Identification of the Reaction Products.—The reaction products were separated by preparative vapor phase chromatography and the structure of the carbon skeletons were confirmed by quantitative hydrogenation in ethanol with 5% Pd–C catalyst. Bicyclo[4.1.0]hept-3-ene (VII),[19] 1-methylcyclohexa-1,4-diene (XII),[21,22] bicyclo[2.2.1]hept-2-ene (XII),[23] and bicyclo[4.1.0]hept-3-ene (XIII)[20,24] were identical with authentic samples.

4-Methylene-1-cyclohexene (VII)[25,26] showed an nmr br singlet (4 H)[27] at 2.1 ppm (allylic CH_2), br singlet (2 H) at 2.7 (double allylic CH_2), br singlet (2 H) at 4.7 (exocyclic CH_2), and a singlet (2 H) at 5.6 (vinyl); infrared bands (CCl_4) at 3062, 3020, 2980, 2930, 2900, 2838, 2085, 1650, 1430, 1414, 880, and 642 cm^{-1}; catalytic hydrogenation (4.0 equiv of hydrogen) to methylcyclohexane.

1-Methylcyclohexa-1,3-diene (VIII)[28] showed an nmr poorly resolved doublet (3 H) at 1.8 ppm (CH_3), br singlet (4 H) at 2.1 (allylic CH_2), br multiplet (3 H) at 5.6–5.8 (vinyl); infrared bands (CCl_4) at 3040, 2970, 2930, 2870, 2830, 1630, 1595, 1485, 1375, 880, and 680 cm^{-1}; catalytic hydrogenation (3.9 equiv of hydrogen) to methylcyclohexane.

Tricyclo[4.1.0.0^{3,7}]heptane (XI)[9] showed an nmr complex spectra containing no vinyl hydrogens; infrared bands (CCl_4) at 3068, 3039, and 2971 cm^{-1}; catalytic hydrogenation (1.9 equiv of hydrogen) to bicyclo[2.2.1]heptane.

Analysis of Deuterated Reaction Mixtures.—Recovered bicyclo[4.1.0]hept-2-ene and 4-methylene-1-cyclohexene from reaction mixtures containing D_2O were spectrally identical with authentic samples and did not contain a C–D stretching band at about 2100 cm^{-1} in the infrared spectrum.[29]

Registry No.—IV, 13428-09-6; VII, 13407-18-6; VIII, 1489-56-1; XI, 279-18-5.

(19) An authentic sample of bicyclo[4.1.0]hept-2-ene was prepared by the Simmons–Smith synthesis from cyclohexa-1,3-diene[20] (Columbia Organic Chemicals Co., Columbia, S. C.).

(20) H. E. Simmons and R. D. Smith, *Org. Syn.*, **41**, 72 (1961).

(21) We would like to gratefully acknowledge a generous sample of 1-methylcyclohexa-1,4-diene from Columbia Chemicals Co.

(22) An authentic sample of XI was obtained from Columbia Chemicals, Co.

(23) An authentic sample of XII was obtained from the Matheson Co.

(24) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(25) W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *ibid.*, **78**, 2804 (1956).

(26) An authentic sample of IX was prepared by the pyrolysis of Δ^3-cyclohexenylcarbinyl acetate prepared from Δ^3-cyclohexenecarboxaldehyde by reduction with borohydride followed by acetylation with acetic anhydride.

(27) The integrated peak heights reported below were within 0.1 proton intensity of the predicted theoretical height.

(28) A. Mondrous, P. Potin, and R. Wylde-Lachazette, *Bull. Soc. Chim. France*, 1549 (1962).

(29) R. T. Coneley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, 1966, pp 26, 280.

