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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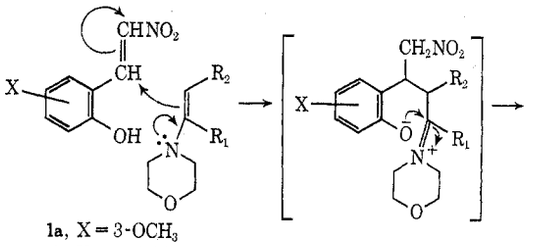
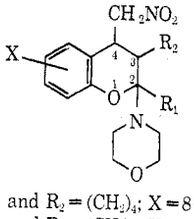
Received April 19, 1973

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.

only one compound was generally isolated from the reaction mixture. This is, in part, due to the ability of these cyclic O,N ketals to epimerize[1b] at C-2 and, in part, because of the stereospecificity of the addition reaction which restricts the spatial arrangement at C-3 and C-4 to a cis configuration.[4]

The reactions were effected by heating equimolar amounts of the enamine and nitrostyrene in dioxane at reflux for 1–2 hr, giving generally a 50% yield of the product. The cyclic nature of the compounds was confirmed by the absence of a phenolic OH, C=O, or C=C or C=CN stretching frequency in the ir. The nmr was in agreement with the assigned structures. The spectrum of the xanthene **2a** consisted of a multiplet at δ 6.85 (3 H, phenyl aromatics), octet at 4.8 (2 H, CH_2NO_2), quartet at 4.18 (1 H, benzylic proton), singlet at 3.9 (3, H, OCH_3), 3.62 (4 H, morpholine CH_2O), 2.68 (4, H, morpholine CH_2N) and 1–2.4 (9 H, the methylene envelope). The nmr spectrum of the benzodihydropyran **2c** was analogous.

Reductive Rearrangement of Benzodihydropyrans. The pyrans **2a–c** are formally O,N ketals of γ-nitro ketones. The reduction of γ-nitro ketones has been utilized in the formation of pyrroline and pyrroline 1-oxides.[5] We have now determined that analogous transformations could be achieved with cyclic O,N ketals such as the benzodihydropyran derivatives **2a–c**.

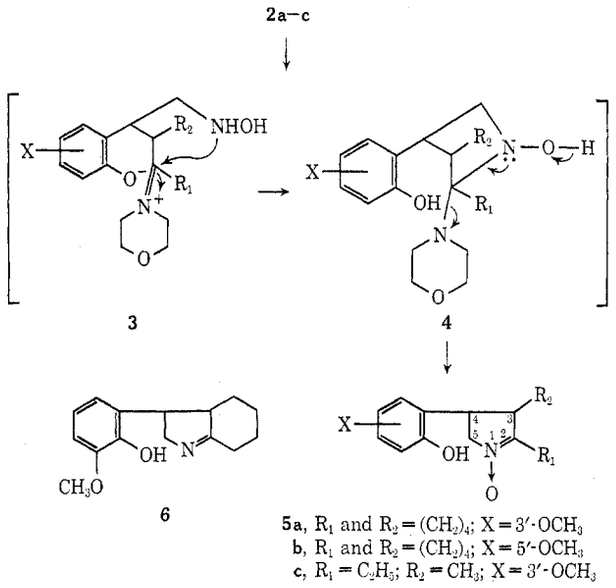
Hydrogenation of **2a** with palladium in ethanol–acetic acid gave the pyrroline 1-oxide derivative **5a**. Assignment of this phenolic nitrone structure rather than the anticipated product of simple reduction, a 4-(aminomethyl)benzodihydropyran, was made on the basis of physical properties, *i.e.*, water solubility, and spectral data: ir (CH_2Cl_2) 3500 (OH), 1620 cm^{-1} (C=N); nmr 2 H multiplet at δ 4.18–4.5 [CH_2N-(O)=C].

The nitrone **5a** could arise through partial reduction of the nitro group to the hydroxylamine followed by cyclization and rearrangement of the hydroxylamine group to the nitrone with elimination of morpholine. The cyclization step probably occurs in the ring-opened form (**3**) (Scheme I), which exists in equilibrium with the closed form.[1b] Consideration of Dreiding models reveals that a direct displacement of morpholine in the presence of the intact pyran ring is unlikely because of severe steric hindrance to the approach of the hydroxylamine moiety. An alternate mechanism would involve hydrolysis of **3** to a ketone with ring closure to **5**.

