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), $n^{25}\text{D}$ 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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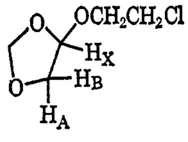
The chlorination of 1,3-dioxolane (**1**) has been reported by Baker and Shannon[4] to yield an inseparable mixture of 2-chloro-1,3-dioxolane (**2**) and 4-chloro-1,3-dioxolane (**3**). However, Baganz and Domaschke,[5] repeating this experiment, found the main product to be β-chloroethyl formate (**4**), 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-

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[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.

[2] Dalhousie University Postdoctoral Research Fellow, 1967–1968. To whom inquiries should be directed.

[3] (a) Dalhousie University; (b) Purkyně University; (c) German Academy of Sciences.

[4] W. Baker and A. Shannon, *J. Chem. Soc.*, 1598 (1933).

[5] H. Baganz and L. Domaschke, *Chem. Ber.*, **91**, 653 (1958).

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[9] M. Kratochvíl, *Collect. Czech. Chem. Commun.*, **27**, 742 (1960); M. Kratochvíl, J. Jonas, O. Bartes, and H. Gross, *Chem. Ber.*, **99**, 1218 (1966).

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[11] T. A. Crabb and R. C. Cookson, *Tetrahedron Lett.*, 679 (1964).

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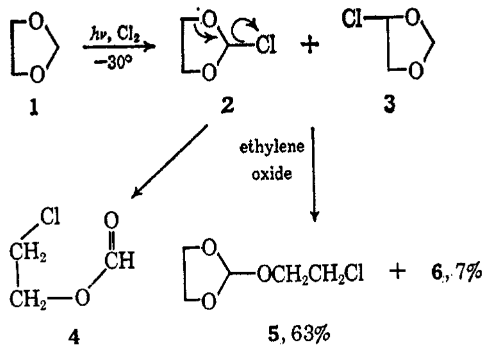
ically. The cochlorination, carried out at −10° afforded once again the halogeno ester (**4**) as the main product.[13]

Undoubtedly, the reaction of **2** with ethylene oxide proceeds more readily than the rearrangement at −30°, whereas the reverse is true above −10°.

With regard to the fact that the reaction of ethylene oxide with reactive α-halogeno ethers proceeds with almost quantitative yields, our results indicate that in the photochlorination of **1**, under the conditions used, **2** and **3** are formed in the ratio of 9:1 with an over-all yield of 70% (Scheme I).

SCHEME I



Experimental Section

Elemental analyses were performed by M. H. W. Laboratories. Nmr spectra were obtained with a Varian A-60 instrument in deuteriochloroform containing tetramethylsilane as an internal reference. Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrometer.

Chlorination of 1,3-Dioxolane (1).—Liquified chlorine (1 mol) was bubbled with nitrogen into a mixture of 1 mol (74 g) of **1** and 100 ml of carbon tetrachloride at −30°, at a rate which maintained the mixture colorless. The mixture was stirred and irradiated with an ultraviolet lamp (2537 Å). After the chlorine had been added (about 4.5 hr), nitrogen was bubbled through the mixture for another 0.5 hr to remove hydrogen chloride and the mixture was distilled *in vacuo*. The distillation yielded 68 g (65%) of β-chloroethyl formate (**4**): bp 38–39° (15 mm); bp 130–131° (750 mm); $n^{25}D$ 1.4248 (lit.[5] bp 131° (760 mm), $n^{25}D$ 1.4250).

Chlorination of 1,3-Dioxolane (1) and Reaction with Ethylene Oxide.—**1** (1 mol) was photochlorinated as above. After the chlorination was completed, 100 ml of ethylene oxide was added so that the temperature did not exceed −15°. The mixture was kept standing over night, treated with 40 ml of triethylamine to remove any hydrogen chloride which did not react with ethylene oxide, and washed with 100 ml of H_2O. The organic layer was separated and the aqueous layer was extracted twice with 25 ml of diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered, and distilled *in vacuo*, yielding 65 g (60%) of β-chloroethyl formate (**4**), 10.5 g (7%) of 4-(β-chloroethoxy)-1,3-dioxolane (**6**), bp 82.5–83° (15 mm), bp 192–193° (760 mm), $n^{25}D$ 1.4462, and 4.6 g (3%) of 2-(β-chloroethoxy)-1,3-dioxolane (**5**), bp 93–95° (15 mm), $n^{25}D$ 1.4485 (lit.[14] bp 92° (11 mm), $n^{25}D$ 1.4489).

