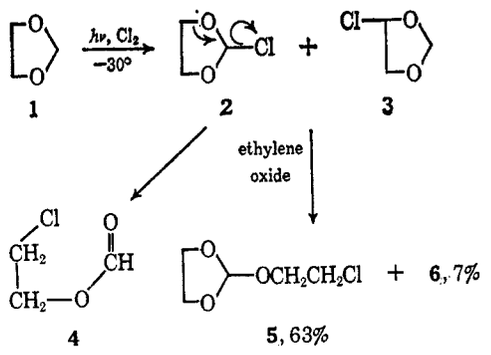
ically. The cochlorination, carried out at −10° afforded once again the halogeno ester (4) as the main product.[13]

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.

Acknowledgments.—Financial assistance of the National Research Council of Canada and the award of an Izaac Walton Killam Postdoctoral Scholarship to J. J. are gratefully acknowledged.

(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]

MAKHLUF J. HADDADIN AND ABDO S. SALAMEH

Department of Chemistry, American University of Beirut, Beirut, Lebanon

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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

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

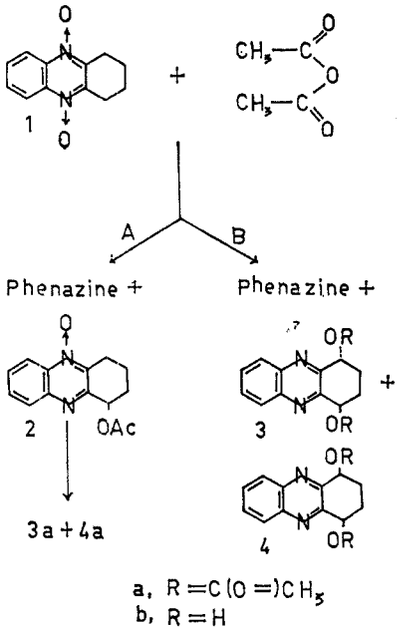
(2) (a) V. Boekelheide and W. J. Linn, *J. Amer. Chem. Soc.*, **76**, 1286 (1954); (b) O. H. Bullitt, Jr., and J. T. Maynard, *ibid.*, **76**, 1370 (1954); (c) J. A. Berson and T. Cohen, *ibid.*, **77**, 1281 (1955); (d) V. J. Traynelis and R. F. Martello, *ibid.*, **80**, 6590 (1958); (e) *ibid.*, **82**, 2744 (1960); (f) S. Oae, T. Kitao, and Y. Kitaoka, *ibid.*, **84**, 3359 (1962); (g) V. J. Traynelis and P. T. Pacini, *ibid.*, **86**, 4917 (1964); (h) S. Oae and S. Kozuka, *Tetrahedron*, **20**, 2677, 2685 (1964); (i) P. W. Ford and J. M. Swan, *Australian J. Chem.*, **18**, 867 (1965); (j) V. J. Traynelis and A. I. Gallager, *J. Amer. Chem. Soc.*, **87**, 5710 (1965); (k) S. Oae, S. Tamagaki, and S. Kozuke, *Tetrahedron Lett.*, 1513 (1966).

(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).

SCHEME I



and C_3), multiplet at τ 6.96 (2 H at C_4), unsymmetrical doublet at τ 3.96 (1 H at C_1), and multiplets at τ 2.9, 2.08, and 1.6 (4 H, aromatic). Phenazine was identified by comparison with an authentic sample.

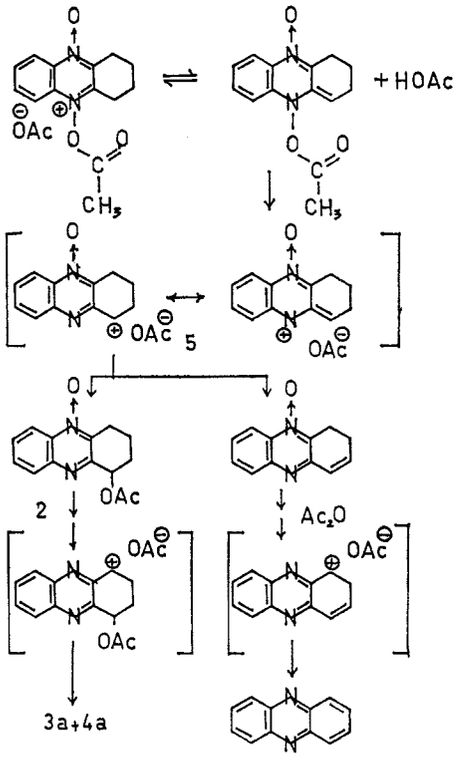
Treatment of **1** with acetic anhydride–acetic acid at reflux temperature (path B) gave phenazine, and two isomeric diacetates which we consider to be *trans*-1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**3a**), and *cis*-1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**4a**). The structures of **3a** and **4a** are based on elemental analysis and spectroscopic data. As nmr data failed to establish the *trans–cis* configuration in **3a** and **4a**, the present assignment is purely speculative.[6]

