Hydrocarbons

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1. Saturated Hydrocarbons

The class of saturated hydrocarbons comprises a myriad of individual compounds. A large number of the theoretically possible saturated hydrocarbons is known [1], although only a limited number of individual saturated hydrocarbons are used as raw materials in the chemical industry.

1.1. Physical Properties

Saturated hydrocarbons are colorless nonpolar substances, immiscible with polar solvents, but miscible with many nonpolar organic solvents. Some physical properties are given in Table 1. The boiling points and, starting with C_3, melting points of *n*-alkanes increase with increasing molecular mass. At 20 °C and atmospheric pressure, C_1 to C_4 *n*-alkanes are gases, C_5 to C_{16} are liquid, and from C_{17} solid. *i*-Alkanes do not display a definite correlation between the number of carbon atoms and their boiling- and melting points. The boiling points of *i*-alkanes all are lower than those of the corresponding *n*-alkanes; this is also true for many of the melting points. Furthermore, the boiling points of isomeric alkanes decrease with increasing degree of branching. The boiling points and melting points of cycloalkanes are generally higher than those of *n*-alkanes having the same number of carbon atoms (Table 1).

The density of the saturated hydrocarbons in the liquid state at 20 °C is <1 g/cm^3; it varies from 0.6 g/cm^3 for compounds with low carbon numbers to 0.8 g/cm^3 for compounds with high carbon numbers (Table 1). Additional physical properties are compiled in Tables 2–5.

1.2. Chemical Properties

Alkanes and cycloalkanes are saturated, nonpolar, and lack functional groups; such hydrocarbons can undergo reaction only after cleavage of C−H or C−C bonds. Consequently, the scope of primary reaction steps is essentially limited to dehydrogenation, substitution, and chain- or ring cleavage. Saturated hydrocarbons cannot undergo addition reactions, which represent a versatile synthetic tool for unsaturated hydrocarbons (see Chap. 2). Most industrial reactions involving saturated hydrocarbons are radical reactions, e.g., thermal cracking, oxidation, sulfoxidation, halogenation, sulfochlorination, and nitration. Industrial ionic reactions of saturated hydrocarbons are restricted to acid-catalyzed processes with strong acids. Such reactions are employed mainly in the processing of petroleum by catalytic cracking, isomerization, and alkylation; they yield complex mixtures of products. Other ionic reactions of saturated hydrocarbons can be carried out with super acids (e.g., $FSO_3H - SbF_5$, $HF - SbF_5$): the alkylation of alkanes by alkanes [3], alkylation of benzene by alkanes [3], and ionic chlorination [5] and bromination [6] of alkanes have been explored, but are not used industrially (see also → Acylation and Alkylation).

Reactions of saturated hydrocarbons, because of the lack of functional groups, are nonselective, with respect to both the region of attack (regioselectivity) and the number of reaction sites (degree of substitution), unless the molecule possesses specific structural features, e.g., tertiary hydrogen atoms. Such reactions frequently afford mixtures of isomeric or structurally analogous compounds which can only be separated with difficulty or not at all.

On the basis of free enthalpy of formation (see Table 2) most of the saturated hydrocarbons are thermodynamically unstable with respect to the elements carbon and hydrogen. They are, however, kinetically stable at ambient temperature. Thermal decomposition of saturated hydrocarbons proceeds stepwise by loss of hydrogen or hydrocarbon fragments with concomitant formation of industrially useful unsaturated cracking products, such as acetylene, olefins, or aromatic hydrocarbons.

On ignition, mixtures of saturated hydrocarbons and oxygen or air may lead to combustion or explosion, depending on the ratio of hydrocarbon and oxygen. Such reactions can be initiated either by imposed ignition or, if the ignition temperature of the mixture is exceeded, by self-ignition. These reactions are the basis for the use of hydrocarbons as heating- and engine fuel. Pertinent fuel properties of individual saturated hydrocarbons are summarized in Table 4.

1.3. Production

By far the largest amount of saturated hydrocarbons is obtained from the natural sources *natural gas* and *petroleum*, either by isolation or by suitable conversion reactions. Additional sources

Table 1. Physical properties of saturated hydrocarbons [2]

Compound	Empirical formula	CAS registry number	mp, °C	bp, °C	η (20 °C), mPa · s	ϱ (20 °C), g/cm³	n_D^{20}
Methane	CH_4	[74-82-8]	−182.5[a]	−161.5			
Ethane	C_2H_6	[74-84-0]	−183.27[a]	− 88.6			
Propane	C_3H_8	[74-98-6]	−187.69[a]	− 42.1		0.5005[b]	
Cyclopropane	C_3H_6	[75-19-4]	−127.4	− 32.8			
n-Butane	C_4H_{10}	[106-97-8]	−138.4	− 0.5		0.5788[b]	1.3326[b]
Cyclobutane	C_4H_8	[287-23-0]	− 90.7	12.5		0.6943[b]	1.365[a]
2-Methylpropane	C_4H_{10}	[75-28-5]	−159.6	− 11.7		0.5572[b]	
n-Pentane	C_5H_{12}	[109-66-0]	−129.7	36.1	0.234	0.62624	1.35748
Cyclopentane	C_5H_{10}	[287-92-3]	− 93.9	49.3	0.438	0.74538	1.40645
2-Methylbutane	C_5H_{12}	[78-78-4]	−159.9	27.9	0.224	0.61967	1.35373
2,2-Dimethylpropane	C_5H_{12}	[463-82-1]	− 16.6	9.5		0.5910[b]	1.342[b]
n-Hexane	C_6H_{14}	[110-54-3]	− 95.3	68.7	0.3117	0.65937	1.37486
2-Methylpentane	C_6H_{14}	[107-83-5]	−153.7	60.3		0.65315	1.37145
3-Methylpentane	C_6H_{14}	[96-14-0]		63.3		0.66431	1.37652
2,2-Dimethylbutane	C_6H_{14}	[75-83-2]	− 99.9	49.7		0.64916	1.36876
2,3-Dimethylbutane	C_6H_{14}	[79-29-8]	−128.5	58.0		0.66164	1.37495
n-Heptane	C_7H_{16}	[142-82-5]	− 90.6	98.4	0.4169	0.68376	1.38764
2-Methylhexane	C_7H_{16}	[591-76-4]	−118.3	90.1		0.67859	1.38485
3-Methylhexane	C_7H_{16}	[589-34-4]		91.9		0.68713	1.38864
3-Ethylpentane	C_7H_{16}	[617-78-7]	−118.6	93.5		0.69816	1.39339
2,2-Dimethylpentane	C_7H_{16}	[590-35-2]	−123.8	79.2		0.67385	1.38215
2,3-Dimethylpentane	C_7H_{16}	[565-59-3]		89.8		0.69508	1.39196
2,4-Dimethylpentane	C_7H_{16}	[108-08-7]	−119.2	80.5		0.67270	1.38145
3,3-Dimethylpentane	C_7H_{16}	[562-49-2]	−134.46[d]	86.1		0.69327	1.39092
2,2,3-Trimethylbutane	C_7H_{16}	[464-06-2]	− 24.9	80.9		0.69011	1.38944
n-Octane	C_8H_{18}	[111-65-9]	− 56.8	125.7	0.5450	0.70252	1.39743
2-Methylheptane	C_8H_{18}	[592-27-8]	−109.0	117.6		0.69792	1.39494
3-Methylheptane	C_8H_{18}	[589-81-1]	−120.5	118.9		0.70582	1.39848
4-Methylheptane	C_8H_{18}	[589-53-7]	−121.0	117.7		0.70463	1.39792
2,2,3-Trimethylpentane	C_8H_{18}	[564-02-3]	−112.3	109.8		0.71602	1.40295
2,2,4-Trimethylpentane	C_8H_{18}	[540-84-1]	−107.4	99.2	0.69193	1.39145	
2,3,3-Trimethylpentane	C_8H_{18}	[564-02-3]	−100.7	114.8		0.72619	1.40750
2,3,4-Trimethylpentane	C_8H_{18}	[565-75-3]	−109.2	113.5		0.71906	1.40422
2,2,3,3-Tetramethylbutane	C_8H_{18}	[594-82-1]	−100.7	106.5			
n-Nonane	C_9H_{20}	[111-84-2]	− 53.5	150.8	0.7139	0.71763	1.40542
n-Decane	$C_{10}H_{22}$	[124-18-5]	− 29.7	174.1	0.9256	0.73005	1.41189
n-Undecane	$C_{11}H_{24}$	[1120-21-4]	− 25.6	195.9	1.185	0.74024	1.41725
n-Dodecane	$C_{12}H_{26}$	[112-40-3]	− 9.6	216.3	1.503	0.74869	1.42160
n-Tridecane	$C_{13}H_{28}$	[629-50-5]	− 5.4	235.4	1.880	0.75622	1.42560
n-Tetradecane	$C_{14}H_{30}$	[629-59-4]	5.9	253.5	2.335	0.76275	1.42892
n-Pentadecane	$C_{15}H_{32}$	[629-62-9]	9.9	270.6	2.863	0.76830	1.43188
n-Hexadecane	$C_{16}H_{34}$	[544-76-3]	18.2	286.8	3.474	0.77344	1.43453
n-Heptadecane	$C_{17}H_{36}$	[629-78-7]	21.98	302.2	4.196[c]	0.7779[c]	1.4368[c]
n-Octadecane	$C_{18}H_{38}$	[593-45-3]	28.2	316.7		0.7818[c]	1.4389[c]
n-Nonadecane	$C_{19}H_{40}$	[629-92-5]	31.9	330.6		0.7854[c]	1.4408[c]
n-Icosane	$C_{20}H_{42}$	[112-95-8]	36.4	343.8		0.7886[c]	1.4425[c]
n-Triacontane	$C_{30}H_{62}$	[638-68-6]	65.8	449.7		0.8096[c]	1.4535[c]
n-Tetracontane	$C_{40}H_{82}$	[4181-95-7]	81.5	525		0.8204[c]	1.4592[c]

[a] For saturation pressure (triple point).
[b] At saturation pressure.
[c] For the super-cooled liquid below the normal melting point.
[d] Value for the melting point of the metastable crystalline form.

include various products derived from coal processing. A number of saturated hydrocarbons, unavailable from natural sources, are produced by special synthesis or by conversion processes.

1.3.1. From Natural Gas and Petroleum

Natural Gas contains methane as the single major component (see also → Methane; →

Table 2. Molar enthalpies of fusion, vaporization and combustion [2]

	Molar enthalpy, kJ/mol		
	Fusion	Vaporization (25 °C)	Combustion[a]
Methane	0.942		802.861
Ethane	2.86	5.02	1 428.787
Propane	3.53	15.1	2 045.377
Cyclopropane	5.44		1 960.637
n-Butane	4.66	21.1	2 658.827
Cyclobutane	5.78	23.7	2 569.523
2-Methylpropane	4.54	19.1	2 650.454
n-Pentane	8.41	26.8	3 274.287
Cyclopentane	4.89	28.5	3 101.707
2-Methylbutane	5.15	24.8	3 266.248
2,2-Dimethylpropane	3.15	21.8	3 254.735
n-Hexane	13.1	31.7	3 886.81
2-Methylpentane	6.27	30.0	3 879.07
3-Methylpentane		30.4	3 881.71
2,2-Dimethylbutane	0.579	27.8	3 869.78
2,3-Dimethylbutane	0.80	29.2	3 877.86
n-Heptane	14.1	36.6	4 501.44
n-Octane	20.8	41.5	5 115.57
n-Dodecane	35.9	61.3	7 580.076
n-Hexadecane	51.9	81.1	10 040.616
n-Icosane	69.9	100.9[b]	12 501.198

[a] For the reaction: Hydrocarbon (g) → CO_2 (g) + H_2O (g).
[b] For the supercooled liquid, below the normal melting point.

Natural Gas). Depending on the particular source, natural gas may also contain acyclic saturated hydrocarbons up to C_5 in proportions that permit their isolation [10]. The isolation of

Table 3. Enthalpy of formation, entropy, and free energy of formation for saturated hydrocarbons as gases (25 °C) [53]

	ΔH^0, kJ/mol	S^0, J mol^{-1} K^{-1}	ΔG^0, kJ/mol
Methane	− 74.898	186.313	−50.828
Ethane	− 84.724	229.646	−32.908
Propane	−103.916	270.090	−23.505
Cyclopropane	+ 53.382	237.810	104.503
n-Butane	−126.232	310.326	−17.166
Cyclobutane	+ 27.256	265.569	110.741
2-Methylpropane	−134.606	294.834	−20.934
n-Pentane	−146.538	349.179	− 8.374
Cyclopentane	− 77.079	293.076	38.895
2-Methylbutane	−154.577	343.820	−14.654
2,2-Dimethylpropane	−166.090	306.599	−15.240
n-Hexane	−167.305	388.661	− 0.293
2-Methylpentane	−174.422	380.789	− 5.024
3-Methylpentane	−171.743	380.036	− 2.135
2,2-Dimethylbutane	−185.685	358.474	− 9.923
2,3-Dimethylbutane	−177.897	366.010	− 4.103
n-Heptane	−187.945	428.058	+ 8.039
n-Octane	−208.586	467.038	16.412
n-Dodecane	−291.066	622.912	50.074
n-Hexadecane	−373.588	778.829	83.820
n-Icosane	−456.068	934.745	117.398

Table 4. Critical data and molar heat capacities of saturated hydrocarbons [2]

Compound	T_c, °C	p_c, MPa	c_p,[a] J mol^{-1} K^{-1}
Methane	−82.6	4.60	35.74
Ethane	32.28	4.88	52.67
Propane	96.7	4.25	73.56
Cyclopropane	125.1	5.57	56.27
n-Butane	152.0	3.80	97.51
Cyclobutane	187	4.99	72.26
2-Methylpropane	135.0	3.65	96.88
n-Pentane	196.5	3.37	120.3
Cyclopentane	238.5	4.50	82.98
2-Methylbutane	187.2	3.38	118.9
2,2-Dimethylpropane	160.6	3.20	121.7
n-Hexane	234.2	3.01	143.2
2-Methylpentane	224.3	3.01	144.3
3-Methylpentane	231.2	3.12	143.2
2,2-Dimethylbutane	215.6	3.08	142.0
2,3-Dimethylbutane	226.8	3.13	140.6
n-Heptane	267.0	2.74	166.1
n-Octane	295.6	2.49	189.0
n-Nonane	321.4	2.29	211.8
n-Decane	344.4	2.10	234.7
n-Undecane	365.6	1.97	257.6
n-Dodecane	385.1	1.82	280.5
n-Tridecane	402.6	1.72	303.4
n-Tetradecane	418.7	1.62	326.3
n-Pentadecane	433.6	1.52	349.2
n-Hexadecane	447.4	1.42	372.0
n-Heptadecane	460.2	1.32	394.9
n-Octadecane	472.1	1.22	417.8
n-Nonadecane	483	1.12	440.7
n-Icosane	494	1.12	463.6

[*] Based on 25 °C and ideal gas state.

individual compounds from natural gas (see Figure 1) can be performed either by absorption or by partial condensation at low temperature, followed by distillation.

Petroleum is the most abundant source of saturated hydrocarbons, both with respect to the absolute amount and to the variety of individual compounds. Petroleum is separated into individual fractions by distillation in a refinery (see also → Oil Refining). Such fractions contain several (liquefied petroleum gas, LPG; → Liquefied Petroleum Gas) or many individual hydrocarbons (all other fractions); these fractions can be used as such or processed further for use as heating- or engine fuels, as lubricants, as raw materials for the production of petrochemicals (synthesis gas → Gas Production, 1. Introduction, acetylene, olefins, aromatics), or for the recovery of industrially important alkanes and cycloalkanes.

From the liquefied petroleum gas fraction, propane, n-butane, and *i*-butane are isolated by

Table 5. Fuel properties of saturated hydrocarbons

	Flash point,[a] °C	Explosion limits (20 °C),[b]		Ignition temperature,[a] °C	Octane number,[c] RON
		lower	upper		
Methane		5.00	15.00	595	
Ethane		3.00	12.50	515	
Propane		2.12	9.35	470	
Cyclopropane		2.40	10.40	495	
n-Butane		1.86	8.41	365	93.8
Cyclobutane		1.8[a]			
2-Methylpropane		1.8[a]	8.5[a]	(460)[d]	
n-Pentane	<−20	1.40	7.80	285	61.7
Cyclopentane	<−20			380	102.5
2-Methylbutane	<−20	1.32	7.6[a]	420	92.3
2,2-Dimethylpropane		1.38	7.50	(450)[d]	85.5
n-Hexane	<−20	1.18	7.40	240	24.8
i-Hexane	<−20	ca. 1[d]	ca. 7.4[d]	ca. 260	
2,2-Dimethylbutane	<−20	1.2[a]	7.0[a]	435	91.8
2,3-Dimethylbutane	<−20	1.2[a]	7.0[a]	415	103.5
n-Heptane	−4	1.10	6.70	215	0
i-Heptane	<−4	ca. 1[c]	ca. 7[c]	ca. 220	
2,3-Dimethylpentane	<0	1.12	6.75	330	91.9
2,2,3-Trimethylbutane	<0			450	112.1
2,3-Dimethylhexane	<12	0.95	6.5[a]	210	
n-Octane	12	0.95	6.5[a]		71.3
i-Octane	−12	1.0	6.0	410	100
2,2,3-Trimethylpentane	<21			430	109.5
2,3,3-Trimethylpentane	<21			425	106
n-Nonane	31	0.83[d]	5.6[a,d]	205	
n-Decane	46	0.77[d]	5.35[d]	205	
n-Dodecane	74	0.6[a,d]		200	
n-Hexadecane	>100			205	
n-Icosane	>100				

[a] Ref. [7]
[b] Ref. [8]
[c] Ref. [9]
[d] Approximate values.
[e] Values are valid for $t > 20$ °C.

distillation. n-Pentane and i-pentane can be isolated from the liquid components of natural gas or from light gasoline (naphtha) either by molecular sieve separation or by superfractionation [11]. Steam-cracking of light gasoline provides, among other products, cyclopentadiene (→ Cyclopentadiene and Cyclopentene), benzene (→ Benzene), and 1,3-butadiene (→ Butadiene); these can, in turn, be converted into the C_5-, C_6-, C_8-, and C_{12}-cycloalkanes. Catalytic reforming of heavy gasoline provides C_6- to C_8-aromatics, which can subsequently be converted into cyclohexane (→ Cyclohexane), e.g., the C_7- and C_8-aromatics are hydrodealkylated, and the ensuing benzene subsequently hydrogenated. From the higher boiling petroleum, gas-oil, and wax distillate fractions, mixtures of homologous n-alkanes are isolated by techniques, such as molecular sieve separation or urea extractive crystallization. Paraffin waxes can also be isolated by precipitation with suitable solvents.

Higher boiling petroleum distillates and distillation residues can be converted into mixtures of lower molecular mass hydrocarbons by hydrocracking [12], [13]. From such mixtures, saturated C_3– C_5-hydrocarbons and a broad spectrum of higher n-alkanes can be recovered.

Although petroleum and the various petroleum distillates contain a large variety of other saturated hydrocarbons in addition to those already mentioned, the recovery and subsequent industrial use of individual compounds is largely confined to those depicted in Figure 1; the increasing number of structural isomers with increasing molecular
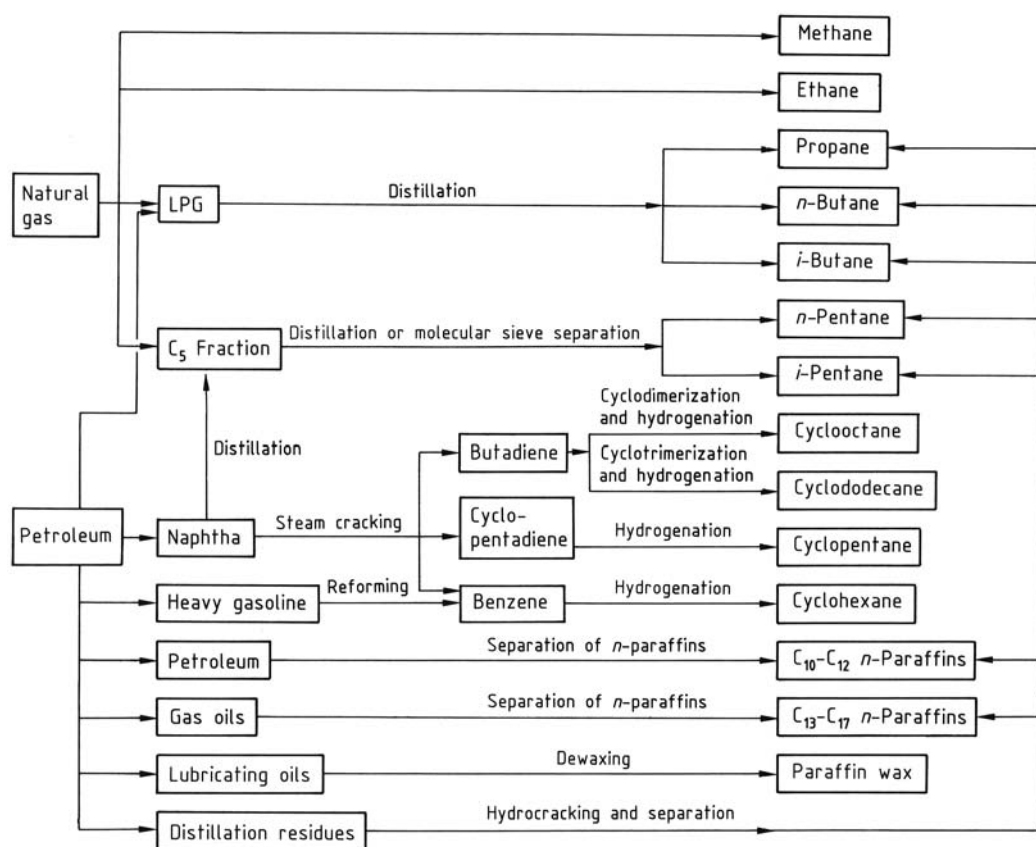
Figure 1. Saturated hydrocarbons from natural gas and from petroleum

mass poses severe limitations on the economical separation of individual compounds from such distillate mixtures on an industrial scale.

1.3.2. From Coal and Coal-Derived Products

For a long time the most important sources of saturated hydrocarbons were coal and the products derived from the liquefaction, coking, and gasification of coal ($\rightarrow$ Coal; $\rightarrow$ Coal Liquefaction; $\rightarrow$ Coal Pyrolysis). These sources became less important when natural gas and petroleum became essential raw materials for organic chemicals [14], [15].

The *liquefaction of coal* provided the greatest variety of saturated hydrocarbons. The Fischer – Tropsch Synthesis can produce alkanes in the range C_1 to C_{30} or higher, depending on the process variant ($\rightarrow$ Coal Liquefaction) [16–18]: the fluidized bed synthesis affords pre-dominantly liquid hydrocarbons in the gasoline range, along with gases from C_1 to C_4. The liquid hydrocarbons contain considerable proportions of branched and olefinic compounds. The fixed bed synthesis provides higher molecular mass hydrocarbons in the range of diesel oil or paraffin wax. These products are rich in n-alkanes and are, therefore, suitable raw materials for detergents and for wax products. Suitable fractions may also serve as raw materials for cracking and reforming processes.

The various processes for the *hydrogenation of coal* [19–21] or of coal tar afford predominantly liquid products in the boiling range of gasoline, which are rich in aromatics, and minor amounts of C_1- to C_4-alkanes. From the gasoline fractions, benzene can be recovered and hydrogenated to cyclohexane. After the recovery of benzene, the remaining mixtures can be used as feed materials for steam crackers for the production of olefins.

Coking of Coal produces methane. In addition, high temperature processes produce benzene, which can be hydrogenated to cyclohexane [22], [23]. Low temperature coking of soft coal provides a tar, from which paraffin wax may be recovered.

Gasification of Coal [24] affords mainly carbon monoxide and hydrogen, which can be converted into methane by nickel-catalyzed reactions or into a range of alkanes by the Fischer – Tropsch process. Up to 10 % of methane and higher hydrocarbons such as naphtha and benzene are formed in addition to carbon monoxide and hydrogen if the gasification is carried out at elevated pressure [25].

1.3.3. By Synthesis and by Conversion of other Hydrocarbons

The major processing techniques are *cyclization, hydrogenation,* and *isomerization,* forming the basis of the industrial production of most cycloalkanes. Other techniques include *alkylation* of alkenes with alkanes to provide *i*-alkanes, and hydrocracking to give predominantly low molecular mass *i*- and *n*-alkanes, including methane.

Cyclization and Hydrogenation. Among the cycloalkanes only those containing a 5- or a 6-membered ring are directly available from natural sources, i.e., from petroleum or coal-derived products. Steamcracking of naphtha or gas oil produces cyclopentadiene as a byproduct, which can be converted into cyclopentane by catalytic hydrogenation. Similarly, cyclohexane is produced by catalytic hydrogenation of benzene, which in turn is formed by steam cracking of liquid hydrocarbons, by catalytic reforming of heavy gasoline, or by coking of coal.

