TABLE V
PHYSICAL CONSTANTS OF PURE SAMPLES OF ALKYL CYCLOHEXENES

Compound	B.p., °C.	$n^{20}D$
1-Methylcyclohexene[b]	108 [109][a]	1.4500 [1.4497][a]
3-Methylcyclohexene[c]	102 [104]	1.4439 [1.4445]
4-Methylcyclohexene[d]	102 [102–103]	1.4419 [1.4418]
1-Ethylcyclohexene[e]	134–136 [134–136]	1.4570 [1.4576]
3-Ethylcyclohexene[f]	132–133 [133]	1.4510 [1.451]
4-Ethylcyclohexene[g]	132 [133]	1.4491 [1.449]
1-Isopropylcyclohexene[h]	155 [155–157]	1.4576 [1.4594]
3-Isopropylcyclohexene[i]	152 [150]	1.4552 [1.4542]
4-Isopropylcyclohexene[j]	155 [150–152]	1.4543 [1.4560]
1-*t*-Butylcyclohexene[g]	170 [173]	1.4623 [1.4638]
3-*t*-Butylcyclohexene[k]	170 [66 (23 mm.)]	1.4595 [1.4593]
4-*t*-Butylcyclohexene[l]	172 [172]	1.4589 [1.4587]
1-Cyclohexylcyclohexene[m]	112 (16 mm.) [88 (4 mm.)]	1.4945 [1.4916]
3-Cyclohexylcyclohexene[n]	109 (13 mm.)	1.4941
4-Cyclohexylcyclohexene[o]	233 [236]	1.4922

[a] The value in brackets represents the literature values. [b] K. Auwers and P. Ellinger, *Ann.*, **387**, 200 (1912). [c] G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 327. [d] R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950). [e] O. Wallach, *et al.*, *Ann.*, **360**, 48 (1908). [f] S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, Inc., New York, N. Y., 1955, p. 33. [g] See footnote *f*, p. 50. [h] See footnote *f*, p. 42. [i] A. Berlande, *Bull. soc. chim. France*, **9**, 644 (1942). [j] H. Pines, R. C. Olberg, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4872 (1952). [k] W. R. Biggerstaff, A. P. Menditto, and I. Yokoyama, *J. Org. Chem.*, **19**, 934 (1954). [l] See footnote *c*, p. 343. [m] F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933). [n] *Anal.* Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.53; H, 12.42. [o] W. Schrauth and K. Gorig, *Ber.*, **56**, 1900 (1923).

The 4-alkylcyclohexenes were prepared by the sequence: 4-alkyl phenol → 4-alkyl cyclohexanol → 4-alkyl cyclohexyl acetate → 4-alkyl cyclohexene. The final pyrolysis step was patterned after that described by Bailey.[9] Table V lists the physical constants of these alkenes.

Equilibration of Methyl- and *t*-Butylcyclohexenes (Table IV).—The following isomerizing conditions were studied.

A. Alumina at 350°.—Passing an olefinic mixture over an alumina column at 350° caused considerable aromatization. When the temperature was lowered to 220°, little change in composition occurred on several consecutive passes through the column.

B. *p*-Toluenesulfonic Acid.—This catalyst proved more efficient and effective than alumina. The olefin was refluxed under nitrogen in acetic acid with a trace of *p*-toluenesulfonic acid. Periodically, about 2 ml. of material was withdrawn, neutralized with excess 10% sodium hydroxide solution, and taken up in 2 ml of ether. The organic layer was analyzed on a Fisher–Gulf partitioner equipped with a 12-ft. β,β′-oxidipropionitrile on C-22 firebrick column operated at 75–85° and at 20 p.s.i.

As noted in Table IV, the amount of 1-methylcyclohexene present in an equilibrium mixture of the methylcyclohexenes was 91–93%. An equilibrium mixture of the *t*-butylcyclohexenes contained 76–79% of the 1-olefin.

In one of the isomerization trials a material balance was calculated. When starting with 15.9 g. of a mixture containing 39% 1-*t*-butylcyclohexene, 11.0 g. of material containing 74% 1-*t*-butylcyclohexene was recovered. Thus the actual amount of 1-olefin increased from 6.2 g. to 8.05 g.

