TABLE I

INTERACTION OF NITROSOBENZENE WITH PHENYLHYDRAZONES. REACTION CONDITIONS AND RESULTS

Expt[a]	Phenylhydrazone	Registry no.	1/2, mmol	Yield of 3,[b] % (mp, °C)[c]
A	Benzaldehyde	588-64-7	1:1	65 (112, lit.[d] 114)
B	Benzaldehyde		1.25:1	71
C	Benzaldehyde		1.50:1	86
D	Benzaldehyde		2.00:1	100[e]
E[f]	Benzaldehyde		1:1	~90[g]
F[h]	Benzaldehyde		1:1	35[i]
G	Benzaldehyde		1:1[j]	56
H	Benzaldehyde		1:1[k]	63
I	*p*-Nitrobenzaldehyde	2829-27-8	1:1	63 (187–188, lit.[d] 189)
J	*m*-Nitrobenzaldehyde	7539-23-3	1:1	63 (149–150, lit.[d] 154)
K	*p*-Chlorobenzaldehyde	2829-26-7	1:1	38[c] (153, lit.[l] 153–154)
L[m]	Fluorenone	15718-00-0	1:1	17 (192–193, lit.[n] 195–196.5)
M[o]	Fluorenone		2:1	49

[a] A 2-hr reaction time, benzene solvent, nitrogen atmosphere, except as noted. [b] Material recovered directly from chromatography, except as noted. [c] After recrystallization. [d] O. H. Wheeler and P. H. Gore, *J. Amer. Chem. Soc.*, **78**, 3363 (1956). [e] Traces of azoxybenzene isolated. [f] Air atmosphere. [g] Includes some crude material from which traces of impurities could not be removed. [h] Diethyl ether solvent. [i] Benzene produced in 39% yield. [j] Water added, H_2O/nitrosobenzene = 5 mmol. [k] Solvent benzene dried over sodium and distilled directly into reaction vessel. [l] V. Bellavita, *Gazz. Chim. Ital.*, **65**, 889 (1935). [m] A 19-hr reaction time. [n] A. W. Johnson, *J. Org. Chem.*, **28**, 252 (1963). [o] A 15-hr reaction time.

Experimental Section

Reagents.—Unless otherwise specified, commercially available reagents and solvents were used without purification. Melting points are corrected. Most nitrosobenzene was supplied by Aldrich; one batch was synthesized, mp 61–65° (lit.[9] mp 64–67°), by the method of Coleman, *et al.*[9] Phenylhydrazones were prepared according to the procedure outlined by Shriner, *et al.*[10]

Reaction of Nitrosobenzene with Benzaldehyde Phenylhydrazone. Neat Reaction.—Benzaldehyde phenylhydrazone (0.392 g, 2.0 mmol) was added to a three-necked flask fitted with a pressure-equalizing dropping funnel. The flask was flushed with nitrogen and cooled with an ice bath. A 0.214-g (2.0 mmol) portion of nitrosobenzene was added, but no change was noted until the ice bath was removed, at which time a sudden and highly exothermic reaction occurred and the mixture grew very dark. After 10 min, the reaction mixture was taken up in 30 ml of ether (previously flushed with nitrogen), and the solution was stirred briefly. The ether solution was evaporated, and the residue was taken up in a minimum amount of benzene. Chromatography on silica gel using benzene and benzene–methanol as solvents yielded 0.179 g of benzaldehyde phenylhydrazone (46% recovery) and 0.029 g of α-phenyl-N-phenyl nitrone (14% conversion).

Identification of the nitrone was made on the basis of its melting point, 112° from cyclohexane (lit.[11] mp 114°), infrared spectrum (bands matching those reported by Shindo and Umezawa[12]), and ultraviolet spectrum (λ_{max} matching those reported by Wheeler and Gore[11]). The nitrone was found to be stable to column chromatographic conditions described.

