same solution is very similar, but cleaner (of course, the absorptions for dimethylamine would be absent from the latter solution): 1631, 1598, 1551, 1486, 1455, 1380, and 1339 cm^{-1}. It seems clear that the latter two solutions contain sodium *o*-hydroxylaminobenzoate.

Alkaline Hydrolysis of *N*,*N*-Dimethylbenzamide.—A solution of 152.5 mg (1.022 mmol) of *N*,*N*-dimethylbenzamide dissolved in 1 equiv of the same solution of NaOH used for the cleavage of 4 was left at room temperature (*ca.* 23°) for 432 hr and then extracted with CH_2Cl_2 (eight 5-ml portions). The dried extract yielded 85.5 mg (56%) of residue, the infrared spectrum of which was identical with that of the starting amide.

***N*-Acetyl-2,1-benzisoxazolone.**—Acetyl chloride (5 drops) was added to a solution of 18 mg (0.13 mmol) of 2,1-benzisoxazolone in 10 drops of dioxane. The solution was gently warmed over a flame and then cooled. Water was added (crystals formed) and the mixture was extracted with ether. The residue from evaporation of the ether was precipitated from an alcoholic solution with water to give 9.4 mg (44%) of white crystals: mp 116–118° (lit.[10] mp 117.5–118.5°); ir ($CHCl_3$) 3040 (w), 1786 (s), 1704 (s), 1613 (w), 1477 (m), 1464 (s), 1379 (s),1350 (m), 1332 (s), 1299 (w), 1153 (w), 1112 (w), 1074 (w), 1042 (w), 980 cm^{-1} (m, broad); mass spectrum, direct probe (since the peak at m/e 43, the acetyl cation, was extremely intense and off-scale, the values in parentheses are percentages of the 135 peak) 178 (6.3), 177 (53.1), 136 (21), 135 (100), 104 (28), 91 (32), 79 (95), 77 (14), 76 (65), 75 (16), 74 (17), 64 (49), 63 (37), 62 (16), 52 (52), 51 (24), 50 (73), 44 (97), 43 (off scale).

Reduction of 2,1-Benzisoxazolone.—2,1-Benzisoxazolone (65.8 mg, 0.488 mmol) was added in small portions to a slurry of 4.1 mg of 10% Pd/C in a solution of 97 mg (2.6 mmol) of sodium borohydride in 3.2 ml of water and 0.28 ml of methanol in an ice bath. After the solution had been stirred for 15 min, the catalyst was removed by filtration, the basic solution was extracted with chloroform (five 1-ml portions), acidified to *ca.* pH 3 with 18% hydrochloric acid, and then extracted again. Evaporation of the solvent from the combined, dried ($MgSO_4$) extract left 50.0 mg (76%) of off-white crystals, mp 143–147°, the infrared spectrum of which matched that reported[17] for anthranilic acid. Sublimation at 100° (0.5 Torr) yielded material of mp 146.5–147.0 (lit.[18] mp 144.9–145.4°; lit.[19] mp 144–145°).

Registry No.—**1,** 2018-71-5; **2,** 118-92-3; **3,** 6526-66-5; **4,** 33047-10-8; **5,** 31499-90-8; **5** *N*-acetyl derivative, 33047-12-0.

Acknowledgments.—We wish to thank the National Institutes of Health for providing the LKB 9000 combined gas chromatograph–mass spectrometer (Grant RR 00273), and Mr. John Naworal for recording the mass spectra.

The Reaction Rates of Alkyl Dihydroxybenzoates in a Nucleophilic Fused Salt[1]

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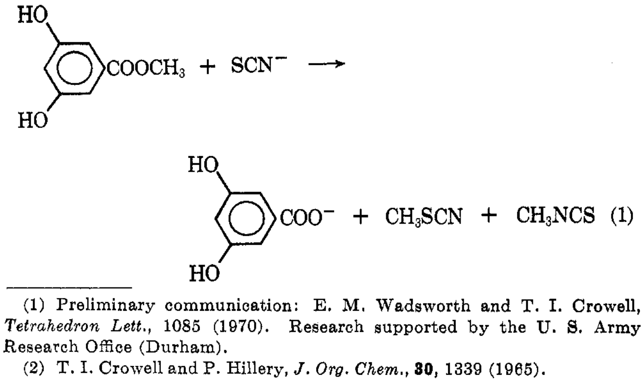
Received September 29, 1971

