tone-*d*), ^1H at τ 2.23 (broad, 2, $=NNH_2$), 4.37 (broad doublet, 1, $J_{NH/CH}$ = 9.5 Hz, $-NHNH_2$), 5.22 (eight lines, 1, doublet ($J_{CH/NH}$ = 9.5 Hz into overlapping quadruplets, J_{H/CF_3} = 7.3 Hz, CH), and 6.66 (singlet, 2, $NHNH_2$); ^{19}F at 68.2 (quadruplet, 3, J_{CF_3/CF_3} = 3.2 Hz, $CF_3C{=}N$) and 73.4 ppm (eight lines, 3, doublet, $J_{CF_3/H}$ = 7.3 Hz into overlapping quadruplets, J_{CF_3/CF_3} = 3.2 Hz, CF_3CH); mass spectrum 224 (5), 194 (42), 155 (21), 145 (16), 113 (27), 111 (17), 105 (23), 95 (28), 93 (20), 75 (19), 69 (48), 43 (39), 31 (100), 29 (23), 28 (52).

Anal. Calcd for $C_4H_6F_6N_4$: C, 21.43; H, 2.70; F, 50.86; N, 25.00; mol wt, 224. Found: C, 22.10; H, 2.88; F, 50.94; N, 24.86; mol wt, 224 (mass spectrometer).

B. Low-Melting Isomer.—A mixture of 32 g (1.0 mol) of anhydrous hydrazine and 100 ml of acetonitrile was stirred and cooled at 0° while 58 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene was added dropwise over 30 min. The mixture was stirred an additional 0.5 hr, during which time it was allowed to warm spontaneously to 34°. It was then filtered, and the solid filter cake was rinsed with acetonitrile. Evaporation of the solvent from the combined filtrate and washings, followed by distillation in a short-path still, afforded 26 g of the crude hydrazone (low-melting isomer), bp *ca.* 80° (0.5 mm). Redistillation in a molecular still under 0.5-mm pressure with the pot at 90° gave 23.8 g (42%) of hydrazone as a distillate which solidified to a white solid, mp 51–53°.

A 17.4-g sample of this hydrazone was dissolved in methylene chloride, and the less soluble high-melting isomer was filtered off. The filtrate was evaporated to a low volume, and petroleum ether (bp 30–60°) was added until cloudiness persisted. The mixture was filtered again and cooled to 0°. The precipitate of low-melting isomer was filtered off and further purified by sublimation at 45° (1 mm) to give 12.1 g of the low-melting isomer of 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone as colorless crystals, mp 52–53°. This was resublimed before analysis: ir (KBr) 2.92 (sh), 3.00, 3.05, and 3.13 (sh) (NH, NH_2), 3.45 (saturated CH), 6.15 (sh) and 6.25 μ (NH_2); nmr ($CDCl_3$), ^1H at τ 2.40 (broad, 2, $=NNH_2$), 5.77 (quadruplet, 1, J_{H/CF_3} = 7.5 Hz, CH), and 6.55 (singlet, 3, $NHNH_2$); ^{19}F at 67.6 (quadruplet, 3, J_{CF_3/CF_3} = 3.7 Hz, $CF_3C{=}N$) and 70.2 ppm (six lines, 3, doublet, $J_{CF_3/H}$ = 7.5 Hz into overlapping quadruplets, J_{CF_3/CF_3} = 3.7 Hz, CF_3CH); mass spectrum 224 (10), 194 (79), 174 (24), 155 (38), 125 (16), 113 (30), 111 (29), 105 (41), 93 (33), 75 (22), 69 (60), 66 (17), 43 (54), 32 (39), 31 (100), 29 (35), 28 (57), 17 (25).

Anal. Calcd for $C_4H_6F_6N_4$: C, 21.43; H, 2.70; F, 50.86; N, 25.00; mol wt, 224. Found: C, 21.90; H, 2.88; F, 50.78; N, 25.69; mol wt, 222, 238 (fp benzene); 224 (mass spectrometer).

Registry No.—*syn* **2**, 17603-96-2; *anti* **2**, 17603-97-3; **3**, 17603-98-4; **6**, 17603-99-5; **7**, 17604-00-1; *syn* **9**, 17604-01-2; *anti* **9**, 17604-02-3; **10**, 17604-03-4; **11**, 17604-30-7; **12**, 17604-31-8; **13**, 17604-32-9; **14**, 17604-33-0.

Fluoronitroaliphatics. IV.[1] Some Reactions of 2-Fluoro-2,2-dinitroethanol

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A variety of reactions of 2-fluoro-2,2-dinitroethanol, primarily involving its hydroxyl function, are described. In certain of its reactions this material parallels other polynitroethanols; in others its reactivity behavior differs markedly. A possible basis for this dual reactivity is suggested.

In a previous paper[2] we reported the first synthesis of fluorodinitromethyl compounds by the perchloryl fluoride fluorination of the corresponding 1,1-dinitroalkane salts as well as improvements and extensions in scope of the preparative methods for such materials which resulted from the Grakauskas aqueous fluorination procedure.[3] In the light of the extensive polynitroaliphatic chemistry which has centered on 2,2,2-trinitroethanol, 2,2-dinitroethanol and 2,2-dinitropropanol as intermediates,[4,5] 2-fluoro-2,2-dinitroethanol (**1**) seemed the most interesting and potentially the most useful of the new fluoro derivatives described. We have therefore investigated the chemistry of **1** in greater detail and wish now to report that it is, indeed, a highly versatile reagent for the introduction of the fluorodinitroethoxy, the fluorodinitroethyl and, indirectly, the fluorodinitromethyl groups into organic molecules.

It was expected that in its reactivity **1** would resemble other highly negatively substituted acidic alcohols such as 2,2,2-trinitroethanol, 2-substituted 2,2-dinitroethanols, and 2,2,2-trifluoroethanol.[4–6] In the course of the present investigation this expectation was confirmed in a number of respects. It will be shown, however, that, in certain other regards, primarily in its behavior with bases, the reactions of **1** deviate considerably from established pathways.