Nitrogen was produced from both neat and solution reactions; it was trapped over water and identified by diffusion-rate molecular-weight determination. Equimolar amounts of reagents in benzene liberated *ca.* $^2/_3$ mol of nitrogen. A heterogeneous surface (conveniently provided by 10–20 mg of charcoal per 1 mmol of reagent) enhanced the rate of gas production but not the volume.

Reactions of Phenylhydrazones with Nitrosobenzene in Solution.—A reaction using diethyl ether as a solvent was run in order to check for benzene production. Benzaldehyde phenylhydrazone (0.196 g, 1.0 mmol) was introduced into a three-necked flask fitted with magnetic stirrer, pressure-equalizing dropping funnel, and drying tube protected condenser. A 45-ml portion of dry ether was added to the funnel and degassed with dry nitrogen which proceeded *via* the funnel side-arm to flush the reaction flask before being emitted through the condenser. After 20 min, 15 ml of the ether was added to the reaction flask with stirring, and nitrosobenzene (0.107 g, 1.0 mmol) and 1.5 mmol of cyclohexane were dissolved in ether remaining in the dropping funnel. The nitrosobenzene solution was added in one portion to the reaction vessel, and immediate gas production was noted. The reaction mixture was stirred under a nitrogen atmosphere for 2 hr, and an aliquot was analyzed by vpc (6 ft × 0.25 in. SE-30 on firebrick column). With cyclohexane as an internal standard, benzene was found to be produced in 39% yield. The bulk of the reaction mixture was evaporated and subjected to column chromatography. The yield of nitrone was *ca.* 65 mg (35%), and *ca.* 60% of the phenylhydrazone of benzaldehyde was recovered.

The series of reactions run in benzene utilized essentially the same procedure as that outlined above, except that the nitrosobenzene in benzene was added dropwise to phenylhydrazone in benzene over a period of 20 min. Results are summarized in Table I, along with results of reactions of substituted phenylhydrazones with nitrosobenzene.

Reaction of Phenylhydrazine with Nitrosobenzene in the Presence of Benzaldehyde.—A solution of 0.107 g (1.0 mmol) of nitrosobenzene and 0.106 g (1.0 mmol) of benzaldehyde in 30 ml of dry, degassed benzene was added dropwise to a solution of 0.108 g (1.0 mmol) of phenylhydrazine in dry, degassed benzene. Upon chromatographic work-up, 57 mg (29%) of nitrone and 95 mg (48%) of crude benzaldehyde phenylhydrazone were isolated.

Registry No.—Nitrosobenzene, 586-96-9.

Acknowledgment.—A portion of this work was supported by the National Science Foundation (Grant GW-2900), for which we are sincerely grateful.

(9) G. H. Coleman, C. M. McCloskey, and F. A. Stuart, *Org. Syn.*, **25**, 80 (1945).

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, p 147. Melting points corresponded to tables in the text.

(11) Footnote *d*, Table I.

(12) H. Shindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 492 (1962).

Direct Fluorination of Secondary Nitronate Salts[1]

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Received June 23, 1969

A number of 1-fluoro-1,1-dinitro alkanes have been prepared by the direct fluorination of aqueous solutions

(1) This work was supported in part by the Office of Naval Research under Contract Nonr 2655(00) and by the U. S. Naval Ordnance Laboratory in collaboration with the U. S. Air Force Armament Laboratory, Air Force Systems Command, under Contract N60921-67-C-0290.

of nitro nitronate salts.[2-4] The application of this reaction to salts of mononitro compounds has been used to prepare simple α-fluoronitro compounds,[2,5] as well as α-fluoronitro-substituted malonates,[6] cyanoacetates,[6] ketones,[5] nitriles,[5] and an alcohol, 2-fluoro-2-nitropropanediol.[7] This reaction has now been used to prepare simple 2-fluoro-2-nitro alcohols and a 2-fluoro-2-nitro ester; some chemical properties of these compounds are described.

