as is catalysis by the ortho hydroxyl group in the hydrolysis of salicylate esters. Bender has, however, presented convincing evidence that the latter type of catalysis is not general for addition of all nucleophiles to the carbonyl group, only the water molecule.[22]

The fact that methyl 3,5-dihydroxybenzoate undergoes thiocyanate displacement seven times as fast as methyl 2,4-dihydroxybenzoate shows that the factors discussed above are in fact not the most important ones affecting the rate at 140–160° and suggests that the displacement is uncatalyzed and occurs prior to, not simultaneously with, decarboxylation. The difference in the admittedly uncertain activation energies of these two compounds is not large enough to change the rate ratio drastically at other attainable temperatures, the isokinetic temperature falling near room temperature. The isotope effect (k_{OH}/k_{OD} = 0.97 at 150.7°) is also nearly negligible.

The fraction of isothiocyanate formed by the reaction of the ambident nucleophile with the methyl esters, 4–5%, is comparable with similar displacements.[23] The higher proportion (46%) from the ethyl ester is not due to thermal isomerization of ethyl thiocyanate; we found the rate constant for formation of EtNCS from EtSCN in contact with molten eutectic to be only 3×10^{-6} sec^{-1} at 150° (half-life 3 days) and 6×10^{-6} at 170°. The published value[24] for methyl thiocyanate is 8.5×10^{-7} sec^{-1} at 136°. The ethyl thiocyanate, which is collected in the cold trap within a few minutes of its formation, cannot isomerize appreciably in this time. The large amount of iso product must then be formed directly. The evidence does not enable us to determine whether the cause is increased SN1 or "pull–push" character of the displacement[25] or a structural effect on solvation in the neighborhood of the reaction center.

Registry No.—Sodium thiocyanate, 540-72-7; potassium thiocyanate, 333-20-0; methyl 2,4-dihydroxybenzoate, 2150-47-2; methyl 3,5-dihydroxybenzoate, 2150-44-9; ethyl 3,5-dihydroxybenzoate, 4142-98-7; isopropyl 3,5-dihydroxybenzoate, 33046-40-1.

(22) M. L. Bender, F. J. Kézdy, and B. Zerner, *J. Amer. Chem. Soc.*, **85**, 3017 (1963).
(23) A. Fava, A. Iliceto, and S. Bresadola, *ibid.*, **87**, 4791 (1965).
(24) C. N. R. Rao and S. N. Balasubrahmanyam, *Chem. Ind. (London)*, 625 (1960).
(25) N. Kornblum, *et al.*, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

Fluoronitroaliphatics. VI.[1] Preparation of *N*-(2,2,2-Fluorodinitroethyl)amides

HORST G. ADOLPH

Advanced Chemistry Division, U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910

Received August 6, 1971

The reaction of 2,2,2-fluorodinitroethylamine with acid chlorides was used to prepare a variety of fluorodinitroethyl-substituted amides, urethanes, and ureas. Urethanes were also prepared by the addition of alcohols to 2,2,2-fluorodinitroethyl isocyanate. The use of the *tert*-butyl group as a protecting group in the synthesis of *N*-(2,2,2-fluorodinitroethyl)amides is described.

N-(2,2,2-Trinitroethyl)amides, urethanes, and ureas, some of which are of interest as explosive ingredients, are generally prepared by amidoalkylation of trinitromethane (eq 5, R = NO_2). The reaction has been carried out by reacting either trinitromethane with a hydroxymethyl amide, or 2,2,2-trinitroethanol with an amide *via* generation of the methylol amide and trinitromethane *in situ*.[2,3,4]

There are apparently no reports in the literature regarding the analogous amidoalkylation of 1,1-dinitroalkanes (R = alkyl). When we attempted to employ this reaction to prepare *N*-(2,2,2-fluorodinitroethyl)-amides (R = F) it failed completely. 2,2,2-Fluorodinitroethanol was unreactive toward a variety of amides as well as urethane and urea, and fluorodinitromethane acted as a demethylolating agent upon hydroxymethyl amides, urethane, and urea. This behavior can be rationalized by examining the equilibria involved in the desired reaction (eq 5).

$$RC(NO_2)_2CH_2OH \rightleftharpoons RC(NO_2)_2^- + CH_2O + H^+ \quad (1)$$

$$RC(NO_2)_2H \rightleftharpoons RC(NO_2)_2^- + H^+ \quad (2)$$

$$R'CONH_2 + CH_2O \rightleftharpoons R'CONHCH_2OH \quad (3)$$

$$R'CONHCH_2OH + H^+ \rightleftharpoons R'CONHCH_2^+ + H_2O \quad (4)$$

$$R'CONHCH_2^+ + R{-}C(NO_2)_2^- \longrightarrow R'CONHCH_2C(NO_2)_2R \quad (5)$$

It follows from the anomalously low acidity of fluorodinitromethane[5,6] that when R = F, in complete contrast to the case where R = NO_2, equilibria 1 and 2 are shifted completely to the left under pH conditions where equilibrium 4 can provide a supply of carbonium ions sufficient for the reaction to proceed at an observable rate.

