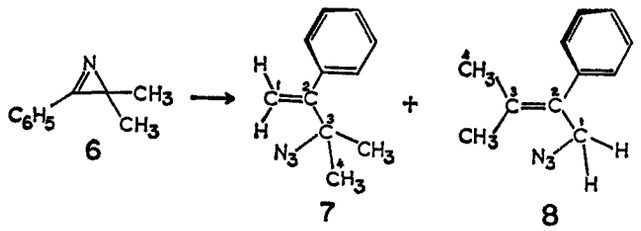
in 10% conversion and in a ratio (per cent) of 25:75 ± 10.[25] The reaction of the representative azirines **1** and



6 with diazomethane is in contrast to the reaction of 2-phenyl-1-azirine[26,27] with dimethylsulfonium methylide communicated by Hartmann and Robertson.[28] The latter combination produces an azabicyclobutane, 3-phenyl-1-azabicyclo[1.1.0]butane.

Experimental Section

3-Methyl-2-phenyl-1-azirine (1).—Propiophenone dimethylhydrazone methiodide was prepared[29] and crystallized from ethanol–ethyl acetate: mp 155–156°; yield 58%; ν_{max}^{Nujol} 1610 cm^{-1}; nmr (DMSO-d_6, TMS) τ 8.97 (t, 3 H), 6.76 (q, 2 H), 6.33 (s, 9 H), 2.67–2.14 (m, 5 H).

Anal. Calcd for $C_{12}H_{19}IN_2$: C, 45.28; H, 5.97; N, 8.81. Found: C, 45.34; H, 5.99; N, 8.82.

A solution of 15.9 g (0.05 mol) of the quaternary hydrazone in 150 ml of dimethyl sulfoxide was treated with 2.4 g of a 51% dispersion of sodium hydride in mineral oil. The reaction mixture was stirred at room temperature for 3 hr and then poured into 700 ml of water and extracted with ether. The combined ethereal extracts were washed with water and dried ($MgSO_4$). Removal of solvent gave a yellow oil (6.2 g) which was fractionated under reduced pressure to give 4.1 g (63%) of **3-methyl-2-phenyl-1-azirine (1)**[30] as a colorless oil; bp 88° (8 mm); $n^{25}D$ 1.5375; ν_{max}^{film} 1730 cm^{-1} (C=N); nmr ($CDCl_3$) τ 8.68 (d, J = 4.5 cps, 3 H), 7.74 (q, J = 4.5 cps, 1 H), 2.64–2.00 (m, 5 H).

Anal. Calcd for C_9H_9N: C, 82.40; H, 6.92. Found: C, 82.38; H, 6.85.

The residue from the distillation gave, on dilution with ether, 0.28 g of 2,5-dimethyl-3,6-diphenylpyrazine as colorless prisms: mp 121–122° (lit.[31] mp 125–128°); nmr ($CDCl_3$) τ 7.37 (s, 6 H), 2.80–2.30 (m, 10 H).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.09; H, 6.17; N, 10.96.

Reaction of Azirine 1 with Diazomethane. Formation of Allylic Azides 2, 3, and 4.—A solution of 2.62 g (0.02 mol) of **1** in 20 ml of ether was treated with excess of an ethereal solution of diazomethane followed by 2 ml of methanol.[9] The reaction mixture was allowed to stand at room temperature for 3 days. The solvent was removed, and the residual oil (2.72 g) was chromatographed over silica gel to give 0.74 g (21.4%) of the mixture of **2**, **3**, and **4**, a colorless oil, as the benzene eluate. The compounds showed a single spot on silica gel plates in several solvent systems (R_f 0.625 in benzene). Most of the remaining material was the unreacted azirine **1**, which was eluted with benzene–ether. The allylic azide mixture showed ν_{max}^{film} 2100, 1630, 875, 830 cm^{-1}; λ_{max}^{EtOH} 235 mμ (ε 8650); the nmr spectra in CCl_4 (Varian A60 and HA 100 instruments) showed absorptions of chemical shift, area, and splitting patterns described in the Discussion (see also Figure 1).

Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26; mol wt, 173.21. Found: C, 69.39; H, 6.48; N, 24.44; mol wt, 179 (osmometric in benzene).

