precipitated by the addition of glacial acetic acid. The white crystals were collected, washed with water, and dried *in vacuo* over P_2O_5 at 78°, 30 mg (74%).

1-Hydroxyxanthine.—To a cooled, stirred solution of 1-hydroxyguanine (10 mg) in 5 ml of 2 *N* HCl was added 1 ml of a 2 *M* solution of $NaNO_2$. After 8 hr the solution was evaporated to dryness and the residue was chromatographed over Dowex-50. The uv spectrum of the main fraction, eluted first with 1 *N* HCl, was identical with that of authentic 1-hydroxyxanthine.[5] Traces of 1-hydroxyguanine and an unidentified product were eluted with further 1 *N* HCl.

Guanine.—1-Hydroxyguanine (10 mg) was suspended in 1 ml of concentrated HI, warmed on a steam bath for 1 hr, and evaporated to dryness. The residue was chromatographed over Dowex-50. Elution with 1 *N* HCl removed a trace of unreduced 1-hydroxyguanine, and guanine, identified by its uv spectrum, was eluted with 2 *N* HCl.

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Registry No.—**1**, 5383-06-2; **2**, 40519-34-4; **3**, 40519-35-5; **4**, 40519-36-6; **5**, 40519-37-7; **6**, 40550-38-7; **7** hydrochloride, 40429-65-0; adenosine 1-*N*-oxide, 146-92-9; benzyl bromide, 100-39-0; benzoyl isothiocyanate, 4461-33-0.

Reaction of Thiete 1,1-Dioxide with α-Pyrone[1]

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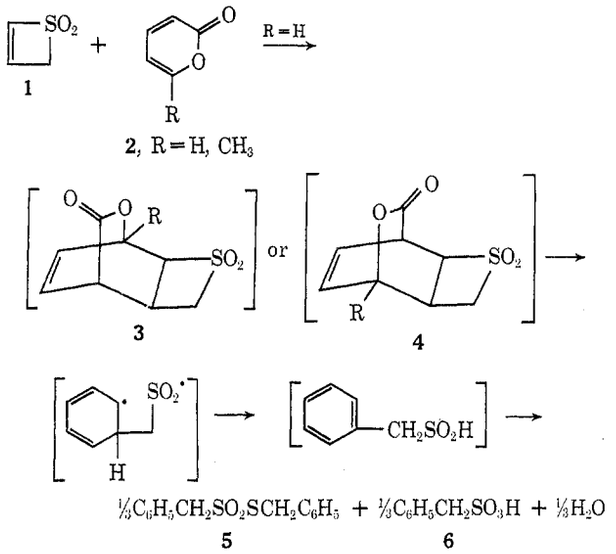
Thiete 1,1-dioxide (thiete sulfone)[2] behaves erratically in cycloaddition reactions. On the one hand it undergoes, in a normal fashion, additions of butadiene,[3] furans,[3,4] anthracene,[5] dienamines,[6] enamines,[6] ynamines,[6] and diazoalkanes.[7] On the other hand, the attempted Diels–Alder cycloaddition of tetraphenylcyclopentadienone to thiete sulfone resulted in evolution of sulfur dioxide and formation of a tetraphenylcycloheptatriene and a bicyclic octadienone in yields of 65 and 15%, respectively.[3]

α-Pyrone[8] is a reactive diene in Diels–Alder reactions and is a useful reagent for introducing the C_4H_4 moiety.[9] Treatment of thiete sulfone, **1** (10 mmol), with α-pyrone, **2** (10 mmol), under nitrogen in refluxing *m*-xylene for 24 hr gave benzyl α-toluenethiosulfonate, **5** (2.59 mmol), and benzylsulfonic acid, **6** (1.05 mmol),



instead of the expected product of the Diels–Alder cycloaddition. The properties of the α-toluene thiosulfonate were identical with those of an authentic sample prepared by oxidation of dibenzyl disulfide with hydrogen peroxide in acetic acid.[10] The benzylsulfonic acid was identified by conversion to benzylsulfonyl chloride, whose properties were identical with those of an authentic sample.[11] No reaction of thiete sulfone and α-pyrone was observed at 50° or 100°.

No reaction was observed between thiete sulfone and 6-methyl-2-pyrone[12] (**2**, R = CH_3) under the same conditions.

A possible scheme for the formation of benzyl α-toluenethiosulfonate involves the disproportionation of benzylsulfinic acid derived from the Diels–Alder adduct of α-pyrone and thiete sulfone. Although there are conflicting reports in the literature concerning the ease of disproportionation of benzylsulfinic acid, the conditions under which those disproportionation reactions were attempted were different from our conditions.[10,13,14] We have found that both benzyl α-toluenethiosulfonate (65.4%) and benzylsulfonic acid (40.8%) are formed when benzylsulfinic acid is refluxed in *m*-xylene for 30 hr. Disproportionation of sulfinic acids to thiosulfonates and sulfonic acids is well known and the mechanism has been established by Kice and his coworkers.[15] The possible involvement of free radicals in thermolysis of sulfones has been noted previously.[16]

The attempt to distinguish between possible inter-

(1) We are grateful to the National Institutes of Health for support of this work (Grant CA 08250).