The configuration at C-3 and C-4, which has been shown above to be cis in **2**, is trans for the two chiral centers in **5**. This change in the spatial arrangement is a consequence of the rotation around the C-4, C-3 axis in the course of the pyrroline ring formation.

A chemical reduction of **2** using aqueous zinc–ammonium chloride[6a,b] also gave **5** in good yield. The pyrroline 1-oxide **5c** was prepared by this method from **2c**. A more complete reduction of **2a** to the 3-(*o*-hydroxyphenyl)hexahydroindole **6** was obtained catalytically with Raney nickel and methanol solvent.

SCHEME I



Experimental Section[7]

1,2,3,4,4a,9a-Hexahydro-5-methoxy-4a-morpholino-9-(nitromethyl)xanthene (2a).—A solution of 145 g (0.74 mol) of 2-hydroxy-3-methoxy-ω-nitrostyrene,[8] 800 ml of dioxane, and 69.6 g (0.8 mol) of cyclohexanone morpholine enamine[9] was heated on the steam bath for 2 hr. About 500 ml of dioxane was removed at reduced pressure and 200 ml of 2-propanol was added to the thick residue. The separated orange crystals were filtered and washed with 2-propanol and then with petroleum ether (bp 30–60°) to give 85 g (32%) of **2a**, mp 198–200°. A total yield of 40–50% of **2a** was isolated by addition of water to the filtrate to precipitate additional crude. Pure material was obtained by recrystallization from tetrahydrofuran–petroleum either, mp 199–201°.

Anal. Calcd for $C_{19}H_{26}N_2O_5$: C, 62.96; H, 7.23; N, 7.73. Found: C, 63.15; H, 7.28; N, 7.48.

7-Methoxy Isomer of 2a (2b).—This compound was prepared from 2-hydroxy-5-methoxy-ω-nitrostyrene by the same procedure used for **2a**: yield 50%; recrystallization from tetrahydrofuran–petroleum ether gave mp 165–167°.

Anal. Calcd for $C_{19}H_{26}N_2O_5$: C, 62.96; H, 7.23; N, 7.73. Found: C, 63.00; H, 7.20; N, 7.59.

2-Ethyl-3,4-dihydro-8-methoxy-3-methyl-2-morpholino-4-(nitromethyl)-2*H*-1-benzopyran (2c).—This compound was prepared from 2-hydroxy-3-methoxy-ω-nitrostyrene and the morpholine enamine of diethyl ketone[10] by a procedure similar to that used for **2a**: yield 50%; recrystallization from tetrahydrofuran–petroleum ether gave mp 176–178°.

Anal. Calcd for $C_{18}H_{26}N_2O_5$: C, 61.70; H, 7.48; N, 8.00. Found: C, 61.81; H, 7.46; N, 7.91.

3,3a,4,5,6,7-Hexahydro-3-(2-hydroxy-3-methoxyphenyl)-2*H*-indole 1-Oxide (5a).—A solution of 271.5 g (0.75 mol) of **2a**, 750 ml of glacial acetic acid, and 3 l. of ethanol was hydrogenated for 16 hr at low pressure using 15 g of 10% Pd/C. The catalyst was filtered and the filtrate was concentrated at reduced pressure

(5) J. Hammer and A. Macaluso, *Chem. Rev.*, **64**, 473 (1964); F. R. Delpierre and M. Lamchen, *Quart. Rev., Chem. Soc.*, 329 (1965).

(6) The use of aqueous zinc ammonium chloride in the reduction of γ-nitro ketones to Δ^1-pyrroline 1-oxides has been reported: (a) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2094 (1959); (b) M. C. Kloetzel, F. L. Chubb, R. Gobran, and J. L. Pinkus, *J. Amer. Chem. Soc.*, **83**, 1128 (1961).