The skeletons of all other industrially produced cycloalkanes are synthesized from acyclic precursors. Although there is a wide variety of synthetic procedures for such reactions, only a limited number are used industrially. Of prime importance are cycloaddition reactions of acyclic unsaturated compounds followed by hydrogenation of the resulting unsaturated cyclic products: Thus, [4 + 2]-cycloaddition (Diels – Alder reaction) of conjugated dienes and monoolefins yields saturated 6-membered ring compounds via cyclo-

hexene intermediates, e.g., the synthesis of cyclohexane from 1,3-butadiene and ethylene [26]:

the catalyzed [4 + 4]-cycloaddition of 1,3-butadiene to give cyclooctane via 1,5-cyclooctadiene;

and the catalyzed [4 + 4 + 4]-cyclotrimerization of 1,3-butadiene to form cyclododecane via 1,5,9-cyclododecatriene:

Cyclizations that lead to small (C_3-, C_4-) rings are not industrially important, although various laboratory methods are available [27]. Examples include the coupling of terminal carbon atoms by elimination of suitable α,ω-substituents from acyclic compounds, e.g., α,ω-dihalides, ω-halogenated ketones, esters, or nitriles (Eq. 1), addition of carbenes, to olefins to give cyclopropanes (Eq. 2) and [2 + 2]-cycloadditions of suitable unsaturated compounds, such as olefins, allenes, or acetylenes, to give cyclobutanes (Eq. 3) [28]:

$$X-CH_2-(CH_2)_n-CH_2-Y \xrightarrow{-XY} \underset{CH_2}{\overset{CH_2}{\mid}}>(CH_2)_n \qquad (1)$$

$$(2)$$

$$(3)$$

Most of these synthetic methods yield substituted or unsaturated cyclic compounds in the cyclization step. These primary products can be subsequently converted into the corresponding cycloalkanes by suitable measures.

Isomerization and Alkylation. On account of their specific properties (antiknock activity, possibility for selective reactions), some *i*-alkanes

are in higher demand than can be met by natural sources. *i*-Alkanes are produced either by acid-catalyzed isomerization of *n*-alkanes or by acid-catalyzed alkylation of olefins with *i*-alkanes. The most important isomerizations are the conversion of *n*-butane to *i*-butane, *n*-pentane to *i*-pentane, and *n*-hexane to *i*-hexane [29], [30]. Industrially important alkylations include the reaction of *i*-butane with propylene or with butenes to give highly branched C_7- or C_8-alkanes, respectively (see also → Oil Refining). The latter exhibit high octane numbers [30], [31].

Hydrocracking.   A range of acyclic saturated hydrocarbons having low carbon numbers is accessible by catalyzed hydrocracking of heavy distillates or distillation residues. Hydrocracking of distillates can be optimized by adjusting the reaction conditions, so that the products are predominantly in the range of liquefied petroleum gases, including *i*-butane [13], or in the range of middle distillates [32]. The cracking of petroleum distillates with steam over a nickel catalyst produces methane [33], [34].

1.4. Uses

The major use of saturated hydrocarbons is as a mixture, sometimes with unsaturated or aromatic compounds, as heating fuels, motor fuels and lubricants. Saturated hydrocarbons also serve as raw materials for the production of carbon black. In the chemical industry, the following processes are important (Fig. 2).

Thermal Cracking.   Thermal cracking of individual or mixed saturated hydrocarbons is the
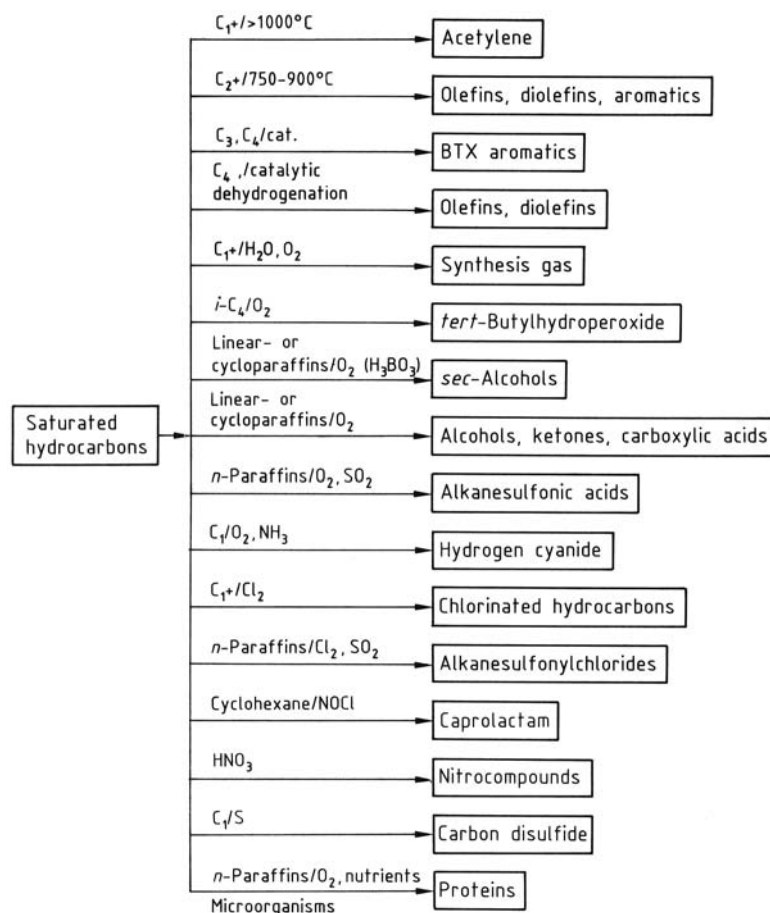
Figure 2. Industrial use of saturated hydrocarbons

basis for the petrochemical production of acetylene, olefins, diolefins, and to some extent BTX aromatics: high temperature pyrolysis at $>1000\,^\circ$C affords acetylene ($\rightarrow$ Acetylene) and, depending on the hydrocarbon feed and the particular process applied, ethylene. The range of hydrocarbon feed materials can vary from methane to crude oil. Medium temperature pyrolysis at $750 - 900\,^\circ$C in the presence of inert diluents such as steam (steam-cracking) or hydrogen (hydropyrolysis) yields ethylene ($\rightarrow$ Ethylene). A wide range of hydrocarbons, e.g., ethane, liquefied petroleum gas, naphtha, and gas oil may serve as raw material, and increasing proportions of C_3- to C_5-olefins, C_4- and C_5-dienes, and C_6- to C_8-aromatics are coproduced with increasing molecular mass of the feed material. Pyrolysis of petroleum waxes at $500 - 600\,^\circ$C affords mixtures of homologous olefins with predominantly terminal double bonds.

Catalytic Dehydrogenation. Catalytic dehydrogenation of acyclic saturated hydrocarbon atoms yields mono- and/or diolefins with the same number of carbon atoms. Industrial processes include the production of butenes and butadiene from *n*-butane, of isoprene from *i*-pentane, and C_6- to C_{19}-monoolefins, mainly with internal double bonds, from the corresponding *n*-alkanes [35]. More recently, improved processes for the production of ethylene, propene, and *i*-butene by catalytic dehydrogenation of the corresponding saturated hydrocarbons have been developed [36]. Catalytic dehydrogenation of cyclohexane and methyl cyclohexanes yields benzene and methylbenzenes, respectively.

Catalytic Dehydrocyclooligomerization of propane and *n*-butane over modified zeolite catalysts represents a new method for the production of BTX-aromatics [37]. The process is apparently ready for industrial application.
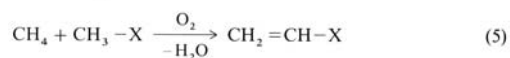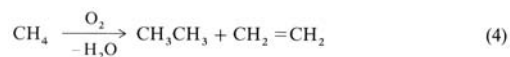
Partial Oxidation. Partial oxidation of saturated hydrocarbons either by catalyzed reaction with steam (steam reforming) or by noncatalyzed reaction with deficient amounts of oxygen affords a mixture of carbon monoxide and hydrogen, which is used as town gas or as synthesis gas ($\rightarrow$ Gas Production, 1. Introduction). Desulfurized saturated hydrocarbons from methane to compounds with *bp* ca. $200\,^\circ$C are suitable feed materials for catalytic processes; for noncatalytic

processes all hydrocarbons may be used from methane to distillation residues.

Selective Oxidation. Selective oxidation represents the most important tool for the introduction of oxygen-containing functional groups into saturated hydrocarbons: Liquid-phase autoxidation of *i*-butane with air yields *tert*-butylhydroperoxide; the latter is used for the selective oxidation of propene to propylene oxide [38]. Liquid-phase oxidation of *n*-alkanes or cycloalkanes in the presence of boric acid affords the corresponding secondary alcohols. The reaction is used industrially for the oxidation of C_{10}- to C_{20}-*n*-alkanes, providing raw materials for detergents and for the oxidation of cyclododecane to cyclododecanol as an intermediate for the production of nylon 12. Catalyzed liquid-phase oxidation of *n*-alkanes and cycloalkanes in the absence of boric acid leads to mixtures of secondary alcohols and ketones or to carboxylic acids, depending on the reaction conditions: oxidation of cyclohexane leads to a mixture of cyclohexanol and cyclohexanone ($\rightarrow$ Cyclohexanol and Cyclohexanone); oxidation of *n*-butane gives acetic acid ($\rightarrow$ Acetic Acid, Section 4.2.); oxidation of longer chain *n*-alkanes produces mixtures of fatty acids; and oxidation of cyclohexane gives adipic acid. ($\rightarrow$ Adipic Acid, Chap. 4.). Liquid phase oxidation of bicyclo [4.4.0] decane yields the corresponding tertiary hydroperoxide, which is eventually converted into sebacic acid by a sequence of reaction steps [39].

Heterogeneously catalyzed gas-phase oxidation of *n*-butane has been used industrially as an attractive alternative for the production of maleic anhydride [40]. Selective oxidation of methane to methanol [41] or formaldehyde [42] and of *i*-butane to methacrylic acid [43] has been examined, but is not yet used industrially.

Oxidative Couplings. Oxidative coupling of methane either with itself to give ethane and ethylene [44] (Eq. 4), or with compounds having activated methyl groups (Eq. 4) to give terminal olefinic compounds [45] has been investigated, but is not yet industrially used.

$$CH_4 \xrightarrow[-H_2O]{O_2} CH_3CH_3 + CH_2=CH_2 \qquad (4)$$

$$CH_4 + CH_3-X \xrightarrow[-H_2O]{O_2} CH_2=CH-X \qquad (5)$$

$$X = -CH=CH_2, -C(CH_3)=CH_2, -C_6H_5, -C\equiv N$$

Three-Component Oxidation. Three-component oxidation allows introduction of hetero atoms or groups of hetero atoms other than oxygen into saturated hydrocarbons. The radical-induced action of both oxygen and sulfur dioxide (sulfoxidation) on alkanes yields the corresponding alkanesulfonic acids. The latter, produced from C_{14}– to C_{18}– n-alkanes, are useful as raw materials for detergents. The heterogeneously catalyzed reaction of oxygen and ammonia with methane (ammoxidation) affords hydrogen cyanide. The latter reaction can be also carried out in the absence of oxygen as a two-component codehydrogenation. The reaction of oxygen and ammonia with propane to give acrylonitrile has recently been explored.

Chlorinations. Chlorination of saturated hydrocarbons yields mono- or polychlorinated hydrocarbons, depending on conditions. The following reactions are used industrially: Chlorination of methane to give the four chloromethanes ($\rightarrow$ Chloromethanes); the chlorination of n-alkanes to give mono- or polychlorinated alkanes having the same number of carbon atoms and chlorinolysis of low molecular mass alkanes or chloroalkanes to give tetrachloroethene and tetrachloromethane. Reaction of chlorine and sulfur dioxide together with alkanes yields alkanesulfonyl chlorides, which in turn can be converted into the corresponding sulfonic acids, sulfonates, sulfonamides, or sulfonic esters.

Photonitrosation. Photonitrosation of saturated alkanes with nitrosyl chloride yields oximes via labile secondary nitroso compounds. The method has been used for the production of caprolactam from cyclohexane ($\rightarrow$ Caprolactam, Section 4.2.).

Nitrosation. Nitrosation of saturated hydrocarbons with nitric acid has been carried out with low molecular mass alkanes, particularly with propane in the gas phase. The reaction gave mixtures of nitro compounds with the same number of and fewer carbon atoms than those of the starting alkanes. Such mixtures are useful as specialty solvents, e.g., for polymers.

Reaction with Sulfur. Reaction of methane with sulfur gives carbon disulfide in high yields with hydrogen sulfide as byproduct. The reaction can be performed by thermal or catalytic methods ($\rightarrow$ Carbon Disulfide, Chap. 4.).

Fermentation. Fermentation of certain saturated hydrocarbons by microorganisms (yeast, bacteria) yields single cell proteins [46–50]. The microorganisms oxidize the hydrocarbons in the presence of oxygen and nutrients with concomitant formation of protein-containing cells. Certain microorganisms are specific for the fermentation of n-alkanes. Industrial processes have therefore been developed both for the fermentation of isolated n-alkanes and for n-alkanes in admixture with branched or cyclic hydrocarbons (e.g., diesel oil). The products obtained are used as animal feed.

1.5. Individual Saturated Hydrocarbons

Methane, Cyclohexane, and *Waxes* are separate keywords. Of the other saturated hydrocarbons only those used industrially will be discussed.

Ethane. Ethane is present in many natural gas sources and in refinery gases; it can be recovered for industrial use. Furthermore, ethane is formed in thermal- and hydrocracking of hydrocarbons ($\rightarrow$ Oil Refining) and in the liquefaction of coal ($\rightarrow$ Coal Liquefaction). The single most important industrial use for ethane is the production of ethylene by steam-cracking ($\rightarrow$ Ethylene, Section 5.1.3.). Thermally-induced chlorination of ethane yields predominantly monochloro-, 1,1-dichloro-, or 1,1,1-trichloroethane, depending on the conditions used. Combined chlorination and oxichlorination of ethane in a salt melt affords vinyl chloride [51]. Reaction of ethane with nitric acid in the gas phase yields nitroethane and nitromethane ($\rightarrow$ Nitro Compounds, Aliphatic).

Propane. Propane is a component of liquefied petroleum gas (LPG), which is derived from natural gas or petroleum. Propane can be recovered from LPG by distillation. The major industrial use of propane is the production of ethylene and propene by the steam cracking process ($\rightarrow$ Ethylene, Section 5.1.3.). Chlorinolysis of

propane at elevated temperature yields a mixture of tetrachloroethene and tetrachloromethane. The conversion of propane into BTX aromatics by zeolite-catalyzed dehydrocyclooligomerization has been developed recently and may find industrial application. Liquefied propane is used for the deasphalting of petroleum residues.

n-Butane. n-Butane can be recovered from LPG by distillation; it has a variety of industrial uses: steamcracking yields ethylene and propene, catalytic dehydrogenation yields butadiene ($\rightarrow$ Butadiene), and acid-catalyzed isomerization provides i-butane. Oxidation of n-butane in the gas phase with heterogeneous catalysis is a modern process for the production of maleic anhydride [40]. Noncatalyzed oxidation of n-butane in the liquid or gas phase has been used industrially to produce acetic acid [52] ($\rightarrow$ Acetic Acid, Section 4.2.).

i-Butane. i-Butane can be obtained either by recovery from LPG or by isomerization of n-butane. Traditional industrial uses include the production of high octane engine fuel by the alkylation of olefins [30], [31] and liquid-phase autoxidation of i-butane to give tert-butylhydroperoxide. Recent developments comprise improved processes for the catalytic dehydrogenation of i-butane [53] to satisfy the increasing demand for i-butene as a pecursor for methyl tert-butyl ether (MTBE) ($\rightarrow$ Methyl Tert-Butyl Ether), and the production of methacrylic acid from i-butane by oxidation [43].

n-Pentane and i-Pentane. Both isomers are present in light gasoline fractions and can be recovered individually by superfractionation [11], [54], possibly in combination with molecular sieve separation. n-Pentane is used as a solvent and for the production of i-pentane by acid-catalyzed isomerization [26]. i-Pentane is used as a blending component for high octane gasoline and for the production of isoprene by catalytic dehydrogenation [53], [54].

n-Hexane. n-Hexane can be isolated from suitable sources (e.g., light gasoline or BTX raffinates) by superfractionation, or by molecular sieve separation. It is used for the extraction of vegetable oils (e.g., from soybeans), as a solvent in chemical reactions (e.g., for coordination complex catalyzed polymerization of olefins) and in adhesive formulations.

Higher n-Alkanes. n-Alkanes having more than six carbon atoms are not isolated individually but as mixtures of several homologues. Suitable sources are the appropriate petroleum distillate fractions, from which the n-paraffins can be isolated in high isomeric purity ($\geq 95\%$ linearity) by selective separation (e.g., molecular sieve separation or urea extractive crystallization). They are used mainly in applications for which i-alkanes are not acceptable for biological reasons, e.g., the production of detergents or proteins. Catalyzed gas-phase dehydrogenation of n-alkanes over noble metal catalysts and at low conversion (ca. 10 %) yields the corresponding n-alkenes with predominantly internal double bonds. The alkenes can be isolated in high purity by selective molecular sieve processes [35], [56]. n-Alkenes in the range C_7 to C_{10} are used as raw materials for the production of flexibilizers, by oxo-synthesis with hydrogen and carbon monoxide. n-Alkenes in the range C_{10} to C_{19} are used for the production of biodegradable detergents: acid-catalyzed reaction of C_{10}- to C_{13}-n-alkenes with benzene, followed by sulfonation and neutralization of the ensuing alkylbenzene sulfonic acids, affords linear alkylbenzenesulfonate (LABS) detergents. Oxo-reaction of C_{10}- to C_{19}-n-alkenes yields C_{11}- to C_{20}-alcohols, which are converted into nonionic detergents by reaction with ethylene oxide, or into anionic detergents by reaction with sulfur trioxide or chlorosulfonic acid. Liquid-phase oxidation of n-alkanes with oxygen in the presence of boric acid yields predominantly secondary alcohols. The latter can be dehydrated to the corresponding n-alkenes. The C_{12}- to C_{19}-alcohols are also used for the production of both ionic and nonionic detergents.

Chlorination of n-alkanes yields mono- or polychlorinated alkanes, depending on the conditions. Mixtures of C_{10}- to C_{13}-monochloroalkanes are used for the production of linear alkylbenzenes as raw materials for LABS-detergents. For this, the chloroalkanes are either directly reacted with benzene or they are dehydrochlorinated to the corresponding n-alkenes, which are then used to alkylate benzene. Polychlorinated n-alkanes are used in a number of special applications.

n-Alkanes in the range of C_{10} to C_{21} are suitable substrates for the production of single cell proteins by fermentation. The microorganisms used selectively attack *n*-alkanes, so that industrial processes have been developed in which either isolated *n*-alkanes or the appropriate petroleum distillates containing *n*-alkanes (petroleum-, gas oil-, or lube oil fractions) are used as starting materials.

Solid *n*-alkanes (paraffin waxes) are used in a variety of applications, both as such and as feed materials in cracking, oxidation and chlorination.

Cycloalkanes. Of the various accessible cycloalkanes, only cyclohexane and cyclododecane are used industrially on a large scale; cyclooctane is used on a relatively small scale. The strained C_3- and C_4-cycloalkanes are not produced industrially. *Cyclopentane* is present in natural hydrocarbon sources and is formed as a byproduct in the processing of cracking products, e.g., by hydrogenation of cyclopentadiene or cyclopentene in the C_5-fraction of steamcracked products. No important industrial use exists for cyclopentane.

Cyclooctane is accessible by catalytic hydrogenation of 1,5-cyclooctadiene. Liquid-phase oxidation of the former with air yields 1,8-octanedicarboxylic acid, which is used on a moderate scale for the production of nylon 68.

Cyclododecane is produced by liquid-phase hydrogenation of 1,5,9-cyclododecatriene over nickel catalysts. Liquid-phase oxidation of cyclododecane with air in the presence of boric acid yields mixtures of cyclododecanol and cyclododecanone in high selectivity. Further oxidation of such alcohol – ketone mixtures with nitric acid gives 1,12-dodecanedicarboxylic acid, used for the production of polyamides, polyesters, and synthetic lubricating oils. Catalyzed dehydrogenation of alcohol-ketone mixtures in the liquid phase yields cyclododecanone, which is then converted into laurinlactam and nylon 12.

Bicyclo [4.4.0] decane (decalin) is obtained by catalytic hydrogenation of naphthalene. Liquid-phase oxidation of decalin with oxygen gives the corresponding tertiary hydroperoxide, which is eventually converted into 1,10-decanedicarboxylic acid (sebacic acid) by a four-step sequence [39].

$$HOOC - (CH_2)_8 - COOH$$
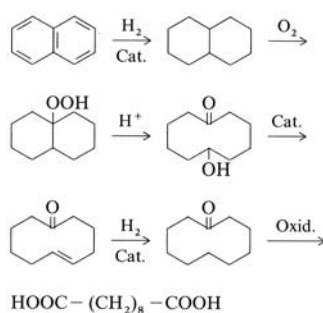
2. Olefins

Olefins are aliphatic hydrocarbons containing at least one carbon−carbon double bond. Monoolefins (alkenes) contain a single C=C double bond and form a homologous series with the empirical formula C_nH_{2n}. Hydrocarbons with two double bonds are differentiated according to the relative positions of the double bonds: in cumulated dienes (cumulenes, allenes) they are immediately adjacent to each other; in conjugated dienes they are separated by a single bond; and in other diolefins, the double bonds are isolated from each other.

More highly unsaturated polyenes are known, e.g., trienes, tetraenes. The name olefin is derived from the property of these compounds to form oily liquids on reaction with halogens (*gaz oléfiant,* oil-forming gas).

The industrial importance of olefins started in the 1950s when the lower olefins became widely available from thermal cracking of wet natural gas and petroleum fractions, displacing acetylene (ethyne) as the dominant commodity chemical (→ Acetylene). In the time since then, ethene (ethylene), propene, 1,3-butadiene, and isoprene (2-methyl-1,3-butadiene) have found wide application, especially for synthetic polymers (→ Butadiene; → Ethylene; → Isoprene; → Propene).

2.1. Monoolefins

The low molecular mass monoolefins ethylene, propene, styrene, cyclopentene, and the butenes are separate keywords: (→ Butenes; → Cyclopentadiene and Cyclopentene; → Ethylene). Among the higher olefins ($C_6 – C_{18}$), the linear α-olefins are of particular industrial interest.

2.1.1. Properties

Physical Properties. Under normal conditions, the olefins from ethylene to the butenes are gases; from the pentenes to 1-octadecene liquids; and from 1-icosene onwards solids. These thermal phase transitions do not differ significantly from those of the corresponding saturated hydrocarbons (Chap. 1). The density of olefins ranges from 0.63 to 0.79 g/cm^3, only a few percent higher than those of the corresponding alkanes.

The heats of combustion of alkenes and the corresponding alkanes are also nearly identical. Olefins have low solubility in water or are insoluble; they dissolve well in most organic solvents, e.g., alcohols, ethers, and aromatic hydrocarbons. Some physical properties of important monoolefins are listed in Table 6.

Chemical Properties. The chemistry of monoolefins is dominated by the reactive double bond. Some important reactions of olefins are summarized in Table 7.

Most *addition reactions* proceed by an electrophilic mechanism via carbonium ions. Chlorination and bromination yields the trans adducts. Hydrohalogenation generally follows Markovnikov's rule to give a product containing halogen linked to secondary carbon. Addition of sulfuric acid to olefins affords alkyl sulfates, which are readily hydrolyzed to alcohols; the reaction corresponds to the acid-catalyzed addition of water. Ethanol, isopropylalcohol, and *tert*-butyl alcohol are produced industrially by this method from ethylene, propene, and isobutene, respectively (→ Alcohols, Aliphatic, Section 2.3.7.).

Hydrogenation of olefins to alkanes requires a catalyst: Raney nickel is most frequently used industrially, although platinum-group metals are also used (→ Hydrogenation and Dehydrogenation).

Epoxidation of ethylene may be carried out with oxygen in the presence of a silver catalyst. Higher olefins are converted to epoxides using hydroperoxides or peracids (→ Epoxides). A related reaction is the hydroxylation of olefins with hydrogen peroxide in glacial acetic acid: an epoxide is initially formed, which subsequently reacts with water in the acidic medium to form a glycol. Another olefin oxidation is the *Wacker oxidation* of ethylene to acetaldehyde (→ Acetaldehyde, Section 4.3.1.). The stoichiometric reaction of ethylene with water and palladium(II) chloride yields acetaldehyde and palladium metal. Addition of copper(II) chloride converts the stoichiometric reaction into a catalytic process, wherein the copper(II) chloride reoxidizes the palladium to palladium(II) chloride the resulting copper(I) chloride is reoxidized to copper(II) chloride by atmospheric oxygen in hydrochloric acid solution.

Ozonolysis is used mainly for structure determination of olefins, but may also be used preparatively. Reaction of olefins with carbon monoxide and additional reagents (e.g., hydrogen, water, alcohols) leads to a plethora of valuable products (e.g., aldehydes, alcohols, carboxylic acids, esters). These reactions proceed under catalysis by transition metals, e.g., hydroformylations (Oxo process) with rhodium- or cobalt carbonyls.