General Directions for the Reductions of Alkylbenzenes in Primary Amines at −7° (Table I).—In each instance lithium wire was added to a solution of alkylbenzene in the amine. The reaction flask was immersed in a cooling bath held at −5 to −9° in the case of ethyl- and *n*-propylamine. Stirring was continued until the lithium had been consumed. With methyl- and ethylamine as solvents, the amine was evaporated before hydrolysis. With *n*-propylamine, water was added directly to the reduction mixture when the metal was completely consumed. At no time during the reductions in *n*-propylamine did the solvent become blue throughout. A blue color was discerned intermittently around the pieces of reacting lithium. The results of these reductions are listed in Table I.

Attempted Isomerization of 4-Methylcyclohexene by Lithium Methylamide.—Lithium methylamide was generated by the reduction of 7.8 g. (0.1 mole) of benzene with 2.8 g. (0.4 g.-atom) of lithium in 200 ml. of methylamine. After all the lithium was gone, 9.6 g. of a mixture of 97% 4-methylcyclohexene and 3% 1-methylcyclohexene was added. After the mixture was stirred for 6 hr., the amine was evaporated. After work-up, an analysis showed 95% 4-methylcyclohexene and 5% 1-methylcyclohexene.

Acknowledgment.—The authors are grateful to the National Institutes of Health and the National Science Foundation for fellowship aid which made this work possible.

(9) W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

Stereochemistry of the Deamination of Aziridines[1a,b]

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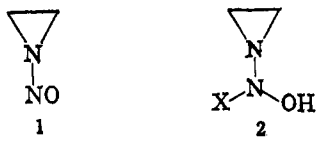
The reaction of stereoisomers of 2,3-dimethylaziridine with nitrosating agents such as 3-nitro-N-nitrosocarbazole, nitrosyl chloride, and methyl nitrite results in the formation of nitrous oxide and 2-butene with greater than 99% stereoselective deamination. At temperatures below −20°, a yellow intermediate was isolated that exhibited infrared, ultraviolet, and n.m.r. spectra characteristic of an N-nitrosoaziridine. The *trans*-dimethyl intermediate decomposed in a first-order rate with a half-life of 11 min. in methanol at −15°, and it formed nitrous oxide and *trans*-2-butene. The yellow product could be isolated as an oil and purified by low temperature chromatography on Florisil. Certain other nitrosoaziridines, including *cis*-dimethyl, methyl, ethyl, and tetramethyl, were less stable, but nitrosoaziridine itself was more stable. The deamination of aziridines with nitrosyl chloride also led to the formation of aziridine hydrochlorides that were stable at −78°. Although the salts tended to polymerize at higher temperatures, they could be converted to stable derivatives by exchanging anions with silver 2,4,6-trinitrobenzenesulfonate.

Preliminary to a study of the cleavage of nitrogen–carbon single bonds and the synthesis of various β-substituted amines, we have investigated the possibility that N-nitroso derivatives of selected aziridines might be sufficiently stable for isolation and study. It had been shown by Bumgardner, McCallum, and Freeman[2] that aziridine was deaminated readily by 3-nitro-N-nitrosocarbazole to yield ethylene and nitrous oxide. They proposed that the mechanism of the reaction involved either formation of the nitrosamine (1) or a

(1) (a) Supported in part by Cancer Research Funds of the University of California; (b) abstracted in part from the Ph.D. thesis of R. D. Clark, University of California, 1963.

(2) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 4417 (1961).



1 2

related intermediate (2). Very recently, Rundel and Müller[3] reported the preparation of an ethereal solution of N-nitrosoaziridine (1), from the low temperature reaction of aziridine with nitrosyl chloride.

We now wish to report that the reaction of 2,3-dimethylaziridine with nitrosyl chloride, 3-nitro-N-nitrosocarbazole, or methyl nitrite led to nitrous oxide and 2-butene with a very high degree of stereospecificity. Furthermore, a yellow intermediate whose properties were consistent with those expected for the N-nitroso derivative was isolated and purified by low temperature chromatography. Analogous intermediates were formed from other alkyl-substituted aziridines.

