

commodate coplanar dialkylamino groups, the  $C_1-C_2-N(O_2)$  and  $C_1-C_6-N(O_2)$  angles in A rotomers might be expanded from  $120^\circ$  and  $C_1-C_2$  and  $C_1-C_6$  bond distances could also increase from normal values. Internal ring angles might also change, and even bending or folding of the benzene ring is not out of the question.<sup>14</sup> Increased molecular distortions of these types with increasing substituent bulk in compounds closely related to **5** and **6** may be observed in a comparison of total crystal structures of N-nitro-N-methylpicramide (tetryl)<sup>15</sup> and N-nitro-N-trifluoroethylpicramide.<sup>16</sup>

Ingraham has commented on a slight bathochromic effect of molecular distortion in benzene derivatives.<sup>17</sup> Additional effects of these types, which would be expected to increase from dimethyl to diethyl, might account for the increased  $\Delta\nu_{\max}$ .

It deserves comment that, had we considered the spectrum of **6** *ab initio*, an analysis such as the above would have been all but impossible. Only by examin-

(14) In the crystal, the ring of 2,3,4,6-tetranitroaniline shows a slight boat shape in the  $C_1-C_4$  axis. Bond distances and internal and external bond angles also differ appreciably from normal values.<sup>8</sup>

(15) H. Cady, *Acta Crystallogr.*, **23**, 601 (1967).

(16) J. R. Holden and C. Dickinson, to be published.

(17) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 500.

ing trends, first on monoalkylation, then on dialkylation, and by observing the progressive growth of one band and concomitant shrinking of another with increasing alkyl bulk, were we able to arrive at the above assignments.

### Experimental Section

All materials were commercially available or prepared by literature methods from picryl chloride and the appropriate mono- or dialkylamine. They were purified by standard means to meet conventional spectrophotometric criteria of purity. Absorption spectra were determined in methanolic solution using a Cary Model 14 recording spectrophotometer with matched 1-cm silica cells. Concentrations were  $3-5 \times 10^{-5} M$ . Previously described precautions<sup>18</sup> were taken to guard against photochemical transformations.

**Registry No.**—**1**, 489-98-5; **2**, 1022-07-7; **3**, 7449-27-6; **4**, 16876-54-3; **5**, 2493-31-4; **6**, 13029-07-7.

**Acknowledgments.**—Helpful discussions with Drs. J. C. Dacons and L. A. Kaplan and Messrs. C. Dickinson and D. J. Glover are gratefully acknowledged. The work was done under Foundational Research Task FR-44 of the U. S. Naval Ordnance Laboratory.

(18) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

## Fluoronitroaliphatics. II. Fluorodinitromethyl Compounds. Synthetic Approaches and General Properties<sup>1</sup>

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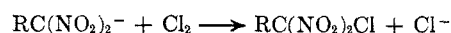
Preparative procedures are described for a new class of compounds containing the  $FC(NO_2)_2^-$  moiety. Three general synthesis methods are most useful in this series: (1) fluorination of 1,1-dinitro carbanion salts with perchloryl fluoride; (2) aqueous fluorination of 1,1-dinitro carbanions (the Grakauskas reaction); (3) reactions of fluorotrinitromethane with a variety of nucleophiles.

In the course of studies concerning the chemistry of polynitroaliphatic compounds, a program was initiated at this laboratory with the aim of developing synthesis methods for fluorodinitromethyl analogs, then undescribed, of known trinitromethyl and other halodinitromethyl compounds.<sup>2-5</sup> In this and the following papers, we wish to report some of the results of this work and, in addition, describe a number of

novel fluorodinitromethyl derivatives for which the corresponding  $C(NO_2)_3^-$  or  $RC(NO_2)_2^-$  analogs are as yet unknown.

Pathways for the synthesis of fluorodinitromethyl compounds considered at the outset and during the course of this investigation included (a) introduction of a second nitro group into compounds already containing the fluoronitromethyl function; (b) introduction of two nitro groups into simple or activated monofluorohydrocarbons; (c) introduction of fluorine into 1,1-dinitro compounds. Since 1,1-dinitroalkanes had previously been reported in considerable number and were fairly readily available,<sup>2</sup> we have directed our attention primarily to pathway c.

An analogy for the introduction of fluorine existed in the ease with which 1,1-dinitro carbanions reacted with chlorinating and brominating agents to form the corresponding chloro- and bromodinitromethyl compounds.<sup>2</sup>



Accordingly, the problem was one of finding suitable fluorinating agents which would selectively attack the dinitromethyl anion in a manner similar to the reaction with chlorine, while leaving intact as wide as

(1) Part I: H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966). See also 1-fluoro-1,1-dinitroalkanes [M. J. Kamlet, U. S. Patent 3,366,897 (Jan 30, 1968)] and 4-fluoro-4,4-dinitrobutyric acid [M. J. Kamlet, U. S. Patent 3,356,714 (Dec. 5, 1967)].

(2) P. Noble, F. G. Borgardt, and W. L. Reed [*Chem. Rev.*, **61**, 19 (1964)] provide a comprehensive review of the polynitroaliphatic chemistry field through 1963.

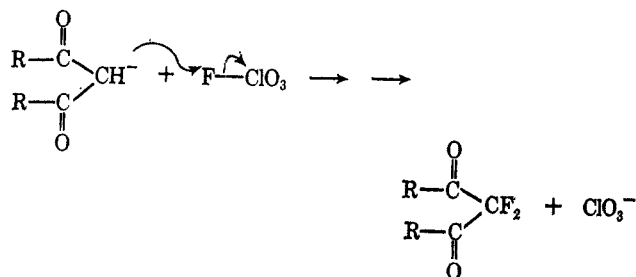
(3) Occasional reports on fluorodinitromethyl compounds have appeared in the literature during the past year, but these generally make reference to earlier work by us or Grakauskas and Baum (see following paper<sup>4</sup>) in the form of private communications. These include fluorodinitroalkyl esters of monocarboxylic acids [O. S. Schaeffer, U. S. Patent 3,316,292 (April 25, 1967)], fluorodinitroalkane preparation [M. Graff, W. E. McQuiston, and J. W. Sterling, U. S. Patent 3,274,264 (Sept 20, 1966)], and heat of formation and properties of fluorotrinitromethane [M. F. Zimmer, R. A. Robb, E. E. Baroody, and G. A. Carpenter, *J. Chem. Eng. Data*, **11**, 577 (1966)]. While the present paper was in process of revision, a report appeared describing solid phase fluorinations of potassium nitroform and dipotassium 1,1,2,2-tetranitroethane to yield, *inter alia*, some of the products reported here. A fluorine-nitrogen mixture was passed over these salts in a matrix of potassium fluoride and granulated copper.<sup>5</sup>

(4) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(5) L. T. Eremenko, F. Ya. Natsibullin, and I. P. Borovinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 429, 431 (1968).

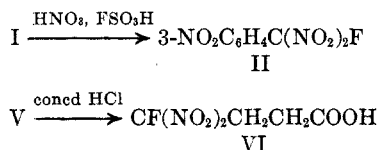
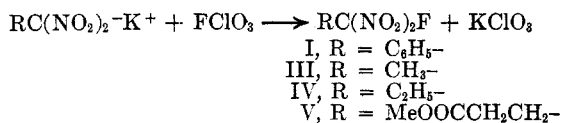
possible a variety of other type functionality in the molecule.

**Fluorination with Perchloryl Fluoride.**—Although no such agents were known to us when this study was undertaken,<sup>6</sup> the first reports on perchloryl fluoride as a selective fluorinating agent were published soon thereafter by Inman, Oesterling, and Tyezkowski,<sup>7</sup> who described the reactions of the sodium salts of such active methylene compounds as acetoacetic ester, malonic ester, and 2,4-pentanedione with perchloryl fluoride to yield primarily the difluoro derivatives at the active methylene sites.