Nucleophilic Opening of the Oxirane Ring of 1-Methyl-4-phenyl-3,4-epoxypiperidine

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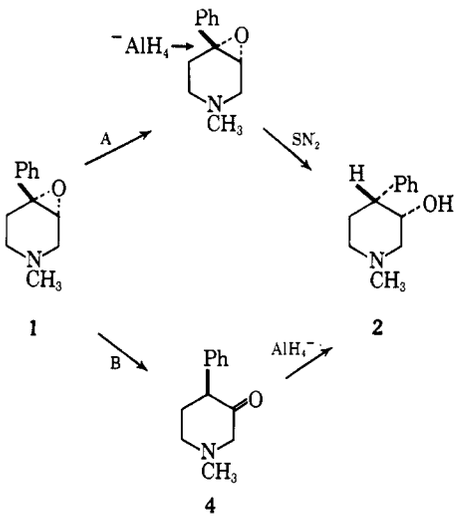
The opening of the oxirane ring of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) by reduction with lithium aluminum hydride or diborane occurs by a displacement at the 4 position to give *cis*-1-methyl-4-phenyl-3-piperidinol. The reaction of **1** with Grignard or lithium reagents gives an elimination reaction at room temperature to form 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol, although at higher temperatures addition does occur. The reaction pathways are considered.

The reaction of 1-methyl-4-phenyl-3,4-epoxypiperidine (**1**) with lithium aluminum hydride to give *cis*-1-methyl-4-phenyl-3-piperidinol (**2**)[2] was highly unexpected in view of the direction of ring opening of epoxides reported previously.[3] From the reduction in ether there was no evidence for the formation of the expected product, 1-methyl-4-phenyl-4-piperidinol (**3**). In view of the unusual reactivity of **1**, a study of its properties was made.

The conversion of **1** to **2** could occur by either of two pathways (Scheme I). The usual ring opening of the epoxide occurs by a nucleophilic displacement on carbon and such a sequence at the C-4 position is represented by path A. An alternative pathway, B, in which a pinacollike rearrangement occurred, owing to a Lewis acid activity of the lithium aluminum hydride or an impurity, to give 1-methyl-4-phenyl-3-piperidone (**4**) would provide a plausible explanation for the unusual direction of ring opening.[3] The latter route, B, was disfavored since the reduction of **4** with lithium aluminum hydride had been shown to give both *cis*- and *trans*-1-methyl-4-phenyl-3-piperidinol;[2] this reaction sequence was completely eliminated by showing

SCHEME I



that the product of reduction of **1** with lithium aluminum deuteride was 1-methyl-4-phenyl-3-piperidinol-d_4 (**2**-d_4). The product of the reaction of **1** with lithium aluminum deuteride was shown by gas phase chromatography to be homogeneous and to have a retention time identical with that of unlabeled **2**. A comparison of the nmr spectra of **2** and **2**-d_4 showed that the integrated intensities of the signals (τ 6.20) for the carbinol protons at position C-3 were identical. Thus the pro-

(1) This research represents a portion of the thesis of W. E. Krueger presented to the Graduate Faculty of the University of New Hampshire in partial fulfillment of the requirements of the Ph.D. degree.

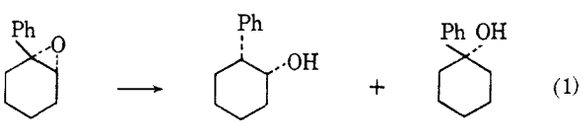
(2) R. E. Lyle and W. H. Krueger, *J. Org. Chem.*, **30**, 394 (1965).

(3) E. L. Eliel, *J. Am. Chem. Soc.*, **80**, 1744 (1958), and previous papers in this series; J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

ton at this position must have been attached to this carbon in the starting material **1**. The multiplet centered at τ 7.43 in **2**, assigned as the C-4 benzylic proton, was not evident in the nmr spectrum of **2**-d_4. Thus there can be little doubt that the conversion of **1** to **2** occurred by a direct nucleophilic displacement of epoxide oxygen by hydride with inversion of the C-4 carbon (A).