We recently reported the synthesis of 2,2,2-fluorodinitroethylamine, only the second primary 2,2-dinitroethylamine to be described in the literature, and found it to be an isolable and reasonably stable species.[6] In view of the above difficulties we examined its utility for the preparation of *N*-(2,2,2-fluorodinitroethyl)amides, urethanes, and ureas by reaction with a variety of acid chlorides.

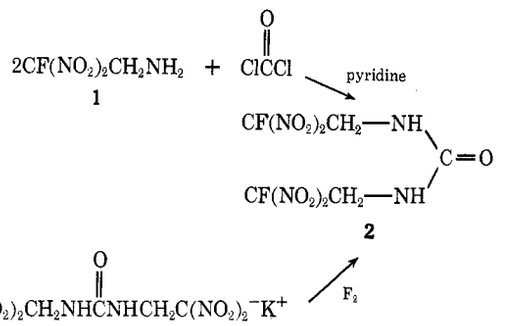
The reaction in methylene chloride solution of acetyl chloride with a 1:1 mixture of 2,2,2-fluorodinitroethylamine (**1**) and pyridine was straightforward and gave *N*-(2,2,2-fluorodinitroethyl)acetamide in >95% yield. In the reaction of **1** with this and other acid

(1) Part V: H. G. Adolph, *J. Org. Chem.*, **35**, 3188 (1970).
(2) H. Feuer and U. E. Lynch-Hart, *ibid.*, **26**, 391, 587 (1961).
(3) P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **61**, 19 (1964).
(4) A. Wetterholm, *Sv. Kem. Tidskr.*, **76**, 628 (1964).
(5) H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966).
(6) H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, **34**, 47 (1969).

chlorides the order of addition of the reactants is of some importance; because of the sensitivity of **1** to acids in the presence of water[6] it is desirable to keep the reaction medium basic until all **1** has reacted, *i.e.*, to add the acid chloride slowly to the mixture of **1** and base. The reaction of **1** with 4,4-dinitroheptanedioyl chloride was carried out in a similar manner. The product, *N,N'*-bis(2,2,2-fluorodinitroethyl)-4,4-dinitroheptanedioic amide, was obtained in 57% yield. **1** and oxalyl chloride in a ratio of 2:1 in the presence of 2 equiv of pyridine gave *N,N'*-bis(2,2,2-fluorodinitroethyl)oxamide (**10**) in excellent yield. Isolation of the intermediate oxamic acid chloride was not attempted.

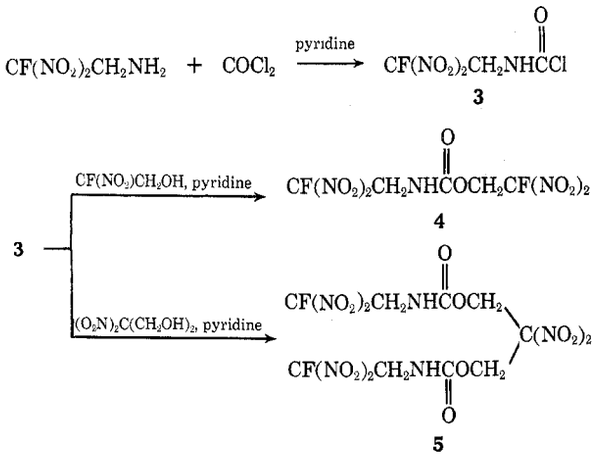
Depending on the ratio of reactants and the nature of the base employed as hydrogen chloride scavenger, the main products of the reaction of **1** with phosgene were *N,N'*-bis(2,2,2-fluorodinitroethyl)urea (**2**), *N*-(2,2,-2-fluorodinitroethyl)carbamyl chloride (**3**), and 2,2,2-fluorodinitroethyl isocyanate.

In a ratio of 2:1:2 in benzene or methylene chloride solution, **1**, phosgene, and pyridine reacted readily to give the urea **2**, which had been prepared previously by

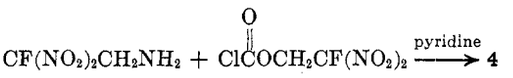


the aqueous fluorination of dipotassium *N,N'*-bis-(2,2-dinitroethyl)urea.[7]

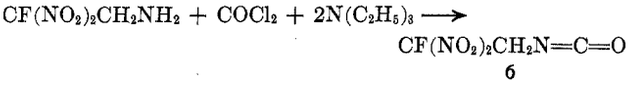
With a 1:phosgene:pyridine ratio of 1:1:1, *N*-(2 2,2-fluorodinitroethyl)carbamyl chloride (**3**), was produced. This material was not obtained pure but was characterized by conversion to the corresponding urethanes on reaction with 2,2,2-fluorodinitroethanol and 2,2-dinitropropane-1,3-diol in the presence of pyridine.