Methyl and ethyl 3,5-dihydroxybenzoates, in molten potassium–sodium thiocyanate eutectic, react by a pseudo-first-order $B_{Al}2$ displacement on the alkyl group to form alkyl thiocyanates and isothiocyanates. The methyl ester, which reacts 49 times as fast as the ethyl at 150°, shows an activation energy of 26 kcal/mol. The product compositions are 96% MeSCN, 4% MeNCS and 54% EtSCN, 46% EtNCS. Methyl 2,4-dihydroxybenzoate reacts similarly except that the 2,4-dihydroxybenzoate ion immediately decarboxylates, evolving 0.5 mol of carbon dioxide per mole of ester and following the rate equation $\ln a/(a - 2x) = 2kt$. Neither the *o*-hydroxyl group nor the decarboxylation accelerates the displacement, as this ester reacts slightly more slowly than the 3,5-dihydroxy compound. The isotope effect is small ($k_{OH}/k_{OD} = 0.97$).

Noting the high nucleophilicity and low melting point of potassium thiocyanate, we initiated a study of nucleophilic displacement reactions in this molten salt, an ionic, aprotic medium which represents the upper concentration limit of a solution. Suitable substrates, undergoing simple displacement reactions with moderate rates at elevated temperatures and containing hydroxyl groups to confer solubility by hydrogen bonding with the solvent[2] are difficult to devise. Benzoic esters with two phenolic hydroxyl groups, however, have these properties. For example, methyl 3,5-dihydroxybenzoate reacts with thiocyanate ion with alkyl–oxygen cleavage, of the type[3] $B_{Al}2$ (eq 1).



Nucleophilic displacements at the saturated carbon atom in ester hydrolysis or alcoholysis can be observed only under the following conditions: (1) special structural features favor alkyl–oxygen cleavage as in the reaction of β-lactones with water[4] or methanol;[5] (2) the competing attack at the carbonyl group ($B_{Ac}2$) is hindered as in methyl 2,4,6-tri-*tert*-butyl benzoate[6] or is designed to be a symmetrical transesterification;[7] (3) the nucleophile is unreactive toward carbonyl groups. The very few examples of this last case include the cleavage of simple methyl esters by trimethylamine[8] and by lithium halides in pyridine[9a] or 2,4,5-collidine.[9b] Thiocyanate ion also belongs to this small group of nucleophiles preferentially attacking the carbon atom of the alkyl group in esters, effecting a slow displacement of the carboxylate ion. Packham and

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Rackley[10] obtained methyl isothiocyanate in 25% yield from the heterogeneous system, methyl acetate–fused NaSCN-KSCN at 300°. This paper describes homogeneous kinetic studies of eq 1 and related reactions in fused KSCN-NaSCN eutectic at 140–160°.

Experimental Section

A Colura Ultra-Thermostat circulating bath, filled with Dow-Corning 210 silicone oil, maintained temperature ±0.2°.

Solvent.—The sodium thiocyanate–potassium thiocyanate (25–75 mol %) binary eutectic[11] melting at 133° was prepared from the reagent grade salts (minimum assay 99.3 and 99.7%) which were dried at 110° for 15 hr, then combined, melted in a beaker, and mixed. The melt was poured into an open dish, allowed to cool in a desiccator, pulverized in a drybox, and dried under vacuum at room temperature. For each kinetic run, 10 g of the molten salt was dried at 10^{-3} Torr at the temperature of the run for at least 24 hr. Karl Fisher titration showed the water content of the eutectic to be 0.2% after this treatment. When deuterated esters were to be used as substrates, the eutectic was wet with D_2O before the drying procedure.

Methyl 2,4-Dihydroxybenzoate.—To 35 g (0.23 mol) of 2,4-dihydroxybenzoic acid was added 40 g (1.25 mol) of methanol and 4 g of concentrated sulfuric acid. After 30 hr at reflux, excess methanol and water were distilled off and the residual liquid (about 25 ml) was neutralized to pH 7 with sodium carbonate solution. The precipitated ester was extracted with ether. The tan solid obtained on evaporation of the extracts was recrystallized from benzene as white crystals (21.4 g, 56%): mp 116–117° (lit.[12] 117–118°); homogeneous by tlc; ir (KBr) 3360 (OH stretch), 1640 (carbonyl), 1275 (C–O stretch), 1625 (aromatic ring stretch), 1370 cm^{-1} (methyl C–H bend); nmr (acetone-d_6) methyl singlet 3.46 ppm from TMS.