This direction of ring opening of the oxirane ring could not be rationalized on the basis of the arrangement of substituents, since α,β-disubstituted styrene oxides have been reported to give α-phenylethanol derivatives.[3] The conformational preference for the diaxial arrangement of bonds after the opening of an oxirane ring fused to a six-membered ring also did not provide an explanation for the product, for there is no obvious difference in the stability of the two conformers of **1**.

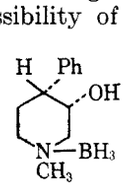
In an attempt to determine whether or not the heterocyclic nitrogen was important in determining the direction of the epoxide ring opening, the carbocyclic analog of **1**, 1-phenyl-1,2-epoxycyclohexane (**5**),[4] was investigated. The product of the reaction of **5** with lithium aluminum hydride in ether was shown to contain a maximum of 8% of 2-phenylcyclohexanol (**6**), and 78% of 1-phenylcyclohexanol (**7**), the expected product, was isolated and characterized (eq 1). Thus the basic nitrogen of **1** must be of importance in causing the nucleophilic substitution at the tertiary position. The role of the basic nitrogen may be in providing a convenient site for an intramolecular nucleophilic displacement.



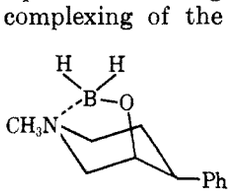
(1)

5 **6** **7**

That an intramolecular reaction facilitated the ring opening to form the less-substituted alcohol was shown by investigating the ring opening of the epoxide of **1** with diborane. Pasto and co-workers have shown this to be a slow reaction with an uncontaminated solution of diborane in tetrahydrofuran.[5] The reaction of **1** with an excess of diborane, generated externally, in dimethoxyethane gave the amine borane of (**2a**) *cis*-1-methyl-4-phenyl-3-piperidinol. This ring opening must have occurred very rapidly, for simply passing diborane into a solution of **1** in ether gave an immediate precipitation of **8**. The absence of O–H stretching absorption and the presence of B–H stretching bands in the infrared spectrum along with the elemental analyses established the cyclic structure of **8**. The formation of the piperidinol **2** rather than 1-methyl-4-phenyl-3,4-piperidinediol on acid hydrolysis of **8** confirms that the oxirane ring has been opened in forming **8**. Thus the possibility of initial complexing of the diborane with the heterocyclic nitrogen seemed to facilitate and to direct the ring opening of *the epoxide*.[5]



2a



8

The direction of the ring opening of **1** with the hydrides suggested that the heterocyclic nitrogen atom was important in providing a site for complexing of the hydride in the transition state.[6] Aluminum hydride or lithium from the lithium aluminum hydride or boron hydride from the diborane may also complex with the oxirane oxygen leading to a high degree of carbonium ion character in the transition state for the nucleophilic displacement.

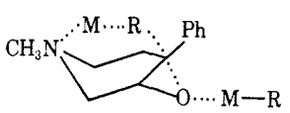
The apparent participation of the heterocyclic nitrogen of **1** in the reaction with hydrides prompted a similar study of the reactions of **1** with organometallic reagents. Again the participation of the nitrogen in a cyclic transition state apparently directed the course of the reaction and the greater steric bulk of the nucleophile caused elimination rather than addition at reaction temperatures near room temperature.[6] Thus the product of the reactions of several lithium and magnesium reagents with **1** was 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol (**9**).[7]

The reaction of **1** with phenyl Grignard reagent in boiling anisole occurred with some elimination to form **9**, but two products of addition were also isolated (eq 2). These addition compounds were not identical with either of the diasterioisomers of 1-methyl-3,4-diphenyl-3-piperidinol formed by the addition of phenyl Grignard to 1-methyl-4-phenyl-3-piperidone.[2] One of the compounds was shown to be 1-methyl-4,4-diphenyl-3-piperidinol (**10**) on the basis of the elemental analyses, spectra, and comparison with reported melting point.[8] Compound **10** was probably formed in a manner comparable with that of **2** from the hydride reductions, for **9** was inert to further reaction with phenyl Grignard reagent under these conditions.