Sulfonation of olefins leads to alkenesulfonic acids, which are used as detergents (→ Laundry Detergents, 2. Ingredients and Products). Hydroboration is used to generate primary alcohols via trialkylboranes. In contrast to the direct addition of water, this pathway is regioselective to yield the anti-Markovnikov products.

Olefins may undergo a number of reactions resulting in new C-C bonds. With aromatic compounds alkylaromatics are formed by the Friedel – Crafts reaction; with isoalkanes chain-lengthened, branched hydrocarbons, which are used in motor fuels, are formed (→ Automotive Fuels). Olefins may also react with themselves or each other to form oligomers and polymers.

The industrial use of the higher monoolefins is discussed in Section 2.1.3.

2.1.2. Production of Higher Olefins

Olefins are synthesized on a laboratory scale by a variety of routes: e.g., selective hydrogenation of alkynes; dehydration of alcohols; pyrolysis of alkyl lithium compounds; the Wittig reaction; the Peterson reaction; and deoxygenation of vicinal diols. Only processes starting with cheap raw materials have gained industrial importance for the production of higher olefins. The following discussion considers processes that start either with long-chain alkanes (Section 2.1.2.1) or those that build up longer chain olefins from their lower molecular mass homologues (Section 2.1.2.2).

Table 6. Physical properties of monoolefins

Olefin	CAS registry number	mp, °C	bp, [a] °C	d^{20}	n^{20}
Ethylene	[74-85-1]	−169.5	−103.8	0.5699 (−103.8 °C)	1.363 (−100 °C)
Propene	[115-07-1]	−185.3	− 47.7	0.6095 (−47.4 °C)	1.3640 (−50 °C)
				0.5139	
1-Butene	[106-98-9]	−185.3	−6.26	0.6356 (−15.1 °C)	1.3791 (−25 °C)
cis-2-Butene	[590-18-1]	−138.9	3.7	0.6447 (0 °C)	1.3783 (0 °C)
trans-2-Butene	[624-64-6]	−105.5	0.88	0.6269 (0 °C)	1.3696 (−20 °C)
Isobutene	[115-11-7]	−140.4	−6.9	0.6398 (−20 °C)	1.3776
1-Pentene	[109-67-1]	−167.2	29.97	0.6405	1.3718
cis-2-Pentene	[627-20-3]	−151.3	37.1	0.6554	1.3828
trans-2-Pentene	[646-04-8]	−140.2	36.4	0.6482	1.3798
2-Methyl-1-butene	[58718-78-8]	−137.5	31.2	0.6504	1.3778
3-Methyl-1-butene		−168.5	20.1	0.6332	1.3640
2-Methyl-2-butene	[26760-64-5]	−133.6	38.6	0.6625	1.3874
1-Hexene	[592-41-6]	−140.0	63.5	0.6732	1.3878
cis-2-Hexene	[7688-21-3]	−141.8	68.8	0.6969	1.3976
trans-2-Hexene	[4050-45-7]	−133.5	67.5	0.6780	1.3935
cis-3-Hexene	[7642-09-3]	−137.8	66.5	0.6794	1.3951
trans-3-Hexene	[13269-52-8]	−113.4	68.0	0.6778	1.3937
1-Heptene	[592-76-7]	−119.6	93.8	0.6993	1.3998
cis,trans-2-Heptene		−109.5	98.2	0.7034	1.4041
cis-3-Heptene	[7642-10-6]	136.6	95.8	0.7030	1.4059
trans-3-Heptene	[14686-14-7]	−136.3	95.7	0.6981	1.4043
1-Octene	[111-66-0]	−102.7	121.3	0.7160	1.4086
cis-2-Octene	[7642-04-8]	−100.5	125.6	0.7243	1.4146
trans-2-Octene	[13389-42-9]	− 87.8	124.5	0.7184	1.4132
cis-3-Octene	[14850-22-7]	−126	122.7	0.7223	1.4140
trans-3-Octene	[14919-01-8]	−110.0	123.3	0.7149	1.4129
cis-4-Octene	[7642-15-1]	−118.1	122.5	0.7212	1.4150
trans-4-Octene	[14850-23-8]	− 93.8	122.3	0.7136	1.4120
1-Nonene	[124-11-8]	− 81.6	146.8	0.7292	1.4157
2-Nonene	[2216-38-8]		149.4	0.7407	1.4201
3-Nonene	[20063-77-8]		148.2 (102 kPa)	0.7334	1.4191
4-Nonene	[2198-23-4]		148.0	0.7313	1.4200
1-Decene	[872-05-9]	− 66.6	170.6	0.7408	1.4215
2-Decene	[6816-17-5]				
3-Decene	[19348-37-9]		173 – 173.5	0.7447	1.4221
4-Decene	[19689-18-0]		170.6	0.7404	1.4243
cis-5-Decene	[7433-78-5]	−112	169.5 (98.5 kPa)	0.7445	1.4252
trans-5-Decene	[7433-56-9]	− 73	170.2	0.7412	1.4235
1-Undecene	[821-95-4]	− 49.1	192.67	0.75033	1.4261
5-Undecene	[4941-53-1]		192.2	0.7511	1.4289
1-Dodecene	[25378-22-7]	− 33.6	213.3	0.7583	1.4300
6-Dodecene	[7206-29-3]		212.9 (99.3 kPa)	0.7597	1.4328
1-Tridecene	[2437-56-1]	− 22.2	104 (1.33 kPa)	0.7654	1.4335
1-Tetradecene	[1120-36-1]	− 12	125 (1.85 kPa)	0.7726	1.4367
1-Pentadecene	[13360-61-7]	− 3.8	133.5 (1.33 kPa)	0.7763	1.4389
1-Hexadecene	[629-73-2]	4.0	155 (2.0 kPa)	0.7811	1.4412
1-Heptadecene	[6765-39-5]	10.7	159 (1.33 kPa)	0.7860	1.4436
1-Octadecene	[112-88-9]	18.0	176 – 178 (1.85 kPa)	0.7888	1.4450
1-Icosene	[3452-07-1]	28.5	151 (0.2 kPa)		1.4440 (30 °C)
1-Heneicosene	[1599-68-4]	35.5	134 (0.005 kPa)	0.7985	1.4510
1-Triacontene	[18435-53-5]	62 – 63	218 (0.07 kPa)	0.7620 (100 °C)	

[a] At 101.3 kPa, unless otherwise noted.

2.1.2.1. Production from Paraffins

Thermal Cracking of Waxes.   Thermal cracking of long chain alkanes yields mainly α-olefins.

$$R^1 - CH_2CH_2CH_2CH_2 - R^2 \longrightarrow$$
$$R^1 - CH = CH_2 + R^2 - CH = CH_2 + H_2$$
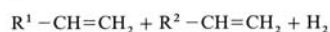
Table 7. Important reactions of olefins

Reaction	Reagents	Products
Halogenation	Cl_2, Br_2	dihaloalkanes
Hydro-halogenation	HCl, HBr	alkylhalides
Sulfation	H_2SO_4	alkyl sulfates
Hydration	H_2O; catalyst: H^+	alcohols
Hydrogenation	H_2; catalyst: Ni, Pt	alkanes
Epoxidation	a) O_2 catalyst: Ag	ethylene oxide
	b) RCOOOH, ROOH	epoxides
Hydroxylation	H_2O_2; catalyst: H^+	glycols
Wacker oxidation	H_2O; catalyst: Pd – Cu	acetaldehyde, ketones
Ozonolysis	O_3	aldehydes, ketones
Hydro-formylation	CO, H_2; catalyst: Co, Rh	aldehydes
Hydrocar-boxylation	CO, H_2O; catalyst: Ni, Co	carboxylic acids
Sulfonation	SO_3, NaOH	alkene-sulfonates
Hydroboration	B_2H_6	trialkyl-boranes
Alkylation	a) of aromatics, with a Friedel – Crafts catalyst	alkyl-aromatics
	b) of isoalkanes, catalyst: H^+	branched alkanes
Polymerization	Catalyst: radicals, metal complexes	polymers
Oligomerization	Catalyst: metal complexes, BF_3	oligomers

Table 8. Composition of fractions (wt %) obtained in a paraffin cracking process (Chevron process)

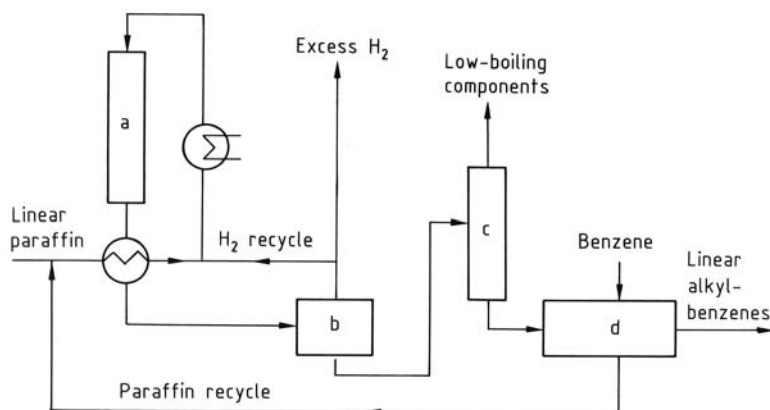|	C_6–C_7	C_8–C_{10}	C_{11}–C_{12}	C_{13}–C_{14}	C_{15}–C_{18}	C_{18}–C_{20}
α-Olefins	83	83	88	88	89	86
Internal olefins	12	11	5	5	3	1
Diolefins	3	4	5	5	6	4
Paraffins	2	2	2	2	2	9
Aromatics	0.4	0.2	0	0	0	0

urea molecules assemble to form cavities having a diameter of 0.53 nm, in which only linear alkanes can be accommodated. The alkanes are then liberated by subsequent decomposition of the complex, e.g., with water at 75 °C. Industrial processes use solid urea (Nurex process) or its saturated aqueous solution (Edeleanu process).

The long-chain paraffins are then cracked by first heating the vapor to 400 °C within a few seconds, followed by thermolysis at 500 – 600 °C in the presence of steam. Rapid quenching of the reaction mixture reduces side reactions such as isomerization or cyclization.

Using C_{18} – C_{36} alkanes as starting material, α-olefins with even and odd numbers of carbon atoms in the range C_6 – C_{20} are obtained; only small amounts of paraffins are present. Byproducts include nonterminal olefins, conjugated and nonconjugated dienes, and traces of aromatics. Typical composition of the olefin fractions from paraffin cracking are given in Table 8.

The dependence of product quality on the starting material and process parameters is discussed in a review [66]; catalytic cracking and cracking in the presence of oxygen are also reviewed. The latter processes have not gained acceptance because of the presence of numerous byproducts, e.g., branched olefins and oxidation products.

The first industrial paraffin cracking plant was brought into service in 1941 by Shell at Stanlow (United Kingdom). Other plants were built at Pernis (The Netherlands) and Berre (France). A U.S. paraffin cracking plant owned by Chevron is located in Richmond, California. Future expansion of paraffin cracking processes is unlikely because of the limited flexibility of paraffin cracking plants with respect to carbon number distribution, the limited supply of paraffin-containing crudes, the high percentage (≥ 10 %) of byproducts in the α-olefin cut, and because of more efficient competitive processes.

Thermal cracking involves a radical mechanism. Cleavage of a C-C bond leads to carbon radicals, which are converted into olefins by loss of a hydrogen atom. The latter predominantly combine to form hydrogen; a small fraction reacts with carbon radicals to form alkanes.

To generate linear α-olefins, linear alkanes (waxes) must be used. Suitable sources are the petroleum, diesel oil, and lubricant fractions of paraffin-based crude oils. One possibility of enriching the linear paraffin content of such fractions is to dilute with a suitable solvent, followed by chilling to crystallize a mixture of paraffins. Linear paraffins can be separated from their branched and cyclic analogs by subsequent treatment with molecular sieves. Another method for the separation of *n*-paraffins, especially suitable for long-chain (>C_{20}) species, is *extractive crystallization with urea*. This process uses the property of urea to form inclusion compounds with linear paraffins, but not with branched or cyclic alkanes, or aromatics. During crystallization the

Figure 3.   Simplified flow diagram for a combination of the UOP PACOL process and benzene alkylation
a) Pacol reactor; b) Separator; c) Stripper; d) Alkylation reactor

Catalytic Dehydrogenation.   Catalytic dehydrogenation of paraffins leads to olefins with the same number of carbon atoms and with random location of the double bond along the chain. Thermally, this reaction cannot be carried out economically because the energy required to cleave a C-H bond (365 kJ/mol) significantly exceeds that for breaking a C-C bond (245 kJ/mol). Cracking of longer chain hydrocarbons is, therefore, favored over dehydrogenation; however, the use of a catalyst facilitates the dehydrogenation of linear paraffins to linear olefins having predominantly the same number of carbon atoms (see also → Hydrogenation and Dehydrogenation).

The most important industrial process is the Pacol (paraffin catalyst olefin) process of Universal Oil Products (UOP). The reaction is carried out at 450 – 510 °C and 0.3 MPa using a hydrogen : carbon ratio of 9 : 1. A supported platinum catalyst, ca. 0.8 wt % Pt, on alumina, activated by addition of lithium and arsenic or germanium, is used. To minimize the formation of byproducts, especially aromatic hydrocarbons, which reduce catalyst activity, relatively low conversion rates of 10 – 15 % are used. This results in paraffin – olefin mixtures that are separated by means of the UOP Olex (olefin extraction) process. The Olex process employs molecular sieves, which absorb olefins more strongly than alkanes. The combination of both processes is known as the Pacol – Olex process [67]. In 1983, there were four Pacol – Olex plants worldwide, as well as 18 other plants where the Pacol process was combined with the alkylation of aromatics [68]. A simplified flow diagram of a Pacol benzene alkylation unit is shown in Figure 3.

Fresh *n*-alkane is added to the circulating paraffin, heated via heat exchangers, and dehydrogenated in the Pacol fixed-bed reactor (a) in the presence of hydrogen and at high throughput velocity. The products are separated into hydrogen and hydrocarbons in the separator (b) and volatile cracking products are removed in the stripper (c); these are then used chiefly as fuel. The stripper sump contains the higher linear monoolefins, which are reacted with benzene under acid catalysis to yield alkylbenzenes. The unreacted *n*-alkanes are returned to the Pacol reactor [69].

Chlorination – Dehydrochlorination.
Another method for generating linear olefins from linear paraffins consists of chlorinating the paraffins to chloroalkanes, followed by a catalyzed second step in which hydrogen chloride is eliminated. Chlorination is carried out continuously in the liquid phase at 120 °C; the conversion is limited to a maximum of 30 %, to avoid excessive formation of dichlorides. A random mixture of linear olefins results from the dehydrohalogenation because the chlorine substituents are almost randomly distributed along the alkyl chain. The dehydrochlorination of chlorinated paraffins occurs in the presence of iron or iron alloy catalysts at 250 °C. The lower boiling olefins and paraffins are drawn off at the still head; the unreacted, higher boiling chlorinated paraffins remain in the reactor. Separating
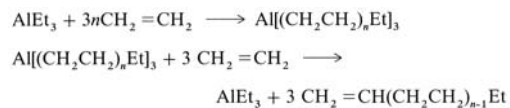
products in this manner requires that rather narrow cuts be taken, because the boiling points of the *n*-olefins and the chloroparaffins are quite close together [70], [71].

2.1.2.2. Oligomerization of Lower Olefins

All the methods described so far for the production of olefins from paraffins suffer from the disadvantage that crude oil containing linear paraffins with the required distribution of carbon atoms is in short supply. Several companies have, therefore, developed alternative routes to olefins that are based on oligomerization of olefins, especially of ethylene. Such starting materials are readily available from the pyrolysis of liquefied natural gas, naphtha, and gas oil fractions. The worldwide capacity for ethylene alone was ca. 50×10^6 t in 1983. Ethylene supplies appear assured for the forseeable future because it can be generated by the Mobil process from methanol, which is derived from coal-based synthesis gas.

The methods for buildup of longer chain olefins vary greatly. In the following sections syntheses via organoaluminum compounds, transition metal catalyzed oligomerization, and acid-catalyzed processes will be discussed.

Ethylene Oligomerization in the Presence of Organoaluminum Compounds. The first process for the industrial oligomerization of ethylene was discovered by ZIEGLER in the early 1950s [72]. The reaction proceeds in two stages: first a growth step followed by an elimination step.

$$AlEt_3 + 3n\,CH_2 = CH_2 \longrightarrow Al[(CH_2CH_2)_n Et]_3$$
$$Al[(CH_2CH_2)_n Et]_3 + 3\,CH_2 = CH_2 \longrightarrow$$
$$AlEt_3 + 3\,CH_2 = CH(CH_2CH_2)_{n-1}Et$$

The growth step occurs at ca. 100 °C under 10 MPa ethylene pressure. In the second stage, the high temperature displacement reaction, the alpha-olefins are displaced by ethylene at ca. 300 °C and 1 MPa. The composition of the product mixture corresponds to a Poisson distribution. This process suffers from the disadvantage of requiring stoichiometric quantities of reaction components, i.e., industrial plants would require large quantities of aluminum alkyls. Consequently, Gulf Oil and Ethyl Corporation developed two process variants that require less triethylaluminum.

The Gulf Oil Process. In the Gulf process, only catalytic quantities of triethylaluminum are used and growth step and elimination reactions occur simultaneously in the same reactor [73]. The reaction is carried out at <200 °C and ca. 25 MPa. The product mixture consists of a Schulz – Flory distribution of linear olefins. A typical composition of individual fractions from $C_6 - C_{18}$ is listed in Table 9.

The Gulf process produces markedly purer α-olefins than can be obtained with paraffin cracking (see Table 8). The major impurities in the α-olefins (trade name: Gulftenes) obtained by the Gulf process are ca. 1.4 % paraffins; with increasing carbon number, an increasing amount of β-branched α-olefin is also formed. The occurrence of these vinylidene and 2-ethyl compounds may be rationalized by consecutive reactions of α-olefins with the aluminum alkyls, as follows:

$$Al(CH_2CH_2R^1)_3 + 3\,CH_2 = CH - R^2 \longrightarrow$$
$$Al(CH_2\overset{\underset{\displaystyle R^2}{|}}{C}HCH_2CH_2R^1)_3 \xrightarrow{3\,CH_2=CH_2}$$
$$AlEt_3 + 3\,CH_2 = \overset{\underset{\displaystyle R^2}{|}}{C} - CH_2CH_2R^1$$
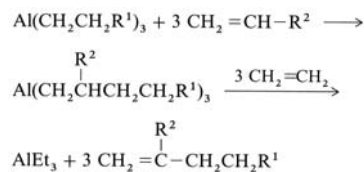
The Gulf Oil Co. uses the Gulf process to produce linear α-olefins in the $C_4 - C_{30}$ range at their plant in Cedar Bajou, Texas. Mitsubishi Chemical Industries uses the same process at Mizushima.

Table 9. Composition of fractions (wt %) obtained from the Gulf process[*]

	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
Linear α-olefins	97.0	96.0	95.0	94.0	93.0	92.0	91.0
β-Branched α-olefins[**]	1.4	2.5	3.4	4.6	5.6	6.6	7.8

[*] *n*-Alkane content 1.4 %.

[**] Including traces of olefins with internal double bonds.
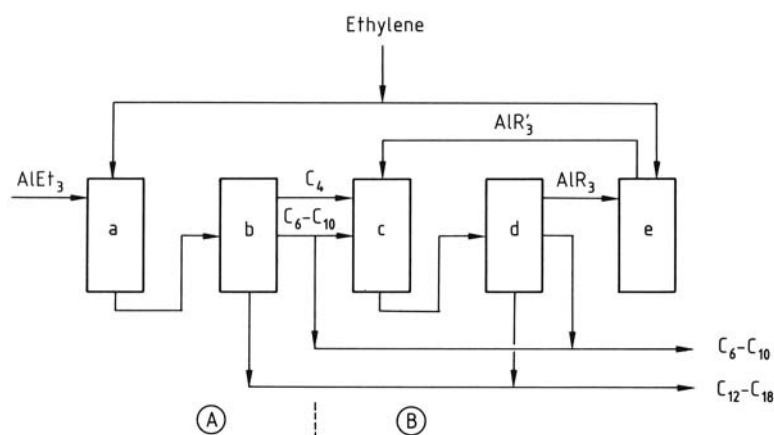
Figure 4.   Typical flow diagram of Ethyl process
A) Catalytic step; B) Stoichiometric step;
a) Catalytic reactor; b) First distillation; c) Transalkylation reactor; d) Second distillation; e) Stoichiometric reactor

Ethyl Process.   The Ethyl process combines a stoichiometric and a catalytic stage [74]. This modified Ziegler process is capable of controlling the chain length of the resulting α-olefins much more precisely, because the shorter chain olefins may be subjected to further chain growth.

The Ethyl process is illustrated schematically in Figure 4. Ethylene is first oligomerized using catalytic quantities of triethylaluminum in analogy to the Gulf process. The resulting products are fractionated (b) in Fig. 4) yielding fractions containing C_4, $C_6 – C_{10}$, and $C_{12} – C_{18}$. The higher boiling fractions may be used directly, whereas the shorter α-olefins, especially C_4, are subjected to transalkylation with long chain aluminum alkyls (c) in Fig. 4). This reaction releases the desired long-chain α-olefins; short-chain trialkylaluminum compounds are simultaneously formed. The aluminum trialkyls are separated in the second distillation step (Fig. 4, (d)) and transformed in another reactor (e) in Fig. 4) into longer chain alkyls by stoichiometric reaction with ethylene. The latter are then recycled to the transalkylation.

The Ethyl Corporation has operated a plant in Pasadena, Texas using this process since 1970; the initial capacity was 110 000 t/a. The process permits 95 % conversion of ethylene into higher α-olefins, a conversion efficiency not achievable by the single-step catalytic Gulf Oil process. This advantage is however, counterbalanced by a much lower product quality of the long-chain α-olefins. The $C_{16}– C_{18}$ cut consists of only 63 % linear α-olefins (Table 10), the remainder being mainly β-branched α-olefins and internal olefins.

Ethylene Oligomerization with Transition-Metal Catalysis. In the presence of nickel, cobalt, titanium, or zirconium catalysts, ethylene may be converted into oligomers [75]. Commercial importance has been attained exclusively by the *Shell higher olefin process* (*SHOP*).

Shell Higher Olefin Process.   The SHOP process is the most recent development in α-olefin synthesis. It works in the liquid phase using a nickel catalyst and yields α-olefins of unusually high purity [76–78]. Monoolefins are formed

Table 10. Composition of fractions (wt %) obtained from the Ethyl process

	C_6	C_8	C_{10}	C_{12}	$C_{12}– C_{14}$	$C_{14}– C_{16}$	$C_{16}– C_{18}$
Linear α-olefins	97.5	96.5	96.2	93.5	87.0	76.0	62.7
Internal olefins	0.6	1.2	1.6	1.5	4.2	5.0	8.2
β-Branched α-olefins	1.9	2.3	2.2	5.0	8.8	19.0	29.1
Alkanes	0.1	0.6	0.3	0.4	0.4	0.4	0.8

Table 11. Composition of α-olefin fractions (wt %) obtained from the SHOP process

	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
All monoolefins	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Linear α-olefins	97.0	96.5	97.5	96.5	96.0	96.0	96.0
Branched olefins	1.0	1.0	1.0	2.0	2.5	2.5	2.5
Internal olefins	2.0	2.4	1.0	1.5	1.5	1.5	1.5
Dienes	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05
Aromatics	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05
Alkanes	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05

almost exclusively; analytical data indicate only trace amounts of dienes, aromatics, and alkanes. The content of α-olefin for the carbon numbers is in the range 96 – 97 %. A typical product composition is given in Table 11.

The SHOP process involves a combination of three different reactions: *oligomerization, isomerization,* and *metathesis*. This integration of chain lengthening and shortening steps makes the SHOP process very flexible. Whereas all other α-olefin processes permit only limited control over product distribution, with the SHOP process it is possible to achieve almost any olefin cut desired. The SHOP process is shown schematically in Figure 5 [78–81].

Oligomerization is carried out in a polar solvent such as ethylene glycol or 1,4-butanediol. The catalyst is produced in situ from a nickel salt, e.g., nickel chloride, sodium borohydride, and a chelating ligand. Suitable ligands are compounds of the general formula $RR^1P-CH_2-COR^2$, e.g., diphenyl phosphinoacetic acid, dicyclohexyl-

phosphinoacetic acid, or 9-(carboxymethyl)-9-phosphabicyclo [3.3.1]- nonane. Ethylene is oligomerized to α-olefins with a Schulz – Flory distribution at 80 – 120 °C and 7 – 14 MPa. The olefins formed are immiscible with the polar solvent; product and catalyst phases are thereby readily separated so that the catalyst can be recycled repeatedly. Oligomerization is accomplished in a series of reactors interspersed with heat exchangers to remove the heat of reaction. The reaction rate can be regulated by the amount of catalyst. A high partial pressure of ethylene is required for high product linearity and a suitable rate of reaction. The chain length of the α-olefins is determined by the geometric factor K of molar growth:

$$K = \frac{n(C_{n+2}-\text{olefins})}{n(C_n-\text{olefins})}$$

where n is the number of moles.

