Dielectric constants, D, for anisole and bromobenzene were obtained from the equation for total polarization (*10*), P,

$$P = \frac{D-1}{D+2}\,\frac{M}{d} = P' + \frac{A}{T}$$

where d is density, M is molecular weight, A is a constant, P' is the distortion polarization, and T is the absolute temperature. Using the molar refraction to estimate (*10*) P' and literature values for D and d at a known T, values for A were calculated. Then values for D at 144.4° C. were obtained by use of the density values at 144.4° C. The D value for n-decane was obtained from the relation $n^2 = D$ for strictly nonpolar compounds.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Aldridge, G.R., Murphy, G.W., *J. Am Chem. Soc.* **73**, 1158 (1951).
(2) Berndt, D.C., Zuika, M., Clark, M.S., Jr., *Chem. Ind.* (*London*) **1965**, p. 139.
(3) Berndt, D.C., *J. Org. Chem.* **32**, 482 (1967).
(4) Cope, A.C., Hancock, E.M., *J. Am. Chem. Soc.* **60**, 2644 (1938).
(5) Gibson, D.H., Pettit, R., *Ibid.*, **87**, 2620 (1965) and references therein indicate that certain hydrocarbons may react by different pathways.
(6) Hildebrand, J.H., Scott, R.L., "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.
(7) LeFevre, R.J.W., "Advances in Physical Organic Chemistry," 3, p. 1, V. Gold, ed., Academic Press, New York, 1965.
(8) Reichardt, C., *Angew. Chem. Intern. Eng. Ed.* **4**, 29 (1965).
(9) Rhoads, S.J., "Molecular Rearrangements," 1, Chap. 11, P. de Mayo, ed., Interscience Publishers, New York, 1963.
(10) Smith, J.W., "Electric Dipole Moments," Chap. 1, Butterworths Publications, London, 1955.
(11) Swinbourne, E.S., *J. Chem. Soc.* **1960**, p. 2371.
(12) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. II, p. 204, Elsevier Publishing Co., New York, 1965.
(13) Weissberger, A., ed., "Techniques of Organic Chemistry," VII, 2nd ed., Interscience Publishers, New York, 1955.

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Substituted Aziridines

Relative Rates of Reaction and Direction of Ring Opening

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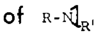
Relative reaction rates have been measured for the ring opening of various *N*-substituted aziridines and 2-methylaziridines by carboxylic acids. In diglyme solution, the order of decreasing reactivity for the substituent attached to the nitrogen atom is: alkyl > dialkylphosphinyl > phosphinylidene > dialkylphosphonyl > diphenylphosphinyl > diphenylphosphonyl > alkylsulfonyl > arylsulfonyl. In addition, *N*-substituted aziridines react more rapidly than the corresponding 2-methylaziridines. The reaction rates were much higher in chlorobenzene than in diglyme. In general, ring opening of *N*-substituted 2-methylaziridines occurred by rupture of the bond between nitrogen and the unsubstituted carbon atom, and by cleavage of the bond between nitrogen and the methyl-bearing ring carbon atom.

ALTHOUGH RING-OPENING REACTIONS of aziridines have been studied by several workers, the reactions of N-substituted aziridines with carboxylic acids have received little attention (*2*). The present study was undertaken to examine, first, the effect of aziridine substituents upon the rate of ring opening with carboxylic acids; second, the effect of the nature of the solvent upon the reaction rates; and third, the direction of ring opening of unsymmetrically substituted aziridines.

The relative rates of reaction of various N-substituted aziridines and (2-methyl)aziridines with carboxylic acids were determined by heating a solution containing the aziridine and butyric acid at 125° C. and titrating the unreacted acid with sodium hydroxide in ethanol. The results of relative rate studies in diglyme (diethylene glycol dimethyl ether) solution are shown in Table I. The choice of solvent was dictated by the fact that several of the aziridines had very low solubility in the more common solvents, and it was desirable to run as many of the reactions as possible in the same solvent. The rates are reported in terms of the quarter life and half life of butyric acid and allow

Table I. Relative Rates of Reaction of  with Butyric Acid

(Diglyme, 125° C.)