(4) D. H. Kelly, Ph.D. Thesis, University of Oklahoma, 1963.

(5) D. J. Pasto, C. C. Cumbo, and J. Hickman, *J. Am. Chem. Soc.*, **88**, 2201 (1966).

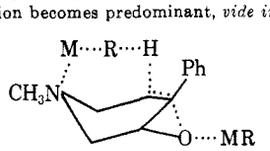
(6) One referee suggested that the direction of the oxirane ring opening might result from the possibility of a "six-membered ring transition state," i, for the formation of **2** while a five-membered ring would be required to give the anticipated product, 1-methyl-4-phenyl-4-piperidinol. Such a complex



i

M = metal or boron
R = H, alkyl, aryl

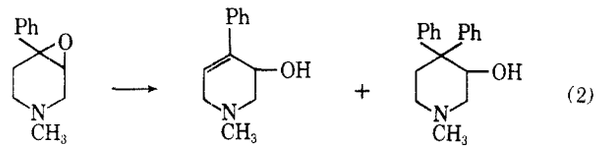
also provides a convenient rationale for the course of the reaction of **1** with organomagnesium and -lithium reagent. The greater bulk of the R group in these reagents causes the "six-membered" cyclic transition state involving the pseudoaxial hydrogen on position 5 (ii) to have lower energy than i and the elimination reaction becomes predominant, *vide infra*.



ii

(7) It is not necessary to invoke a transition state involving nitrogen participation[6] to explain the formation of the elimination product, for similar products have been reported with nonnitrogeneous epoxides and organometallic reagents: (a) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6370 (1960), and A. C. Cope and J. K. Heeren, *ibid.*, **87**, 3125 (1966); (b) W. Rieve and L. W. Fine, *ibid.*, **86**, 880 (1964); (c) D. F. Hoeg, J. E. Forrette, and D. I. Lusk, *Tetrahedron Letters*, No. 30, 2059 (1964).

(8) F. F. Blicke and J. Krapcho, *J. Am. Chem. Soc.*, **74**, 4001 (1952).



1 9 10 (2)

The second product of addition was probably 1-methyl-3,4-diphenyl-4-piperidinol; however, the data were not conclusive. At the higher temperatures the Grignard reaction occurs by two different mechanisms.

Experimental Section

Reaction of 1-Methyl-4-phenyl-3,4-epoxypiperidine (1) with Lithium Aluminum Deuteride.—A slurry of 0.31 g (0.007 mole) of lithium aluminum deuteride in 10 ml of anhydrous ether was prepared under nitrogen in a three-neck flask. A solution of 0.80 g (0.004 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) in 20 ml of anhydrous ether was added and stirring was continued overnight. The excess lithium aluminum deuteride was hydrolyzed with water and the solid was separated by filtration. The filter cake was washed four times with 15-ml portions of ether. The combined organic layers were dried over potassium carbonate and evaporated to dryness to give 0.79 g (97%) of a white solid. Recrystallization of this solid from *n*-heptane gave 0.75 g (92%) of white needles, mp 95–97°; *cis*-1-methyl-4-phenyl-3-piperidinol (2) had mp 95–97°.[2] The nmr spectrum of these needles had a signal at τ 6.02 (carbinol proton), but not at 7.43 (benzylic hydrogen). On this basis the structure was assigned as that of *cis*-1-methyl-4-phenyl-3-piperidinol-d_4 (2-d_4).