The mass distribution of various α-olefins relative to the growth factor K is shown in Figure 6.

Controlling the growth factor is extremely important for the overall process because K determines both the product distribution and the
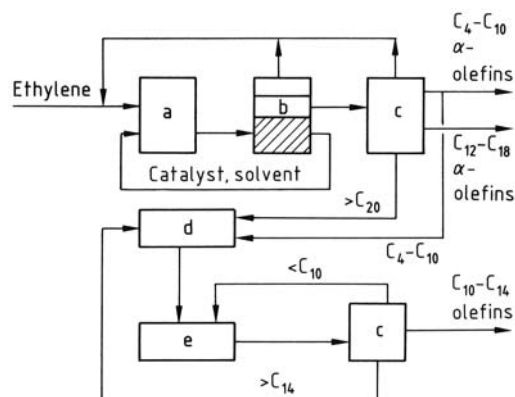

Figure 5. Typical flow diagram of SHOP process
a) Oligomerization reactor; b) Phase separator; c) Distillation; d) Isomerization reactor; e) Metathesis reactor
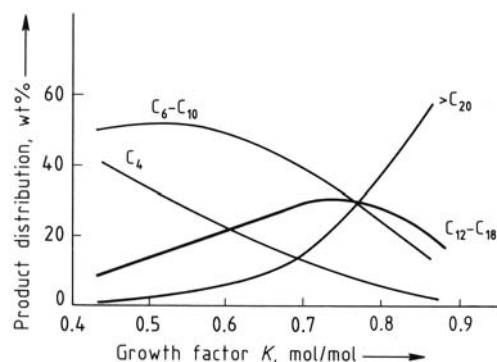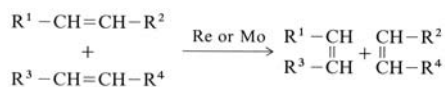

Figure 6. Product distribution as a function of growth factor K

median chain length of the olefins obtained. It is, therefore, advantageous to be able to vary the K-factor by the composition of the catalyst.

After separation of the catalyst and product phase, the latter is washed with fresh solvent to remove the last traces of catalyst. In a subsequent distillation (see Fig. 5) the mixture is separated into the desired $C_{12} - C_{18}$ α-olefins and into low ($C_4 - C_{10}$) and high-boiling ($>C_{20}$) fractions. The $C_4 - C_{10}$ fraction can then be further fractionated, if desired, into individual compounds, for example, those used as comonomers for the manufacture of linear low density polyethylene (LLDPE). However, the $C_4 - C_{10}$ fraction and the $C \geq 20$ fractions are generally combined for isomerization and subsequent metathesis. These two steps require only moderate reaction conditions: $80 - 140\ °C$, $0.3 - 2$ MPa. The heat of reaction of both steps is quite low; because in isomerization only intramolecular migration of double bonds occurs, in metathesis carbon – carbon bonds are simultaneously cleaved and reformed. *Isomerization* takes place in the liquid phase in the presence of magnesium oxide catalyst [82]. About 90 % of the terminal olefins are converted to internal olefins in this reaction.

$$R-CH=CH_2 \xrightarrow{\text{MgO}} R^1-CH=CH-R^2$$
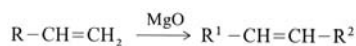
The subsequent joint *metathesis* of the internal, low, and high molecular mass olefins, mainly over heterogeneous rhenium or molybdenum catalysts, yields a mixture of internal olefins having a new chain length distribution, i.e., a random mixture of olefins of even and odd numbers of carbon atoms.

$$\begin{array}{c} R^1-CH=CH-R^2 \\ + \\ R^3-CH=CH-R^4 \end{array} \xrightarrow{\text{Re or Mo}} \begin{array}{c} R^1-CH \quad CH-R^2 \\ \parallel \quad + \quad \parallel \\ R^3-CH \quad CH-R^4 \end{array}$$

The products of metathesis are distilled and the $C_{11} - C_{14}$ fraction, representing ca. $10 - 15\%$ of the mixture, is separated for production of alcohols used in the detergent industry (see Section 2.1.3).

The composition of the internal $C_{11} - C_{14}$ olefins produced by the SHOP process is given in Table 12; more than 99.5 % is monoolefins, with only small amounts of dienes, aromatics, and paraffins.
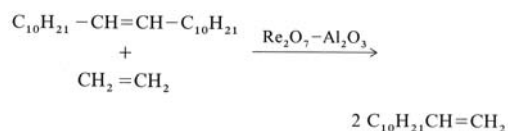
Table 12. Composition of internal olefins (wt %) obtained from the SHOP process

	$C_{11}- C_{12}$	$C_{13}- C_{14}$
All monoolefins	>99.5	>99.5
Linear olefins	>96	>96
Branched olefins	3	3
Dienes	<0.1	<0.1
Aromatics	<0.1	<0.1
Paraffins	<0.5	<0.5

Although the double bonds of the olefins at the beginning of metathesis are distributed almost at random over the carbon backbone, they are shifted in the end product toward the chain end, a result of the high concentration of short-chain olefins (2-butene, 2-hexene, 3-hexene) in the metathesis feed.

Distillation of the metathesis products also yields low- and high-boiling components in addition to the $C_{11} - C_{14}$ fraction. One of the great advantages of the SHOP process is that these fractions do not have to be discarded but can be recycled. The fraction consisting of compounds with less than 11 carbon atoms is returned directly to the metathesis reactor; the fraction containing olefins with more than 14 carbon atoms is again subjected to isomerization before it reaches the metathesis stage. By combining oligomerization, isomerization, and metathesis, the SHOP process is capable of converting almost all the ethylene feed into olefins having the desired number of carbon atoms.

An interesting alternative of the SHOP process described above is the metathesis of the isomerized $C \geq 20$ fraction together with a ten-fold molar excess of ethylene [82]. Olefins, predominantly α-olefins, within the desired carbon range may be prepared in the presence of a rhenium catalyst (20 % Re_2O_7 on aluminum oxide).

$$\begin{array}{c} C_{10}H_{21}-CH=CH-C_{10}H_{21} \\ + \\ CH_2=CH_2 \end{array} \xrightarrow{Re_2O_7-Al_2O_3} $$
$$2\ C_{10}H_{21}CH=CH_2$$

The first SHOP processing plant was built in 1977 by Shell Oil Corporation at Geismar, Louisiana (see Section 2.1.4); annual capacity was 200 000 t.
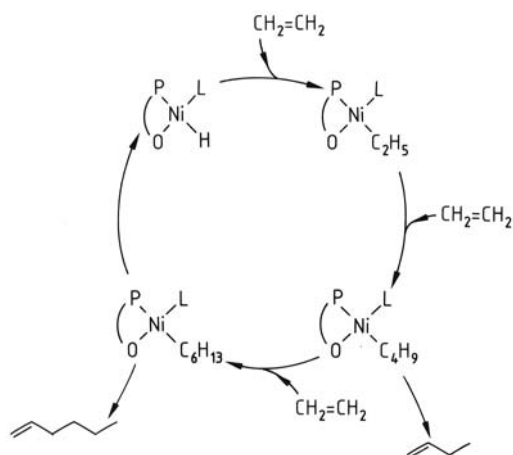
Figure 7. Mechanism of ethylene oligomerization in the presence of nickel P−O-chelate complex catalyst (for P−O ligand see text)

The mechanism of the highly selective ethylene oligomerization with nickel chelate catalysts has been largely elucidated by the research group of W. KEIM [76], [83–87]. A chelated nickel hydride complex is formed initially. This complex reacts with ethylene (Fig. 7) to form alkyl nickel complexes. Linear α-olefins are eliminated from the alkyl nickel complexes; the nickel hydride species is formed simultaneously to reenter the catalytic cycle.

The SHOP process is by far the most important method for oligomerization of ethylene involving transition-metal catalysts. To complete the picture, two other processes will be described below, although they have not yet reached commercial importance.

Exxon Process. The Exxon Corporation has developed a process in which ethylene is converted to high molecular mass olefins in the presence of a catalyst consisting of a transition-metal component and a soluble alkyl aluminum chloride [88]. Titanium chloride or an alkoxy titanium chloride are favored as the transition metal components. The catalyst is soluble in saturated hydrocarbons and active at $25 - 70 \,^\circ\text{C}$. This process yields linear α-olefins in the range $C_4 - C_{100}$ or higher; it appears to be especially useful for the production of high-melting waxes, i.e., olefins higher than C_{20}.

Alphabutol Process. In the Alphabutol process, developed by the Institut Français du Pétrole (IFP), ethylene is selectively dimerized to 1-butene [89] using a homogeneous titanium catalyst. In contrast to the SHOP process, the mechanism does not involve metal hydrides but a titanium(IV) cyclopentane species that decomposes under the reaction conditions ($50 - 60 \,^\circ\text{C}$, slight positive pressure) with β-hydrogen transfer to 1-butene:
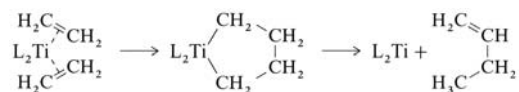
The 1-butene, which contains only traces of impurities (hexenes, 2-butene, butanes) may be used as comonomer in the production of LLDPE.

Oligomerization of Propene and Butenes with Transition-Metal Catalysis. Ziegler catalysts consisting of nickel compounds and aluminum trialkyls can be used to dimerize or codimerize propene and butene to give predominantly branched olefins. This process was also developed by the Institut Français du Pétrole and is referred to as the Dimersol process [90–95]. IFP research began as early as the mid 1960s. The first commercial Dimersol-G plant was brought into production in 1977 by Total in Alma, Michigan. In the *Dimersol G process*, propene (in admixture with propane) is dimerized mainly (80 %) to isohexenes; small amounts of propene trimers (18 %) and tetramers (2 %) are also formed:

$$2\ C_3H_6 \longrightarrow$$

n-Hexenes + 2-methylpentenes + 2,3-dimethylbutenes

The reaction takes place in the liquid phase without solvent. The pressure in the reactor is adjusted so that the C_3 compounds remain liquid at the operating temperature. The product mixture leaving the reactor head is fed to a vessel where the catalyst is neutralized with alkali. The product (trade name: Dimate) is then washed with water and freed of any remaining propane and propene on a stabilizing column.

The *Dimersol X process* is similar, although the starting materials are butenes or a mixture of propene and butenes. The products formed are,

accordingly, isooctenes or mixtures of $C_6 - C_8$ olefins. The first Dimersol X plant was started in 1980 by Nissan Chem. in Kashima, Japan. A typical starting material for the Dimersol X process is the raffinate II obtained from the C_4 cut of the steam cracker, after removal of butadiene and isobutene. The resulting C_8 olefins can be converted by Oxo-synthesis into nonanols, which are used for the synthesis of plasticizers (dinonyl phthalate).

A more recent development is the *Dimersol E* process, which employs the exhaust gases of fluid catalytic crackers (FCC) that contain ethylene and propene. A gasoline fraction can be obtained from this product after hydrogenation. The first experiments with cracker exhaust gases from the Elf cracker near Feyzin (France) began in 1984.

By 1982, IFP had licensed 16 Dimersol plants, eight of which were in production. In addition to IFP, other industrial and academic groups have investigated the transition metal-catalyzed oligomerization of lower olefins [96–104]. The observation that in the propene dimerization with nickel-based Ziegler catalysts the addition of phosphines may significantly affect the isohexene product distribution is of interest. With the catalyst $[NiBr(\eta^3\text{-}C_3H_5)(PCy_3)]$ – $EtAlCl_2$ (Cy = cyclohexyl) a remarkable turnover of 800 000 mol propene per mol nickel h^{-1} could be achieved. A turnover of 60 000 s^{-1} was calculated for operation at room temperature. This value is of an order of magnitude usually achieved only by enzyme reactions.

Oligomerization of Propene and Butene by Acid Catalysis. Mineral acids such as phosphoric or sulfuric acid can also be used as catalysts for the oligomerization of olefins; the major products are branched olefins. Alkylbenzenes were once prepared from tetramers of propenes (tetrapropylene). This reaction is now rarely used in Europe because of the low biodegradability of the alkylbenzenesulfonates obtained.

Oligomerization of isobutene leads to the formation of diisobutene, triisobutene, and tetraisobutene; after hydrogenation, these may be added to gasoline to improve the octane rating (polymer gasoline, oligomer gasoline). In the *cold acid process*, isobutene-containing C_4 fractions are treated with 60 – 70 % sulfuric acid at room temperature. Isobutene dissolves in the sulfuric acid as *tert*-butyl sulfate. This solution is then oligomerized at 100 °C. The products, mainly diisobutenes, separate as a second phase. In the *hot acid process*, the *n*-butenes of the C_4 fraction are also converted, forming i-C_4 – n-C_4 cooligomers.

The oligomerization can also be performed with poly(styrene sulfonic acid) resins as catalysts. This process is used by Erdölchemie – Dormagen using the raffinate I (C_4 fraction after extraction of butadiene). The reaction is performed in loop reactors at 100 °C and 1.5 – 2.0 MPa with residence times of 20 – 60 min. The product is composed of 36 % diisobutene, 22 % C_8 codimers, 38 % triisobutene, and 4 % tetraisobutene. The product distribution may be changed by recycling specific fractions.

2.1.3. Uses of Higher Olefins

The most important uses of linear olefins are described below.

Synthesis of Oxo-Alcohols. Linear α-olefins can be converted to linear primary alcohols, which are used in the synthesis of plasticizers ($<C_{11}$) or detergents ($>C_{11}$) by hydroformylation (oxo synthesis). The reaction can also be used to give aldehydes as the major products.

$$R-CH=CH_2 \xrightarrow[\text{Cat.}]{CO, H_2}$$
$$R-CH_2CH_2CH_2OH \text{ or } R-CH_2CH_2CHO$$
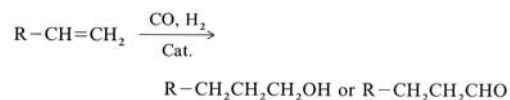
The yield of linear products can be increased to >90 % if phosphine-modified cobalt- or rhodium catalysts are used.

The described synthesis route for long-chain alcohols has strong competition, however, from the natural fatty alcohols and from the Alfoles, generated from ethylene by an organo aluminum synthesis with subsequent oxidation.

In the United States Monsanto has produced oxo alcohols from $C_6 - C_{10}$ α-olefins since 1971. Exxon has used the oxo process since 1983 to produce plasticizer alcohols in the $C_7 - C_{11}$ range at Baton Rouge, Louisiana. Shell also converts olefins to alcohols. In recent years, olefins derived from paraffin crackers as starting materials have been replaced by internal olefins from the SHOP process.

The possibility of converting olefin-derived aldehydes to short-chain synthetic fatty acids by oxidation is also notable:

$$R-CH_2CH_2CHO \xrightarrow{\text{Oxid.}} R-CH_2CH_2COOH$$
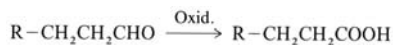
In 1980 Celanese (now Hoechst-Celanese) built a plant in Bay City, Texas with an annual capacity of 18 000 t to produce heptanoic and nonanoic acids from 1-hexene and 1-octene, respectively, which are used in the production of lubricants. Again, there is strong competition from the natural products, which are generally less expensive. In addition, lubricant production requires highly linear acids. Fatty acids from oxo aldehydes have a linearity of >95 %; natural fatty acids have a linearity of almost 100 % ($\rightarrow$ Fatty Acids).

Synthesis of Linear Alkylbenzenes. Currently the most important class of detergents for domestic use is still the linear alkylbenzenesulfonates (LAS or LABS). They are prepared by Friedel – Crafts reaction of benzene with linear olefins followed by sulfonation:

LAB   LABS
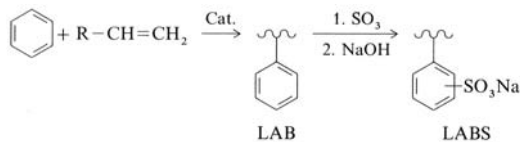
Total estimated production of LAS in Western Europe, Japan, and the United States in 1982 was ca. 1.1×10^6 t. In Europe, Asia, South Africa, and South America linear alkylbenzenes are produced from C_{10}– C_{15} *alpha*-olefins. In 1982, 420 000 t of LAB were synthesized in Western Europe from ca. 80 000 t of linear olefins.

Synthesis of α-Alkenesulfonates. α-Alkene sulfonates (α-olefin sulfonates, AOS or OS) are obtained by direct sulfonation of C_{14} – C_{18} α-olefins ($\rightarrow$Detergents). An ionic mechanism results in a product mixture of 40 % isomeric alkenesulfonic acids (with the double bond predominantly in the β- or the γ-position) and 60 % 1,3- or 1,4-alkanesulfones. Following hydrolysis with sodium hydroxide, a mixture of alkenesulfonates and hydroxyalkanesulfonates is obtained:

AOS
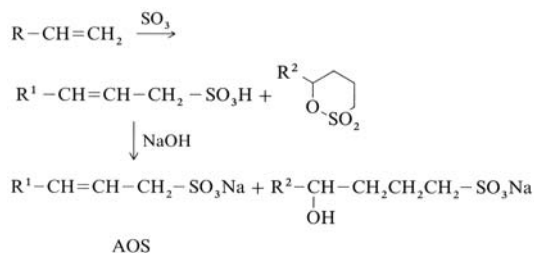
The double bonds and the hydroxyl groups contribute to the excellent water solubility of the AOS compounds. They are effective laundry agents even in hard water and at low concentration and are used increasingly in liquid soaps and cosmetics. In order to be used in such products the AOS must be of high quality, especially with regard to color; this is only possible with α-olefins that contain no more than traces of dienes.

Although AOS compounds have been known since the 1930s, they gained commercial importance only in the late 1960s. In 1982, ca. 7000 t of AOS were produced in the United States from α-olefins, with the Stepan Company and Witco Chemical Corporation being the largest U.S. producers. AOS represents an interesting alternative to alkyl sulfates and alkyl ether sulfates in cosmetic products.

Synthesis of Bromoalkanes and Derived Products. An important reaction of α-olefins is radical hydrobromation to give primary bromoalkanes. These compounds are valuable intermediates for, e.g., thiols, amines, amine oxides, and ammonium compounds:
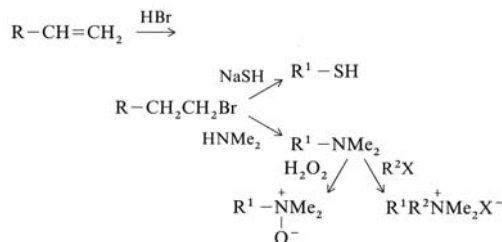
Thiols are produced by this route in Europe and in the United States by Pennwalt Corp. and Phillips Petroleum Co. They are used in the synthesis of herbicides, pesticides, pharmaceuticals, in the textile industry, or as polymer regulators.

In 1982, ca. 15 000 t of alkyldimethylamine (ADA) was produced from linear α-olefins in the United States by Ethyl Corporation and by Procter & Gamble. Most of these amines were directly converted to fatty amine oxides (FAO) or quaternary ammonium salts (Quats). Fatty amine oxides are nonionic surfactants that, because they are biodegradable and do not irritate the skin, are incorporated into numerous products, e.g., into rinsing agents. Quats are produced by alkylation of amines, e.g., with benzylchloride. Benzyl-Quats possess biocidal and antimicrobial properties and are incorporated, for example, into disinfectants and deodorants.

Production of Synthetic Lubricants (→ Lubricants, 2. Components). Oligomerization of α-olefins in the middle C-number range, in particular 1-decene, to isoparaffins (mostly trimers with a few tetramers and pentamers) leads to lubricants known as poly(α-olefins) (PAO) or synthetic hydrocarbons (SHC). They are used industrially, and in the automobile and aircraft sectors [105], [106]. They are in many instances superior to natural mineral oils, especially at lower temperature, because of their favorable viscosity, low volatility, high flash point, and high thermal stability. Oligomerization of the α-olefins can be performed with, e.g., BF_3, to which protonic cocatalysts, e.g., water or alcohols, are added.

In 1982, ca. 25 000 t of PAO were produced in the United States. The major producers are Mobil Oil, Gulf Oil, National Distillers, Burmah-Castrol, and Ethyl Corporation.

Production of Copolymers. Linear α-olefins, in particular 1-butene, 1-hexene, and 1-octene, are used as comonomers in the production of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). By adding α-olefins the density and other properties of the polymers may be significantly modified.

HDPE copolymers contain only relatively small quantities of α-olefins, generally 0.5 – 3 %. The density of the HDPE homopolymer ($0.965 – 0.955$ g/cm^3) is reduced to $0.959 – 0.938$ g/cm^3 for the HDPE copolymer. The most frequently employed comonomer is 1-hexene, followed by 1-butene.

On the other hand, 4 – 12 % α-olefin is generally added to LLDPE to reduce the density to 0.935 – 0.915. The more α-olefins added to the polymer, the greater the number of short-chain branches and the lower the density. Addition of 1-butene is preferred in many of the gas-phase processes, e.g., in the Unipol process introduced by Union Carbide in 1977 [107], whereas 1-octene and 1-hexene are preferred in liquid-phase processes.

Major United States producers are Dow Chemical, DuPont, Exxon, Gulf Oil, Union Carbide, Soltex Polymer Corporation, Phillips Petroleum Company, and Allied Corporation. An estimated 85 000 t of α-olefins were copolymerized in HDPE and LLDPE in the United States in 1982.

Because Shell began marketing SHOP olefins in Western Europe, the use of HDPE and LLDPE copolymers has increased in these countries. Olefins derived from paraffin cracking plants are unsuitable as comonomers for polyethylene because of the impurities they contain.

Additional Reactions of α-Olefins.   The reaction of α-olefins with peracid to form epoxides is an interesting route to bifunctional derivatives [108]. Some examples are given below (see also → Epoxides, Section 2.1.).
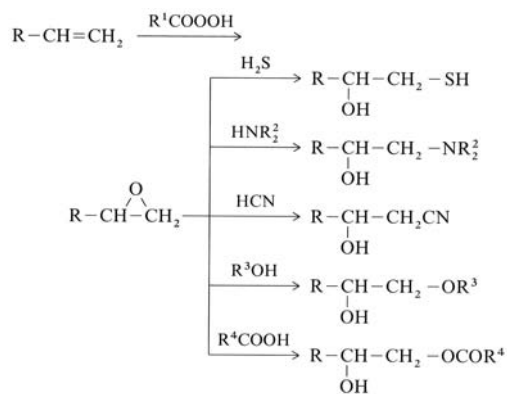
α-Olefin epoxides have also been used in polymer chemistry, e.g., for the modification of epoxy resins. United States producers of α-olefin epoxides include: Union Carbide, Viking, and Dow Chemical.

Another use of α-olefins is conversion into secondary monoalkylsulfates, which are readily degradable surfactants useful in wetting agents and household detergents. They are synthesized by reaction with concentrated sulfuric acid at low

temperature (10 – 20 °C) and with short reaction times (5 min):

R−CH=CH$_2$ $\xrightarrow{H_2SO_4}$ R−CH−CH$_3$ (OSO$_3$H) $\xrightarrow{NaOH}$ R−CH−CH$_3$ (OSO$_3$Na)
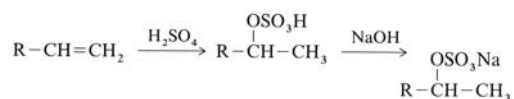
Hydrocarboxylation of α-olefins leads to odd-numbered carboxylic acids. This reaction is carried out with carbon monoxide and water at 200 °C and 20 MPa. The formation of linear carboxylic acids is favored in the presence of cobalt carbonyl – pyridine catalysts. Both the free acids and their esters are used as lubricant additives.

R−CH=CH$_2$ $\xrightarrow[Co]{CO, H_2O}$ R−CH−CH$_3$ (COOH) + R−CH$_2$CH$_2$COOH
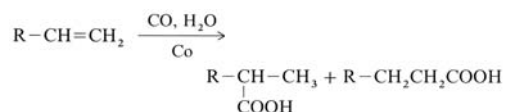
The alkenylsuccinic anhydrides (ASA) should also be mentioned. They are obtained by heating maleic anhydride with α- or internal olefins, and are used as lubricant additives, detergents, and in leather and paper production.

Olefins with more than 30 carbon atoms are waxy and can be used as paraffin substitutes. In 1984 ca. 8000 t of α-olefins were used in the United States for the production of candles, crayons, and coatings.

2.1.4. Economic Aspects of Higher Olefins

Production facilities for α-olefins and their capacities (1984) are listed in Table 13.

The α-olefin market has been subject to fluctuations [109]. Ethyl Corporation, the largest United States α-olefin producer, announced at the end of 1987 the intention to build a large α-olefin plant in Europe with an annual capacity of 250 000 t [110]. This plant would make Ethyl the largest α-olefin producer in Europe.

Shell has also been planning for some time to expand its SHOP processing capacity. The SHOP plant in Geismar, United States, which has been operating since 1977, was expanded in 1982 to an annual capacity of 270 000 t. Construction of a second SHOP unit in Geismar had been announced for 1984 [111]. According to [112], this second plant should come on stream in 1989 with an annual capacity of 243 000 t. Additional expansion is to bring the total annual capacity at Geismar to 590 000 t.