These reactions presumably involved attack of the carbanion on fluorine with displacement of chlorate ion and seemed to parallel the desired fluorination of 1,1-dinitroalkane ions mechanistically. The question remained to be answered, however, as to whether the less basic dinitro carbanions would be sufficiently reactive and whether their ambident nature<sup>2</sup> would lead to a multiplicity of products deriving from C and O fluorination.<sup>8</sup>

In four instances the reactions of the potassium salts of the 1,1-dinitro compounds with perchloryl fluoride in methanol or aqueous methanol at 25–40° proved to be relatively straightforward. From potassium dinitromethylbenzene we obtained in 95% yield fluorodinitromethylbenzene (I) which on nitration with HNO<sub>3</sub>–FSO<sub>3</sub>H was converted into a mononitro derivative, presumably  $\alpha$ -fluoro- $\alpha,\alpha,3$ -trinitrotoluene (II). Potassium 1,1-dinitroethane and potassium 1,1-dinitropropane yielded 54% pure 1-fluoro-1,1-dinitroethane (III) and 59% 1-fluoro-1,1-dinitropropane (IV), respectively. Potassium methyl 4,4-dinitrobutyrate gave 93% methyl 4-fluoro-4,4-dinitrobutyrate (V), characterized as the corresponding butyric acid (VI), into which it was converted in prac-



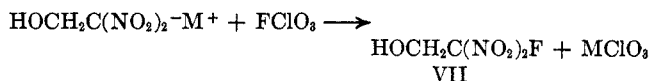
(6) Our original intent was to investigate nitryl fluoride as a fluorinating agent. We had earlier found that, depending on the solvent and substrate, nitryl chloride reacted with 1,1-dinitro carbanion salts to yield either the trinitro or the chlorodinitro derivative: unpublished information.

(7) C. E. Inman, R. E. Oesterling, and E. A. Tyezkowski, *J. Amer. Chem. Soc.*, **80**, 6533 (1958); H. Gershon, *et al.*, *J. Org. Chem.*, **31**, 916 (1966).

(8) While this work was in progress, H. Shechter and A. B. Roberson, Jr. [*J. Org. Chem.*, **25**, 175 (1960)] reported that C fluorination occurred in the reaction of a number of mononitro carbanions with PF in methanol, but that oxidation (presumably arising from O fluorination) was a major side reaction.

tically quantitative yield by refluxing with concentrated hydrochloric acid.

With potassium or sodium 2,2-dinitroethanol the fluorination reaction was very much more complex. Under a variety of conditions the best yields of 2-fluoro-2,2-dinitroethanol (VII) ranged from 20 to 25%. Of



the solvents tried in this case, only in aqueous methanol and in DMF, in which the salts are somewhat soluble,<sup>9</sup> did reaction take place at a reasonable rate. In such solvents the dinitroethanol anion participates in a series of formylation–deformylation equilibria involving 2,2-dinitro-1,3-propanediol together with smaller amounts of dinitromethane, 2,2,4,4-tetranitro-1-butanol (from dinitroethanol and dinitroethylene), and 2,2,4,4-tetranitro-1,5-pentanediol.<sup>10</sup> Certain of these species would also be expected to react with perchloryl fluoride and, by contrast with the previous examples, the products obtained from the fluorinations of the dinitroethanol salts were complex mixtures. Only by repeated fractional distillation was a reasonably pure sample of VII obtained.

Unsuccessful attempts to fluorinate 1,1-dinitroalkane salts with perchloryl fluoride involved 2,2-dinitroethylamine zwitterion<sup>11</sup> in a methanol–water–ether mixture and potassium nitroform in a variety of solvents. The failure of the latter to react was not unexpected in view of the lower basicity (pK of nitroform = ca. 0)<sup>12</sup> and nucleophilicity of the trinitromethide anion compared with those of the dinitro carbanions (pK values of parent dinitro compounds range from 3.5 to 6.5).<sup>12</sup>

**Fluorination with Elemental Fluorine.**—Soon after our initial work on the perchloryl fluoride fluorination of dinitro carbanions, it was shown by Grakauskas that many types of fluorination reactions could be carried out by the surprisingly simple expedient of passing a stream of a nitrogen–fluorine mixture into an aqueous solution of the appropriate substrate.<sup>13</sup> Among the reactions carried out by Grakauskas to demonstrate the versatility of this most useful technique were aqueous fluorinations of the potassium salts of 1,1-dinitroethane and 2,2-dinitroethanol. The products, 1-fluoro-1,1-dinitroethane and 2-fluoro-2,2-dinitroethanol, were the same as we had obtained by the perchloryl fluoride method, but the yields as well as the purity of the product in the fluorodinitroethanol preparation were vastly improved.

(9) See Experimental Section for a discussion of factors governing choice of solvents in perchloryl fluoride fluorinations.

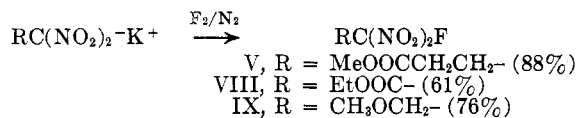
(10) Summary Report No. 461, Aerojet Engineering Corp., Azusa, Calif., July 20, 1950 (available through the Defense Documentation Center, Cameron Station, Alexandria, Va.); K. Klager, J. P. Kispersky, and E. Hamel, *J. Org. Chem.*, **26**, 4368 (1961).

(11) M. J. Kamlet and J. C. Dacons, *ibid.*, **26**, 3005 (1961).

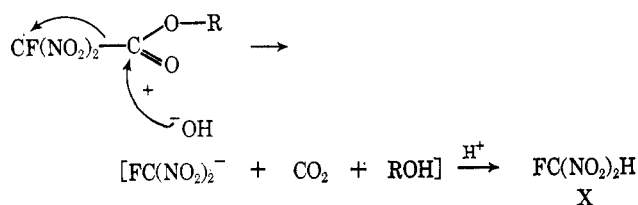
(12) (a) V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, L. I. Biryukova, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 655 (1966). (b) M. E. Sitzmann, H. G. Adolph, and M. J. Kamlet, *J. Amer. Chem. Soc.*, **90**, 2815 (1968).

(13) Because of the novelty, extreme versatility, and utility of this procedure, we have taken the liberty of naming it the Grakauskas reaction. Very little of Grakauskas' work has yet appeared in print (what has, indeed, is reported by other later workers) and we wish to thank Dr. Grakauskas for making much of this information available to us in a series of private communications. See following paper.<sup>4</sup>

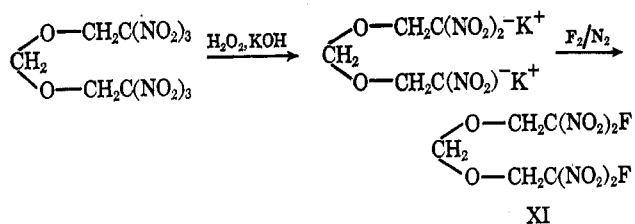
We have extended the aqueous fluorination of dinitro carbanions to compounds containing a variety of additional functional groups to explore the scope of the Grakauskas reaction.



Since attack of fluorine occurs on the carbanion, and since partially ionized 1,1-dinitroalkanes tend to undergo various types of self-condensation,<sup>14</sup> the reaction mixture is preferably maintained at a pH which ensures essentially complete ionization of the substrate. Most aqueous fluorinations of 1,1-dinitro compounds were therefore carried out in a pH range of 8–10. In the fluorination of potassium ethyl dinitroacetate, the presence of base led to the formation of *ca.* 20% fluorodinitromethane (X) as a by-product, probably as a result of hydroxide attack on the ethyl fluorodinitroacetate.<sup>15</sup>



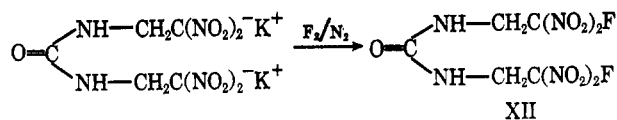
The aqueous fluorination of dipotassium bis(2,2-dinitroethyl)formal, obtained by the alkaline hydroperoxide reduction of bis(2,2,2-trinitroethyl)formal, proceeded smoothly at both ends of the chain, affording bis(2-fluoro-2,2-dinitroethyl)formal (XI)<sup>16</sup> in 55% over-all yield.



