eration. The analytical gas–liquid chromatography was carried out on a Beckman GC-4 gas chromatograph equipped with a flame ionization detector which was interfaced with a Perkin-Elmer PEP-1 data processor. The 6 ft × 0.125 in. stainless steel chromatographic column was packed with 20% diethylene glycol adipate polyester and 3% phosphoric acid on 60/80 mesh Gas-Chrom P.

Experimental Procedures. The reaction mixture containing 5 ml of methanol, approximately 0.05 g of each of the two acids, and 0.01 ml of concentrated hydrochloric acid was esterified at 40 ± 0.04 °C. Reaction times ranged from less than 1 h to more than 1 month. The calculation of r, the relative rate, is based on the equation

$$k_1/k_2 = \ln A/\ln B = r$$

where A is the fraction of acid 1 and B the fraction of acid 2 remaining after the partial esterification. Two GLC methods of analysis were used to determine A and B. In the first method, the analyses were carried out with the column at 160 °C. The reaction mixture also contained 0.05 g of methyl myristate as an internal standard. Determinations of A and B are based on the results of two chromatograms, one taken before and one after the partial esterification; for example

$$A = [\text{final acid 1}][\text{initial standard}]/[\text{initial acid 1}][\text{final standard}]$$

where the items in brackets refer to the GLC areas of the components in the chromatograms. Neither hydrolysis of the internal standard nor esterification occurring in the chromatographic system during analysis was found to be significant. For the second GLC analytical method, in which case the acids and esters are analyzed, the temperature of the column was held at 100 °C for 4 min and then programmed to 160 °C over an 8-min period. No internal standard is needed for this method and only the chromatogram of the partly esterified mixture is used to determine A and B; for example

$$A = (\text{acid 1})/[(\text{acid 1}) + c\ (\text{ester 1})]$$

where c is the mole-area correction factor for the acid–ester pair. The correction factor of 0.92, determined for 2-ethylhexanoic acid and methyl 2-ethylhexanoate, was assumed to hold for the five octanoate entries in Table I.

In two cases, as indicated in Table I, the esterification was carried out with each acid in a separate container because the GLC separation of the mixture was not adequate for good analysis. This means that the esterification environment was not exactly the same for each acid because of different amounts of water produced during the reaction. However, the results should not be particularly affected since under the experimental conditions the "wetness" of the alcohol does not greatly increase during the esterification.

How errors in measuring A and B affect the computation of r has been previously considered.[6] In the present case the relative standard deviation in reproducing the chromatographic peaks was found to be about 3%. Although in the first GLC analytical method, the error in r decreases the further the esterification proceeds, data cannot be used where the hydrolysis reaction becomes significant. Therefore acid pairs were chosen with somewhat similar rates and data was taken when the faster reacting component had esterified from 50 to 80%. For the second method of analysis, based on the relative amounts of each acid and its ester in the partly esterified mixture, the extent of esterification has little influence in the computational error of r. Data can therefore be taken during the early stages of the reaction. This advantage over the first method is somewhat offset by the more complex analytical procedure. Most of the esterification experiments were carried out by the first method described. The values of r in Table I are averages from at least four determinations. The relative standard deviation for r averaged 8%.

Esterification rate coefficients for 2-ethyl-3-methylbutanoic acid and 2,2-diethylbutanoic acid were determined by the procedures used in obtaining the data in ref 2. Samples containing 0.5 M carboxylic acid and 0.005 M hydrogen chloride in dry methanol were sealed in glass ampules and kept at 40 ± 0.04 °C for 413 h. Analysis was carried out by acid titrations. The value of k in liters per mole per second for 2-ethyl-3-methylbutanoic acid was 7.47×10^{-5} (7.80×10^{-5} previously reported) and for 2,2-diethylbutanoic acid was 2.99×10^{-6} (21.4×10^{-6} previously reported). The ratio of the two rates as entered in Table I is $7.47 \times 10^{-5}/2.99 \times 10^{-6} = 25.0$.

Acknowledgments. The author wishes to thank Dr. Stanley Sojka of the Naval Research Laboratory for determining and interpreting the NMR spectra, and John Mulloy of the Dow Chemical Co. for a sample of 2-ethyl-3,3-dimethylbutanoic acid.