Shell has also announced changes in Europe [113]. The plant at Stanlow, United Kingdom, operating since 1982, is to be expanded to an annual capacity of 220 000 t; once this plant is fully operational, the plant at Pernis, The Netherlands which for some time has produced only 60 000 – 70 000 t/a, is to be closed down.

Mitsubishi Petrochemical has expressed an interest in constructing a SHOP plant in Kashina, Japan in a joint venture with Shell [114]. Other projects under discussion are SHOP plants in New Zealand and in Canada [115].

Uses of linear olefins in the United States and in Western Europe are given in Table 14.

2.2. Dienes and Polyenes

2.2.1. Low Molecular Mass 1,3-Dienes

Industrially, the most important 1,3-dienes are butadiene, isoprene, and cyclopentadiene (→ Butadiene; → Cyclopentadiene and Cyclopentene;

Table 13. Linear α-olefin producers (January 1984)

Manufacturer	Location	Process	Annual capacity (10^3 t)
Gulf Oil	Cedar Bayou, Texas	Oligomerization (Gulf process)	90
Mitsubishi	Mizushima, Okayama	Oligomerization (Gulf process)	30
Ethyl Corp.	Pasadena, Texas	Oligomerization (Ethyl process)	450
Chevron	Richmond, California	Paraffin cracking	40
Shell	Berre (France)	Paraffin cracking	90
	Pernis (The Netherlands)	Paraffin cracking	170
	Geismar, Louisiana	SHOP	270
	Stanlow (UK)	SHOP	170
		Total	1310

Table 14. Uses of higher linear olefins (1982) (estimate by the Stanford Research Institute)

Final products	Olefin consumption (10^3 t)	
	United States[*]	Western Europe
Oxo alcohols	67	145 – 160
Amines and derivatives	13 – 17	**
α-Olefinsulfonates (AOS)	7	3
Linear alkylbenzenes (LAB)	1 – 2	75 – 80
Copolymers (HDPE, LLDPE)	85	**
Synthetic lubricants (SHC)	25	**
Lubricant additives	15	20

[*] Figures refer exclusively to α-olefins.
** Unknown.

→ Isoprene). The conjugated dienes listed below are of lesser importance.

Piperylene (1,3-pentadiene) is present at a level of >10 % in the C_5 steam cracker fraction; it is expensive to separate from the C_5 cut. Polymers and copolymers with, for example, butadiene have been produced but have not yet found a technical application.

2,3-Dimethylbutadiene was the first monomer to be converted on an industrial scale to a synthetic rubber, referred to as methyl rubber. It was developed by HOFFMANN in 1910 and produced during 1914 – 1918. It suffered, however, from several disadvantages (excessive hardness, sensitivity to oxidation) and later lost its importance. The early synthesis of the monomer involved conversion of acetone to pinacol, which is then dehydrogenated to the diene in the presence of aluminum oxide as catalyst. Modern synthesis starts with propene, which is dimerized to 2,3-dimethylbutene [103], [104] and subsequently dehydrogenated:
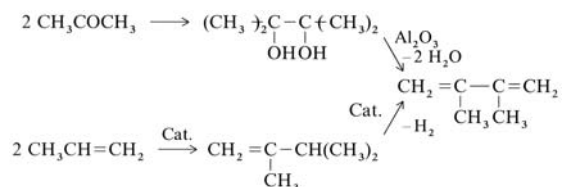
Chloroprene (→ Chloropropanes, Chlorobutanes, and Chlorobutenes), $CH_2=CCl-CH=CH_2$, 2-chloro-1,3-butadiene, is used to form polychloroprene (neoprene), which is extremely resistant to oil, abrasion, and ageing. As with all poly-

mers containing a large proportion of halogen, these products are resistant to ignition. Vulcanized polychloroprene is used in, for example, conveyer belts, cable shielding, and protective clothing. Nonvulcanized polymers are used as contact adhesives in plastics manufacturing.

Chloroprene can be produced by two routes. In the older process, acetylene is first dimerized to vinyl acetylene and hydrogen chloride then added to the triple bond; both steps take place in the presence of CuCl as catalyst. The second process involves chlorination of butadiene, at 300 °C with chlorine to yield a mixture of dichlorobutenes. The 1,2-adduct is subsequently dehydrochlorinated to yield chloroprene. The 1,4-adduct can be isomerized to the 1,2-adduct:
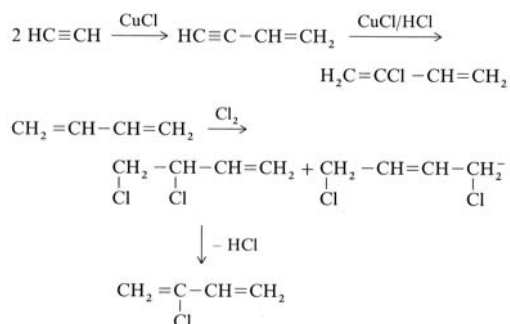
2.2.2. Synthesis of Dienes and Polyenes by Oligomerization

A multitude of linear and cyclic dienes and polyenes can be synthesized by transition metal-catalyzed oligomerization or by cooligomerization [75]. Only a few examples will be described below, some of which are used commercially.

Butadiene can be converted into six cyclooligomers in a nickel-catalyzed reaction [116]. The synthesis can be steered in the desired direction by a suitable choice of catalyst.
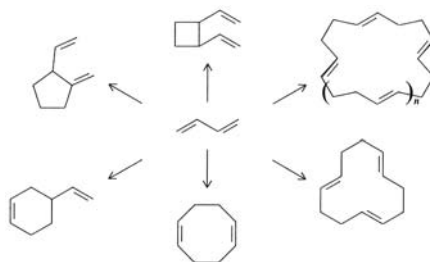
1,5-Cyclooctadiene is produced by Shell and by Hüls and is used, for example, as starting material for suberic acid and poly(octenamer) (→ Cyclododecatriene, Cyclooctadiene, and 4-Vinylcyclohexene).

1,5,9-Cyclododecatriene is produced by Du-Pont, Shell, and Hüls using nickel or titanium as catalyst; it is used in the synthesis of nylon 12, dodecandioic acid, and hexabromocyclododecane.

4-Vinylcyclohex-1-ene is also accessible from butadiene but is, as yet, of little commercial importance. The possibility of using it as a precursor in styrene synthesis has been discussed.

An example of catalytic cooligomerization is the reaction between butadiene and ethylene [117].
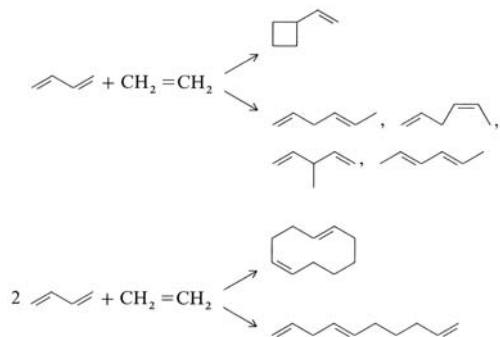

Whereas the cyclic 1:1 product vinylcyclobutane and the C_{10} oligomers cyclodecadiene and 1,4,9-decatriene are not yet used commercially, the linear oligomer, 1,4-hexadiene, is produced as a monomer for the production of ethylene – propene – diene (EPDM) elastomers. Homogeneous catalysis with rhodium or palladium complexes leads to *trans*-1,4-hexadiene; cobalt and iron catalysts yield predominantly the *cis*-1,4-product. Rhodium catalysts are used in commercial production.

Ethylidenenorbornene, also a comonomer for EPDM polymers, is also accessible via cooligomerization. One of the routes employs the Diels – Alder reaction starting with butadiene and cyclopentadiene, the other couples norbornadiene and ethylene in the presence of a nickel catalyst. Vinylnorbornene is formed as an intermediate in both routes.
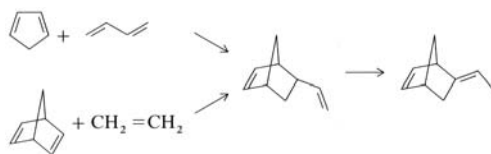

2.2.3. Synthesis of Dienes and Polyenes by Metathesis

Metathesis offers a simple path to α,ω-diolefins that are not easily obtained by other routes [118]. Starting materials are cycloolefins, which can be prepared, for example, by cyclooligomerization of butadiene (see Section 2.2.2) and subsequent partial hydrogenation. Metathetic conversion with ethylene opens the cycloolefin to an α,ω-diene. In this manner, 1,5-cyclooctadiene gives two molecules of 1,5-hexadiene; cyclooctene forms 1,9-decadiene; and cyclododecene leads to 1,13-tetradecadiene.
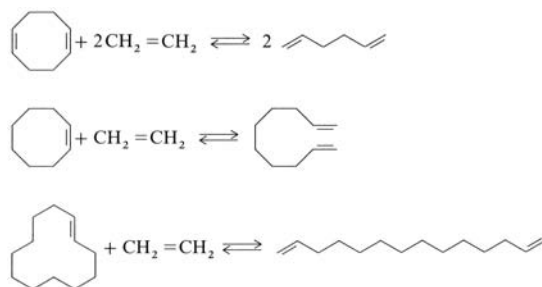
Heterogeneous rhenium catalysts are preferred because they allow the reaction to proceed under very mild conditions (5 – 20 °C, 0.1 – 0.2 MPa ethylene). A plant with an annual capacity of 3000 t using this FEAST (Further Exploitation of Advanced Shell Technology) process was brought on stream by Shell in Berre (France) in 1987. The products are suitable for the synthesis of numerous fine chemicals, e.g., production of long-chain diketones, for dibromides, diepoxides, dialdehydes, dithiols, and diamines.

4-Vinylcyclo-1-hexene undergoes self metathesis. Elimination of ethylene yields 1,2-bis (3-cyclohexenyl)ethylene, which has been used as a starting material for fire retardants.
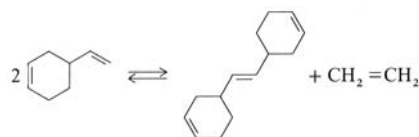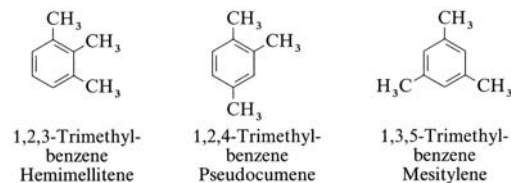
3. Alkylbenzenes

→ Toluene, → Xylenes, and → Ethylbenzene are separate keywords.

3.1. Trimethylbenzenes

Properties. The three isomers of trimethylbenzene are colorless liquids. Some of their physical properties are listed in Table 15.

1,2,3-Trimethyl-
benzene
Hemimellitene

1,2,4-Trimethyl-
benzene
Pseudocumene

1,3,5-Trimethyl-
benzene
Mesitylene

The methyl groups of trimethylbenzenes are converted to carboxyl groups on oxidation. Dilute nitric acid oxidizes mesitylene to the corresponding tricarboxylic acid, trimesic acid [554-95-0]. In pseudocumene the preferred site of reaction for halogenation, sulfonation, and nitration is the 5-position; disubstitution leads to 3,5-derivatives. Mild oxidation of pseudocumene or mesitylene, with manganese- or lead dioxide, or electrolytically, leads to 2,4- or 3,5-dimethylbenzaldehyde, respectively.

Production. Hemimellitene, pseudocumene, and mesitylene are found in coal tar oil. The compounds can be isolated by distillation and purified by the differential hydrolysis of their sulfonic acids [120]. More important industrially is the occurrence of trimethylbenzenes in some mineral oils, and their formation during processing of crude oil, especially catalytic cracking and reforming. Pseudocumene is obtained in 99 % purity by superfractionation from the C_9 cut of crude oil refining [121].

Table 15. Physical properties of alkylbenzenes [119]

Compound	CAS registry number	M_r	mp, °C	bp, °C	d_4^{20}, g/cm^3	n_D^{20}
1,2,3-Trimethylbenzene, hemimellitene	[526-73-8]	120.19	−25.4	176.1	0.8944	1.5139
1,2,4-Trimethylbenzene, pseudocumene	[95-63-6]	120.19	−43.8	169.3	0.8758	1.5048
1,3,5-Trimethylbenzene, mesitylene	[108-67-8]	120.19	−44.7	164.7	0.8652	1.4994
1,2,3,4-Tetramethylbenzene, prehnitene	[488-23-3]	134.22	− 6.2	205	0.9052	1.5203
1,2,3,5-Tetramethylbenzene, isodurene	[527-53-7]	134.22	−23.7	198	0.8903	1.5130
1,2,4,5-Tetramethylbenzene, durene	[95-93-2]	134.22	79.2	196 – 198	0.8380[a]	1.4790 [a]
Pentamethylbenzene	[700-12-9]	148.25	54.5	232	0.917	1.527
Hexamethylbenzene, mellitene	[87-85-4]	162.28	166 – 167	265	1.0630[b]	
1,2-Diethylbenzene	[135-01-3]	134.22	−31.2	183.5	0.8800	1.5035
1,3-Diethylbenzene	[141-93-5]	134.22	−83.9	181.1	0.8602	1.4955
1,4-Diethylbenzene	[105-05-5]	134.22	−42.8	183.8	0.8620	1.4967
1,2,3-Triethylbenzene	[42205-08-3]	162.27				
1,2,4-Triethylbenzene	[877-44-1]	162.27		217.5[c]	0.8738	1.5024
1,3,5-Triethylbenzene	[102-25-0]	162.27	−66.5	215.9	0.8631	1.4969
1,2,3,4-Tetraethylbenzene	[642-32-0]	190.33	11.8	251[d]	0.8875	1.5125
1,2,3,5-Tetraethylbenzene	[38842-05-6]	190.33	−21	247[d]	0.8799	1.5059
1,2,4,5-Tetraethylbenzene	[635-81-4]	190.33	10	250	0.8788	1.5054
Pentaethylbenzene	[605-01-6]	218.38	<−20	277	0.8985[e]	1.5127
Hexaethylbenzene	[604-88-6]	246.44	129	298	0.8305[f]	1.4736[f]
1-Ethyl-2-methylbenzene, 2-ethyltoluene	[611-14-3]	120.19	−80.8	165.2	0.8807	1.5046
1-Ethyl-3-methylbenzene, 3-ethyltoluene	[620-14-4]	120.19	−95.5	161.3	0.8645	1.4966
1-Ethyl-4-methylbenzene, 4-ethyltoluene	[622-96-8]	120.19	−62.3	162	0.8614	1.4959

[a] At 81 °C.
[b] At 25 °C.
[c] 100.4 kPa.
[d] 97.6 kPa.
[e] At 19 °C.
[f] At 130 °C.

Pseudocumene and hemimellitene can be obtained by extractive crystallization of the C_9 cut with urea [122]. Trimethylbenzenes can be produced by Friedel – Crafts methylation of toluene or xylene with chloromethane in the presence of aluminum chloride. Trimethylbenzenes, especially pseudocumene and mesitylene, are also formed by liquid-phase disproportionation of xylene in the presence of aluminum chloride. These reactions can be carried out in the gas phase at high temperature on aluminum silicate catalysts.

A more recent method for the methylation of xylene with methanol or dimethyl ether on fluorine-containing crystalline borosilicate, aluminosilicate, or boroaluminosilicate (ZSM-5) at 300 °C and atmospheric pressure yields pseudocumene and durene almost exclusively, both of which may be isolated at >99 % purity [123]. Trimethylbenzenes are also generated in the reaction of toluene with synthesis gas over a dual catalyst consisting of a metal oxide component and an aluminum silicate, at 200 – 400 °C and up to 20 MPa [124]. Pseudocumene is also generated from methanol as a byproduct of the Mobil MTG (methanol to gasoline) process (see Section 3.2). Fusel oils and other fermentation products may be reacted on the zeolite catalyst HZSM-5 to form aromatic compounds, including trimethylbenzenes [125].

Uses. Mesitylene is used in the synthesis of dyes and antioxidants, and as a solvent. Pseudocumene is a starting material for dyes, pharmaceuticals and, especially, for trimellitic anhydride [552-30-7], which is then converted to heat-resistant polyamideimides and polyesterimides (see also → Carboxylic Acids, Aromatic, Section 4.3.). Hemimellitene is an intermediate in the production of fragrances (→ Flavors and Fragrances).

3.2. Tetramethylbenzenes

Properties. Some physical properties of the three tetramethylbenzene isomers are listed in Table 15. Prehnitene and isodurene are colorless liquids; durene forms colorless, monoclinic crystals that sublime slowly at room temperature and that have an odor reminiscent of camphor.

1,2,3,4-Tetramethyl-
benzene
Prehnitene

1,2,3,5-Tetra-
methylbenzene
Isodurene

1,2,4,5-Tetramethyl-
benzene
Durene
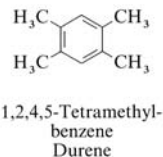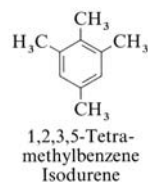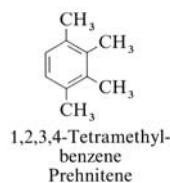
Tetramethylbenzenes are readily soluble in aromatic hydrocarbons, acetone, ether, and alcohol. Durene is highly reactive; nitration, chlorination, sulfonation, and chloromethylation occur almost as readily as with phenol. The methyl groups may be successively oxidized to carboxylic acids; the presence of the corresponding mono-, di-, tri-, and tetracarboxylic acids can be demonstrated during liquid-phase oxidation of durene in the presence of cobalt catalyst [126].

Production. The tetramethylbenzenes also occur in coal tar from anthracite and lignite, and in the reformed fraction of oil refineries. The isolation of durene by crystallization is aided by its relatively high melting point; isodurene becomes enriched in the mother liquor. Methylation of xylene leads to an isomeric mixture, from which durene, prehnitene, and isodurene can be obtained [120]. Durene is produced by liquid-phase methylation of pseudocumene with chloromethane in the presence of aluminum chloride [127]. In more recent processes durene is produced by reaction of xylene or pseudocumene with methanol in the gas phase over aluminum silicates; the most successful process uses the zeolites ZSM-5 and TSZ [128], [129]. In the MTG process, commercialized in New Zealand since 1986, the production of automotive fuels from methanol over ZSM-5 yields an unacceptable quantity of durene, which has to be removed from the fuel to avoid carburetor clogging by the high melting point impurity. The durene is currently removed by catalytic isomerization, disproportionation, and reductive demethylation. The possibility of isolating durene from the MTG process is being investigated [130].

Uses. Oxidation of durene leads to the commercially important pyromellitic dianhydride [*89-32-7*] used as a starting material for heat-resistant polyimides (→ Polyimides) and as a hardener for epoxy resins (→ Epoxy Resins). Pyromellitic esters serve as migration-resistant plasticizers for poly(vinyl chloride) (→ Carboxylic Acids, Aromatic, Section 4.2.).

3.3. Penta- and Hexamethylbenzene

Properties. Some physical properties are listed in Table 15. Both compounds are crystalline at room temperature; they dissolve easily in benzene and ethanol. The methyl groups are readily oxidized to carboxyl groups. Irradiation with light converts hexamethylbenzene into its valence isomer hexamethyl Dewar benzene (1,2,3,4,5,6-hexamethylbicyclo [2.2.0] hexa-2,5-diene, [*7641-77-2*]). Electrophilic substitution on the free ring site of pentamethylbenzene proceeds readily.

Production. Penta- and hexamethylbenzene are generated by liquid-phase Friedel – Crafts alkylation of xylene or pseudocumene with chloromethane in the presence of aluminum chloride [127]. If the reaction is carried out at 140 – 180 °C in *o*-dichlorobenzene, hexamethylbenzene with a purity of 98 % can be crystallized directly from the reaction mixture [131]. In a more recent method, penta- and hexamethylbenzene can be produced simultaneously by reaction of phenol and methanol in toluene in the presence of a zinc aluminate catalyst at 330 – 360 °C [132]. The products are then separated by fractional crystallization. Hexamethylbenzene is formed by thermal rearrangement of hexamethyl Dewar benzene, which is readily obtained from 2-butyne [133].

Uses. Pentamethylbenzene is of little commercial importance. Hexamethylbenzene is an intermediate in the fragrance industry. It is of scientific interest in studies of charge transfer complexes and exciplexes, in which, like other methylbenzenes, it may function as donor [134].

3.4. Diethylbenzenes

Properties. For some physical properties see Table 15.

1,2-Diethyl-benzene   1,3-Diethyl-benzene   1,4-Diethyl-benzene
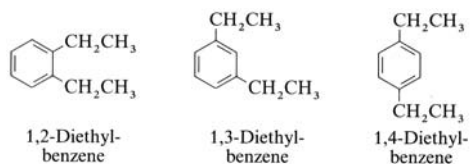
Production. The three isomeric diethylbenzenes (DEB) occur as byproducts in the production of ethylbenzene from benzene and ethylene but are, generally, recycled to undergo transalkylation (→ Ethylbenzene). In the liquid-phase Friedel – Crafts process with aluminum chloride an increase in the feedstock ratio of ethylene to benzene may raise the DEB concentration in the output to 35 %. The DEB fraction consists of ca. 65 % 1,3-DEB, 30 % 1,4-DEB, and only 5 % 1,2-DEB. A similar isomer distribution is found in the product mixture from gas-phase alkylation of ethylbenzene with ethylene on an unmodified HZSM-5 zeolite catalyst. By modifying the catalyst, the zeolite pore may be narrowed to such an extent that, based on geometry alone, only 1,4-diethylbenzene is formed, rather than the bulkier 1,2- and 1,3-isomers. The Mobil gas-phase alkylation, which is based on such a shape-selective zeolite, converts ethylbenzene to DEB at 400 °C and 0.7 MPa with 88 % selectivity; more than 99 % of the DEB is the 1,4-isomer [135]. Nearly quantitative formation of 1,3-DEB occurs at low temperature in the liquid phase by disproportionation of ethylbenzene in the presence of at least 10 vol % HF and 0.3 – 0.5 mol BF_3 per mol ethylbenzene.

Uses. Diethylbenzenes may be converted to divinyl benzenes by catalytic dehydrogenation (→ Hydrogenation and Dehydrogenation). The latter are useful in the production of cross-linked polystyrenes. DEB is contained in the product of the MTG process (see Section 3.2) and improves the properties of the gasoline.

3.5. Triethylbenzenes and More Highly Ethylated Benzenes

Properties. For some physical properties see Table 15.

Production. The more highly ethylated benzenes are produced in the liquid phase in a similar manner as that described for diethylbenzene. 1,3,5-Triethylbenzene may be generated in excellent yield by disproportionation of diethylbenzene with BF_3 and HF at 75 °C. The same result is obtained with $AlCl_3$ – HCl as catalyst. 1,3,5-Triethylbenzene is also formed by cyclocondensation of 2-butanone in the presence of sulfuric acid. Hexaethylbenzene is formed in nearly quantitative yield when ethylene is passed into the $AlCl_3$ complex of aromatics until a mass of crystals is formed, which is then worked up with water.

3.6. Ethylmethylbenzenes (Ethyltoluenes)

Properties. Some physical properties are collected in Table 15.

Production. Ethyltoluene is produced in similar fashion to ethylbenzene, i.e., by ethylation of toluene. Alkylation of toluene with ethylene in the presence of $AlCl_3$ and HCl gives all three isomers of ethyltoluene and more highly ethylated derivatives. A typical reaction mixture contains 48 % unreacted toluene, about 12 % 4-ethyltoluene, 19 % 3-ethyltoluene, 4 % 2-ethyltoluene, 14 % higher aromatics, and barely 1 % tar [135]. According to a Dow process, subsequent distillation gives a mixture of 3- and 4-ethyltoluenes [136]. 2-Ethyltoluene, toluene, and the more highly alkylated toluenes are then recycled. The gas-phase ethylation of toluene on unmodified HZSM-5 zeolite catalyst at 350 °C gives 23 % 4-ethyltoluene, 53 % 3-ethyltoluene, 8 % 2-ethyltoluene, and 10 % higher aromatics [137]. Formation of the 2- and 3-isomers in the ethylation of toluene can be almost completely suppressed by the use of a shape-selective ZSM-5 zeolite that has been modified by addition of phosphorus, boron, or other elements, and by suitable physical treatment. In a Mobil process, 4-ethyltoluene of 97 % purity is generated in this manner at 350 – 400 °C [137]. A patent granted to Universal Oil Products claims a process for the production of an alkylbenzene mixture, which also contains ethyltoluene, from toluene and synthesis gas [124].

Uses. The mixture of 3- and 4-ethyltoluene obtained by the Dow process is catalytically dehydrogenated to the corresponding mixture of methylstyrenes, known commercially as vinyltoluene [25013-15-4], and then polymerized to "poly(vinyltoluene)." Dehydrogenation of the practically pure 4-ethyltoluene from the Mobil process to 4-methylstyrene [622-97-9] occurs analogously on the route to "poly(p-methylstyrene)". A plant for the alkylation of toluene to 4-ethyltoluene by the Mobil process was opened in 1982 by Hoechst (now Hoechst-Celanese) in Baton Rouge, Louisiana [138]; the plant has an annual capacity of 16 000 t of 4-methylstyrene and has been purchased by Deltech in 1989. The output of the two products vinyltoluene and p-methylstyrene is estimated at 25 000 t/a [139] ($\rightarrow$ Polystyrene and Styrene Copolymers).