This illustrates a general method whereby a trinitro compound may be reduced to the dinitro carbanion salt with alkaline hydroperoxide<sup>17</sup> or potassium iodide<sup>18</sup> and thence converted into the corresponding fluorodinitro derivative.

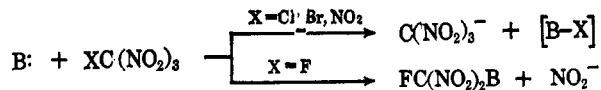
Under the conditions of the aqueous fluorination, fluorine also attacks amides, amines, and urethans on nitrogen.<sup>19</sup> The fluorination of dipotassium *N,N'*-bis(2,2-dinitroethyl)urea, which in addition to the car-

bation sites can also undergo reaction at the urea nitrogens, therefore provided an opportunity to obtain qualitative information about the relative reactivity of the two nucleophilic centers. Although both reactions proceeded at not markedly dissimilar rates, C fluorination was somewhat more rapid, permitting the isolation of *N,N'*-bis(2-fluoro-2,2-dinitroethyl)urea (XII) in moderate yield; in addition, *N*-fluorinated but otherwise unidentified by-products were formed.



In isolated instances, perchloryl fluoride may be the more advantageous for the fluorination of 1,1-dinitro salts. Thus, it has been shown that carbon-carbon double bonds are attacked by fluorine under conditions of aqueous fluorination, while the use of perchloryl fluoride in the fluorination of 4,4-dinitro-1-butene salts left the unsaturation in the molecule intact.<sup>20</sup> It is also possible that, with compounds containing an amide function in addition to the dinitromethyl group, perchloryl fluoride will give better results because of its relative inertness toward amide nitrogen. In general, however, the Grakauskas method with elemental fluorine is to be preferred. It is safer,<sup>21</sup> gives at least as good or better yields in most cases where both procedures have been tried, and, except for the initial setup of the fluorination apparatus, is more convenient to carry out because of a generally much simpler work-up of the reaction mixture.

**Preparation of Fluorodinitromethyl Compounds from Fluorotrinitromethane.**—Although perchloryl fluoride and aqueous fluorination allow the preparation of a wide variety of substituted fluorodinitromethanes, a third method, which is indirectly based on the Grakauskas reaction, permits the synthesis of a variety of materials for which the corresponding 1,1-dinitro carbanion salts are not accessible. We have found that fluorotrinitromethane, obtained by the aqueous fluorination of nitroform salts,<sup>22</sup> reacts with certain nucleophiles with formal substitution of one of the nitro groups. This is in marked contrast to tetranitromethane and chloro- and bromotrinitromethane, whose reactions with a variety of bases and reducing agents generally lead to nitroform anion.<sup>23</sup>



Thus, the reactions of fluorotrinitromethane with sodium ethoxide and sodium trifluoroethoxide, using

(20) Private communication, Dr. M. B. Frankel, Rocketdyne Corp., Canoga Park, Calif.

(21) See Experimental Section for a discussion of some hazards in perchloryl fluoride fluorinations. We know of at least one very serious accident resulting from the use of this material: private communication, Professor E. D. Bergmann, The Hebrew University, Jerusalem.

(22) K. Baum and V. Grakauskas, private communication. Later workers (Zimmer, *et al.*)<sup>3</sup> have acknowledged us as the authors of a private communication regarding the synthesis of this material, while in fact we were only transmitting information first obtained from Baum and Grakauskas. See following paper.<sup>4</sup>

(23) (a) A. Hantzsch, *Chem. Ber.*, **39**, 2479 (1906); Chattaway and Harrison, *J. Chem. Soc.*, **109**, 173 (1916). (b) A. K. Macbeth and D. D. Pratt, *ibid.*, **119**, 333 (1921); K. Klager, *Anal. Chem.*, **23**, 534 (1951).

(14) For example, an autocondensation product is formed wherever 1,1-dinitroethane coexists in appreciable concentrations with its carbanion: J. S. Belew, C. E. Grabiell, and L. B. Clapp, *J. Amer. Chem. Soc.*, **77**, 1110 (1955).

(15) A similar cleavage of negatively substituted esters which does not proceed through the corresponding carboxylic acid has been reported by, among others, E. Bergman, *J. Org. Chem.*, **23**, 476 (1958).

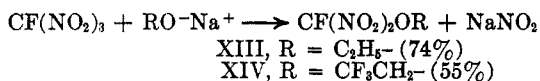
(16) This material was first prepared by the condensation of VII with formaldehyde in strong sulfuric acid by Dr. F. E. Martin of the Aerojet-General Corp., whose priority in this regard we herewith acknowledge. A single trial at perchloryl fluoride fluorination of dipotassium bis(2,2-dinitroethyl)formal yielded *ca.* 3% XI.

(17) D. J. Glover, *Tetrahedron, Suppl. 1*, **19**, 219 (1963), and references cited therein.

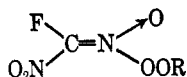
(18) D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

(19) V. Grakauskas, "Direct Fluorination of Alkyl Carbamates in Solution," Third International Symposium on Fluorine Chemistry, Munich, 1965.

the parent alcohols as solvents, gave the corresponding fluorodinitromethyl ethers in moderate to good yields.

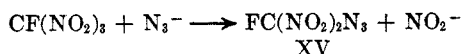


The structures of these ethers were assigned on the basis of analytical results which confirmed the presence of nitro and ethoxy groups in XIII in the ratio of 2:1 (see Experimental Section). A peroxide or O-ether structure of the type

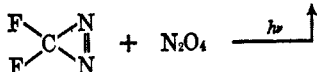
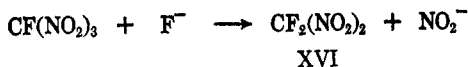


was ruled out primarily on the basis of the ultraviolet spectrum which showed  $\lambda_{\text{max}}^{\text{MeOH}}$  285 m $\mu$  ( $\epsilon$  ca. 95). Low intensity absorption near 280 m $\mu$  is characteristic of unconjugated nitro- and polynitroaliphatics<sup>24</sup> ( $\epsilon$  25 to 35 per nitro group),<sup>25</sup> and is in marked contrast with the spectral behavior of 1,1-dinitroalkane *aci*-ethers which typically show high intensity absorption at 315–320 m $\mu$  ( $\epsilon$  6000–9000).<sup>26</sup>

The analogous reaction of fluorotrinitromethane with sodium azide in dimethylformamide afforded fluorodinitromethyl azide in approximately 35% yield.



With potassium fluoride in sulfolane, the corresponding reaction provided difluorodinitromethane (XVI), which has also been reported to result from photochemical addition of N<sub>2</sub>O<sub>4</sub> or NO<sub>2</sub>Cl to difluorodiaziridine.<sup>27</sup>



Although no unequivocal evidence is available at this time, it is likely that these reactions involve simple nucleophilic substitutions of a nitro group with the nucleophile attacking on carbon rather than on nitrogen or oxygen as is more frequently observed in polynitroaliphatic chemistry,<sup>17,18</sup> or on halogen, as must be the case with the other halotrinitromethanes. Two factors may contribute to the different pathways taken in the reactions of B: with X-C(NO<sub>2</sub>)<sub>3</sub> or R-C(NO<sub>2</sub>)<sub>3</sub>. The carbon atom is, of course, sterically most accessible where X = F, leading to an increased rate of nucleophilic attack on carbon; the decreased stability of the fluorodinitromethide leaving group relative to trinitromethide or other dinitro carbanions [evidenced by the following *pK*'s: C(NO<sub>2</sub>)<sub>3</sub>H, 0.17; ClC(NO<sub>2</sub>)<sub>2</sub>H, 3.53; BrC(NO<sub>2</sub>)<sub>2</sub>H, 3.6; CH<sub>3</sub>C(NO<sub>2</sub>)<sub>2</sub>H, 5.21; FC(NO<sub>2</sub>)<sub>2</sub>-H, 7.70]<sup>1,28</sup> may contribute to a lowered rate of nucleophilic attack on oxygen or nitrogen.