(7) Melting points were determined with the Thomas-Hoover capillary melting point apparatus which was calibrated against known standards. Infrared spectra were determined with a Baird Model 544 double-beam instrument. Nmr spectra were measured with a Varian A-60 spectrophotometer.

(8) C. B. Gairaud and G. R. Lappin, *J. Org. Chem.*, **18**, 1 (1953).

(9) G. Stork, A. Brizzolava, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(10) R. Jacquier, C. Petrus, and F. Petrus, *Bull. Soc. Chim. Fr.*, **9**, 2845 (1966).

to remove most of the solvent. The residue was dissolved in water (750 ml) and enough potassium carbonate was added to neutralize and saturate the solution. The separated material was dissolved in 1.5 l. of methylene chloride and the solution was dried over potassium carbonate, filtered, and concentrated. Ether (300 ml) was added to generate 130 g (66%) of solid **5a**, mp 110–115°. Recrystallization was effected by dissolution in a minimum volume of hot methylene chloride, concentration to about ½ volume, and addition of an equal volume of ethyl acetate: mp 120–122°; nmr δ 6.82 (m, 3, aromatics), 4.18–4.5 (m, 2), 3.9 (s, 3, OCH_3), 2.9–3.7 (m, 3), 1–2.3 (m, 8, methylene envelope).

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.69; H, 7.35; N, 5.36.

Alternate Preparation of 5a.—A solution of 0.54 g (0.01 mol) of ammonium chloride in 15 ml of water was added to a solution of 3.6 g (0.01 mol) in **2a** in 75 ml of THF. With vigorous stirring, under nitrogen, zinc powder (7 g) was added over a 2-min period. The mixture was stirred for 45 min and filtered and the filtrate was treated with 50 ml of 1 *N* hydrochloric acid. After 15 min this solution was neutralized with solid potassium carbonate excess and the THF phase was dried further with anhydrous potassium carbonate, filtered, and concentrated. Upon addition of ether to the viscous residue, 2.2 g (85%) of solid **5a** developed, mp 105–110°. Recrystallization was effected as above, mp 118–121°.

2-Hydroxy-5-methoxyphenyl Isomer of 5a (5b).—This compound was prepared from **2b** by the above alternate zinc–NH_4Cl method: yield 78%, mp 180–182°.

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.19; H, 7.44; N, 5.24.

2-Ethyl-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-pyrroline 1-Oxide (5c).—A solution of 5.4 g of ammonium chloride in 150 ml of water was added to a warm solution (35°) of 35 g (0.1 mol) of **2c** in 750 mol of tetrahydrofuran. The vigorously stirred mixture was treated with 70 g of zinc powder over the next several minutes. In 15 min, the zinc paste developed into a suspended solid. After ½ hr the reaction was worked up in a fashion similar to that for the alternate preparation of **5a** to give 20.5 g (82.3%) of crude **5c**, mp 101–103°. Recrystallization from EtOAc gave pure nitrone, mp 107–109°.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.30; H, 7.82; N, 5.57.

3,3a,4,5,6,7-Hexahydro-3-(2-hydroxy-3-methoxyphenyl)-2*H*-indole (6).—A mixture of 108.6 g (0.3 mol) of **2a**, 3 l. of methanol, and 30 g of Raney nickel was hydrogenated at low pressure at a temperature of 50° for 16 hr. After filtration of the catalyst, the solution was concentrated to 1-l. volume. A volume of 350 ml of 2 *N* hydrochloric acid was added and the solution was heated on the steam bath for 10 min. Ice water was added to precipitate some red solid. After filtration, concentrated ammonium hydroxide was added to precipitate the tacky base. Recrystallization was effected by dissolution in 200 ml of hot methanol and addition of 100 ml of water to give 25 g (34%) of **6**, mp 135–140°. Recrystallization from absolute ethanol gave pure **6**: mp 140–145°; ir (Nujol) 1655 (C=N), 2500 cm^{-1} (C=NH^+); ir ($CHCl_3$) 1650 (C=N), 3550 cm^{-1} (OH).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.46; H, 7.77; N, 5.89.

