TABLE III

Compound	ϵ_1	V_1, ml/g	α	β, ml/g	P_2, cc	MR_D, cc	μ, D
Tetrahydrofuran[a,b]	2.2280	0.63085	8.59	0.4667	88.59	20.08	1.82
Tetrahydrothiophene[b]	2.2267	0.63078	8.90	0.3344	107.80	26.41	1.98
Tetrahydroselenophene[b]	2.2268	0.63085	3.98	0.1069	85.86	29.19	1.64
Tetrahydrofuran[c]	2.2725	1.14445	4.02	−0.0243	77.62	20.08	1.66
Tetrahydrothiophene[c]	2.2725	1.14445	4.34	−0.1542	97.94	26.41	1.85

[a] ϵ = dielectric constant, V_1 = specific volume, $\alpha = (\epsilon_{12} - \epsilon_1)/W_2$, $\beta = (V_{12} - V_1)/W_2$, W = weight fraction, P = polarization, MR_D = molar refraction. Subscripts: 1, solvent; 2, solute; 12, solution. [b] Measurements carried out in carbon tetrachloride. [c] Measurements carried out in benzene.

designed by Sayce and Briscoe;[19] the air capacitance is 25.99 pF. The cell constant, C_0, was determined from the capacitance, C_a, of the cell containing dry air and the capacitance, C_x, of the cell containing a liquid of known dielectric constant, ϵ, such as benzene or carbon tetrachloride.[20] The cell constant is given by $C_0 = (C_a\epsilon - C_x)/(\epsilon - 1)$.

Solution densities were measured at 25° with a pycnometer that had been calibrated with pure benzene, bp 79.6° (746 mm) (lit.[21] bp 79.6° (746 mm)).

The method of Halverstadt and Kumler[22] was used to calculate the dipole moments. The advantages of this method of treating solution data have been evaluated by Smyth.[23] The electronic polarization is taken as equal to the molar refraction of the solute. The atomic polarization may be assumed, with negligible error,[23] equal to 5% of the electronic polarization. The molar refractions are calculated from electron group refractions.[24] The dipole moments are calculated as

$$\mu = 0.22125({}_{\infty}P_2 - 1.05\mathrm{MR_D})^{1/2}$$

In this case, dielectric constants and specific volumes of the carbon tetrachloride and benzene solutions are found to be linear functions of the solute weight fraction over the range studied. The experimental and calculated quantities used to compute the dipole moment are given in Table III.

Registry No.—Benzene, 71-43-2; cyclopentane, 287-92-3; tetrahydrofuran, 109-99-9; tetrahydrothiophene, 110-01-0; tetrahydroselenophene, 3465-98-3; tetrahydrotellurophene, 3465-99-4; cyclopentanone, 120-92-3; tetramethylenesulfone, 126-33-0; methylenecyclopentane, 1528-30-9.

Acknowledgments.—The authors wish to thank L. E. Nelson for making the nmr measurements and Mobil Research and Development Corp. for permission to publish this work.

(19) L. A. Sayce and H. V. A. Briscoe, *J. Chem. Soc.*, 315 (1925).

(20) R. J. W. LeFevre, "Dipole Moments," Methuen and Co., Ltd., London, 1953, p 53.

(21) "Handbook of Chemistry and Physics," K. C. Weast, Ed., The Chemical Rubber Publishing Co., Cleveland, 1964, p D-124.

(22) I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

(23) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N.Y. 1955, p 224.

(24) See ref 23, p 409.

Acid-Catalyzed Ring Opening of 6,8-Dinitro-1,3-benzodioxane

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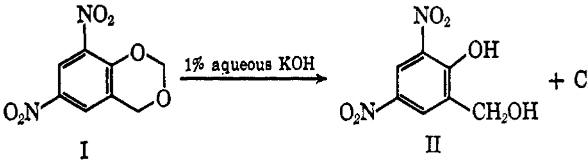
The preparation of 6,8-dinitro-1,3-benzodioxane (I) by the nitration of 6-nitro-1,3-benzodioxane was first described by Chattaway and Irving.[1] Their subsequent investigation[2] revealed that the 6,8-dinitro-1,3-benzodioxane was easily cleaved by dilute alkali to give 2-hydroxy-3,5-dinitrobenzyl alcohol (II).