Reaction of Azirine 6 with Diazomethane.—A solution of 1.45 g (0.01 mol) of 3,3-dimethyl-2-phenyl-1-azirine (**6**)[2,29] in 20 ml of ether was treated with diazomethane in ether over a period of 2 days. The reaction mixture was allowed to stand at room temperature for 4 days, then worked up and chromatographed as described above to give 0.195 g (10.4%) of a mixture of **3-azido-3-methyl-2-phenyl-1-butene (7)** and **1-azido-3-methyl-2-phenyl-2-butene (8)** in addition to 1.29 g of unreacted starting material (**6**). Thus, the yield was nearly quantitative if based on unrecovered starting material. Product analysis was carried out by nmr spectroscopy: nmr (CCl_4) τ 8.63 (methyls of **7**), 8.33 and 8.08 (methyls of **8**), 6.00 (C-1 protons of **8**), 4.88 and 4.60 (C-1 olefinic protons of **7**), 2.90–2.53 (aromatic protons).

Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00. Found: C, 70.89; H, 7.09.

Registry No.—**1**, 16205-14-4; **2**, 16205-15-5; **3**, 16223-64-6; **4**, 16205-16-6; **7**, 16205-17-7; **8**, 12605-18-8; diazomethane, 334-88-3.

(25) Professor N. J. Leonard has informed me that Professor P. Gassman of Ohio State University (private communication) has carried out the reaction of diazomethane with other azirines and has also obtained allylic azide products.

(26) (a) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); (b) G. Smolinsky and B. I. Feuer, *ibid.*, **31**, 1423 (1966).

(27) S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jap.*, **40**, 1014 (1967).

(28) A. G. Hortmannn and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967).

(29) E. F. Parcell, *Chem. Ind.* (London), 1396 (1963).

(30) A. Hassner and F. W. Fowler, *Tetrahedron Lett.*, 1545 (1967).

(31) P. A. S. Smith, *J. Amer. Chem. Soc.*, **70**, 323 (1948).

Azetidines. III.[1] A Convenient Synthesis of 1-Alkyl-3,3-dimethylazetidines[2,3]

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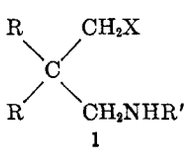
In the course of studies on tertiary and quaternary derivatives of azetidines,[1] need arose for a convenient synthesis for 1-substituted 3,3-dimethylazetidines. The method that was developed is described in this paper.

Consideration of the elegant route to 3-substituted azetidines *via* lithium aluminum hydride reduction of β-lactams[4] and malonimides[5] revealed that the use of N-substituted compounds gave ring cleavage to the corresponding aminopropanol.[6] Thus formation of a secondary azetidine, acylation, and then a second hydride reduction was required to obtain a tertiary azetidine.[7] A more direct route was therefore sought.

The acyclic structure (**1**) appeared to be favorable as a precursor as side reactions such as bimolecular sub-



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stitution and elimination would be hindered or precluded, respectively. Also no examples of fragmentation[8] were found for acyclic compounds in which halogen

(1) Paper I: A. G. Anderson, Jr., and M. T. Wills, *J. Org. Chem.*, **32**, 3241 (1967); paper II: *ibid.*, **33**, 536 (1968).

(2) From the Ph.D. Thesis of Max T. Wills, University of Washington.

(3) Supported in part by State of Washington Initiative 171 Funds for Research in Biology and Medicine.

(4) E. Testa, L. Fontanella, and G. F. Christiani, *Ann.*, **626**, 114 (1959).

(5) E. Testa, L. Fontanella, G. F. Christiani, and L. Mariani, *Helv. Chim. Acta*, **42**, 2370 (1959).

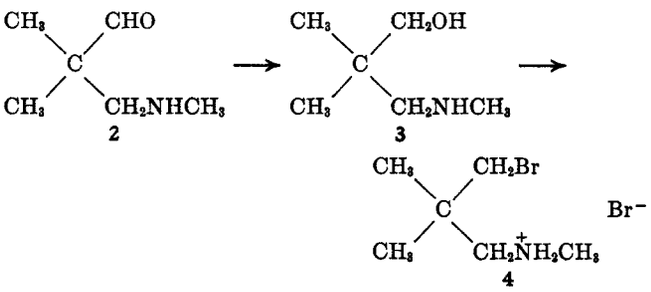
(6) (a) M. E. Speeter and W. H. Maroney, *J. Amer. Chem. Soc.*, **76**, 5810 (1954); F. F. Blicke and W. A. Gould, *J. Org. Chem.*, **23**, 1102 (1958); (b) W. R. Vaughan, R. S. Klonowski, R. S. McElhinney, and B. B. Millward, *ibid.*, **26**, 138 (1961).