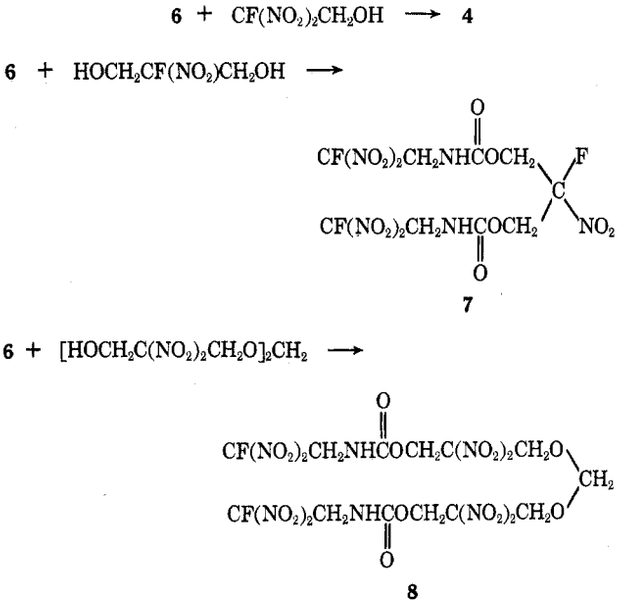
4 was also prepared by the alternate pathway of reacting **1** with 2,2,2-fluorodinitroethyl chloroformate.



N-(2,2,2-Fluorodinitroethyl)carbamyl chloride (**3**) did not readily lose hydrogen chloride on further treatment with pyridine, but was converted to 2,2,2-fluorodinitroethyl isocyanate (**6**) on reaction with triethylamine. Alternatively, **1**, phosgene, and triethylamine in a ratio of 1:1:2 in benzene solution reacted at room temperature to give **6** in *ca.* 20% yield.

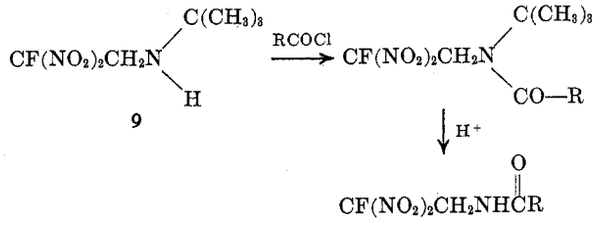


A distillable, colorless liquid, **6** was storable at room temperature for several days. On prolonged contact with triethylamine in benzene, it formed a cyclic trimer, mp *ca.* 150° dec. It underwent addition reactions when treated with a variety of nitrosubstituted alcohols in methylene chloride solution in the presence of catalytic amounts of pyridine.



It has been pointed out[6] that neat 2,2,2-fluorodinitroethylamine is unstable under ambient conditions; even in relatively dilute methylene chloride solution (<25%) appreciable decomposition takes place on extended storage at ambient temperatures. Another problem in treating **1** with acid chlorides on a larger scale is presented by its sensitivity toward acids, particularly in the presence of water, which could lead to vigorous decomposition taking place during the reaction.

In attempts to circumvent these hazards involved in the direct synthesis of 2,2,2-(fluorodinitroethyl)-amides, an alternative route for their preparation was examined consisting in the acylation of *tert*-butyl-(2,2,2-fluorodinitroethyl)amine (**9**) with acid chlorides

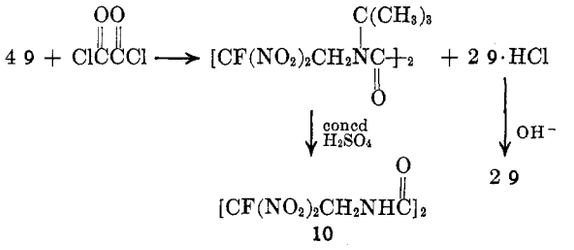


(7) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

or anhydrides followed by de-*tert*-butylation of the resulting amide by strong acid.

The starting material, **9**, was prepared readily and in almost quantitative yield by addition of *tert*-butylamine to an aqueous solution of 2,2,2-fluorodinitroethanol; the oil that separated was essentially pure **9**. It is stable to extended storage at room temperature and its salts with strong acids are stable in aqueous solution.