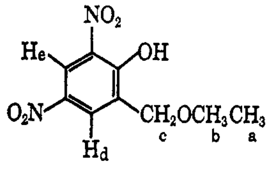
I II

In contrast to this, 6-nitro-1,3-benzodioxane was stable to boiling 25% aqueous alkali or alcoholic potassium ethoxide. Chattaway and Irving then postulated that the stability of this dioxane system toward alkali was decreased by electron-withdrawing groups in the 8 position.

The present investigation has led to the discovery of an acid-catalyzed ring cleavage of 6,8-dinitro-1,3-benzodioxane.

Results and Discussion

The yield of expected product from the nitration of 6-nitro-1,3-benzodioxane was dependent upon the reaction conditions employed. After 20 min at 0° the nitration gave good yields. Prolonged acid treatment at 40–50° led to oxidation and formation of dinitrosalicylic acid as well as the expected product. At intermediate temperatures (10–20°) small quantities of another by-product were formed. This acidic compound (NE 240 ± 2) was precipitated by the addition of water to the ethanolic mother liquor of recrystallization of crude 6,8-dinitro-1,3-benzodioxane and was shown to be 2,4-dinitro-6-ethoxymethylphenol (III) by synthesis using a previously described[3] procedure.



III

Nmr, δ
a, 1.33 (t)
b, 3.71 (q)
c, 4.66 (t, J = 0.7 Hz)
d, 8.62 (d, J = 3.0 Hz)
e, 8.97 (d, J = 3.0 Hz)

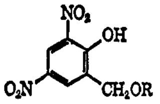
The ethoxy compound III and the corresponding methyl ether were found to arise from the dioxane I on treatment with the respective alcohols containing nitric acid. To avoid complications caused by the oxidative properties of nitric acid, the reaction was then performed using an aprotic Lewis acid. A butanol solution of 6,8-dinitro-1,3-benzodioxane containing 1 ml of boron

(1) F. D. Chattaway and H. Irving, *J. Chem. Soc.*, **1931**, 2492.

(2) F. D. Chattaway and H. Irving, *ibid.*, **1934**, 325.

(3) (a) Indian Patent 91,371 (June 1965); (b) French Patent 1,403,658 (Oct 1965).

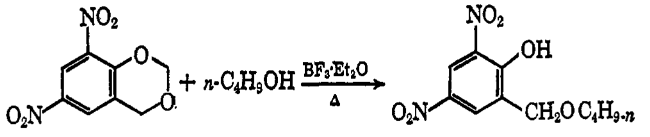
TABLE I
2-ALKOXYMETHYL-4,6-DINITROPHENOLS



No.[i]	R	Reacn conditions Time, hr	Reacn conditions Temp, °C	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1	CH_3	3	140[a]	84	64[b]	$C_8H_8N_2O_6$	42.11	3.53	12.28	42.18	3.55	12.41
2	C_2H_5	9	130[a]	67	66[c]	$C_9H_{10}N_2O^9$	44.60	4.16	11.62	44.48	4.39	11.88
3	$(CH_3)_2CH$	3	140[a]	99	87[d]	$C_{10}H_{12}N_2O_6$	46.88	4.72	10.93	46.78	4.91	11.26
4	$H_2C{=}CHCH_2$	3	140[a]	55	46	$C_{10}H_{10}N_2O_6$	47.25	3.96	11.02	47.30	4.17	11.03
5	n-C_4H_9	24	118	83	51[e]	$C_{11}H_{14}N_2O_6$	48.86	5.22	10.41	48.80	5.26	10.68
6	*sec*-C_4H_9	68	100	83	82[f]	$C_{11}H_{14}N_2O_6$	48.86	5.22	10.41	49.19	5.23	10.65
7	i-C_5H_{11}	24	130	88	51	$C_{12}H_{16}N_2O_6$	50.67	5.67	9.90	50.97	5.75	9.80
8	n-C_5H_{11}	4	135	46	47[g]	$C_{12}H_{16}N_2O_6$	50.67	5.67	9.90	50.95	5.63	10.21
9	n-C_6H_{13}	20	140	39	46	$C_{13}H_{18}N_2O_6$	52.34	6.08	9.39	52.61	6.15	9.34
10	$(C_2H_5)_2CHCH_2$	10	140	36	44	$C_{13}H_{18}N_2O_6$	52.34	6.08	9.39	52.55	6.15	9.49
11	$C_6H_5CH_2$	48	108	54	90	$C_{14}H_{12}N_2O_6$	55.24	3.97	9.25	55.42	4.06	9.14
12	$\underbrace{CH_2(CH_2)_4CH}-$	6.5	130	70	91[h]	$C_{13}H_{16}N_2O_6$	52.67	5.44	9.50	52.93	5.46	9.52
13	$(CH_3)_2\underbrace{CCH(OH)C(CH_3)_2CH}-$	6	110	15	107	$C_{15}H_{20}N_2O_7$	52.96	5.88	8.24	53.15	6.02	8.65