(7) E. Testa, L. Fontanella, L. Mariani, and G. F. Christiani, *Ann.*, **633**, 56 (1960); E. Testa, A. Bonati, G. Pagani, and E. Gatti, *ibid.*, **647**, 92 (1961).

(8) C. A. Grob, "Kekule Symposium on Theoretical Chemistry," Butterworth's Scientific Publications, London, 1959, pp 114–127; C. A., Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Lett.*, 2901 (1964).

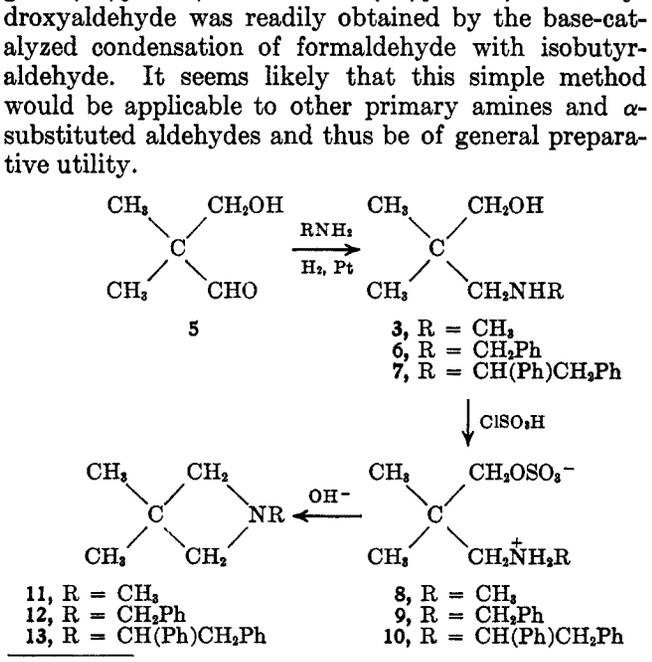
was bonded to a primary carbon, and the formation of 1,3,3-trimethylazetidine in good yield from methyl-3-bromo-2,2-dimethylpropylammonium bromide (4) plus alkali[9] served as a model.

The route in the literature consisted of condensation of isobutyraldehyde with formaldehyde and methylammonium chloride to give 2,2-dimethyl-3-(methylamino)propanal (2)[10] which was reduced with sodium amalgam to the corresponding alcohol (3). Conversion of 3 into 4 required heating with hydrobromic and acetic acids in a sealed tube. The number of primary amines and aldehydes that can be condensed with formaldehyde in this fashion is very limited,[11] however, and a further complication was the spontaneous dimerization of 2. The latter was less serious since reversion



to the monomer could be effected by strong acid. The finding in the present work that the inconvenient sealed tube reaction to form 4 could be replaced by a facile conversion into the sulfato derivative (*vide infra*) prompted the search for a more general synthesis of 3 and related N-alkyl alcohols.

The reduction of 2 with a twofold excess of lithium aluminum hydride gave a 33% yield of 3.[12] A more satisfactory and general route to the aminoalcohols (3,6,7) was found to be the low pressure reductive alkylation of the appropriate primary amine with 2,2-dimethyl-3-hydroxypropanal (5). The yields were good (68% for 3) to excellent (91% for 6). The hydroxyaldehyde was readily obtained by the base-catalyzed condensation of formaldehyde with isobutyraldehyde. It seems likely that this simple method would be applicable to other primary amines and α-substituted aldehydes and thus be of general preparative utility.