(2) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961); P. L. Chang and D. C. Dittmer, *ibid.*, **34**, 2791 (1969); D. C. Dittmer, M. E. Christy, N. Takashina, R. S. Henion, and J. M. Balquist, *ibid.*, **36**, 1324 (1971).

(3) D. C. Dittmer, K. Ikura, J. M. Balquist, and N. Takashina, *ibid.*, **37**, 225 (1972).

(4) D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964); L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

(5) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

(6) L. A. Paquette, R. M. Houser, and M. Rosen, *J. Org. Chem.*, **35**, 905 (1970).

(7) D. C. Dittmer and R. Glassman, *ibid.*, **35**, 999 (1970).

(8) H. E. Zimmerman, G. L. Grunwald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

(9) For examples, see H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960); L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965); A. B. Evnin and D. Seyferth, *J. Amer. Chem. Soc.*, **89**, 952 (1967).

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(11) T. B. Johnson and J. A. Ambler, *J. Amer. Chem. Soc.*, **36**, 372 (1914).

(12) M. Rey, E. Dunkelblum, R. Allain, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 2159 (1970); E. Dunkelblum, M. Rey, and A. S. Dreiding, *ibid.*, **54**, 6 (1971).

(13) T. B. Johnson and I. B. Douglass, *J. Amer. Chem. Soc.*, **61**, 2548 (1939).

(14) C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957).

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mediates **3** and **4** by use of 6-methyl-2-pyrone was unsuccessful. No reaction was observed with thiete sulfone under the same conditions used with α-pyrone. Although the result was negative, one might, as a consequence, favor the stereochemistry of **3** over **4** because steric hindrance between the methyl group and the oxygens of the sulfone would inhibit reaction. The regiospecificity implied in the formation of **3** also may result from minimization of the opposition of the strong dipoles of the sulfone and carbonyl groups (*i.e.*, they tend to be as far apart as possible). For this reason, an endo configuration of the initial adduct would be expected.

The reaction of α-pyrone with 3-phenyl-2-thiete 1,1-dioxide[17] also failed even after 10 days at 140°. The phenyl group would have blocked aromatization and the adducts corresponding to **3** or **4** perhaps could have been isolated.

Experimental Section[18]

Reaction of α-Pyrone and Thiete Sulfone.—Thiete sulfone[2] (1.04 g, 10 mmol) was added to α-pyrone[8] (0.960 g, 10 mmol, distilled prior to its use) in *m*-xylene (30 ml). The mixture was refluxed and stirred for 24 hr under nitrogen. The *m*-xylene was removed *in vacuo* and the mixture was chromatographed on Florisil (60–100 mesh). Benzyl α-toluenethiosulfonate (0.720 g, 2.59 mmol) was eluted with hexane and with hexane–benzene. The toluene thiosulfonate was recrystallized from ether: mp 106–107.5° (lit.[10] mp 107–108°); ir (KBr) 1320 (s), 1120 cm^{-1} (s); nmr[19] ($CDCl_3$) δ 4.01 (s, 1), 4.21 (s, 1), 7.35 (s, 5); mass spectrum (70 eV) *m/e* 278 (parent), 214 (parent − SO_2), 91 (C_7H_7). A mixture of starting materials (0.420 g) was eluted with ether. Benzylsulfonic acid (0.180 g, 1.05 mmol) was eluted with ether–ethanol (1:2), dissolved in water, and neutralized with 30% sodium hydroxide. Most of the water was removed *in vacuo* and a white solid (0.130 g) was obtained: mp 250°; ir (KBr) 1200 (b, s), 1130 (s), 1050 (s), 1020 cm^{-1} (s). This solid was treated at 70° with phosphorus pentachloride (0.130 g) in 2 ml of phosphorus oxychloride. Benzylsulfonyl chloride (0.084 g) separated when the reaction mixture was added to water: mp 89.5–90.5°, undepressed by admixture with an authentic sample (lit.[20] mp 91–93°); ir (KBr) 1340 (s), 1250 (s), 1190 (s), 1150 (s), 1120 cm^{-1} (s); nmr ($CDCl_3$) δ 4.88 (s, 2), 7.54 (s, 5); mass spectrum (70 eV) *m/e* 192, 190 (parent), 128, 126 (parent − SO_2), 101 ($SO_2{}^{37}Cl$), 99 ($SO_2{}^{35}Cl$), 91 (C_7H_7). Finally, a water-soluble acidic tarry fraction (0.400 g) was eluted with ethanol.

