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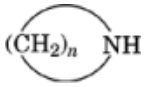
IMINES, CYCLIC

Ethyleneimine (aziridine, azacyclopropane) is the smallest cyclic imine consisting of a three-membered *N*-heterocyclic ring ($n = 2$):



This article describes ethyleneimine and the most important aziridine derivatives, not the higher homologues azetidine ($n = 3$), pyrrolidine ($n = 4$), or piperidine ($n = 5$). Reviews of these compounds are available (1–19). Unsubstituted ethyleneimine [151-56-4] is industrially the most important representative of the aziridine class. This substance was first prepared in the laboratory in 1888 (20, 21), and independently confirmed in 1899 (22, 23). Ethyleneimine was first synthesized industrially in 1938 by I. G. Farbenindustrie AG. After World War II ethyleneimine was produced by the Badische Anilin- und Soda-Fabrik Aktiengesellschaft (BASF AG) in Germany and by several companies in the United States (Chemirad Corporation, Dow Chemical Company, Cordova Chemical Company). In the 1960s, Interchemical Corporation and Union Carbide Corporation began large-scale production of ethyleneimine derivatives such as 2-methylaziridine and 1-(2-hydroxyethyl)aziridine. The BASF group is by far the largest manufacturer of ethyleneimine and has production plants in Germany and the United States. Another important producer is the Nippon Shokubai Company Ltd. of Japan.

1. Physical Properties

Ethyleneimine (EI) and its two most important derivatives, 2-methylaziridine [75-55-8] (propyleneimine) (PI) and 1-(2-hydroxyethyl)aziridine [1072-52-2] (HEA) are colorless liquids. They are miscible in all proportions with water and the majority of organic solvents. Ethyleneimine is not miscible with concentrated aqueous NaOH solutions ($>17\%$ by weight) (24). Ethyleneimine has an odor similar to ammonia and is detectable only at concentrations ≥ 2 ppm. The physical properties of ethyleneimine and the derivatives mentioned are given in Table 1. Thermodynamic data can be found in the literature (32).

2. Chemical Properties

Unlike the other structural isomers of C_2H_5N, *N*-methylenemethylamine (33, 34), ethylideneimine (35), and vinylamine [593-67-9] (36, 37) and the analogous phosphorus compound, phosphirane (38), ethyleneimine is stable at room temperature provided CO_2 is excluded from the air (39). Unexpectedly, ethyleneimine has the highest calculated relative heat of formation of the C_2H_5N isomers (40). Relative calculated heats of

Table 1. Physical Properties of Ethyleneimine and Derivatives

Property	EI	PI[a]	HEA[b]	Refs.
solidification point, °C	−74	−65		(1, 25)
boiling point, °C	57	66	156	(1, 26, 27)
density, g/mol	0.837[c]	0.8017[d]	1.088	(26–28)
refractive index n_D	1.4130[c]	1.4084[d]	1.453[d]	(1, 26, 27)
flashpoint, °C	−13	−10	67	(25, 26, 28)
ignition temperature, °C	322			29
ignition limits in air at 20°C, 101.3 kPa[e]				
lower explosion limit, vol %	3			29
upper explosion limit, vol %	55			29
viscosity at 25°C, mPa·s(=cP)	0.418	0.491		(1, 27)
surface tension at 25°C, mN/m(=dyn/cm))	32.8			1
dielectric constant at 25°C	18.3			1
dipole moment, C·m[f]	7.8×10^{-30}			1
specific conductivity, $(\Omega \cdot cm)^{-1}$	8×10^{-6}			1
heat of vaporization, kJ/mol[g]	34	33.2		(1, 26, 27)
heat capacity at 20°C, J/(g·K)[g]	2.48			
heat of combustion at 25°C, kJ/mol[g]	1.59×10^3			30
heat of formation, liquid, 25°C, kJ/mol[g]	92			30
heat of formation, gas, 25°C, kJ/mol[g]	127			1
heat of polymerization, kJ/kg[g]	2.3×10^3			(1, 26)
heat of mixing with 80% H_2O, kJ/mol[g]	13.8			1
vapor pressure, kPa[e] (°C)	30.76 (27)	18.6		(31, 27)

[a] Propyleneimine.
[b] Hydroxyethylaziridine.
[c] At 20°C.
[d] At 25°C.
[e] To convert kPa to mm Hg, multiply by 7.5.
[f] To convert C·m to debye, multiply by 2.99×10^{29}.
[g] To convert J to cal, divide by 4.184.

formation are ethylideneimine, 0.0; vinylamine, 26.9; *N*-methylenemethylamine, 32.2; and ethyleneimine, 85.3 kJ/mol (20.4 kcal/mol).

The special types of bonding in three-membered ethyleneimine rings (41–43) have been studied using microwave spectroscopy (44–47), electron diffraction (48), and photoelectron spectroscopy (49–51), and have occupied theoretical chemists up to the present day (52). These studies reveal that ethyleneimine has a distinctly shortened C—C bond of 0.148 nm (as compared to 0.154 nm in open-chain compounds) and a noticeably lengthened C—N bond of 0.149 nm (compared to 0.146 nm). Because of the high *s* character of the free electron pair on the nitrogen, ethyleneimine also shows a lower basicity ($pK_a = 7.98$) than noncyclic aliphatic amines such as dimethylamine ($pK_a = 10.7$) (53).

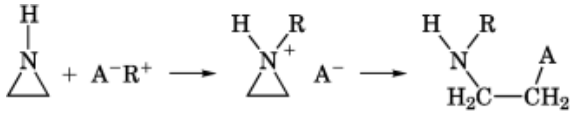
2.1. Reactions

Depending on the experimental conditions used, the basicity or the ring strain can be the driving force in reactions involving ethyleneimine. With catalysis by Brönsted or Lewis acids, the aziridine ring can be opened by a large number of nucleophiles to give β-substituted ethylamines. In the absence of strong nucleophiles and at elevated temperatures, preparation of polyethyleneimines from aziridines is possible by acid-catalyzed reaction of the aziridine with itself. On the other hand, ethyleneimine and other aziridines substituted only on carbon show the typical reactions of a secondary amine, such as addition onto unsaturated systems, complex formation with metals, and reaction with halogen compounds. At low temperatures and alkaline pH the

N-substituted aziridines are generally formed in these reactions. High temperatures and catalysis by acids or nucleophiles promote secondary reactions with opening of the three-membered ring, and these can be used for synthesis of heterocyclic compounds.

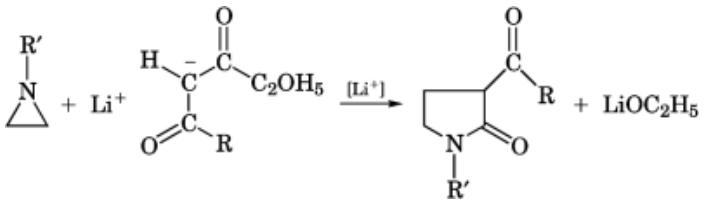
2.1.1. Nucleophilic Ring Opening

Opening of the ethyleneimine ring with acid catalysis can generally be accomplished by the formation of an intermediate aziridinium salt, with subsequent nucleophilic substitution on the carbon atom which loses the amino group. In the following, R represents a Lewis acid, usually H^+; A^- = the nucleophile.

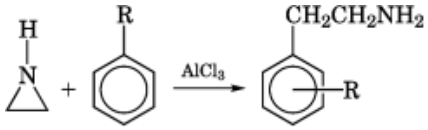


Because of the rapid ring opening by the nucleophile, aziridinium salts cannot usually be isolated. However, in a few cases it is possible to isolate such compounds (54), eg, at low temperatures, when the aziridinium salts are sparingly soluble or where there is steric hindrance to substitution. Stable ethyleneiminium salts can be prepared by reaction of ethyleneimine with acids not containing nucleophilic anions, for example HBF_4 (55).

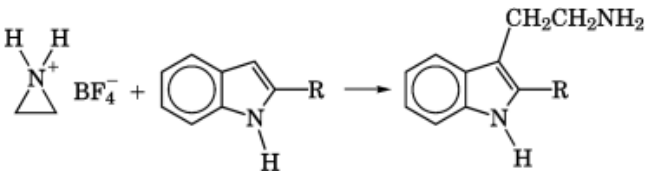
2.1.1.1. Reaction with Carbon Nucleophiles. Unactivated aziridines react with the lithium salts of malonates or β-keto esters in the presence of lithium salts to yield 3-substituted pyrrolidinones (56–59), where R′ = alkyl and aryl, and R = alkoxyl, alkyl, and aryl.

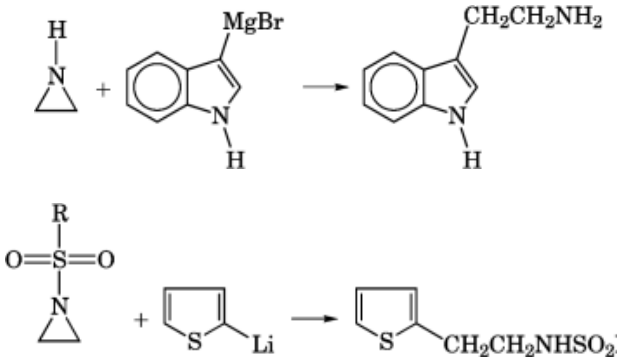


Carbocyclic aromatic compounds ($R = H$, C_2H_5, Cl, OCH_3) can be aminoethylated in the presence of $AlCl_3$ (60–62).

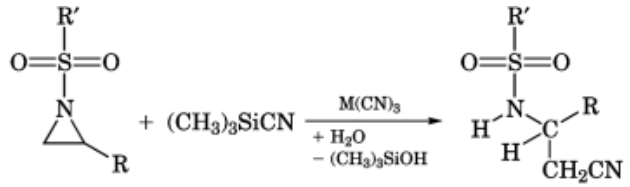


N-sulfonated aziridines have also been used in Friedel-Crafts reactions (qv) (63). The successful C-alkylation of the heteroaromatic compounds indole (qv) [120-72-9] (64–66) and thiophene [110-02-1] (67) with aziridines has also been reported:





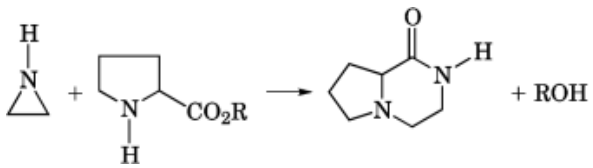
Direct reaction of hydrocyanic acid with ethyleneimine does not yield the desired β-aminopropionitrile (68). However, ring opening of tosylated aziridines to give the corresponding tosylated β-aminopropionitriles is possible using trimethylsilyl cyanide [7677-24-9] with lanthanoid tricyanide catalysis (69, 70).



where M = Yb, Y, Ce; R = C_6H_5, C_4H_9, $C_2H_4SCH_3$, $CH_2C_6H_5$; R′ = $C_6H_4CH_3$

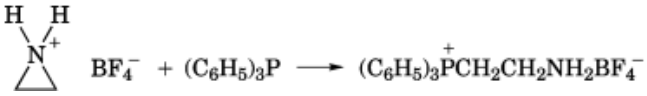
2.1.1.2. Reaction with Nitrogen Nucleophiles. The acid-catalyzed reaction of primary, secondary, and tertiary amines with ethyleneimine yields asymmetrically substituted ethylenediamines (71). Steric effects dominate basicity in the relative reactivity of various amines in the ring-opening reaction with ethyleneimine (72). The use of carbon dioxide as catalyst in the aminoethylation of aliphatic amines, for which a patent application has been filed (73), has two advantages. First, the corrosive salts produced when mineral acids are used as catalysts (74, 75) are no longer formed, and second, the reaction proceeds with good yields under atmospheric pressure.

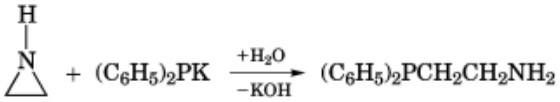
Aluminum chloride [7446-70-0] is a useful catalyst in the reaction of aromatic amines with ethyleneimine (76). Solid catalysts promote the reaction of ethyleneimine with ammonia in the gas phase to give ethylenediamine (77). Not only ammonia and amines, but also hydrazine [302-01-2] (78), hydrazoic acid [7782-79-8] (79–82), alkyl azidoformates (83), and acid amides, eg, sulfonamides (84) or 2,4-dioxopyrimidines (85), have been used as ring-opening reagents for ethyleneimine with nitrogen being the nucleophilic center (1). The 2-oxopiperazine skeleton has been synthesized from α-amino acid esters and ethyleneimine (86–89).



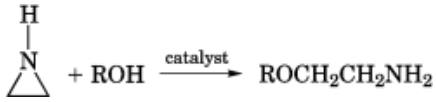
Ethyleneimine dimer has been synthesized using catalytic amounts of an alkali metal amide of ethyleneimine under alkaline conditions (89, 90).

2.1.1.3. Reaction with Phosphorus Nucleophiles. The ethyleneimine ring can be opened using phosphines (91) or alkali metal phosphides (92):



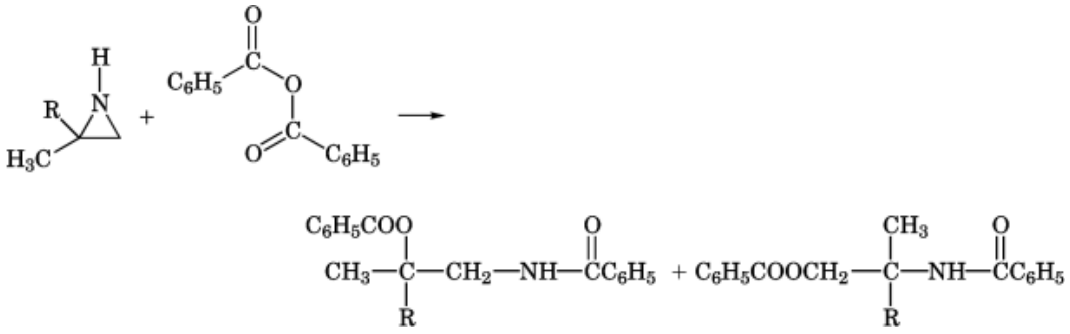


2.1.1.4. Reaction with Oxygen Nucleophiles. In the presence of strong acids, eg, H_2SO_4, HBF_4, or BF_3, aziridines react with alcohols to form β-amino ethers (93):

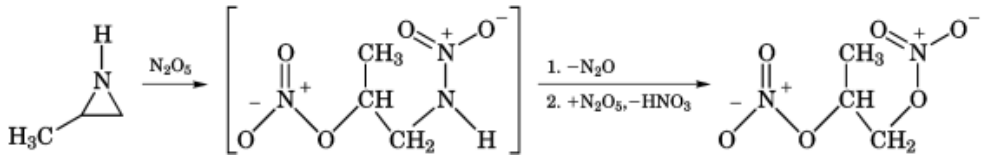


The reaction of a hydroperoxide with 2-methylaziridine [75-55-8] has been described (94). The reaction of ethyleneimine with phenols (95) and carboxylic acids (96, 97) produces ethylamine ethers and esters, respectively. However, these reactions frequently yield product mixtures which contain polyaminoalkylated oxygen nucleophiles and polymers, in addition to the desired products (1). The selectivity of the reaction can often be improved by using less than the stoichiometric amount of the aziridine component (98, 99).

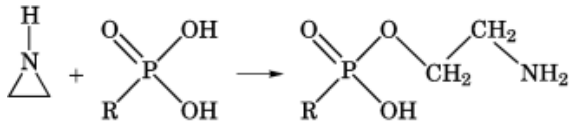
Rearrangement of the initial products to give amides or *N*-nitrophenylmonoethanolamines may occur as secondary reactions when aziridines react with carboxylic acids and phenols which have nitro groups in the ortho and para positions (1, 100). In the reaction of aziridines with anhydrides, the attacking reagent simultaneously acts as oxygen nucleophile and as electrophilic agent. Ester amides are formed when carboxylic anhydrides react with aziridines (101–104).