Reduction of 1-Phenylcyclohexene Oxide (5) with Lithium Aluminum Hydride.—To a suspension of 1.0 g (0.025 mole) of lithium aluminum hydride in 30 ml of dry ether was added 1.0 g (0.006 mole) of 1-phenyl-1,2-epoxycyclohexane(1-phenylcyclohexene oxide) (5). Stirring was continued for 3 hr. The excess lithium aluminum hydride was hydrolyzed with water and the solid which formed was separated by filtration. The filter cake was washed three times with 20-ml portions of ether. The combined organic layers were dried over magnesium sulfate. The reaction was worked up as above to give a yellow oil which solidified on standing. Gas chromatographic analysis of the crude product using a 1-m Carbowax 20 M on Chromosorb W column showed that it contained 1-phenylcyclohexanol (7) and 2-phenylcyclohexanol (6) in a 19:1 ratio. Recrystallization of the solid from *n*-heptane gave 0.78 g (78%) of a white solid, mp 60–62°, whose melting point (63–63.5°),[9] infrared spectrum, and vpc retention time were identical with those of 1-phenylcyclohexanol (7) prepared by the reaction of phenylmagnesium bromide with cyclohexanone.

Reaction of 1-Methyl-4-phenyl-3,4-epoxypiperidine (1) with Diborane. A.—A large excess of diborane generated externally[10] was bubbled through a solution of 11.0 g (0.06 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) in 150 ml of 1,2-dimethoxyethane. The reaction was stirred for 6 hr. The solvent was removed under reduced pressure and the residue was dissolved in methanol. An equal volume of ether was added and the white solid that separated was collected by filtration. Recrystallization of the solid from toluene gave 7.5 g (64%) of *cis*-1-methyl-4-phenyl-3-piperidinol amine borane (2a) as a white solid: mp 137–140° dec; ν_{mull} 3550 (OH), 2300, and 2450 cm^{-1} (BH).

Anal. Calcd for $C_{12}H_{20}BNO$: C, 70.92; H, 9.91; N, 6.87. Found: C, 69.48; H, 10.16; N, 6.89.[11]

Treatment of the amine borane 2a with 6 *N* hydrochloric acid gave 2. The reaction of 2 with diborane gave a compound identical in decomposition point and infrared spectrum with this amineborane (2a).

B.—A large excess of diborane generated as above was bubbled through a solution of 9.0 g (0.05 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) in anhydrous ether. The white solid that formed was collected by filtration. Recrystallization of the solid from ether–petroleum ether gave 5.2 g (54%) of an amine borane, mp 105–108°, not identical with the amine borane of 2 isolated from part A. Hydrolysis of 8 with 6 *N* hydrochloric acid gave *cis*-1-methyl-4-phenyl-3-piperidinol (2), mp 102–105°. The infrared spectrum of 8 showed no absorption bands above 3100 cm^{-1} (no OH), but the boron–hydrogen stretching absorption at 2300 and 2450 cm^{-1} was evident.

Anal. Calcd for $C_{12}H_{18}BNO$: C, 71.62; H, 9.00. Found: C, 70.81; H, 9.17.[11]

1-Methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol (9). A.—The lithium reagent was prepared from 0.30 g (0.04 mole) of lithium ribbon and excess methyl bromide in ether. The excess methyl bromide was removed by heating and sweeping with nitrogen for 0.5 hr. A solution of 4.0 g (0.02 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) in ether was added in 0.5 hr and the reaction was heated for an additional 12 hr. Water and potassium carbonate were added and the water layer was drawn off and extracted three times with 50-ml portions of ether. The combined organic layers were dried over potassium carbonate and evaporated to give 2.4 g (60%) of a dark oil. The oil was taken up in an equal volume of *n*-heptane and on standing a white solid separated. Recrystallization of the solid from *n*-heptane gave 1.8 g (45%) of 9 as white needles: mp 104–106°; $\lambda_{max}^{i\text{-PrOH}}$ 244 mμ, log ϵ 4.06.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99. Found: C, 76.31; H, 8.18.

Treatment of an acetone solution of the crude product obtained from 5.0 g (0.03 mole) of 1 with dry hydrogen chloride gave, after recrystallization of the salt from wet isopropyl alcohol, 4.35 g (73%) of 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol (9) hydrochloride, mp 211–214°.