Stereochemical Course of Deamination.—The reaction of 2,3-dimethylaziridines with nitrosyl chloride was carried out in carbon tetrachloride solution. For the comparable reaction with 3-nitro-N-nitrosocarbazole, refluxing benzene was used according to the procedure of Bumgardner, *et al.*[2] The yields in the two reactions were compable (Table I) if it was assumed that one

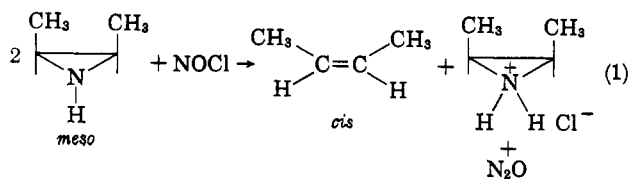
TABLE I

YIELD OF OLEFIN FROM ALKYL AZIRIDINES AND NITROSATING AGENTS

Compound	Yield, %
Aziridine	40[a]
2-Methylaziridine	57–71[b]
2-Ethylaziridine	53[b]
meso-2,3-Dimethylaziridine	43–53[c]
	43–53[b]
dl-2,3-Dimethylaziridine	19–38[c]
	37–53[b]
2,2,3,3-Tetramethylaziridine	27[d]

[a] As reported by Bumgardner, *et al.*[2] [b] Using nitrosyl chloride. [c] Using 3-nitro-N-nitrosocarbazole. [d] Using nitrosyl chloride in *p*-xylene.

additional equivalent of aziridine was consumed by the acid formed in the nitrosyl chloride reaction (eq. 1). Such a salt was isolated as a crystalline by-product.



(1)

It polymerized exothermically and gave a water-soluble product at room temperature. A similar polymerization was noted by Jones, *et al.*,[4] in the addition of anhydrous hydrogen chloride to aziridine in ether.

The stereochemical course of the deamination reactions was followed by the use of *meso*- and *dl*-2,3-dimethylaziridine. The results are shown in Table II.

The stereoisomeric 2,3-dimethylaziridines were prepared from the corresponding 2-butenes *via* the epoxides

(3) W. Rundel and E. Müller, *Ber.*, **96**, 2528 (1963).

(4) G. D. Jones, A. Langsjoen, Sister M. M. C. Neumann, and J. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).

TABLE II

STEREOSPECIFICITY OF THE DEAMINATION OF 2,3-DIMETHYLAZIRIDINES

Isomer	Reagent	Product butene, % *cis*	Product butene, % *trans*	Starting butene,[a] % *cis*	Starting butene,[a] % *trans*
cis	NOCl	99.1	0.9	99.9	0.1
trans	NOCl	0.3	99.7	1.0	99.0
cis	3-Nitro-N-nitroso-carbazole	99.6	0.4	99.9	0.1
trans	3-Nitro-N-nitroso-carbazole	0.5	99.5	1.0	99.0
trans	Methyl nitrite	<10[b]	>90[b]	1.0	99.0

[a] The sequence involved 2-butene → epoxide → aziridine → [nitrosoaziridine] → 2-butene. [b] The reaction mixture exploded and only a trace of product was recovered.

by a series of five steps.[5,6] Since both the *trans* epoxide and the *trans*-imine have lower boiling points than the *cis* isomers, it can be assumed that during their purification some of the *cis* contaminant was removed. This would account for the increase in purity of the product butene compared with the starting butene in the complete synthetic cycle (Table II). On the other hand, it would have been more difficult to effect purification of the higher boiling components in the *cis* series. Thus the increase of *trans* contaminant concentration during the cycle was not necessarily related to the deamination reaction. The deamination was most certainly better than 99% stereospecific.

It was observed by Bumgardner[7] that the treatment of *cis*-2,3-diphenylaziridine with N-nitroso-3-nitrocarbazole in refluxing benzene yielded a mixture of stilbenes containing about 10% of the *trans* isomer. The presence of *trans* isomer was accounted for by stilbene isomerism rather than from a nonstereospecific deamination mechanism because isomerization of *cis*-stilbene occurred to about the same extent under the reaction conditions.