Alkaline hydrolysis of **3a** and **4a** yielded diols **3b** and **4b**, respectively. Either of these diols could be converted into its parent diacetate (**3b** → **3a**, **4b** → **4a**), indicating that no epimerization took place during hydrolysis.

An interesting feature of this work is the formation of phenazine as a by-product of the reaction of **1** with acetic anhydride. Phenazine could possibly arise through an elimination of two molecules of acetic acid from diacetate **3a** and/or diacetate **4a**. This possibility can be dismissed since neither **3a** nor **4a** give phenazine when refluxed with acetic anhydride–acetic acid. Moreover, phenazine is formed from **1** and acetic anhydride–acetic acid at room temperature while no diacetates are detected. Another source of phenazine could be product **2**. However, treatment of the latter with acetic anhydride–acetic acid at reflux temperature gives **3a** and **4a** in about equal amounts but no phenazine, as shown by thin layer chromatography. It is clear therefore that, although **2** can be a precursor for **3a** and **4a**, neither **2** nor **3a** nor **4a** are intermediates in the formation of phenazine. Furthermore, the yield of phenazine in the reaction at room temperature (path A) is not appreciably affected by the presence of free radical initiators such as benzoyl peroxide and 2,2′-azobis(2-methylpropionitrile), or of free radical inhibitors such as hydroquinone and nitrobenzene.

Recent mechanistic studies[3] on the reaction of α-picoline N-oxide and γ-picoline N-oxide with acid anhydrides have shown that the products, picolyl acetates, arise mainly through an ionic mechanism. By analogy, we present Scheme II to explain the formation of **2**, **3a**, **4a** and phenazine from the reaction of **1** with acetic anhydride.

SCHEME II



According to this mechanism, the observed products of this reaction are postulated to arise from a common species (**5**), which finally gives rise to either **2** (and hence **3a** and **4a**) or phenazine. Although the reaction is not stereoselective, it is of value in the preparation of **2**, **3a**, and **4a** which are not easily accessible by other methods.

Experimental Section[7]

1,2,3,4-Tetrahydrophenazine Di-N-oxide (**1**).—To a warm methanolic solution of benzofurazan oxide (13 g),[8] 1-morpholino-1-cyclohexene (17 g)[9] was added in portions. A deep red coloration developed with rise in the temperature of the reaction mixture. Concentration of the methanolic solution under reduced pressure resulted in the precipitation of a pale red solid which was collected by suction filtration, Chromatography on neutral alumina and fast elution with chloroform afforded a yellow solid, which upon recrystallization from methanol gave yellow prisms

(6) Isomer **3a** has a higher melting point than isomer **4a** and, being less polar, emerges first from the chromatography column.

(7) Melting points are uncorrected. Alumina used for chromatography was neutral, Grade I "Woelm," to which 3% water was added. Solvents for chromatography are indicated thus: PE = petroleum ether (bp 30–75°), B = benzene, E = ether. Elemental analyses were performed by F. Pascher, Germany. Ultraviolet spectra were measured in methanol solution, in a Perkin-Elmer ultraviolet-visible spectrophotometer, Model 202. Unless specified otherwise, infrared spectra were determined in Nujol using a Perkin-Elmer infrared spectrophotometer, Model 137. Nuclear magnetic resonance spectra were run in deuterated chloroform on a Varian A60 spectrometer.

(8) F. B. Mallory, "Organic Synthesis," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 75.