The anhydride of nitric acid, N_2O_5, reacts with 2-methylaziridine to give the dinitrate (105). In the case of *N*-substituted aziridines, the reaction stops at the stage of the nitramine nitrate prior to elimination of N_2O (106).

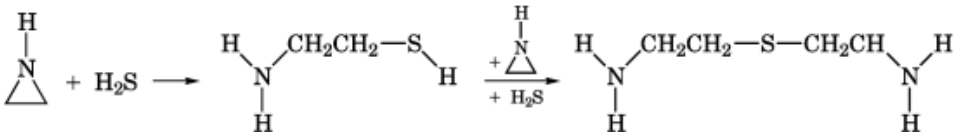


Phosphoric acid, monoalkyl phosphates, and phosphonic acids, but not dialkyl phosphates (107), can be aminoalkylated on the oxygen (108–110).

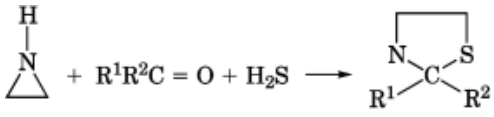


where R = hydroxy, alkoxy, alkyl

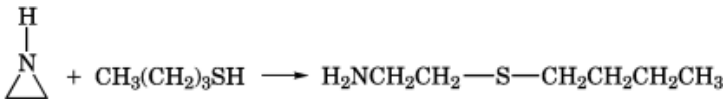
2.1.1.5. Reaction with Sulfur Nucleophiles. Because sulfur is highly nucleophilic, reactions of aziridines with sulfur nucleophiles generally proceed rapidly (111) and with good yields. The reaction of hydrogen sulfide [7783-06-4] with ethyleneimine yields cysteamine [60-23-1] (2-mercaptoethylamine) or bis(2-aminoethyl)sulfide [871-76-1] (2, 112) depending on the molar ratio of the reactants. The use of NaHS for the synthesis of cysteamine has also been described (113).



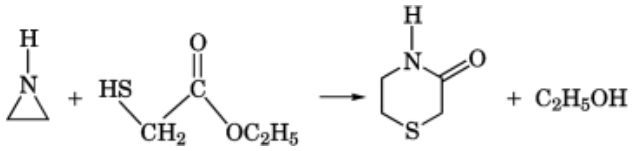
The reaction of hydrogen sulfide with aziridines in the presence of aldehydes or ketones provides a simple route to two-substituted thiazolidines (2, 114–116).



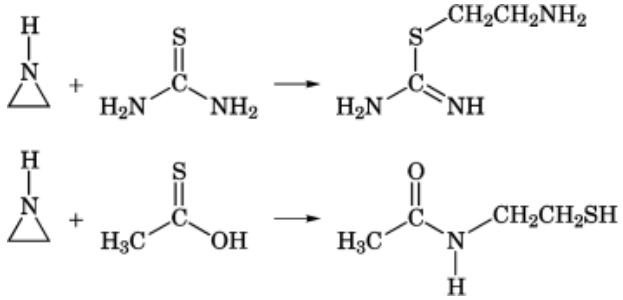
The reaction of aliphatic and aromatic mercaptans with aziridines yields thioethers (117–119).



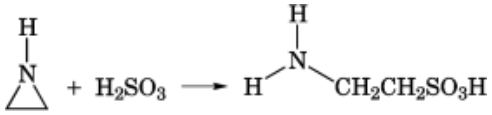
The di- or tetrahydro-1,4-thiazine skeleton is obtained if mercaptans which have a carbonyl group in the β-position react with ethyleneimine (120–124)



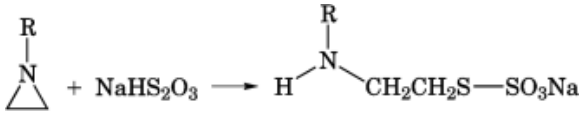
The reaction of thioethers with ethyleneimine in the presence of acid yields sulfonium compounds. The reaction is reversible under alkaline conditions (125). Compounds in which double-bonded sulfur can exist in tautomerism with a form having a free SH group, such as thiourea (126, 127), thiocarboxylic acids (128), and thiophosphates (129), react to give aminoalkylated products. The β-aminoethyl thiocarboxylate rearranges to give the amide.



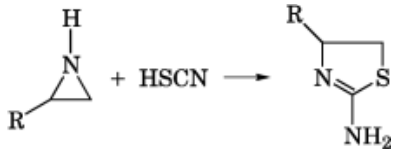
Ethyleneimine reacts rapidly with sulfurous acid to give taurine [107-35-7] in high yield, a reaction of importance not only for the preparation of this amino sulfonic acid but also for the decontamination of ethyleneimine solutions (130).



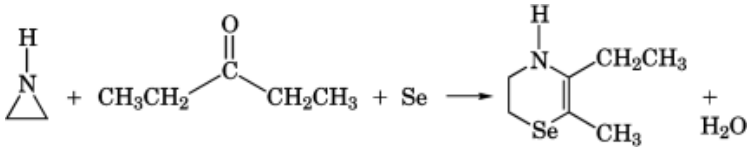
The reaction of aziridines ($R = H$, triazinyl) with thiosulfate yields *S*-alkyl thiosulfates (131, 132), which are known as Bunte salts (133).



2-Amino-2-thiazolines are formed from thiocyanic acid [463-56-9] and aziridines where $R = H$ or CH_3 (116, 134).

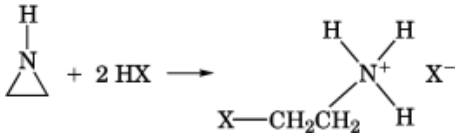


2.1.1.6. Reaction with Selenium Nucleophiles. The reactions of selenium nucleophiles are similar to those of the sulfur nucleophiles: selenophosphates can be aminoalkylated (135). A dihydroselenazine has been obtained by reaction of diethyl ketone, elementary selenium, and ethyleneimine (136).



Selenosulfate reacts with ethyleneimine in the same way as thiosulfate to give 2-aminoethaneselenosulfuric acid. However, the reaction of ethyleneimine using selenous acid does not yield a stable product (137).

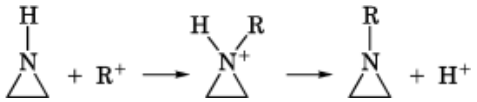
2.1.1.7. Reaction with Halogen Nucleophiles. Hydrochloric acid [7647-01-0], hydrobromic acid [10035-10-6], and hydroiodic acid [10034-85-2] react readily with ethyleneimine (3) to give the corresponding β-halogenoethylamines (20, 21).



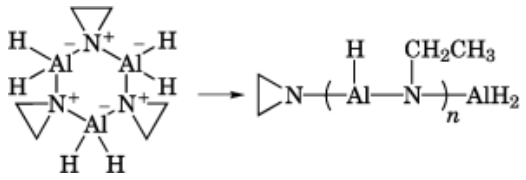
β-Fluoroethylamines are accessible by ring opening of aziridines with hydrogen fluoride in pyridine or with hydrogen fluoride and $SOCl_2$ at low temperatures in ether (138–141). β-Bromoalkylcyanamides have also been obtained by reaction of *N*-alkylated aziridines with cyanogen bromide (142). In this reaction nucleophilic ring opening by bromide and electrophilic attack by the CN group of cyanogen bromide on the aziridine nitrogen take place.

2.1.2. Electrophilic Reactions on the Aziridine Nitrogen

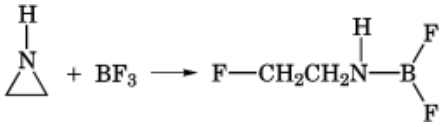
The generalized reaction of aziridines with an electrophile (R^+) is as follows.



2.1.2.1. Reactions with Electrophiles of Group IIIA (B,Al,Ga,In). Ethyleneimine forms cyclic trimers with hydrides or alkyls of elements of Group IIIA, with the liberation of hydrogen or hydrocarbons (143–146). In the case of diborane or trimethylboron, the initial adducts can be isolated (147–150). These aziridine boranes on the one hand undergo electrophilic reactions with opening of the aziridine ring, and on the other hand have the reducing properties of aziridine boranes (149) (see Hydroboration). Aziridinylalane trimer polymerizes on standing with reductive ring opening (145, 151).

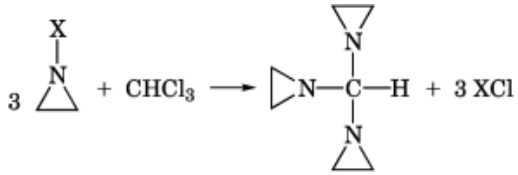


The reaction of 2-methylaziridine with boron trichloride [10294-34-5] leads to replacement of all three chlorides by aziridine rings to form tri(methylethyleneimine) boron [17862-61-2] (152). The reaction of boron trifluoride [7637-07-2] with ethyleneimine at $-78^{\circ}C$ proceeds via substitution and subsequent ring opening to yield *N*-β-fluoroethyl-*B*-difluoroborazene (153).

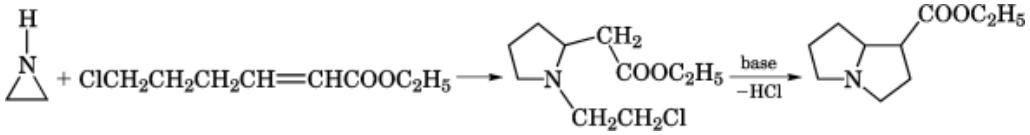


2.1.2.2. Reaction with Carbon Electrophiles. Halogenated carbon compounds, heterocyclic three-membered rings, and unsaturated carbon compounds containing a carbon–carbon or carbon–hetero atom multiple bond can act as electrophiles attacking the aziridine nitrogen via the carbon. The initial products are frequently capable of undergoing ring expansion to form larger heterocycles (7, 8).

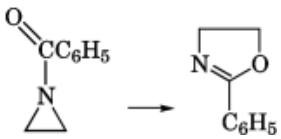
Aziridines ($X = H$) can be alkylated on the nitrogen, with retention of the three-membered ring, by reaction with aliphatic and aromatic halides in the presence of base (2, 154). The reaction can also be carried out, in some cases with very good yields, under phase-transfer conditions using 30% NaOH and optionally an organic solvent (155). If the halides do not react readily, the alkali metal salts ($X =$ Na) of the corresponding aziridine can be used (156–158) to form, for example, triethyleneiminemethane [23974-29-0]..



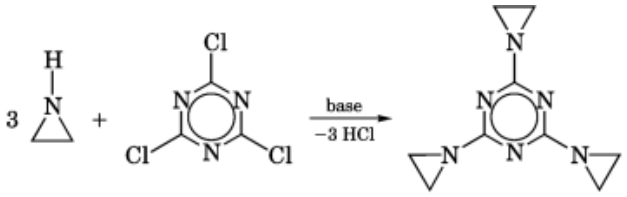
In the absence of a base, the aziridine ring can be quaternized and opened by the nucleophile. A pyrrolizidine synthesis, in which such a reaction proceeds intramolecularly followed by a Michael addition (159), is shown as follows:



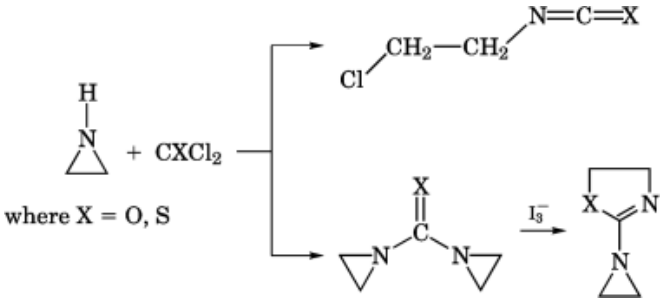
In the presence of a base, acid chlorides react readily with aziridines to give acylated aziridines (2, 22, 160–163). In the absence of a base, however, ring opening takes place and 2-chloroethylamides are obtained (2, 164). Under suitable conditions acylated trialkylammonium salts of ethylenediamine can be prepared from acid chlorides, ethyleneimine, and tertiary amines (71). Acylated aziridines can be rearranged to 2-oxazolines by the action of heat, nucleophiles, or acids. The rearrangement of thioacylaziridines proceeds analogously (7, 8, 165–171).



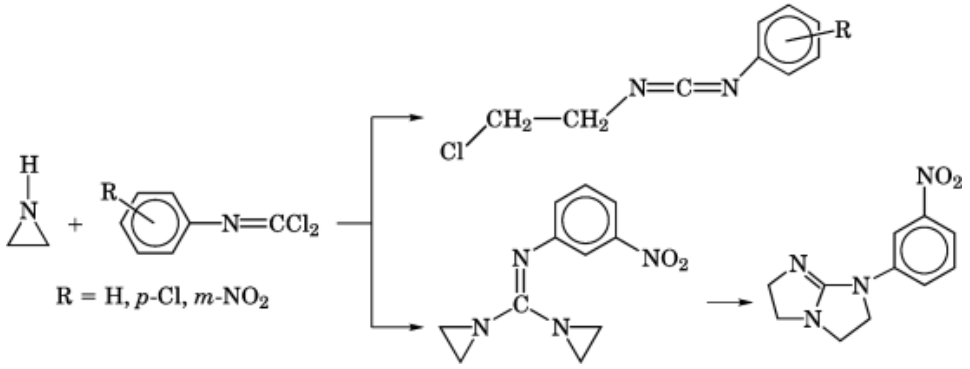
Reaction of cyanuric chloride [108-77-0] with ethyleneimine yields triethylenemelamine [51-18-3] (172).



The reaction of phosgene [75-44-5] or thiophosgene [463-71-8] with ethyleneimine yields either a bisaziridine compound (1,1′-carbonylbisaziridine [1192-75-2] or 1,1′-thiocarbonylbisaziridine [13163-23-0]) or a 2-chloroethyliso(thio)cyanate, depending on the reaction conditions. The former can be isomerized by catalysis with triiodide to give 1-aziridinyl-2-oxazoline [19587-77-0] or 1-aziridinyl-2-thiazoline [17205-48-0] (173–177).



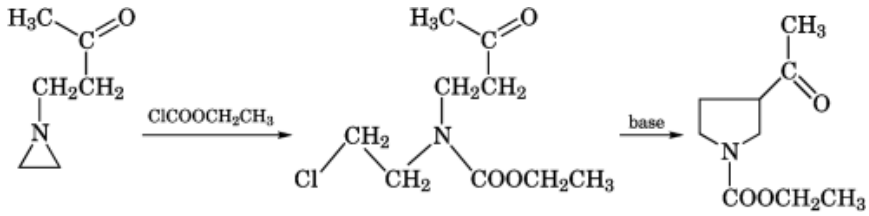
Bisaziridine compounds and *N*-(2-chloroethyl)carbodiimides have also been prepared using isocyanide dichlorides and ethyleneimine (178, 179). The iodide-catalyzed rearrangement of the formerly mentioned compounds provides a method for preparing the tetrahydroimidazoimidazole system:



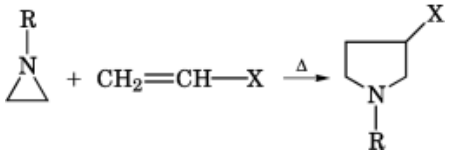
Ethyleneimine reacts with epoxides to form hydroxyalkylated products, eg, *N*-(*β*-hydroxyethylaziridine) [1072-52-2]. The epoxide component is frequently used in substoichiometric amount in order to prevent multiple alkoxylation (180–190). Ethyleneimine and episulfides react to give complex product mixtures, since the 1-(2-mercaptoethyl)aziridine produced initially can easily react further with both reactants (191, 192).