11, R = CH_3
12, R = CH_2Ph
13, R = $CH(Ph)CH_2Ph$

8, R = CH_3
9, R = CH_2Ph
10, R = $CH(Ph)CH_2Ph$

(9) C. Mannich and G. Baumgarten, *Ber.*, **70**, 210 (1937).
(10) C. Mannich and H. Wieder, *Ber.*, **65**, 385 (1932).
(11) B. Reichart, "Die Mannich-Reaktion," Springer-Verlag, Berlin, 1959, pp 35–37.
(12) The use of a large excess of the hydride reagent has been reported to give a 72% yield: K. Hayes and G. Drake, *J. Org. Chem.*, **15**, 873 (1950).

The creation of a suitable leaving group was achieved by conversion of the hydroxyl function into a sulfate.[6b] The products were obtained as the dipolar ion salts (8, 9, 10). The procedure of Reeves and Guthrie[13] (chlorosulfonic acid and carbon tetrachloride) gave very good (68–83%) yields. The transformation of 6 to 9 was also effected with concentrated sulfuric acid.[6b]

Treatment of the inner salts with aqueous alkali[6b] formed the corresponding tertiary azetidines (11, 12, 13) in excellent (84–92%) yields. The azetidines readily formed a series of quaternary salts. The nmr spectra were recorded for the different azetidines and quaternary salts prepared. It was observed that the chemical shift for the geminal methyl hydrogens was essentially independent of the N-substituents in the tertiary amines, but was very sensitive to the groups on nitrogen in the quaternary salts. In the latter case the methyl group *cis* to the larger group on the nitrogen was the more shielded. The chemical shift of the ring hydrogens in the azetidines and in the quaternary salts was only slightly affected by the size of the substituent on nitrogen, but if the latter was asymmetric or consisted of two dissimilar groups an AB splitting pattern resulted. The asymmetry of two tertiary azetidines and one quaternary salt having substituents on carbon 2 had previously been found to result in different shielding for the geminal methyl groups and methylene hydrogens.[1]

Experimental Section[14]

2,2-Dimethyl-3-(methylamino)propanal (2).—This compound was prepared in *ca.* 35% yield as described by Mannich and Wieder.[10] The product was collected as the fraction boiling at 43–47° (8 mm) (lit.[10] bp 48° (10 mm)). The dimeric by-product was also obtained (*ca.* 40%) as long colorless needles, mp 68–69° after recrystallization from acetone (lit.[10] mp 71.5°).

2,2-Dimethyl-3-hydroxypropanal (5).—This compound was prepared in 68% yield as described in the literature.[15] The product was collected as the fraction boiling at 100–120° (25 mm), mp 80–91° (lit.[15] bp 83–86° (15 mm), mp 96–97°) and was used without further purification.

2,2-Dimethyl-3-(methylamino)-1-propanol (3). A. From 2.—To a stirred solution of 7 g (0.185 mol) of lithium aluminum hydride in 800 ml of dry ether was added, dropwise, 40 g (0.35 mol) of 2. Then 13.5 ml of water was added, dropwise, and the mixture was refluxed for 1 hr. Filtration and evaporation of the ether from the filtrate left 33 g of a partially crystalline yellow residue which was distilled under reduced pressure. Compound 3 was obtained as colorless needles (11 g, 28%), mp 51–53° (lit.[10] mp 52°), from the first fraction (bp 44–60° (1 mm)) after two recrystallizations from petroleum ether (20–40°). Refractionation of the second fraction, bp 60–85° (1 mm), afforded an additional 2 g of 3 for a total yield of 33%.

B. From 5.—A mixture of 20 g (0.196 mol) of 5, 15.5 g (0.2 mol) of 40% aqueous methylamine, 0.5 ml of concentrated hydrochloric acid, and 150 ml of 95% ethanol was treated with hydrogen in the presence of 200 mg of platnium oxide catalyst in a low pressure Paar apparatus at 3 atm. The theoretical quantity of hydrogen was taken up after 2 hr. After removal of the catalyst

(13) W. A. Reeves and J. D. Guthrie, *J. Amer. Chem. Soc.*, **75**, 4101 (1953).
(14) Melting points and boiling points are uncorrected. Melting points were taken with a Thomas-Hoover capillary melting point apparatus. Infrared spectra of compounds 3, 6, 11, 12, 13, and of the quaternary salts were recorded with a Perkin-Elmer Model 21 spectrophotometer. The nmr spectra were recorded (carbon tetrachloride solvent for azetidines and trifluoroacetic acid solvent for azetidinium salts) on a Varian Associates Model A-60 spectrometer and values are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. Chemicals shifts for doublets are reported as the midpoint. Elementary analyses were performed by Dr. A. Bernhardt, Microanalytical Laboratory, Max-Planck Institute, Mülheim (Ruhr), Germany.
(15) E. T. Stiller, S. A. Harris, J. Finkelstein, J. C. Keresztesy, and K. Folkers, *J. Amer. Chem. Soc.*, **62**, 1785 (1940).