Direct fluorination of salts of 2-nitro alcohols in aqueous solution afforded 2-fluoro-2-nitro-1-butanol, 2-fluoro-2-nitro-1-pentanol, 2-fluoro-2-nitro-1-hexanol, and 2-fluoro-2-nitro-1-heptanol in yields of 21–42.5%. As in the fluorinations of other mononitro salts, an acid-forming side reaction resulted in the liberation of unfluorinated nitro compounds, but the boiling points differed sufficiently from those of the products to allow isolation by fractional distillation.

$$CH_3(CH_2)_n\overset{\overset{NO_2^-}{\|}}{C}CH_2OH \xrightarrow[H_2O]{F_2} CH_3(CH_2)_n\overset{\overset{NO_2}{|}}{\underset{\underset{F}{|}}{C}}CH_2OH \qquad n = 1\text{–}4$$

The activating effect of a carboalkoxy group was demonstrated using ethyl 2-nitropentanoate. The fluorination of the nitronate salt gave ethyl 2-fluoro-2-nitropentanoate in 85% yield (54.5% conversion).

$$CH_3CH_2CH_2\overset{\overset{NO_2^-}{\|}}{C}CO_2C_2H_5 \xrightarrow[H_2O]{F_2} CH_3CH_2CH_2\overset{\overset{NO_2}{|}}{\underset{\underset{F}{|}}{C}}CO_2C_2H_5$$

Sodium 4,4-dinitro-2-pentanenitronate, available in connection with another study,[8] was also fluorinated, and 2-fluoro-2,4,4-trinitropentane was isolated in 11.5% yield. In this case column chromatography was used to isolate the product.

$$CH_3\overset{\overset{NO_2}{|}}{\underset{\underset{NO_2}{|}}{C}}CH_2\overset{\overset{NO_2^-}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{NO_2}{|}}{\underset{\underset{NO_2}{|}}{C}}CH_2\overset{\overset{NO_2}{|}}{\underset{\underset{F}{|}}{C}}CH_3$$

Since 2-nitro alcohols and 2-nitro acids readily undergo deformylation and decarboxylation, respectively, the fluoro derivatives could be expected to serve as convenient precursors to 1-fluoro-1-nitro alkanes. One must bear in mind, however, that α fluorines have been shown to decrease the acidity of substituted nitro methanes,[9] and this destabilization of nitronate salts would also tend to inhibit the deformylation and decarboxylation reactions.

Attempts to deformylate 2-fluoro-2-nitro alcohols in the presence of base did not lead to 1-fluoro-1-nitro alkanes. However, 2-fluoro-2-nitro-1-butanol reacted with aqueous sodium hypobromite solution to give 1-bromo-1-fluoro-1-nitropropane. Thus the α-fluoronitronate salt must be capable of at least transitory existence. The reaction of 1-bromo-1-fluoro-1-nitropropane with difluoramine in strong acid to give 1-bromo-1-difluoramino-1-fluoropropane has been reported.[8]

$$CH_3CH_2\overset{\overset{F}{|}}{\underset{\underset{NO_2}{|}}{C}}CH_2OH \xrightarrow[H_2O]{NaOBr} CH_3CH_2\overset{\overset{F}{|}}{\underset{\underset{NO_2}{|}}{C}}Br$$

The oxidation of 2-fluoro-2-nitro-1-heptanol with aqueous chromic acid gave only caproic acid. Under the same conditions, 2-fluoro-2,2-dinitroethanol gave fluorodinitromethane in 63% yield (47% conversion). This reaction provides a convenient laboratory synthesis of fluorodinitromethane; the previously reported synthesis by alkaline deformylation of 2-fluoro-2,2-dinitroethanol requires isolation of the hazardous nitronate salt intermediate.[9] The probable path of these oxidations involves carboxylic acid intermediates which undergo decarboxylation, and in the case of 2-fluoro-2-nitro-1-heptanol, further oxidation and hydrolysis.

$$FC(NO_2)_2CH_2OH \xrightarrow[H_2O]{H_2CrO_4} FC(NO_2)_2H$$

$$R\overset{\overset{F}{|}}{\underset{\underset{NO_2}{|}}{C}}CH_2OH \longrightarrow RCO_2H$$