Aziridines can add to carbon–carbon multiple bonds. Elevated temperature and alkali metal catalysis are required in the case of nonpolarized double bonds (193–195). On the other hand, the addition of aziridines

onto the conjugated polarized double or triple bonds of α,β-unsaturated nitriles (196–199), ketones (197, 200), esters (201–205), amides (197), sulfones (206–209), or quinones (210–212) in a Michael addition-type reaction frequently proceeds even at room temperature without a catalyst. The adducts obtained from the reaction of aziridines with α,β-unsaturated ketones, eg, 4-aziridinyl-2-butanone [503-12-8] from 3-buten-2-one, can be converted to 1,3-substituted pyrrolidines by subsequent ring opening with acyl chlorides and alkaline cyclization (213).

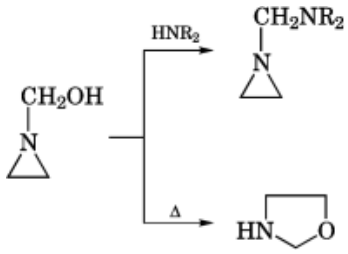


At temperatures $>300^{\circ}C$, substituted pyrrolidines can be obtained by reaction of substituted aziridines ($R = CH_3, C_2H_5$) and conjugated olefins ($X = CN, CO_2CH_3, CH{=}CH_2$) with C—C cleavage in the three-membered ring (214–216).

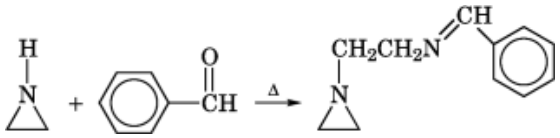


Reactions between vinyl ethers or vinyl acetate and ethyleneimine have not been satisfactory (198), but ethyleneimine does add onto the double bond of *N*,*N*-dimethylvinylamine to give 1-dimethylamino-1-ethyleneiminoethane [5498-98-6] (217).

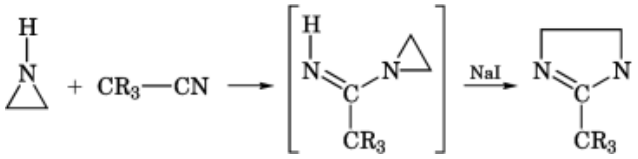
Aliphatic aldehydes and ketones react with aziridines to form relatively stable half aminals, eg, aziridine reacts with formaldehyde to form *N*-hydroxymethylaziridine [20276-43-1]. Half aminals can be converted to full aminals by reaction with a further secondary amine, isomerized to oxazolidines by the action of heat or used in a Mannich reaction for the ring aminomethylation of phenols, although this reaction gives only moderate yields (218–227).



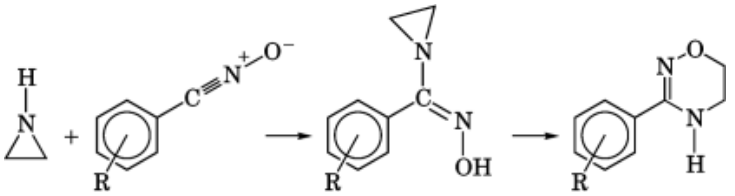
Schiff's bases of ethyleneimine dimer are obtained from the reaction of aromatic aldehydes, eg, benzaldehyde [100-52-7] or furfural [98-01-00], and ethyleneimine (228).



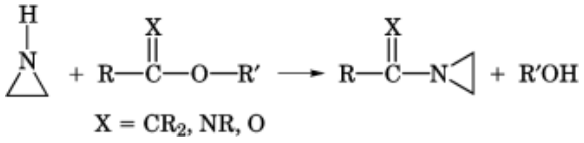
The reaction of ethyleneimine with nitriles in the presence of HBF_4 gives Δ^2-imidazolines (229). If trichloroacetonitrile [545-06-2] ($R = Cl$) is used as the nitrile component, the intermediate amidine can be isolated (230).



1-Aroylaziridine oximes are accessible from aromatic nitrile oxides and aziridines and can rearrange to give the 1,2,4-oxadiazine derivatives (231–233).

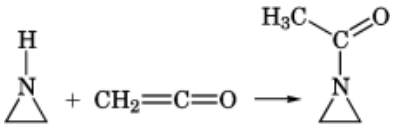


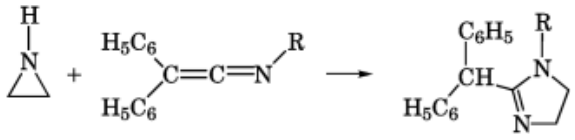
Acyl carbonates (234), alkoxyquinones (235) as vinylogous esters, imino ethers (236), and diketene (237) react with ethyleneimine to give the corresponding acylated ethyleneimines.



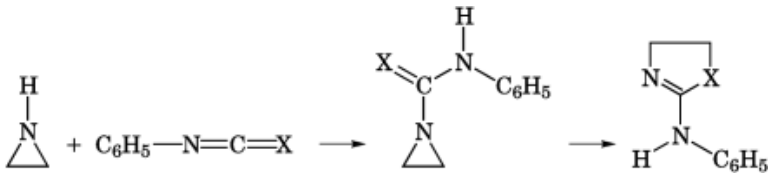
Reaction with esters of strong acids, such as formates or oxalates, yields the acyl derivatives of ethyleneimine dimer (238, 239).

The reaction of heterocumulenes of the ketene type (ketenes, *N*-arylketeneimines, carbon suboxide) with aziridines leads to the formation of acylaziridines or imidoylaziridines (240–242). In a reaction analogous to the ring expansion of acylaziridines, imidoylaziridines rearrange in acids to give 2-substituted 2-imidazolines. These imidazolines are obtained directly in the reaction of ethyleneimine with keteneimines containing an aliphatic substituent on the nitrogen (242).

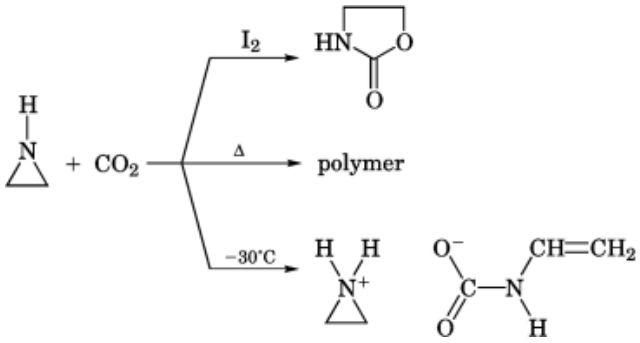




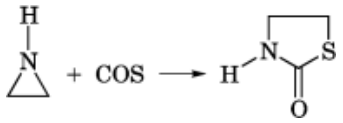
Carbodiimides ($X = NC_6H_5$), isocyanates ($X = O$), and isothiocyanates ($X = S$) also react with aziridines to give amidinoaziridines, carbamoylaziridines, and thiocarbamoylaziridines, respectively. As activated aziridine derivatives, these can rearrange to give derivatives of 2-amino-2-imidazoline, 2-amino-2-oxazoline, and 2-amino-2-thiazoline, respectively (243–250).



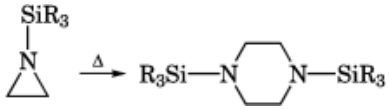
The iodine-catalyzed reaction of aziridines with carbon dioxide leads to 2-oxazolidinones (251). Because carbon dioxide effectively polymerizes ethyleneimine, only low yields are obtained when unsubstituted ethyleneimine reacts with CO_2. However, direct insertion of carbon dioxide [124-38-9] into aziridines can be accomplished, with better yields, by ethoxycarbonylation of aziridines with subsequent elimination of ethylene under flash vacuum conditions (252). 1-Phenylaziridine [696-18-4] can react with CO_2 under antimony [7440-36-0] catalysis to give *N*-phenyl-2-oxazolidinone in good yields (253). At low temperatures and with the exclusion of atmospheric humidity, the reaction of ethyleneimine with carbon dioxide produces the unstable ethyleneiminium salt [31645-38-2] of *N*-vinylcarbamic acid (254, 255).



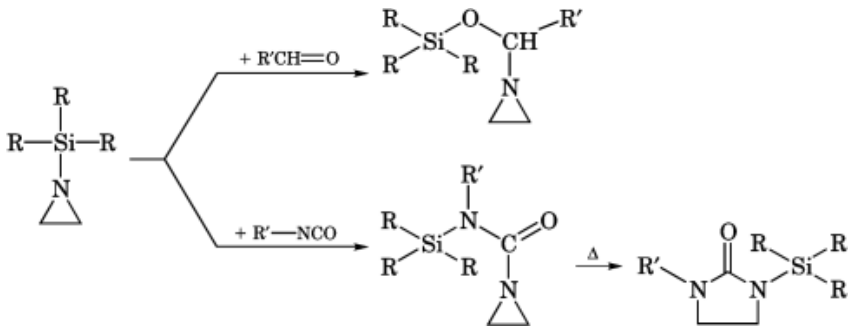
The reaction of ethyleneimine (and derivatives) with carbon oxysulfide yields 2-thiazolidinone [2682-49-7] (256, 257). Carbon disulfide and ethyleneimine react to give 2-thiothiazolidine (258–260). Carbon diselenide reacts with aziridines to form 2-selenazolidineselenones (261).



2.1.2.3. Reaction with Further Electrophiles of Group IVA (Si,Ge,Sn). *N*-Silylated aziridines can be prepared from ethyleneimine by amination of chlorosilanes in the presence of an HCl acceptor, by dehydrocondensation with an organosilicon hydride or by cleavage of a silicon–carbon bond in 2-furyl-, 2-thienyl-, benzyl-, or allylsilanes in the presence of an alkali metal catalyst (262–266). *N*-Silylated aziridines can react with carboxylic anhydrides to give acylated aziridines, eg, *N*-acetylaziridine [460-07-1] in high yields (267). At high temperatures, *N*-silylaziridines can be dimerized to piperazines (268). Aldehydes can be inserted

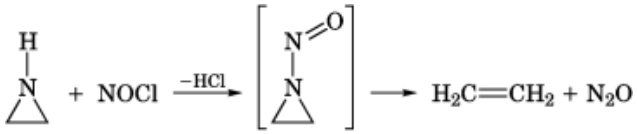


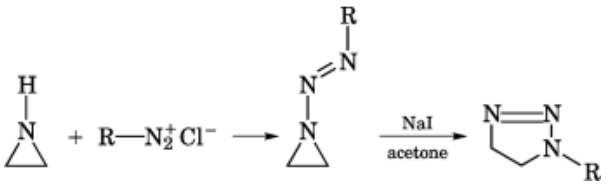
in the nitrogen–silicon linkage (269). The insertion of isocyanates with subsequent thermolysis and hydrolysis provides a method for the preparation of 1-alkyl-2-imidazolidinones (270).



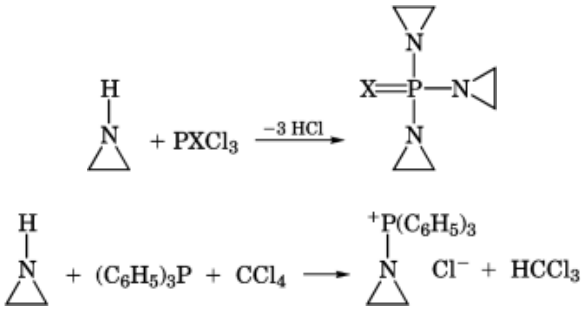
Alkylgermylaziridines of 2- and 4-valent germanium have also been described (271–273). Acetone can be inserted in the germanium–nitrogen linkage of triethylgermylaziridine (273) analogously to the above-mentioned reaction of silylaziridines with carbonyl compounds. *N*-Trimethylstannylaziridine [1481357-1] has been prepared by transamination of *N*-trimethylstannyldimethylamine with ethyleneimine (274), or by lithioamination of trimethyltin chloride or trimethyltin acetate [1118-14-5] with *N*-lithioethyleneimine (275). Carbon dioxide, carbon disulfide, phenyl isocyanate, acetone, or diethyl acetylenedicarboxylate can be inserted in the tin–nitrogen linkage (275).

2.1.2.4. Reaction with Electrophiles of Group VA (N,P,As). The reaction of aziridines with nitrosyl chloride (276, 277) and other nitrosating reagents such as HNO_2, C_4H_9ONO, or $NOBF_4$ (18) proceeds via the thermally unstable *N*-nitrosoaziridines and leads to deamination. Coupling of aromatic diazonium salts with aziridines gives 1-arylazoaziridines, many of which are explosive. The 1-arylazoaziridines can be rearranged with sodium iodide in acetone to give *N*-substituted Δ^2-1,2,3-triazolines (278, 279).



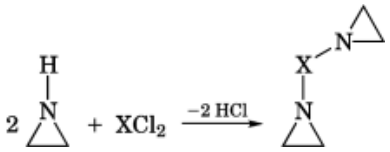


Suitable methods for linking a phosphorus–nitrogen bond to the aziridine ring are the aminolysis of halogenated phosphorus compounds (2, 280–282), the transamination of phosphoramines with excess aziridine (283), the reaction with phosphites (284) and phosphoramidites (285) which have a free OH group, or the reaction of phosphines with aziridines and carbon tetrachloride (286).



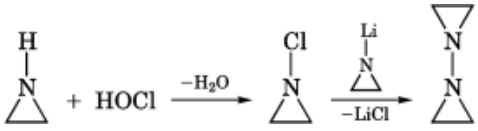
The reaction of monoalkylarsenic(III) halides and dialkylarsenic(III) halides with ethyleneimine has been described (287). This reaction proceeds successfully, unlike the reaction with $AsCl_3$, which can lead to an explosion when purification by distillation is attempted.

2.1.2.5. Reaction with Sulfur Electrophiles. Bisaziridine compounds can be prepared from sulfur dichloride, thionyl chloride, or sulfuryl chloride and ethyleneimine (288). The products are, respectively, 1,1′-thiobisaziridine [2881-79-0] (X = S), 1,1′-dithiobisaziridine [1623-84-3] (X = S—S), 1,1′-sulfinylbisaziridine [1192-76-3] (X = SO), and 1,1′-sulfonylbisaziridine [931-92-0] (X = SO_2).



Diaziridinylsulfanes $S_x(C_2H_4N)_2$, where $x = 1 - 5$, are also obtainable via diimidazolylsulfanes (289). These compounds tend to explode on distillation.

2.1.2.6. Reaction with Halogen Electrophiles. The synthesis of 1-haloaziridines, which are prone to explosion, has been carried out using hypohalites (290, 291). 1-Chloroaziridine [10165-13-6] produced in this way reacts with 1-lithiated ethyleneimine to give 1,1′-diaziridine [4388-03-8]. Perchlorylaziridine [112405-46-6] has been prepared by reaction of ethyleneimine with dichlorine heptoxide at $-20°C$ (292).

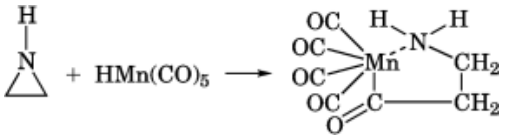


2.1.3. Reactions with Transition-Metal Compounds

The numerous published products of reactions of transition-metal compounds with aziridines can be divided into complexes in which the aziridine ring is intact, compounds formed by reaction of aziridine with the ligands of a complex, and complexes in which the aziridine molecule is fragmented (imido complexes).