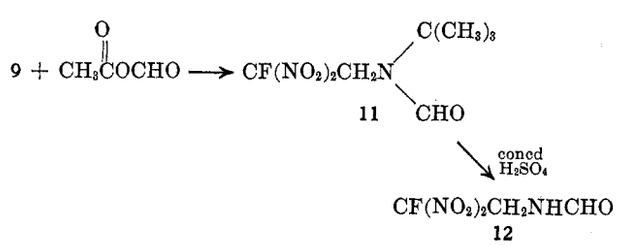
9 was found to be less reactive toward acylating agents than **1**, as might be expected because of steric hindrance by the *tert*-butyl substituent. It was also found that in the reaction with a number of acid chlorides, *e.g.*, acetyl chloride and oxalyl chloride, pyridine and trialkylamines were not satisfactory as hydrogen chloride scavengers; these bases reacted with the acid chloride without participation of **9**. The desired amide in the reaction with oxalyl chloride was obtained, however, by using an excess (which was readily recovered) of **9** to neutralize the hydrogen chloride.



10

Removal of the *tert*-butyl groups in the oxamide was effected by the method of Lacey,[8] stirring a suspension of the material in concentrated sulfuric acid, trifluoroacetic acid, or a mixture of concentrated sulfuric and acetic acids for several hours at room temperature.

N-(2,2,2-Fluorodinitroethyl)formamide (**12**) was also prepared *via* **9** in the manner outlined above. Treating **9** with acetic–formic anhydride gave *tert*-butyl-(2,2,2-fluorodinitroethyl)formamide (**11**) in 71% yield. The *tert*-butyl group in this compound was less readily removed than in other carboxamides. Treatment with trifluoroacetic acid at ambient or reflux temperatures, for example, was ineffective. However, prolonged action of concentrated sulfuric acid converted **11** to **12** in moderate yield.



11

12

Experimental Section

Caution. Many compounds described herein are explosive in nature and appropriate care should be taken in their handling. Precautions recommended in working with fluorodinitromethyl compounds, especially 2,2,2-fluorodinitroethanol, have been described elsewhere.[7] Neat 2,2,2-fluorodinitroethylamine (**1**) must be handled with extreme care.[6]

Melting and boiling points are uncorrected; elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Nmr spectra were obtained on a Varian HA-100 spectrometer; chemical shifts are relative to TMS as internal standard.

Preparation of Amides from 2,2,2-Fluorodinitroethylamine (1) and Acid Chlorides. General Procedure.—**1** was prepared as described in ref 6. For the initial preparation of an unknown amide distilled **1** (caution, see above) was used; for subsequent preparations the methylene chloride solution of crude **1** as obtained from the reaction of 2,2,2-fluorodinitroethanol with ammonia was found satisfactory; a 70% yield of **1** from 2,2,2-fluorodinitroethanol was assumed in the latter preparations.

The methylene chloride solution of **1** (15–20 g/100 ml) was cooled in an ice bath and pyridine, the calculated amount plus 10% excess, was added with stirring. With continued cooling, a solution of the acid chloride in methylene chloride was added and the mixture was stirred, initially in an ice bath, later at room temperature, for 2 to 15 hr depending on the reactivity of the acid chloride. The methylene chloride solution was then washed with small amounts of dilute sulfuric acid and water, dried, and freed from solvent, and the crude amide was recrystallized from the appropriate solvent.

***N*-(2,2,2-Fluorodinitroethyl)acetamide.**—The crude amide was difficult to crystallize without seed crystals. These were obtained by depositing a small quantity of crude amide on a short column of silica (G. F. Smith, Columbus, Ohio), washing with methylene chloride, eluting with 1:1 methylene chloride–ether, and freeing the main product containing fraction from solvent. The remaining oil crystallized on standing.

Using seed crystals, the crude amide was recrystallized from chloroform–hexane (2:1), mp 57–58°, yield (based on 2,2,2-fluorodinitroethanol) 71%.

Anal. Calcd for $C_4H_6FN_3O_5$: N, 21.53; F, 9.74; mol wt, 195.1. Found: N, 21.2, 21.4; F, 10.0, 10.1; mol wt (in CH_3CN), 190.

***N*,*N*′-Bis(2,2,2-fluorodinitroethyl)-4,4-dinitroheptanedioic Amide.**—4,4-Dinitroheptanedioyl chloride was prepared by the procedure of Herzog, *et al.*[9] The reaction mixture was refluxed for 3 hr and poured into dilute sulfuric acid, the solvent was allowed to evaporate, and the solid product was recrystallized from ethylene dichloride–dimethoxyethane. From 4.85 g of acid chloride there was obtained 6.5 g of crude amide. After repeated fractional crystallization the product melted at 170.5–171.5°, nmr (CD_3CN) δ 2.63 (sym m), 4.65 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps).