Anal. Calcd for $C_{12}H_{16}ClNO$: C, 63.85; H, 7.14; N, 6.21. Found: C, 63.61; H, 7.02; N, 6.30.

B.—The reaction of 2.0 g (0.01 mole) of 1 with 0.02 mole of phenyllithium gave 0.9 g (45%) of 9, mp 103–105°.

C.—To the Grignard reagent from 3.1 g (0.02 mole) of bromobenzene and 0.5 g (0.02 mole) of magnesium turnings was added a solution of 1.9 g (0.01 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) in ether. After stirring overnight, the reaction mixture was decomposed with 100 ml of 4 *N* hydrochloric acid and 50 g of ice. The water layer was removed and the ether layer was extracted twice with 25-ml portions of 2 *N* hydrochloric acid. The combined acid layers were neutralized with 50% sodium hydroxide solution and saturated with potassium carbonate. The resulting mixture was extracted with ether and the ether extracts were dried over potassium carbonate and evaporated to give a dark solid. Recrystallization of this solid from *n*-heptane gave 1.05 g (52%) of 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol (9) identical in melting point and infrared spectrum with 9 prepared by methods A and B.

The Reaction of 1-Methyl-4-phenyl-3,4-epoxypiperidine (1) with Grignard Reagents at Elevated Temperatures.—A solution of 14.9 g (0.09 mole) of bromobenzene in 100 ml of anisole was treated with 2.2 g (0.09 g-atom) of magnesium turnings at 150°. After all the magnesium had undergone reaction, an anisole solution of 5.7 g (0.03 mole) of 1-methyl-4-phenyl-3,4-epoxypiperidine (1) was added and the solution was heated under reflux for 5 hr. The reaction was hydrolyzed with 200 ml of 4 *N* hydrochloric acid and 50 g of ice. The acidic water layer was removed and the organic layer was extracted with 2 *N* hydrochloric acid. The combined acidic water layers were made basic with 50% sodium hydroxide and an excess of potassium carbonate was added. The basic solution was extracted with ether and the combined organic layers were dried and concentrated to give 6.25 g of a dark oil. Analysis of the dark oil by gas chromatography using a 1-m silicone GE XE-60 column indicated the presence of 1-methyl-4-phenyl-1,2,3,6-tetrahydro-3-pyridinol (9) and two products of addition in a ratio of 2:3. Crystallization of the oil from 5 ml of *n*-heptane and recrystallization from ethanol gave 2.1 g (30%) of a white solid, mp 128–135°.

The solid was chromatographed using a 30-cm column of Florisil with acetone as the eluent. Fractions of 25 ml were collected. The fractions from 325 to 425 ml gave a white solid. Recrystallization from acetone gave 1-methyl-3,4-diphenyl-4-piperidinol, mp 157–159°.

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.81; H, 8.02; N, 5.13.

(9) I. Heilbron, "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1953, p 116.

(10) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(11) The combustion of boron-containing compounds may lead to boron carbide and hence low analytical values for carbon: R. L. Letsinger and A. J. Wyosick, *J. Org. Chem.*, **28**, 3199 (1963).

The fractions after 500 ml gave 1-methyl-4,4-diphenyl-3-piperidinol (**10**), mp 162–165° (lit.[8] mp 158–159°). The infrared spectrum showed an OH stretching absorption and the nmr spectrum gave a signal (quartet) at τ 5.32, a carbinol CH of an ABX system.

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.50; H, 7.93; N, 5.41.

Registry No.—1, 2206-30-6; 2-d_4, 13427-20-8; **2a**, 13427-21-9; **7**, 1589-60-2; **8**, 13441-17-3; **9**, 1891-24-3; **9** hydrochloride, 13427-23-1; **10**, 7507-74-6; 1-methyl-3,4-diphenyl-4-piperidinol, 13427-24-2.