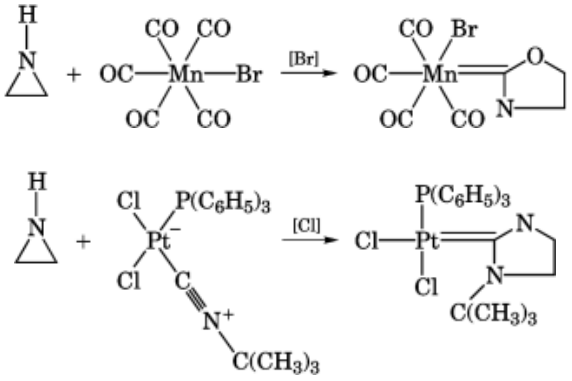
2.1.3.1. Aziridine Complexes in Which the Aziridine Ring is Intact. Central atoms which have been used for complexes in which the aziridine ring is intact include U (293), Ti (294–296), Zr (296), Cr (288–299), Mo (299), Wo (299), Mn (298–300), Fe (301), Co (297, 298, 300, 302–304), Rh (305, 306), Ni (298, 300, 303, 307), Pd (297, 298), Pt (297, 298, 308–310), Cu (298, 300), Ag (300, 311), Zn (300, 311, 312), Cd (300, 311), and Hg (300). The metals Rh and Pt in low oxidation states form stable and inert aziridine complexes (313, 314). Aziridine complexes of Zn and Ti are highly labile with respect to polymerization (313). The aziridine complexes of Co, Ni, and Cu fall between these two extremes. In complexes with central atoms of this type, the aziridine ligand can be dimerized to give 1-(2-aminoethyl)aziridine (299, 311) or hexamerized to give 1,4-bis[2-(2-aminoethyl)aminoethyl]piperazine (315). Secondary reactions of the coordinated ethyleneimine with ring opening are also able to proceed with external nucleophiles, for example in nickel complexes with ammonium thiocyanate to give coordinated 2-amino-2-thiazoline (316).

2.1.3.2. β-Aminoacyl Complexes. Metalcarbonyl hydrides of Mo, W, Mn, and Co react with aziridines with ring opening of the aziridines and subsequent CO insertion to give β-aminoacyl complexes (317–319).

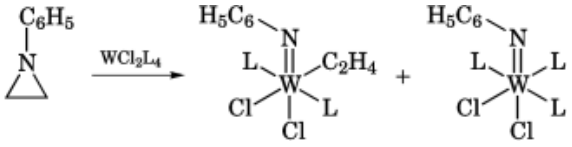


Oxidative cleavage of β-aminoacyl complexes can yield β-amino acid derivatives (320, 321). The rhodium(I)-catalyzed carbonylation of substituted aziridines leads to β-lactams, presumably also via a β-aminoacyl–metal acyclic compound as intermediate. The substituent in the aziridine must have π or *n* electrons for coordination with the rhodium (322, 323).

2.1.3.3. Cyclic Carbene Complexes. The reaction of aziridines with carbonyl, thiocarbonyl, or isonitrile ligands in Mn, Re, Fe, Ru, Pd, or Pt complexes leads to formation of cyclic carbene complexes (324–331).

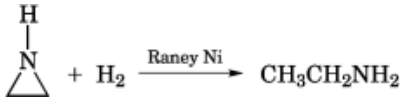


2.1.3.4. Imido Complexes. The reaction of aziridines with tungsten(II) complexes leads to the formation of tungsten(IV) imido complexes (332):



2.1.4. Reductive Ring Opening

Aziridines can be hydrogenated to ethylamines with catalysis by Raney nickel, palladium, or platinum (2,333–335). Lithium in ethylamine has also been used as reducing agent (336). Reductive ring opening of acylated aziridines has been performed using tributyltin hydride and methanol (337).

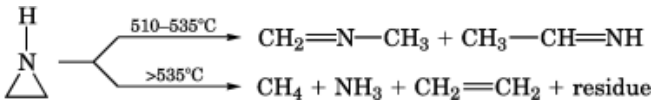


2.1.5. Oxidative Ring Opening

Many oxidizing reagents, such as peracids, ozone [10028-15-6], or FeI_2, are suitable for oxidative deamination of aziridines to give olefins (18). On the other hand, oxidation of bicyclic 2,3-polymethyleneaziridines with lead tetraacetate leads to retention of the nitrogen in the molecule with the formation of ω-keto nitriles (338).

2.1.6. Thermal and Photochemical Reactions

Unsubstituted ethyleneimine has astonishing thermal stability. The reaction of ethyleneimine diluted with argon proceeds to give a mixture of unidentified compounds only at temperatures above 400°C (339). In a flow pyrolysis system under pressures of <1.33 kPa (<10 mm Hg) on quartz wool, isomerization to give *N*-methylenemethylamine and ethylideneimine was observed only in the temperature range 510–535°C. Higher temperatures result in fragmentation (340).



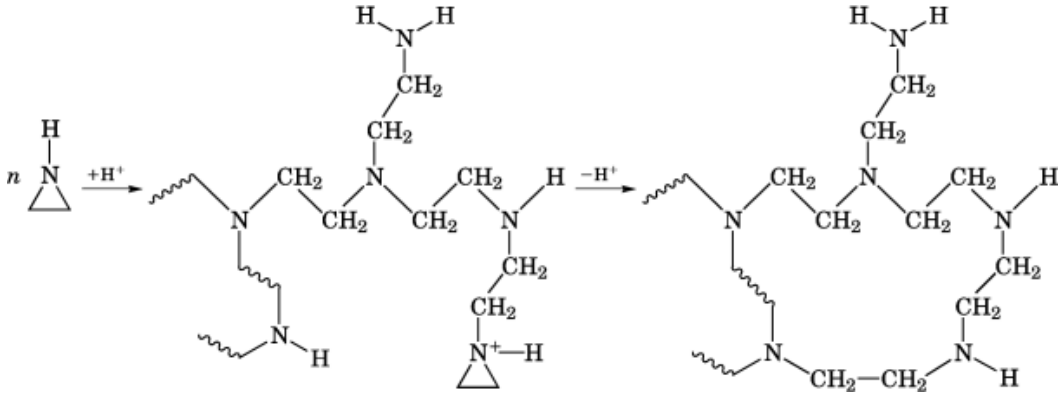
Irradiation of ethyleneimine (341, 342) with light of short wavelength in the gas phase has been carried out directly and with sensitization (343–349). Photolysis products found were hydrogen, nitrogen, ethylene, ammonium, saturated hydrocarbons (methane, ethane, propane, *n*-butane), and the dimer of the ethyleneimino radical. The nature and the amount of the reaction products is highly dependent on the conditions used. For example, the photoproducts identified in a fast flow photoreactor included hydrocyanic acid and acetonitrile (345), in addition to those found in a steady state system. The reaction of hydrogen radicals with ethyleneimine results in the formation of hydrocyanic acid in addition to methane (350). Important processes in the photolysis of ethyleneimine are nitrene extrusion and homolysis of the N—H bond, as suggested and simulated by *ab initio* SCF calculations (351). The occurrence of ethyleneimine as an intermediate in the photolytic formation of hydrocyanic acid from acetylene and ammonia in the atmosphere of the planet Jupiter has been postulated (352), but is disputed (353).

2.1.7. Polymerization

The polymerization of aziridines takes place in the presence of catalytic amounts of acid at elevated temperatures. The molecular weight can be controlled by the monomer–catalyst ratio, the addition of amines as stoppers, or the use of bifunctional initiators. In order to prevent a vigorous reaction, the heat liberated during

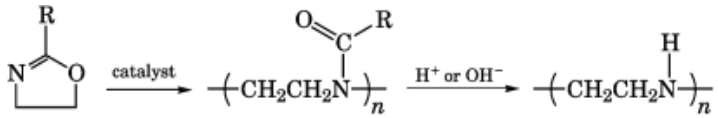
the highly exothermic polymerization must be removed by various measures, ie, suitable dilution, controlled metering of the aziridine component, or external cooling after the reaction has started.

The polymerization of ethyleneimine (16, 354–357) is started by a catalytically active reagent (H^+ or a Lewis acid), which converts the ethyleneimine into a highly electrophilic initiator molecule. The initiator then reacts with nitrogen nucleophiles, such as the ethyleneimine monomer and the subsequently formed oligomers, to produce a branched polymer, which contains primary, secondary, and tertiary nitrogen atoms in random ratios. Termination takes place by intramolecular macrocycle formation.



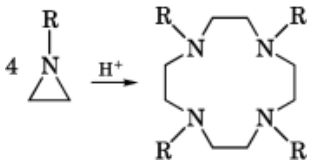
These branched polyethyleneimines are marketed, or have been marketed in the past, under the following trade names: Polymin (BASF Group, Germany and United States), Epomin (Nippon Shokubai, Japan), Corcat (Cordova Chemical Company, United States), and PEI (Dow Chemical Company, United States). In general, the reaction conditions employed for the polymerization of ethyleneimine do not have a significant effect on the degree of branching in the resulting polymers, so polyethyleneimines with extremely high degrees of branching are synthesized by other routes.

Linear polyethyleneimine results only in low yields from low temperature polymerization of ethyleneimine for very long reaction times. It can, however, be synthesized in a targeted manner by polymerization of 2-oxazolines with subsequent hydrolytic cleavage of the resulting polyamides (355, 358).



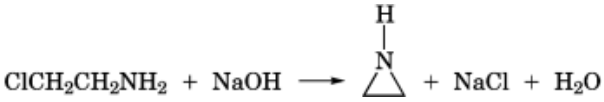
The polymerization of *N*-(2-tetrahydropyranyl)aziridine with subsequent hydrolysis of the resulting polymers has been described as an alternative route for the synthesis of linear polyethyleneimine (359). Linear polyethyleneimine, in contrast to branched polyethyleneimines, is only sparingly soluble in water at room temperature.

Polyethyleneimines with mainly tertiary and primary amino groups are synthesized by subjecting tris(2-aminoethyl)amine, as initiator core, to peraminoalkylation with methanesulfonylaziridine, and the methanesulfonyl protective groups are then removed by hydrolysis. Spherical starburst dendrimers, which contain tertiary amino groups on the inside and primary amino groups on the surface, are obtained by repeating this synthesis sequence several times (360). The reaction of 1-alkylaziridines, in particular 1-benzylaziridines, with catalytic amounts of acids in ethanol leads to the formation of cyclic oligomers, which are normally composed of four aziridine units (361–363).

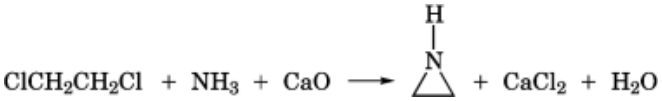


3. Preparation

Ethyleneimine was first prepared commercially in 1938 from 2-chloroethylamine and NaOH by a modified Gabriel synthesis (21).

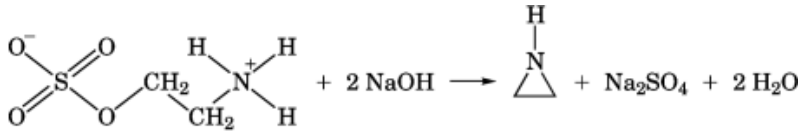


In the 1960s and 1970s ethyleneimine was produced by the dichloroethane–ammonia process by the Dow Chemical Co.

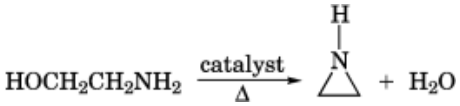


The problems inherent to these two processes are not only the production of corrosive salts, but also the possibility of product contamination by 2-chloroethylamine [689-98-5], as starting material or intermediate. This substance can initiate polymerization of ethyleneimine with the elimination of HCl.

The Wenker process (364), carried out by BASF and various other companies since the end of the 1960s, is a distinct improvement. In this process the hemisulfate of monoethanolamine, a nonvolatile, crystalline substance, is used in place of volatile 2-chloroethylamine for the alkaline cyclization. The reaction can be carried out under pressure (365).



A production plant for salt-free ethyleneimine synthesis by catalytic dehydration of monoethanolamine [141-45-5] in the gas phase has started operation at the Japanese company Nippon Shokubai (366).



4. Economic Aspects

Because of its toxicity, ethyleneimine monomer is not sold by the BASF group or Nippon Shokubai, currently the only large producers. Ethylenimine is used on-site for further reaction to produce polymers and intermediates. The BASF Corp. has started production of ethyleneimine in the United States in Freeport, Texas. The current world ethyleneimine production capacity is more than $12,000$ t/yr. In the United States alone, the consumption of polyethyleneimines approximately doubled between 1983 and 1990. One of the largest markets worldwide is the paper industry, which uses ethyleneimine polymers and their derivatives as process chemicals for paper making. Large amounts of ethyleneimine-based polymers are also used as oil field chemicals and flocculating (aggregating) agents. In addition, ethyleneimine derivatives can be used for a large number of special applications, such as enzyme immobilization, textile finishing, membranes, etc.

5. Analytical and Detection Methods, Storage

In addition to modern spectroscopic methods (^{1}H nmr spectroscopy, ftir spectroscopy) and chromatographic methods (gc, hplc), HBr titration (29) is suitable for the quantitative analysis of ethyleneimine samples which contain relatively large amounts of ethyleneimine. In this titration, the ethyleneimine ring is opened with excess HBr in glacial acetic acid, and unconsumed HBr is back-titrated against silver nitrate.

Aziridine traces in aqueous solution can be determined by reaction with 4-(*p*-nitrobenzyl)pyridine [1083-48-3] and potassium carbonate [584-08-7]. Quantitative determination is carried out by photometric measurement of the absorption of the blue dye formed (367, 368). Alkylating reagents interfere in the determination. Aziridine traces in the air can be detected discontinuously by absorption in Folin's reagent (1,2-naphthoquinone-4-sulfonate) [2066-93-5] (369, 370) with subsequent chloroform extraction and hplc analysis of the red dye formed (371, 372). The detection limit is ca 0.1 ppm. Nitrogen-specific thermal ionization detectors can be used for continuous monitoring of the ambient air.

5.1. Storage

Resistant materials for the storage and handling of ethyleneimine are low carbon steel, V2A and V4A chrome nickel steel, and (strengthened) glass and enamel. Copper, silver, and solders containing these metals must be avoided since they are attacked by ethyleneimine and can form potentially explosive compounds. The majority of plastics swell on contact with ethyleneimine and are unsuitable for its storage. Polytetrafluoroethylene can be used as sealing material for a limited period. When storing ethyleneimine, contact with acids, acid-producing substances, oxidizing agents, and sources of ignition must be avoided in order to avoid uncontrolled decomposition, which in the worst case can proceed with explosive force. Nitrogen is a suitable blanketing gas for use when storing ethyleneimine, and is used to prevent contact with the carbon dioxide in the air. Storage tanks should be fitted with a temperature monitoring device and a linked facility for NaOH metering.

6. Health and Safety Factors

6.1. Toxicology

Ethyleneimine is highly toxic on inhalation, on contact with the skin, and if swallowed (373). Inhalation of ethyleneimine vapors can cause damage to the mucous membranes of the respiratory tract and bronchi, with associated difficulty in breathing and irritation of the throat, and pulmonary edema. There can be a latency period of several hours between inhalation and onset of symptoms. Ethyleneimine vapors and liquid

Table 2. Acute Toxicities for Ethyleneimine

Mode of administration	Species	LD_{50}	Reference
inhalation (10 min),	mouse	4 mg/Lair	378
injection,	rat	4 mg/kg	379
ingestion,	rat	15 mg/kg	380
absorption through the skin,	guinea pig	14 μL/kg	381

ethyleneimine can cause damage to the eyes, which can lead to blindness. Liquid ethyleneimine penetrates the skin very rapidly and produces severe burns and necroses (localized death of living tissue). In addition to the local effect, absorption of ethyleneimine can cause nausea and vomiting and states of agitation with profuse sweating, frequently only after a latency period of several hours. In the extreme case, ethyleneimine poisoning can be fatal.