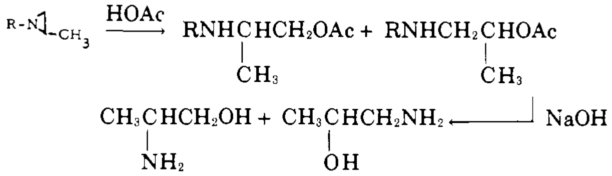
R	R′	$T_{1/4}$[a], Hr.	$T_{1/2}$[a], Hr.
$—C_2H_4SO_2C_2H_4—$	H	0.10	0.38
$—C_2H_4SO_2C_2H_4—$	CH_3	0.15	0.55
$(C_4H_9)_2PO—$	H	1.22	2.25
$(C_4H_9)_2PO—$	CH_3	1.00	3.42
$PO(-)_3$	H	1.13	2.41
$PO(-)_3$	CH_3	2.16	6.66
$(C_4H_9O)_2PO—$	H	9.5	26
$(C_4H_9O)_2PO—$	CH_3	12.25	40
$(C_6H_5)_2PO—$	CH_3	27.5	78
$(C_6H_5O)_2PO—$	H	52	. . .
$(C_6H_5O)_2PO—$	CH_3	135	. . .
$C_4H_9SO_2—$	H	129	263
$C_4H_9SO_2—$	CH_3	445	1075
$C_6H_5SO_2—$	CH_3	375	1310

[a] $T_{1/4}$ represents time to 25% reaction; $T_{1/2}$, time to 50% reaction.

a qualitative ranking of functional groups with respect to rate of reaction of the aziridine. The order of decreasing reactivity was: alkyl > dialkylphosphinyl > phosphinylidene > dialkylphosphonyl > diphenylphosphinyl > diphenylphosphonyl > alkylsulfonyl > arylsulfonyl. The 2-methylaziridines react more slowly than the compounds which have no substituent on the ring carbon atoms.

To examine the effect of a solvent with a different dipole moment, several aziridines were treated with butyric acid in chlorobenzene, again at 125° C. Reaction rates in chlorobenzene and diglyme are compared in Table II. Apparently reaction rates are two to four times as high in chlorobenzene [dipole moment 1.73×10^{-18} electrostatic unit (*1*)] as in diglyme (dipole moment zero).

The direction of ring opening of several *N*-substituted-(2-methyl)-aziridines was investigated to determine if a change in reaction solvent would produce a change in direction of ring opening as well as significant changes in the reaction rates. The aziridines were heated with acetic acid in both chlorobenzene and diglyme. The addition products obtained in this manner were hydrolyzed with base, and the mixture of amino alcohols was analyzed by vapor-phase chromatography using a commercial sample of 2-hydroxy-1-propylamine and a sample of 2-amino-1-propanol, prepared from alanine (*3*), as reference compounds. The reaction sequence is shown below, where -N◁ represents the aziridine ring. The results of the ring-opening experiments are detailed in Table III. In most instances, ring opening occurred to give both possible products. For several compounds there was a significant difference in the ring opening in the two solvents, as indicated by the differences in the percentages of the amino alcohols obtained. The effect of solvent was most marked in the reaction of the carboxylic acid with 1-(dibutylphosphonyl)-2-methylaziridine. In chlorobenzene, 60% of the product resulted from cleavage of the bond between nitrogen and the unsubstituted carbon atom. In diglyme, however, no product of this type of cleavage could be detected. Instead, all of the product isolated was 2-hydroxy-1-propylamine, indicating cleavage between the nitrogen atom and the substituted carbon atom.



The consequences of changing to a solvent with a higher dipole moment are clear in the case of reaction rates, since a significant enhancement in rate occurred in each instance. However, the effect of such a change on the direction of ring opening is less obvious. In most cases, the reactions in chlorobenzene yielded larger amounts of 2-hydroxy-1-propylamine than those in diglyme. This is the product which would be expected if a carbonium ion or an ion pair were involved in the reaction mechanism. In diglyme it is possible that the reaction normally occurs by both ionic and concerted paths. The unprecedented results with dibutylphosphonyl-(2-methyl)aziridine could be interpreted as a result of failure to utilize the concerted path, thereby forcing the reaction to occur by a slower ionic mechanism in diglyme.

Table II. Effect of Solvent on Reaction Rate of R-N◁$_{R'}$

R	R′	$T_{1/2}$ (Diglyme), Hr.	$T_{1/2}$ (Chlorobenzene), Hr.
$—C_2H_4SO_2H_4—$	CH_3	0.55	0.15
$(C_4H_9)_2PO—$	CH_3	3.42	1.60
$PO(-)_3$	CH_3	6.66	1.25
$(C_4H_9O)_2PO—$	H	26.0	12.0

EXPERIMENTAL

Aziridines used in this study were synthesized by methods reported previously (*5*) or supplied by the Interchemical Corp. All melting points and boiling points are uncorrected. Reaction rates were obtained by dissolving redistilled butyric acid and freshly prepared aziridine in previously dried and distilled solvent, placing samples of the solution in a constant temperature bath, and periodically withdrawing and titrating the unreacted butyric acid. The following examples illustrate both the relative rate studies and the ring-opening experiments.