Isolation of N-Nitrosoaziridines.—When the nitrosyl chloride reaction was carried out with *trans*-2,3-dimethylaziridine in a Dry Ice–acetone bath, a bright yellow solution was formed which was stable for several weeks at that temperature. However, when the solution was allowed to warm to room temperature, there was rapid disappearance of the yellow color and concomitant production of nitrous oxide and *trans*-2-butene. In order to isolate the colored intermediate, the nitrosation reaction was carried out in methyl ether at Dry Ice temperature, the reaction solution was decanted to separate the solid by-product, and the solvent was removed at −35 to −40° on a rotary evaporator. The oily residue was further purified by dissolving it in butane and chromatographing it on Florisil at about −50°. The solvent was again removed by evaporation at low temperature and pressure to give a product that was considered to be essentially pure.[8]

Rundel and Müller[3] carried out their nitrosation reaction using aziridine in ether at −60° with triethylamine to remove the hydrogen chloride produced.

(5) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2396 (1936).

(6) F. H. Dickey, W. Fickett, and H. J. Lucas, *ibid.*, **74**, 944 (1952).

(7) C. L. Bumgardner, private communication.

(8) Decomposition of the intermediate was sufficiently exothermic that it became violent if the temperature was allowed to approach ambient. Because of this, no attempts were made to obtain data on molecular weight or elemental analyses.

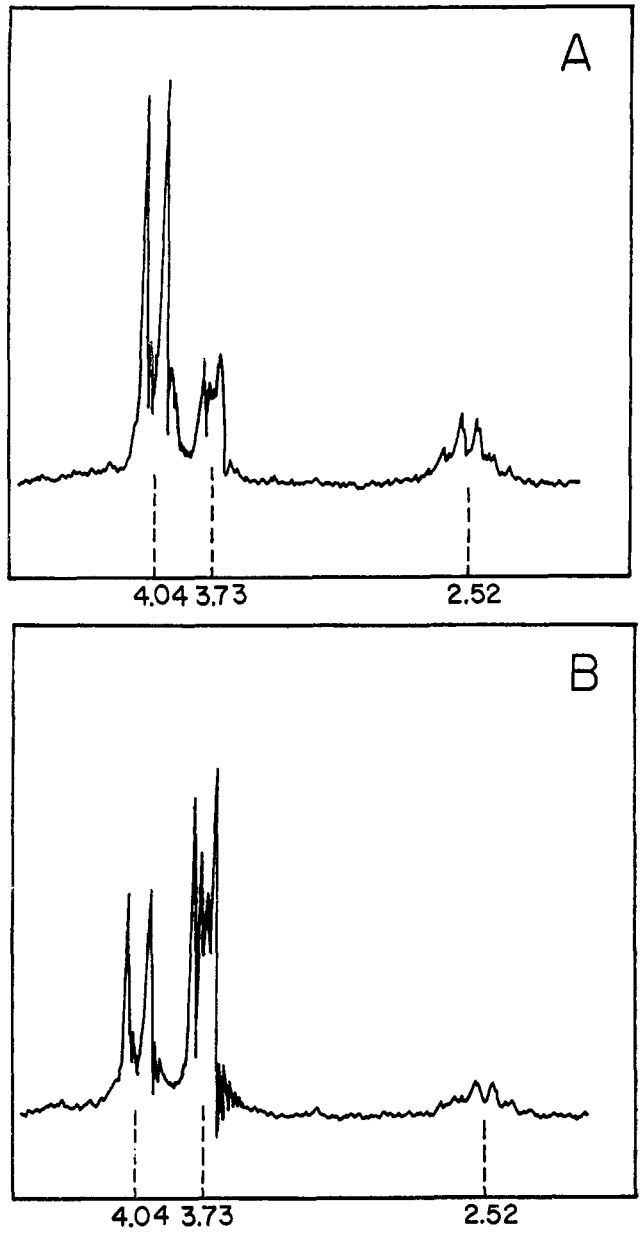


Fig. 1.—Proton n.m.r. spectra of *trans*-2,3-dimethyl-N-nitrosoaziridine in methylene chloride at −22°; shifts in p.p.m. upfield from the solvent: A, fresh sample with trace of 2-butene decomposition product at 3.73 p.p.m.; and B, same sample after more extensive decomposition.