Anal. Calcd for $C_{11}H_{14}F_2N_8O_{14}$: C, 25.39; H, 2.71; F, 7.30. Found: C, 25.3; 25.3; H, 2.6, 2.7; F, 7.6, 7.7.

***N*,*N*′-Bis(2,2,2-fluorodinitroethyl)urea (2).**—The reaction mixture obtained by the slow addition of a solution of phosgene in methylene chloride to the **1** + pyridine solution was stirred at room temperature overnight and then poured into dilute sulfuric acid. The solid remaining after evaporation of the methylene chloride was filtered and recrystallized from carbon tetrachloride–acetonitrile, mp 218–219°. The yield, based on 2,2,2-fluorodinitroethanol, was 66%. A lower melting polymorph of this material had previously been obtained by aqueous fluorination of dipotassium bis(2,2-dinitroethyl)urea.[7] The two polymorphs showed slight differences in their ir spectra (in KBr), but had identical nmr spectra, nmr (DMSO-d_6) δ 4.60 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 7.14 (t).

***N*-(2,2,2-Fluorodinitroethyl)carbamyl Chloride (3).**—To a solution of 11.5 g of phosgene in 50 ml of benzene was added dropwise at 5–10° a solution of 17.7 g of **1** and 9.5 g of pyridine in 30 ml of benzene. After complete addition the mixture was heated to 50° for 1 hr and the solvents were removed *in vacuo*. The residual oil was diluted to 100 ml with methylene chloride and reacted further as described below.

***N*,*O*-Bis(2,2,2-fluorodinitroethyl)carbamate (4).**—To 40 ml of the above solution of crude fluorodinitroethylcarbamyl chloride was added 5.6 g of 2,2,2-fluorodinitroethanol[6,7] and, dropwise and with cooling in an ice bath, 3.1 g of pyridine. The mixture was stirred at room temperature for 2 hr, diluted with 100 ml of methylene chloride, washed with dilute sulfuric acid, dried, and concentrated. Repeated chilling, filtration, and concentration of the mother liquor gave several fractions of **4** containing diminishing amounts of **2** as impurity. The crude yield totaled 3 g. The product was purified by recrystallization from methylene chloride–hexane: mp 63–64°; nmr (CD_3CN) δ 4.54 (pair of d,

(8) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

(9) L. Herzog, M. H. Gold, and R. D. Geckler, *J. Amer. Chem. Soc.*, **73**, 749 (1951).

J_{HF} = 16, J_{NH-H} = 6.5 cps), 5.28 (d, J_{HF} = 16 cps), 6.74 (broad t).

Anal. Calcd for $C_5H_5F_2N_5O_{10}$: C, 18.04; H, 1.51; F, 11.40. Found: C, 17.8; H, 1.5; F, 11.3.

1,13-Difluoro-1,1,7,7,13,13-hexanitro-3,11-diaza-5,9-dioxatridecane-4,10-dione (5).—The above solution of crude fluorodinitroethylcarbamyl chloride (60 ml) was treated with 4.6 g of 2,2-dinitropropane-1,3-diol and 4.6 g of pyridine in the manner described for **4**. The methylene chloride solution of the crude product was concentrated until crystallization started. A second crop was obtained by addition of hexane to the mother liquor of the first crop; total yield 4.5 g. The product was contaminated with **2**, which is less soluble than **5** and could be removed by fractional crystallization from methylene chloride–hexane. A purer sample of **5** was obtained by addition of 2,2-dinitropropane-1,3-diol to fluorodinitroethyl isocyanate (see below), mp 128.5–130.5°, nmr (acetone-d_6) δ 4.53 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 5.02 (s), NH not reported.

Anal. Calcd for $C_9H_{10}F_2N_8O_{16}$: C, 20.62; H, 1.92; F, 7.25; N, 21.37; mol wt, 524.23. Found: C, 20.8; H, 2.0; F, 7.1; N, 21.4; mol wt (acetone), 528.

4 by Reaction of 2,2,2-Fluorodinitroethylamine with 2,2,2-Fluorodinitroethyl Chloroformate.—2,2,2-Fluorodinitroethyl chloroformate was prepared *in situ* as follows. To an ice-cooled solution of 15.4 g of 2,2,2-fluorodinitroethanol[6,7] and *ca.* 12 g of phosgene in 100 ml of methylene chloride was added dropwise 9 g of pyridine. The mixture was stirred at ambient temperature for 3–4 hr, then washed rapidly with ice-cold dilute sulfuric acid, and dried, and the solvent and excess phosgene were removed *in vacuo*. The remaining oil was taken up in 25 ml of methylene chloride and added dropwise and with stirring and cooling to an ice-cold solution of 11 g of **1** and 6.3 g of pyridine in 100 ml of methylene chloride. The mixture was stirred overnight at room temperature and freed from solvent, and the residue was digested with dilute sulfuric acid. The crude product was recrystallized from methylene chloride–hexane to give 21 g (88.6% based on **1**) of **4**.