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Oxidation of Thiols and Disulfides to Sulfonic Acids by Dimethyl Sulfoxide

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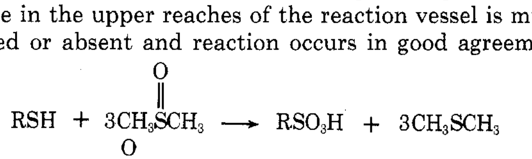
The oxidizing ability of dimethyl sulfoxide (Me_2SO) is well known;[1] still, its ability to oxidize organic sulfur compounds to sulfonic acids has received little recognition. Such oxidations would include certain decompositions of Me_2SO in the presence of bromine, hydrogen bromide, or iodine giving, among other products, methanesulfonic acid or its trimethylsulfonium salt.[2] Methanethiol[2a] and the corresponding sulfenic and sulfinic acids[2d] and sulfinyl halides[2b,c] have been suggested as intermediates.

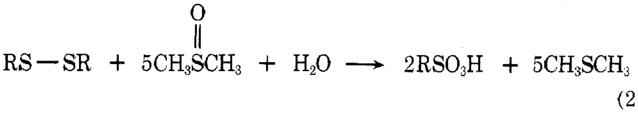
As for specific examples of the oxidation of thiols and disulfides, Toland[3] has described the oxidation of dodecanethiol to dodecanesulfonic acid in the presence of ammonium bromide at temperatures approaching 170 °C; yet, a similar, preparative decomposition of Me_2SO to methanesulfonic acid at 175 °C is also described. Further, Lipton and Bodwell[4] have reported that cystine is oxidized to cysteic acid by minor amounts of Me_2SO under conditions used for the acid-catalyzed hydrolysis of proteins.

The above Me_2SO decompositions also produce paraformaldehyde and dimethyl sulfide (DMS) and may be hazardous.[2a,5] Thus, application of Me_2SO to oxidation of thiols and disulfides has the disadvantage of both hazard and contamination of product sulfonic acid with methanesulfonic acid.

I have now found that, in the presence of a catalytic amount of bromine or iodine or their hydrogen halide, thiols and disulfides may conveniently be oxidized to the corresponding sulfonic acid with little Me_2SO decomposition through the simple expedient of having water present during the oxidation of thiols (eq 1) and excess water present during the oxidation of disulfides (eq 2). With such presence of water, the characteristic deposit of paraformaldehyde in the upper reaches of the reaction vessel is much reduced or absent and reaction occurs in good agreement



$$RSH + 3CH_3\overset{\overset{O}{\|}}{S}CH_3 \longrightarrow RSO_3H + 3CH_3SCH_3 \qquad (1)$$



$$RS{-}SR + 5CH_3\overset{\overset{O}{\|}}{S}CH_3 + H_2O \longrightarrow 2RSO_3H + 5CH_3SCH_3 \qquad (2)$$

Table I. Effect of Water on Oxidations[a]

H_2O/RSH or RSSR, molar ratio	Nature of reaction	Deposit, $(CH_2O)_n$	DMS yield, % theory	Acidity, % theory
	Benzenethiol (1.57 M, at 110 °C)			
0	Rapid and vigorous	Abundant	131	154
0.71	Moderate	Absent	86	107
	Dimethyl Disulfide (1.13 M, at 90 °C)			
1.00	Eventually vigorous	Abundant	183	191
1.44	Gradual	Trace	103	109

[a] 0.0356 M HBr catalyst.

Table II. Effect of Variables on Completion Time in Oxidation of DMDS[a] **(1.13 M, HBr Catalyst)**

Temp, °C	Water/DMDS molar ratio	Catalyst concn, M	Completion time, h
90	1.44	0.0356	10.75
90	2.00	0.0356	>12
90	4.00	0.142	6.5
100	2.00	0.0356	6.5
100	3.00	0.0712	5
110–120	2.00	0.0178	6.5
110–120	2.00	0.0356	3.25

[a] Dimethyl disulfide.