Esterification.—Reactions of fluorodinitroethanol with a variety of acid chlorides proceeded smoothly in the manner described previously for 2,2-dinitroalkanols.[7] Acetyl chloride, for example, reacted readily with **1** in the absence of catalyst or base. With *p*-toluenesulfonyl chloride, the condensation reaction proceeded in the presence of pyridine or pyridine N-oxide.[8]

As with 2,2,2-trichloro-, tribromo-, trifluoro-, and trinitroethanol,[9,10] aluminum chloride has proven an effective catalyst for the esterification of **1** with less reactive acid chlorides. A preferred method of effecting the reaction is to treat **1** with 1 equiv of aluminum chloride in an inert solvent to form the soluble fluoro-

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[1] Part III: H. G. Adolph, R. E. Oesterling, and M. E. Sitzmann, *J. Org. Chem.*, **33**, 4296 (1968).

[2] M. J. Kamlet and H. G. Adolph, *ibid.*, **33**, 3073 (1968).

[3] V. Grakauskas and K. Baum, *ibid.*, **33**, 3080 (1968).

[4] A detailed review of the chemistry of 2,2,2-trinitroethanol and 2,2-dinitroethanol may be found in Reports No. 461 and 494, Aerojet Engineering Corp., Azusa, Calif., available through the Defense Documentation Center, Cameron Station, Alexandria, Va.

[5] Several dozen papers and scores of patents describe derivatives of these polynitro alcohols. An excellent review through 1962 is given by P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **61**, 19 (1964).

[6] Booklet DC-1254, "Trifluoroethanol," Pennsalt Chemicals Corp., Three Penn Center, Philadelphia 2, Pa.

[7] L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, *J. Org. Chem.*, **28**, 2491 (1963); H. E. Ungnade and L. W. Kissinger, *ibid.*, **31**, 369 (1966).

[8] T. N. Hall, *J. Org. Chem.*, in press.

[9] M. E. Hill, *J. Amer. Chem. Soc.*, **76**, 2329 (1954); **75**, 3020 (1953).

[10] M. E. Hill, U. S. Patent 3,375,266 (March 26, 1968); *Chem. Abstr.*, **61**, 106545 (1968).

$$\begin{tikzcd}
 & \underset{\mathbf{2}}{CF(NO_2)_2CH_2OCOCH_3} \\
\underset{\mathbf{1}}{CF(NO_2)_2CH_2OH} \arrow[ur, "CH_3COCl"] \arrow[dr, "p\text{-}CH_3C_6H_4SO_2Cl"', "C_5H_5N \text{ or } C_5H_5N\rightarrow O"] & \\
 & \underset{\mathbf{3}}{CF(NO_2)_2CH_2OSO_2C_6H_4CH_3\text{-}p}
\end{tikzcd}$$

dinitroethyl dichloroaluminate (**4**) which, with the acid chloride, forms an ester–aluminum chloride complex from which the free ester may be recovered on treatment with dilute mineral acid. 2-Fluoro-2,2-dinitroethyl 3,5-dinitrobenzoate (**5**) was prepared in this manner in 78% yield.

$$FC(NO_2)_2CH_2OH + AlCl_3 \longrightarrow \underset{\mathbf{4}}{[FC(NO_2)_2CH_2OAlCl_2]} \xrightarrow[2.\ H^+,\ H_2O]{1.\ 3,5\text{-}(NO_2)_2C_6H_3COCl} \underset{\mathbf{5}}{3,5\text{-}(NO_2)_2C_6H_3COOCH_2C(NO_2)_2F}$$

Because of the greater stability of the fluorodinitromethyl group in general and fluorodinitroethanol in particular toward alkaline conditions, it is also possible to effect reactions of **1** with still less reactive acid chlorides through the use of more strongly basic reagents such as would cause deformylation or other decomposition with trinitroethanol or the dinitroalkanols. Thus, for example, attempts to prepare 1-(2-fluoro-2,2-dinitroethoxy)-2,4,6-trinitrobenzene (**6**) by the reaction of **1** with picryl chloride in the presence of pyridine were unsuccessful but, when anhydrous potassium carbonate was used, **6** was obtained in good yield.

$$\mathbf{1} + 2,4,6\text{-}(NO_2)_3C_6H_2Cl \xrightarrow[\text{benzene}]{K_2CO_3} \underset{\mathbf{6}}{2,4,6\text{-}(NO_2)_3C_6H_2OCH_2C(NO_2)_2F}$$

In company with other negatively substituted alcohols, uncatalyzed or *p*-toluenesulfonic acid catalyzed esterifications of **1** proceed at negligible rates, even under forcing conditions. As shown by Frankel[11] and by Conly[12] for trinitroethanol, however, direct esterifications of **1** with carboxylic acids may be effected in strong sulfuric acid or in oleum. Representative of this procedure in the fluorodinitro series are the preparations[13] of 2,2,2-trinitroethyl 4-fluoro-4,4-dinitrobutyrate (**7**), 2-fluoro-2,2-dinitroethyl 4-fluoro-4,4-dinitrobutyrate (**8**), and 2-fluoro-2,2-dinitroethyl 4,4,4-trinitrobutyrate (**9**).

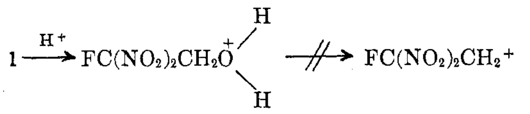
$$XC(NO_2)_2CH_2CH_2COOH + YC(NO_2)_2CH_2OH \xrightarrow[\text{or oleum}]{H_2SO_4} XC(NO_2)_2CH_2CH_2COOCH_2C(NO_2)_2Y$$

$\mathbf{7}$, $X = F$; $Y = NO_2$
$\mathbf{8}$, $X = Y = F$
$\mathbf{9}$, $X = NO_2$; $Y = F$

Formation of Ethers and Formals.—Few attempts at preparation of alkyl 2-fluoro-2,2-dinitroethyl ethers by direct etherification of **1** have been made because fluorination of the readily available alkyl 2,2-dinitroethyl ether salts[14] appeared to provide an easy access route to this class of compounds.[2] Diazomethane reacted rather sluggishly with **1** and only in the presence of boron trifluoride as a catalyst.[15] The product, obtained in low yield, was identified as 2-fluoro-2,2-dinitroethyl methyl ether (**10**) by comparison with a sample obtained earlier by the fluorination of potassium 2,2-dinitroethyl methyl ether.[2]

$$\mathbf{1} \xrightarrow{CH_2N_2} \underset{\mathbf{10}}{FC(NO_2)_2CH_2OCH_3} \xleftarrow[H_2O]{F_2/N_2} K^+\ \bar{C}(NO_2)_2CH_2OCH_3$$