Their evidence for the nitroso intermediate was based on its ultraviolet spectrum and largely unsuccessful attempts to isolate a stable derivative. Although we have also been unsuccessful so far in isolating a stable, solid derivative, we have additional evidence for the nitrosamine structure based on infrared, n.m.r., and ultraviolet spectroscopy.

The infrared spectrum of the yellow intermediate from *trans*-2,3-dimethylaziridine was obtained in carbon tetrachloride by warming the solution just above the melting point of the solvent and passing it through a standard 0.5-mm. sodium chloride cell. A continuous flow of solution was maintained so that fresh, cold material was always present in the cell. Spectra obtained in this manner were compared with those from the solution after it had been allowed to come to room temperature. With one minor exception, the peaks in the "warm" spectrum could be identified as belonging to carbon dioxide, nitrous oxide, and the appropriate 2-butene. The one extraneous peak occurred at 6.16 μ, and, since it also occurred in the "cold" spectrum, it was assumed to result from an impurity. The "cold" spectrum showed no N–H or O–H bands, but it did show peaks at 6.72, 6.95, and 7.62 μ related to the nitroso group and a peak at 9.60 μ related to the N–N group, in agreement with the values reported for dialkyl nitrosamines.[9] A peak at 8.25 μ was taken as evidence that the aziridine ring was still intact.[10] A peak expected at about 11.5 μ, assigned to the aziridine ring,[10] was not observed, but it was also absent in the spectrum of *trans*-2,3-dimethyl-N-methylaziridine.

The proton n.m.r. spectra[11] at −22° of the intermediate from *trans*-2,3-dimethylaziridine and its decomposition products are shown in Fig. 1. Methylene chloride was used as the solvent and internal standard. In a freshly prepared sample (Fig. 1A), two bands were observed at 2.52 and 4.04 p.p.m. upfield from the solvent and were attributed to the intermediate. The band at 4.04 p.p.m. was split into a doublet by about 5 c.p.s. and was assigned to the methyl protons. The second band, at 2.52 p.p.m., was assigned to the ring protons. It was expected that the band from these protons would be split into a quartet by the methyl group. In addition, further splitting by the *trans* proton, to give a more complex spectrum, was possible. Six peaks were easily distinguished, indicating that the splitting was more complex than that due only to the methyl group, and that the two ring protons were not identical. A very similar spectrum was observed for *trans*-2,3-dimethylaziridine, with the methyl doublet occurring at 4.3 p.p.m. and the multiplet at 3.8 p.p.m. The areas of the peaks in either case were in the ratio of 3:1. The third band (Fig. 1), at 3.73 p.p.m., was due to the methyl protons of *trans*-2-butene. The vinyl protons were masked by the solvent. As the intermediate decomposed, this peak slowly increased in magnitude while the other two peaks decreased (Fig. 1B). After the sample was warmed and the yellow color had disappeared, the butene peak was the only one remaining. Assignment of this peak was verified by comparing the shift and splitting with that of a known sample of *trans*-2-butene under the experimental conditions.

The n.m.r. spectrum of the unsubstituted nitrosoaziridine showed a single sharp peak at 2.70 p.p.m. that disappeared completely when the sample was warmed. No product peak was observed, and it was assumed that it was masked by the solvent.

The visible and ultraviolet spectra were similar to those reported for nitrosoaziridine.[3] Except for a shift in the position of maxima and somewhat less fine structure, they were also quite comparable with those of dimethylnitrosamine.[12] The ratio of intensities of the $n\rightarrow\pi^*$ band (457 mμ) and the $\pi\rightarrow\pi^*$ band (254 mμ) was about 1:100 as estimated by dilution technique. It was impossible to determine values for absorbancy because of the instability of the compound.