The other alkyl dihydroxybenzoates, prepared by similar procedures but with 3–5-hr reflux periods, were ethyl 2,4-dihydroxybenzoate, 41% yield, mp 69–70.5° (lit.[13] 69–70°); methyl 3,5-dihydroxybenzoate, 70%, mp 167–168° (lit.[14] 163–165°); and ethyl 3,5-dihydroxybenzoate, 32%, mp 127–128° (lit.[15] 128.5). Isopropyl 3,5-dihydroxybenzoate was vacuum distilled. A fraction obtained at 185–190° (0.3 Torr), which contained both starting acid and product (tlc), was dissolved in benzene-acetone (95:5%), chromatographed on a silica gel (0.2–0.5 mm, 20 g) column, and eluted with benzene–acetone (95:5 then 90:10%). The ester containing fractions were combined and evaporated under reduced pressure to a viscous oil which could not be solidified: yield 0.77 g (6%); ir (DMSO-d_6) 3450–3550 (OH stretch), 1720 (C=O), 1610 (aromatic ring), 1245 cm^{-1} (CO); nmr (DMSO-d_6) methyl doublet δ 1.30, methine multiplet δ 5.13.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17. Found: C, 61.16; H, 6.28.

Sodium 2,4-dihydroxybenzoate was prepared by neutralizing the acid with 0.2 *M* sodium hydroxide and evaporating to dryness under vacuum. The monosodium salt of methyl 2,4-dihydroxybenzoate (presumably sodium 3-hydroxy-4-carbomethoxyphenoxide) was obtained similarly from a methanol solution of the ester after adding 1 equiv of sodium methoxide. Methyl 2,4-dideuteroxybenzoate was prepared by heating 0.7 g of methyl 2,4-dihydroxybenzoate in 12.5 ml of D_2O (99.8%) until it dissolved. The solution was cooled and filtered and the process was repeated. The ir spectrum of the vacuum-dried solid showed equally strong OD (KBr, 2440 cm^{-1}; reported[16] for phenol in D_2O, 2432 cm^{-1}) and OH (3370 cm^{-1}) peaks. Taking into account the lower absorption intensity of OD, about 75% exchange was indicated. This product was again heated with D_2O. After the solvent was evaporated under vacuum, the ir spectrum of the ester showed about 87% exchange in the hydroxyl groups. This was confirmed by the nmr spectrum; the aromatic A_2B pattern moreover was similar to that of the undeuterated ester.

Methyl and ethyl thiocyanate[17] and isothiocyanate[18] were prepared by standard methods.

Procedure.—The Pyrex reaction vessel, 22 × 150 mm, containing about 10 g of the thiocyanate eutectic, was immersed in the oil bath and evacuated for the final stage of the drying procedure. It was then opened and 1.5–2.5 mmol of ester was introduced through a funnel and stirred with a heated rod until dissolved (5–15 min).

The reactions of the 3,5-dihydroxybenzoate esters were followed by weighing the mixture of alkyl thiocyanate and isothiocyanate produced. After introduction of the ester, the system was closed and evacuated to a pressure of 20 Torr. The vapor of the products passed through glass tubing (maintained at about 100° by a heating coil to prevent condensation) into a Dry Ice trap. After the desired time interval, a stopcock next to the trap was closed to isolate it temporarily from the reaction and a clean trap was substituted for the first one. The collected product (about 100 mg) was redistilled on the vacuum line, the vapors passing through calcium chloride to remove traces of water, and finally weighed. This procedure, tested on samples of methyl thiocyanate mixed with much more water (50%) than was produced in the kinetic runs, gave results only 2% high.

Methyl 2,4-dihydroxybenzoate, on the other hand, undergoes decarboxylation as displacement by thiocyanate takes place, and is conveniently followed by measuring the volume of carbon dioxide evolved. A cold finger, containing circulated refrigerant at −10°, was located in the reaction vessel to minimize the partial pressure of methyl thiocyanate before it was completely removed by a Dry Ice trap between the reaction vessel and the rest of the vacuum system. After the ester was dissolved in the molten salt, the system was closed and partially evacuated. (Complete evacuation caused bumping and undue sublimation of the ester.) From the volume of the whole system and the pressure measured on a mercury manometer, the quantity of carbon dioxide formed in the reaction could be calculated at any time.