Table III. Effect of Added Methanesulfonic Acid on Completion Time, Oxidation of DMDS (1.13 M; Water, 2.22 M)

Catalyst (concn, M)[a]	Temp, °C	Added CH_3SO_3H, M	Completion time, h
I_2 (0.0316)	130	None	4.5
I_2 (0.0316)	110	0.40	5
HBr (0.0356)	90	None	Negligible rxn
HBr (0.0356)	90	0.40	⅓ complete in 7

[a] I_2 expressed as HI equivalents.

with theory (reaction 1 or 2) in DMS yield and titratable acidity (Table I).

Chlorine and hydrogen chloride are known to catalyze sulfoxide oxidation of thiols to disulfides,[6] but on checking for further oxidation of disulfides, there was only a slow evolution of DMS. Thus, they do not provide practical catalysis for oxidation to sulfonic acid; though, in the presence of a minor amount of iodine or hydrogen iodide, good catalysis is obtained.

The oxidations are conducted with excess Me_2SO as solvent and at elevated temperatures with distillation of produced DMS so that the progress of the oxidation may be followed. In satisfactory oxidations, completion is indicated by a marked slowing or near cessation of DMS formation at about the theoretical amount. For successful application with negligible Me_2SO decomposition, the concentrations of thiol or disulfide, water, and catalyst and reaction temperature must be adjusted in relation to one another.

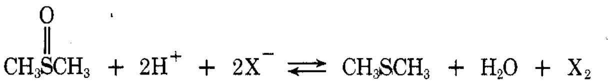
Water has a marked moderating effect. As its concentration is increased, the oxidation becomes excessively sluggish, but this may be compensated for by an increase in catalyst concentration or reaction temperature (Table II). However, with increased catalyst concentration and temperature, particularly if not appropriately compensated for with more water, there is a greater probability of Me_2SO decomposition, further oxidation to sulfuric acid and, generally, a more impure product.

An induction period for the formation of DMS is regularly observed. This period can be decreased and oxidation time shortened through the addition of acid, e.g., sulfuric acid, though addition of the same acid as expected from the oxidation is most convenient preparatively. Addition of acid also permits satisfactory oxidation at somewhat lower temperatures (Table III).

The use of a high concentration of thiol or disulfide (about 4.8 and 2.4 M, respectively) resulted in oxidations that were difficult to control. In practice thiol concentration was kept below 2.4 M, and disulfide, below 1.2 M. Bromine–hydrogen bromide catalyzed oxidations were generally conducted at about 110 °C, and iodine–hydrogen iodide catalyzed oxidations at somewhat higher temperatures. Lower temperatures were often suitable where the above catalysts were used in conjunction with HCl or other added acid. The use of high catalyst concentrations and temperatures so as to have short reaction times was avoided. For separation of the product sulfonic acid from excess Me_2SO, the use of ion exclusion chromatography[7] was found to be convenient; though, generally, the reaction mixture was neutralized with aqueous sodium hydroxide and the salt recovered after addition of a precipitant.

The oxidation was applied successfully to a number of aliphatic and aromatic thiols and disulfides. Table IV summarizes these experiments. The method compares favorably with other oxidation procedures.[8] The oxidation of 2-methyl-2-propanethiol and bis(*tert*-butyl) disulfide led to decomposition, and only sodium sulfate was identified after neutralization.

The subject oxidation has much in parallel with the halogen–hydrogen halide catalyzed oxidations of aliphatic thiols to disulfides by sulfoxides.[6] In addition to the same oxidant and catalysts, there is retardation or moderation by water, enhancement of catalysis by addition of a nonhydrohalic acid, and satisfactory mixed chlorine–iodine species catalysis contrasted with inferior chlorine species catalysis. The principal distinction is a higher reaction temperature without a reduced reaction time. Again, reaction 3 accounts for catalysis by both halogen and its hydrogen halide. The produced halogen may play a leading role in the actual oxidation.



$$CH_3\overset{\overset{O}{\|}}{S}CH_3 + 2H^+ + 2X^- \rightleftharpoons CH_3SCH_3 + H_2O + X_2 \tag{3}$$

In view of the greater ease of oxidation of a thiol to its disulfide, the disulfide would appear to be an intermediate in oxidation of thiol to the sulfonic acid. Color changes such as those reported for iodine–hydrogen iodide catalyzed oxidation to disulfide[6] have been observed part way through the oxidation to the sulfonic acid. Thereafter, the mixture retained the amber, iodine color.