(9) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).
(10) H. T. Hoffman, Jr., G. E. Evans, and G. Glockler, *J. Am. Chem. Soc.*, **73**, 3028 (1951).
(11) Spectra were obtained with a Varian Associates V-4300 spectrometer operating at 56.4 Mc.
(12) W. S. Layne, H. H. Jaffé, and H. Zimmer, *J. Am. Chem. Soc.*, **85**, 435 (1963).

Electrochemical reduction of the yellow intermediate could be observed by polarographic means. At −25° half-wave potentials of −1.20 v. and −1.65 v. *vs.* a mercury pool were observed in ethyl ether–methanol (50% by volume) containing 0.25 *M* lithium chloride. Both waves were found to diminish with time and disappeared completely when the solution had been warmed sufficiently for the discharge of the yellow color. Large scale constant potential reduction failed to yield any significant amount of reduced product because the rate of decomposition of the nitroso compound was too rapid.[13]

An attempt was made to obtain some thermodynamic values from the polarographic data. At −15° the decomposition was followed by maintaining a constant potential of −1.5 v., but at lower temperatures (−20°, −25°, and −30°) the polarograph was placed on a 10-min. cycle. Periodic degassing was required to prevent the formation of a maximum in the polarographic wave, presumably caused by the build-up of gaseous products in the solution. The activation energy was found to be approximately 16 kcal./mole and the entropy of activation about −13 e.u. It was impossible to correlate these data closely with the rates obtained spectrophotometrically because of the use of mixed solvent and the presence of lithium chloride.

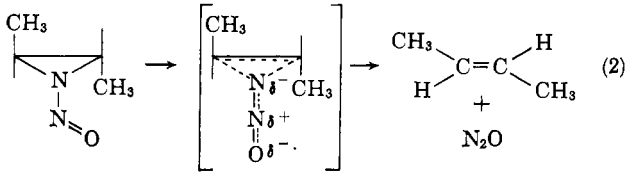
In general agreement with the data of Rundel and Müller,[3] the rate of decomposition of the intermediate was found to be first order. Additionally, in the spectrophotometric determination of rates in pure solvents, it was also observed that a tenfold increase in rate occurred when the solvent was changed from pentane to dimethylformamide (Table III).

TABLE III

RATE OF DECOMPOSITION OF *trans*-2,3-DIMETHYL-N-NITROSOAZIRIDINE IN VARIOUS SOLVENTS AT −15°

Solvent	$k_1 \times 10^2$, min.$^{-1}$	Approximate half-life, min.
Pentane	1.2 ± 0.3	58
Ethyl ether	1.8 ± 0.3	38
Methanol	6.3 ± 0.4	11
Dimethylformamide	13 ± 4	5

Since the reaction was first order in nitrosamine, and product formation was stereospecific, it seemed likely that the transition state involved a concerted cleavage of the two C–N bonds (eq. 2). The charge



(2)

separation related to the incipient formation of the nitrous oxide molecule could account for a small-to-moderate solvent dependence of reaction rates. In contrast, in the desulfurization of 2,3-dimethylthiirane with triphenylphosphine[14] in which a similar concerted bond cleavage was postulated, the observed change of rate with change in solvent was very small.

Maximum thermal stability among the various substituted nitrosoaziridines was observed with the *trans*-dimethyl isomer. The corresponding *cis*-dimethyl isomer decomposed so rapidly that it could not be purified at −35 to −40°. The methyl, ethyl, and tetramethyl intermediates were also less stable than the *trans*-dimethyl intermediate. However, the unsubstituted material was more stable, having a half-life in ethyl ether at −15° of about 256 min., compared to about 38 min. for the *trans* isomer.

The decomposition of *trans*-2,3-dimethyl-N-nitrosoaziridine was found to be catalyzed by acids. Although the compound was stable for long periods of time at −78°, the presence of a small amount of sulfuric acid induced a noticeable rate of decomposition. Better solvation in the transition state through hydrogen bonding or more formal protonation would be expected in the presence of acids. Such interactions have been proposed[12,15] as an explanation for the effect of acids on the spectra of dialkyl nitrosamines.