The odor threshold for detection of ethyleneimine is 2 ppm. The maximum permissible concentration of ethyleneimine in the air at the place of work is 0.5 ppm (as specified in statutory regulations in the United States (374) and in Germany (375)). Animal experiments have shown ethyleneimine to be both carcinogenic (376) and mutagenic (377) (Table 2).

6.2. Handling Precautions

It is essential that inhalation of vapors and contact with the skin is avoided when handling ethyleneimine. Suitable personal protection includes a full protection suit, preferably made of butyl rubber, and a breathing and face mask (hood with independent air supply). Reactions with ethyleneimine carried out in the laboratory must be conducted as far as possible in closed apparatus in an efficient hood. Ethyleneimine and other low molecular weight aziridines are very highly flammable and can form explosive mixtures with air (Table 1). Possible sources of ignition (open flames, electric sparks, static charges, etc) must be removed when using ethyleneimine. Aziridines stored in the monomer form should be stabilized with solid NaOH to prevent spontaneous polymerization by traces of acid, eg, by carbon dioxide from the air. Ethyleneimine can be destroyed by slow introduction into sodium bisulfite solution.

7. Applications

Ethyleneimine and its derivatives have many industrial applications. Polymers based on ethyleneimine have a very high nitrogen:carbon ratio. This results in a high cation activity, which results in a high affinity for naturally occurring anions (29). However, the potential of ethyleneimine is based not only on autocondensation but also on the aminoethylation of functional groups. By grafting ethyleneimine onto oligomers or polymers, it is possible to adjust the cation activity of these compounds, and to tailor the compounds to suit the intended application (1, 29).

The biological activity of ethyleneimine derivatives is utilized in both medicine and in crop protection (1). Derivatization of the aziridine ring results in a great variety of useful compounds. Derivatives of methylaziridine have a higher affinity for lipophilic substrates, and thus have widespread use as biologically active substances. The complexing properties of polyaziridines can be modified by the use of ethyleneimine derivatives such as *N*-(2-hydroxyethyl)aziridine as starting monomers (1).

7.1. Paper Industry

The principal use of ethyleneimine is as polymer in paper making. Polyethyleneimines (PEIs) promote the flocculation of wood and cellulose fibers and thus increase the retention of the fibers and fillers (382–384). The introduction of paper making in a neutral medium and the associated reduced use or abandonment of aluminum sulfate is increasing the demand for synthetic retention agents (385). Polyamidoamines are also suitable for this application, and the nitrogen content of these compounds can be increased by grafting with ethyleneimine (386–388). Because of their high positive charge density, PEIs fix negatively charged resin particles and interfering substances and thus facilitate problem-free paper production even in the case of closed water circulation (389, 390), which is increasingly used. These fixing properties also can increase the quality of the paper. Ink-jet paper, which has to absorb ink easily, is produced with the addition of PEI (391). The fixing of sizing emulsions also serves the same purpose (392). In addition, both dry compaction (393) and wet compaction (394) are improved by the addition of polyethyleneimines.

7.2. Extraction and Complexing

The basic nitrogen atoms in PEI are able to absorb gases. This is utilized in, for example, cigarette filters, which can be impregnated with PEIs or derivatives (395), to remove aldehydes by chemical absorption (396). Acid gases can also be neutralized and absorbed by cross-linked PEIs (397) or by carriers impregnated with PEI (398). The complex-forming properties of PEI can also be used for the retention of metal ions (399–401) and for the catalysis of chemical reactions (402, 403).

PEI derivatives have proven to be effective carriers of cations in liquid membrane systems (404). This technology led to the development of ion-exchange resins (405), which are also suitable for extracting uranium from seawater (406).

Polyelectrolytes based on ethyleneimine are also used to treat drinking water and process water, and as agents for preventing lime deposits (407) in water extraction. The binding power of PEI is utilized for the treatment of effluents (408). Biochemical reactions can be catalyzed by using the complex-forming properties of PEIs and their affinity for organic substrates (409).

7.3. Additives

Because of their versatility, imparted via chemical modification, the applications of ethyleneimine encompass the entire additive sector. The addition of PEI to PVC plastisols increases the adhesion of the coatings by selective adsorption at the substrate surface (410). PEI derivatives are also used as adhesion promoters in paper coating (411). The adducts formed from fatty alcohol epoxides and PEI are used as dispersants and emulsifiers (412). They are able to control the viscosity of dispersions, and thus facilitate transport in pipe systems (413). Fatty acid derivatives of PEI are even able to control the viscosity of pigment dispersions (414). The high nitrogen content of PEIs has a flame-retardant effect. This property is used, in combination with phosphorus compounds, for providing wood panels (415), cellulose (416), or polymer blends (417, 418) with a flame-retardant finish.

7.4. Immobilization

The fixing property of PEIs has previously been discussed. Another application of this property is enzyme immobilization (419). Enzymes can be bound by reactive compounds, eg, isothiocyanate (420) to the PEI skeleton, or immobilized on solid supports, eg, cotton by adhesion with the aid of PEIs. In every case, fixing considerably simplifies the performance of enzyme-catalyzed reactions, thus facilitating preparative work. This technique has been applied to glutaraldehyde-sensitive enzymes (421), α-glucose transferase (422), and pectin lyase, pectin esterase, and endopolygalacturonase (423).

Substances other than enzymes can be immobilized. Examples include the fixing of heparin on polytetrafluoroethylene with the aid of PEI (424), the controlled release of pesticides which are bound to PEI (425), and the inhibition of herbicide suspensions by addition of PEI (426). The uptake of anionic dyes by fabric or paper is improved if the paper is first catonized with PEI (427). In addition, PEI is able to absorb odorizing substances such as fatty acids and aldehydes. Because of its high molecular weight, PEI can be used in cosmetics and body care products, as well as in industrial elimination of odors, such as the improvement of ambient air quality in sewage treatment plants (428).

7.5. Textile Finishing

Polyethyleneimine-*N*-methylolurea derivatives improve the crease and wear resistance of cotton (429, 430). The adhesion between individual wool fibers is improved by pretreatment with amines, which leads to improved shrink resistance (431). An antimicrobial finish can be applied to cotton by using a combination of PEI and ureas to bind zinc pyrithione to the fabric (432). After wool has been provided with a flameproof finish using fluorozirconate or fluorotitanate, the wool can be neutralized with PEI (433). Conventional neutralizing agents cannot be used for this purpose since they impair the flameproof characteristics of the impregnated fabric.

7.6. Flocculation

The interaction of the cationic PEIs with anionic substrates leads to substrate flocculation. Applications of this property include the coagulation of latex (434), commercial application in effluent treatments (435–437), and stabilization of highly loaded coal–water mixtures in mining (438).

7.7. Material Protection

The graft copolymers of ethylene sulfide on polyethyleneimine can be used as an antifouling anticorrosion substrate for iron (439). PEIs or their derivatives are also used in electrolysis baths as brighteners in the electrochemical deposition of metals (440, 441).

7.8. Medicine

There are many applications of PEI in the medical sector. Analytical methods, such as the quantitative determination of the surface charge of serum lipoproteins (442), are aided by use of PEI, and it is also used as a carrier in the development of polymer drugs (443, 444). Platinum–polyethyleneimine complexes prevent the division of bacteria, and are being tested as carriers in the treatment of cancer and viruses (445–447). Encapsulated PEIs containing nucleic acid bases activate the neutrophils in human blood (448).

Aziridines occur naturally in the form of mitomycins (Table 3), which have antibiotic activity (1, 449). Mytomycin C is used clinically as one of the most effective agents in the chemotherapy of cancer (450).

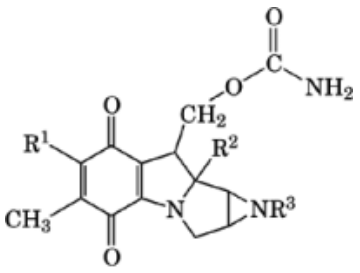


Table 3. Structures of Mytomycins

Name	CAS Registry Number	R^1	R^2	R^3
mitomycin A	[4055-40-7]	CH_3O—	CH_3O—	H—
mitomycin B	[4055-39-4]	CH_3O—	HO—	CH_3—
mitomycin C	[50-07-7]	H_2N—	CH_3O—	H—
porfiromycin	[801-52-5]	H_2N—	CH_3O—	CH_3—

7.9. Membranes and Osmosis

Membranes based on PEI can be used for the dehydration of organic solvents such as 2-propanol, methyl ethyl ketone, and toluene (451), and for concentrating seawater (452–454). On exposure to ultrasound waves, aqueous PEI salt solutions and brominated poly(2,6-dimethylphenylene oxide) form stable emulsions from which it is possible to cast membranes in which submicrometer capsules of the salt solution are embedded (455). The rate of release of the salt solution can be altered by surface–active substances. In membranes, PEI can act as a proton source in the generation of a photocurrent (456). The formation of a PEI coating on ion-exchange membranes modifies the transport properties and results in permanent selectivity of the membrane (457). The electrochemical testing of salts (458) is another possible application of PEI.

7.10. Miscellaneous Applications

PEIs and their derivatives are used as cementation auxiliaries in crude oil exploration (459), and for breaking crude oil emulsions (460) in crude oil extraction. Seed coatings of water-soluble copolymers containing polyethyleneimine have been developed (461). Polyethyleneimine derivatives have positive photoresist properties (462); amidated polyethyleneimines improve the flow properties of cement (463); and with few exceptions, *N*-acylaziridines act as chemical sterilizers for insects (464).

7.11. Derivatives

The most important data for 2-methylaziridine and 1-(2-hydroxyethyl)aziridine, which previously had some industrial significance, are given in Table 1. Like ethyleneimine, these compounds are used in polymer form and as intermediates. The use of activated aziridines, eg, *N*-acylaziridines, for amino ethylation, under alkaline conditions, is of preparative interest (1).

BIBLIOGRAPHY

"Imines, Cyclic" in *ECT* 2nd ed., Vol. 11, pp. 526–548, by O. C. Dermer, Oklahoma State University, and A. W. Hart, The Dow Chemical Co.; in *ECT* 3rd ed., Vol. 13, pp. 142–166, by G. E. Ham, Dow Chemical U.S.A.

Cited Publications

1. O. C. Dermer and G. E. Ham, *Ethylenimine and Other Aziridines*, Academic Press, Inc., New York, 1969.
2. H. Bestian, *Ann. Chem.* **566**, 210 (1950).
3. H. Bestian, in E. Müller, ed., *Methoden der Organischen Chemie (Houben-Weyl)*, Georg Thieme Verlag, Stuttgart, 1958, p. 227.
4. P. E. Fanta, in A. Weissberger, ed., *Heterocyclic Compounds with Three- and Four-Membered Rings*, Part I, Interscience Publishers, New York, 1964, p. 524.
5. P. A. Gembitskii, N. M. Loim, and D. S. Zhuk, *Russ. Chem. Rev.* **35**, 105 (1966).

6. S. Hirai and W. Nagata, *Kagaku No Ryoiki Zokan* **87**, 213 (1969).
7. F. N. Gladysheva, A. P. Sineokov, and V. S. Etlis, *Russ. Chem. Rev.* **39**, 118 (1970).
8. H. W. Heine, *Mech. Mol. Migr.* **3**, 145 (1971).
9. J. W. Lown, *Rec. Chem. Progr.* **32**, 51 (1971).
10. J. W. Lown and K. Matsumoto, *Yuki Gosei Kagaku Kyokai Shi* **29**, 760 (1971).
11. G. Maerker, in F. D. Gunstone, ed., *Topics in Lipid Chemistry*, Vol. **2**, Logos Press Limited, London, 1971, p. 159.
12. G. E. Ham, in K. C. Frisch, ed., *High Polymers*, Vol. **26**, John Wiley & Sons, Inc., New York, 1972, p. 313.
13. G. J. Matthews and A. Hassner, in J. Fried and J. A. Edwards, eds., *Organic Reactions in Steroid Chemistry*, Vol. **2**, 1972, p. 1.
14. O. Cervinka, *Method Chim.* **6**, 603 (1975).
15. G. E. Ham, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Suppl. Vol. **1**, John Wiley & Sons, Inc., New York, 1976, p. 25.
16. G. E. Ham, in E. J. Goethals, ed., *Polymeric Amines and Ammonium Salts*, Pergamon Press, New York, 1980, p. 1.
17. M. Kodo, *Kagaku Keizai*, 41 (1982).
18. J. A. Deyrup, in A. Weissberger and E. C. Taylor, eds., *The Chemistry of Heterocyclic Compounds*, Vol. 42, Part 1, John Wiley & Sons, Inc., New York, 1983, p. 1.
19. A. Padwa and A. D. Woolhouse, in A. R. Katritzky and C. W. Rees, eds., *Comprehensive Heterocyclic Chemistry*, Vol. **7**, Pergamon Press, Oxford, U.K., 1984, p. 47.
20. S. Gabriel, *Ber.* **21**, 1049 (1988).
21. *Ibid.*, p. 2664.
22. C. C. Howard and W. Marckwald, *Ber.* **32**, 2036 (1899).
23. W. Marckwald, *Ber.* **33**, 764 (1900).
24. P. F. Pascoe and W. A. Sherbrock-Cox, *J. Appl. Chem.* **13**, 564 (1963).
25. Sorbe, *Sicherheitstechnische Kenndaten Chemischer Stoffe*, Ecomed Verlagsgesellschaft GmbH, Landsberg/Lech, 1983, p. 11.
26. Internal technical research report, *Ethylenimin*, BASF AG, Ludwigshafen, Germany, 1970.
27. E. W. Flick, ed., *Industrial Solvents Handbook*, 3rd ed., Noyes Data Corp., Park Ridge, N.J., 1985, p. 569.
28. Ref. 25, p. 9.
29. Technical data, BASF AG, Ludwigshafen, Germany, 1964.
30. R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Standards* **48**, 206 (1952).
31. *Vapour Pressures and Critical Points of Liquids XI: Heterocyclic Nitrogen Compounds*, Engineering Sciences Data Unit 77019, London, 1977.
32. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, 1969, 468–469, and references therein.
33. J. Hinze and R. F. Curl, Jr., *J. Am. Chem. Soc.* **86**, 5068 (1964).
34. U.S. Pat. 2,729,679 (Nov. 19, 1951), J. L. Anderson (to E. I. du Pont de Nemours & Co., Inc.).
35. K. Hashigushi and co-workers, *J. Mol. Spectroscopy* **105**, 81 (1984).
36. J. L. Ripoll, H. Lebrun, and A. Thuillier, *Tetrahedron* **36**, 2497 (1980).
37. Y. Hamada and co-workers, *J. Mol. Spectroscopy* **105**, 93 (1984).
38. R. I. Wagner and co-workers, *J. Am. Chem. Soc.* **89**, 1102 (1967).
39. G. D. Jones and co-workers, *J. Org. Chem.* **9**, 125 (1944).
40. L. Siggel and S. Brode, technical data, BASF AG, Ludwigshafen, Germany, 1992.
41. R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).
42. R. Hoffmann and W. D. Stohrer, *J. Am. Chem. Soc.* **93**, 6941 (1971).
43. R. Gleiter, *Topics Curr. Chem.* **86**, 197 (1979).
44. W. S. Wilcox and co-workers, *J. Chem. Phys.* **21**, 563 (1953).
45. T. E. Turner and co-workers, *J. Chem. Phys.* **21**, 564 (1953).
46. T. G. Tuner, V. C. Flora, and W. M. Kendrick, *J. Chem. Phys.* **23**, 1966 (1955).
47. R. D. Johnson, R. J. Myers, and W. D. Gwinn, *J. Phys. Chem.* **21**, 1425 (1953).
48. M. Igarashi, *Bull. Chem. Soc. Jpn.* **34**, 369 (1961).
49. H. B. Basch and co-workers, *J. Chem. Phys.* **51**, 52 (1969).
50. P. Rademacher and co-workers, *J. Mol. Struct.* **197**, 291 (1989).

