the ester in 5 g of diethylamine for 2 hr resulted in the isolation of only starting material.

Reaction of Ethyl 2-Fluoro-2-nitropentanoate with Hydrochloric Acid.—A mixture of 1.93 g (0.010 mol) of ethyl 2-fluoro-2-nitropentanoate, 15 ml of concentrated hydrochloric acid, and 15 ml of water was refluxed for 2.5 hr. The solution was saturated with sodium chloride and extracted with three 15-ml portions of methylene chloride. Distillation gave 0.85 g (97% yield) of butyric acid, bp 164°.

Registry No.—2-Fluoro-2-nitro-1-butanol, 22538-29-0; 2-fluoro-2-nitro-1-pentanol, 22538-30-3; 2-fluoro-2-nitro-1-hexanol, 22538-31-4; 2-fluoro-2-nitro-1-heptanol, 22538-32-5; ethyl 2-fluoro-2-nitropentanoate, 22554-93-4; 2-fluoro-2,4,4-trinitropentane, 22538-33-6; 1-bromo-1-fluoro-1-nitropropane, 22538-34-7.

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One-Step Monobromination of Resorcinol Ethers

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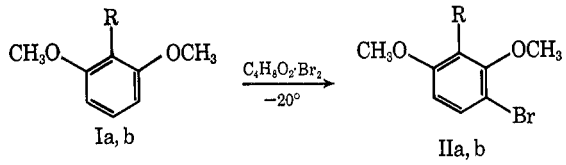
In the course of recent synthetic work, we found it necessary to monobrominate the highly activated aromatic ring of resorcinol dimethyl ether and 2-methylresorcinol dimethyl ether. Several earlier workers[2-4] had used multistep procedures to accomplish this, because direct bromination yielded a mixture of products. We have found, however, that bromination of these reactive systems with dioxane dibromide[5] in ether at a temperature of −20° gives the readily distilled, pure monobromo products (II) in high yields.



Ia, b IIa, b

I, IIa, R = H
b, R = CH_3

Experimental Section[6]

4-Bromoresorcinol Dimethyl Ether (IIa).—A solution of 18.2 g of anhydrous dioxane dibromide[6] in 100 ml of ether was added to a cooled solution (−20°) of 10.0 g of resorcinol dimethyl ether in 60 ml of ether during 15 min. After the addition, the solution was stirred until it reached room temperature. The ether was extracted twice with water and dried over anhydrous sodium sulfate. Removal of solvent on a rotary evaporator followed by vacuum distillation using a 9-cm Vigreux column gave 12.9 g (82%) of the desired product: bp 80–85° (0.2 mm) [lit.[2] bp 141–142° (14 mm)]; nmr ($CDCl_3$) δ 3.73 (s, 3, OCH_3), 3.80 (s, 3, OCH_3), 6.36 and 6.46 (m, 2, $J_{5,6}$ = 8.5 Hz, $J_{2,5}$ = 0.8 Hz, $J_{2,6}$ = 2.7 Hz, H-2 and H-6), and 7.37 (q, 1, H-5).

4-Bromo-2-methylresorcinol Dimethyl Ether (IIb).—The reaction was carried out exactly as in the preceding paragraph, employing 10.0 g of 2-methylresorcinol dimethyl ether. Simple removal of solvent (without washing) and vacuum distillation as above gave 13.4 g (90%) of the desired product: bp 92–96° (2.5 mm); nmr ($CDCl_3$) δ 2.18 (s, 3, $ArCH_3$), 3.75 (s, 3, OCH_3), 3.77 (s, 3, OCH_3), 6.43 (d, 1, $J_{5,6}$ = 8.7 Hz, H-6), and 7.20 (d, 1, H-5).

Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.75; H, 4.81; Br, 34.63. Found: C, 46.67; H, 4.73; Br, 34.72.

Registry No.—IIa, 77715-69-4; IIb, 22794-95-2.

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(1) National Institutes of Health Predoctoral Trainee in Biophysical Chemistry (Training Grant No. 2TI GM722).
(2) R. A. Benkeser, R. A. Hickner, D. I. Hoke, and O. H. Thomas, *J. Amer. Chem. Soc.*, **80**, 5289 (1958).
(3) R. Preuss and I. Janshen, *Arch. Pharm.*, **293**, 933 (1960).
(4) J. P. Lambooy, *J. Amer. Chem. Soc.*, **78**, 771 (1956).
(5) J. D. Billimoria and N. F. Maclagan, *J. Chem. Soc.*, 3257 (1954).
(6) Nmr spectra were recorded on a Varian A60-A spectrometer.

Amide–Hydrogen Halides Adducts from the Reaction of Acyl Halides and Amines

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Amide–acid adducts[2] (1) are commonly prepared through reaction of an amide with a protonic acid.[3-7]

$$RC(=O)NR_2' + HX \longrightarrow RC(=O)NR_2' \cdot HX$$

As a result of a study of the reaction of acetyl chloride with various amines, Dehn postulated, in 1912, an additional route for formation of the adducts[8] (eq 1).

$$CH_3C(=O)Cl + R_2NH \longrightarrow CH_3C(=O)NR_2 \cdot HCl \qquad (1)$$

Recently, Cook has suggested that adducts similar to 1 cannot be prepared by this route, since free amine would immediately convert the transient adduct into amide and the amine salt[9] (eq 2). We wish to confirm

$$1 + R_2'NH \longrightarrow RC(=O)NR_2' + R_2'NH_2^+X^- \qquad (2)$$

Dehn's postulate by reporting the isolation of amide–acid adducts from the reaction of acetyl halides with secondary amines, both in solution and in the gas phase.

In the course of a gas-phase reaction of acetyl chloride with dimethylamine, expected to produce N,N-di-

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(2) The term "amide salt," frequently used in describing these compounds, implies high ionic character. Alternatively, "amide–acid adduct" suggests lesser ionicity. Because compounds described here possess measurable vapor pressures at room temperature, the term "adduct" will be used with recognition that ionicity may vary considerably with changes in structure of both the amide and the acid.
(3) J. R. Blackborow, *J. Chem. Soc., C*, 739 (1969).
(4) O. D. Bonner, K. W. Bunzl, and G. B. Woolsey, *Spectrochim. Acta*, **22**, 1125 (1966).
(5) D. Cook, *Can. J. Chem.*, **42**, 2721 (1964).
(6) W. D. Kumler, *J. Amer. Chem. Soc.*, **83**, 4983 (1961).
(7) E. Spinner, *Spectrochim. Acta*, **15**, 95 (1959).
(8) W. H. Dehn, *J. Amer. Chem. Soc.*, **34**, 1399 (1912).
(9) D. Cook, *Can. J. Chem.*, **40**, 2362 (1962).