

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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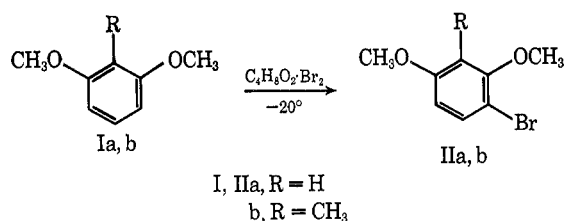
### One-Step Monobromination of Resorcinol Ethers

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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<sup>2-4</sup> 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<sup>5</sup> in ether at a temperature of -20° gives the readily distilled, pure monobromo products (II) in high yields.



#### Experimental Section<sup>6</sup>

**4-Bromoresorcinol Dimethyl Ether (IIa).**—A solution of 18.2 g of anhydrous dioxane dibromide<sup>5</sup> 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.<sup>2</sup> bp 141–142° (14 mm)]; nmr (CDCl<sub>3</sub>) δ 3.73 (s, 3, OCH<sub>3</sub>), 3.80 (s, 3, OCH<sub>3</sub>), 6.36 and 6.46 (m, 2, J<sub>5,6</sub> = 8.5 Hz, J<sub>2,5</sub> = 0.8 Hz, J<sub>2,6</sub> = 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<sub>3</sub>) δ 2.18 (s, 3, ArCH<sub>3</sub>), 3.75 (s, 3, OCH<sub>3</sub>), 3.77 (s, 3, OCH<sub>3</sub>), 6.43 (d, 1, J<sub>5,6</sub> = 8.7 Hz, H-6), and 7.20 (d, 1, H-5).

*Anal.* Calcd for C<sub>9</sub>H<sub>11</sub>BrO<sub>2</sub>: 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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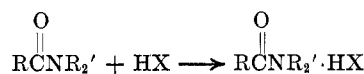
### Amide-Hydrogen Halides Adducts from the Reaction of Acyl Halides and Amines

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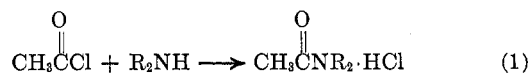
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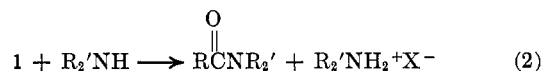
Amide-acid adducts<sup>2</sup> (1) are commonly prepared through reaction of an amide with a protonic acid.<sup>3-7</sup>



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<sup>8</sup> (eq 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<sup>9</sup> (eq 2). We wish to confirm



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.

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(6) Nmr spectra were recorded on a Varian A60-A spectrometer.

TABLE I

X	Mode of formation	CHARACTERIZATION OF $\text{CH}_3\text{CN}(\text{CH}_3)_2 \cdot \text{HX}$				Mp, °C	Lit.	
		Calcd		Found			Mp, °C	Ref
		Equiv wt	X, %	Equiv wt	X, %			
Cl	Gas phase	123.5	28.7	123.6	28.8	120-121	121-122	<i>b</i>
Cl	Ether			124	28.8	120-121		
Br	Gas phase	168	47.6	169	47.6	169-170	167-168	<i>b</i>
Br	Ether			168	47.6	167-168 <sup>c</sup>		
Br <sup>d</sup>	Gas phase	196	...	187	...	120-124	120-124	<i>e</i>
I	Gas phase	215	59.1	216	59.0	140-143 dec	140-143 dec	<i>b</i>
I'	Gas phase	233	54.5	230	54.8	64-68		

<sup>a</sup> Sealed tube unless otherwise indicated. <sup>b</sup> Reference 5. <sup>c</sup> Unsealed tube. <sup>d</sup> Reaction with diethylamine to give  $\text{CH}_3\text{CON}(\text{C}_2\text{H}_5)_2 \cdot \text{HBr}$ . <sup>e</sup> E. H. White, *J. Amer. Chem. Soc.*, **77**, 6215 (1955). <sup>f</sup> Monohydrate.

methylacetamide and hydrogen chloride, reaction-vessel walls became coated with small droplets which rapidly crystallized. Since it seemed reasonable that the liquid might have been the desired amide and the observed crystallization might have been due to increasing contamination with dimethylammonium chloride, vacuum distillation of the amide from the sides of the flask was attempted. Instead, sublimation occurred with separation of two crystalline phases: a colorless residue identified as dimethylammonium chloride, and a similar, but acidic, sublimate which proved to be the hydrochloride of *N,N*-dimethylacetamide. Yields of the adduct vary with reaction conditions but can approach quantitative amounts.