51. R. Ellerbrock and P. Rademacher, *J. Mol. Struct.* **265**, 93 (1992).
52. C. Liang and L. C. Allen, *J. Am. Chem. Soc.* **113**, 1878 (1991) and references therein.
53. G. J. Buist and H. J. Lucas, *J. Am. Chem. Soc.* **79**, 6157 (1957).
54. D. R. Crist and N. J. Leonard, *Angew. Chem.* **81**, 953 (1969) and references therein.
55. U. Harder, E. Pfeil, and K. F. Zenner, *Chem. Ber.* **97**, 510 (1964).
56. H. Stamm, *Angew. Chem.* **74**, 694 (1962).
57. H. Stamm, *Angew. Chem.* **77**, 738 (1965).
58. H. Stamm, *Chem. Ber.* **99**, 2556 (1966).
59. H. Stamm, *Arch. Pharm.* **299**, 965 (1966).
60. G. I. Bras, *Dokl. Akad. Nauk SSSR* **87**, 589 (1952).
61. G. I. Bras, *Dokl. Akad. Nauk SSSR* **87**, 747 (1952).
62. N. Milstein, *J. Heterocycl. Chem.* **5**, 339 (1968).
63. H. Stamm and co-workers, *J. Org. Chem.* **54**, 193 (1989).
64. R. Bucourt and M. Vignau, *Bull. Soc. Chim. Fr.*, 1190 (1961).
65. E. Pfeil and U. Harder, *Angew. Chem.* **79**, 188 (1967).
66. J. Legters, L. Thijs, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **111**, 16 (1992).
67. R. Fikentscher, R. Brückmann, and R. Betz, *Ann. Chem.*, 113 (1990).
68. E. D. Schilling and F. M. Strong, *J. Org. Chem.* **22**, 349 (1957).
69. S. Matsubara, T. Kodama, and K. Utimoto, *Tetrahedron Lett.* **31**, 6379 (1990).
70. K. Utimoto and co-workers, *Yuki Gosei Kagaku Kenkyusho Koenshu* **5**, 101 (1991).
71. L. B. Clapp, *J. Am. Chem. Soc.* **70**, 184 (1948); Brit. Pat. 1,363,299 (Nov. 26, 1970), F. Miksovsky and R. Fikentscher (to BASF AG); Brit. Pat. 1,383,127 (Jan. 11, 1971), F. Miksovsky and R. Fikentscher (to BASF AG).
72. A. R. Dalin and co-workers, *Zh. Obshch. Khim.* **58**, 2098 (1988).
73. Eur. Pat. 422,534 A2 (Jan. 19, 1994), A. Hohmann, W. Reuther, and W. Bochnitschek (to BASF AG).
74. G. I. Bras and V. A. Skorodumov, *Compt. Rend. Acad. Sci. USSR* **55**, 315 (1947).
75. G. I. Bras and V. A. Skorodumov, *Dokl. Akad. Nauk SSSR* **59**, 489 (1948).
76. G. H. Coleman and J. E. Callen, *J. Am. Chem. Soc.* **68**, 2006 (1946).
77. Eur. Pat. 370,730 A2 (Nov. 22, 1988), (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
78. Ger. Pat. 1,108,223 (Oct. 9, 1959), K. Eiter and E. Truscheit (to Bayer AG).
79. R. D. Guthrie and co-workers, *Proc. Chem. Soc.*, 84 (1963).
80. E. Bertele and co-workers, *Angew. Chem.* **76**, 393 (1964).
81. G. Swift and D. Swern, *J. Org. Chem.* **32**, 511 (1967).
82. J. Cleophax, S. D. Gero, and J. Hildesheim, *Chem. Commun.*, 94 (1968).
83. Y. Hata and M. Watanave, *Tetrahedron* **30**, 3569 (1974).
84. Ger. Pat. 1,198,471 (Aug. 30, 1961), A. Tartter, G. Lützel, and W. Rohland (to BASF AG).
85. R. T. Markiw, *J. Org. Chem.* **37**, 2165 (1972).
86. M. E. Freed and A. R. Day, *J. Org. Chem.* **25**, 2108 (1960).
87. H. B. Sullivan and A. R. Day, *J. Org. Chem.* **29**, 326 (1964).
88. C. R. Rasmussen and D. L. Shaw, *J. Org. Chem.* **39**, 1560 (1974).
89. U.S. Pat. 3,502,654 (Apr. 12, 1967), J. D. Young (to Dow Chemical Co.).
90. C. R. Dick, *J. Org. Chem.* **32**, 72 (1967).
91. W. Reuther, technical data, BASF AG, Ludwigshafen, Germany, 1989.
92. K. Issleib and D. Haferburg, *Z. Naturforsch.* **B 20**, 916 (1965).
93. U. Harder, E. Pfeil, and K. F. Zenner, *Chem. Ber.* **97**, 510 (1964).
94. U.S. Pat. 2,703,816 (Sept. 26, 1951), W. S. Emerson and B. S. Wildi (to Monsanto Chemical Co.).
95. L. B. Clapp, *J. Am. Chem. Soc.* **73**, 2584 (1951).
96. R. Ghirardelli and H. J. Lucas, *J. Am. Chem. Soc.* **77**, 106 (1955).
97. A. Hassner and C. Heathcock, *J. Org. Chem.* **30**, 1748 (1965).
98. U.S. Pat. 3,336,358 (July 23, 1964), R. T. McFadden (to Dow Chemical Co.).
99. U.S. Pat. 3,338,954 (Oct. 8, 1964), R. T. McFadden and C. R. Dick (to Dow Chemical Co.).
100. L. B. Clapp and co-workers, *J. Am. Chem. Soc.* **77**, 5116 (1955).
101. Ger. Pat. 1,081,473 (Mar. 18, 1954), H. G. Trieschmann, L. Reuther, and W. Arend.

102. Brit. Pat. 784,058 (Mar. 18, 1954), W. Arendt, L. Reuter, and H. Trieschmann (to BASF AG).
103. Brit. Pat. 784 059 (Mar. 18, 1954), W. Arendt, L. Reuter, and H. Trieschmann (to BASF AG).
104. P. Loewrigkeit and co-workers, *J. Org. Chem.* **33**, 3344 (1968).
105. P. Golding and co-workers, *Tetrahedron Lett.* **32**, 4985 (1991).
106. P. Golding and co-workers, *Tetrahedron Lett.* **29**, 2735 (1988).
107. D. M. Brown and G. O. Osborne, *J. Chem. Soc.*, 2590 (1957).
108. H. N. Christensen, *J. Biol. Chem.* **135**, 399 (1940).
109. Y. S. Tsizin and N. A. Preobrazhenskii, *J. Gen. Chem. USSR* **33**, 2800 (1963).
110. S. Z. Ivin and co-workers, *J. Gen. Chem. USSR* **37**, 1556 (1967).
111. J. E. Earley, *J. Am. Chem. Soc.* **80**, 3458 (1958).
112. S. Gabriel and G. Eschenbach, *Ber.* **30**, 2494 (1897).
113. Eur. Pat. 320,727 A2 (Dec. 12, 1987), A. Hohmann and co-workers (to BASF AG).
114. R. G. Kostyanovskii, *Dokl. Akad. Nauk SSSR* **135**, 853 (1960).
115. J. L. Larice, J. Roggero, and J. Metzger, *Bull. Soc. Chim. Fr.*, 3637 (1967).
116. R. A. Wohl and D. F. Headley, *J. Org. Chem.* **37**, 4401 (1972).
117. G. Tsatsas, C. Sandris, and D. Kontonassios, *Bull. Soc. Chim. Fr.*, 3100 (1964).
118. H. Rübner, *Arzneim. Forsch.* **15**, 796 (1965).
119. G. Meguerian and L. B. Clapp, *J. Am. Chem. Soc.* **73**, 2121 (1951).
120. H. Lehr, S. Karlan, and M. W. Goldberg, *J. Med. Chem.* **6**, 136 (1963).
121. F. Asinger, F. J. Schmitz, and S. Reichel, *Ann. Chem.* **652**, 50 (1962).
122. F. Asinger, H. Diem, and W. Schäfer, *Monatsh. Chem.* **95**, 1335 (1964).
123. F. Asinger and co-workers, *Monatsh. Chem.* **101**, 1281 (1970).
124. *Ibid.*, p. 1295.
125. U.S. Pat. 3,793,370 (Apr. 21, 1970), F. Miksovsky and R. Fikentscher (to BASF AG).
126. S. L. Holton and co-workers, *Can. J. Chem.* **42**, 2147 (1964).
127. L. D. Spicer and co-workers, *J. Org. Chem.* **33**, 1350 (1968).
128. Ger. Pat. 893,795 (Apr. 26, 1951), R. Kuhn and G. Quadbeck (to BASF AG).
129. S. Akerfeldt, *Acta Chem. Scand.* **17**, 329 (1963).
130. P. Rumpf, *Compt. Rend.* **204**, 592 (1937).
131. F. C. Schaefer, J. T. Goeghegan, and D. W. Kaiser, *J. Am. Chem. Soc.* **77**, 5918 (1955).
132. E. Allen and W. Seaman, *Anal. Chem.* **27**, 540 (1955).
133. H. Distler, *Angew. Chem.* **79**, 520 (1967).
134. J. E. Earley and co-workers, *J. Am. Chem. Soc.* **80**, 3458 (1958).
135. S. Akerfeldt and L. Fagerlind, *J. Med. Chem.* **10**, 115 (1966).
136. F. Asinger, H. Berding, and H. Offermanns, *Monatsch. Chem.* **99**, 2084 (1968).
137. D. L. Klayman, *J. Org. Chem.* **30**, 2454 (1965).
138. A. Barama, R. Condom, and R. Guedj, *J. Fluorine Chem.* **16**, 183 (1980).
139. T. N. Wade and R. Guedj, *Tetrahedron Lett.*, 3247 (1978).
140. T. N. Wade, F. Gaymard, and R. Guedj, *Tetrahedron Lett.*, 2681 (1979).
141. Rus. Pat. 244,339 (Feb. 27, 1967), M. Woronkow, L. Fedotowa, and D. Rinkis (to Institut für organische Synthese der Akademic der Wissenschaften der Lehischen sozialistischen sowjet Republik).
142. R. C. Elderfield and H. A. Hageman, *J. Org. Chem.* **14**, 605 (1949).
143. J. L. Atwood and G. D. Stucky, *J. Am. Chem. Soc.* **92**, 285 (1970).
144. A. Storr and B. S. Thomas, *J. Chem. Soc.* (A), 3850 (1971).
145. A. Storr, B. S. Thomas, and A. D. Penland, *J. Chem. Soc. Dalton Trans.*, 326 (1972).
146. J. Müller, K. Margiolis, and K. Dehnicke, *J. Organomet. Chem.* **46**, 219 (1972).
147. H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.* **72**, 2926 (1950).
148. B. P. Robinson and K. A. H. Adams, *Tetrahedron Lett.*, 6169 (1968).
149. S. Akerfeldt, K. Wahlberg, and M. Hellström, *Acta Chem. Scand.* **23**, 115 (1969).
150. H. Ringertz, *Acta Chem. Scand.* **23**, 137 (1969).
151. R. Ehrlich and co-workers, *Inorg. Chem.* **3**, 628 (1944).
152. U.S. Pat. 3,393,184 (Dec. 4, 1964), J. A. Hoffman (to American Cyanamid Co.).

153. M. G. Voronkov and L. A. Fedotova, *Khim. Geterotsikl. Soedin.* **2**, 408 (1966).
154. U.S. Pat. 3,197,463 (Mar. 10, 1961), G. C. Tesoro, D. Ferry, and S. B. Sello (to J. P. Stevens and Co.).
155. M. T. Maurette and co-workers, *C.R. Acad. Sci. Paris, Ser. C* **282**, 599 (1976).
156. R. G. Kostyanovskii and A. K. Prokof'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 159 (1965).
157. W. Funke, *Ann. Chem.* **725**, 15 (1969).
158. R. G. Kostyanovskii, Y. I. El'natanov, and K. Khafizov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1815 (1970).
159. T. Kametani and co-workers, *Israel J. Chem.* **27**, 57 (1986).
160. S. S. Skorokhodov and co-workers, *Zh. Obshch. Khim.* **31**, 3382 (1961).
161. W. D. Stephens and co-workers, *J. Chem. Eng. Data* **8**, 625 (1963).
162. C. W. Woods, A. B. Borkovec, and F. M. Hart, *J. Med. Chem.* **7**, 371 (1964).
163. Y. Iwakura and A. Nabeya, *J. Org. Chem.* **25**, 1118 (1960).
164. H. W. Heine, *J. Am. Chem. Soc.* **85**, 2743 (1963).
165. H. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.* **31**, 2662 (1966).
166. P. Reynaud, R. C. Moreau, and P. Fodor, *C.R. Acad. Sci. Paris, Ser. C* **266**, 632 (1968).
167. T. Nishiguchi and co-workers, *J. Am. Chem. Soc.* **91**, 5835 (1969).
168. T. A. Foglia, L. M. Gregory, and G. Maerker, *J. Org. Chem.* **35**, 3779 (1970).
169. J. F. Bieron and F. J. Dinan, in J. F. Bieron and F. J. Dinan, *The Chemistry of Amides*, Wiley-Interscience, New York, 1970, p. 246.
170. F. A. Vingiello, M. P. Rorer, and M. A. Ogliaruso, *J. Chem. Soc., Chem. Commun.*, 329 (1971).
171. S. P. McManus, R. A. Hearn, and C. U. Pittman, Jr., *J. Org. Chem.* **41**, 1895 (1976).
172. V. P. Wystrach, D. W. Kaiser, and F. C. Schaefer, *J. Am. Chem. Soc.* **77**, 5915 (1955).
173. C. K. Johnson, *J. Org. Chem.* **32** 1508 (1967).
174. D. A. Tomalia, N. D. Ojha, and B. P. Thill, *J. Org. Chem.* **34**, 1400 (1969).
175. D. A. Tomalia, *J. Heterocycl. Chem.* **3**, 384 (1966).
176. D. A. Tomalia, *J. Heterocycl. Chem.* **4**, 419 (1967).
177. D. A. Tomalia, *Tetrahedron Lett.*, 2559 (1967).
178. D. A. Tomalia, T. J. Giacobbe, and W. A. Sprenger, *J. Org. Chem.* **36**, 2142 (1971).
179. E. V. Dehmlow and H. J. Westendorf, *Z. Naturforsch.* **B 25**, 1191 (1970).
180. A. Funke and G. Benoit, *Bull. Chem. Soc. Chim. Fr.*, 1021 (1953).
181. Ger. Pat. 1,004,614 (June 26, 1954), K. Vierling, H. Oettel, and G. Wilhelm (to BASF AG).
182. Ger. Pat. 1,031,307 (Oct. 24, 1956), H. Metzger, K. Vierling, and G. Wilhelm (to BASF AG).
183. Ger. Pat. 1,054,998 (Oct. 9, 1957), (to BASF AG).
184. Ger. Pat. 1,064,500 (Sept. 5, 1956), (to BASF AG).
185. Ger Pat. 1,115,256 (Apr. 26, 1957), (to BASF AG).
186. E. J. Reist, I. G. Junga, and B. R. Baker, *J. Org. Chem.* **25**, 1673 (1960).
187. E. J. Reist and co-workers, *J. Org. Chem.* **26**, 2139 (1961).
188. F. Fischer and H. Rönsch, *Chem. Ber.* **94**, 901 (1961).
189. P. W. Feit, *Acta Chem. Scand.* **16**, 522 (1962).
190. H. A. Staab and W. Rohr, *Chem. Ber.* **95**, 1298 (1962).
191. Brit. Pat. 1,138,738 (Dec. 1, 1966), D. D. Reynolds (to Eastman Kodak Co.).
192. Ger. Pat. 1,029,000 (Oct. 24, 1956), H. Metzger, H. Oettel, and G. Wilhelm (to BASF AG).
193. U.S. Pat. 3,520,875 (Aug. 25, 1966), (to Dow Chemical Co.).
194. U.S. Pat. 2,654,737 (Sept. 26, 1949), H. Bestian (to Hoechst AG).
195. Brit. Pat. 692,368 (Sept. 26, 1949), M. W. Erlenbach and A. Sieglitz (to Hoechst AG).
196. J. M. Stewart, *J. Am. Chem. Soc.* **76**, 3228 (1954).
197. D. Rosenthal and co-workers, *J. Org. Chem.* **30**, 3689 (1965).
198. Y. Oshiro, T. Agawa, and S. Komori, *Osaka Diagaku (Technol. Rep. Osaka Univ.)*, 541 (1967).
199. Y. I. El'natanov and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1661 (1988).
200. Ger. Pat. 1,111,637 (Dec. 14, 1957), F. Reicheneder, K. Dury, and H. J. Sasse (to BASF AG).
201. J. E. Dolfini, *J. Org. Chem.* **30**, 1298 (1965).
202. E. I. Grinblat and I. Y. Postovskii, *Dokl. Akad. Nauk SSSR* **133**, 873 (1960).
203. I. A. Postovskii, E. I. Grinblat, and L. F. Trefilova, *Zh. Obshch. Khim.* **31**, 363 (1961).