(24) V. I. Slovetskii, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1709 (1960); 330 (1961).

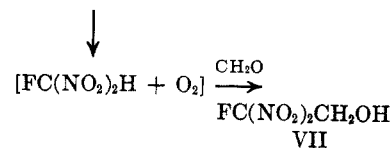
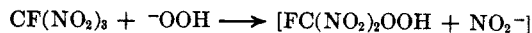
(25) The slightly higher extinction coefficient for XIII causes us no concern since this absorption is superimposed on the tail of a high-intensity shorter wavelength band whose maximum is below 200 m $\mu$ . This latter band seems to be displaced bathochromically (as best one can judge from its tail) relative to the corresponding band for other nitroaliphatics.

(26) A. I. Ivanov, I. E. Chlenov, V. A. Tartakovskii, V. I. Slovetskii, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1491 (1965).

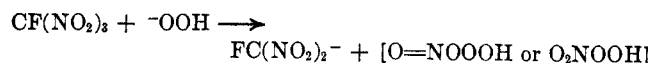
(27) R. A. Mitsch, *J. Heterocycl. Chem.*, 1, 233 (1964).

(28) A. I. Ivanov, V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, A. A. Fainzil'berg and S. S. Novikov, *Zh. Fiz. Khim.*, 40, 2298 (1966).

A possibly related reaction of fluorotrinitromethane, which constitutes a useful synthesis of 2-fluoro-2,2-dinitroethanol (VII), was found in its reduction by alkaline hydrogen peroxide in the presence of formaldehyde.

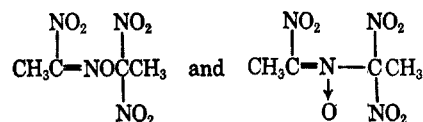


In this case, however, the over-all result of the reaction can also be explained in terms of attack by hydroperoxide ion on oxygen or nitrogen of one of the nitro groups with displacement of fluorodinitromethide ion.<sup>29</sup>

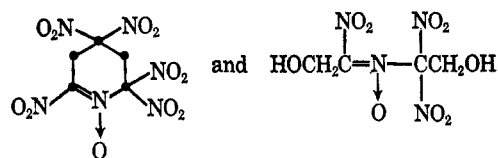


When this reaction is carried out in the absence of formaldehyde, fluorodinitromethane is obtained, but only in moderate yield because of the instability of this material under the reaction conditions.<sup>30</sup>

Referring to the ethers XIII and XIV, it should be mentioned that references to compounds containing the -O-C(NO<sub>2</sub>)<sub>2</sub>- moiety are few. Belew, Grabiell, and Clapp<sup>14</sup> have suggested

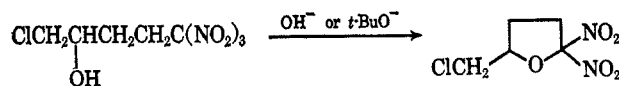


as possible structures for the autocondensation product of 1,1-dinitroethane. Although the available information did not allow an unequivocal choice, they expressed a preference for the -C=NOC(NO<sub>2</sub>)<sub>2</sub>- structure and, more recently, spectra of this material and its derivatives were reported to provide confirmatory evidence in this regard.<sup>31</sup> It is worth comment, however, that compounds closely analogous to the alternative nitron structure, *i.e.*



are likely intermediates in the reported<sup>32</sup> self-condensation of potassium 2,2-dinitroethanol in dilute sulfuric acid to form 2,4,6-trinitropyridine 1-oxide.

More closely akin to XIII and XIV, both in structure and in proposed mode of formation, is 5-chloromethyl-2,2-dinitrotetrahydrofuran, which is reported<sup>33</sup> to arise from the oxy anion of 1-chloro-5,5,5-trinitro-2-pentanol



(29) J. C. Hoffsummer has shown that in the analogous reaction of tetranitromethane with *t*-butyl hydroperoxide the nucleophile attacked on oxygen of one of the nitro groups: Ph.D. Dissertation, George Washington University, Washington, D. C., 1965.

(30) The chemistry and properties of fluorodinitromethane will be described in a subsequent paper in this series.

(31) A. I. Ivanov, L. A. Ustynyuk, V. I. Slovetskii, A. A. Fainzil'berg, and S. S. Novikov, *Zh. Organ. Khim.*, 2, 763 (1966).

(32) K. D. Gundermann and H. U. Alles, *Angew. Chem.*, 78, 906 (1966).

(33) E. Steininger, *ibid.*, 77, 427 (1965).

TABLE I  
 PREPARATION AND PHYSICAL PROPERTIES OF FLUORODINITROMETHYL COMPOUNDS

No.	Compound Z- = FC(NO <sub>2</sub> ) <sub>2</sub> -	Method of preparation <sup>a</sup>	Yield, %	Mp, °C	Bp, °C (mm)
X	Z-H	Hydrolysis of VIII	<i>b</i>		65 (80)
III	Z-CH <sub>3</sub>	Reduction of FC(NO <sub>2</sub> ) <sub>3</sub>	~40		125 (760)
		PF fluorination	54		41 (20)
		Aqueous fluorination	65		57 (44)
IV	Z-CH <sub>2</sub> CH <sub>3</sub>	PF fluorination	59		145 (760)
VII	Z-CH <sub>2</sub> OH	PF fluorination	25	12	55 (0.5)
		FC(NO <sub>2</sub> ) <sub>3</sub> reduction + CH <sub>2</sub> O	90		
IX	Z-CH <sub>2</sub> OCH <sub>3</sub>	Aqueous fluorination	76		48 (4.0)
XI	[Z-CH <sub>2</sub> O] <sub>2</sub> CH <sub>2</sub>	PF fluorination	~3	0 <sup>h</sup>	
		Aqueous fluorination	55	11-12	
XII	[Z-CH <sub>2</sub> NH] <sub>2</sub> C=O	Aqueous fluorination	30	218-219 <sup>i</sup>	
		PF fluorination	(93) <sup>c</sup>	(2-3) <sup>c</sup>	
V	Z-CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	Aqueous fluorination	(88) <sup>c</sup>		
		Hydrolysis of V	77 <sup>d</sup>	38-39	
I	Z-C <sub>6</sub> H <sub>5</sub>	PF fluorination	(95) <sup>e</sup>		
II	Z-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> - <i>m</i>	Nitration of I	73 <sup>f</sup>	31-32	
VIII	Z-COOC <sub>2</sub> H <sub>5</sub>	Aqueous fluorination	61 <sup>g</sup>		
XIII	Z-OCH <sub>2</sub> CH <sub>3</sub>	FC(NO <sub>2</sub> ) <sub>3</sub> + ethoxide	74		61 (20)
XIV	Z-OCH <sub>2</sub> CF <sub>3</sub>	FC(NO <sub>2</sub> ) <sub>3</sub> + CF <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	55		45 (15)
XV	Z-N <sub>3</sub>	FC(NO <sub>2</sub> ) <sub>3</sub> + azide	34		45 (60)
XVI	Z-F	FC(NO <sub>2</sub> ) <sub>3</sub> + fluoride	59		

<sup>a</sup> PF = perchloryl fluoride. <sup>b</sup> Obtained in ca. 20% yield in aqueous fluorination leading to VIII. <sup>c</sup> Values in parentheses are for crude products; material was not purified, but was characterized by conversion into VI. <sup>d</sup> Over-all yield for two steps (aqueous or PF fluorination and hydrolysis) based on potassium methyl 4,4-dinitrobutyrate. <sup>e</sup> Yield is for crude material. Characterized by conversion into II. <sup>f</sup> Yield based on crude I. <sup>g</sup> X (ca. 20%) obtained as a by-product. <sup>h</sup> Metastable polymorph. <sup>i</sup> A metastable polymorph has been found, mp 185-186°.

through an apparently analogous displacement of a nitro group by an alkoxy group with the assistance of ring formation.