3.7. Cumene

Properties. Cumene [98-82-8], 2-phenylpropane, isopropylbenzene, C_9H_{12}, M_r120.19, is a colorless, mobile liquid with a characteristic, aromatic odor.
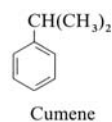
Cumene

The effect of cumene in increasing the octane rating of motor fuels ($\rightarrow$ Octane Enhancers) has long been known. Large plants for production of cumene, which was used as a component of aviation fuel, were constructed in the United States during the early 1940s. Some physical properties of cumene are listed below [140], [141]:

mp, °C	−96.04
bp, °C	152.39
d^{20}, g/cm^3	0.86179
n_D^{20}	1.49145
Specific heat (25 °C), J g^{-1} K^{-1}	1.96
Heat of vaporization, kJ/mol	
at 25 °C	44.23
at 152.4 °C	37.74
T_{crit}, K	631
p_{crit}, MPa	3.21
V_{crit}, cm^3/mol	428
Flash point, °C	43
Ignition temperature, °C	425

The variation of vapor pressure with temperature is given below:

t, °C	2.9	38.3	66.1	88.1	129.2
Vapor pressure, kPa	0.13	1.33	5.33	15.33	53.33

For more thermodynamic data, see [142]. Explosion limits for the system cumene vapor – oxygen – nitrogen at standard pressure and at 0.56 MPa are given in [143]. For cumene – air mixtures the explosion limits are 0.8 – 6.0 vol % cumene, corresponding to a cumene concentration of 40 – 300 g/m^3 [144]. Cumene forms azeotropes with water, aliphatic carboxylic acids, ethylene glycol ethers, cyclohexanol, and cyclohexanone.

Production. Cumene is produced from benzene [71-43-2] and propene [115-07-1] in the presence of an acidic catalyst:

$$C_6H_6 + C_3H_6 \longrightarrow C_6H_5CH(CH_3)_2 \quad \Delta H = -113 \text{ kJ/mol}$$

Two processes are employed industrially (see also→ Acylation and Alkylation). In the *UOP process* a fixed bed consisting of polyphosphoric acid on a silica support is used as the catalyst [145]. The reaction takes place mainly in the gas phase at ≥200 °C and ≥2 MPa. Pure propene or propene with a propane content ≥5 % is used as raw material, together with benzene (min. purity 99.5 %) in up to 12-fold molar excess; this leads to high distillation costs in the product work-up. The yield of cumene is 97 % based on benzene and 90 % based on propene [146]. The losses are caused by overalkylation and oligomerization of the propene. The high-boiling residue contains 50 – 60 % diisopropylbenzenes (*o*- : *m*- : *p*- ratio 1 : 2 : 2 – 3) and numerous other byproducts. It is not possible to recycle these products to the alkylation reactor, because polyphosphoric acid has no transalkylation properties.

The *second industrial process* works in the liquid phase at 50 – 80 °C; aluminum chloride or the liquid double compound formed from aluminum chloride, (isopropyl-)benzene, and hydrogen chloride is employed as the catalyst. This complex is separated from the product stream, as a heavy phase and is returned to the alkylation reactor. Except for a small purge stream higher alkylated byproducts are recycled to the alkyl-ation step, whereby essentially complete use of both benzene and propene bound in di- and triisopropylbenzenes is achieved by transalkylation. The yield of cumene, referred to benzene and propene, is 99 % and 98 %, respectively. The UOP process is used predominantly. Higher selectivity and the lower energy requirements, however, are now making the aluminum chloride process more attractive [146].

Uses. The production capacity for cumene in Western Europe, the United States, and Japan amounts to 2×10^6, 2×10^6, and 4×10^5 t/a, respectively. Cumene is used almost exclusively for the production of phenol [108-95-2] and acetone [67-64-1] (→ Acetone, Section 4.1.; → Phenol). This process is based on the discovery in 1944 that cumene hydroperoxide [80-15-9], obtained by oxidation of cumene with oxygen, can be cleaved under the catalytic action of strong acids:

$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH$$
$$C_6H_5C(CH_3)_2OOH \longrightarrow C_6H_5OH + CH_3COCH_3$$
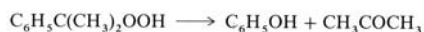
Both reactions are exothermic; the enthalpy of reaction amounts to 121 and 255 kJ/mol, respectively. (For cumene quality specifications, see → Acetone.)

Pure α-methylstyrene can be obtained as a byproduct of the phenol process. Cumene hydroperoxide is used as a radical initiator for the copolymerization of styrene with butadiene and acrylates, and also for the radical cross-linking of unsaturated polyester resins. Addition of cumene hydroperoxide to α-methylstyrene gives dicumyl peroxide, used for radical cross-linking of polyolefins. Hydrogenation of the aromatic nucleus in cumene gives isopropylcyclohexane (hydrocumene), a cycloaliphatic solvent with a high boiling point (154.5 °C) and a low freezing point (−90 °C).
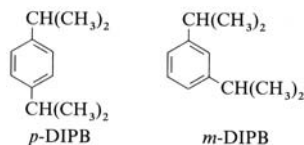
3.8. Diisopropylbenzenes

1,4-Diisopropylbenzene [100-18-5] *p*-diisopropylbenzene, *p*-DIPB, $C_{12}H_{18}$, M_r162.26, 1,3-diisopropylbenzene [99-62-7], *m*-diisopropylbenzene, *m*-DIPB, and mixtures of these isomers, are industrially important. Some physical properties of diisopropylbenzenes are

Table 16. Physical properties of diisopropylbenzene isomers [140]

Property	m-DIPB	o-DIPB	p-DIPB
CAS registry number	[99-62-7]	[577-55-9]	[100-18-5]
mp, °C	−63.13	−56.68	−17.07
bp, °C	203.18	203.75	210.35
d^{20}, g/cm^3	0.8559	0.8779	0.8568
η_D^{20}	1.4883	1.4960	1.4893

given in Table 16.

p-DIPB   *m*-DIPB

The flash point of DIPB mixtures is 77 °C; the ignition temperature is 449 °C. Inhalation of DIPB vapor can lead to the appearance of narcotic effects.

Production. Diisopropylbenzenes are present in the high boiling fractions, in which they may account for 50 – 70 wt %, of cumene plants, together with numerous other byproducts. Processes for the production of *m*- and *p*-DIPB from these fractions have been suggested [147], [148]. The high-boiling fraction of the aluminum chloride process frequently contains 1,1,3-trimethylindan [2613-76-5], bp 204.8 – 204.9 °C, which cannot be separated from the *m*- and *p*-DIPB at a justifiable cost.

For production from benzene and propene alkylation catalysts that possess high isomerization and transalkylation activities are employed. Examples include aluminum chloride – hydrogen chloride [149], [150], silica – alumina [151], [152], boron trifluoride-treated alumina [153], and zeolithes [154]. The process is controlled in such a way that cumene formed at a later stage is alkylated with propene. The desired DIPB isomer is isolated by distillation and the undesired DIPB isomer, together with triisopropylbenzenes, are converted to cumene by reaction with benzene in a transalkylation step. The aim in both the alkylation and the transalkylation steps is to reach thermodynamic equilibrium, at which the *o*-diisopropylbenzene is present at only ca. 0.1 %.

Uses. 1,3-Diisopropyl- and 1,4-diisopropylbenzene are the starting materials for new synthetic routes to resorcinol (→ Resorcinol) and hydroquinone (→ Hydroquinone), respectively [155], which are used industrially in Japan and the United States [152]. Furthermore, a process for the production of phloroglucin, 1,3,5-trihydroxybenzene, from 1,3,5-triisopropylbenzene has been developed [156]. The monohydroperoxides of 1,3- and 1,4-diisopropylbenzene are used as initiators for the thermal cross-linking of unsaturated polyester resins, and for the emulsion polymerization of dienes, styrene, and acrylates. Oxidation gives *a,a,a′,a′*-tetramethylphenylenebiscarbinols. Dehydrogenation gives diisopropenylbenzenes, which by reaction with phenol or aniline give bisphenols or bisanilines, respectively, which are used as building blocks for polycarbonates, polyamides, polyesteramides, and polyurethanes (→ Polyamides; → Polycarbonates; → Polyurethanes). Addition of isocyanic acid to diisopropenylbenzenes yields diisocyanates, from which light-stable polyurethanes can be produced [157]. Bis(*tert*-butylperoxyisopropyl)benzene, preferably prepared from the mixture of the corresponding biscarbinols of 1,3- and 1,4-DIPB, is used as a cross-linking agent for polyolefins.

3.9. Cymenes; C$_4$- and C$_5$-Alkylaromatic Compounds

The compounds listed in Table 17 are industrially important. Mixtures of 3-isopropyltoluene (*m*-cymene) and 4-isopropyltoluene (*p*-cymene) can be obtained by propylation of toluene in the presence of an isomerization-active Friedel – Crafts catalyst. These two isomers can be separated by distillation only with difficulty. The mixture is used for the production of *m*- and

Table 17. Physical properties of some alkylbenzenes

Compound	CAS registry number	mp, °C	bp, °C	η_D^{20}
3-Isopropyltoluene	[535-77-3]	−63.75	175.05	1.4929
4-Isopropyltoluene	[99-87-6]	−67.94	177.10	1.4909
2-Isopropyltoluene	[527-84-4]	−71.54	178.15	1.5005
Isobutylbenzene	[538-93-2]	−51.48	172.76	1.4864
tert-Butylbenzene	[98-06-6]	−57.85	169.12	1.4926
4-*tert*-Butyltoluene	[98-51-1]	−53	192.7	1.4919
5-*tert*-Butyl- *m*-xylene	[98-19-1]	−18.3	209	1.4956
tert-Pentylbenzene	[2049-95-8]		192.38	1.4958

p-cresol, ($\rightarrow$ Cresols and Xylenols, Section 1.4.3.), [158]. Treatment of (methyl-)aromatic compounds with isobutene yields *tert*-butyl-substituted compounds, which are used as solvents (*tert*-butylbenzene) and for the production of fragrances, pharmaceuticals, and herbicides.

m-Cymene   *p*-Cymene
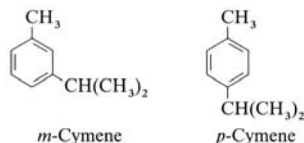
The introduction of a *tert*-pentyl group can be achieved by the use of *tert*-pentyl chloride as the alkylating agent and aluminum chloride, iron(III) chloride, or zirconium tetrachloride as the catalyst. 2-*tert*-pentylanthraquinone, obtained from *tert*-pentylbenzene and phthalic anhydride, is employed in the industrial production of hydrogen peroxide. Isobutylbenzene, required for the synthesis of pharmaceuticals and fragrances, is produced in industrial quantities by treatment of toluene with propene over catalysts containing alkali metals, such as potassium – graphite inclusion compounds or sodium – potassium on a support [159].

3.10. Monoalkylbenzenes with Alkyl Groups >C_{10}

Monoalkylbenzenes with secondary alkyl groups C_{10} to ca. C_{14} are used as starting materials for the production of alkylbenzenesulfonates (ABS) ($\rightarrow$ Surfactants). Only secondary alkylbenzenesulfonates with unbranched (linear) side chains (LABS) are of practical importance as raw materials for detergents, as they are extensively degraded (>90 %) by microorganisms in sewage plants after a relatively short period of time.

Before the introduction of LABS, which took place in the Federal Republic of Germany in 1962, alkylbenzenesulfonates with highly branched C_{12} side chains were used. These compounds, tetrapropylene benzenesulfonates, were produced from the products of alkylation of benzene with propene tetramer, itself obtained by the tetramerization of propene by contact with phosphoric acid. These sulfonates possess excellent detergent properties, but their biological degradeability is insufficient.

Production. Linear secondary alkylbenzenes are obtained industrially by reaction of benzene with secondary alkyl chlorides (chloroparaffins) or with olefins under the influence of a Friedel – Craft catalyst such as aluminum chloride, hydrofluoric acid, or sulfuric acid ($\rightarrow$ Acylation and Alkylation, $\rightarrow$ Acylation and Alkylation, Section 2.1.1.). The following methods have been described for the production of the required alkyl chlorides and olefins [160]:

1. Dehydrogenation of $C_{10} - C_{13}$-*n*-alkanes, according to the Pacol process of UOP (see Section 2.1.2.1), on a fixed bed at 400 – 500 °C, with a conversion of 10 – 15 %; the ensuing mixture of internal olefins and unreacted alkanes is used for the alkylation of benzene. The *n*-$C_{10} - C_{13}$-alkanes used in the dehydrogenation are obtained from the kerosene fraction of crude oil by adsorption on molecular sieves, according to well known processes such as IsoSiv of Union Carbide, or Molex of UOP.
2. By chlorination of $C_{10} - C_{13}$-alkanes at ca. 100 °C to a conversion of ca. 30 %, and use of the resulting mixture of alkanes and secondary monochloroalkanes for alkylation of benzene.
3. By chlorination of $C_{10} - C_{13}$-*n*-paraffins as in 2) above, followed by dehydrochlorination (elimination of hydrogen chloride) of the monochloroalkanes at 200 – 300 °C over an iron catalyst to give linear alkenes with internal double bonds; these alkenes, in admixture with unreacted paraffins, are then used to alkylate benzene.
4. Metathesis of higher (>C_{18}) with lower (<C_{10}) internal olefins from the Shell SHOP process (see Section 2.1.2.2) to give olefins of intermediate molecular mass.

A $C_{10} - C_{13}$-α-olefin fraction suitable for use in detergents can also be obtained by thermal cleavage of $C_{20} - C_{40}$-*n*-paraffins at 500 – 600 °C, according to the older wax-cracking process of Shell (see Section 2.1.2.1).

The alkylation of benzene with chloroparaffin – paraffin mixtures takes place in the presence of aluminum chloride at ca. 50 °C. A relatively high proportion of 2-phenylalkanes is characteristic of secondary alkylbenzenes obtained in this manner [161], [162].
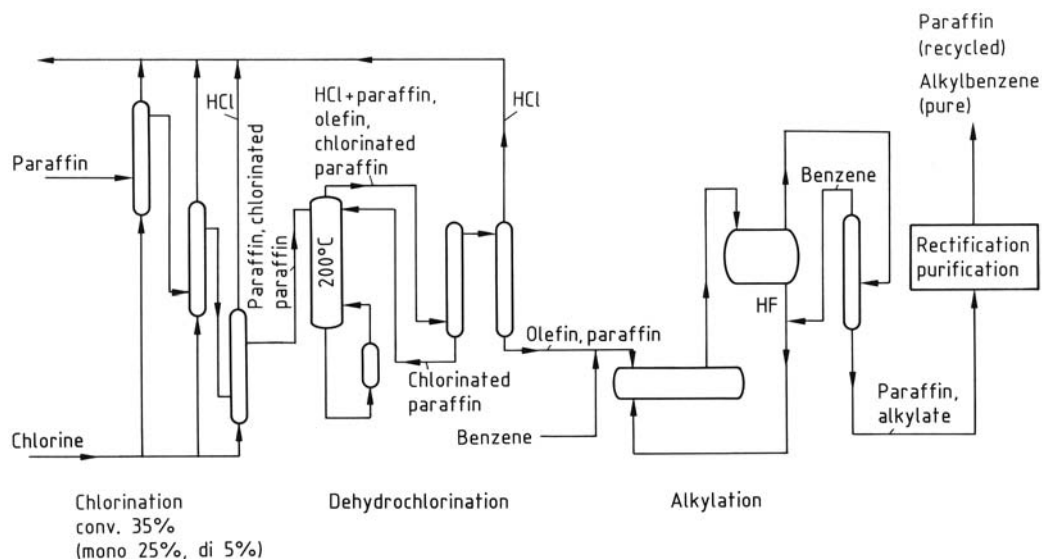
Figure 8.   Production of alkylbenzenes, process of Hüls AG [165]

Dichloroalkanes, always present in the mixture of chloroparaffins even at low levels of chlorination, can lead to the formation of diphenylalkanes, 1,4-dialkyltetralins, and 1,3-dialkylindans. For formation and analytical detection see [163]. The removal of these compounds from monoalkylbenzenes is difficult. Formation of these byproducts can be largely avoided by carrying out the alkylation of benzene with olefins from the dehydrochlorination, where dichloroalkanes are dehydrochlorinated to give tar-like products that are easily separated. In industrial production the reaction of $C_{10} - C_{13}$-olefins with benezene is carried out with a 1 : 10 molar ratio in the presence of anhydrous hydrofluoric acid at 10 °C, a process that dates back to 1949 [164]. The industrial process using the steps paraffin chlorination – dehydrochlorination – alkylation in the presence of hydrofluoric acid was first realized by Chemische Werk Hüls in 1962 [162]. This process is shown in Figure 8. In this way a quality standard for alkylbenzenes for use in detergents was created; in ecological terms, this standard is still valid.

3.11. Diphenylmethane

Diphenylmethane [*101-81-5*] benzylbenzene, $C_{13}H_{12}$, M_r168.24, was first prepared in 1871 by ZINCKE from benzyl chloride and benzene in the presence of zinc dust or copper (I) oxide.
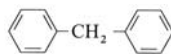
Physical   Properties.   Diphenylmethane forms colorless prismatic needles with a harsh herbaceous odor reminiscent of geranium leaves. It is insoluble in water, soluble in alcohol, ether, chloroform, and benzene.

mp	26 – 27 °C
bp	
101.3 kPa	261 – 262 °C
1.33 kPa	125.5 °C
d_4^{20}	1.006
Flash point ca.	130 °C
Enthalpy of formation	
(room temperature)	109.6 kJ/mol
Enthalpy of combustion	
(20 °C)	41.2×10^3 kJ/kg

Chemical Properties.   As an araliphatic hydrocarbon, diphenylmethane displays the chemical properties of both aromatic and aliphatic compounds. It is difficult to limit substitution in the phenyl radicals to one of the rings; therefore, controlled syntheses of particular

unsymmetrically substituted diphenylmethanes must be carried out by different paths. Under suitable reaction conditions the methylene group can also be substituted, e.g., by halogen or nitro groups. Benzophenone can be produced by oxidation, for example, with oxygen over various catalysts, chromic acid or dilute nitric acid. Hydrogenation in ethanol over a nickel catalyst leads to dicyclohexylmethane. When diphenylmethane is passed over platinum – charcoal at 300 °C, cyclization to fluorene takes place.

Production. Of the many known methods to synthesize diphenylmethane only a few are used commercially.

The Friedel – Craft reaction of benzyl chloride with benzene in the presence of aluminum chloride is an important method for production of diphenylmethane:

$$C_6H_5CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5$$

Other known catalysts of this process are elemental aluminum, iron(III) chloride, antimony pentachloride, zinc chloride – hydrogen chloride and boron fluoride dihydrate. When sulfuric acid is used as a condensation agent diphenylmethane yields are 83 % [166] and with polyphosphoric acid yields are over 90 % [167].

Condensation of benzene with formaldehyde in presence of 85 % sulfuric acid yields 79 % diphenylmethane [168].

$$2\ C_6H_6 + HCHO \xrightarrow{H_2SO_4} C_6H_5CH_2C_6H_5$$

Quality Specifications. Commercial diphenylmethane should be at least 97 % pure (GC). It must be free of halogens and have a minimum melting point of 24 °C.

Uses. Diphenylmethane is used in the fragrance industry both as a fixative and in scenting soaps. It can serve as a synergist for pyrethrin in pesticides and insecticides [169], [170]. Diphenylmethane is recommended as a plasticizer to improve the dyeing properties [171], as a solvent for dyes [172], and as a dye carrier for printing with disperse dyes [173]. The addition of diphenylmethane to saturated, linear polyesters improves their thermal stability [174], and its addition to jet fuels increases their stability and lubricating properties [175].

Substituted diphenylmethanes are used as solvents for pressure-sensitive recording materials [176].

4. Biphenyls and Polyphenyls

In the series of aromatic hydrocarbons with polyphenyls or polyaryls of the general formula $C_6H_5(C_6H_4)_nC_6H_5$, only the lowest members ($n = 0, 1$) are economically important. Higher polyphenyls ($n > 2$) are also known and may be isolated from coal tar or from aryl halides by the Ullmann reaction.

4.1. Biphenyl

Biphenyl [*92-52-4*], phenylbenzene, diphenyl, $C_{12}H_{10}$, M_r154.2, was discovered in 1862 by FITTIG by the reaction of bromobenzene with sodium metal. BERTHELOT obtained the compound in 1867 by passing benzene vapor through a heated tube. In 1875 BÜCHNER demonstrated the presence of biphenyl in coal tar [177].
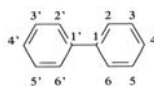

Physical Properties. Pure biphenyl is a white solid; when only slightly impure it has a yellow tint. It crystallizes from solution results as glossy plates or monoclinic prisms. Biphenyl is almost insoluble in water, but is easily soluble in organic solvents such as ethanol, diethyl ether, and benzene. The dipole moment and X-ray measurements demonstrate that the two benzene rings are coplanar in the solid state. In the melt, in solution, and in the vapor free rotation about the central C-C bond can take place; in substituted biphenyls, however, this rotation may be severely restricted, e.g., in dinitrodiphenic acid, leading to the existence of optically active isomers. The most important physical properties are listed below:

mp	69.2 °C [178]
bp (101.3 kPa)	255.2 °C [178]
d_4^{20} (solid)	1.041
d_4^{77} (liquid)	0.9896 [179]
n_D^{77}	1.5873
T_{crit}	515.7 °C [180]
p_{crit}	4.05 mPa
Flash point	113 °C [181]
Ignition temperature	570 °C
Heat of combustion	6243.2 kJ/mol
Heat of vaporization	53.9 kJ/mol
Heat of fusion	18.60 kJ/mol

The variation of some physical properties with temperature is given in Table 18.

Chemical Properties. Biphenyl is a very stable organic compound; in an inert atmosphere it remains unchanged even at a temperature >300 °C. The compound sublimes, distills with steam, and undergoes various substitution reactions; the reactivity is similar to, but less than that of benzene. Substitution reactions, e.g., chlorination, nitration, and sulfonation, occur at the 2- and 4-positions, the latter being the preferred site of attack in Friedel – Crafts reactions.

Production. *Hydrodealkylation of Benzene.* Biphenyl is currently obtained mainly as a by-product in the production of benzene by thermal or catalytic hydrodealkylation of toluene ($\rightarrow$ Benzene, Section 5.3.1.) [182–185]. The reaction is carried out in a hot tube reactor at 700 °C with a hydrogen pressure of 4 MPa; the ratio of hydrogen to toluene is 4 : 1. Toluene conversion ranges from 35 to 85 %, with methane being formed at 2.5 mol % above the stoichiometric.
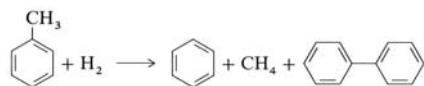
Biphenyl is obtained as the pot residue, following removal of gas and distillation of benzene and toluene; about 1 kg of biphenyl is obtained

Table 18. Temperature dependence of some physical properties of biphenyl [179]

t, °C	100	200	300	350
Vapor pressure, kPa		25.43	246.77	558.06
Liquid density, g/cm^3	0.97	0.889	0.801	0.751
Heat capacity, J/g	1.786	2.129	2.468	2.640

per 100 kg benzene. The biphenyl can be enriched to a purity of 93 – 97 % by distillation.

Thermal Dehydrocondensation of Benzene. Until the early 1970s, biphenyl was produced exclusively by specific thermal dehydrocondensation of benzene [186]. This process yields a higher quality product than the toluene route, e.g., distilled material with a purity >99.5 %; varying quantities of terphenyl isomers and several higher homologues are also obtained.

$$n = 1, 2$$
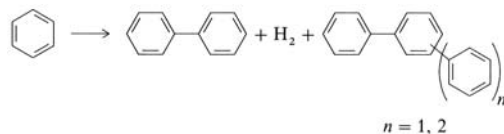
The slightly endothermic dehydrocondensation ($\Delta H = + 8$ kJ/mol [187]) of benzene to biphenyl and terphenyl has been investigated intensively [188], [189]. The formation of biphenyl from benzene starts at ca. 480 °C and increases with increasing temperature and residence time.

Industrially, the reaction is carried out in a multitube reactor, heated electrically [190] or by heat exchanger, at 700 – 850 °C using residence times of the order of seconds. An optimal tube length of 45 – 75 m and diameter of 100 – 120 mm have been reported [191–194]. None of the published procedures work in equilibrium because carbon black formation increases with increasing temperature and longer residence time.

The preferred residence time is ca. 10 s, which results in a benzene conversion of ca. 10 % [192], [195]. By recycling the benzene, 1 kg of starting material may yield 0.8 – 0.85 kg biphenyl, 0.07 – 0.12 kg terphenyl, and some higher polyphenyls. The major technical problem in the production of biphenyl by dehydrocondensation of benzene is carbonization at the high temperature required [196]. The carbon deposit on the reactor tube walls and the release of large carbon flakes at bends or narrow passages within the tubes may lead to blockages. Countermeasures include addition of about 0.1 % oxygen or sulfur compounds, such as methanol, ethanol, acetone, or carbon disulfide [197–199] to the benzene feedstock, the use of special alloys [200], [201], uniform heating of the reactor by means of circulating gases, and high feedstock velocity,

and the use of turbulent flow [192]. A proposal for further improving the process is to carry out the reaction in fluidized beds. Quartz sand [202] or sintered corundum [203] is used as energy carrier in this process; these materials are recycled after the carbon deposits have been removed by burning them outside of the reactor.