Product Analysis.—Alkyl thiocyanates and isothiocyanates were identified by their ir spectra (KBr) and by gas chromatography. A column of 20% Carbowax 600 on Anakrom ABS 50/60 support (0.25 × 120 in.) was used. The flame ionization detector response was found to be identical for methyl thiocyanate and methyl isothiocyanate, using 1,2-dimethoxyethane as reference compound in the Micro-Tek gas chromatograph. The relative amounts of isomers produced could therefore be calculated from peak areas without further correction. The volatile products from ethyl 3,5-dihydroxybenzoate gave two peaks showing similar retention times to the methyl products and were assumed without calibration to correspond to ethyl thio- and isothiocyanate. The higher proportion of ethyl isothiocyanate (50% as compared to 5% for the methyl esters) was confirmed by the ir spectrum of the mixture.

Methyl 2,4-dihydroxybenzoate was stable for 3 days at 150°. Dissolved in the thiocyanate melt at 150°, this ester slowly evolved carbon dioxide (identified by mass spectrum), methyl thio- and isothiocyanate (identified as above) and, as a sublimate just above the bath oil level, resorcinol (ir in KBr). Sodium 2,4-dihydroxybenzoate was decarboxylated very rapidly in the melt. Methyl and ethyl 3,5-dihydroxybenzoates, however, showed no evolution of noncondensable (−78°) gas, the pressure remaining constant within 7 mm (methyl) and 1 mm (ethyl) as alkyl thiocyanates formed and passed into the Dry Ice trap. This important observation demonstrated the absence of carbon dioxide, methane, ethane, and ethylene and illustrated the convenience of a vacuum system for handling nonvolatile fused salts.

Results

In the reaction of methyl 3,5-dihydroxybenzoate, 90% of the theoretical weight of product was obtained composed of 96% methyl thiocyanate and 4% methyl isothiocyanate. The product from the ethyl ester was 54% ethyl thiocyanate and 46% isothiocyanate.

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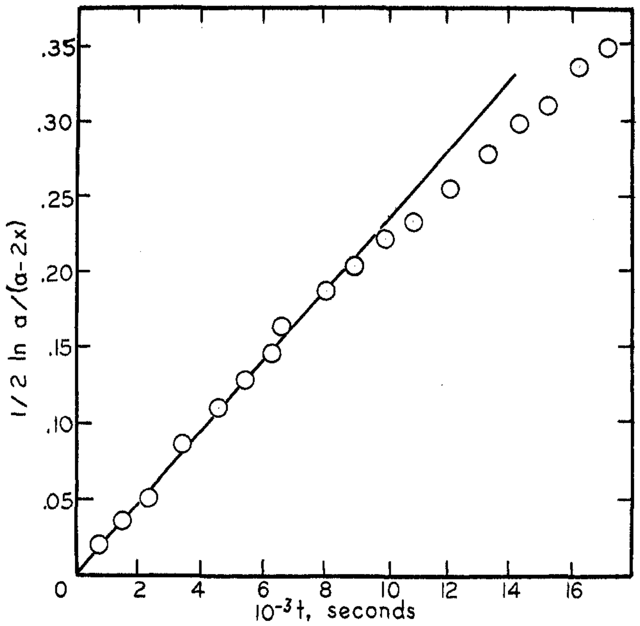


Figure 1.—Kinetic plot for solvolysis of methyl 2,4-dihydroxybenzoate in molten K^+, Na^+/SCN^- at 140.5°.

The rate constants, shown in Table I, were obtained from plots of ln $a/(a - x)$ (linear to 75% reaction)

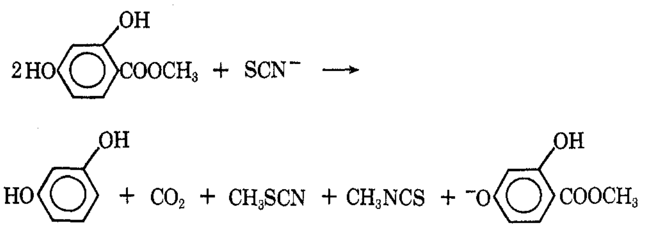
TABLE I

Ester	Temp, °C	No. of runs	10^4k,[a] sec^{-1}	Mean % devn
Me 3,5	140.5	2	1.53	0.5
	150.4	3	3.20	4.7
	160.2	2	6.32	1.3
Et 3,5	150.5	3	0.065	11.7
Me 2,4	140.5	3	0.232	1.3
	150.5	2	0.467[b]	1.3
	160.6	2	0.794	1.1
Me 2,4[c]	150.7	2	0.485	1.0

[a] Mean value of k for given number of runs. [b] This rate constant for thiocyanate displacement is one-half the value given in ref 1 for total ester consumption. [c] Methyl 2,4-dideuterioxybenzoate.

where a is the amount of ester, in millimoles, dissolved in 10 g of melt, and x the millimoles of product at time t. The three-point Arrhenius plot for the methyl ester is linear, the calculated activation energy E_a being 26 kcal/mol and the entropy of activation −16 cal/deg. Isopropyl 3,5-dihydroxybenzoate is insoluble in the melt.