[a] Reaction performed in an autoclave. [b] Lit.[3a] mp 60–61°. [c] Lit.[3a] mp 84–85°. [e] Lit.[3a] mp 49–51°. [f] Lit.[3b] mp 81.5°. [g] Lit.[3a] mp 47–49°. [h] Lit.[3b] mp 87–89°. [i] Registry no.: 1, 2534-05-6; 3, 2542-34-9; 4, 16607-33-3; 6, 2634-04-0; 7, 16607-35-5; 8, 16607-36-6; 9, 16607-37-7; 10, 16607-38-8; 11, 16607-39-9; 12, 2633-96-7; 13, 16607-41-3.

trifluoride etherate was heated to reflux for 24 hr. The product isolated from this reaction was 2-butoxymethyl-4,6-dinitrophenol (IV).



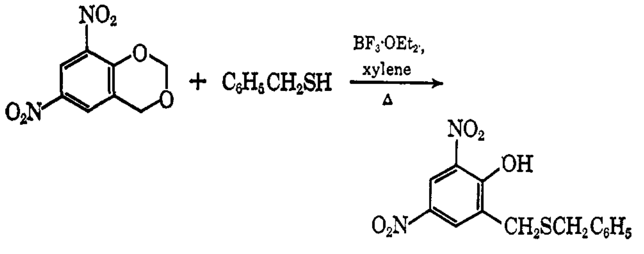
IV

This type of reaction was then extended to other alcohols and the products which were obtained are described in Table I. The reaction required prolonged heating whenever the temperature was maintained below 110°. This required reaction time was dramatically shortened when volatile alcohols were heated under pressure to effect the dioxane cleavage. For example, ethanol was converted in 67% yield into the ethoxymethyl derivative after 9 hr at 130° in an autoclave (41 psig), whereas only a 4% conversion into product was realized after 48 hr at normal reflux temperatures. Several other volatile alcohols were converted into the corresponding benzyl ethers in this fashion.

The scope of this reaction was partially defined when a variety of alcohols were employed as reagents. Formation of 2-alkoxymethyl-4,6-dinitrophenols by this method is apparently limited to the use of sterically unhindered alcohols. Attempted reactions of *t*-butyl alcohol, *t*-pentyl alcohol, diisobutylcarbinol, 4-methyl-2-pentanol, neohexanol and neooctanol all failed to give the desired benzyl ethers. One relatively hindered secondary alcohol, 2,2,4,4-tetramethylcyclobutane-1,3-diol, gave a 15% yield of the 1:1 benzylic ether adduct. In this case, the cyclobutane ring dictated the geometry of the system and minimized the interaction of the hydroxyl with the β-methyl groups. This reaction also proved that a diol could be converted into a 1:1 adduct in spite of the possibility of reaction at each hydroxyl. No attempt was made to isolate any other product.