I suggest that a further intermediate or intermediates[9] have the structure 1 where X is the halogen species employed as catalyst and that the beneficial role of water is to hydrolyze such intermediates, thereby limiting undesirable reaction with Me_2SO. Such a hydrolysis would also regenerate catalyst. An example of undesirable reaction with Me_2SO is the case of a sulfonyl chloride (n = 2).[10] The Me_2SO oxidation of such possible intermediates and their hydrolysis products is presently being investigated.

$$RSO_nX$$

1, n = 0, 1 or 2

Table IV. Summary of Oxidations to Sulfonic Acid[a]

Registry no.	Thiol or disulfide	Concn, M	Catalyst ($M \times 10^2$)[b]	Temp, °C	Rxn time, h	DMS yield % theory	Acidity, % theory[c]	Na sulfonate yield, %[d]	Na$_2$SO$_4$ yield, %[e]
624-92-0	Dimethyl	1.126	I$_2$ (3.16)	130	4.25	89	105	96	<0.1
	Dimethyl	1.126	I$_2$ (1.58)	130	6.25	90	103		
	Dimethyl	1.126	HI (3.48)	130	4.5	88	104		
	Dimethyl	1.126	Br$_2$ (3.66)	110	3	90	105		
	Dimethyl	1.126	HBr (3.56)	110	3.25	89	106	92	<0.1
	Dimethyl	1.126	HBr (1.78)	110	6.5	91	103		
	Dimethyl	1.126	HCl (3.60)[f]	100	6.25	81	105	97	<0.1
110-81-6	Diethyl	0.972	I$_2$ (3.16)	120	6	88	108	84	8
	Diethyl	0.972	HBr (3.56)	110	3.75	85	107	82	0.6
109-79-5	Butane-	1.850	I$_2$ (3.16)	120	7	86	113	71	20
	Butane-	1.850	HBr (3.56)	110	5.75	92	110	89	4
75-33-2	2-Propane-	1.692	HBr (3.56)	110	7.75[g]	88	107	90	2.4
	2-Propane-	1.692	HCl (3.60)[f]	110	17[g]	120	147	44	45
108-98-5	Benzene-	1.568	I$_2$ (3.16)	130	4.75	85	106	87	Trace
	Benzene-	1.368	HBr (3.56)	110	3.5	83	107	88	Trace
882-33-7	Diphenyl	0.732	I$_2$ (3.16)	130	3.75	83	108	94	Trace
1155-00-6	Bis(2-nitrophenyl)[h]	0.520[i]	HBr (7.12)	[j]	7	118	143	90	4.5
	Bis(2-naphthyl)	0.502[i]	HBr (3.56)	110	4.75	91	130	84[k]	
5586-15-2	Bis(2-naphthyl)	0.628[i]	HCl (3.60)[f]	105	4.25	94	117	79[k]	

[a] Oxidations were conducted in 50 ml of Me$_2$SO. The water concentration was 1.11 M with thiols and 2.22 M with disulfides except as indicated. [b] Halogen concentrations are expressed as equivalents of hydrogen halide. [c] Based upon the amount of 5 N NaOH solution required to neutralize the reaction mixture. Theory according to reaction 1 or 2, as applicable. [d] Yield of crude product less yield of Na$_2$SO$_4$ except as indicated. [e] Based upon thiol or disulfide. [f] Iodine also present, 0.64–0.66 × 10^{-2} M as HI. [g] Temperature of the reaction mixture was gradually increased from 70 to 110 °C in 2–3 h before start of this heating period. [h] Water concentration was 1.11 M. [i] Incompletely soluble initially. Went into solution as the oxidation progressed. [j] See Experimental Section. [k] Yield after recrystallization from water.