Chlorofluoronitroacetate esters have been reported to yield chlorofluoronitromethane at ambient temperature on reaction with diethylamine[10] or water.[6] Ethyl 2-fluoro-2-nitropentanoate, however, was unreactive under these conditions or with refluxing diethylamine or aqueous sodium hydroxide solution at 0°. Refluxing aqueous sodium hydroxide gave a complex mixture of degradation products, whereas refluxing 18% hydrochloric acid gave a quantitative yield of butyric acid.

$$CH_3CH_2CH_2\overset{\overset{NO_2}{|}}{\underset{\underset{F}{|}}{C}}CO_2C_2H_5 \xrightarrow{HCl} CH_3CH_2CH_2COOH$$

Infrared and nmr spectra of the new compounds are described in the Experimental Section. An unusual feature of the proton spectra of the fluoronitro alcohols and 2-fluoro-2,4,4-trinitropentane is that methylenes adjacent to fluoronitro groups have the appearance of a singlet and an AB quartet of 1 H area each. The methylene hydrogens are nonequivalent because of the adjacent asymmetric center, and the observed ABX profile can result[11] from equality of the difference in chemical shifts to $^1/_2(J_{AX} - J_{BX})$.

Experimental Section

General.—Fluorinations were carried out in glass apparatus as described previously.[2] The fluorine was diluted fourfold–sixfold with nitrogen.

(2) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).
(3) M. J. Kamlet and H. G. Adolph, *ibid.*, **33**, 3073 (1968).
(4) L. T. Eremenko and F. Ya. Natsibullin, *Izv. Akad. Nauk SSSR*, 912 (1968).
(5) H. Feuer, Progress Report No. 28, Contract Nonr-1100(13), Dec 1966. Available through the Defense Documentation Center, Cameron Station, Alexandria, Va.
(6) H. G. Adolph, R. E. Oesterling, and M. E. Sitzmann, *J. Org. Chem.*, **33**, 4296 (1968).
(7) H. J. Marcus, presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.
(8) K. Baum, *J. Org. Chem.*, **34**, 2049 (1969).
(9) H. G. Adolph and M. J. Kamlet, *ibid.*, **34**, 45 (1969).
(10) I. V. Martynov and Y. L. Kruglyak, *Zh. Obshch. Khim.*, **37**, 1221 (1967).
(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 132–135; "High Resolution NMR Spectra Catalog," Vol. 2, Varian Associates, New York, N. Y., 1963, Spectrum No. 382.

2-Fluoro-2-nitro-1-butanol.—A solution of 230 g (1.93 mol) of 2-nitro-1-butanol and 85.1 g (2.12 mol) of sodium hydroxide in 4 l. of water was treated with 2 mol of fluorine at 5–10° over a 2-hr period. The solution was saturated with sodium chloride and extracted with five 400-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled through a 10-cm Vigreux column to give 110 g of impure 2-fluoro-2-nitro-1-butanol, bp 57–60° (0.8 mm), and 37 g of 2-nitro-1-butanol, bp 65–72° (0.8 mm). Redistillation gave 91.3 g (34.5% conversion, 42.5% yield) of 2-fluoro-2-nitro-1-butanol, bp 102–104° (13 mm). A total of 43 g of starting material was recovered.

Anal. Calcd for $C_4H_8NO_3F$: C, 35.04; H, 5.84; N, 10.22. Found: C, 34.90; H, 5.90; N, 10.11.

The fluorine nmr spectrum (CCl_4 solution) consisted of a symmetrical multiplet at ϕ^* 139.8. The proton nmr spectrum consisted of a triplet for the methyl at δ 1.01 (J = 7.5 cps), a multiplet for the methylene of the ethyl group at δ 2.23, a broad singlet at δ 3.0 shifted by dilution for the hydroxyl, and the AB portion of an ABX pattern for $-CH_2OH$ (δ_A 4.00, δ_B 4.14, J_{AB} = 14.0 cps, J_{AX} = 26.2 cps, J_{BX} = 9.8 cps). Prominent infrared bands were at 3.0, 6.40, 9.3, and 12.0 μ.