by filtration and evaporation of the ethanol under reduced pressure, 100 ml of 50% sodium hydroxide was added and the organic layer was then extracted into ether. Distillation of the dried (sodium sulfate) ethereal solution afforded 15.7 g (68%) of **3** as the fraction boiling at 110–120° (25–30 mm), mp 45–48°. Recrystallization from petroleum ether (20–40°) gave colorless needles, mp 51–52°. (lit.[10] mp 52°).

3-Benzylamino-2,2-dimethyl-1-propanol (6).—A mixture of 125 g (1.15 mol) of benzylamine, 101 g (1 mol) of **5**, six drops of concentrated hydrochloric acid, and 550 ml of absolute ethanol in the presence of 0.25 g of platinum oxide catalyst was treated with hydrogen as described for the preparation of **3** (method B). The theoretical quantity of hydrogen was taken up after 3 hr. After removal of the catalyst by filtration and the solvent by distillation under reduced pressure, the residue was dissolved in an excess of 10% sulfuric acid. The acidic solution was washed several times with ether and was then made strongly alkaline with 50% sodium hydroxide. The organic layer which formed was extracted into ether. Distillation of the dried (sodium sulfate) ethereal solution gave 175 g (91%) of **6** as a colorless oil: bp 124–127° (1 mm); $n^{25}D$ 1.5160. The nmr spectrum (carbon tetrachloride) showed singlets at 0.84, 2.47, 3.30, 3.68 and 7.20, and a broad, unresolved peak at 2.95 ppm with respective areas corresponding to six, two, two, two, five, and two hydrogens.

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.78; H, 10.00; N, 7.13.

1,2-Diphenylethylamine.—A mixture of 40 g (0.2 mol) of desoxybenzoin, 37 g (0.8 mol) of formamide, and 5 ml of formic acid was heated to 180°. After 30 min, an additional 10 ml of formic acid was added and the mixture was then maintained at 170–175° for 24 hr. During the first 12 hr water was slowly distilled from the reaction mixture. The mixture was cooled and then extracted with benzene. The solvent was evaporated from the benzene solution, 50 ml of concentrated hydrochloric acid was added to the residue and the mixture was refluxed for 1 hr. Enough water was added to the cooled solution to dissolve the precipitate which had separated and the solution, after extraction with ether, was basified with 100 ml of 50% sodium hydroxide. The organic layer was extracted with ether, and evaporation of the solvent from the dried (sodium sulfate) ethereal solution and then distillation gave 30 g (75%) of a colorless oil: bp 111–112° (0.3 mm) (lit.[16] bp 142–143° (2.9 mm)); $n^{25}D$ 1.5792.

2,2-Dimethyl-3-(1,2-diphenylethylamino)-1-propanol (7).—A mixture of 10 g (0.05 mol) of 1,2-diphenylethylamine, 5 g (0.05 mol) of **5**, two drops of concentrated hydrochloric acid, and 75 ml of absolute ethanol in the presence of 150 mg of platnium oxide catalyst was treated with hydrogen as described for the preparation of **3** (method B). Hydrogen uptake ceased at 0.035 mol after 8 hr. The catalyst was removed by filtration, 150 ml of 5% sulfuric acid was added, and the ethanol was then removed by distillation. The remaining acidic solution was extracted twice with ether and then was basified with 50% sodium hydroxide. The organic layer which formed was extracted into ether. Evaporation of the ether from the dried (sodium sulfate) ethereal solution and distillation of the residue gave 10 g (70%) of **7** as a colorless, viscous oil (bp 155–157° (0.1 mm), $n^{25}D$ 1.5482) which solidified on standing, mp 57–60°.

Anal. Calcd for $C_{19}H_{25}NO$: C, 79.94; H, 9.54; N, 4.91. Found: C, 80.24; H, 9.34; N, 5.06.