204. K. C. Tsou, K. Hoegerle, and H. C. F. Su, *J. Med. Chem.* **6**, 435 (1963).
205. Y. I. El'natanov and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR*, 302 (1988).
206. Ger. Pat. 1,010,063 (May 22, 1953), W. Riemenschneider (to Hoechst AG).
207. W. E. Truce and D. G. Brady, *J. Org. Chem.* **31**, 3543 (1966).
208. W. E. Truce and L. D. Markley, *J. Org. Chem.* **35**, 3275 (1970).
209. W. E. Truce and D. W. Onken, *J. Org. Chem.* **40**, 3200 (1975).
210. U.S. Pat. 2,770,617 (Apr. 30, 1954), A. Marxer (to Ciba Pharmaceutical Products, Inc.).
211. T. S. Lin and co-workers, *J. Med. Chem.* **32**, 1467 (1989).
212. T. S. Lin and co-workers, *J. Med. Chem.* **34**, 1634 (1991).
213. J. E. Dolfini and D. M. Dolfini, *Tetrahedron Lett.*, 2053 (1965).
214. M. Fremery, *Angew. Chem.* **78**, 1024 (1966).
215. U.S. Pat. 3,342,833 (Aug. 7, 1964), M. I. Fremery (to Shell Oil Co.).
216. U.S. Pat. 3,259,632 (Aug. 7, 1964), M. I. Fremery (to Shell Oil Co.).
217. U.S. Pat. 3,236,835 (Nov. 24, 1961), W. J. Rabourn and L. Jackson (to Dow Chemical Co.).
218. A. Dornow and W. Schacht, *Ber.* **82**, 464 (1949).
219. Ger. Pat. 935,545 (Jan. 3, 1954), K. Vierling (to BASF AG).
220. W. J. Rabourn and W. L. Howard, *J. Org. Chem.* **27**, 1039 (1962).
221. R. G. Kostyanovskii and V. F. Bystrov, *Izv. Akad. Nauk SSSR* **8**, 1404 (1962).
222. R. G. Kostyanovskii and V. F. Bystrov, *Doklady Akad. Nauk SSSR* **148**, 97 (1963).
223. P. G. Kostyanovskii and O. A. Pan'shin, *Izv. Akad. Nauk SSSR*, 182 (1963).
224. S. C. Kuo and W. H. Daly, *J. Org. Chem.* **35**, 1861 (1970).
225. Ger. Pat. 1,445,525 (Mar. 13, 1964), B. Sander and F. Becke (to BASF AG).
226. J. B. Doughty, C. L. Lazzell, and A. R. Collett, *J. Am. Chem. Soc.* **72**, 2866 (1950).
227. H. Fillion and co-workers, *Chem. Pharm. Bull.* **39**, 493 (1991).
228. Y. Ohshiro, K. Yamamoto, and S. Komori, *Yuki Gosei Kagako Kyokai Shi* **24**, 945 (1966).
229. E. Pfeil and U. Harder, *Angew. Chem.* **77**, 505 (1965).
230. F. Lautenschlaeger, *J. Heterocycl. Chem.* **7**, 1283 (1970).
231. P. Rajagopalan and C. N. Talaty, *J. Am. Chem. Soc.* **88**, 5048 (1966).
232. T. Sasaki and T. Yoshioka, *Bull. Chem. Soc. Jpn.* **42**, 556 (1969).
233. T. Sasaki, T. Yoshioka, and Y. Suzuki, *Bull. Chem. Soc. Jpn.* **44**, 185 (1971).
234. R. Schwyzer, *Helv. Chim. Acta* **XXXV**, 1903 (1952).
235. Ger. Pat. 1,087,131 (Oct. 11, 1958), W. Gauß and S. Petersen (to Bayer AG).
236. D. Bormann, *Angew. Chem. Int. Ed.* **12**, 768 (1973).
237. T. Kato, Y. Yamamoto, and M. Sato, *Yagugaku Zasshi* **91**, 384 (1971).
238. Ger. Pat. 1,941,175 (Aug. 13, 1969), R. Fikentscher and F. Miksovsky (to BASF AG).
239. R. Kostyanovskii and co-workers, *Izv. Akad. Nauk SSSR*, 2576 (1988).
240. U.S. Pat. 2,339,046 (Apr. 1, 1940), H. Bestian (to Hoechst AG).
241. L. B. Dashkevich and V. G. Beilin, *Zh. Obshch. Khim.* **32**, 2391 (1962).
242. N. Murai and co-workers, *J. Org. Chem.* **42**, 847 (1977).
243. B. Adcock and A. Lawson, *J. Chem. Soc.* **474** (1965).
244. A. B. Borkovec and C. W. Woods, *J. Med. Chem.* **8**, 545 (1965).
245. H. Najer and co-workers, *Compt. Rend.* **253**, 2369 (1961).
246. H. Najer and co-workers, *Bull. Soc. Chim. Fr.*, 323 (1963).
247. E. Pfeil and K. Milzner, *Angew. Chem.* **78**, 677 (1966).
248. A. S. Deutsch and P. E. Fanta, *J. Org. Chem.* **21**, 892 (1956).
249. J. C. Howard and G. Klein, *J. Org. Chem.* **27**, 3701 (1962).
250. Y. Iwakura and A. Nabeya, *Nippon Kagaku Zasshi* **77**, 773 (1956).
251. K. Soga and co-workers, *J. Chem. Soc., Chem. Commun.*, 617 (1976).
252. M. R. Banks and co-workers, *J. Chem. Soc. Perkin. Trans.*, 961 (1991).
253. H. Matsuda, A. Ninagawa, and H. Hasegawa, *Bull. Chem. Soc. Jpn.* **58**, 2717 (1985).
254. A. Seher, *Annalen* **575**, 153 (1952).
255. H. M. Rauen and H. Schriewer, *Arzneim. Forsch.* **21**, 518 (1971).

256. Rus. Pat. 2,235,876 A2 (Sep. 18, 1990), M. Kitano and M. Yagisawa (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
257. V. I. Markov and D. A. Danileiko, *Zh. Org. Khim.* **10**, 1262 (1974).
258. L. B. Clapp and J. W. Watjen, *J. Am. Chem. Soc.* **75**, 1490 (1953).
259. C. S. Dewey and R. A. Bafford, *J. Org. Chem.* **30**, 491 (1965).
260. T. A. Foglia and co-workers, *J. Org. Chem.* **36**, 1068 (1971).
261. F. A. Devillanova and G. Verani, *Spectrochim. Acta* **36A**, 371 (1980).
262. S. F. Thames, J. E. McClesky, and P. L. Kelly, *J. Heterocycl. Chem.* **5**, 749 (1968).
263. Ger. Pat. 834,990 (Oct. 2, 1948), J. Heyna and A. Bauer (to Hoechst AG).
264. DDR 20,378 (Nov. 14, 1958), E. J. Birr and W. Walther.
265. N. S. Nametkin, V. N. Perchenko, and L. G. Batalova, *Dokl. Akad. Nauk SSSR* **158**, 953 (1964).
266. N. S. Nametkin, V. N. Perchenko, and G. K. Kadorkina, *Dokl. Akad. Nauk SSSR* **187**, 522 (1969).
267. N. S. Nametkin and co-workers, *Dokl. Akad. Nauk SSSR* **219**, 860 (1974).
268. N. S. Nametkin, V. N. Perchenko, and L. G. Batalova, *Dokl. Akad. Nauk SSSR* **160**, 167 (1965).
269. N. S. Nametkin and co-workers, *Khim. Geterotsikl. Soedin.* **3**, 75 (1967).
270. O. Scherer and M. Schmidt, *Chem. Ber.* **98**, 2243 (1965).
271. P. Riviere, M. Riviere-Baudet, and J. Satge, *J. Organome. Chem.* **96**, C7 (1975).
272. J. Barrau and co-workers, *J. Organomet. Chem.* **243**, 281 (1983).
273. M. Riviere-Baudet and J. Satge, *Rec. Trav. Chem. Pays-Bas* **89**, 1281 (1970).
274. R. G. Kostyanovskii and A. K. Prokof'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 469 (1967).
275. M. E. Bishop and J. J. Zuckerman, *Inorg. Chem.* **16**, 1749 (1977).
276. W. Rundel and E. Müller, *Ber.* **96**, 2528 (1963).
277. R. D. Clark and G. K. Helmkamp, *J. Org. Chem.* **29**, 1316 (1964).
278. H. W. Heine and D. A. Tomalia, *J. Am. Chem. Soc.* **84**, 993 (1962).
279. H. W. Heine, *Angew. Chem.* **74**, 772 (1962).
280. L. A. Fedotova and M. G. Voronkov, *Khim. Geterotsk. Soed.* **3**, 570 (1969).
281. J. G. Pomonis, D. T. North, and R. G. Zaylskie, *J. Med. Chem.* **13**, 989 (1970).
282. U.S. Pat. 2,858,306 (May 8, 1957) (to Olin Mathieson Chemical Corp.).
283. E. E. Nifant'ev, A. I. Zavalisina, and M. R. Ter-Ovanesjan, *Z. Obsc. Chim.* **39**, 28 (1969).
284. E. E. Nifant'ev, A. I. Gavrilova, and N. K. Bliznjuk, *Z. Obsc. Chim.* **36**, 363 (1966).
285. V. S. Abramov and N. A. Il'ina, *Z. Obsc. Chim.* **39**, 177 (1969).
286. R. Appel and co-workers, *Chem. Ber.* **103**, 3631 (1970).
287. G. Kamai and Z. L. Khisamova, *Dokl. Akad. Nauk SSSR* **156**, 485 (1964).
288. M. G. Voronkov, L. A. Fedotova, and D. O. Rinkis, *Khim. Geterotsikl. Soedin.*, 488 (1965).
289. F. Feher and B. Degen, *Angew. Chem.* **79**, 690 (1967).
290. F. Graefe and R. E. Meyer, *J. Am. Chem. Soc.* **80**, 3939 (1958).
291. J. M. Kanabus-Kaminska and J. Lange, *Rocz. Chem.* **51**, 1253 (1977).
292. W. Hennrichs and J. Jander, *Z. Anorg. Allg. Chem.* **547**, 233 (1987).
293. R. G. Jones and co-workers, *J. Am. Chem. Soc.* **78**, 6027 (1956).
294. H. Bürger and U. Dämmgen, *Z. Anorg. Allg. Chem.* **394**, 209 (1972).
295. H. Bürger and U. Dämmgen, *Z. Anorg. Allg. Chem.* **407**, 201 (1974).
296. A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Organomet. Chem. Lausanne* **23**, 165 (1970).
297. T. B. Jackson and J. O. Edwards, *Inorg. Chem.* **1**, 398 (1962).
298. H. P. Fritz and G. Hierl, *Z. Anorg. Chem.* **371**, 229 (1969).
299. R. Höfer, W. Beck, and A. Engelmann, *Chem. Ber.* **106**, 2590 (1973).
300. T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.* **83**, 355 (1961).
301. I. Morishima and co-workers, *J. Am. Chem. Soc.* **102**, 2429 (1980).
302. W. Hieber and R. Wiesboeck, *Chem. Ber.* **91**, 1146 (1958).
303. R. W. Kiser and T. W. Lapp, *Inorg. Chem.* **1**, 401 (1962).
304. D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *J. Am. Chem. Soc.* **92**, 6159 (1970).
305. M. R. Hoffmann and J. O. Edwards, *Inorg. Nucl. Chem. Lett.* **10**, 837 (1974).
306. J. Scherzer and co-workers, *Inorg. Chem.* **5**, 847 (1966).
307. C. A. Root and J. Williams Allison, *Inorg. Chem.* **9**, 2791 (1970).