Other Synthetic Routes. In addition to these two industrial processes for the production of biphenyl, other synthetic routes have been described:

1. Ullmann reaction: heating halogenobenzenes with copper powder [204].
2. Pyrolysis of coal tar in the presence of molybdenum oxide – alumina catalyst [205], [206].
3. Reduction of phenyldiazonium chloride solution with copper and zinc [207].
4. Heating phenylmagnesium halides with copper(II) salts [208].
5. Oxidative dehydrocondensation of benzene [209–214]. Benzene is oxidized to biphenyl by platinum- or palladium salts in glacial acetic acid at 120 °C; the salts are reduced to the pure metals, and stoichiometric quantities of the salts are required.
6. Dehydrocondensation of benzene in the presence of catalytic quantities of noble metal salts requires reoxidation of the metals during the course of the reaction. This may be done with pure oxygen, but a partial pressure of 6 MPa is required [215]. Additives such as β-diketones [216], heteropolyacids [217], or organic copper salts [218] are incapable of significantly lowering the required oxygen pressure, so that a potentially explosive regime cannot be avoided [217]. Yields of biphenyl are ca. 260 mol %, calculated on the palladium salt charge.
7. Hydrodimerization of benzene to phenylcyclohexane, followed by dehydrogenation to biphenyl [219–223]:
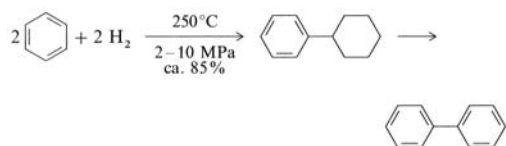
Suitable catalysts for this dimerization are noble metals on molecular sieve, alkali metals on alumina or carbon, and transition metals such as nickel, tungsten, or zinc on the zeolites faujasite or mordenite. A selectivity of up to 87 % has been claimed. Subsequent dehydrogenation is carried out at about 400 °C over Pt – Al$_2$O$_3$ [223], Cr$_2$O$_3$ – Na$_2$O – Al$_2$O$_3$ [222], [224], Cr$_2$O$_3$ – K$_2$CO$_3$ – Fe$_2$O$_3$ [225], or Cr$_2$O$_3$ – MgO – Al$_2$O$_3$ [226] giving yields of up to 99 %. Data concerning residence times over the catalyst are not available, either for the hydrodimerization or the dehydrogenation processes.

Analysis. Gas chromatography is used to analyze biphenyl and its derivatives.

Storage and Transportation. Biphenyl is marketed as a solid in the form of plates, flakes, or pellets, containing <10 ppm benzene and with a biphenyl content of >99.5 %; it is transported in bags or fiber drums; in the molten state (ca. 120 °C) in tank cars. It is not a regulated material for transportation, on account of its toxicity; there are no restrictions for transportation by sea, land, or air. The greatest hazards in handling biphenyl are the risk of dust explosions and the ignition of biphenyl vapor – air mixtures over the molten product.

Uses. Biphenyl is an important heat transfer agent, because of its high thermal stability. It is used as a composite with diphenyl ether, especially as a melting point depressant. The eutectic mixture of 26.5 % biphenyl and 73.5 % diphenyl ether is marketed under the trade names Diphyl (Bayer), Dowtherm A (Dow), Thermic (ICI), Gilotherm (Rhône-Poulenc), Therm S 300 (Nippon Steel), Santotherm VP and Therminol VP-1 (both Monsanto) for use at up to 400 °C. The eutectic begins to boil at 256 °C; the vapor pressure at the maximum operating temperature (400 °C) is ca. 1.1 MPa.

A further large quantity of biphenyl is used as a dye carrier [227], [228]. Until a few years ago, polychlorinated biphenyls (PCBs), generated by chlorination of biphenyl, were produced in large quantities for use as nonflammable hydraulic fluids and as transformer dielectrics. Production has largely ceased on ecological considerations (→ Chlorinated Benzenes and Other Nucleus-hlorinated Aromatic Hydrocarbons). Among the hydroxy derivatives, *o*- and *p*-hydroxybiphenyl and *p,p′*-dihydroxybiphenyl are used industrially. *o*-Hydroxybiphenyl is used as a preservative and fungicide. It is synthesized mainly from cyclohexanone
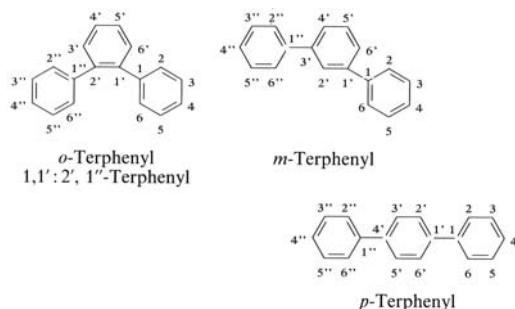
(→ Phenol Derivatives). *p*-Hydroxybiphenyl and *p,p′*-dihydroxybiphenyl are generated by sulfonation of biphenyl, followed by fusion with alkali.

Economic Aspects. According to a 1976 estimate, 67 % of the annual United States production of 40 000 t biphenyl was produced by dealkylation of toluene and 33 % by thermal dehydrocondensation of benzene [229].

The annual production for 1984 is estimated at 15 000 t, with an increasing proportion from dealkylation of toluene. The production capacities of the major producers, Monsanto, (United States), Bayer (Federal Republic of Germany), and Monsanto (United Kingdom) have not been disclosed. Based on the legal restrictions imposed on the use of PCBs, capacity should far exceed current demand.

4.2. Terphenyls

Physical Properties. The three isomeric terphenyls, $C_{18}H_{14}$, M_r230.29, are colorless to pale yellow crystalline solids [230–235]. Some physical properties are listed in Table 19.

o-Terphenyl
1,1′:2′, 1″-Terphenyl

m-Terphenyl

p-Terphenyl

Table 20. Terphenyl substitution pattern

	Position for substitution			
	First	Second	Third	Fourth
o-Terphenyl	4-	4″-	4′-	5′-
m-Terphenyl	4′-	4-	4″-	
p-Terphenyl	4-	4″-	2′-	

Chemical Properties. Terphenyls, like biphenyls, are thermally extremely stable organic compounds, again offering a potential for use as heat transfer media. Terphenyls are sublimable, steam volatile, and show the typical substitution reactions of aromatic hydrocarbons, such as bromination and nitration. The substitution pattern for the preferred positions of the three terphenyls is shown in Table 20.

Production. Terphenyls are byproducts in the production of biphenyl by dehydrocondensation of benzene; they are found in the high-boiling fraction of the pyrolysis products. The pot residue has the following approximate composition [240]:

3 – 8 %	*o*-Terphenyl
44 %	*m* – Terphenyl
24 %	*p* – Terphenyl
1.5 %	Triphenylene
22 – 27 %	Higher polyphenylenes and tar.

When, in the early 1960s, terphenyl was proposed to be used as coolant and moderator in nuclear reactors [241], numerous reports were published of attempts to enhance the yield of

Table 19. Physical properties of terphenyls

Property	*o*-Terphenyl [84-15-1]	*m*-Terphenyl [92-06-8]	*p*-Terphenyl [92-94-4]	Reference
mp, °C	59	87	212	[233]
bp (101.3 kPa), °C	332	365	376	[234]
Flash point, °C	171	206	210	[236]
T_{crit}, °C	613	603	621	[237]
P_{crit}, MPa	3.903	3.503	3.330	[238]
Heat of vaporization (at *bp*), kJ/mol	58.3	64.2	62.6	[234]
Vapor pressure, kPa				
93 °C	0.01172	0.00165		[233], [239]
204 °C	2.834	0.8274	0.789	
315.6 °C	64.4	27.3	24.56	
426.7 °C	439.9	240.6	174.4	

terphenyl in dehydrocondensation reactions. Increasing the temperature or residence time was ruled out because of increased carbonization. These procedures also enhanced the biphenyl fraction, so that the latter had to be recycled to the reactor [193], [197], [242–244]. Recycling a concentration of up to 30 % biphenyl has been described [193]. A practical level appears to be using benzene with 10 % biphenyl [210]. Attempts have also been made to recycle the extremely high melting p-terphenyl, after isolation from the reaction mixture, to obtain a lower melting terphenyl mixture [242]. The o-derivative is readily separated from the terphenyl isomer mixture by distillation; m- and p-terphenyl distill together and the pure isomers can be obtained by zone refining [245]. Terphenyl isomers, including hydrogenated terphenyl, can be analyzed by gas chromatography. The sole producer of terphenyl in the United States is Monsanto. The market amounts to several thousand tons per year. Terphenyl is available in Europe from Bayer.

Storage and Transportation. Solid terphenyl is shipped as flakes in laminated bags or in fiber drums, liquid, hydrogenated terphenyl in tank cars, steel drums, or barrels. Terphenyls and hydrogenated terphenyls possess a low toxicity, and are therefore not regarded as dangerous goods for the purpose of transportation.

Uses. Terphenyl is used as a heat transfer agent because of its excellent thermal stability; a mixture with a composition of 2 – 10 % o-terphenyl, 45 – 49 % m-terphenyl, 25 – 35 % p-terphenyl, and 2 – 18 % higher polyphenyls is used. This composition approximates the pot residue from the distillation of biphenyl. This mixture has bp ca. 360 °C; a disadvantage is the high mp, 145 °C. The largest fraction is partially hydrogenated to yield a clear oil, miscible with hydrocarbons and chlorinated hydrocarbons. Hydrogenation lowers the setting point and the viscosity but unfortunately also reduces the thermal stability. Partially hydrogenated terphenyl [246] is used mainly as a dye carrier for pressure sensitive recording materials and copy paper, and as a heat transfer oil. Heat transfer oils consisting of partially hydrogenated terphenyl isomers are marketed under the following trade names:

Santotherm 66 or 88, Therminol (Monsanto, United States), Gilotherm (Rhône-Poulenc, France), and Therm S 900 (Nippon Steel, Japan). Their usage range extends to 340 °C.

4.3. Polyphenyls

Polyphenyls with four or more phenyl residues have generally been synthesized as p-linked isomers and are used as scintillators [247]. They are economically unimportant.

A symmetrical hydrocarbon within this class is 1,3,5-triphenylbenzene, $C_{24}H_{18}$, mp 174 °C, prepared by condensation of three molecules of acetophenone.

5. Hydrocarbons from Coal Tar

→ Anthraceneand → Naphthalene and Hydronaphthalenes are separate keywords.

Hydrocarbons from coal tar are generally recovered in large-scale operations by distillation and crystallization, after the polar, co-boiling components, phenols and nitrogen bases, have been separated by extraction (→ Tar and Pitch). Supplies of coal tar as a raw material have been sufficient to date to meet the demand for these hydrocarbons, so that no other production processes, such as syntheses, have yet been developed to the stage of commerciality. Hydrocarbons from coal tar are used predominantly in the synthesis of dyes, plastics, and pharmaceuticals.

5.1. Acenaphthene

Acenaphthene [83-32-9], $C_{12}H_{10}$, M_r 154.21, was discovered in coal tar in 1867 by BERTHELOT.
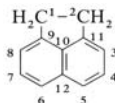
Physical Properties. Acenaphthene forms colorless needles; readily soluble in chloroform, toluene, and hot ethanol; soluble in cold ethanol, hot diethyl ether, and benzene; insoluble in water.

mp	95.4 °C
bp (101.3 kPa)	277.5 °C
ϱ (25 °C)	1.2195 g/cm^3
n_D^{100}	1.6048
T_{crit}	530 °C
Heat of fusion	1.344×10^5 J/kg
Heat of vaporization (40 °C)	3.48×10^5 J/kg
Heat of combustion (25 °C)	4.033×10^7 J/kg

Chemical Properties. Acenaphthene reacts with halogens, preferentially at 3-, 5-, and 6-positions, or at the 1-position when irradiated with visible light. Nitration and sulfonation occur at the 3-, 5-, or 6-positions. Catalytic hydrogenation leads to tetra- and decahydroacenaphthene. Decahydroacenaphthene can be isomerized in the presence of Lewis acids to 1,3-dimethyladamantane. Oxidation of acenaphthene gives naphthalic acid or its anhydride, acenaphthenequinone, acenaphthenol, and acenaphthenone.

Production. High-temperature coal tar contains, on average, 0.3 % of acenaphthene; in addition, it is formed under the conditions of coal tar distillation by hydrogenation of acenaphthylene, which is found in crude tar at a level of 2 %. Acenaphthene is concentrated to ca. 25 % in the coal tar fraction boiling between 230 and 290 °C (wash oil), which is recovered at ca. 7 % in continuous tar distillation. The readily crystallizable acenaphthene fraction, boiling at 270 – 275 °C, is obtained from the wash oil by redistillation, or by removing it directly during primary tar distillation. From this, technical acenaphthene (95 – 99 % pure) is produced by crystallization in agitated coolers and centrifuges, or by continuous counter-current crystallization [256], [259]. The pure compound is obtained by further distillation and recrystallization.

Uses. Acenaphthene is used on a large-scale for synthesis of naphthalic anhydride by gasphase with air oxidation at 300 – 400 °C, in the presence of vanadium containing catalysts [258], [259]. Liquid-phase oxidation with chromate or air in the presence of cobalt- or manganese acetate at 200 °C [260], or cobalt resinate at 120 °C [261] produces naphthalic acid (→ Carboxylic Acids, Aromatic, Section 4.4.). Production of naphthalene-1,4,5,8-tetracarboxylic acid from acenaphthene by condensation with malonic acid dinitrile [262] is at present not industrially important. A technically feasible procedure has been developed using 5-methyl-*peri*-acenaphthindene-7-one [*42937-13-3*] (by reaction of acenaphthene with diketene in HF) (→ Carboxylic Acids, Aromatic), [263]. Naphthalic anhydride and naphthalene-1,4,5,8-tetracarboxylic acid are used as intermediates for production of perylene and perinone pigments (→ Pigments, Organic) [262]. Other valuable intermediates, particularly for the production of dyes and optical brighteners, and also for pharmaceuticals and pesticides, are produced from, e.g., 4-bromacenaphthene [264] (for 4-bromonaphthalic anhydride or naphthalic anhydride-4-sulfonic acid), from 5,6-dichloracenaphthene (for 4,5-dichloronaphthalic anhydride) [265] and from 3,5,6-trichloracenaphthene [266]. Nitration and oxidation of acenaphthene produce 4-nitronaphthalic anhydride, from which the fluorescent pigment Solvent Yellow 44 can be made [267]. Reaction of acenaphthalene with sodium cyanate in hydrofluoric acid gives acenaphthene-5,6-dicarboxylic acid imide, which can be used as an intermediate for dyes [268].

Bromination of acenaphthene in the presence of, e.g., iron(III)- or aluminum chloride, followed by further bromination by the addition of a radical initiator, such as azobisisobutyronitrile (AIBN), and subsequent dehydrobromination produces condensed bromacenaphthene, which is particularly well-suited for rendering plastics nonflammable and radiation-resistant [269]. Thermally stable plastics can be obtained from acenaphthene in the following ways: 1) by condensation with formaldehyde; 2) oxidation and reaction with an aromatic polyamine [270]; by cocondensation with phenol and formaldehyde [271]; and by condensation with terephthaloyl chloride [272]. Acenaphthene also serves as a feedstock for the production of acenaphthenequinone, acenaphthene, and dimethyladamantane [273].

Derivatives.
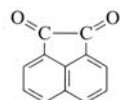

Acenaphthenequinone   Acenaphthylene

Acenaphthenequinone [*82-86-0*], C$_{12}$H$_6$O$_2$, M_r182.17; mp 261 °C; yellow needles; slightly soluble in ethanol; soluble in hot benzene and

toluene. It is formed by liquid-phase oxidation of acenaphthene with hydrogen peroxide or dichromate in acetic acid, by chlorination of dibromacenaphthylene followed by acid hydrolysis, or by condensation of acenaphthene with ethyl nitrite and separation of the dioxime. Acenaphthenequinone is suitable for use as an insecticide and fungicide and can be converted into vat dyes.

Acenaphthylene [*208-96-8*], $C_{12}H_8$, M_r 152.18; *mp* 92 – 93 °C; yellow prisms; soluble in ethanol, diethyl ether, and benzene; insoluble in water. It is found in coal tar at a concentration of 2 % and can be produced industrially by catalytic dehydrogenation of acenaphthene in the gas phase. Thermal, ionic, radical, or radiochemically induced polymerization produces polyacenaphthylene [274]. Polyacenaphthylene and copolymers with other olefins are characterized by high thermal and mechanical stability together with good electrical insulation properties. The thermal stability of polystyrene can be significantly increased by copolymerisation with acenapthylene [274]. Polymerisation of acenaphthylene with acetylene in the presence of a Lewis acid catalyst gives electrically conductive polymers; they are used for electronic engineering and for the antistatic finishing of plastics [275]. Thermosetting resins with good resistance to heat and chemicals can be obtained by cocondensation with phenol and formaldehyde [271]. Acenaphthylene possesses excellent properties as an antioxidant in cross-linked polyethylene and ethylene – propylene rubber [274]. Thermal trimerization of acenaphthylene leads to decacyclene, which can be further processed to sulfur dyes [276].

5.2. Indene

Indene [*95-13-6*], C_9H_8, M_r 116.16, was discovered in coal tar in 1890 by KRAEMER and SPILKER.
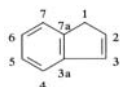
Physical Properties. Indene is a colorless liquid; insoluble in water; soluble in ethanol; it is miscible with diethyl ether, naphtha, pyridine, carbon tetrachloride, chloroform, and carbon disulfide.

mp	−1.5 °C
bp (101.3 kPa)	183 °C
ϱ (20 °C)	0.9966 g/cm³
n_D^{20}	1.5763
Heat capacity (25 °C)	1.610×10^3 J/kg
Heat of fusion	8.33×10^4 J/kg
Heat of combustion (25 °C)	4.132×10^7 J/kg
Dipole moment (in CCl₄)	0.85 D

Chemical Properties. Indene polymerizes readily at ambient temperature and in the dark. Polymerization is accelerated by heat, acid, and Friedel – Crafts catalysts. Depending on reaction conditions, oxidation leads to dihydroxyindan, homophthalic acid, or phthalic acid. Hydrogenation produces indan. Halogenation occurs at the 2,3-double bond. Diene adducts are formed with maleic anhydride and hexachlorocyclopentadiene.

Production. Indene is found in high-temperature coal tar at an average concentration of 1 %. Pyrolysis residual oils from olefin production contain varying amounts of indene [277], which can be separated by extractive distillation with *N*-methyl-2-pyrrolidone [278] or by crystallization [279]. Indene is recovered industrially from dephenolated and debased tar light oil by rectifying distillation followed by crystallization. When the phenol extraction is omitted a highly concentrated indene fraction can also be obtained by azeotropic distillation of an indene – phenol fraction with water, whereby the phenol is separated as a bottom product [280].

Uses. Indene is used as a comonomer in coal-tar derived indene – coumarone and petroleum-derived aromatic hydrocarbon resins (→ Resins, Synthetic). Technical pure indene is used for the production of indan and its derivatives. Esters of indene-1-carboxylic acid, which are effective as acaricides, can be synthesized from indene for use in, e.g., tick collars [281].
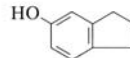
Derivatives.
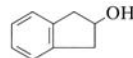
Indan   2-Indanol   5-Indanol

4-Indanol

Indan [*496-11-7*], hydrindene, C_9H_{10}, M_r 118.18;

mp	−51.4 °C
bp (1013 kPa)	176 °C
ϱ (20 °C)	0.9644 g/cm^3

Indan is a colorless liquid; insoluble in water; soluble in ethanol and diethyl ether. It is found at a concentration of 0.1 % in coal tar, but is mainly produced by catalytic hydrogenation of indene. Alkylated indans are used in the production of synthetic lubricants ($\rightarrow$ Lubricants and Lubrication). Indan is used for the synthesis of indanols ($\rightarrow$ Phenol Derivatives).

2-Indanol [*4254-29-9*], $C_9H_{10}O$, M_r 134.18; *mp* 69 °C; colorless crystals. It is obtained by hydrogenation of 2-indanone prepared by reaction of indene with hydrogen peroxide and boiling in sulfuric acid over a platinum catalyst in ethanol. 2-indanol is used in the synthesis of the coronary therapeutic, Aprindine [*37640-71-4*], *N*-(3-diethylaminopropyl)-*N*-indan-2-ylaniline; ($\rightarrow$ Cardiovascular Drugs), [282] and can be employed as an intermediate for other pharmaceuticals, e.g., for antihypertonics [283].

5-Indanol [*1470-94-6*], $C_9H_{10}O$, M_r 134.18; *mp* 55 °C; colorless crystals. It is produced by fusion of indan-5-sulfonic acid with potassium hydroxide [284]. 5-Indanol is used in the synthesis of the multi-purpose antibiotic, Carindacillin [*26605-69-6*] (6-[2-phenyl-2-(5-indanyloxycarbonyl)acetamido] penicillanic acid; $\rightarrow$ Antibiotics, 1. General), [285]. 5-Indanylesters of substituted picolinic acids can be used as antihypertonic [286]. 5-Indanol itself may be used as an antidandruff additive in hair shampoos ($\rightarrow$ Hair Preparations) [287].

4-Indanol [*1641-41-4*], $C_9H_{10}O$, M_r 134.18; *mp* 49 – 50 °C; colorless crystals. Analogous to 5-indanol it is synthesized by potassium hydroxide fusion of indan-4-sulfonic acid, which is produced as a byproduct in indan sulfonation. Catalytic gas-phase amination of 4-indanol produces 4-aminoindan [288], which is required as an intermediate, e.g., for pharmaceuticals. Clorindanol (7-chloro-4-indanol) is used as an antiseptic.

5.3. Fluorene

Fluorene [*244-36-0*], $C_{13}H_{10}$, M_r 166.22, was discovered in coal tar in 1867 by BERTHELOT.
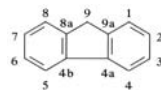
Physical Properties. Fluorene forms colorless flakes with slight violet fluorescence; sublimes readily; insoluble in water; soluble in benzene, diethyl ether, carbon disulfide, and hot ethanol; soluble with difficulty in cold ethanol.

mp	115 °C
bp (101.3 kPa)	298 °C
ϱ (20 °C)	1.181 g/cm^3
Heat of fusion	1.21×10^5 J/kg
Heat of combustion (25 °C)	3.994×10^7 J/kg

Chemical Properties. Fluorene is capable of numerous chemical reactions, through both the aromatic rings and especially the reactive methylene group. Oxidation produces fluorenone. Reaction with dialkyl carbonate and alkali metal hydride or alcoholate, followed by neutralization and saponification of the resulting ester produces fluorene-9-carboxylic acid; the latter is also produced by metalation with butyl lithium followed by carboxylation. Nitration leads predominantly to 2-nitrofluorene, chloromethylation to 2-chlormethylfluorene. Halogenation, depending on the reaction conditions, gives the mono-, di-, or tri-haloderivatives, substitution taking place at the 2-, 2,7-, or 2,4,7-positions; in the presence of catalysts waxy products containing ca. 50 wt % chlorine are formed.

Production. High-temperature coal tar contains on average, 2 % fluorene. The latter is recovered industrially by redistillation of coal tar wash oil or by direct removal of a fluorene fraction during primary distillation of coal tar, followed by recrystallization of the fluorene fraction (dephenolated and debased if necessary) e.g., from solvent naphtha or naphtha [289]. Fluorene can be isolated from a ≥60 % fluorene fraction by continuous counter-current crystallization [290]. It is possible to refine the technical product further

via the sodium compound (by reaction with sodium or sodium amide), or by sulfuric acid purification and crystallization from methanol.

Uses. Fluorene is the starting material for production of fluorenone and fluorene-9-carboxylic acid. Fluorene-9-carboxylic acid is an intermediate in the production of antidiabetic and antiarrhythmic drugs, and plant growth regulators [291]. Plant growth regulators are also obtained by reaction of fluorene with phthalic anhydride [292]. Fluorene-2-acetic acid (by acylation of fluorene) can be used as a precursor in the synthesis of anti-inflammatory drugs [293]. Reaction of fluorene with sulfur produces electrically conductive polymers [294]. The azine dye Sirius Light Violet FRL is produced from 2-aminofluorene (→ Azine Dyes, Section 5.2.). The fluorene analog of malachite green dye is obtainable from 3,6-bis-(dimethylaminofluorene) [295]. 2,7-Diiodofluorene can be employed in the production of styryl dyes for optical brighteners [296]; heptabromofluorene can be used as a fire-retardant for plastics [297]. Fluorene itself can be used in admixture with biphenyl and phenyltoluene as a carrier for dyeing polyester fibers [298].