2,2,2-Fluorodinitroethyl Isocyanate (6).—To a solution of 6 g of phosgene in 50 ml of methylene chloride was added dropwise at 0–5° and with stirring a solution of 9.2 g of **1** and 6.2 g of triethylamine in 25 ml of methylene chloride. After the exothermic reaction had subsided, another 6.2 g of triethylamine was added dropwise, and the mixture was stirred at room temperature for 1 hr, filtered rapidly, and freed from solvent *in vacuo*. The liquid portion of the remaining semisolid material was dissolved in methylene chloride–hexane (1:1), and the solution was filtered and concentrated. Vacuum distillation of the remaining oil gave 2 g of **6** as a pale yellow liquid, bp *ca.* 45° (0.1 mm), exhibiting a single peak in the glpc chromatogram and a strong band in the ir at 2250 cm^{-1}. The compound was characterized further by the following reactions with nitro alcohols.

Addition to 6 of 2,2,2-Fluorodinitroethanol, 2,2-Dinitropropane-1,3-diol, 2,2,8,8-Tetranitro-4,6-dioxa-1,9-nonanediol, and 2-Fluoro-2-nitropropane-1,3-diol.—The alcohol was added at room temperature to a methylene chloride solution of **6**. When necessary, ether was added until the mixture was homogeneous. A few drops of pyridine were added and the mixture was stirred at room temperature overnight. The product was isolated by filtration or removal of the solvents. **4** and **5** prepared in this manner were identical with samples obtained from the reaction of fluorodinitroethyl carbamyl chloride (**3**) with the corresponding alcohol and pyridine. The two additional carbamates prepared from **6** are described below.

1,19-Difluoro-1,1,7,7,13,13,19,19-octanitro-3,17-diaza-5,9,11,15-tetraoxa-4,16-nonadecanedione (8).—The crude product from 1.8 g of **6** and 1.7 g of 2,2,8,8-tetranitro-4,6-dioxa-1,9-nonanediol[10] weighed 3.4 g. It was taken up in methylene chloride, filtered through a short column of silica (G. F. Smith, Columbus, Ohio) to remove colored material, and recrystallized from methylene chloride: mp 94–96°; nmr (CD_3CN) δ 4.55 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 4.46, 4.79, 5.04 (three s), 6.63 (broad peak, NH).

Anal. Calcd for $C_{13}H_{16}F_2N_{10}O_{22}$: C, 22.23; H, 2.30; F, 5.41. Found: C, 22.5; 22.4; H, 2.2, 2.1; F, 5.2, 5.3.

1,7,13-Trifluoro-1,1,7,13,13-pentanitro-3,11-diaza-5,9-dioxa-4,10-tridecanedione (7).—From 1.8 g of **6** and 0.7 g of 2-fluoro-2-nitro-1,3-propanediol[11] there was obtained 2.3 g of crude product. After recrystallization from ethylene dichloride–acetonitrile and drying at 80° (0.1 mm) for 2 days the material melted at 135–137°, resolidified when kept at this temperature, and melted again at 156–157°: nmr (CD_3CN) δ 4.53 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 4.61, 4.66, 4.81 (three s),[12] NH not reported.

Anal. Calcd for $C_9H_{10}F_3N_7O_{14}$: C, 21.75; H, 2.03; F, 11.46; N, 19.71. Found: C, 21.8, 21.7; H, 2.0, 2.1; F, 11.8, 11.7; N, 19.6, 19.6.

***N,N'*-Bis(2,2,2-fluorodinitroethyl)oxamide (10).**—A mixture of 100 g of 2,2,2-fluorodinitroethanol,[6,7] 100 ml of water, and 100 ml of methylene chloride was cooled in an ice bath, 70 g of 28% aqueous ammonia was added gradually, and the mixture was stirred for 0.5 hr at ice bath temperature and 6 hr at 25–30°. The phases were separated, the aqueous phase was extracted with 200 ml of methylene chloride, and the combined methylene chloride solutions were washed with 100 ml of 0.1 *N* NaOH and dried ($MgSO_4$). This solution of crude **1** was filtered and cooled in an ice bath; 36.3 g of pyridine was added, then slowly a solution of 29 g of oxalyl chloride in 200 ml of methylene chloride. Toward the end of the acid chloride addition the mixture was allowed to warm to *ca.* 40°. Methylene chloride (100 ml) was added and stirring was continued for another 7 hr. The precipitate was filtered off, washed with methylene chloride, and digested with dilute sulfuric acid to remove ammonium salts. The crude product weighed 68.5 g (58.6%). After two recrystallizations from acetic acid it melted at 224–225°: nmr (moist DMSO-d_6) δ 4.73 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 9.75 (t).