(9) S. Hunig, E. Lucke, and W. Brenninger, *Org. Syn.*, **41**, 65 (1961).

of 1,2,3,4-tetrahydrophenazine di-N-oxide (11 g, 51% yield), mp 183–184° dec.

Reaction of 1,2,3,4-Tetrahydrophenazine Di-N-oxide (1) with Acetic Anhydride. A. Path A, at Room Temperature.—1,2,3,4-Tetrahydrophenazine di-N-oxide (1, 1 g) was dissolved in a mixture of acetic anhydride (4 ml) and glacial acetic acid (1 ml) with gentle warming. After standing at room temperature for 48 hr, the reaction mixture was poured onto ice with stirring. A pale yellow solid precipitated which was collected by suction, washed with water, and dried (0.8 g). Thin layer chromatography of this crude product on silica gel, with benzene–chloroform (1:1) as eluent, indicated the presence of phenazine (detected by comparison with authentic phenazine and by its deep red coloration with concentrated sulfuric acid),[10a] and 1-acetoxy-1,2,4,4-tetrahydrophenazine 5-N-oxide (2) as the major product. The latter was obtained pure after two recrystallizations from methanol (0.6 g, 50% yield): mp 140–141°; infrared spectrum, 1725, 1560, 1475, 1335, 1225, 1050, 965, 910, 850, and 765 cm^{-1}; ultraviolet spectrum, λ_{max} 244.5, 329, 344 mμ (log ε 3.6, 3.9, and 3.8, respectively); nmr, envoloped singlet at τ 7.8 (7 H, three for one acetate and four for protons at C_2 and C_3), multiplets at τ 6.96 (2 H, at C_4), unsymmetrical doublet at τ 3.96 (1 H at C_1), and multiplets at τ 2.9, 2.08, and 1.6 (4 H, aromatic).

Anal. Calcd for $C_{14}H_{14}O_3N_2$ (258.27): C, 65.10; H, 5.46; N, 10.85. Found: C, 65.12; H, 5.50; N, 10.70.

B. Path B, at Reflux Temperature.—A mixture of 1,2,3,4-tetrahydrophenazine di-N-oxide (1, 11 g), acetic anhydride (44 ml), and glacial acetic acid (11 ml) was refluxed for 75 min. The cold tan solution was poured onto ice and the resulting greenish yellow solid was collected by suction filtration, washed with water, and dried (8.5 g). The solid was dissolved in the minimum amount of benzene and chromatographed on neutral alumina (290 g). Elution with PE–B 8:2, 7:3, 3:2, 2:3, 1:4 (400, 400, 450, 800, 800 ml, respectively), B (650 ml), B–E 8.5:1.5, 4:1, 7:3, 3:2, 1:1 (250, 350, 100, 100, 300 ml, respectively), and evaporation of the fractions yielded three products.

Phenazine (125 mg) was identified by its melting point, 171–173°, (lit.[10b] mp 171–173°), mixture melting point with authenic phenazine, and superimposable infrared and ultraviolet spectra with those of authentic phenazine.

***trans*-1,4-Diacetoxy-1,2,3,4-tetrahydrophenazine (3a, 1.83 g).**—Recrystallization from methanol gave colorless needles, mp 164–165°. Nmr spectroscopy showed a singlet at τ 7.87 (6 H, for two acetates), a multiplet at τ 7.68 (4 H, at C_2 and C_3), a multiplet at τ 3.7 (2 H, at C_1 and C_4), and a symmetrical multiplet at τ 2.3 and 1.9 (A_2B_2 system, 4 H, aromatic); infrared spectrum, 1700, 1685, 1220, 1190, 1145, 1080, 1025, 965, and 765 cm^{-1}; in chloroform, 1740, 1360, 1225, 1020, and 965 cm^{-1}; ultraviolet spectrum, λ_{max} 239, 315, 325 mμ (log ε 4.5, 3.8, and 3.9, respectively).

Anal. Calcd for $C_{16}H_{16}O_4N_2$ (300.30): C, 63.99; H, 5.37; N, 9.33. Found: C, 63.94; H, 5.35; N, 9.47.