Acknowledgment.—The authors wish to express appreciation to the National Heart Institute of the National Institutes of Health for partial support of this research by Grant No. HE-01713 and continuation grants. The Varian A-60 nmr spectrometer was made available by a National Science Foundation Grant G 27718 which the authors gratefully acknowledge.

Derivatives of Azidosulfonic Acid. Halides, Amides, and Salts

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Received April 7, 1967

The preparation of sulfuryl azide chloride, sulfamoyl azide, and several aromatic sulfamoyl azides was achieved by the metathetical reaction of sodium azide and the related chloro derivatives. A broadly applicable synthesis of substituted sulfamoyl azides was found in the reaction of sulfuryl azide chloride and amines. Previously developed preparations of inorganic azidosulfonate salts were utilized in the synthesis of quaternary ammonium azidosulfonates. The reactions of selected products indicated that these materials have chemical properties similar in kind to those of sulfonyl azides.

A number of derivatives of azidosulfonic acid are known. Sulfuryl azide, $SO_2(N_3)_2$,[1] sulfuryl azide fluoride, FSO_2N_3,[2] pyrosulfuryl azide, $N_3SO_2OSO_2N_3$,[3] N,N-dialkylsulfamoyl azides, $R_2NSO_2N_3$,[4] and azidosulfonate salts, N_3SO_3M,[3,5-7] have been reported. We now wish to describe the preparation of additional examples of azidosulfonic acid derivatives and to suggest, from the results of a brief study of their reactions, that their chemical properties are similar to those of the sulfonyl azides.

Sulfuryl Azide Chloride

The synthesis of the explosive liquid, sulfuryl azide chloride (I), was accomplished in high yield by the reaction of sulfuryl chloride fluoride with sodium azide in the presence of a catalytic amount of dimethylformamide. The preferential replacement of fluoride by azide is in accord with previously described reactions of sulfuryl chloride fluoride and amines.[8,9] In the absence of dimethylformamide, the yields of azide I are not consistent, while an excess of the amide causes decomposition of the product.

$$ClSO_2F + NaN_3 \longrightarrow \underset{\text{I}}{ClSO_2N_3} + NaF \qquad (1a)$$

It was suggested that a trace of moisture promotes the formation of sulfuryl azide from sulfuryl chloride.[1] It has now been found that azide I can be isolated when the reaction is carried out under anhydrous conditions.

$$SO_2Cl_2 + NaN_3 \longrightarrow ClSO_2N_3 + NaCl \qquad (1b)$$

Another synthesis of sulfuryl azide fluoride[2] (eq 2) was found in the reaction of sulfuryl fluoride and lithium azide. Attempts to obtain this product from fluoride exchange reactions with azide I were unsuccessful.

$$SO_2F_2 + LiN_3 \longrightarrow FSO_2N_3 + LiF \qquad (2)$$

In a reaction which is characteristic of azides,[10] compound I and tetramethylethylene combine to form the iminosulfonyl chloride II which, upon treatment with dimethylamine, is converted to the sulfamide III.

$$(CH_3)_3CC(CH_3)=NSO_2X$$

II, X = Cl
III, X = $N(CH_3)_2$

Sulfamoyl Azides

Sulfamoyl azide (IV) was isolated as a low melting, explosive solid from the reaction of sulfamoyl chloride and sodium azide (eq 3). The sulfamoyl azides V and VI were obtained from similar reactions of N-chlorosulfonylformanilide and N-chlorosulfonyl-*p*-toluenesulfonanilide.[11] Since the synthesis of aromatic sulfamoyl chlorides appears to be limited to compounds having an electronegative substituent on the nitrogen atom, the

$$XSO_2Cl + NaN_3 \longrightarrow \underset{\text{IV–VI}}{XSO_2N_3} + NaCl \qquad (3)$$

IV, X = NH_2–
V, X = $C_6H_5N(CHO)$–
VI, X = $C_6H_5N(Tos)$–

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