Anal. Calcd for $C_6H_6F_2N_6O_{10}$: F, 10.55; N, 23.34; mol wt, 360.16. Found: F, 10.8, 10.5; N, 22.5, 22.8; mol wt, 379, 346.

***N*-*tert*-Butyl-*N*-(2,2,2-fluorodinitroethyl)amine (9).**—*tert*-Butylamine (8.5 g) was added with stirring and cooling to a solution of 15 g of 2,2,2-fluorodinitroethanol in 60 ml of water and the mixture was stirred at room temperature for 2 hr. The oil was separated and dried with a small amount of magnesium sulfate. It was shown by nmr to be pure **9** and was used for further reactions without purification. The yield was essentially quantitative: bp 54–55° (0.5 mm); nmr ($CDCl_3$) δ 1.05 (s), 1.23 (broad peak, NH), 3,81 (d, J_{HF} = 16 cps).

Preparation of 10 *via* 9.—A solution of 16.8 g of **9** in 50 ml of methylene chloride was cooled to 5–10° and 2.6 g of oxalyl chloride in 10 ml of methylene chloride was added. The mixture was stirred for 1 hr at room temperature, heated to reflux for 6 hr, and poured into dilute sulfuric acid, and the organic solvent was allowed to evaporate. Filtration gave 8.7 g of crude *N,N'*-(*tert*-butyl)-*N,N'*-bis(2,2,2-fluorodinitroethyl)oxamide, mp 159–160°. The filtrate was made alkaline and extracted with methylene chloride. Upon removal of the solvent from the extract 8.3 g of **9** was recovered.

A mixture of 10 g of the crude oxamide, 18 ml of acetic acid, and 12 ml of concentrated sulfuric acid was stirred for 2 hr at ambient temperature, ice and water was added, and the solid was filtered off to give 7.5 g of crude **10**. After recrystallization from acetic acid the material was identical with a sample prepared from **1** as described above.

***N*-(2,2,2-Fluorodinitroethyl)formamide (12) *via* 9.**—A mixture of 10.5 g of **9** and 30 ml of formic acid was cooled, 30 ml of acetic anhydride was added, and the mixture was stirred overnight. On drowning the reaction mixture in water and filtering off the precipitate there was obtained 8.5 g (71.4%) of *N*-(*tert*-butyl)-*N*-(2,2,2-fluorodinitroethyl)formamide (**11**).

Nine grams of **11** was added to 15 ml of concentrated sulfuric acid, and the mixture was stirred for 6 hr at 25–30°, drowned on crushed ice, and the solution diluted to 125 ml with water. Charcoal was added to remove a brown, oily material and the solution was filtered, saturated with sodium sulfate, and extracted with five 50-ml portions of ether. Drying ($MgSO_4$) and removing the solvent gave 5 g of crude **12**. The product was degassed and distilled in a molecular still at 80–90° (0.1 mm). Nmr and glpc analysis indicated the distillate to be about 95% pure, nmr (CD_3CN) δ 4.64 (pair of d, J_{HF} = 16, J_{NH-H} = 6.5 cps), 7.22 (broad peak, NH), 8.16 (s).

(10) T. N. Hall and K. G. Shipp, U. S. Patent 3,288,863 (Nov 29, 1966).

(11) L. T. Eremenko and G. V. Oreshko, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 380 (1965).

(12) See K. Baum, *J. Org. Chem.*, **35**, 846 (1970), for a discussion of anomalies in the nmr spectra of 2-fluoro-2-nitroalkanols.

Anal. Calcd for $C_3H_4FN_3O_5$: C, 19.91; H, 2.23; F, 10.49; N, 23.21. Found: C, 20.6, 20.5; H, 2.7, 2.6; F, 9.8, 10.1; N, 23.0, 23.0.

Registry No.—**1**, 18139-02-1; **2**, 17003-80-4; **4**, 33046-31-0; **5**, 33191-89-8; **6**, 33046-32-1; **7**, 33147-03-4; **8**, 33046-33-2; **9**, 33046-34-3; **10**, 33191-90-1; **12**, 33046-35-4; *N*-(2,2,2-fluorodinitroethyl)acetamide, 22691-71-0; *N*,*N*′-bis(2,2,2-fluorodinitroethyl)-4,4-dinitroheptanedioic amide, 33046-37-6; *N*,*N*′-di(*tert*-butyl)-*N*,*N*′-bis(2,2,2-fluorodinitroethyl)oxamide, 33046-38-7.

Acknowledgment.—The work described here was carried out under NOL Task IR-144, "Explosives Chemistry."