Acknowledgment.—The authors are indebted to the Analytical and Physical Chemistry Department under the supervision of Mr. A. D. Lewis. In particular, we wish to thank Dr. C. Greenough for the spectral data and Mrs. U. Zeek for analytical determinations. We also wish to thank the Chemical Development Department under the supervision of Dr. A. W. Ruddy for the large-scale preparation of intermediates.

Registry No.—**2a**, 36848-01-8; **2b**, 40697-22-1; **2c**, 40697-23-2; **5a**, 40697-85-6; **5b**, 40697-86-7; **5c**, 40697-87-8; **6**, 40697-88-9; 2-hydroxy-3-methoxy-ω-nitrostyrene, 1986-06-7; cyclohexanone morpholine enamine, 670-80-4; 2-hydroxy-5-methoxy-ω-nitrostyrene, 35467-98-2; diethyl ketone morpholine enamine, 13654-48-3.

Synthesis of 1,7- and 1,11-Dihydrobenzo[1,2:4,5]dicycloheptene and 1*H*-Benzo[1,2:4,5]dicycloheptenium Tetrafluoroborate(1−)

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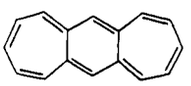
Received March 14, 1973

The dihydrobenzo[1,2:4,5]dicycloheptenes (*e.g.*, **3** and **4**) are molecules of considerable synthetic interest, since, in principle, these compounds can act as precursors to a variety of novel conjugated systems. Thus, removal of hydride could provide the monocation **5** and the 14-π-electron dication, proton removal the 18-π-electron dianion, and loss of hydrogen the 16-π-electron hydrocarbon **1**. We now report the synthesis



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of 1,7- (**3**) and 1,11-dihydrobenzo[1,2:4,5]dicycloheptene (**4**), and the conversion of these isomers into 1*H*-benzo[1,2:4,5]dicycloheptenium tetrafluoroborate(1−) (**5**).[1]

1,2,3,4,5,7,8,9,10,11-Decahydrobenzo[1,2:4,5]dicycloheptene (**2**), prepared by a known route,[2,3] was treated with 4 molar equiv of *N*-bromosuccinimide, and a complex mixture of bromides was formed. The total mixture was dehydrobrominated with 1,5-diazabicyclo[5.4.0]undec-5-ene in dimethylformamide, and the resulting mixture was chromatographed on silica, eluting with petroleum ether (bp 40–60°). A crystalline material was obtained, which on fractional crystallization or chromatography gave mixtures of varying composition of the isomers **3** and **4** (see Experimental Section). Attempts to separate these isomers completely proved unsuccessful, but the mixtures gave satisfactory mass spectral and analytical data. The nmr spectrum of the mixtures showed a singlet in the aromatic region at τ 2.92, assigned to the equivalent aromatic protons of **3**, and singlets at τ 2.75 and 3.06, assigned to the nonidentical aromatic protons of **4**. The allylic protons of **3** and **4** appeared as a doublet (τ 6.97) and the chemical shifts and coupling pattern of the olefinic protons was consistent with structures **3** and **4**.

A mixture (1:2) of the isomers **3** and **4** was treated with trityl fluoroborate in dry acetonitrile under nitrogen, and 1*H*-benzo[1,2:4,5]dicycloheptenium tetrafluoroborate(1−) (**5**) was formed as dark red needles. The nmr spectrum (CD_3CN) was complex [τ 6.49 (H^A, d, $J \approx 6$ Hz), 3.97 (dd, H^B, $J \approx 6$, 10 Hz), 3.68 (H^C, dd, $J \approx 6$, 10 Hz) 3.07 (H^D, dd, $J \approx 6$, 12 Hz), 2.52 (H^E, d, $J \approx 12$ Hz), 1.18–1.46 (H^H, $H^{H'}$, H^F, H^J, m), 0.92 (H^I, dd, $J \approx 10$ Hz), 0.47 (H^G, $H^{G'}$, d, $J \approx 10$

(1) We thank Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service, for helpful discussions concerning the correct name for the cation.

(2) R. Legros and P. Cagniant, *C. R. Acad. Sci.*, **252**, 2733 (1961).

(3) For a second method of preparation, see R. H. Wightman, R. J. Wain, and D. H. Lake, *Can. J. Chem.*, **49**, 1360 (1971).