2,2-Dimethyl-3-methylamino-1-sulfatopropane (8).—In a procedure patterned after that of Reeves and Guthrie[13] 16 g (9 ml, 0.137 mol) of chlorosulfonic acid was added to a solution of 16 g (0.137 mol) of **3** in 300 ml of carbon tetrachloride cooled to 5° in an ice bath at such a rate that temperature of the reaction mixture did not exceed 10°. The ice bath was then removed and the mixture was stirred overnight during which time hydrogen chloride was evolved and a granular mass separated. The solvent was removed under reduced pressure and recrystallization of the residue from aqueous 80% ethanol gave 22.5 g (83%) of **8** as short, colorless needles, mp 254–256° dec. The substance was water soluble and did not give a precipitate with barium chloride solution.

Anal. Calcd for $C_6H_{15}NO_4S$: C, 36.53; H, 7.67; N, 7.10. Found: C, 36.69; H, 7.58; N, 6.98.

3-Benzylamino-2,2-dimethyl-1-sulfatopropane (9). A. Chlorosulfonic Acid Method.[13]—In the manner described for the preparation of **8**, a solution of 171 g (0.9 mol) of **6** in 2.5 l. of carbon tetrachloride was treated with 60 ml (0.9 mol) of chlorosulfonic acid. Recrystallization of the solid remaining after removal of the solvent (reduced pressure) gave 155 g (68%) of **9** as colorless needles, mp 274–275° dec. The filtrate was distilled until the temperature of vapors reached 100°. To the cooled residue was added 35 g of sodium hydroxide and the organic layer was then extracted into ether. Distillation of the dried (sodium sulfate) ether solution gave 52 g (0.27 mol) of **6**, bp 105–107° (0.1 mm). The net yield of **9** was 98%.

Anal. Calcd for $C_{12}H_{19}NO_4S$: C, 52.74; H, 7.00; N, 5.13. Found: C, 53.01; H, 7.15; N, 5.05.

B. Sulfuric Acid Method.—A solution of 19.3 g (0.1 mol) of **6** in 20 ml of concentrated sulfuric acid was warmed to 80° over a period of 15 min, then cooled and diluted with 200 ml of 95% ethanol. During the heating period the color of the mixture became a dark red brown. On dilution with ethanol the color faded and a colorless solid separated. Recrystallization of the collected solid from 300 ml of 75% aqueous ethanol gave 17.7 g (65%) of **9**, mp 275–276° dec, which was identical (mmp 274–275° dec) with the product from procedure A.

1,3,3-Trimethylazetidine (11).—To a solution of 10 g (5.1 mmol) of **8** in 50 ml of water was added 50 ml of 50% potassium hydroxide. The mixture was warmed on a steam bath (reflux condenser) for 2 hr and was then steam distilled until 170 ml of distillate had been collected. The distillate was chilled in an ice bath and was made strongly alkaline with solid potassium hydroxide. Distillation of the separated organic layer gave 2.9 g (57%) of **11**: bp 77–79°; $n^{25}D$ 1.4002 (lit.[9] bp 73–74°). The nmr spectrum showed singlets at 1.16, 2.17, and 2.83 ppm corresponding to the geminal methyl, N-methyl, and ring methylene hydrogens, respectively. The picrate after recrystallization from ethanol melted at 222–224°.

1,1,3,3-Tetramethylazetidinium Iodide.—To a solution of 20 g (0.1 mol) of **8** in 200 ml of water was added 50 g of solid potassium hydroxide. The mixture was warmed on a steam bath (reflux condenser) for 2.5 hr and then was steam distilled until the distillate was no longer basic to litmus. The chilled distillate was made alkaline with 50 g of solid potassium hydroxide and the organic layer was extracted into two 50-ml portions of ether. To the dried (sodium sulfate) ether extract was added 100 ml of acetonitrile and most of the ether was then removed by distillation through a 50-cm column packed with glass helices. The residual solution was cooled and treated wih 19 g (0.135 mol) of methyl iodide. After 5 min an excess of ether was added and the precipitate which formed was separated and recrystallized from a minimum of absolute ethanol. There was obtained 20.2 g (84%) of product as colorless, glistening needles, mp 188–189° dec (lit.[9] mp 190°). The nmr spectrum showed singlets at 1.50, 3.34, and 4.27 ppm corresponding to the geminal methyl, N-methyl, and ring methylene hydrogens, respectively.