2-Fluoro-2-nitro-1-pentanol.—A solution of 102 g (0.99 mol) of 1-nitrobutane, 40 g (1.0 mol) of sodium hydroxide, and 84 g (1.0 mol) of formalin in 1250 ml of water was treated with 1 mol of fluorine. The product was isolated as above, but using a 25-cm Holzmann column for the distillation, to give 31.0 g (21% yield) of 2-fluoro-2-nitro-1-pentanol, bp 29–30° (0.025 mm).

Anal. Calcd for $C_5H_{10}NO_3F$: C, 39.74; H, 6.67; N, 9.27. Found: C, 39.71; H, 6.63; N, 9.40.

The fluorine nmr spectrum (CCl_4 solution) consisted of a multiplet at ϕ^* 138.1 with a profile identical with that of 2-fluoro-2-nitro-1-butanol. The proton nmr spectrum consisted of a triplet (J = 7 cps) at δ 1.00 for the methyl, multiplets at δ 1.5 and 2.1 for the propyl methylenes, a broad singlet at δ 3.3 for the hydroxyl, and the AB portion of an ABX pattern for the carbinol protons (δ_A 4.12, δ_B 3.98, J_{AB} = 13.8 cps, J_{AX} = 25.1 cps, J_{BX} = 10.4 cps). Prominent infrared bands were at 2.9, 6.40, 9.18, and 11.85 μ.

2-Fluoro-2-nitro-1-hexanol.—The fluorination of a solution of 52.0 g (0.445 mol) of 1-nitropentane, 17.8 g (0.445 mol) of sodium hydroxide, and 37.4 g (0.445 mol) of formalin in 600 ml of water by the above procedure gave 21.2 g (28.4%) of 2-fluoro-2-nitro-1-hexanol, bp 42–43° (0.025 mm).

Anal. Calcd for $C_6H_{12}NO_3F$: C, 43.63; H, 7.33; N, 8.45. Found: C, 43.67; H, 7.51; N, 8.13.

The fluorine nmr spectrum consisted of a multiplet at ϕ^* 138.2. The proton spectrum (pyridine solution) consisted of a triplet (J = 6.1 cps) at δ 0.77 for the methyl, multiplets at δ 1.3 and 2.2 for the butyl methylenes, and the AB portion of an ABX pattern for the carbinol protons (δ_A 4.52, δ_B 4.35, J_{AB} = 13.4 cps, J_{AX} = 30.4 cps, J_{BX} = 9.7 cps). Prominent infrared bands were at 2.9, 6.40, 9.1, and 11.85 μ.

2-Fluoro-2-nitro-1-heptanol.—The above procedure with 60 g (0.457 mol) of 1-nitrohexane gave 20.0 g (24.5%) of analytically pure 2-fluoro-2-nitro-1-heptanol. Two redistillations were required to remove 2-nitro-1-heptanol.

Anal. Calcd for $C_7H_{14}NO_3F$: C, 46.93; H, 7.82; N, 7.82. Found: C, 46.76; H, 7.97; N, 7.47.

The fluorine nmr spectrum (pyridine solution) consisted of a multiplet at ϕ^* 137.7. The proton spectrum showed a triplet (J = 4.9 cps) at δ 0.82 for the methyl, multiplets at δ 1.2 and 2.3 for the pentyl methylenes, and the AB portion of an ABX pattern for the carbinol methylene (δ_A 4.35, δ_B 4.52, J_{AB} = 13.8 cps, J_{AX} = 30.3 cps, J_{BX} = 9.8 cps). Prominent infrared bands were at 2.95, 6.40, 9.1, 9.4, and 11.88 μ.