Reaction of 1-(Diphenylphosphinyl)-2-methylaziridine with Butyric Acid in Diglyme. A solution of 1-(diphenylphosphinyl)-2-methylaziridine (10.996 grams, 0.0397 mole) and butyric acid (3.4976 grams, 0.0397 mole) in diglyme was diluted to volume with solvent at 125° C. in a 100-ml. volumetric flask. Ten 10-ml. samples were withdrawn and placed in 25-ml. tubes in a constant temperature bath at 125° C. Samples were withdrawn at appropriate intervals and titrated for unreacted butyric acid with 0.2*N* ethanolic sodium hydroxide, using phenolphthalein as the indicator.

Ring Opening Reaction of 1-(Dibutylphosphinyl)-2-methylaziridine in Chlorobenzene. A solution of the aziridine (5.0 grams, 0.026 mole) and glacial acetic acid (1.8 grams, 0.30 mole) in 50 ml. of chlorobenzene was heated at reflux for 8 hours (reaction times were chosen on the basis of half lives shown in Table II, so that the extent of reaction would be greater than 90%). At the end of this time, the solution was concentrated in vacuo, yielding 7 grams (95%) of the isomeric addition compounds as a clear oil.

The residual oil was added to 30 ml. of diethylene glycol containing 6.6 grams of 85% potassium hydroxide pellets, and the mixture was heated at 125° C. for 6 hours with stirring. The resulting solution was then distilled and the fraction collected with boiling point 100° to 185° C. Vapor

Table III. Direction of Ring Opening of *N*-Substituted 2-Methylaziridines

	Chlorobenzene			Diglyme		
N-Substituent	Amino alcohol, yield, %	2-Hydroxy-1-propylamine, yield, %	2-Amino-1-propanol, yield, %	Amino alcohol, yield, %	2-Hydroxy-1-propylamine, yield, %	2-Amino-1-propanol, yield, %
$(C_6H_5)_2PO—$	86	54	46	100	40	60
$PO(-)_3$[a]	96	53	47	95	40	60
$(C_6H_5O)_2PO—$	95	42	58	80	38	62
$(C_4H_9O)_2PO—$	96	40	60	54	100	0
$(C_4H_9)_2PO—$	78	80	20	100	66	34

[a] Lambert, Thompson, and Kristofferson report a product containing 40% 2-hydroxy-1-propylamine and 60% 2-amino-1-propanol for this reaction in refluxing toluene (*4*).

phase chromatographic analysis of the distillate (2-foot column of 10% Carbowax 6000 on Haloport F at 100° C. and a helium flow rate of 54 cc. per minute) was made by reference to a standard calibration curve in which the concentrations of known mixtures of the amino alcohols had been plotted.

The ring opening was allowed to proceed to the extent of 96.8% before exposure to hydroxide ion. This means that base-catalyzed ring opening could not have exceeded 3.2%. For the other compounds the maximum is less than 10%.

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LITERATURE CITED

(1) Daniels, F., "Outlines of Physical Chemistry," p. 90, Wiley, New York, 1953.
(2) Fanta, P.E., in "Heterocyclic Compounds—Three- and Four-Membered Heterocycles," A. Weissberger, Ed., Part I, Chap. II, Interscience, New York, 1964.
(3) Karrer, P., Karrer, W., Thomann, H., Horlacher, E., Mader, W., *Helv. Chim. Acta* **4**, 76 (1921); *CA* **15**, 1288 (1921).
(4) Lambert, R.F., Thompson, G., Kristofferson, C.E., *J. Org. Chem.* **29**, 3116 (1964).
(5) Stephens, W.D., Moffett, L.R., Hill, W.E., Taylor, C.O., Brown, S.P., J. Chem. Eng. Data **8**, 625 (1963).