***cis*-1,4-Diacetoxy-1,2,3,4-tetrahydrophenazine (4a, 1.50 g).**—Recrystallization from methanol yielded needles melting at 158°. Nmr spectroscopy displayed a singlet at τ 7.86 (6 H, for two acetates), a multiplet at τ 7.70 (4 H, at C_2 and C_3), a multiplet at τ 3.84 (2 H, at C_1 and C_4), and symmetrical multiplets at τ 2.3 and 1.9 (A_2B_2 system for 4 H, aromtic): infrared spectrum, 1720, 1250, 1220, 1040, 970, and 765 cm^{-1}; in chloroform, 1740, 1360, 1225, 1040, and 965 cm^{-1}; ultraviolet, λ_{max} 239, 317, 325 mμ (log ε 4.4, 3.7, and 3.7, respectively).

Anal. Calcd for $C_{16}H_{16}O_4N_2$ (300.30): C, 63.99; H, 5.37; N, 9.33. Found: C, 63.78; H, 5.33; N, 9.52.

Decoupling experiments of the 1,4-protons by irradiation of the 2,3-protons were run at room temperature (27°) in deuterated chloroform and in deuterated benzene at 100 MHz. The two protons at C_1 and C_4 appeared as a singlet in both **3a** and **4a** in each solvent.

Reaction of 1-Acetoxy-1,2,3,4-tetrahydrophenazine 5-N-Oxide (2) with Acetic Anhydride.—A solution of 1-acetoxy-1,2,3,4-tetrahydrophenazine 5-N-oxide (2 g), acetic anhydride (8 ml), and glacial acetic acid (2 ml) was refluxed for 75 min. The cold solution was poured onto ice and the resulting precipitate was collected, washed with water, and dried (1.62 g). The product was chromatographed on neutral alumina (125 g) and eluted with PE (250 ml); PE–B 9:1, 17:3, 4:1, 7:3, 3:2, 1:1, 2:3, 3:7, 1:4, (250, 200, 200, 350, 500, 350, 400, 950, 100 ml, respectively) and B ((1300 ml). Evaporation of the fractions yielded *trans*-1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**3a**) and *cis*-1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**4a**). Products **3a** and **4a** from this reaction were identical with **3a** and **4a** from path B. Thin layer chromatography of the crude product on silica gel, with benzene or benzene–chloroform as eluents, indicated the absence of phenazine.

Treatment of *cis*-1,4-Diacetoxy-1,2,3,4-tetrahydrophenazine (4a) with Acetic Anhydride.—A solution of **4a** (100 mg) in acetic anhydride–glacial acetic acid (ten drops and two drops, respectively) was refluxed for 75 min. The cold solution was poured onto ice and the product was collected, washed with water, and dried (78 mg), and was shown to be unchanged starting material **4a** (melting point, mixture melting point, and infrared spectrum). Thin layer chromatography of the crude product on silica gel (chloroform or benzene–chloroform as eluents) showed the absence of phenazine.

Treatment of 3a with Acetic Anhydride.—The previous procedure was applied to *trans*-1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**3a**, 100 mg), giving unchanged **3a** (89 mg). Thin layer chromatography of the crude product did not reveal the presence of phenazine.

Hydrolysis of *cis*-1,4-Diacetoxy-1,2,3,4-tetrahydrophenazine (4a).—A solution of 5% sodium bicarbonate was added to a stirred methanolic solution of **4a** (0.25 g in 10 ml). The precipitated solid was dissolved in water (5 ml) and methanol (5 ml). The solution was allowed to stand at room temperature for 4 hr. Upon concentration, *cis*-1,4-dihydroxy-1,2,3,4-tetrahydrophenazine (**4b**) precipitated. The product was collected by suction filtration, washed with water followed by methanol, and dried (125 mg, 70% yield). Colorless plates (80 mg) were obtained from methanol. On heating, diol **4b** developed a pale red color at 147° and melted with decomposition at 167.5–169° giving a deep red coloration: infrared spectrum, 3030, 1480, 1430, 1280, 1080, 1065, 1055, 1000, 965, and 785 cm^{-1}; ultraviolet spectrum, λ_{max} 239, 315, 324 mμ (log ε 4.4, 3.6, and 3.7, respectively). A sample of diol **4b** (50 mg) was dissolved in pyridine (0.8 ml) and acetic anhydride (0.8 ml). The usual work-up gave a product (42 mg, 61% yield) identical with **4a**.