Attempts to prepare bis(2-fluoro-2,2-dinitroethyl) ether by direct etherification were unsuccessful. In no case was the desired product isolated when **1** was subjected to usual dehydrating agents and procedures. Since such a reaction would probably require the intermediacy of fluorodinitroethyl carbonium ion, its failure was not unexpected in view of the recent observation that alcohols with several electron-withdrawing β substituents and no carbonium ion stabilizing α substituents do not proceed beyond the oxygen protonation stage in the FSO_3H–SbF_5–SO_2 system.[16]



$$\mathbf{1} \xrightarrow{H^+} FC(NO_2)_2CH_2\overset{+}{O}H_2 \;\not\longrightarrow\; FC(NO_2)_2CH_2^+$$

The preparation of formals of negatively substituted alcohols by reaction with formaldehyde in concentrated sulfuric acid has been reported recently.[17] Fluorodinitroethanol reacted analogously with polyformaldehyde[18] (80% yield) as well as with dimethoxymethane (65% yield) to afford bis(2-fluoro-2,2-dinitroethyl)formal (**11**), whose preparation by the aqueous fluorination of dipotassium bis(2,2-dinitroethyl)formal was described earlier.[2]

$$\mathbf{1} + (CH_2O)_n \text{ or } CH_3OCH_2OCH_3 \xrightarrow[H_2SO_4]{\text{concd}} \underset{\mathbf{11}}{FC(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2F}$$

When the reaction was conducted in the presence of excess formaldehyde and in weaker (80–90%) sulfuric acid, the oxymethylene homologs **12**–**14** were also

$$FC(NO_2)_2CH_2O(CH_2O)_nCH_2C(NO_2)_2F$$

$\mathbf{11}$, $n = 1$ $\mathbf{13}$, $n = 3$
$\mathbf{12}$, $n = 2$ $\mathbf{14}$, $n = 4$

formed. The effects of formaldehyde concentration and water content of the reaction medium are illustrated in Table I.

The rather striking effect of relatively small amounts of water on this reaction may be rationalized if it is assumed that oligomers of formaldehyde condense

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[11] M. B. Frankel, *J. Org. Chem.*, **27**, 331 (1962).

[12] J. C. Conly, U. S. Patent 3,160,654 (Dec 8, 1964).

[13] M. J. Kamlet, U. S. Patent 3,356,714 (Dec 5, 1967); *Chem. Abstr.*, **61**, 29259 (1968).

[14] Reference 5, p 28.

[15] E. Mueller and W. Rundel, *Angew. Chem.*, **70**, 105 (1958).

[16] G. A. Olah and C. U. Pittman, *J. Amer. Chem. Soc.*, **88**, 3310 (1966).

[17] K. G. Shipp and M. E. Hill, *J. Org. Chem.*, **31**, 853 (1966).

[18] The preparation of **11** by the reaction of **1** with formaldehyde was first carried out by Dr. F. E. Martin of the Aerojet-General Corp., Azusa, Calif., whose priority in this regard we herewith acknowledge.

TABLE I
PRODUCT COMPOSITIONS[a] FROM THE REACTION OF 2-FLUORO-2,2-DINITROETHANOL WITH EXCESS POLYFORMALDEHYDE[b]

Trial no.	Reaction medium	% excess formaldehyde	Yield, % 11	12	13	14	Total yield (crude), %
1	96% H_2SO_4	100	80	20	Nil	Nil	80
2	96% H_2SO_4	200	75	25	Trace	Nil	80
3	90% H_2SO_4	100	55	39	6	Nil	80
4	80% H_2SO_4	200	Trace	36	64	Trace	65

[a] Estimated from glpc peak areas. [b] 10 g of alcohol, 10 ml of H_2SO_4, 2 hr, *ca.* 25°.

with **1** during the reaction and that the oxymethylene chains of these products are subsequently cleaved *via* oxygen protonation until an equilibrium composition is reached. With its reduced protonating power, 80% sulfuric acid[19] might be considerably less effective than 96% sulfuric acid at cleaving **12** and **13**, which would explain their preponderance in the product of trial 4, while the formal **11** prevails in the product of trial 2. The same effect, though less drastic, is noted when trials 1 and 3 are compared.

These arguments are supported by the results of the reaction of **1** with dimethoxymethane in the presence of BF_3, which leads only to the formation of 2-fluoro-2,2-dinitroethylmethylformal (**15**). In concentrated sulfuric acid the latter unsymmetrical formal reacts with a second molecule of **1** to produce the bis(fluorodinitroethyl)formal.

$$\mathbf{1} + CH_3OCH_2OCH_3 \xrightarrow{BF_3} \underset{\mathbf{15}}{FC(NO_2)_2CH_2OCH_2OCH_3} \xrightarrow[H_2SO_4]{\mathbf{1}} \mathbf{11}$$

The structure assignments for **12** and **13** are based mainly on analytical and spectral data (see Experimental Section). The structure of **12** was further substantiated by an alternative synthesis from **1** and bis(chloromethyl) ether in the presence of boron trifluoride. Samples prepared by this method were identical with **12** isolated from trials 3 and 4 (Table I).

The presence of stoichiometric amounts or an excess of aluminum chloride in the reaction of **1** with bis(chloromethyl) ether led to cleavage of the central ether linkage in **12** and formation of chloromethyl 2-fluoro-2,2-dinitroethyl ether (**16**) in 68% yield. A primary by-product (*ca.* 15%) was **11**, probably formed by the further reaction of **16** with **1**.

$$\mathbf{1} + ClCH_2OCH_2Cl \begin{cases} \xrightarrow{BF_3} \underset{\mathbf{12}}{FC(NO_2)_2CH_2O(CH_2O)_2CH_2C(NO_2)_2F} \\ \xrightarrow{AlCl_3} \underset{\mathbf{16}}{FC(NO_2)_2CH_2OCH_2Cl} \xrightarrow[AlCl_3]{\mathbf{1}} \mathbf{11} \end{cases}$$

All of the above reactions are readily rationalized on the understanding that the basicity of the ether oxygens in **12–15** (tendency toward protonation or complex formation with $AlCl_3$ or BF_3) and the stability of the carbonium ions formed on cleavage fall off rapidly as they approach the $FC(NO_2)_2-$ grouping.