1-Benzyl-3,3-dimethylazetidine (12).—To a suspension of 30 g (0.11 mol) of **9** in 300 ml of water was added 100 ml of 50% sodium hydroxide solution. The mixture was refluxed for 3 hr and then was steam distilled until the distillate was no longer basic to litmus. The distillate was extracted with three 100-ml portions of ether. Evaporation of the ether from the combined, dried (sodium sulfate) extracts left 17.7 g (92%) of **12** as a colorless oil. Distillation of a 6.3-g sample gave 6 g (95% recovery, 87.5% over-all yield) of pure product: bp 40–41° (0.1 mm); $n^{25}D$ 1.4993. The nmr spectrum showed singlets at 1.15, 2.84, and 3.47 ppm corresponding to the geminal methyl, ring methylene, and benzylic hydrogens, respectively.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.25; H, 9.64; N, 8.11.

1-Benzyl-1,3,3-trimethylazetidinium Iodide.—A cooled (ice bath), stirred solution of 17.7 g (0.1 mol) of **12** in 100 ml of acetonitrile was treated slowly with 14 g (0.1 mol) of methyl iodide and the mixture was stirred for 4 hr. Dilution with 200 ml of ether precipitated 30.4 g (96%) of the quaternary salt. Recrystallization from 175 ml of absolute ethanol gave 29 g (91.5%) of colorless needles, mp 163–164° dec. The nmr spectrum showed singlets at 1.25 and 1.57 (two geminal methyls), singlets at 3.40 (N-methyl) and 4.73 (benzylic methylene), and doublets (J = 11 cps) at 4.16 and 4.67 ppm (ring methylenes) of the correct relative areas.

Anal. Calcd for $C_{13}H_{20}NI$: C, 49.22; H, 6.36; N, 4.41. Found: C, 49.37; H, 6.34; N, 4.48.

1,1-Dibenzyl-3,3-dimethylazetidinium Bromide.—To a cooled (ice bath), stirred solution of **12** as obtained from 30 g (0.11 mol) of **9** in 200 ml of acetonitrile was added 22 g (0.13 mol) of

(16) H. E. Baumgarten and J. M. Peterson, *J. Amer. Chem. Soc.*, **82**, 459 (1960).

benzyl bromide. The mixture was stirred for 2.5 hr and then was diluted with 200 ml of ether. Recrystallization of the precipitate which formed from absolute ethanol gave 31.1 g (82% from 9) of fine, colorless needles, mp 152–152.5°. The nmr signal for the phenyl hydrogen was observed at 7.53 ppm. The nmr spectrum showed singlets at 0.92, 4.32, and 4.58 ppm corresponding to the geminal methyl, ring methylene, and benzyl hydrogens, respectively.

Anal. Calcd for $C_{19}H_{24}NBr$: C, 65.89; H, 6.99; N, 4.04. Found: C, 66.01; H, 6.99; N, 4.13.

3,3-Dimethyl-1-(1,2-diphenylethyl)azetidine (13).—In the manner described for the preparation of **8**, a suspension of 3.5 g (12.5 mmol) of **7** in 30 ml of carbon tetrachloride was treated with 1.45 g (12.5 mmol) of chlorosulfonic acid. The mixture was stirred for 2 hr after removing the ice bath. Dissolution of the residue remaining after removal of the solvent (reduced pressure) in the minimum of absolute ethanol and then dilution with 15 volumes of ether gave 3.42 g (75%) of colorless crystals presumed to be **10**, mp 248–250° dec. Treatment of this product with base as described for the preparation of **11** gave 2.26 g (90%) of **13** as a colorless oil: bp 121–122° (0.5 mm), $n^{25}D$ 1.5408. The nmr spectrum showed a singlet at 1.17 (geminal methyls) and doublets (J = 1.5 cps) at 2.78 and 2.82 ppm (ring methylenes) having the correct relative areas.

The picrate after recrystallization from ethanol melted at 209–211°.

Anal. Calcd for $C_{25}H_{26}N_4O_7$: C, 60.72; H, 5.30; N, 11.33. Found: C, 60.71; H, 5.25; N, 11.42.