Isolation of Aziridine Salts.—The aziridine hydrochlorides formed from the reaction of aziridines with nitrosyl chloride were isolated as crystalline solids after the nitrosamines were separated. Although they appeared to be stable indefinitely at −78°, all except the salt of tetramethylaziridine polymerized exothermically when allowed to warm to room temperature. A similar polymerization was reported for the hydrochloride formed from aziridine and anhydrous hydrogen chloride in ether.[4] On the other hand, the hydrochloride of 2,2-dimethylaziridine, isolated in 90% yield from an ether solution at −77°, was found to be stable in dry air at room temperature for several days.[16] This hydrochloride, shown to be a monomer by quantitative conversion to the known picrate, polymerized to a water-soluble polymer at its melting point of 54–56°.[16]

The yield of polymer in the nitrosyl chloride reaction was usually somewhat greater than 100% based on the previously suggested stoichiometry. Up to 94% of the original aziridine was accounted for in the specific case of 2-methylaziridine, where 71% propene and 117% polymer were isolated. The excess material in the polymer was probably a complex mixture of side products formed by ring cleavage and diazotization of the resulting amine.

The unstable hydrochlorides of aziridine and 2-methylaziridine were converted to stable derivatives by treating them with an acetonitrile solution of silver 2,4,6-trinitrobenzenesulfonate.[17] After the precipitated silver chloride was removed by filtration, the aziridine trinitrobenzenesulfonate was precipitated by the addition of ether. The hydrochloride could not be converted directly to the trinitrobenzenesulfonate with the acid because the resulting product was unstable, probably owing to hydrogen chloride trapped in the product.

Structure proof for the aziridinium salts was based on syntheses by independent routes. The trinitrobenzenesulfonates were prepared directly by the reaction of the aziridine with trinitrobenzenesulfonic

(13) That an intermediate of type **2**, where X = Cl, was not present in the original solution was shown by the absence of any precipitate when the solution was treated with silver nitrate.

(14) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960).

(15) W. S. Layne, H. H. Jaffé, and H. Zimmer, *ibid.*, **85**, 1816 (1963).

(16) L. B. Clapp, private communication; data from the Ph.D. thesis of V. B. Schatz, Brown University, 1954.

(17) The authors are indebted to D. J. Pettitt for providing the silver 2,4,6-trinitrobenzenesulfonate.

acid or indirectly by forming the hydrochloride at low temperatures and converting this with silver trinitrobenzenesulfonate. Salts from all sources were found to have identical infrared spectra, melting points, and mixture melting points. Furthermore, the materials had the expected elemental analyses for a simple salt and the correct molecular weight for a monomeric species.

Experimental

Aziridines.—Aziridine was donated by the Dow Chemical Company, Midland, Mich. The 2-methylaziridine and 2-ethylaziridine were purchased from Interchemical Corporation, 67 West 44th Street, New York 36, N. Y. Stereospecific *cis*- and *trans*-2,3-dimethylaziridine were prepared from the corresponding 2-butene isomers *via* the epoxide.[5,6] The 2,2,3,3-tetramethylaziridine was prepared according to the method of Closs and Brois.[18]

***trans*-2,3-Dimethyl-N-nitrosoaziridine.**—A solution of 3.30 g. (0.0503 mole) of nitrosyl chloride in 50 ml. of methyl ether was added slowly and with stirring to 7.1 g. (0.100 mole) of freshly distilled *trans*-2,3-dimethylaziridine in 100 ml. of the same solvent in a bath at −78°. After about 2 hr. at this temperature, when the precipitated aziridine hydrochloride had settled, the yellow solution was separated by decantation. The residue was washed with several 25-ml. portions of cold methyl ether. The solvent in the combined ethereal solutions was removed in a rotary evaporator at 25-mm. pressure and −35 to −40°. Ther esidual oil was dissolved in a small amount of butane and placed on a Florisil chromatographic column kept at about −50°. Methanol at about −50° was continuously circulated through a jacket surrounding the column, and a vacuum jacket surrounded the entire working length of the apparatus. The yellow material was eluted with butane containing a small amount of methyl ether and collected in a cold receiver. The purified product was reisolated by evaporation of the solvent as previously described.