308. S. Gabriel and C. Hirsch, *Ber.* **29**, 2747 (1896).
309. J. N. Kukuskin and V. B. Ukraincev, *Z. Neorg. Chim.* **15**, 60 (1970).
310. I. A. G. Roos, A. J. Thomson, and S. Mansy, *J. Am. Chem. Soc.* **96**, 6484 (1974).
311. H. P. Fritz and G. Hierl, *Z. Naturforsch.* **26B**, 476 (1971).
312. N. S. Nametkin and co-workers, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1874 (1972).
313. V. B. Ukraintsev and Y. N. Kukushkin, *Zh. Obshch. Khim.* **56**, 2292 (1986) and references therein.
314. V. B. Ukraintsev, S. V. Yakovlev, and Y. N. Kukushkin, *Zh. Obshch. Khim.* **59**, 1602 (1989).
315. V. B. Ukraintsev and co-workers, *Zh. Obshch. Khim.* **58**, 389 (1988).
316. V. B. Ukraintsev, S. V. Yakovlev, and Y. N. Kukushkin, *Zh. Obshch. Khim.* **53**, 2066 (1983).
317. W. Beck, W. Danzer, and R. Höfer, *Angew. Chem.* **85**, 87 (1973).
318. W. Beck and co-workers, *Angew. Chem.* **88**, 511 (1976).
319. W. Danzer and co-workers, *Z. Naturforsch.* **39B**, 167 (1984).
320. P. K. Wong and co-workers, *J. Am. Chem. Soc.* **99**, 2823 (1976).
321. L. S. Hegedus and co-workers, *Inorg. Chem.* **16**, 1887 (1977).
322. H. Alper, F. Urso, and J. H. Smith, *J. Am. Chem. Soc.* **105**, 6737 (1985).
323. H. Alper, *Pure Appl. Chem.* **60**, 35 (1988).
324. M. M. Singh and R. J. Angelici, *Angew. Chem.* **95**, 160 (1983).
325. M. M. Singh and R. J. Angelici, *Angew. Chem. Suppl.*, 184 (1983).
326. M. M. Singh and R. J. Angelici, *Inorg. Chem.* **23**, 2691 (1984).
327. *Ibid.*, p. 2699.
328. R. Bertani and co-workers, *NATO ASI Ser., Ser. C, Adv. Met. Carbene Chem.*, **269** 67 (1989).
329. R. A. Michelin and co-workers, *Inorg. Chim. Acta* **174**, 3 (1990).
330. L. Zanotto, R. Bertani, and R. A. Michelin, *Inorg. Chem.* **29**, 3265 (1990).
331. R. Bertani and co-workers, *Inorg. Chim. Acta* **189**, 175 (1991).
332. L. M. Atagi and co-workers, *J. Am. Chem. Soc.* **113**, 870 (1991).
333. U.S. Pat. 3,242,166 (May 26, 1965), C. G. Krespan and W. J. Middleton (to E. I. du Pont de Nemours & Co., Inc.).
334. C. H. Wang and S. G. Cohen, *J. Org. Chem.* **26**, 3301 (1961).
335. C. L. Stevens and co-workers, *J. Org. Chem.* **29**, 3146 (1964).
336. A. Kubik, K. Piatkowski, and H. Kuczynski, *Roczniki Chemii* **48**, 1225 (1974).
337. J. Werry and co-workers, *Tetrahedron* **45**, 5015 (1989).
338. T. Hiyama, H. Koide, and H. Nozaki, *Bull. Chem. Soc. Jpn.* **48**, 2918 (1975).
339. S. V. Zotova, G. V. Loza, and M. Y. Lukina, *Bull. Acad. Sci. USSR*, 415 (1967).
340. J. Meier, F. Akermann, and H. H. Günthard, *Helv. Chim. Acta* **51**, 1686 (1968).
341. N. R. Bertoniere and G. W. Griffin, in O. L. Chapman, ed., *Organic Photochemistry*, Vol. **3**, Marcel Dekker, Inc., New York, 1973, p. 158.
342. S. Braslavsky and J. Heicklen, *Chem. Rev.* **4**, 473 (1977).
343. C. Luner and H. Gesser, *J. Phys. Chem.* **62**, 1148 (1958).
344. R. F. Klemm, *Can. J. Chem.* **43**, 2633 (1965).
345. A. Jones and F. P. Lossing, *Can. J. Chem.* **45**, 1685 (1967).
346. R. F. Klemm, *Can. J. Chem.* **45**, 1693 (1967).
347. M. Kawasaki and co-workers, *J. Chem. Phys.* **59**, 6321 (1973).
348. M. Kawasaki, M. Iwasaki, and I. Tanaka, *J. Chem. Phys.* **59**, 6328 (1973).
349. A. A. Scala and D. Salomon, *J. Chem. Phys.* **65**, 4455 (1976).
350. W. S. Jamieson and C. A. Winkler, *J. Phys. Chem.* **60**, 1542 (1956).
351. B. Bigot, A. Devaquet, and A. Sevin, *J. Org. Chem.* **45**, 97 (1980) and references therein.
352. J. A. Kaye and D. F. Strobel, *Icarus* **54**, 417 (1983).
353. J. P. Ferris and Y. Ishikawa, *J. Am. Chem. Soc.* **110**, 4306 (1988).
354. E. J. Goethals, in K. J. Ivin and T. Saegusa, eds., *Ring-Opening Polymerization*, Vol. **2**, Elsevier Applied Science Publishers, New York, 1984, p. 715.
355. D. A. Tomalia and G. R. Killat, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **1**, John Wiley & Sons, Inc., New York, 1985, p. 680.
356. S. Kobayashi, *Progr. Polym. Sci.* **15**, 751 (1990).

357. E. J. Goethals and R. DeClercq, in W. J. Mijs, ed., *New Methods for Polymer Synthesis*, Plenum Press, New York, 1992, p. 67.
358. T. Saegusa and S. Kobayashi, in Ref. 16, p. 55.
359. K. F. Weyts and E. J. Goethals, *Polymer Bulletin* **19**, 13 (1988).
360. D. A. Tomalia, A. M. Naylor, and W. Goddard III, *Angew. Chem.* **102**, 119 (1990).
361. G. R. Hansen and T. E. Burg, *J. Heterocycl. Chem.* **5**, 305 (1968).
362. S. Tsuboyama and co-workers, *Tetrahedron Lett.*, 1367 (1970).
363. U.S. Pat. 4,093,615 (June 6, 1978), G. E. Ham and R. L. Krause (to Dow Chemical Co.).
364. H. Wenker, *J. Am. Chem. Soc.* **57**, 2328 (1935).
365. H. Kindler and co-workers, *Chemie-Ing.-Techn.* **37**, 400 (1965).
366. M. Ueshima and Y. Shimasaki, *Kagaku to Kogyo* **43**, 349 (1990).
367. J. Epstein, R. W. Rosenthal, and R. J. Ess, *Anal. Chem.* **27**, 1435 (1955).
368. R. Preussmann, H. Schneider, and F. Epple, *Arzneimittel-Forsch.* **19**, 1059 (1969).
369. D. H. Rosenblatt, P. Hlinka, and J. Epstein, *Anal. Chem.* **27**, 1290 (1955).
370. T. R. Crompton, *Analyst* **90**, 107 (1965).
371. D. J. Evans, R. J. Mayfield, and I. M. Russell, *J. Chromatog.* **115**, 391 (1975).
372. R. Morales, J. F. Stampfer, and R. E. Hermes, *Anal. Chem.* **54**, 1340 (1982).
373. A. M. Thiess, *Arch. Toxikol.* **21**, 67 (1965).
374. *U.S. Code of Federal Regulations: Occupational Safety and Health Standards*, U.S. Government Printing Office, Washington, D.C., 1973, Title 29, part 1910.93, p. 114.
375. Technische Regeln für Gefahrstoffe (TRGS) 102, *Technische Richtkonzentrationen (TRK) für gefährliche Stoffe*, Kuehn, Birett, Bonn, Germany, 1993.
376. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, Some Aziridines, N-, S- and O-Mustards and Selenium*, Vol. **9**, International Agency for Research on Cancer, Geneva, Switzerland, 1975.
377. L. Verschaeve and M. Kirsch-Volders, *Mutat. Res.* **238**, 39 (1990).
378. S. D. Silver and F. P. McGrath, *J. Ind. Hyg. Toxicol.* **30**, 7 (1948).
379. R. M. V. James, *Biochem. Pharmacol.* **14**, 915 (1965).
380. H. F. Smyth, Jr., J. Seaton, and L. Fischer, *J. Ind. Hyg. Toxicol.* **23**, 259 (1941).
381. C. P. Carpenter, H. F. Smyth, Jr., and C. B. Shaffer, *J. Ind. Hyg. Toxicol.* **30**, 2 (1948).
382. D. Horn and F. Linhart, in J. C. Roberts, ed., *Paper Chemistry*, Blackie, London, 1991, p. 44.
383. D. Horn and J. Melzer, *Das Papier* **29**, 534 (1975).
384. J. Weigl, J. Hlavatsch, and W. Scheid, *Wochenblatt für Papierfabrikation* **13**, 587 (1989).
385. R. Nicke and M. Tappe, *Zellstoff und Papier* **37**, 16 (1988).
386. U.S. Pat. 3,520,774 (Sept. 28, 1967), H. H. Roth (to Dow Chemical co.).
387. Eur. Pat. 0 025,515 (Aug. 14, 1980), (to BASF AG).
388. M. Hoffmann, *Zellstoff und Papier* **34**, 134 (1985).
389. F. Linhart and co-workers, *Tappi J.* **70**, 79 (1987).
390. J. G. Penniman, *Paper Trade J.* **162**, 36 (1978).
391. Rus. Pat. 6 0071-795-A (Sept. 27, 1983), (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
392. Ger. Pat. 3,316,179 A1 (May 4, 1983), F. Reichel and G. Frey (to BASF AG).
393. Ger. Pat. 3,719,480-A (Aug. 5, 1986), H.-J. Degen, S. Pfohl, and A. Stange (to BASF AG).
394. L. Westfelt, *Cellul. Chem. Technol.* **13**, 813 (1979).
395. Eur. Pat. 374,861-A (Dec. 20, 1988), R. Cohen and G. Luzio (to Hercules Inc.).
396. Ger. Pat. 2,911,533 (Apr. 10, 1978), E. Litzinger (to British-American Tobacco Co. Ltd.).
397. A. G. Andreopoulos, *Polym. Adv. Technol.* **2**, 87 (1991).
398. Rus. Pat. 2,225,244-A (Mar. 27, 1986), S. Yuji and co-workers (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
399. H. Thiele and K. H. Gronau, *Makromol. Chem.* **59**, 207 (1963).
400. S. Kobayashi and co-workers, *Macromolekules* **20**, 1496 (1987).
401. K. Geckeler, B. Rivas, and R. Zhou, *Angew. Makromol. Ch.* **193** 195 (1991); B. Rivas and K. Geckeler, *Adv. Polym. Sci.* **102**, 171 (1992).
402. Y. Bao and C. Pitt, *J. Polymer Sci., Polymer Chemistry Edition* **28**, 741 (1990).
403. Y. Nakamura and H. Hirai, *Chem. Lett.*, 1997 (1972).

404. J. Anzai and co-workers, *Bl. Chem. Soc. Japan* **56**, 2541 (1983).
405. B. Rivas and co-workers, *Polymer Bull.* **14**, 239 (1985).
406. M. Morita, M. Higuchi, and I. Sakata, *J. Appl. Polymer Sci.* **34**, 1013 (1987).
407. D. Mortimer, *Polymer Int.* **25**, 29 (1991).
408. Eur. Pat. 61,169 (Mar. 25, 1981), (to BASF AG).
409. Y. Kurimura, *Adv. in Polymer Sci.* **90**, 105 (1989).
410. G. Karpuchina and co-workers, *Plasticheskie Massy* **10**, 43 (1988).
411. G. V. Karpuchina and co-workers, *Plasticheskie Massy* **10**, 43 (1988).
412. Ger. Pat. 3,309,866 (Mar. 19, 1982), N. Kobayashi and A. Funamoto (to Nippon Soda Co. Ltd.).
413. Ger. Pat. 3,517,107 (May 11, 1985), D. Stoeckigt and co-workers (to BASF AG).
414. U.S. Pat. 4,415,705 (July 19, 1982), F. Hutter (to Inmont Corp.).
415. U.S. Pat. 4,165,409 (Feb. 23, 1978), J. Maine.
416. U.S. Pat. 4,086,385 (Nov. 5, 1975), S. Rowland (to ., represented by the Secretary of Agriculture).
417. U.S. Pat. 4,454,254 (Dec. 1, 1982), C. Reichel, J. Patton, Jr., and T. Narayan (to BASF Wyandotte Corp.).
418. Anonymous, *Süddeutsches Kunststoff-Zentrum Würzburg*, Fachtagung, Stuttgart, Germany, 1984, p. 1.
419. W. Marconi, *Reactive Polymers, Ion Exchangers, Sorbents* **11**, 1 (1989).
420. G. Manecke and S. Heydolph, *Makromol. Ch. and Physics, Basel* **182**, 2641 (1981).
421. Ger. Pat. 2,915,135 (Apr. 19, 1978), M. Gestrelius (to Novo Ind.).
422. Brit. Pat. 2,082,591 (Aug. 21, 1980), J. Shimizu, K. Suzuki, and Y. Nakajima (to Mitsui Sugar Co. Ltd.).
423. P. Lozano and co-workers, *Process Biochem.* **23**, 75 (1988).
424. Ger. Pat. 2,828,369 (July 1, 1977), H. Mano (to Sumitomo Electric Ind.).
425. J. Batulin and B. L. Rivas, *J. Makromol. Ch., Rapid Comm.* **2**, 375 (1981).
426. U.S. Pat. 4,808,215 (Apr. 3, 1987), J. S. Gill and R. G. Varsanik (to Calgon Group).
427. Ger. Pat. 3,111,713 (Mar. 25, 1981), (to BASF AG).
428. World Pat. 8,201,993 (Dec. 18, 1980), H. Meyer.
429. H. E. Bille and R. R. Fikentscher, *Chem. Aftertreat. Text.*, (1971).
430. N. R. Bertoniere, M. K. Black, and S. P. Rowland, *Textile Res. J.* **48**, 664 (1978).
431. J. R. Cook and D. E. Rivett, *Text. Res. J.* **51**, 596 (1981).
432. C. E. Morris and C. M. Welch, *Text. Res. J.* **53**, 725 (1983).
433. P. E. Ellingham, P. G. Gordon, and J. Rosevaer, *Text. Res. J.* **53**, 577 (1983).
434. Jpn. Pat. 55 065,234 (Nov. 9, 1978), T. Hiroshi and T. Hidetoshi (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
435. K. Matsumoto, A. Suganuma, and D. Kunui, *Powder Technol.* **25**, 1 (1980).
436. Jpn. Pat. 9 133,000 A (Jan. 21, 1983), J. Masa-Mitsu and co-workers (to Nippon Shokubai Kagaku Kogyo Co., Ltd.).
437. V. Valtschev and co-workers, *Zellstoff und Papier* **34**, 88 (1985).
438. A. Naka and co-workers, *Nippon Kagaku Kaishi* **10**, 1342 (1986).
439. G. D. Jones and R. C. Asperger, *J. Macromol. Sci., Chem. J. Macromol. Sci.* **A13**, 835 (1979).
440. L. I. Metelskaja and co-workers, *Ukr. Chim. Z.* **54**, 387 (1988).
441. Eur. Pat. 561 (July 28, 1977), (to BASF AG).
442. Ger. Pat. 2,934,228 (Aug. 24, 1979), C. C. Heuck, E. Lueddecke, and D. Horn (to BASF AG).
443. A. G. Ludwick and C. G. Overberger, *Rev. Roumaine Chim.* **25**, 1011 (1980).
444. R. E. Wingard, Jr., *Organic Coatings and Appl. Polymer Sci. Proceedings* **44**, 69 (1981).
445. L. Wayne Noell and C. C. Cherry, *J. Med. Chem.* **11**, 63 (1968).
446. C. E. Carraher, Jr. and co-workers, *Organic Coatings and Applied Polymer Sci. Proceedings* **49**, 210 (1983).
447. C. E. Carraher, Jr. and co-workers, *J. Polym. Mat.* **1**, 116 (1984).
448. T. Sato and co-workers, *Polymer Preprints, Japan, Engl. Ed.* **38**, E 357 (1989).
449. R. W. Franck, *Fortschritted. Chem. Org. Naturst.* **38**, 1 (1979).
450. H. Waldmann, *Nachr. Chem. Tech. Lab.* **40**, 235 (1992) and references therein.
451. U.S. Pat. 5,032,278 (Aug. 6, 1990), (to Texaco Inc.).
452. T. Sata, *Pure Appl. Chem.* **58**, 1613 (1986).
453. J. E. Cadotte and co-workers, *J. Makromol. Sci., Part A: Chemistry* **A15**, 727 (1981).
454. Y. Maeda and co-workers, *Polymer J.* **23**, 501 (1991).
455. M. F. Tsai and M. Levy, *J. Polymer Sci., Polym. Chem. Ed.* **22**, 2523 (1984).

456. K. Uehara and K. Kawai, *Polymer Preprints, Japan, Engl. Ed.* **38**, E 551 (1989).
457. T. Sata and R. Iuzo, *Angew. Macrom. Chem.* **171**, 101 (1989).
458. L. E. Bromberg, *J. Member. Sci.* **62**, 131 (1991).
459. Eur. Pat. 147,743 (Dec. 14, 1984), R. Baur, K. Oppenländer, and K. Barthold (to BASF AG).
460. Eur. Pat. 444 542 (Mar. 2, 1990), K. Oppenländer and co-workers (to F Corp.).
461. Ger. Pat. 3,712,317 (Apr. 11, 1987), H.-P. Seelmann-Eggebert and co-workers (to BASF AG).
462. K. Takemoto and Y. Inaki, *Macromol. Sci., Part A: Chem* **A25**, 5–7, 757 (1988).
463. Eur. Pat. 174,644 A (Sept. 11, 1985), T. Teraji and co-workers (to Fujisawa Pharmaceutical Co., Ltd.).
464. L. W. Woods, A. B. Borkevec, and F. M. Harz, *J. Med. Chem.* **7**, 371 (1964).

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