Experimental Section

Reagents. The Me$_2$SO, halogens, and hydrohalic acids were reagent grade. The concentrations of the acids follow: HI, 57%; HBr, 48%; and HCl, 37%. Ordinary quality, commercial thiols and disulfides were used directly when available. Practical grades were redistilled. Bis(2-naphthyl) disulfide was prepared by oxidation of 2-naphthalenethiol.[6]

General Aspects of the Oxidation Procedure. The reactants were heated by means of an oil bath in a flask equipped with a distillation head suitable for collection of DMS. Temperatures were approximate. Such heating was continued until the rate of DMS distillation went through a maximum and slowed to less than about $\frac{1}{3}$ ml per 15-min period per 100 mmol of expected sulfonic acid. Unless indicated otherwise, the reaction mixture was neutralized by addition of sodium hydroxide solution. The sodium salt was precipitated (preferably after removal of water under vacuum) by addition of acetone and ethyl acetate (about 200 ml of each per 100 mmol of expected sulfonate). The salt was dried at 130 °C and then recrystallized from ethanol[11] to separate from any sodium sulfate. Recrystallized salt was treated with phosphorus pentachloride and then concentrated aqueous ammonia to obtain the sulfonamide. In each case, the melting point of the sulfonamide agreed with the reported value.[12]

The following experiments are given as examples. Melting and boiling points are uncorrected.

Methanesulfonic Acid. A solution of 15 ml (169 mmol) of DMDS, 6 ml (333 mmol) of water, and 0.60 ml (5.34 mmol) of hydrobromic acid in 150 ml of Me$_2$SO was heated at 100–110 °C. After a bit, a distillation at 38–45 °C commenced. Heating was continued until the distillation temperature dropped and distillation slowed to less than 1 ml in a 15-min period (about 4.25 h). Distillate (56.5 ml) was obtained and proved to be mainly DMS. It redistilled at 37–39 °C and gave a mercuric chloride derivative melting at 159–161 °C (reported for the DMS derivative, 156–158 °C).[13]

Two-thirds of the reaction mixture was removed, and after dilution with 200 ml of water, the acid pesent was separated from excess Me$_2$SO by ion exclusion chromatography[7] on Dowex ion exchange resin (50-X8, acid form). The acid fraction was concentrated, then methanesulfonic acid distilled at 1 mm. Obtained was 19.6 g (90% of theory). The melting and boiling points agreed with literature values.

The remaining third of the reaction mixture was neutralized by addition of 24.3 ml of 5 N NaOH. Addition of 250 ml of acetone and 150 ml of ethyl acetate gave 12.4 g of crude sodium methanesulfonate (93% of theory). After recrystallization from 95% alcohol, the melting point was 353–355 °C (reported, 345 °C).[14]

2-Nitrobenzenesulfonic Acid. A mixture of 8.0 g (26.0 mmol) of bis(2-nitrophenyl) disulfide, 1 ml (55.5 mmol) of water, 0.40 ml (3.56 mmol) of hydrobromic acid, and 50 ml of Me$_2$SO was initially heated at 120 °C, but the temperature was gradually allowed to drop to 106 °C. In 7 h, 11.2 ml of DMS distilled.[15] NaOH (5 N, 15.2 ml) was required to neutralize the residue. After water was removed by heating under vacuum, 200 ml of ethyl acetate was added, and the mixture triturated. This was repeated with 100 ml of fresh ethyl acetate. Crude sodium 2-nitrobenzenesulfonate (10.9 g) was obtained. The yield was 90% after correction for 0.33 g of sodium sulfonate removed by crystallization from 95% alcohol.

Registry No.—Me$_2$SO, 67-68-5; methanesulfonic acid, 75-75-2; ethanesulfonic acid, 594-45-6; 1-butanesulfonic acid, 2396-47-2; 2-propanesulfonic acid, 14159-48-9; benzenesulfonic acid, 98-11-3; 2-nitrobenzenesulfonic acid, 80-82-0; 2-naphthalenesulfonic acid, 120-18-3.

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(11) Except sodium 2-naphthalenesulfonate. See Table IV, footnote *k*.
(12) Z. Rappoport, Ed., "Handbook of Tables for Organic Compound Identification", 3d ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, pp 392–405.
(13) F. Challenger and M. I. Simpson, *J. Chem. Soc.*, 1593 (1948).
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(15) Bis(2-nitrophenyl) disulfide was notably resistant to oxidation, and these conditions somewhat pressed the stability limits of Me_2SO. Though distillation of DMS had slowed by 7 h, it was still continuing at more than the usual rate.