Anal. Calcd for **6**, $C_5H_9O_3Cl$ (152.5): C, 39.34; H, 5.94; Cl, 23.25. Found: C, 40.06; H, 5.91; Cl, 23.23.

Cochlorination of 1,3-Dioxolane (1) and Ethylene Oxide at −30°.—A mixture of 1 mol (74 g) of **1**, 100 ml of carbon tetrachloride, and 100 ml of ethylene oxide was chlorinated with dried chlorine for 4.5 hr so that it remained colorless. The mixture was kept at −30°, stirred, and irradiated with an ultraviolet lamp. The mixture was then worked up as in the previous experiment and distilled *in vacuo*. The distillation afforded 10.2 g (7%) of 4-(β-chloroethoxy)-1,3-dioxolane (**6**), bp 82–83° (14 mm), $n^{25}D$ 1.4463, and 95.5 g (63%) of 2-(β-chloroethoxy)-1,3-dioxolane (**5**), bp 92–94° (14 mm), $n^{25}D$ 1.4487. No β-chloroethyl formate (**4**) was isolated. When the reaction mixture is not treated with triethylamine, the yield of **5** is lowered to about 60 g, and higher boiling compounds, presumably formed from **5** by the action of hydrogen chloride, are present.

Cochlorination of 1,3-Dioxolane (1) and Ethylene Oxide at −10°.—The reaction carried out as above (only 3 hr needed for complete chlorination of **1**) but at −10° gave the same products as when the raw reaction mixture after chlorination of **1** was treated with ethylene oxide.

Registry No.—**1**, 646-06-0; **4**, 1487-43-0; **5**, 16162-30-4; **6**, 16162-31-5.

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[13] To make sure that ethylene oxide rather than ethylene chlorohydrin (formed from the former by the action of hydrogen chloride) is involved as the species reacting with **2** and **3**, cochlorination of equimolar amounts of **1** and ethylene chlorohydrin with 1 mol equiv of chlorine has been carried out at −30°. After the usual work-up, the reaction mixture was analysed gas chromatographically, revealing **4** and **6**, and no **5**. Hence, **5** is formed exclusively by the reaction of **2** with ethylene oxide, whereas the both ways of forming **6** from **3** are possible.

[14] H. Baganz and L. Domaschke, *Chem. Ber.*, **91**, 650 (1958).

Reactions of 1,2,3,4-Tetrahydrophenazine Di-N-oxide with Acetic Anhydride[1]

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The reaction of acetic anhydride with aromatic N-oxides, especially picoline N-oxides, has been extensively studied.[2,3] At the outset of this work, we knew of no reports on the analogous reaction of acetic anhydride with aromatic di-N-oxides of the quinoxaline series.[4] As a typical compound in this class we chose 1,2,3,4-tetrahydrophenazine di-N-oxide (**1**) because it can be readily prepared[5] and because the presence of the cyclohexene ring in the molecule provides the opportunity of studying the stereoselectivity of the reaction.

Treatment of **1** with acetic anhydride–acetic acid at room temperature (path A, Scheme I) gave 1-acetoxy-1,2,3,4-tetrahydrophenazine 5-N-oxide (**2**) and traces of phenazine. The structure of **2** was assigned on the basis of its infrared spectrum, which displayed bands at 1725 (C═O of acetate), 1335 cm^{-1} (N→O), and of its nmr spectrum, which showed an enveloped singlet at τ 7.8 (7 H, 3 H for one acetate and 4 H at C_2

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[1] Abstracted in part from the M. S. thesis of A.S., American University of Beirut, Beirut, Lebanon, 1967.

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[3] (a) T. Koenig, *J. Amer. Chem. Soc.*, **88**, 4045 (1966); (b) T. Cohen and G. L. Deets, *ibid.*, **89**, 3939 (1967).

[4] During the course of this study we were informed by Dr. J. D. Johnston of Chas. Pfizer Co., Inc., that he has run some of the reactions described above. His results will appear in a forthcoming publication.

[5] M. J. Haddadin and C. H. Issidorides, *Tetrahedron Lett.*, 3253 (1965).