The products described in Table I had very characteristic infrared spectra. The phenolic O–H stretch absorbed at 3.04–3.08 μ. This assignment was verified by comparison of the spectrum of 2-butoxymethyl-4,6-dinitrophenyl acetate with that of its phenol precursor. A sharp band at 3.05 μ from the phenol was significantly absent after formation of the acetate. Each product exhibited a strong absorption near 6.2 (C=C stretch) as well as a sharp band at 8.2–8.3 μ (OH deformation). The C–O stretch of the ether linkage appeared at 8.8–9.05 μ. In addition to the bands already mentioned, the infrared spectrum of the product from the cyclobutanediol had two sharp bands at 2.78 and 2.85 μ (presumably O–H stretch of *cis* and *trans* isomers).

The preparation of 2-benzylthiomethyl-4,6-dinitrophenol (V) demonstrated that the reaction could be extended to mercaptansm as well as alcohols.

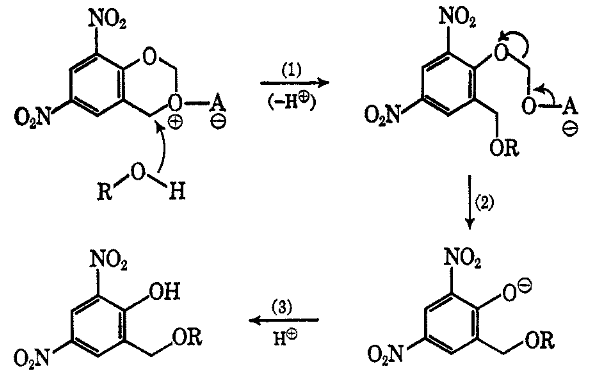


V

A variety of Lewis acids were successfully utilized as catalysts for this reaction. Butanol and 6,8-dinitro-1,3-benzodioxane were maintained at reflux temperature for 24 hr in each case. The catalysts with their corresponding yields of 2-butoxymethyl-4,6-dinitrophenol were as follows: zinc chloride (83%), sulfuric acid (78%), stannic chloride (74%), boric acid (72%), zinc iodide (72%), aluminum chloride (70%), mercuric chloride (70%), boron trifluoride etherate (68%), ferric chloride (59%), and bismuth chloride (41%).

Additional information concerning the scope and limitations of this reaction was obtained by the attempted reaction of 6-nitro-1,3-benzodioxane with butanol. After heating the solution for 24 hr in the presence of boron trifluoride etherate, starting material was quantitatively recovered. The requisite presence of the two nitro groups, in this reaction, led to the postulation of the mechanism in Scheme I where A is a

SCHEME I



Lewis acid. Elimination of formaldehyde from this system (step 2) is evidently dependent upon the formation of the dinitrophenoxide anion. In the absence of the second nitro group, the corresponding *p*-nitrophenoxide anion is considerably less stable as reflected by the fact that 4-nitrophenol is over a 1000-fold less acidic than 2,4-dinitrophenol. This difference in anion stability is so significant that step 2 of the mechanistic pathway is precluded in the mononitro case, and the reverse of step 1 occurs. The proposed mechanism also accounts for the lack of reactivity of sterically hindered alcohols; such attack would perforce create a severe 1,2 interaction with the Lewis acid.

Experimental Section[4]

The 6,8-dinitro-1,3-benzodioxane used as a starting material for this work was prepared according to the method of Chattaway and Irving.[1]

Procedure A is typical of that used to prepare the 2-alkoxymethyl-4,6-dinitrophenols at atmospheric pressure and was also used in the examination of the various Lewis acids as catalysts. Those reactions which were performed under pressure are typified by procedure B.

2-Butoxymethyl-4,6-dinitrophenol. A.—A mixture of 4.5 g (0.02 mol) of 6,8-dinitro-1,3-benzodioxane and 0.2 g of zinc chloride in 40 ml of butanol was stirred and heated to reflux for 24 hr. The resulting solution was chilled (ice bath) and treated with a few drops of water. The yellow platelets which crystallized were collected by suction filtration. Additional product was obtained from the filtrate by the addition of 20 ml of methanol followed by sufficient water to induce crystallization. The combined solids weighed 4.5 g (83% yield) and had mp 48–49°. Recrystallization from aqueous methanol gave an analytical sample.