Benzyl α-Toluenethiosulfonate.—Benzyl α-toluenethiosulfonate was prepared in 52% yield by the method of Boldyrev and Khovalko,[10] mp 106–107.5°. The ir, nmr, and mass spectra were identical with those cited above for this compound.

Benzylsulfonyl Chloride.—Benzylsulfonyl chloride was prepared by the method of Johnson and Ambler,[11] mp 89–91° (lit.[11] mp 92–93°). Its nmr, ir, and mass spectra were identical with those given above for this compound.

Disproportionation of Benzylsulfinic Acid.—Benzylsulfinic acid[14] (0.800 g, 5.13 mmol) was dissolved in *m*-xylene (25 ml); the solution was brought to reflux and stirred 30 hr under nitrogen. Benzyl α-toluenethiosulfonate (0.312 g, 1.12 mmol, 65.5%) and benzylsulfonic acid (0.120 g, 0.70 mmol, 40.8%) were isolated and identified as described above for the reaction of thiete sulfone with α-pyrone.

Registry No.—α-Pyrone, 504-31-4; thiete sulfone, 7285-32-7; benzyl α-toluenethiosulfonate, 16601-40-4; benzylsulfonic acid, 100-87-8; phosphorus pentachloride, 10026-13-8; benzylsulfonyl chloride, 1939-99-7.

(17) W. O. Siegl and C. R. Johnson, *J. Org. Chem.*, **35**, 3657 (1970).

(18) Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU 6E spectrometer. Melting points are uncorrected. *m*-Xylene was distilled from calcium hydride just prior to its use.

(19) δ 4.02, 4.19 reported by P. Allen, Jr., P. J. Berner, and E. R. Malinowski, *Chem. Ind. (London)*, 208 (1963).

(20) E. Fromm and J. Palma, *Ber.*, **39**, 3308 (1936).

The Reaction of Enamines with *o*-Hydroxy-ω-nitrostyrenes. Preparation of Benzodihydropyrans and Hexahydroxanthenes and Their Rearrangement to Pyrroline 1-Oxides and Hexahydroindole 1-Oxides

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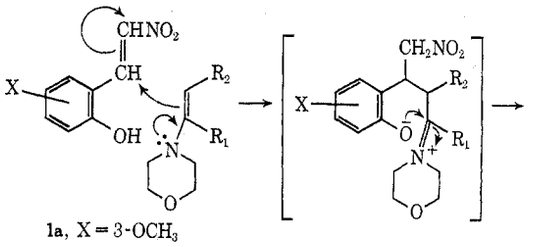
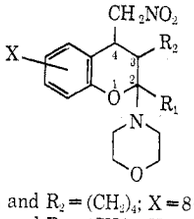
The reaction of enamines with phenolic Mannich bases[1a,b] and *o*-hydroxybenzaldehydes[2] has resulted in the formation of benzodihydropyrans. The present report describes the development of a third method of preparing benzodihydropyrans (**2**) which involves the reaction of enamines with *o*-hydroxy-ω-nitrostyrenes. A useful feature of this approach was the incorporation of a nitromethyl function in the 4 position. The reaction of enamines with nitro olefins has been reported to give good yields of nitrocyclobutanes or nitro ketones.[3,4] In our case the postulated zwitterion intermediate collapsed to a benzodihydropyran **2c** or a hexahydroxanthene **2a,b**, through the intervention of the *o*-hydroxyl, rather than to a nitrocyclobutane or a simple substituted enamine.



1a, X = 3-OCH_3
b, X = 5-OCH_3



2a, R_1 and R_2 = $(CH_2)_4$; X = 8-OCH_3
b, R_1 and R_2 = $(CH_2)_4$; X = 6-OCH_3
c, R_1 = C_2H_5; R_2 = CH_3; X = 8-OCH_3

Both aliphatic and alicyclic enamines were utilized in this reaction; thus, the morpholine enamine of diethyl ketone yielded a 2-morpholino-4-(nitromethyl)-benzodihydropyran (**2c**) and the morpholine enamine of cyclohexanone gave **4a**-morpholino-9-(nitromethyl)-hexahydroxanthenes (**2a,b**).

In spite of the presence of three asymmetric centers,

(1) (a) M. von Strandtmann, M. P. Cohen, and J. Shavel, Jr., *Tetrahedron Lett.*, 3101 (1965); (b) *J. Heterocycl. Chem.*, **7**, 1311 (1970).

(2) L. A. Paquette, *Tetrahedron Lett.*, 1291 (1965).

(3) M. Kuehne and L. Foley, *J. Org. Chem.*, **30**, 4280 (1965).

(4) A. Risaliti, M. Forchiassin, and E. Valentin [*Tetrahedron*, **24**, 1889 (1968)] have shown that the product of reaction of β-nitrostyrenes and morpholine cyclohexanone enamine has the erythro configuration.