**Physical and Spectral Properties of Fluorodinitro Compounds.**—A summary of the physical properties of the new fluorodinitromethyl compounds prepared in this study is given in Table I. Table I also allows a facile comparison of yields where several preparative methods have been used.

As already mentioned, the FC(NO<sub>2</sub>)<sub>2</sub>- group exhibits no distinct absorption in the uv spectrum other than the low-intensity band near 280 mμ characteristic of the unconjugated nitro groups.<sup>24</sup> Similarly, the frequencies of the symmetrical and asymmetrical nitro stretching vibrations in the infrared are only minimally displaced from their positions in the spectra of other negatively substituted nitroaliphatics,<sup>34</sup> and were found in the ranges 1290-1330 and 1600-1630 cm<sup>-1</sup> for all compounds studied. A set of two bands at ca. 800 and 850 cm<sup>-1</sup>, with the rather constant relative ratios 2:1, was found in all FC(NO<sub>2</sub>)<sub>2</sub>- compounds investigated except X (750, 830 cm<sup>-1</sup>) and III (770, 850 cm<sup>-1</sup>). These maxima, which are also found in some trinitromethyl compounds, are probably associated with the C-N bonds and are therefore not necessarily indicative of the fluorodinitromethyl group. Except in one case, specific C-F absorption could not be identified with certainty in these compounds owing to the presence of several bands in the 1000-1100-cm<sup>-1</sup> region. Important features in the infrared spectra of some of the materials discussed here are summarized in Table II.

The pmr spectra of the FC(NO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>- group in various of the compounds reported here exhibited a doublet

 TABLE II  
 PRINCIPAL INFRARED BANDS OF SOME  
 FLUORODINITROMETHYL COMPOUNDS

Compd	NO <sub>2</sub>		C-F	750-900 region	Miscellaneous
	assym	sym			
VII	1600	1320		802, 852	
VIII	1605	1308		795, 845	1780, —COOR
III	1600	1330		770, 850	
IX	1605	1320		800, 850	
V	1600	1322		802, 845	1740, —COOR
XI	1605	1320		798, 850	
X	1610	1325		750, 830	
XVI	1630	1330		805, 860	
FC(NO <sub>2</sub> ) <sub>3</sub>	1625	1290	1018	805, 855	
XIII	1610	?		805, 840	
XIV	1608	1310		800, 850	1185, C—O?

(*J*<sub>HF</sub> = 16-19 cps) at δ 4.5 to 5 (relative to TMS) in CCl<sub>4</sub> or CDCl<sub>3</sub> solutions.

### Experimental Section

**General (Caution!).**—Most of the starting materials and products described in this paper are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, or other means. They should therefore be handled with care. Furthermore, many fluorodinitro compounds 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 Mr. D. J. Glover of this laboratory. Methodical difficulties were encountered in obtaining reproducible analytical results on a number of the fluorodinitro compounds reported here and somewhat larger than usual deviations from calculated values were therefore occasionally judged acceptable. Melting and boiling points are uncorrected.

**Fluorination with Perchloryl Fluoride (Caution!).**—Many of the procedures described below involve filtrations of potassium chlorate from mixtures containing both combustible solvents

(34) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955); V. I. Slovet-skii, A. A. Fainzil'berg, V. I. Gulevskaya, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 683 (1961); see also ref 24.

and explosive organic materials and it should be recognized that during these filtrations one goes through a stage where the chlorate-fuel-explosive ratio may represent a potentially hazardous situation. For this reason the filtration operations are well shielded and the filter cakes are exhaustively washed with additional solvent before being allowed to air dry.

Perchloryl fluoride was purchased from the Pennsalt Chemicals Corp. and was used without further purification.<sup>35</sup> Reactions of potassium or sodium dinitro compounds with perchloryl fluoride were carried out by bubbling the gas into a well-stirred suspension of the salt. Apparatus generally involved a gas inlet tube and stirrer in a three-necked, round-bottomed flask surmounted by a reflux condenser and with bubble counters fore and aft. After introducing the salt and solvent, most of the air was purged from the system by blowing through a rapid stream of perchloryl fluoride which was vented to the hood. The rate of input was then cut back until there was a partial vacuum in the system as shown by the liquid level rising in the bubble counter aft, this partial vacuum being due to uptake of the perchloryl fluoride by the solvent in forming a saturated solution. Reaction with the salt of the dinitro compound was then evidenced by a rapid gas input with the partial vacuum being maintained. Generally, where reaction took place, the rate was determined by the speed of solution of the gas. Increasing the stirring rate increased the perchloryl fluoride uptake; decreasing it had the converse effect.

Where reaction took place it was also evidenced by the gradual solution of the yellow dinitro salt and precipitation of white potassium chlorate. Preferred solvents were those in which perchloryl fluoride and the dinitro salt had mutually maximal solubilities. Thus, reactions were extremely slow in ether in which the dinitro salt was insoluble and in water in which the perchloryl fluoride was relatively insoluble. Methanol was a more rapid solvent, aqueous methanol was faster, and dimethylformamide the most rapid solvent tried.

Temperatures were chosen between 0 and 50° to give the most convenient rates and, except in one case, temperature control was easy. The reactions appeared to be slightly exothermic and could be held at the desired temperature by varying the perchloryl fluoride input rate and by moderate cooling. A self-sustaining exothermal decomposition (*fume-off!*) took place with potassium methyl 4,4-dinitrobutyrate in DMF, but in the slower solvent, methanol, the reaction was easily controlled.

**Fluorodinitromethylbenzene (I).**—A suspension of 9.7 g of potassium dinitromethylbenzene in 200 ml of methanol was maintained at 25° while perchloryl fluoride was slowly bubbled in. After the yellow-orange salt had been replaced by a white precipitate and the color of the solution had changed to pale charreux (*ca.* 1.5 hr), 120 ml of ether was added to the reaction mixture, and 5.1 g of potassium chlorate was filtered off. Stripping off the solvent, adding ether, filtering off an additional 0.2 g of potassium chlorate (total 98%), and again stripping off the ether *in vacuo* gave 8.30 g (95%) of crude I as a yellow oil. This material was not purified further, but was converted into and analyzed as its *m*-nitro derivative (see below).

**$\alpha$ -Fluoro- $\alpha,\alpha,3$ -trinitrotoluene (II).**—Portionwise addition of 3.3 g of crude fluorodinitromethylbenzene at 0–5° to a stirred mixture of 10 ml of 96% nitric acid and 10 ml of fluorosulfonic acid caused vigorous bubbling, evolution of brown fumes, and the eventual formation of a homogeneous pale yellow solution. Pouring the mixture over crushed ice gave a yellow oil which slowly solidified on standing. The solid was collected, triturated with a small amount of cold methanol, and filtered to give 3.0 g (73%) of crude II, mp 29–30°. Recrystallization from ether-hexane or methanol-water raised the melting point to 31–32°.

*Anal.* Calcd for C<sub>7</sub>H<sub>4</sub>FN<sub>3</sub>O<sub>6</sub>: C, 34.29; H, 1.63; N, 17.15. Found: C, 34.20; H, 1.85; N, 17.06.