Ethyl 2-Fluoro-2-nitropentanoate.—A solution of 160 g (0.91 mol) of ethyl 2-nitropentanoate[12] and 1.0 mol of sodium hydroxide in 2 l. of water was fluorinated at 0–5° with 1 mol of fluorine. The product was extracted with methylene chloride, dried over sodium sulfate, and distilled through a 25-cm Holzmann column to give 96 g (54.5% conversion, 85% yield) of ethyl 2-fluoro-2-nitropentanoate, bp 36° (0.35 mm), and 57.5 g (0.33 mol) of recovered ethyl 2-nitropentanoate, bp 39° (0.025 mm).

Anal. Calcd for $C_7H_{12}NO_4F$: C, 43.49; H, 6.26; N, 7.25. Found: C, 43.48; H, 6.03; N, 7.14.

(12) N. Kornblum, R. K. Blackwood, and J. Powers, *J. Amer. Chem. Soc.*, **79**, 2507 (1957).

The proton nmr spectrum (CCl_4 solution) consisted of a quartet (J = 5.4 cps) at δ 4.3 for the ethoxy methylene, a doublet (J_{HF} = 20 cps) of triplets (J = 7 cps) at δ 2.40 for CH_2-$CFNO_2$–, and a triplet at δ 1.30 for the ethoxy methyl superimposed over a methylene multiplet near δ 1.30 and a distorted methyl triplet (J = 6.4 cps) at δ 0.98. The fluorine nmr spectrum consisted of a broadened triplet (J = 20.8 cps) at ϕ^* 125.2. The infrared spectrum showed a carbonyl band at 5.74 μ and a nitro band at 6.43 μ.

2-Fluoro-2,4,4-trinitropentane.—2-Nitropropene (4.35 g, 0.050 mol) was added dropwise with stirring to a solution of 6.0 g (0.050 mol) of 1,1-dinitroethane in 40 ml of 1.25 N sodium hydroxide at 0–10°. The resulting suspension of sodium 4,4-dinitro-2-pentanenitronate[8] was fluorinated at 0–5° with 0.05 mol of fluorine. The product was extracted with 80 ml of methylene chloride, dried over sodium sulfate, and distilled to give 4.9 g of liquid, bp 80–110° (0.2 mm). Column chromatography, using a 35 × 220 mm column of neutral active alumina and ethyl ether, gave 0.1 g of residue from the first 300 ml of eluent, 1.30 g from the next 50 ml, and subsequently only 0.08 g. The 1.30-g fraction was identified as 2-fluoro-2,4,4-trinitropentane (11.5% overall yield), bp 53° (0.025 mm).

Anal. Calcd for $C_5H_8N_3FO_6$: C, 26.67; H, 3.55; N, 18.67; F, 8.45. Found: C, 26.97; H, 3.28; N, 18.11; F, 8.51.

The infrared spectrum consisted of peaks at 3.31 (w), 3.36 (w), 3.43 (w), 6.37 (vs), 6.90 (m), 7.17 (s), 7.30 (m), 7.40 (m), 7.57 (s), 8.06 (s), 8.5 (m), 8.66 (m), 11.4 (w), and 11.80 μ (s).

The fluorine nmr spectrum (no solvent) consisted of a symmetrical multiplet at ϕ^* 122.5. The proton spectrum consisted of a doublet (J = 21 cps) at δ 2.07 for $-CF(NO_2)CH_3$, a singlet at δ 2.75 for $-C(NO_2)_2CH_3$, and an ABX pattern for the methylene (δ_A 3.78, δ_B 3.67, J_{AX} = 22.8 cps, J_{BX} = 7.5 cps, J_{AB} = 16.5 cps).