Reactions with Bases.—2-Substituted 2,2-dinitroethanols are fairly acidic alcohols (estimated pK range 10–14).[20] From $\sigma^* = 4.54$ for $C(NO_2)_3-$,[21] $\sigma^* = 4.38$ for $FC(NO_2)_2-$,[22] and $\sigma^* = 2.8$ for alkyl-$C(NO_2)_2-$,[21] **1** should be slightly less acidic than trinitroethanol but appreciably more acidic than the 2,2-dinitroalkanols.

Hall[23] has pointed out that in aqueous media polynitro alcohols enter into equilibria 1 and 2. He has

$$ZC(NO_2)_2CH_2OH + X \xrightleftharpoons{K_1} ZC(NO_2)_2CH_2O^- + XH^+ \quad (1)$$

$$X = \text{general base}$$

$$ZC(NO_2)_2CH_2O^- + H_2O \xrightleftharpoons{K_2} ZC(NO_2)_2^- + CH_2(OH)_2 \quad (2)$$

$$ZC(NO_2)_2H + H_2O \xrightleftharpoons{K_i} ZC(NO_2)_2^- + H_3O^+$$

also shown[24] that for a variety of Z's the over-all dissociation constant in the deformylation reaction ($= K_1K_2$) is reasonably proportional to the ionization constant of the substituted dinitromethane formed (K_i). Although the K's for the individual steps have not been determined, it would seem reasonable from Hall's findings that, lacking strong steric effects with changing Z such as have been the subject of earlier comment,[25] the K_2/K_i ratio should also remain reasonably constant.[26]

Based on estimated nitro alcohol acidities (reaction 1) and Hall's over-all K values,[24] the carbanion–alkoxide equilibrium (reaction 2) is far in the direction of carbanion for most 2-substituted 2,2-dinitroethanols. It has been shown,[27,28] however, that fluorodinitromethane (**17**) is an appreciably weaker acid than other substituted dinitromethanes, the pK's being as follows:[24,25,27,28] $CH_3C(NO_2)_2H$, 5.13; $ClC(NO_2)_2H$, 3.80; $CH_2(NO_2)_2$, 3.57; $C(NO_2)_3H$, 0.06; $FC(NO_2)_2H$, 7.70. From the normal acid strengthening by a fluorine substituent at the 2 position of 2,2-dinitroethanol and the acid-weakening effect of a fluorine atom directly affixed to the ionizing carbon of dinitromethane (the "anomalous fluorine effect"),[29] it should follow that for fluorodinitroethanol the carbanion–alkoxide equilibrium would fall appreciably more in the direction of alkoxide.

Much of the chemistry of **1** in weakly alkaline media is explicable on this basis, *e.g.*, the absence of deformylation attending the use of potassium carbonate as condensing agent in the reaction of **1** with picryl chloride to form **6**. Thus also is explained the fact that **1** is obtained with little or no concomitant formation of difluorodinitromethane by the aqueous fluorination of potassium 2,2-dinitroethanol at pH's of 7–10.[3] In this pH range other 2-substituted 2,2-dinitroethanols go over to the dinitro carbanion which undergoes fluorination.

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[19] Acid strengths given are initial concentrations; since water is produced in the reaction, the acid becomes more dilute as the reaction proceeds.

[20] Estimated from the σ^*'s and from the data on fluoro alcohols by B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965).

[21] J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961).

[22] L. A. Kaplan and H. B. Pickard (of this laboratory), private communication.

[23] T. N. Hall, *J. Org. Chem.*, **30**, 3157 (1965).

[24] T. N. Hall, *ibid.*, **29**, 3587 (1964).

[25] M. E. Sitzmann, H. G. Adolph, and M. J. Kamlet, *J. Amer. Chem. Soc.*, **90**, 2815 (1968).

[26] This is equivalent to saying that carbon basicities and hydrogen basicities of $ZC(NO_2)_2^-$ should change in parallel manners with changing Z.

[27] H. G. Adolph and M. J. Kamlet, *ibid.*, **88**, 4761 (1966).

[28] V. I. Slovetskii, L. V. Okhobystina, A. A. Fainzil'berg, A. I. Ivanov, L. J. Birynkova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2063 (1965).

[29] Possible explanations for this "anomalous fluorine effect" have been suggested in ref 27 and by J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).

$$HOCH_2C(NO_2)_2^- \xrightarrow[\text{pH 7-10}]{F_2/N_2} FC(NO_2)_2CH_2OH \nrightarrow FC(NO_2)_2F$$

$$ZC(NO_2)_2CH_2OH \xrightarrow{\text{pH 7-10}} CH_2(OH)_2 + ZC(NO_2)_2^- \xrightarrow{F_2/N_2} ZC(NO_2)_2F$$

$$Z = NO_2\text{, alkyl, halo, } HOCH_2$$

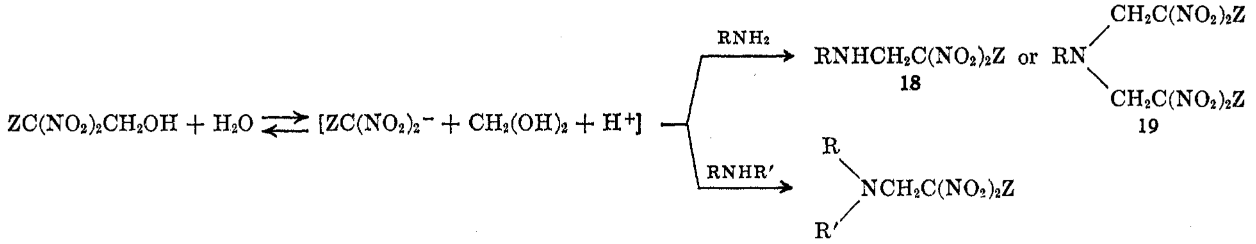
In stronger base reactions of **1** parallel those of other dinitroethanol derivatives. The yellow sparingly soluble salt of **17** precipitates on treatment of **1** with 1

$$1 + KOH \xrightarrow{MeOH} CH_2(OH)_2 + FC(NO_2)_2^-K^+ \xrightarrow{H^+} \underset{\mathbf{17}}{FC(NO_2)_2H}$$