**1-Fluoro-1,1-dinitroethane (III).**—A satisfactory rate of reaction was achieved by bubbling perchloryl fluoride into a suspension of 90 g of potassium 1,1-dinitroethane in 750 ml of methanol plus 200 ml of water at 40°, about 7 hr being required for the complete replacement of the yellow starting material by potassium chlorate. After filtering off the latter material, the solution was diluted with 500 ml of water and extracted with 500 ml of ether. The ether phase was washed several times with water and dried over calcium chloride, and the ether was evaporated off *in vacuo*. Fractionation of the residue yielded 42.5 g

(54%) of pure III, bp 40.5–41.5° (20 mm). About 10 g of a higher boiling oil remained as a pot residue.

*Anal.* Calcd for C<sub>2</sub>H<sub>3</sub>FN<sub>2</sub>O<sub>4</sub>: C, 17.38; H, 2.17; N, 20.25. Found: C, 17.58; H, 2.18; N, 19.81.

**1-Fluoro-1,1-dinitropropane (IV).**—The perchloryl fluoride fluorination of 100 g of potassium 1,1-dinitropropane in a mixture of 750 ml of methanol and 100 ml of water at 35–40° required *ca.* 3.5 hr. Approximately 1 l. of water was added to dissolve most of the potassium chlorate and the product was extracted into chloroform. The extracts were washed with 250 ml of water, 250 ml of 2% sodium carbonate solution, and again with 250 ml of water, and dried over magnesium sulfate, and the chloroform was stripped off *in vacuo*. Fractionation of the residue under reduced pressure gave 51.6 g of IV (59%): bp 45–47° (15 mm), 144.5° (760 mm).

*Anal.* Calcd for C<sub>3</sub>H<sub>5</sub>FN<sub>2</sub>O<sub>4</sub>: C, 23.68; H, 3.29; N, 18.41. Found: C, 23.93; H, 3.29; N, 18.05.

**Methyl 4-Fluoro-4,4-dinitrobutyrate (V).**—At 37° uptake of perchloryl fluoride by a suspension of 73 g of potassium methyl 4,4-dinitrobutyrate in 750 ml of methanol was substantially complete in 5 hr. After cooling the mixture to –10°, 37.5 g of potassium chlorate was filtered off, most of the methanol was stripped off *in vacuo*, an additional 0.8 g of potassium chlorate was filtered off (98.5% total), and the remaining methanol was removed to leave 62 g of crude V as a pale yellow oil which solidified on standing in the freezer, mp *ca.* 2–3°. For analysis, this ester was converted into the corresponding acid (see below).

**4-Fluoro-4,4-dinitrobutyric Acid (VI).**—A 52-g sample of crude V (see above) was refluxed for 2–3 hr with 500 ml of constant-boiling hydrochloric acid. The almost clear solution which resulted was filtered hot through a layer of Celite on a sintered-glass funnel and chilled, and the precipitate was filtered off. Concentration of the mother liquor afforded an additional two crops, leading to a total of 35.9 g (77%) of crude VI, mp 35–38°. Recrystallization from chloroform-carbon tetrachloride afforded pure VI as long white needles, mp 37–38°.

*Anal.* Calcd for C<sub>4</sub>H<sub>5</sub>FN<sub>2</sub>O<sub>6</sub>: C, 24.48; H, 2.55; N, 14.28; F, 9.69. Found: C, 24.73; H, 2.88; N, 13.87; F, 9.46.

**2-Fluoro-2,2-dinitroethanol (VII).**—To a cooled, stirred solution of 53.0 g of 85% potassium hydroxide in 140 ml of water and 500 ml of methanol was added portionwise 132.8 g of 2,2-dinitro-1,3-propanediol in 240 ml of methanol; the temperature was kept below 12°. The precipitated potassium 2,2-dinitroethanol was separated from the solvent through the use of a filter stick and washed twice with 250-ml portions of methanol and once with 350 ml of ether, 500 ml of dimethylformamide was then added, the mixture was cooled to 15°, and perchloryl fluoride was bubbled in at this temperature. The uptake was relatively rapid, with the mixture slowly discoloring until, by the time the perchloryl fluoride uptake was complete, the solution was dark brown. The insoluble material was filtered off and washed with ether. Addition of 2 ml of concentrated sulfuric acid to the dark brown mother liquor caused a color change to bright orange. Most of the solvent was then distilled off below 30° (1.5 mm). The residue was taken up in 250 ml of ether and washed with three 100-ml portions of water, the combined aqueous washes were reextracted with 250 ml of ether, and the combined ether phases were washed with 100 ml of 3% hydrochloric acid.<sup>36</sup> The ether was stripped off and the residual orange oil was fractionated *in vacuo* to yield 30.7 g of VII (25% of theory), bp 55–57° (1.5 mm). A second fractionation gave the analytical sample which was still relatively impure, but whose infrared spectrum and retention volume were essentially identical with those of a purer sample obtained by fluorotrinitromethane reduction (see below).

*Anal.* Calcd for C<sub>2</sub>H<sub>3</sub>FN<sub>2</sub>O<sub>5</sub>: N, 18.20. Found: N, 17.28, 16.99.

**Fluorination with Elemental Fluorine (The Grakauskas Reaction).**—All experiments with elemental fluorine were carried out in a well-shielded and vented area. Fluorine-nitrogen mixtures in ratios of approximately 1:1 to 1:3 were generally used and were delivered through an apparatus constructed essentially according to the recommendations given by the Gen-

(35) Properties and methods of handling this material are described in Pennsalt Chemicals Corp. New Products Booklet DC-1819, "Perchloryl Fluoride," 1957.

(36) In earlier trials where this cumbersome separation procedure was not used, fume-offs occurred during the fractionation step, probably owing to 2,2-dinitro-1,3-propanediol in the pot residue. At the time the work was done it was not known that VII is a moderately stable to weak alkali, which would have simplified the separation appreciably. Also, if we were to repeat the work, we would run the fluorination in the presence of excess weak base.

eral Chemical Division, Allied Chemical Corp.<sup>37</sup> The setup was modified by incorporating a surge tank of about 500-ml capacity between the back pressure control valve and the back pressure indicator in order to minimize bouncing of the rotometer float. Metal to glass connections were of Teflon tubing. The fluorinations were carried out in ordinary glass equipment consisting of a four-neck flask fitted with stirrer, thermometer, gas inlet tube, and condenser; the stirrer was well lubricated with water. Little etching of the apparatus was observed, even after extensive use. Occasionally, where methanol-wet dinitroalkane salts were used as starting materials, small "flashes of blue fire" were observed in the gas inlet tube, accompanied by slight popping sounds, but these were never sufficient to rupture the apparatus and could be avoided easily.

**Methyl 4-Fluoro-4,4-dinitrobutyrate (V).**—A mixture of 51.5 g of potassium methyl 4,4-dinitrobutyrate, 10 g of sodium bicarbonate, and 300 ml of water in a 1-l. standard fluorination apparatus was stirred vigorously and held at 20–25° as a 2:1 nitrogen-fluorine mixture was introduced. The reaction mixture changed in color from yellow to red-orange as the starting material gradually dissolved; after about 45 min a sharp, milky white end point was observed. The system was purged of fluorine with pure nitrogen, the reaction mixture was extracted with ether, and the extracts were washed with water, dried, and concentrated. There remained 41.4 g of crude V (88%) as a yellow oil.

**Methyl 2-Fluoro-2,2-dinitroethyl Ether (IX).**—At 0–5° a 2:1 nitrogen-fluorine mixture was bubbled through a solution of 2.5 g of potassium 2,2-dinitroethyl methyl ether in 100 ml of water until the yellow color disappeared. The reaction mixture was purged with nitrogen and extracted with methylene chloride, and the extract was dried and distilled. Thus was obtained 1.7 g of IX (76%), bp 47–48° (4.0 mm).