Hydrolysis of *trans*-1,4-Diacetoxy-1,2,3,4-tetrahydrophenazine (3a).—The same procedure used in the hydrolysis of **4a** was followed. Product **3a** (0.4 g) was dissolved in methanol–water (30 ml–5 ml) and treated with a solution of 5% sodium bicarbonate (8 ml). The work-up afforded *trans*-1,4-dihydroxy-1,2,3,4-tetrahydrophenazine (**3b**) in 78% yield (225 mg). *trans*-Diol **3b** was recrystallized from methanol to give needles (182 mg), which on heating became pale red at 165°, and melted with decomposition at 182–183° giving a deep red coloration: infrared spectrum, 3030, 1480, 1420, 1055, 1050, 990, 925, 915, and 785 cm^{-1}; ultraviolet spectrum, λ_{max} 239, 315, 324 mμ (log ε 4.4, 3.7, and 3.8 respectively).

Diol 3b (50 mg) was treated with pyridine (0.8 ml) and acetic anhydride (0.8 ml). The solution was allowed to stand at room temperature for 24 hr and poured onto ice. The resulting solid was collected, washed with water, and dried (45 mg, 65% yield), and shown to be identical with 1,4-diacetoxy-1,2,3,4-tetrahydrophenazine (**3a**) (mixture melting point and superimposable infrared spectra).

The Reaction of 1,2,3,4-Tetrahydrophenazine Di-N-oxide (1) with Acetic Anhydride in the Presence of Benzoyl Peroxide, 2,2′-Azobis(2-methylpropionitrile), Nitrobenzene, and Hydroquinone. General Procedure.—A solution of 1,2,3,4-tetrahydrophenazine di-N-oxide (1 g) in acetic anhydride–acetic acid (6 ml and 2 ml, respectively), and the free radical initiator or inhibitor (50 mg) were allowed to stand at room temperature for 48 hr. After the reaction mixture was poured onto ice, the solution was made slightly alkaline with sodium bicarbonate and immediately extracted with ether. The dried ethereal solution

TABLE I

Initiator	Inhibitor	Product 2, mg	Phenazine, mg
Benzoyl peroxide		278	53
2,2′-Azobis(2-methylpropionitrile)		135	21
	Nitrobenzene	100	13
	Hydroquinone	335	57

(10) G. A. Swan and D. G. I. Felton, "The Chemistry of Heterocyclic Compounds: Phenazines," Interscience Publishers, Inc., New York, N. Y., 1957, (a) p 17, (b) p 15.

was evaporated and the residue was chromatographed on neutral alumina (30 g) and eluted with PE (200 ml), PE–B 17:3, 8:2, 5:5 (150 ml each), and B (500 ml). Evaporation of the fractions gave the results shown in Table I.

Registry No.—**1**, 4121-35-1; acetic anhydride, 108-24-7; **2**, 16101-29-4; **3a**, 16101-30-7; **3b**, 16101-31-8; **4a**, 16101-32-9; **4b**, 16101-33-0.

Acknowledgment.—We are indebted to the Arts and Sciences Research Committee of the American University of Beirut for financial support. We are grateful to Professor Costas H. Issidorides for his advice and encouragement. We thank Professors E. P. Papadopoulos and W. T. Smith for the nmr spectra, and Dr. Jean Märki of Varian AG, Zürich, for the nmr decoupling experiments.

Synthesis and Properties of 1H-Naphtho[2,1-*b*]thiete 2,2-Dioxide[1,2]

LEO A. PAQUETTE[3] AND MELVIN ROSEN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

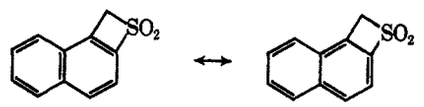
Received December 18, 1967

In recent years, the chemistry of thiete 1,1-dioxide (**1**) and its derivatives has been given considerable attention. In earlier papers of this series, we described the preparation of fused aromatic derivatives of **1** in which the double bond of the four-membered sulfur-containing ring was incorporated into the delocalized π cloud of naphthalene.[4,5] Our interest in such molecules has been associated with the question of whether

1 **2a** **2b**

the steric strain imposed by the heterocyclic ring would cause measurable double-bond fixation in the naphthalene system. Previous results[4a] have indicated that the fusion of a thiete dioxide to the 2,3 bond of naphthalene as in **2** does not significantly alter the ground or excited state properties of the aromatic moiety.