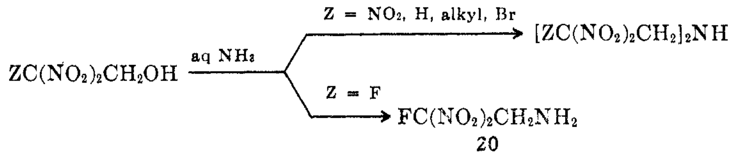
equiv of potassium hydroxide in methanol. In contrast to other dinitromethides, however, salts of fluorodinitromethane are unstable at room temperature and detonate vehemently if allowed to reach temperatures above 0° in a dry state. At lower temperatures the salt has been isolated and handled safely. Conversion of the isolated salt[30] into the free acid by treatment with dilute sulfuric acid afforded fluorodinitromethane in an over-all yield from **1** of 72%. This material was identical with samples of **17** obtained previously by other routes.[2]

The instability of the salts may derive from the same factors which lead to the unusually low acidity of **17**. It is comment worthy that similarly low acidities are shown by fluoromononitromethane derivatives,[27] and similar instability is shown by their carbanion salts.[1]

Reactions with Aqueous Ammonia.—On reaction with primary or secondary amines in water or methanol-water, 2,2-dinitroethanols undergo deformylation and, with proper pH control, subsequent Mannich condensation to give N-alkyl- and N,N-dialkyl-2,2-dinitroethylamines and, in some cases, N-alkylbis(2,2-dinitroethyl)amines[31] (eq 3).



$$ZC(NO_2)_2CH_2OH + H_2O \rightleftharpoons [ZC(NO_2)_2^- + CH_2(OH)_2 + H^+] \xrightarrow{RNH_2} \underset{\mathbf{18}}{RNHCH_2C(NO_2)_2Z} \text{ or } \underset{\mathbf{19}}{RN[CH_2C(NO_2)_2Z]_2}; \xrightarrow{RNHR'} RR'NCH_2C(NO_2)_2Z \quad (3)$$



$$ZC(NO_2)_2CH_2OH \xrightarrow{\text{aq } NH_3} \begin{cases} \xrightarrow{Z\,=\,NO_2,\ H,\ \text{alkyl},\ Br} [ZC(NO_2)_2CH_2]_2NH \\ \xrightarrow{Z\,=\,F} \underset{\mathbf{20}}{FC(NO_2)_2CH_2NH_2} \end{cases} \quad (4)$$

With ammonia, only bis(2,2-dinitroethyl)amines (**19**, R = H) have been obtained.[32] In fact, primary 2,2-dinitroalkylamines (**18**, R = H) were hitherto unknown with the exception of 2,2-dinitroethylamine itself (**18**, R = Z = H) which was shown, however, to derive its stability and probably its existence from the fact that it has the structure of a zwitterion with strong intramolecular hydrogen bonding.[33]

In complete contrast to these observations, 2-fluoro-2,2-dinitroethylamine (**20**) is the only product readily obtained from the reaction of **1** with aqueous ammonia at ambient conditions (eq 4). This primary amine has only limited stability; the neat material must be handled with care. It is a somewhat weaker base than pyridine; moderately stable salts are formed with strong acids in essentially anhydrous media, but on contact with moisture these decompose violently. The chemistry of **20** will be described in greater detail in a subsequent publication.

To effect condensation of **20** with a second fluorodinitroethyl group, more forcing conditions are required. Thus, bis(2-fluoro-2,2-dinitroethyl)amine (**21**) is obtained by adding either **20** or ammonia to a refluxing solution of **1** in aqueous methanol. Yields in the latter reactions were only fair because both **20** and the intermediate fluorodinitromethide ion decomposed partially under the reaction conditions. The secondary amine, **21**, is much more stable than **20**. It is only very weakly basic, may be crystallized unchanged from trifluoroacetic acid, and is essentially insoluble in 50 wt % aqueous sulfuric acid.

$$\underset{\mathbf{20}}{FC(NO_2)_2CH_2NH_2} + [FC(NO_2)_2CH_2OH \rightleftharpoons FC(NO_2)_2^- + CH_2(OH)_2 + H^+] \longrightarrow \underset{\mathbf{21}}{[FC(NO_2)_2CH_2]_2NH}$$

That **20** is capable of existence, while other 2-substituted 2,2-dinitroethylamines apparently are not, may again devolve from the effect of an α-fluorine substituent on the properties of nitro carbanions. It seems reasonable that dinitroethylamines cannot generally be isolated from reactions of dinitroethanols with ammonia because the reverse Mannich reaction predominates. As was the case in reaction 2 to which it

$$ZC(NO_2)_2CH_2NH_2 \rightleftharpoons ZC(NO_2)_2^- + [CH_2{=}NH_2]^+$$

bears formal analogy, where Z = F, this equilibrium is shifted to the left because the fluorodinitromethide ion is less stable and more nucleophilic than the other dinitro carbanions. The increased stability of **20** would thus represent still another manifestation of the "anomalous fluorine effect" which was discussed earlier

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[30] Separation of the salt from the methanolic formaldehyde solution is advisable to prevent regeneration of **1** on acidification.

[31] H. Feuer, G. B. Bachman, and W. May, *J. Amer. Chem. Soc.*, **76**, 5124 (1954); M. B. Frankel and K. Klager, *ibid.*, **79**, 2953 (1957); M. B. Frankel and K. Klager, *J. Chem. Eng. Data*, **7**, 412 (1962); H. Feuer and W. A. Swarts, *J. Org. Chem.*, **27**, 1455 (1962); E. E. Hamel, *Tetrahedron, Suppl. 1*, 85 (1963); M. B. Frankel, *ibid.*, 213 (1963).

[32] M. B. Frankel and K. Klager, *J. Amer. Chem. Soc.*, **79**, 2953 (1957); K. Klager, *J. Org. Chem.*, **23**, 1519 (1958).

[33] M. J. Kamlet and J. C. Dacons, *ibid.*, **26**, 3005 (1961).

in connection with fluoronitromethane acidities,[27,29] fluoronitroethanol deformylations (*vide supra*), and nucleophilic displacements of nitro in fluorotrinitromethane.[2]

Experimental Section

General (CAUTION!).—Most of the starting materials and products described herein are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care. Many fluorodinitromethyl compounds also show varying degrees of toxicity. Fluorodinitromethane and particularly fluorodinitroethanol may cause painful burns when brought into contact with the skin.