Deamination of Aziridines.—As an example of a typical deamination procedure, 7.1 g. (0.10 mole) of freshly distilled *cis*-2,3-dimethylaziridine in 75 ml. of carbon tetrachloride was placed in a 300-ml. flask containing (a) an addition funnel and (b) a reflux condenser connected in series with two Dry Ice traps. A solution of 3.3 g. (0.050 mole) of nitrosyl chloride in 50 ml. of carbon tetrachloride was added with stirring. Both solutions were kept just above the freezing point of the solvent during this period of about 15 min. After the yellow solution was slowly allowed to warm to room temperature, it was refluxed for 2 hr. The yield of butene, determined volumetrically in the liquid phase and based on the stoichiometry of eq. 1, was 43–53%. The distribution of butene isomers was determined by chromatography with a 15-ft. column of Dow 11 silicone oil on firebrick. No other low-boiling hydrocarbon products were detected. Nitrous oxide was isolated by adding a liquid nitrogen trap to the collection system, and it was identified by chromatography on a 6-ft. silica gel column.

Reaction of 2-Methylaziridine with 2,4,6-Trinitrobenzenesulfonic Acid.—A solution of 5.7 g. (0.10 mole) of 2-methylaziridine in 50 ml. of acetonitrile was added to 35 g. (0.12 mole) of 2,4,6-trinitrobenzenesulfonic acid dissolved in a minimum quantity of acetonitrile. The product was precipitated by the addition of anhydrous ether. Recrystallization from acetonitrile–ether yielded 30 g. (86%) of a white solid. The melting point of the product was highly dependent on the rate of heating and the degree of preheating; when the oil bath was preheated to 150° and the rate of heating was about 10°/min., the material decomposed at 173–174°.

Anal. Calcd. for $C_9H_{10}N_4O_9S$: C, 30.86; H, 2.88; N, 16.00; mol. wt., 350. Found: C, 30.90; H, 2.74; N, 15.95; mol. wt. (crystalline material), 352 ± 3.[19]

Aziridinium 2,4,6-Trinitrobenzenesulfonate.—The aziridinium trinitrobenzenesulfonate was prepared in the same manner as the 2-methylaziridinium salt. The product decomposed sharply at 189° when the bath was preheated to 175° and the rate of heating was about 10°/min.

Anal. Calcd. for $C_8H_8N_4O_9S$: C, 28.58; H, 2.40; N, 16.66; mol. wt., 336. Found: C, 28.90; H, 2.75; N, 16.79; mol. wt., 350 ± 6.[19]

Reaction of Aziridine Hydrochlorides with Silver 2,4,6-Trinitrobenzenesulfonate.—A small amount of an aziridine hydrochloride was dissolved in cold acetonitrile and added to an excess of silver 2,4,6-trinitrobenzenesulfonate in the same solvent. In the absence of excess silver salt the solution turns deep red. The solution was filtered to remove silver chloride, and the product was precipitated by the addition of anhydrous ethyl ether. Recrystallization from acetonitrile–ether yielded a product identical with that described above for the direct preparation of the salt.

Kinetic Procedure.—Samples of consistent (but unknown) concentration of the nitrosamines were prepared by adding small amounts of the yellow oil to the cold solvent in a spectrophotometer cell until the absorbancy of the solution was very near unity at 450 mμ. The cell, which had a jacket for circulation of coolant, and which was protected from moisture condensation by an air space isolated by pairs of quartz windows, was quickly brought to the temperature of the kinetic run (as determined by a thermocouple in the nitrosoaziridine solution). The decompotion was followed spectrophotometrically at the indicated wave length.

The addition of pellets of potassium hydroxide to a solution used for kinetic measurement had no effect on the rate of decomposition. Hence it was assumed that separation of nitrosoaziridine from aziridine salt in the synthetic procedure had been complete and no acid catalysis was involved during the rate studies.

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(18) G. L. Closs and S. J. Brois, *J. Am. Chem. Soc.*, **82**, 6068 (1960).

(19) Determined with a Mechrolab Model 301A osmometer using acetonitrile solvent and dimethylamine trinitrobenzenesulfonate as a standard.