Derivatives.   *9-Fluorenone* [*486-25-9*], $C_{13}H_8O$, M_r 180.21;

|	
mp	85 – 86 °C
bp 101.3 kPa)	341.5 °C
ϱ (99.4 °C)	1.130 g/cm^3
n_D (99.4 °C)	1.6369

9-Fluorenone forms yellow crystals; insoluble in water; soluble in hot sulfuric acid; very readily soluble in ethanol and diethylether; volatile in steam. Fluorenone can be produced by catalytic oxidation of fluorene [261], [299–302], or of fluorene fractions in the presence of a quaternary ammonium salt [303], or by catalytic oxidative cracking (oxicracking) of suitable aromatic [304].
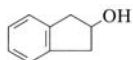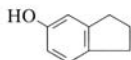

Indan   2-Indanol   5-Indanol

4-Indanol

Di- and trinitrofluorenones are synthesized from fluorenone for use as electron acceptors in electrophotography, e.g., in copying systems [305]. 2,4,7-Trinitrofluorenone is used as an analytical reagent for polynuclear aromatic hydrocarbons. Fluorenone can be used as starting material for the synthesis of imidazolylfluorene salts with antimycotic activity [306]. 9,9-Bis(4-hydroxylphenyl)fluorene (from fluorenone by reaction with phenol [307]) can be used as starting material for thermally stable plastics [308]. 9,9-Bis(4-methylaminophenyl)fluorene (from fluorenone by reaction with phenyl methyl amine) has been suggested as a hardener for epoxy resins [309]. Fluorenone is also suitable as an oxidizing agent in the Oppenauer reaction.

5.4. Fluoranthene

Fluoranthene [*206-44-0*], $C_{16}H_{10}$, M_r 206.26, was isolated from coal tar by Fittig and Gebhardt in 1878.
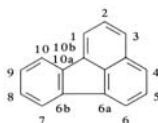
Physical Properties. Colorless crystals with light blue fluorescence; insoluble in water; readily soluble in diethyl ether, boiling ethanol, chloroform, carbon disulfide, and glacial acetic acid.

mp	110 °C
bp (101.3 kPa)	384 °C
ϱ (20 °C)	1.236 g/cm^3
Heat of vaporization	3.29×10^5 J/kg
Heat of combustion (25 °C)	3.913×10^7 J/kg

Chemical Properties. Oxidation of fluoranthene with chromic acid leads to fluorenone-1-carboxylic acid via fluoranthene-2,3-quinone; hydrogenation leads to 1,2,3,10 b-tetrahydrofluoranthene, and to perhydrofluoranthene via decahydrofluoranthene. 2,3-Dihydrofluoranthene is obtained by metalation with sodium. Halogenation, nitration, and sulfonation take place predominantly at the 4-position. Condensation with phthalic anhydride in the presence of aluminum

chloride gives a mixture of 7,8- and 8,9-phthaloyl fluoranthene.

Production. Fluoranthene belongs to the main constituents of high-temperature coal tar, which contains, on average, 3.3 % of fluoranthene. It is recovered from the fluoranthene fraction, which boils at 373 – 385 °C, and is obtained from the high-boiling anthracene oil II and from pitch distillate by redistillation. Subsequent recrystallization of the fluoranthene fraction from solvent naphtha gives 95 % pure fluoranthene. Further refining is carried out by recrystallization from xylene with simultaneous partial sulfonation of the impurities with ca. 1 % of concentrated sulfuric acid, or by recrystallization from a pyridine – water mixture.

Uses. Fluoranthene is used in the production of fluorescent dyes (→ Fluorescent Dyes). Yellow vat dyes are obtained by condensation with phthalic anhydride, via phthaloyl fluoranthenes, whereas bromination [310] and condensation with 1-amino-4-benzoyl-amino anthraquinone produces olive dyes [311]. 2-Benzylfluoranthene (from 2,3-dihydrofluoranthene [312] and benzaldehyde) can also be used for the production of dye intermediates [313]. Fluoranthene and alkyl fluoranthenes can be used as stabilizers in epoxy resin adhesives [314], as additives in electrically-insulating epoxy resin compositions [315], and in electrically-insulating oils [316]. 2,3-Dihydrofluoranthene and 1,2,3,10 b-tetrahydrofluoranthene [317] are used for numerous derivatives, some of which (e.g., their derivatives of phenylethyl amine) are of pharmaceutical interest. 7-Fluoranthenyl aminoalcohols (for cytostatics, anthelmintics, or bactericides [318]) and bis-aminoketones, e.g., 3,8-bis(4-piperidinobutyryl)fluoranthene (as antiviral agents [319]) can be synthesized from fluoranthene.

5.5. Phenanthrene

Phenanthrene [85-01-8], $C_{14}H_{10}$, M_r178.24 was discovered in coal tar by Fittig and Ostermayer in 1872.
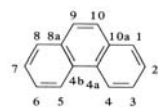
Physical Properties. Colorless flakes with weak blue-violet fluorescence; readily sublimable; insoluble in water; slightly soluble in ethanol; readily soluble in diethyl ether, benzene, carbon disulfide, and glacial acetic acid.

mp	101 °C
bp (101.3 kPa)	338.5 °C
ϱ (20 °C)	1.172 g/cm^3
Heat capacity (25 °C)	1.361×10^3 J/kg
Heat of fusion	1.04×10^5 J/kg
Heat of combustion (25 °C)	3.982×10^7 J/kg

Chemical Properties. Phenanthrene can be oxidized to phenanthrenequinone, diphenic acid, or to phthalic acid, depending on the oxidant. Hydrogenation produces 9,10-di-, tetra-, octa-, or perhydrophenanthrene. Phenanthrene is halogenated predominantly in the 9,10-positions, and nitrated in the 9-position. Sulfonation leads to mixtures of 2-, 3-, and 9-phenanthrene sulfonic acids. For acylation see → Acylation and Alkylation, Section 2.2.2..

Production. Phenanthrene, at a concentration of 5 %, is the second most important coal tar constituent in terms of quantity after naphthalene. During primary distillation of coal tar, it is concentrated in the anthracene oil fraction. After crystallization of the anthracene residues the phenanthrene is recovered as a fraction from the filtrate of this crystallization, or from the top fraction of crude anthracene distillation, by redistillation. Technically pure grades of phenanthrene are obtained by sulfuric acid refining and recrystallization from methanol, or by repeated rectification of the phenanthrene fraction. The accompanying substances can be separated either by partial sulfonation, or by partial condensation with formaldehyde and hydrogen chloride. The most persistent accompanying substance, diphenylene sulfide, can be completely removed by treating the melt with sodium and maleic anhydride.

Uses. Phenanthrene forms the basis for production of 9,10-phenanthrenequinone and 2,2′-diphenic acid (see Chap. 4) [320]. It can be used to synthesize anthracene, via the isomerization product of *sym*-octahydrophenanthrene (→ Anthracene). Electrically conductive substances, e.g., for use in batteries and solar cells, can be

produced by the electrochemical conversion of phenanthrene diazonium salts in a solvent containing a conductive salt, and subsequent doping with various ions (e.g., Na^+, Ba^{2+}, H^+, etc.) [321]. Liquid-crystalline 7-*n*-alkyl-9,10-dihydrophenanthrene-2-carboxylic acid ester, used for optical-electronic applications, can be synthesized from 9,10-dihydrophenanthrene [322]. By cross-linking with *p*-xylylene glycol and 4-toluenesulfonic acid, polycondensed thermosetting resins are obtained for composites or temperature-resistant, electrically insulating coatings [323]. A polyamide – polyimide resin can be produced by oxidation of phenanthrene to phenanthrene-9,10-quinone and -9,10-diol, condensation with formaldehyde, oxidation to the polycarboxylic acid, formation of the anhydride and finally reaction with an aromatic diamine. This resin is suitable for use in high-temperature insulators, printed circuit boards, and laminates [324]. Phenanthrene has been proposed as a plasticizer for plastics and molding compounds [325], phenanthrene and alkylphenanthrenes have been suggested as stabilizers for mineral oil products [326], [327]. Deep khaki vat dyes are prepared by heating a mixture of phenanthrene and anthracene with sulfur [328]. [(Phenanthrylmethyl)amino]-propandiol, which possesses antitumor activity, can be synthesized via phenanthrene-9-carboxaldehyde [329].

Derivatives

Phenanthrene–9–10-quinone [*84-11-7*], $C_{14}H_8 O_2$, M_r 208.91; *mp* 217 °C; orange needles; poorly soluble in water; slightly soluble in ethanol; soluble in boiling water and in diethyl ether; readily soluble in hot glacial acetic acid. Phenanthrene-9,10-quinone is produced by liquid-phase oxidation of phenanthrene with chromates [330], catalytically with oxygen [331], with *tert*-butylhydroperoxide [332], [333] or via phenanthrene-9,10-oxide with nitric acid or hypochlorite [334], [335]. Further oxidation transforms the quinone into 9-hydroxyfluorene-9-carboxylic acid, which is used in the form of its salts or esters (in combination with the herbicide methyl chlorophenoxyacetic acid (MCPA), trade name: Aniten) or as the 2-chloro derivative (trade name: Maintain) as plant growth regulators [336], [337]. Phenanthrene-9,10-quinone has been suggested as an additive for photographic

or electrophotographic applications [308], [338], [339], in UV-curable coatings and adhesives [340], [341] and in production of cellulose by wood pulping [342]. An intermediate for azo pigments can be obtained by condensation with hydrazinobenzoic acid [343]. Condensation with aromatic amines gives intermediates for pharmaceuticals (e.g., immuno-suppressives) or fungicides [344], [345].
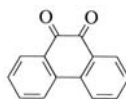
5.6. Pyrene

Pyrene [*129-00-0*], $C_{16}H_{10}$, M_r 202.26, was found in coal tar by GRAEBE in 1871.
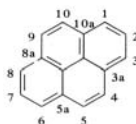
Physical Properties. Colorless crystals with blue fluorescence; insoluble in water; very readily soluble in diethyl ether, benzene, and carbon disulfide; poorly soluble in ethanol.

mp	150 °C
bp (101.3 kPa)	393.5 °C
ϱ (23 °C)	1.271 g/cm³
Heat capacity (18 °C)	1.126×10^7 J/kg
Heat of vaporization	3.21×10^5 J/kg
Heat of combustion (25 °C)	3.878×10^7 J/kg
Dielectric constant (17 °C)	3.21

Chemical Properties. Pyrene is oxidized by mild oxidants such as chromic acid to pyrene-1,6- and 1,8-quinone; further oxidation leads to perinaphthenone [*548-39-0*] and napthalene-1,4,5,8-tetracarboxylic acid. Hydrogenation produces, depending on the reaction conditions, ditetra-, hexa- or decahydropyrenes; halogenation products substituted in the 1-, 1,6-, 1,8-, 1,3,6- and 1,3,6,8-positions. The substitution pattern for halogenation can be changed in favor of the 4-position by Diels – Alder reaction with hexachlorocyclopentadiene [*77-47-4*] in the presence of iron powder or thallium acetate, followed by retro-Diels – Alder reaction. With

nitration and sulfonation the 1-, 1,6-, and 1,3,6,8-substitution products are formed. Pyrene can be condensed with phthalic anhydride by Friedel – Crafts reaction to give diphthaloyl pyrenes, and with benzoyl chloride to the dye pyranthrone [*128-70-1*].

Production. High-temperature coal tar contains an average of ca. 2 % of pyrene. It is recovered from a fraction crystallizing above 110 °C, which is obtained by redistillation of the high-boiling anthracene oil II or pitch distillate. Pure pyrene is produced by recrystallization, e.g., from solvent naphtha [346] or by fractional crystallization from the melt [256], dephenolation and debasing, and by refining with 80 % sulfuric acid. As an alternative to sulfuric acid refining, the pyrene-accompanying brasane (2,3-benzodiphenylene oxide) can also be separated by recrystallization from xylene by adding iron (III) chloride. Traces of tetracene are removed by reaction with maleic anhydride.

Uses. The dye intermediate naphthalene-1,4,5,8-tetracarboxylic acid [*128-97-2*] can be produced by halogenation of pyrene [347], [348] (halogenation of the pyrene fraction is also possible [349]) followed by oxidation ($\rightarrow$ Carboxylic Acids, Aromatic), [350]. Other pyrene-based dyes are Sirius Light Blue F 3 GL from 3-aminopyrene ($\rightarrow$ Azine Dyes, Section 5.2.) and the green fluorescent dye, pyranin (Solvent Green 7), from pyrene-1,3,6,8-sulfonic acid [351]. Anthraquinone dyes (e.g., pyranthrone) may be obtained from dibenzoyl pyrene or diphthaloyl pyrene. Optical brighteners may be synthesized by reaction of pyrene with a complex of cyanuric chloride and aluminum chloride ($\rightarrow$ Optical Brighteners) [352]. By analogy to fluoranthene, pyrene and alkylpyrenes can be used as additives in electro-insulating oils [316], and in epoxy resins for electrical-insulation [315]. In a similar manner to phenanthrene, thermosetting resins may be formed with *p*-xylene glycol and 4-toluenesulfonic acid [323]. Condensation products of 1-bromopyrene or nitropyrene with formaldehyde are used as photoconductive substances in electrophotography [305], [353], [354]. 1,2,3,6,7,8-Hexahydropyrene is effective as a synergist for dialkylsulfide antioxidants in lubricants [355]. On the basis of pyrene, pyrenyl aminoalcohols can be synthesized as cytostatics,

anthelmintics, or bactericides [356]. Pyrene itself can serve as an electron donor to increase the blackness in pencil leads [357].

6. Toxicology and Occupational Health

6.1. Alkanes

Methane is toxicologically virtually inert. In very high concentrations (80 – 90 vol %) it causes respiratory arrest [358]. The bulk of an inhaled dose is exhaled unchanged [359].

Ethane easily causes dyspnea in laboratory animals, beginning at concentrations of approximately 2 – 5 vol % in the air inhaled [360]. At high concentration respiratory arrest occurs [361]. A slight sensitization of the myocard to catecholamines has been described at a concentration of 15 – 19 vol % [362].

Propane has narcotic properties [361]. It is neither a skin nor a mucosal irritant. At very high concentration it also causes respiratory arrest [363]. In dogs adverse effects on circulatory function were found with inspiratory concentrations of 1 % or greater. A negative inotropic effect, a drop in the mean aortic pressure, and an increase in pulmonary vascular resistance were found [364].
MAK (1987): 1000 ppm.

Butane causes slight drowsiness beginning at a concentration of 10 000 ppm in the air inhaled [365]. In the mouse the inhalatory LC_{50} is 680 g/m^3 [366]. It has been proven in the dog that butane also sensitizes the myocardium to the effects of catecholamines [364].
MAK (1987): 1000 ppm.

n-Pentane has a less pronounced narcotic effect than the C_1– C_4 hydrocarbons. In humans the lowest lethal dose after acute inhalatory exposure is apparently 130 000 ppm, the lowest toxic dose 90 000 ppm [367]. Pentane apparently possesses a neurotoxic effect, although it is not very pronounced [368], [369].

n-Hexane possesses a marked neurotoxic effect that distinguishes it from the other alkanes.

The causal factor for peripheral neuropathies is the oxidation product (cytochrome P 450-dependent oxidases) 2,5-hexadione. Toxicity manifests itself clinically in polyneuropathies [370], [371]. Hexane is also a skin irritant. The LC_{50} (inhalation mice) is 120 g/m^3 [372]. In rats the acute oral LD_{50} is 24 – 49 mL/kg [373]. Hexane is absorbed through the skin. Dermal exposure can lead to poisoning (LD dermal in rabbits ca. 5 mL/kg) [374]. In rats subchronic exposure to a concentration of 400 – 600 ppm leads to neuropathies [375], which are characterized by degeneration of both myelin sheaths and axons [376–378].

MAK (1987): 50 ppm.

nHeptane   has narcotic properties. In humans 0.1 % in the inhaled air leads to dizziness and 0.5 % to equilibrial disturbances with loss of motor coordination [365]. Within 3 min 4.8 vol % in the air inhaled leads to asphyxia [379]. Like hexane, heptane is a skin and mucosal irritant [365]. The biotransformation of *n*-heptane, as with hexane, is by oxidation. Heptane apparently also possesses neurotoxic properties [380]. Myocardial sensitization to catecholamines has also been found [381].

MAK (1987): 500 ppm.

n-Octane   is similar to *n*-heptane in regard to its narcotic effect; however, it does not seem to cause any other effects on the nervous system [372]. Octane is also metabolized by oxidation [382].

MAK (1987): 500 ppm

Only limited toxicological data are available on the higher molecular mass alkanes.

6.2. Alkenes

The alkenes under consideration are toxicologically not very active. Higher molecular mass compounds possess narcotic properties. The alkenes are not neurotoxic. The α-olefins generally seem to be more reactive and toxic than the β-isomers.

6.3. Alkylbenzenes

Trimethylbenzenes. The toxicological data available on trimethylbenzenes is mainly rather

old. The acute inhalatory toxic dose for the 1,2,4- and the 1,3,5-isomers is in the range 7000 – 9000 ppm [383], [384].

As a result of their occurrence in automotive fuel and heating oil, low concentrations of trimethylbenzenes can be demonstrated in air and water. For example, measurements in 1974 in a tunnel in Rotterdam indicated a level of 0.015 ppm pseudocumene; see [385] for more details. An analysis of the drinking water of Cincinnati, Ohio, in 1980, revealed a concentration of 45 ng/L hemimellitene, 127 ng/L pseudocumene, and 36 ng/L mesitylene [386]. Trimethylbenzenes are toxic to aquatic organisms; LC_{50} values between 10 and 100 ppm have been reported [387].

The TLV (TWA) level for trimethylbenzene is 25 ppm [388]. The MAK for Trimethylbenzenes (all isomers (1,2,3–;1,2,4–;1,3,5–) has been set at 20 ppm. [389]. The United States toxicity assigment ranges from low to moderately toxic for pseudocumene, to highly toxic for the isomer mixture; disturbances in the central nervous system and abnormal blood pictures have been reported [387].

Tetramethylbenzenes. The oral toxicity of tetramethylbenzenes is low; LD_{50} >5000 mg/kg (rat, oral). Durene is additionally classified as intravenously highly toxic; LD_{50} 180 mg/kg (i.v., mice). Tetramethylbenzenes cause mild skin reactions [387]. Two values are cited for the odor threshold concentration of durene: 0.083 and 0.087 mg/m^3 [385].

Hexamethylbenzene. Hexamethylbenzene has low oral toxicity; LDLo 5000 mg/kg (rat). It is, however, suspected of causing neoplastic effects. Addition of nitromethane to hexamethylbenzene can lead to an explosive reaction [387].

Diethylbenzenes. Diethylbenzene is more toxic than monoethylbenzene (→ Ethylbenzene) [390]. DEB is emitted into the environment from engine fuel and heating oil [386]. Diethylbenzenes are toxic to aquatic organisms; the LC_{50} is between 10 and 100 mg/L [387]. In the cell multiplication inhibition test with protozoa, the toxicity threshold is <10 mg/L [385]. In the Federal Republic of Germany DEB is classified as an aquatic hazard; aquatic hazard class 2. DEB causes mild to moderate irritation of the eye and

mucous membranes. The oral toxicity is low: LDLo 5000 mg/kg (rat) [387]. The vapor possesses an anesthetic action and may cause headache, vertigo, or vomiting; the odor threshold concentration is <10 ppm [391].

Triethylbenzene. The LC_{50} of triethylbenzene (aquatic organisms) is between 100 and 1000 mg/L. The oral toxicity is low: LDLo 5000 mg/kg (rat). Implant experiments with hexaethylbenzene in mice have raised the suspicion that the compound may be carcinogenic [387].

Ethyltoluene. Ethyltoluene can, as with aromatic hydrocarbons, be detected in the environment [385]. The oral toxicity of 2- and 4-ethyltoluene is low: LDLo 5000 mg/kg (rat) [387].

Cumene. Cumene appears to be orally as nontoxic as propylbenzene, it is even less so by inhalation [383], [392], [393]. Cumene has a prolonged depressant effect on the central nervous system [394].

The MAK for cumene has been set at 250 mg/m^3, corresponding to a cumene vapor concentration in air of 50 mL/m^3. The vapor pressure of cumene at 20 °C is 0.5 kPa. There is a risk of cumene being absorbed through the skin [395]. Inhalation of cumene vapor leads to the delayed appearance of a long lasting narcotic effect [396].

6.4. Biphenyls and Polyphenyls

Biphenyls. Biphenyl dust or vapor is irritating to the eye and mucous membrane at a concentration as low as 3 – 4 ppm [390], and to the skin after extended exposure. A concentration of >5 mg/m^3 for long periods is considered a health hazard; systemic toxic effects were elicited in humans by a concentration with inhalatory exposure maxima of 128 ppm [400], [401]. The olfactory threshold is ca. 0.06 – 0.3 mg/m^3. Some toxicity data are listed below [397–399]:

LD$_{50}$ (rat, oral)	3280 mg/kg
LD$_{50}$ (rabbit, oral)	2400 mg/kg
LD$_{50}$ (rabbit, dermal)	2500 mg/kg
TL$_m$ (fathead minnow, 96 h)	1.5 mg/L

Triphenyls are only minimally toxic [402].

Terphenyls. Toxicologically, terphenyl isomers should be treated like biphenyl. The oral LD$_{50}$ is ca. 4.6 – 4.7 g/kg [403]. The toxicity of partially (40 %) hydrogenated terphenyl (LD$_{50}$ 17.5 g/kg) is much less than that of the fully aromatic terphenyls [404–407].

6.5. Hydrocarbons from Coal Tar

The aromatic hydrocarbons under consideration are usually found in complex mixtures of various other polycyclic aromatic hydrocarbons (PAH), which originate from combustion emissions and industrial processes. For this reason toxic phenomena possibly caused by exposure to humans are often unlikely to be attributed to one single aromatic compound. Incorporation of these compounds into the body occurs predominantly by way of the respiratory tract. Skin contact is important with occupational exposure.

6.5.1. Biological Effects

6.5.1.1. Carcinogenicity and Mutagenicity

The aromatic compounds under discussion are considered as noncarcinogens, but pyrene and fluoranthene are able to enhance the carcinogenic potential of benzo[*a*]pyrene [*50-32-8*] when applied simultaneously to mouse skin (cocarcinogenic effect) (→ Carcinogenic Agents) [408]. Phenanthrene resulted in just one positive tumorinitiation test in a series of carcinogenicity studies [408], [409]. Acenaphthene, known as an inhibitor of mitosis in plant cells [410], induced the initial phase of bronchocarcinoma in rats after an inhalation period (4 months) of 4 hours per day with 0.5 – 1.25 mg/m^3 [411], but was negative in repeated topical application to mouse skin [412]. With their low activity in in vivo and in vitro assays, there is limited evidence that phenanthrene and pyrene are mutagenic [408], [409], [413–415]. As for fluoranthene, several more recent positive results indicate a mutagenic potential [408], [416–419].

So far, tests on fluorene have given negative results [408].

6.5.1.2. Mammalian Toxicity and Toxicokinetics

The acute toxicity of the aromatic compounds under consideration is low: LD_{50} (oral and dermal) is 700 – 2700 mg/kg body weight in rodents [408], [409], [411], [413]; LD_{50} (rat, oral) for acenaphthene is 10 000 mg/kg [421]. The LC_{50} (inhalation) of pyrene is reported to be 170 mg/m^3 [413]. No fatalities occurred in rats exposed to indene vapor (800 – 900 ppm) for six inhalation periods of 7.5 h each; however, systemic pathological changes in the vascular system and several organs were observed [412]. Longterm inhalation (4 months) of acenaphthene (0.5 –1.25 mg/m^3) [411], [420] or pyrene (0.3 – 3.6 mg/m^3) [408], [409], [413] caused local irritation and systemic pathological effects in several organs and the blood of rodents. In direct contact at high concentration, the compounds under consideration are irritating to the skin and mucous membranes; the tri- and polycyclic aromatics especially are photosensitizing [408–410], [412], [413]. The compounds under consideration are absorbed on inhalation or oral exposure, and partly leave the body unchanged in the feces and by exhalation [408], [409], [412], [413]. After metabolic conversion to more water-soluble intermediates (hydroxylation and conjugation), they are excreted into the bile or the urine. The half-life of pyrene is estimated to be 24 – 48 h in rats and swine [413].

6.5.1.3. Ecotoxicology

Several studies have shown that the aromatic compounds, in question are microbially decomposed [422–424], although the microbial conversion of indene has not yet been described. These compounds tend to be enriched in sediments, sludges, and aquatic organisms because of their low water solubility. As a result of microbial degradation, biotransformation, and photochemical decomposition, however, accumulation is limited and checked. Nonetheless, a concentration in water of the order of their low solubility ($<0.2 – 4.0$ mg/L) may have adverse effects on aquatic life, as shown for acenaphthene [425], phenanthrene, and pyrene [426], [427].

6.5.2. Safety Regulations

A threshold limit value (TLV) at the work place exists only for indene: 10 ppm (45 mg/m^3) (AC-GIH, United States 1980). No other TLVs have so far been established. The United States standard for exposure to coal tar volatiles (0.2 mg/m^3) was recommended to be used in case of pyrene-containing PAH mixtures, but a maximum level of 0.1 mg/m^3 should be applied in the case of exposure to pure pyrene [413]. With the exception of indene all aromatics are included in the recommended United States list of priority pollutants (United States EPA, 1977) [428].

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