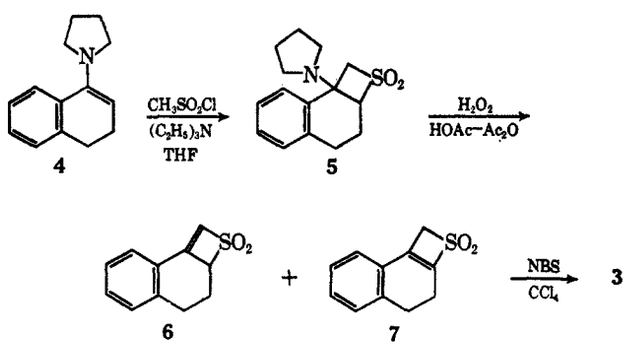
Because the α,β bonds of naphthalene are known to possess greater double bond character than the β,β bonds,[6] the possibility that fusion of a thiete dioxide ring to the 1,2 bond of naphthalene might result in bond fixation was considered. For this reason, it was deemed of interest to prepare **3**; in this paper the synthesis and physical properties of this molecule are described.



3a **3b**

The reaction of 1-(3,4-dihydro-1-naphthyl)pyrrolidine (**4**) with methanesulfonyl chloride and triethylamine in dry tetrahydrofuran afforded, in 58% yield, colorless crystals of the thietane dioxide **5**. The structure of **5** follows from its spectral parameters (see Experimental Section) and from the well-precedented course of sulfene–enamine cycloaddition reactions.[7] In the presence of an acetic acid–acetic anhydride solution of hydrogen peroxide, **5** was converted in 91% yield into a mixture consisting of thiete dioxides **6** and **7** (ratio *ca.* 1.5:1, nmr analyses, See Scheme I). Equilibration of this mixture with powdered potassium hydroxide in tetrahydrofuran gave a solid that was enriched in **7** (ratio *ca.* 1:3). Further attempts at equilibration did not alter this ratio. The question of apparent equilibrium composition[8] is interesting. The results indicate the endocyclic isomer to be more stable in agreement with the Brown–Brewster–Shechter rule.[9] Whether this preference can be attributed to eclipsing interactions, or to angle strain effects, or to a combination of these factors,[10] remains an open question.

SCHEME I



Bromination of either the equilibrated or nonequilibrated mixture with N-bromosuccinimide in carbon tetrachloride solution led to the evolution of hydrogen bromide and the formation of **3** in 50–60% yield. The nmr spectrum of **3** displayed a singlet at δ 5.50 due to the α-sulfonyl protons and a complex six-proton multiplet in the 7.42–8.18 region (aromatic hydrogens). No abnormal chemical shifts are seen; furthermore, the great degree of similarity in the ultraviolet spectra of **3**, **2**, and methyl 2-naphthyl sulfone (**8**) (see Table I) indicates that the naphthalene ring is not unusually affected by the nature of the ring fusion found in **3**.

The mass spectrum of **3** has a molecular ion at *m/e* 204 and a base peak at *m/e* 139, corresponding to an ion formed by the expulsion of a hydrogen and sulfur

(1) Paper XXXVIII of the series entitled "Unsaturated Heterocyclic Systems;" for previous paper, see L. A. Paquette, *Tetrahedron Lett.*, in press.

(2) The authors are grateful to the National Science Foundation for Grant GP-5977 which contributed to the financial support of this research.

(3) Fellow of the Alfred P. Sloan Foundation, 1965–1967.

(4) (a) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); (b) L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

(5) In an independent study, D. C. Dittmer and N. Takashina [*Tetrahedron Lett.*, 3809 (1964)] reported the synthesis of the 3,8-diphenyl derivative of **2**.

(6) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 880.

(7) For a summary of this rather extensive literature, see (a) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967); (b) G. Opitz, *Angew. Chem. Intern. Ed., Engl.*, **6**, 107 (1967); (c) T. J. Wallace, *Quart. Rev.* (London), **20**, 67 (1966).

(8) Owing to the fact that **7** could not be isolated in pure form, the equilibrium could not be approached from both directions However, the same result was obtained in a duplicate run.

(9) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Amer. Chem. Soc.*, **76**, 467 (1954).

(10) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).