Microanalyses and molecular weight determinations were by Professor Mary H. Aldridge, American University, Washington, D. C., and by Mr. D. J. Glover of this laboratory. Difficulties were encountered in obtaining reproducible analytical results on some of the fluorodinitromethyl compounds reported here, and somewhat larger than usual deviations from calculated values were occasionally judged acceptable. Melting and boiling points were uncorrected.

2-Fluoro-2,2-dinitroethyl Acetate (2).—An immediate reaction occurred on mixing fluorodinitroethanol with a small excess of acetyl chloride. Heating to 40° for 1 hr after the exotherm had subsided, pouring over crushed ice, and stirring briefly to hydrolyze unreacted acetyl chloride gave **2** in 93% yield, bp 65° (2 mm).

Anal. Calcd for $C_4H_5FN_2O_6$: F, 9.69; N, 14.29; mol wt, 196. Found: F, 9.28; N, 14.35; mol wt, 199.

2-Fluoro-2,2-dinitroethyl Tosylate (3).—A mixture of 40 g of *p*-toluenesulfonyl chloride, 25 g of **1**, and 24 g of pyridine N-oxide in 50 ml of chloroform was refluxed gently for 3 hr and allowed to cool to room temperature. About 100 ml of methylene chloride was added, the mixture was washed with dilute sulfuric acid, water, and dilute sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solution was then concentrated to about one-third its volume and hexane was added until a precipitate formed. After cooling, 40–42 g of **3** (80–84%) was obtained; further concentration and cooling of the mother liquor afforded a small second crop of less pure material. The analytical sample, mp 83–84°, was obtained by successive recrystallizations from methanol and from carbon tetrachloride.

Anal. Calcd for $C_9H_9FN_2O_7S$: C, 35.07; H, 2.94; N, 9.09. Found: C, 34.9, 35.2; H, 3.2, 3.5; N, 9.0, 8.8.

2-Fluoro-2,2-dinitroethyl 3,5-Dinitrobenzoate (5).—To 4.13 g of **1** in 25 ml of chloroform and 25 ml of carbon tetrachloride was added 3.35 g of anhydrous aluminum chloride which dissolved with evolution of hydrogen chloride. After slight heating to drive off the last of the hydrogen chloride, a solution of 5.75 g of 3,5-dinitrobenzoyl chloride in 20 ml of chloroform and 20 ml of carbon tetrachloride was added and the total heated to reflux for 2 hr. During this time the ester–aluminum chloride complex separated as a gummy brown solid.

Decomposition of the complex was effected by adding to the mixture 100 ml of chloroform, 500 ml of ether, and 200 ml of 20% sulfuric acid and shaking vigorously. The solid material was filtered off (4.50 g), and the organic phase of the filtrate was washed with 100 ml of water, dried, and concentrated to yield two additional crops totalling 2.31 g. Recrystallization of 5.65 g of the combined product from ether–benzene afforded 5.15 g of pure **5**, mp 133.5–134°.

Anal. Calcd for $C_9H_5FN_4O_{10}$: C, 31.05; H, 1.44; N, 16.08. Found: C, 31.4, 31.2; H, 1.6, 1.6; N, 15.5, 15.8.

1-(2-Fluoro-2,2-dinitroethoxy)-2,4,6-trinitrobenzene (6).—To a cooled (0–5°) mixture of 7.7 g of **1**, 12.4 g of picryl chloride, and 20 ml of dry benzene was added portionwise 7 g of anhydrous potassium carbonate. After stirring overnight at room temperature, the mixture was filtered, the filtrate freed from solvent, and the residue recrystallized from methylene chloride–carbon tetrachloride (4:1). Thus was obtained 8.95 g of **6** (49%), mp 99–100°.

Anal. Calcd for $C_8H_4FN_5O_{11}$: C, 26.31; H, 1.10; N, 19.16; mol wt, 365. Found: C, 26.0; H, 1.0; N, 18.5; mol wt, 368.

2,2,2-Trinitroethyl 4-Fluoro-4,4-dinitrobutyrate (7).—A solution of 9.75 g of 4-fluoro-4,4-dinitrobutyric acid[2] and 10.0 g of trinitroethanol in 25 ml of 10% oleum was heated to 50° for 2.5 hr, during which time a second phase separated. The mixture was cooled, poured into a stirred mixture of 150 g of ice and 150 ml of methanol, and filtered to yield 14.9 g (84%) of crude **7** as a white solid, mp 34–38°. Recrystallization from methanol–water yielded 12.0 g of **7** as clean white feathery needles, mp 37.5–40°. A further recrystallization from ether–hexane afforded the analytical sample as clusters of tiny white needles, mp 42.6–43.8°.

Anal. Calcd for $C_6H_6FN_5O_{12}$: C, 20.04; H, 1.67; N, 19.50. Found: C, 20.0; H, 2.0; N, 19.2.

2-Fluoro-2,2-dinitroethyl 4-Fluoro-4,4-dinitrobutyrate (8).—A solution of 3.9 g of fluorodinitrobutyric acid and 4.5 g of **1** in 15 ml of 10% oleum, maintained 2.5 hr at 50° and poured over 100 g of crushed ice, yielded 2.7 g of a gummy white solid, mp 38–41°. Recrystallization from ether–hexane yielded 2.2 g (41%) of pure **8**, mp 41–42°.

Anal. Calcd for $C_6H_6F_2N_4O_{10}$: C, 21.69; H, 1.81; N, 16.86. Found: C, 22.4; H, 2.1; N, 16.6.

2-Fluoro-2,2-dinitroethyl 4,4,4-Trinitrobutyrate (9).—A solution of 9.0 g of **1** and 8.92 g of 4,4,4-trinitrobutyric acid in 30 ml of 10% oleum was held at 55° for 1 hr and poured onto 100 g of crushed ice. The product was extracted into 200 ml of ether, the ether solution washed with 100 ml of water, several 100-ml portions of dilute potassium carbonate solution, and then 100 ml of water and dried over calcium chloride, and the solvent evaporated off. The residual solid was taken up in ether–hexane which on concentration and chilling deposited two crops, totaling 3.52 g, of white needles. Recrystallization of 1.26 g of this material from carbon tetrachloride yielded 1.15 g of the analytical sample of **9**, mp 53.5–54.5°.