The adduct was also prepared by reaction of dimethylamine with acetyl chloride in ether at 0°. Filtration of the colorless precipitate and sublimation yielded 70% of the adduct. Infrared spectra of the adducts prepared by the two methods are identical and consistent with the reported<sup>5</sup> spectrum of  $\text{CH}_3\text{CON}(\text{CH}_3)_2 \cdot \text{HCl}$ .

Sensitivity of the reaction to amine stoichiometry may account for earlier doubts concerning the utility of this approach to preparation of the adducts.<sup>9</sup> Successful preparations require not only use of 1 equiv or less of the amine, but also a mode of mixing which precludes a local excess of amine. Thus in gas-phase reactions the amine must be diluted with helium and added to the acyl halide. In solution reactions the amine must be added slowly to a well stirred acyl halide solution. In general, the adduct must be formed in the presence of a local excess of acetyl halide. On formation, the adduct presumably separates from the reaction medium, effectively preventing its reaction with local excesses of free amine as suggested by Cook.<sup>9</sup>

#### Experimental Section

**Gas-Phase Preparation of *N,N*-Dimethylacetamide Hydrochloride.**—Adducts were prepared in a glass reactor consisting of two bulbs, individually connected to an existing vacuum system and connected to each other by a stopcock. In a typical preparation acetyl chloride (20 cm pressure, 0.011 mol) and dimethylamine (0.011 mol) were transferred, respectively, through the vacuum system into thoroughly dried bulbs. The flask containing amine was charged with dry helium to a total pressure of 40 cm and the connecting stopcock was opened rapidly to permit reaction. The rapid flow of the dimethylamine-helium mixture into the acetyl chloride provided a crude means of mixing the two reactants.

The reactor pressure began dropping immediately and reached 15.3 cm (equivalent to 73% completion) 30 sec after the stopcock had been opened. Concurrent with the pressure drop, a white solid began forming on the walls of the flask containing the

acetyl chloride. In other experiments this condensed phase appeared originally as a colorless liquid which rapidly solidified. When the reactor pressure had dropped to 10 cm, the calculated limit for the reaction, dry helium was added to a pressure of 76 cm. The flask containing most of the solid product was removed quickly and fitted with a cold-finger condenser. Vacuum sublimation of the solids at 40° yielded an acidic, colorless, crystalline sublimate.

Preparations of other adducts were similar except that lower pressures were used occasionally. Variations of molar ratios of the reactants markedly decreased the yields of adducts, particularly when excess amine was used. Because several adducts proved extremely hygroscopic, all handling of sublimed products was carried out in an atmosphere of dry nitrogen. The monohydrate of the HI· adduct was prepared by allowing the newly formed adduct to stand overnight in the presence of 2 cm of water vapor. Results are summarized in Table I.

No adducts were obtained from gas-phase reactions of acetyl cyanide and either dimethylamine or diethylamine, nor from oxalyl chloride and dimethylamine (which produces *N,N,N',N'*-tetramethyloxamide).

**Preparations in Ether.**—The HCl and HBr adducts were prepared in *ca.* 70 and 50% yields, respectively, by slow addition of an ethereal solution of the amine to a similar solution of the acetyl halide. The reaction mixture, protected by a drying tube, was stirred continuously and cooled in an ice-water bath during addition. Filtration, removal of ether under reduced pressure, and repeated sublimation of all solids gave material described in Table I. The hydrogen iodide adduct could not be prepared in good yield by a similar procedure.

**Registry No.**—*N,N*-Dimethylacetamide hydrochloride, 920-54-7; *N,N*-dimethylacetamide hydrobromide, 920-53-6; *N,N*-dimethylacetamide hydriodide, 920-55-8.

#### The Sulfonation of Negatively Substituted *t*-Butylbenzene Derivatives

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The possibility of ring sulfonation *ortho* to a *t*-butyl group is of special interest because of the high steric requirements of both moieties. 2,6-Di-*t*-butylpyridine is the only compound known to react in this manner.<sup>1,2</sup>

(1) N. Muller and W. J. Wallace, *J. Org. Chem.*, **24**, 1151 (1959).

(2) Dr. H. Cerfontain has suggested (privately) that the explanation may lie in ring deformation.