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Reaction of Bis(2,2,2-trinitroethyl) Formal with Potassium Cyanide

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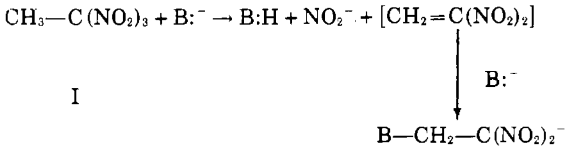
Bis(2,2,2-trinitroethyl) formal reacts with methanolic potassium cyanide to yield dipotassium bis(1-cyano-2,2-dinitroethyl) formal as the main product, together with minor amounts of the corresponding amide-nitrile and diamide. Some properties and reactions of these materials are described.

THE REACTION of 1,1,1-trinitroethane (I) with a variety of nucleophiles yields β-substituted 1,1-dinitroethane salts. Examples include the formation of potassium 3,3-dinitropropionitrile from the reaction of potassium cyanide with I (*7*), potassium methyl 2,2-dinitroethyl ether from potassium methoxide (*6*), potassium ethyl 2,2-dinitroethyl ether from potassium ethoxide (*6*) or ethanolic potassium hydroxide (*2*), potassium ethyl 2-carbethoxy-4,4-dinitrobutyrate from potassium diethyl malonate (*9*), and the zwitterionic salts, ammonium, dimethylammonium, trimethylammonium, guanidinium, and piperidinium *N*-(2-nitroethyl-2-nitronate) from I and the corresponding amines (*3, 9*). Zeldin and Shechter (*9*) have suggested that the reactions proceed through the attack of the base at the β-hydrogen, leading to elimination of nitrous acid and the formation of 1,1-dinitroethylene (never isolated), which serves as a substrate for subsequent Michael addition of the nucleophile.

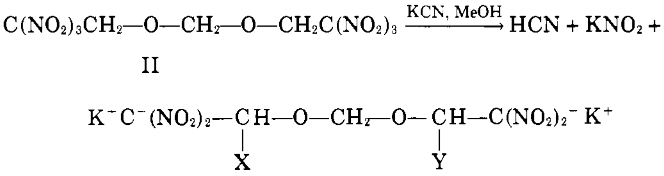


$$\mathrm{CH_3{-}C(NO_2)_3 + B{:}^- \rightarrow B{:}H + NO_2^- + [CH_2{=}C(NO_2)_2]} \xrightarrow{B:^-} \mathrm{B{-}CH_2{-}C(NO_2)_2^-}$$

I

To the best of our knowledge, the literature contains no mention of similar reactions on polynitroaliphatics other than I.

We wish, therefore, to record the closely analogous reactions of bis(2,2,2-trinitroethyl) formal (II) with potassium cyanide in methanol to yield dipotassium bis(1-cyano-2,2-dinitroethyl) formal (III) as the main product (62%). Also formed were minor amounts of the amide-nitrile, IV, and the diamide, V, these hydrolysis products of III probably arising from small amounts of water in the "absolute" methanol.



$$\mathrm{C(NO_2)_3CH_2{-}O{-}CH_2{-}O{-}CH_2C(NO_2)_3} \xrightarrow{\text{KCN, MeOH}} \mathrm{HCN + KNO_2 +}$$

II

$$\mathrm{K^-C^-(NO_2)_2{-}\underset{\displaystyle X}{\underset{|}{C}}H{-}O{-}CH_2{-}O{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}C(NO_2)_2^-\,K^+}$$

III, X = Y = CN
IV, X = CN, Y = $CONH_2$
V, X = Y = $CONH_2$

The dinitrile, III, decomposes slowly in aqueous acid and undergoes hydrolysis in aqueous base, but is relatively stable at intermediate pH's. Its separation from IV and V was readily effected by adding the crude product mixture to water and stirring. Initially an amorphous yellow tar was formed, but this soon turned nicely crystalline as III was transformed to its relatively insoluble monohydrate and IV and V dissolved. In hot aqueous alkali, III was converted in high yield to V, which precipitated as the dihydrate. When isolation and purification of III were sidestepped—i.e., the crude product mixture added directly to hot aqueous alkali—II was converted to V in 80% overall yield.

Attempts in aqueous or nonaqueous media to convert the dinitrile salt to its conjugate diacid, VI, were frustrated by spontaneous decomposition of the latter. A dibromo derivative, VII, was readily obtained, however, by bromination of an ether suspension of III. In the case of the diamide salt, by way of contrast, the conjugate diacid, VIII, which precipitated on acidification of a concentrated aqueous solution of V, was stable, but attempts at bromination led to decomposition. Stable dimethylol derivatives, IX and X, were also obtained by treatment of III and V with formaldehyde and mineral acid; yields were 70 and 84%, respectively.