Methyl 2,4-dihydroxybenzoate yielded methyl thio- and isothiocyanate in the same ratio (95.3:4.7) as the 3,5 ester. Carbon dioxide was evolved as the reaction proceeded, apparently approaching 0.5 mol per mole of reactant. The actual yield was 0.46 mol; volatilization of ester from the hot solution probably accounts for the difference. If the reaction proceeds as shown in eq 2 and all the products on the right side except the anion **1** are removed by volatilization, including resorcinol, the failure of half of the substrate to react is explained if **1** is assumed unreactive. The sodium salt of methyl 2,4-dihydroxybenzoate in fact neither dissolved nor reacted in the melt unless it was heated to 198°. (Sodium 2,4-dihydroxybenzoate, however, dissolved and decarboxylated rapidly at 150°.) It is, therefore, proper to plot ($^1/_2$) ln $a/(a - 2x)$ vs. time, since $2x$ is the number of moles of reactant removed when x mol undergo the displacement reaction. A typical plot for reaction of the ester at 140°, followed by carbon dioxide evolution, is shown in Figure 1. The slope, k, is 2.36×10^{-5} sec^{-1} up to 25% reaction. Note that the initial slope of a plot of ln $a/(a - x)$ vs. t would have this same value, which simply measures the rate of carbon dioxide evolution from the ester at its initial concentration. Equation 2 is suggested as the reason for deviation from first-order kinetics as the reaction proceeds, but the evaluation of k should not markedly depend on whether or not the interpretation is correct.



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(2)

All the results are summarized in Table I, including duplicate runs on ester deuterated in the hydroxyl groups. One run at 150.5°, followed gravimetrically, as described for the 3,5 esters, gave a rate constant of 4.2×10^{-5} sec^{-1} before tapering off as it approached 50% reaction.

The Arrhenius plot for methyl 2,4-dihydroxybenzoate is not quite linear: the activation energy is 25 (140–150°), 19 (150–160°), or 22 kcal/mol overall. The corresponding entropy of activation is −29 cal/deg mol.

Ethyl 2,4-dihydroxybenzoate is insouble in the thiocyanate melt.

Discussion

The reaction of the alkyl dihydroxybenzoates appears to be a direct displacement on the alkyl group. The ratio k_{Me}/k_{Et} is 49 for the 3,5 esters at 150–155°, which is in the normal range for SN2 reactions.[19] The absence of ethylene in the products from ethyl 3,5-dihydroxybenzoate shows that ester pyrolysis is not occurring in this medium (the esters alone are stable at the temperatures used) and, together with the absence of methane from the methyl esters, is evidence against the presence of free radicals.

The 2,4-dihydroxy esters might be expected to react more rapidly than those with both the hydroxyl groups in meta positions. If decarboxylation took place simultaneously with displacement, a driving force characteristic of many fragmentation reactions[20] would increase the displacement rate. Furthermore, the ortho hydroxyl group could, by hydrogen bonding or proton transfer, increase the positive charge on the carbonyl carbon atom and consequently the affinity of the adjacent methyl group for the nucleophilic anion. Catalysis of ester hydrolysis by neighboring hydroxyl groups (the Henbest–Kupchan effect[21]) is well known,

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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 S_N1 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.

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

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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).

$$RC(NO_2)_2CH_2OH \rightleftharpoons RC(NO_2)_2^- + CH_2O + H^+ \tag{1}$$

$$RC(NO_2)_2H \rightleftharpoons RC(NO_2)_2^- + H^+ \tag{2}$$

$$R'CONH_2 + CH_2O \rightleftharpoons R'CONHCH_2OH \tag{3}$$

$$R'CONHCH_2OH + H^+ \rightleftharpoons R'CONHCH_2^+ + H_2O \tag{4}$$

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

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

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