2,4-Dinitro-6-isopropoxymethylphenol. B.—A 300-ml stainless steel microshaker autoclave was charged with 22.6 g (0.10 mol) of 6,8-dinitro-1,3-benzodioxane, 200 ml of isopropyl alcohol, and 1.0 ml of boron trifluoride etherate. The vessel was purged with nitrogen, then shaken, and heated to 140° for 3 hr. When the vessel had cooled to room temperature, the solution was collected and chilled (ice bath). The resulting tan solid was washed with water and had mp 86–87°. This product was dissolved in boiling methanol and the hot solution was decolorized with charcoal. Treatment of the yellow solution with a few drops of water induced crystallization and gave 25.3 g (99% yield) of analytically pure yellow platelets.

2-Benzylthiomethyl-4,6-dinitrophenol.—A mixture of 22.6 g (0.10 mol) of 6,8-dinitro-1,3-benzodioxane, 24.8 g (0.20 mol) of benzyl mercaptan, 1.0 ml of boron trifluoride etherate, and 225 ml of xylene was stirred and heated to 140° for 24 hr. The reaction mixture was cooled to precipitate 5.0 g of unreacted benzodioxane. The solution was then extracted with three 100-ml portions of 1 *M* sodium hydroxide and the combined aqueous extracts were chilled and acidified to pH 2 with 6 *N* hydrochloric acid. A black oil formed which was dissolved in boiling methanol and the solution was decolorized with charcoal. Chilling the red solution followed by the addition of water gave 2.8 g (11% yield) of yellow product, mp 127–129°. Two recrystallizations (first from aqueous ethanol, then from aqueous methanol) failed to change the melting point of the product.

Anal. Calcd for $C_{14}H_{12}N_2O_5S$: C, 52.47; H, 3.77; N, 8.79; S, 10.01. Found: C, 52.95; H, 4.00; N, 8.94; S, 10.31.

2,4-Dinitro-6-ethoxymethylphenol. A.—Boron trifluoride etherate catalysis and 48 hr at 78° gave a 4% conversion into product. The same procedure with sulfuric acid catalysis and 168 hr at reflux gave a 54% yield of product.

B.—After 9 hr at 130° in an autoclave a 67% yield of product was realized.

C.—A well-stirred solution of 11.3 g (0.05 mol) of 6,8-dinitro-1,3-benzodioxane, 50 ml of ethanol, and 0.5 ml of sulfuric acid in 50 ml of *p*-dioxane was heated to reflux for 30 hr. The solution was chilled and treated with 50 ml of water to give 5.0 g (41% yield) of product.

Registry No.—I, 16607-27-5; III, 2544-94-7; IV, 16607-29-7; V, 16607-30-0.

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Ring-Fused *meso* Ionic *s*-Triazole Derivatives[1]

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In a recent communication,[2] a series of *meso* ionic compounds containing the *s*-triazole nucleus was described. One synthetic procedure used in this earlier study has now been found to be of a general nature for the synthesis of *meso* ionic *s*-triazole derivatives. This paper describes the synthesis of several representative ring-fused systems and the route used here should be useful for the synthesis of numerous heterocyclic systems of unusual structure.

Reaction of the appropriate 2-halo heterocycle with methylhydrazine gave the corresponding 1-methyl-1-(2-heteryl)hydrazine, which underwent ready reaction with phosgene, thiophosgene, or cyanogen bromide to give the appropriate *meso* ionic product. Application of these reactions to the pyridine, quinoxaline, and benzothiazole ring systems gave the products described in Table I. As in our earlier work, analytical and spectral data clearly showed that ring closure to the fused ring system had occurred.

Rearrangement of the substitution pattern in the heterocyclic hydrazine, *e.g.*, replacement of 1-methyl-1-(2-pyridyl)hydrazine (1) with 1-amino-2-methylimino-

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(4) All melting points are uncorrected. Melting points were determined on a Mel-Temp capillary melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer; the nmr spectrum was run in deuteriochloroform solution with tetramethylsilane as an internal standard on a Varian A-60 spectrometer.

(1) (a) 1,2,4-Triazoles. Part XIX. (b) Support of this work by U. S. Public Health Service Research Grant CA 08495-01, National Cancer Institute, is gratefully acknowledged.

(2) K. T. Potts, S. K. Roy, and D. P. Jones, *J. Org. Chem.*, **32**, 2245 (1967).