Anal. Calcd for $C_6H_6FN_5O_{12}$: C, 20.04; H, 1.67; N, 19.50; Found: C, 19.8; H, 2.1; N, 19.0.

2-Fluoro-2,2-dinitroethyl Methyl Ether (10).—Fluorodinitroethanol was added to an ether solution of diazomethane prepared from an equivalent amount of nitrosomethylurea. No immediate reaction was evident, but addition of a few drops of boron trifluoride etherate resulted in strong gas evolution. After the reaction had subsided this was repeated. The almost colorless mixture was filtered, the ether was removed from the filtrate, and the remaining oil, which proved to be mainly unreacted **1**, was thoroughly washed with water until the fluorodinitroethanol peak in the vapor phase chromatogram had disappeared. The product, which distilled at 45° (3 mm), contained about 3% an unidentified impurity, but was otherwise identical with a sample of **10** prepared as described previously.[2]

Bis(2-fluoro-2,2-dinitroethyl)formal (11) from Fluorodinitroethanol and Dimethoxymethane.—To a solution of 5.1 g of **1** in 20 ml of concentrated sulfuric acid was added with cooling 1.25 g of dimethoxymethane in 20 ml of methylene chloride and the mixture was stirred vigorously at room temperature for 15 hr. The sulfuric acid phase was extracted with methylene chloride, and the combined extracts were washed with water, dried, and freed from solvent to give 3.4 g (64%) of crude **11**. Purification as detailed in ref 2 gave a material identical with the sample of **11** described therein which had been obtained by aqueous fluorination of dipotassium bis(2,2-dinitroethyl)formal.

Reaction of Fluorodinitroethanol with Polyformaldehyde in Sulfuric Acid. Runs 1–4 of Table I.—The amount of formaldehyde cited in the table was dissolved or slurried in 10 ml of sulfuric acid of the concentration cited and at 0° 10 g of **1** was added dropwise with vigorous stirring. The mixture was allowed to warm to room temperature, stirred an additional 2 hr, and then poured onto crushed ice. The product was extracted into methylene chloride, dried, freed from solvent *in vacuo*, and subjected to glpc analysis (F & M Model 300 gas chromatograph, 36-in. column packed with 10% May-Baker silicon oil on Haloport F).

Isolation of 12 and 13 from Trial 4, Table I.—The crude mixture, consisting mainly of **12** and **13**, was dissolved in methylene chloride–pentane (3:2) and chromatographed on silica (G. F. Smith, Columbus, Ohio). The compositions of the various fractions were determined by glpc as described above. The fractions comprising mainly of the bis(oxymethylene) compound **12** were combined as were those consisting primarily of the tris(oxymethylene) compound **13**. Crude **12** and **13**, obtained in this manner, were rechromatographed twice and then crystallized from methylene chloride–hexane solution in a Dry Ice–acetone bath. A second recrystallization afforded the analytical samples. Since **12** melts at *ca.* 20°, it must be collected on a chilled funnel. It is a colorless oil, stable to storage at room temperature.

Anal. Calcd for $C_6H_8F_2N_4O_{11}$: F, 10.85; mol wt, 350. Found: F, 10.4; mol wt, 342 (in $CHCl_3$).

The nmr spectrum was determined in carbon tetrachloride solution with a Varian HA-100 spectrophotometer with TMS as lock signal. It showed a doublet at δ 4.63 (J_{HF} = 17 cps) and a single peak at 4.80, area ratios 1:1. Major bands in the infrared region (liquid film) were 1600 (NO_2), 1320 (NO_2), 1130 (C–O), 1010 (C–O), 805 and 855 cm^{-1} (C–N?).

The tris(oxymethylene compound) **13** was obtained as colorless thin plates, mp 40–42°.

Anal. Calcd for $C_7H_{10}F_2N_4O_{12}$: F, 10.10; mol wt, 376. Found: F, 9.7; mol wt, 365 (in $CHCl_3$).

The nmr spectrum, obtained as for **12**, showed peaks at δ 4.61 (doublet, J_{HF} = 17 cps, relative area 2), 4.78 and 4.80 (two singlets, combined relative area 3). Major infrared bands (liquid film) were at 1595 (NO_2), 1315 (NO_2), 1125 and 990 (C–O), 805 and 855 cm^{-1} (C–N?).

2-Fluoro-2,2-dinitroethylmethylformal (15).—A mixture of **1**, a fourfold excess of dimethoxymethane, and a catalytic amount of boron trifluoride etherate were heated to reflux for 3 hr; low boiling material was then distilled off by raising the temperature slowly to 90°. The residue was taken up in methylene chloride, the solution was washed with 0.1 *N* sodium hydroxide to remove unreacted **1** and with water and was then dried and freed from solvent to give crude **15** as a colorless liquid, bp 58–61° (1.5 mm).

Alternatively, **1** (2.0 g) and chloromethyl methyl ether (2.5 g) in the presence of a small amount of anhydrous aluminum chloride, warmed to 50° for 1 hr, reacted readily to give, after pouring the mixture over crushed ice, extracting the product into methylene chloride, washing with water, drying, and removing the solvent, **15** of excellent purity and in almost quantitative yield.

Anal. Calcd for $C_4H_7FN_2O_6$: C, 24.25; H, 3.56; F, 9.59; N, 14.14; mol wt, 198. Found: C, 24.6; H, 4.0; F, 9.6; N, 13.8; mol wt, 213 (in CH_3CN).

The nmr spectrum (in CCl_4, δ relative to TMS) showed peaks at 4.58 (doublet, J_{HF} = 17.5 cps), 3.36 and 4.67 (two singlets); area ratio 2:3:2.

Preparation of 12 from 1 and Bis(chloromethyl) Ether.—A mixture of 1.15 g of bis(chloromethyl) ether, 3.1 g of fluorodinitroethanol, and 1 drop of boron trifluoride etherate was heated to 55° for 2.5 days. The product was taken up in methylene chloride; the solution was washed with dilute sodium bicarbonate and with water and dried. The solvent was removed and the remaining oil held at 65° (0.1 mm) for 4 hr to remove unreacted **1** and other low boilers. There was obtained 0.72 g of crude **12**, which was purified by chromatography on silica and recrystallization as described above. Samples of **12** obtained in this manner and by the preceding method were identical by glpc retention times and by infrared and nmr spectra.