Reactions of Fluorodinitroethoxyacetyl Chloride and Fluorodinitroethoxyacetic Anhydride with Friedel–Crafts Catalysts[1]

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Simple aliphatic anhydrides have been reported to react with boron trifluoride to give the symmetrical ketones.[2,3] Simple acid halides and tertiary amines gave ketene dimers, which on hydrolysis gave the corresponding ketones.[4] On the other hand, tertiary carboxylic acids, acid halides, and anhydrides underwent decarbonylation with Friedel–Crafts catalysts;[5] pivalyl chloride and aluminum chloride gave HCl, CO, and isobutylene.[6]

These reactions of fluorodinitroethoxyacetic acid derivatives were investigated as a continuation of our earlier work on this class of compounds.[7,8]

Fluorodinitroethoxyacetic acid and fluorodinitroethoxyacetyl chloride needed for this work were prepared by reported[7] procedures. Fluorodinitroethoxyacetic anhydride, unknown prior to this work, was synthesized in 60% yield by dehydrating fluorodinitroethoxyacetic acid with acetic anhydride:

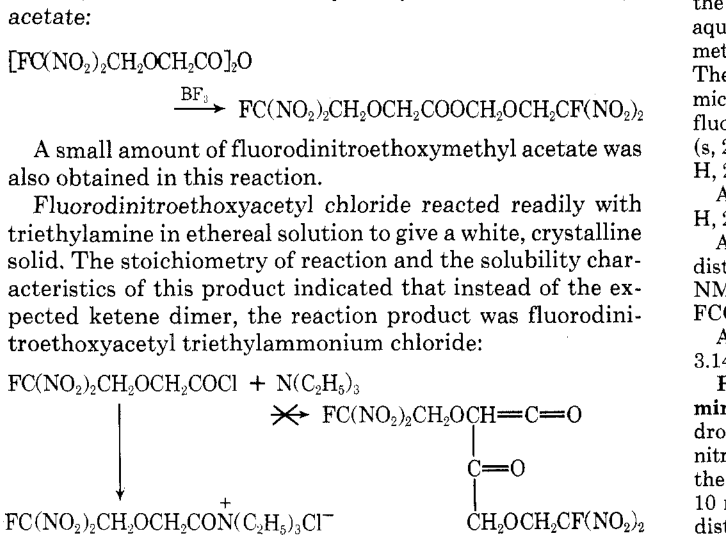
$$2FC(NO_2)_2CH_2OCH_2CO_2H + (CH_3CO)_2O \xrightarrow[\Delta]{} [FC(NO_2)_2CH_2OCH_2CO]_2O$$

Fluorodinitroacetic anhydride reacted with boron trifluoride under the reaction conditions employed by Man and Hauser.[3] The reaction product, however, was not the expected ketone, but fluorodinitroethoxymethyl fluorodinitroethoxyacetate:

$$[FC(NO_2)_2CH_2OCH_2CO]_2O \xrightarrow{BF_3} FC(NO_2)_2CH_2OCH_2COOCH_2OCH_2CF(NO_2)_2$$

A small amount of fluorodinitroethoxymethyl acetate was also obtained in this reaction.

Fluorodinitroethoxyacetyl chloride reacted readily with triethylamine in ethereal solution to give a white, crystalline solid. The stoichiometry of reaction and the solubility characteristics of this product indicated that instead of the expected ketene dimer, the reaction product was fluorodinitroethoxyacetyl triethylammonium chloride:



$$FC(NO_2)_2CH_2OCH_2COCl + N(C_2H_5)_3 \not\rightarrow FC(NO_2)_2CH_2OCH{=}C{=}O \quad (CH{-}C{=}O{-}CH_2OCH_2CF(NO_2)_2)$$

$$FC(NO_2)_2CH_2OCH_2COCl + N(C_2H_5)_3 \longrightarrow FC(NO_2)_2CH_2OCH_2CO\overset{+}{N}(C_2H_5)_3Cl^-$$

Unlike the reported reaction of ketene dimers, this material yielded dark, tarry product on treatment with water which did not contain any 1,3-bis(fluorodinitroethoxy)acetone.