1-Bromo-1-fluoro-1-nitropropane.—To a freshly prepared solution at 10° of 1.25 mol of bromine and 2.50 mol of sodium hydroxide in 1500 ml of water, 68.6 g (0.50 mol) of 2-fluoro-2-nitro-1-butanol was added over a 10-min period and the mixture was allowed to stand for 30 min at 10°. The product was extracted with three 100-ml portions of methylene chloride, dried over sodium sulfate, and distilled through a 25-cm Holzmann column to give 30.0 g (32% conversion, 56.5% yield) of 1-bromo-1-fluoro-1-nitropropane, bp 90° (47 mm), and 22.4 g of recovered 2-fluoro-2-nitro-1-butanol.

Anal. Calcd for $C_3H_5NO_2BrF$: C, 19.37; H, 2.69; N, 7.53. Found: C, 19.37; H, 2.72; N, 7.63.

The proton nmr spectrum consisted of a triplet (J = 7.3 cps) at δ 1.1 for the methyl and a doublet of quartets (J_{HF} = 18 cps, J_{HH} = 7.3 cps) at δ 2.8 for the methylene. The fluorine spectrum consisted of a distorted triplet (J = 18.5 cps) at ϕ^* 85.6. The infrared spectrum consisted of peaks at 3.32 (w), 3.36 (w), 3.41 (w), 6.32 (s), 6.84 (m), 6.98 (m), 7.2 (w), 7.41 (s), 7.5 (s), 7.79 (s), 8.30 (s), 8.90 (s), 9.30 (s), 9.50 (w), 10.00 (s), 10.50 (s), 10.60 (s), 11.30 (m), 11.70 (w), 12.30 (s), 12.9 (sh), and 13.11 μ (m).

Fluorodinitromethane.—A solution of 100 g (0.65 mol) of 2-fluoro-2,2-dinitroethanol in 280 ml of concentrated sulfuric acid and 165 ml of water was added with stirring, over a 30-min period, to a solution of 400 g (1.34 mol) of sodium dichromate dihydrate in 800 ml of water at 25–40°. The solution was allowed to stand at ambient temperature for 66 hr and then extracted with three 300-ml portions of methylene chloride. Distillation through a 25-cm Holzmann column gave 38 g (47% conversion, 63% yield) of fluorodinitromethane,[3] bp 40° (20 mm), and 19.0 g of 2-fluoro-2,2-dinitroethanol, bp 38–39° (0.1 mm). An additional 6.2 g of 2-fluoro-2,2-dinitroethanol was recovered by diluting the aqueous layer with an equal volume of water and extracting with ether.

Oxidation of 2-Fluoro-2-nitroheptanol.—2-Fluoro-2-nitro-1-heptanol (4.0 g, 0.022 mol) was added to a solution of 20 g of sodium dichromate dihydrate and 14 ml of concentrated sulfuric acid in 48 ml of water. After 3 days, the solution was diluted with an equal volume of water and extracted with three 50-ml portions of methylene chloride. Distillation gave 1.92 g (75% yield) of caproic acid, bp 65° (1 mm).

Reaction of Ethyl 2-Fluoro-2-nitropentanoate with Diethylamine.—A solution of 1.93 g (0.010 mol) of ethyl 2-fluoro-2-nitropentanoate in 2 g of diethylamine was allowed to stand for 24 hr at ambient temperature. Distillation gave 1.47 g (76%) of unchanged starting material. Refluxing a solution of 1 g of

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.

Acknowledgment.—The author is indebted to Mr. K. Inouye for elemental analysis, to Mr. L. A. Maucieri and Dr. W. R. Woolfenden for nmr analysis, and to Mr. H. F. Shuey for assistance in the synthesis work.

One-Step Monobromination of Resorcinol Ethers

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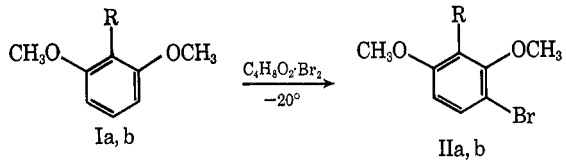
Received September 17, 1969

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.

Acknowledgment.—This research was supported in part by a grant (AI 01278) from the National Institute of Allergy and Infectious Diseases.

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

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Received July 14, 1969

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.
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