*Anal.* Calcd for C<sub>3</sub>H<sub>5</sub>FN<sub>2</sub>O<sub>5</sub>: N, 16.66; F, 11.30. Found: N, 16.85, F, 10.93.

**Bis(2-fluoro-2,2-dinitroethyl)formal (XI).**—Dipotassium bis(2,2-dinitroethyl)formal was prepared by the hydroperoxide reduction<sup>17</sup> of bis(2,2,2-trinitroethyl)formal as follows. To 30.0 g of bis(2,2,2-trinitroethyl)formal in 225 ml of methanol at 0° was added 45 ml of cold 30% hydrogen peroxide; then, dropwise with stirring and continued cooling over a period of 30 min, 36 g of 85% potassium hydroxide in 210 ml of methanol was also added, the temperature being kept below 10°. The mixture was stirred a further 20 min and filtered. The precipitate was washed with three 100-ml portions of methanol, the methanol-wet salt was suspended in a solution of 10 g of sodium carbonate in 500 ml of water, and the mixture was concentrated<sup>38</sup> to a total volume of 400 ml at a temperature not above 50°. The solution was then rapidly cooled to 22° with vigorous stirring to impart small particle size to the reprecipitating salt.

The resulting mixture was fluorinated in the standard fluorination apparatus at 20–25° with a nitrogen-fluorine ratio of 3:1. A milky white end point was reached in about 2 hr, after which time the reaction mixture was purged with nitrogen and the product was extracted into chloroform. The extracts were washed with four 100-ml portions of 5% sodium hydroxide and once with water. After drying, the solvent was stripped off; the last traces were removed by holding the temperature at 70° (1 mm) for several hours. There remained 14.1 g (55%) of very pale yellow XI.

The analytical sample was obtained by thoroughly washing a methylene chloride solution of XI with concentrated sulfuric acid, then with water, dilute sodium hydroxide, again with water, drying, removing the solvent, and recrystallizing the residual oil from methylene chloride-hexane, mp<sup>39</sup> 11–12.

*Anal.* Calcd for C<sub>3</sub>H<sub>5</sub>F<sub>2</sub>N<sub>4</sub>O<sub>10</sub>: C, 18.76; H, 1.89; F, 11.88. Found: C, 19.05; H, 2.02; F, 11.32.

**Ethyl 2-Fluoro-2,2-dinitroacetate (VIII) and Fluorodinitromethane (X).**—A fluorine-nitrogen mixture (3:1) was introduced at 0° with stirring into a solution of 21.6 g of potassium ethyl 2,2-dinitroacetate in 200 ml of water containing 18 g of sodium

bicarbonate. The exit gases were passed through a trap held at –70°. The system was purged with nitrogen, the reaction mixture was extracted with methylene chloride, and the trap contents were combined with the extracts. Removal of the solvent yielded 16.5 g of a pale yellow oil which was shown by glpc (column: 10% May-Baker silicon oil on Haloport F) to be a mixture of two products. By fractional distillation at 40 mm (bath temperature not above 100°), the lower boiling component could be removed almost completely. The remaining oil was distilled in a molecular still at 80° (0.01 mm) to yield 12.0 g of VIII (61.2%) of an estimated purity of 98% (glpc).

*Anal.* Calcd for C<sub>4</sub>H<sub>5</sub>FN<sub>2</sub>O<sub>6</sub>: N, 14.29; F, 9.69. Found: N, 14.10; F, 9.42.

The lower boiling fraction was refractionated at 80 mm to give 2.5 g of fluorodinitromethane (20.3%) as a colorless oil of pungent odor, bp 64–65° (80 mm) and 125° (760 mm).

*Anal.* Calcd for CHFN<sub>2</sub>O<sub>4</sub>: N, 22.58; F, 15.31; neut equiv, 124. Found: N, 22.58; F, 14.92; neut equiv, 121.

**Bis(2-fluoro-2,2-dinitroethyl)urea (XII).**—N,N'-Bis(2,2,2-trinitroethyl)urea (39 g) was added gradually to a stirred mixture of 66 g of potassium iodide in 500 ml of methanol;<sup>18</sup> the mixture was stirred 24 hr at room temperature, cooled in an ice bath, and filtered. The solid was washed with a small amount of methanol and liberally with ether to give 24 g (64.2%) of crude dipotassium N,N'-bis(2,2-dinitroethyl)urea.

The crude salt was dissolved in 400 ml of water containing 10 g of sodium bicarbonate and was fluorinated in the standard apparatus at 0° until the mixture became slightly acidic. The pale yellow, gummy solid was filtered off, dissolved in methylene chloride-ether (1:1), and filtered through a 1 × 15 in. column of silica (G. F. Smith, Columbus, Ohio). The colorless portion of the eluate was collected and concentrated until precipitation started. Addition of methylene chloride and chilling afforded 6.4 g of crude XII (29.8% based on dipotassium salt). After recrystallization from toluene-ethyl acetate, the product melted at 185–186° dec. In later experiments a second polymorph, mp 218–219° dec, was obtained and we can no longer make the metastable 186° form in this laboratory.

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>F<sub>2</sub>N<sub>6</sub>O<sub>8</sub>: N, 25.31; F, 11.42; mol wt, 332. Found: N, 25.29; F, 11.61; mol wt (MEK), 325.

**Reactions with Fluorotrinitromethane.**—Fluorotrinitromethane was prepared by the aqueous fluorination of nitroform salts with slight modifications on a procedure first reported by Grauskas and Baum<sup>22</sup> and was used without further purification.

**Fluorotrinitromethane.**—A solution of 114 g of nitroform in 1000 ml of 5% sodium carbonate solution was fluorinated at 0–5° in the standard apparatus until the mixture was bleached to a milky white suspension of pH 6. The product, a heavy colorless oil, was separated, washed with 5% sodium bicarbonate solution and with water, and dried over magnesium sulfate to give 115 g (90%) of fluorotrinitromethane of 98 mol % purity (glpc).

**Ethyl Fluorodinitromethyl Ether (XIII).**—At –10 to –15° and over a period of 15 min, a solution of sodium ethoxide prepared by dissolving 4.6 g of sodium in 70 ml of ethanol was added to 16.9 g of fluorotrinitromethane in 70 ml of methylene chloride; the mixture was stirred another 10 min below 10°. The mixture was then poured into ice-cold dilute sulfuric acid, the phases were separated, the aqueous phase was extracted with methylene chloride, and the combined extracts were washed with water, dried, and distilled to yield 12.45 g of crude XIII (74%). Refractionation gave 11.2 g of pure material, bp 60–62° (20 mm), λ<sub>max</sub><sup>MeOH</sup> 285 mμ (ε ca. 95).<sup>40</sup>

*Anal.* Calcd for C<sub>5</sub>H<sub>5</sub>FN<sub>2</sub>O<sub>5</sub>: C, 21.44; H, 3.00; F, 11.30; N, 16.66; ethoxyl, 26.8; NO<sub>2</sub>, 54.7. Found: C, 21.55; H, 2.92; F, 10.61; N, 16.12; ethoxyl, 25.3; NO<sub>2</sub>, 50.1.<sup>41</sup>

**2,2,2-Trifluoroethyl Fluorodinitromethyl Ether (XIV).**—A solution of sodium trifluoroethoxide was prepared by dissolving 6.9 g of sodium in 100 ml of hot trifluoroethanol and cooled to ca. 5° with the gradual addition of 25 ml of dimethyl sulfoxide to keep the mixture stirrable. Fluorotrinitromethane (34 g) was added with stirring. The mixture was stirred 5 hr at 20–25° and filtered through a sintered-glass funnel (11 g of sodium nitrite was obtained), and the filtrate was poured into cold dilute sul-

(37) Product Data Sheet PD-TA-85413A, 9-15-1958, Product Development Department, General Chemical Division, Allied Chemical Corp., New York, N. Y.