Chloromethyl 2-Fluoro-2,2-dinitroethyl Ether (16).—Anhydrous aluminum chloride, 3.2 g, was added gradually at room temperature to a mixture of 9.3 g of **1** and 3.45 g of bis(chloromethyl) ether. When the hydrogen chloride evolution ceased, the mixture was heated to 65–70° for 1 hr, then poured onto crushed ice. The product, 11.4 g, was distilled to give 8.9 g of **16** (67.7%), bp 40° (0.3 mm). The distillation residue, 2.2 g, consisted mainly of **11**.

Anal. Calcd for $C_3H_4ClFN_2O_5$: F, 9.38; mol wt, 202.5. Found: F, 9.1; mol wt, 198.

The nmr spectrum (in CCl_4, δ relative to TMS) showed peaks at 4.73 (doublet, J_{HF} = 17 cps), 5.47 (singlet); area ratio 1:1.

Fluorodinitromethane (17).—The potassium salt of **17** was prepared by adding a solution of 25 g of **1** in 50 ml of methanol to a well-stirred solution of 12.5 g of potassium hydroxide in 50 ml of methanol over a 15-min period at 0°. Concomitantly, 50 ml of cold methylene chloride was added to keep the mixture stirrable. After completion of the addition, another 50 ml of cold (0°) methylene chloride was added and the mixture was cooled to below −25° and freed from most of the solvent by means of a sintered-glass filter stick (*CAUTION:* do not allow the semidry salt to warm as it will detonate at temperatures near 0°). The salt was washed twice with methylene chloride which had been precooled to −25°, again using a filter stick to remove the solvent, and converted into **17** by adding 100 ml of cold (0°) 2 *N* sulfuric acid and stirring until the mixture was colorless. The product was extracted into methylene chloride, and the extract dried ($MgSO_4$) and distilled through a small Vigreux column. The yield of pure **17**, identical with material described earlier,[2] was 14.5 g (72%): bp 64–65° (85 mm); fp −25°; $n^{25}{}_D$ 1.4029.

Principal infrared bands (liquid film) appeared at 1600, 1322 (NO_2), 1203 (C–F?), 932, 830, 745 cm^{-1}; ultraviolet at $\lambda\lambda_{max}^{dil\ HONa}$ 252 mμ (ϵ 4700), 382 (19,400).

2-Fluoro-2,2-dinitroethylamine (20).—A mixture of 10 g of **1**, 10 ml of water, and 10 ml of methylene chloride was cooled in an ice bath while 7 g of 28% aqueous ammonia was added with vigorous stirring. The cooling was removed and stirring was continued for 6 hr at 25°. The aqueous phase was extracted with methylene chloride and the extract was washed with 25 ml of 0.1 *N* NaOH and with water and dried. The oil remaining after removal of the solvent was then distilled to give 7.0 g of **20** (70.5%), bp 38–41° (0.3 mm).

CAUTION: Samples of **20** stored neat at ambient temperatures regularly exploded within several hours. On occasion, concentrated solutions (>50%) in methylene chloride have also decomposed violently after extended storage. For this reason the final part of the above preparation should be carried out without interruption in a well-shielded and ventilated area, and the product should be used without delay or diluted with inert solvent. It is not advisable to prepare larger amounts of neat **20**; for most reactions a methylene chloride solution of the crude material is satisfactory.

Principal infrared bands (liquid film) appeared at 3410, 3350 (N–H), 1595, 1315 (NO_2), 1280, 1055, 855, 800 cm^{-1}; nmr (in $CDCl_3$, δ relative to TMS) 3.90 (doublet, J_{HF} = 17 cps), 1.50 (singlet); relative areas 1:1.

Because of its instability, **20** was analyzed as its acetyl derivative, **N-(2-fluoro-2,2-dinitroethyl)acetamide**, which was prepared with acetyl chloride and pyridine in methylene chloride solution.

Anal. Calcd for $C_4H_6FN_3O_5$: N, 21.53; F, 9.74; mol wt. 195. Found: N, 21.3; F, 10.0; mol wt, 190 (in CH_3CN).

Bis(2-fluoro-2,2-dinitroethyl)amine (21). A. From 20 and 1.—A solution of 7 g of **1** in 10 ml of methanol and 15 ml of water was heated to reflux, 6.65 g of **20** in 5 ml of methanol was added and the mixture was refluxed 24 hr. The mixture was then poured onto ice and the solid product filtered off and recrystallized from chloroform(adding a small amount of charcoal and Celite) to give 5.15 g of **21** (41%), mp 44–45°.

Anal. Calcd for $C_4H_5F_2N_5O_8$: C, 16.61; H, 1.74; F, 13.14; N, 24.22; mol wt, 289. Found: C, 17.0; H, 1.70; F, 13.2; N, 24.2; mol wt, 285 (in $CHCl_3$).

Principal infrared bands (liquid film) appeared at 3400 (N–H), 1600, 1315 (NO_2), 852, 805 cm^{-1}; nmr (in $CDCl_3$, δ relative to TMS) 4.13 (double doublet, J_{HF} = 17 cps, J_{NH-H} = 7.5 cps), 2.12 (broadened quintet); area ratio 4:1.

B. From 1 and Aqueous Ammonia.—A solution of 25 g of **1** in 30 ml of methanol and 30 ml of water was heated to a mild reflux (*ca.* 90°), 4.9 g of aqueous ammonia was added dropwise, the mixture was maintained at reflux for 24 hr, then drowned on ice, and the semisolid precipitate was recrystallized from chloroform with the addition of charcoal and Celite. There was obtained 7 g (*ca.* 30%) of crude **21**.

Registry No.—**1**, 17003-75-7; **2**, 18138-90-4; **3**, 18138-91-5; **5**, 18138-92-6; **6**, 18138-93-7; **7**, 15957-53-6; **8**, 15957-54-7; **9**, 18138-96-0; **12**, 18138-97-1; **13**, 18138-98-2; **15**, 18138-99-3; **16**, 18139-00-9; **17**, 7182-87-8; **20**, 18139-02-1; **21**, 18139-03-2.