Reactions of Nitromethane with Hexafluorobenzene at 550°

ELLIS K. FIELDS*

Amoco Chemicals Corporation, Naperville, Illinois 60540

SEYMOUR MEYERSON

Standard Oil Company, Naperville, Illinois 60540

Received June 25, 1971

Nitromethane reacts with hexafluorobenzene at 550° to give products that differ greatly in nature from those with benzene under the same conditions. Pentafluorotoluene and pentafluorophenol are the major products, together with varying amounts of pentafluoroanisole, pentafluorobenzaldehyde, and decafluorobiphenyl. With *p*-difluorobenzene, nitromethane gives *p*-fluorophenol as the only major product. The driving force in reactions of nitromethane with fluorinated aromatics may be the formation of nitrosyl and nitryl fluorides.

Nitromethane reacts with benzene at 500–550° to give aniline, *N*-methylaniline, and biphenyl as major products, together with minor amounts of toluene, anisole, phenol, and *N*-benzylideneaniline.[1] The deuterium content of products from labeled reagents indicated that *N*-methylaniline formed by insertion in benzene of methylnitrene from nitromethane, and aniline by subsequent loss of CH_2 from *N*-methylaniline.[2] Apart from biphenyl, a product derived entirely from benzene, nitrogen compounds comprised about 79% of the total products. It was of interest to find if nitromethane would give analogous products with substituted benzenes. We therefore allowed nitromethane to react with hexafluorobenzene at 550° and determined the products by mass spectrometry, gas chromatography, and directly coupled gas chromatography–mass spectrometry.

Experimental Section

Hexafluorobenzene was from Aldrich Chemical Company. It analyzed 98% hexafluorobenzene and 1% each of penta- and tetrafluorobenzenes. The pentafluoro derivatives of toluene, anisole, aniline, benzaldehyde, and decafluorobiphenyl were from Pierce Chemical Company. Nitromethane was Eastman Reagent Grade, distilled prior to use. The apparatus, procedure, and analytical methods are fully described in previous publications.[3]

In a typical experiment a mixture of 10.72 ml (0.2 mol) of nitromethane and 118 ml (1.0 mol) of hexafluorobenzene was pumped into a Vycor tube filled with Vycor chips at 550° in a stream of argon flowing at 20 ml/min. Liquid products were condensed in a bulb at 0°; gases were collected in gas bulbs for mass spectral analysis. Distillation of the liquid products recovered 171 g, almost all hexafluorobenzene, at 78–80°, and left 12.6 g of a higher boiling residue whose composition is shown in Table II, along with the composition of gases generated in the reaction.

Results and Discussion

Products from the reaction of nitromethane with hexafluorobenzene determined by gas chromatography are listed in Table I. These included various amounts

TABLE I

PRODUCTS FROM NITROMETHANE AND HEXAFLUOROBENZENE[a]

	Products[b]			
Nitromethane, mol	1	0.5	0.2	0.1
Weight of products boiling over 100°, g	26	27	12.6	7.0
Pentafluorotoluene	37.5	53.0	56.0	60.0
Pentafluorophenol	33.0	23.0	20.7	3.0
Pentafluoroanisole	5.9	9.8	9.9	12.7
Pentafluorobenzaldehyde	6.6	3.2	3.0	4.6
Decafluorobiphenyl	6.8	4.7	3.6	2.9
Unknowns	10.2	6.3	6.8	16.8

[a] Conditions: 1 mol hexafluorobenzene; 550°; contact time, 20 sec; argon, 20 ml/min. [b] Weight percent by gas chromatography.

of unknowns, whose molecular weights were determined by mass spectrometry; these are listed in Table II, along with the composition of gaseous products.

The two major products were pentafluorotoluene and pentafluorophenol, with pentafluoroanisole prominent among the less abundant ones. In addition, mass spectrometry showed a compound of molecular weight 180, corresponding to tetrafluoroanisole, tetrafluorobenzyl alcohol, or tetrafluorocresol. Its spectrum is compatible with the structure $CH_3C_6F_4OH$. A pair of peaks of about equal intensities at masses 179 and 180 resembles corresponding pairs in the spectra of $C_6F_5CH_3$[4,5] and $C_6F_4HCH_3$,[5] and thus suggests a methyl group on a fluorinated benzene ring. Masses of other fragments (probable derivations) follow: 161 ($M^+ - F$), 151 ($M^+ - CHO$), 150 ([$M^+ - H$] –

(1) E. K. Fields and S. Meyerson, *Chem. Commun.*, 494 (1967).
(2) E. K. Fields and S. Meyerson, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, **16**, No. 1, B96 (1971).
(3) E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969), and references cited therein.
(4) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).
(5) L. D. Smithson, A. K. Bhattacharya, and C. Tamborski, *Org. Mass Spectrom.*, **4**, 1 (1970).