(38) The purpose of this concentration step was to remove most of the methanol carried in with the starting material (methanol wet for desensitizing purposes), which otherwise caused the "flashes of blue fire" mentioned above.

(39) A lower melting polymorph of mp ca. 0° exists. If seed crystals are not available, the initial crystallization may require cooling to –70° and extensive scratching.

(40) The material decomposed in methanol at a measurable rate with the appearance of characteristic nitrous acid (or methyl nitrite) "fingerprint" absorption centering around 350 mμ.

(41) Determined as nitrite by its absorption at 354 mμ by D. J. Glover of this laboratory; the accuracy of the method has not been established.

furic acid. This was extracted with methylene chloride, the extract was dried and freed from solvent, and the residue was washed twice with water and dried over magnesium sulfate. Distillation of the oil afforded 25 g of XIV (55.3%), bp 44–45° (15 mm).

*Anal.* Calcd for  $C_3H_2F_4N_2O_5$ : N, 12.62; F, 34.22. Found: N, 12.34; F, 33.84.

**Fluorodinitromethyl Azide (XV).**—To a solution of 85 g of fluorotrinitromethane in 175 ml of dimethylformamide was added, at  $-15$  to  $-20^\circ$  and over a period of 10–15 min, 40 g of sodium azide. The mixture was stirred 2 hr at  $-15$  to  $-20^\circ$  (*Caution! at higher temperatures the reaction may get out of hand*) and then poured into ice-water (strong gassing). The product was extracted into methylene chloride, the solvent was removed at a temperature below  $65^\circ$ , and the residue was washed with water, dried, and fractionated at 40 mm of pressure. At ca.  $40^\circ$ , 31.5 g of crude XV containing ca. 10% starting material distilled over (yield ca. 34%). Refractionation at 60 mm (bp  $45^\circ$ ) gave a material which appeared to be pure by glpc (silicon oil on Teflon column), but which exhibited a weak band in the  $1700\text{-cm}^{-1}$  region of the infrared spectrum which suggested the presence of an impurity. The spectrum also showed a strong azide band at  $2200\text{ cm}^{-1}$  in addition to the usual nitro bands at 1325 and  $1610\text{ cm}^{-1}$ .

Fluorodinitromethyl azide decomposes slowly at room temperature and should be handled with care. Further characterization and reactions of this material will be described in a subsequent paper.

**Difluorodinitromethane (XVI).**—A 500-ml, four-necked flask was fitted with a stirrer, thermometer, and a vented addition funnel whose stem extended almost to the bottom of the vessel. The fourth neck was connected to a cold trap held at  $-70^\circ$  during the experiment. The system was purged with a slow stream of dry nitrogen through the vent of the addition funnel, the flask was charged with 35 g of anhydrous potassium fluoride and 250 ml of sulfolane, and the mixture was heated to  $150^\circ$  for 15 min and allowed to cool to  $95^\circ$ . At this temperature, 50.7 g of fluorotrinitromethane was added over a period of 1.5 hr; the mixture was stirred an additional 0.5 hr at  $100^\circ$  and allowed to cool. The trap contents were dried over magnesium sulfate and were shown by glpc and by comparison of the infrared spectrum with that of a sample prepared by the method of Mitsch<sup>27</sup> to be essentially pure XVI, yield 25 g (58.7%).

**2-Fluoro-2,2-dinitroethanol (VII) by FTM Reduction.**—Methanol (90 ml) and 42 ml of 30% aqueous hydrogen peroxide were mixed at  $0^\circ$  in a 500-ml, three-neck flask fitted with stirrer, thermometer, and vented addition funnel. A solution of 14.5 g of sodium hydroxide in 70 ml of water was prepared and 1 ml of this was added at  $-5$  to  $-10^\circ$ . At the same temperature, 30 ml of 36–37% aqueous formaldehyde solution was added gradually (exotherm) followed by 50 g of fluorotrinitromethane.

With the temperature kept at  $-5$  to  $-10^\circ$ , the remainder of the sodium hydroxide solution was added over a 30-min period; the yellow solution was then stirred an additional 15 min while the temperature was allowed to rise to  $0^\circ$ .

Dilute sulfuric acid (equivalent to 5 ml of concentrated  $H_2SO_4$ ) was added dropwise to the reaction mixture with the temperature maintained at  $0^\circ$  until, toward the end of the addition, a strong exotherm raised it to  $10$ – $15^\circ$ . After saturation of the reaction mixture with sodium chloride, it was extracted with one 100-ml and two 50-ml portions of methylene chloride and the extracts were dried and freed from solvent. Vacuum fractionation of the residual oil gave 41.3 g VII (90.6%) of excellent purity (glpc), bp  $55^\circ$  (0.5 mm).

*Anal.* Calcd for  $C_2H_3FN_2O_5$ : N, 18.20; F, 12.33. Found: N, 18.51; F, 12.01.

**Fluorodinitromethane (X) by FTM Reduction.**—To a solution of 5 g of fluorotrinitromethane in 10 ml of methanol was added dropwise at  $-10^\circ$  a mixture of 6.7 g of 30% hydrogen peroxide and 3.3 g of potassium hydroxide in 15 ml of methanol. A thick yellow precipitate formed (efficient stirrer necessary). The mixture was poured into ice-cold dilute sulfuric acid, the resulting clear solution extracted with methylene chloride, the extracts dried, and the solvent distilled off through a Vigreux column. The residue on fractionation gave 1.5 g (41%) of crude X. The product was identical with, although less pure than, the material obtained as a by-product in the aqueous fluorination of potassium ethyl dinitroacetate.

**Registry No.**—I, 17003-70-2; II, 17003-71-3; III, 13214-58-9; IV, 17003-25-7; V, 15895-14-4; VI, 15895-15-5; VII, 17003-75-7; VIII, 17003-76-8; IX, 17003-77-9; X, 7182-87-8; XI, 17003-79-1; XII, 17003-80-4; XIII, 17021-83-9; XIV, 17003-81-5; XV, 17003-82-6; XVI, 1185-11-1;  $FC(NO_2)_3$ , 1840-42-2.

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## Aqueous Fluorination of Nitronate Salts<sup>1</sup>

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The fluorination of aqueous solutions of nitronate salts gave *gem*-fluoronitro compounds. The following compounds were synthesized by this reaction: fluorotrinitromethane, 1-fluoro-1,1-dinitroethane, 1-fluoro-1,1-dinitropropane, 2-fluoro-2,2-dinitroethanol, 1-fluoro-1-nitroethane, and 1-fluoro-1-nitropropane.

Although many examples of the direct chlorination and bromination of nitronate salts to give  $\alpha$ -halonitro compounds are known,<sup>2</sup> only indirect methods have been reported for fluorination. Perchloryl fluoride has been used to convert *gem*-nitronitronate salts<sup>3</sup> and simple secondary nitronate salts<sup>4</sup> into the corresponding fluorine derivatives, but attempts to apply this re-

action to simple primary nitronate salts were unsuccessful. Perfluoropiperidine has also been used as a fluorinating agent to prepare 2-fluoro-2-nitropropane.<sup>5</sup>

The present investigation concerns the preparation of fluoronitro compounds by the direct fluorination of aqueous solutions of nitronate salts, under conditions similar to those generally used for chlorination and bromination of nitronate salts. Although the fluorination of sodium hydroxide in aqueous solution is the standard

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(2) P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **61**, 19 (1964).

(3) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

(4) H. Shechter and E. R. Robinson, Jr., *ibid.*, **25**, 175 (1960).

(5) R. E. Banks and O. E. Williamson, *Chem. Ind. (London)*, 1864 (1964).