Registry No.—**3**, 16047-86-2; **6**, 16047-87-3; **7**, 16047-88-4; **8**, 16047-89-5; **9**,16047-90-8; **11**, 16047-91-9; **12**, 13509-71-2; **13**, 16047-93-1; 1-benzyl-1,3,3-trimethylazetidinium iodide, 16047-94-2; 1,1-dibenzyl-3,3-dimethylazetidinium bromide, 16047-95-3; 13-picrate, 16047-96-4.

Chlorination of 1,3-Dioxolane[1]

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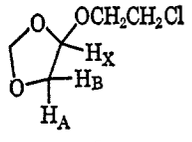
The chlorination of 1,3-dioxolane (**1**) has been reported by Baker and Shannon[4] to yield an inseparable mixture of 2-chloro-1,3-dioxolane (**2**) and 4-chloro-1,3-dioxolane (**3**). However, Baganz and Domaschke,[5] repeating this experiment, found the main product to be β-chloroethyl formate (**4**), probably formed from **2** by a rearrangement similar to that postulated previously for α-bromo acetals.[6] The same rearrangement has been observed recently with unstable 2-chloro-2-trichloromethyl-1,3-dioxolane and 2-bromo-2-(bromodichloromethyl)-1,3-dioxolane.[7] In 1960, Cort and Pearson,[8] having been unaware of the work,[5] confirmed that chlorination and bromination of **1** afforded only **4** and β-bromoethyl formate, respectively. No evidence was reported for the formation of **3**.

We now wish to report a low-temperature photochlorination of **1** with evidence for the formation of **2** and **3**.

Photochlorination of **1** with 1 mol equiv of chlorine at −30° yielded 65% of **4**. Gas chromatographic analysis of the crude reaction mixture indicated the presence of a small amount of a compound having retention data which would be expected for **3**. The compound, decomposing readily, could not be isolated by distillation. Gas chromatographic isolation was prevented by the large amount of hydrogen chloride present in the reaction mixture. However, when the reaction mixture was treated immediately after photochlorination with ethylene oxide, which is known to react readily with α-halogeno ethers,[9] 60% of **4**, 3% of 2-(β-chloroethoxy)-1,3-dioxolane (**5**), and 7% of 4-(β-chloroethoxy)-1,3-dioxolane (**6**) were obtained. The nmr spectrum of **5** showed an one-proton singlet at τ 4.13, assigned to the hydrogen atom at C-2, an A_2B_2 multiplet centered at τ 6.26, assigned to the hydrogen atoms of the β-chloroethoxy group, and a multiplet centered at τ 5.94, typical of the C-4 and C-5 dioxolane protons.[10]

In the nmr spectrum of **6** an ABX pattern is assigned to the protons at C-4 and C-5. The C-2 proton signals appear as singlets at τ 4.94 and 5.01, and the protons of the β-chloroethoxy group give rise to a multiplet between τ 5.95 and 6.47. The signal of the C-4 proton collapsed to a singlet on decoupling from the C-5 protons. No splitting of the C-2 proton singlets has been observed either, when running the spectrum with a 100 Mcps instrument. Hence, the J_{gem} of C-2 protons is zero which is in agreement with values found for other 4-substituted 1,3-dioxolanes.[11] The infrared spectrum of **6** showed bands at 1168, 1097, and 1013 cm^{-1}, characteristic of the dioxolane ring.[12]



6

J, cps	Chemical shift, τ
AB = 8.9	A = 6.22
AX = 4.4	B = 5.99
BX = 2.5	X = 4.68

It is apparent that **2** and **3** are indeed formed on chlorination of **1** but the rearrangement of **2** is so rapid that it is almost complete under these reaction conditions. Having established that **1** reacts with chlorine more readily than does ethylene oxide, we carried out a photochlorination of **1** in the presence of ethylene oxide in order to trap **2** before rearrangement. In such cochlorination at −30°, 63% of **5** and 7% of **6** was isolated; only traces of **4** were found chromatograph-

(1) (a) Part XXXVII of α-Halogeno Ethers; for Part XXXVI see H. Gross, D. Habisch, and E. Gründemann, *J. Prakt. Chem.*, in press. (b) Dedicated to Professor J. Hadáček on the occasion of his 60th birthday.

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