Fluorodinitroethoxyacetyl chloride did not react with weak Friedel–Crafts catalysts such as stannic chloride or ferric chloride. The acid chloride, however, reacted rapidly with aluminum chloride with evolution of a gas. The product of this reaction was characterized as the previously reported[9] chloromethyl fluorodinitroethyl ether.

$$FC(NO_2)_2CH_2OCH_2COCl + AlCl_3 \longrightarrow FC(NO_2)_2CH_2OCH_2Cl + CO$$

These results are consistent with the initial reaction of fluorodinitroethoxyacetic anhydride and fluorodinitroethoxyacetyl chloride with Friedel–Crafts catalysts to give fluorodinitroethoxyacylium cation intermediate. Instead of losing the α proton and yielding fluorodinitroethoxyketene as is the case with simple carboxylic acid derivatives, this intermediate undergoes decarbonylation to give fluorodinitroethoxymethyl cation:

$$FC(NO_2)_2CH_2OCH_2COCl \xrightarrow{AlCl_3} [FC(NO_2)_2CH_2OCH_2CO]^+ + Cl^-$$

$$[FC(NO_2)_2CH_2OCH_2CO]_2O \xrightarrow{BF_3} [FC(NO_2)_2CH_2OCH_2CO]^+ + FC(NO_2)_2CH_2OCH_2COO^-$$

$$[FC(NO_2)_2CH_2OCH_2CO]^+ \xrightarrow{-CO} [FC(NO_2)_2CH_2OCH_2]^+$$

Thus, the fluorodinitroethoxy group appears to promote decarbonylation rather than ketene formation because of oxygen stabilization of the resulting cation, $FC(NO_2)_2CH_2OCH_2^+$.

Experimental Section

Fluorodinitroethoxyacetic Anhydride. A solution of 10 g (0.0472 mol) of fluorodinitroethoxyacetic acid[7] in 15 ml of acetic anhydride was refluxed for 8 h and the excess of acetic anhydride and acetic acid were removed under reduced pressure. The reaction product, 8.3 g, was contaminated with fluorodinitroethoxyacetic acid which was removed by distillation at 175–180 °C (0.1 mm). The degassed material amounting to 6.1 g (64% yield) solidified at room temperature and was crystallized from carbon tetrachloride to give 5.1 g of a white, crystalline solid: mp 54 °C; ^1H NMR ($CDCl_3$) δ 4.32 (d, J_{HF} = 16 Hz, 4 H, $2FCCH_2$–) and 4.69 ppm (s, 4 H, 2 $-CH_2CO-$).

Anal. Calcd for $C_8H_8F_2N_4O_{13}$: C, 23.66; H, 1.98. Found: C, 23.42; H, 2.03.

Fluorodinitroethoxymethyl Fluorodinitroethoxyacetate. A slow stream of boron trifluoride was passed at 0 °C for ca. 50 min into a stirred and cooled solution of 4 g (0.01 mol) of fluorodinitroethoxyacetic anhydride in 3 ml of chloroform. The resulting mixture was added to a solution of 4 g of sodium acetate in 9 ml of water and heated at 95–100 °C for 45 min. Chloroform was allowed to evaporate. The cooled mixture was extracted with 25 ml of methylene chloride and the methylene chloride solution was washed with 50 ml of saturated aqueous sodium bicarbonate solution followed by 50 ml of water. The methylene chloride solution was dried and stripped to give 2.2 g of oil. The crude material was distilled at 150 °C (0.1 mm) in a short-path micro distillation apparatus to give 1.9 g of fluorodinitroethoxymethyl fluorodinitroethoxyacetate, a colorless oil: ^1H NMR ($CDCl_3$) δ 5.25 (s, 2 H, $-COOCH_2O-$), 4.62 and 4.68 (two doublets, $J_{HF} \simeq$ 16 Hz, 4 H, 2 $FCCH_2$–), and 4.23 ppm (s, 2 H, $-OCH_2COO-$).

Anal. Calcd for $C_7H_8F_2N_4O_{12}$: C, 22.24; H, 2.13. Found: C, 22.36; H, 2.18.

A few drops of a colorless liquid obtained as a forerun in the above distillation was identified as fluorodinitroethoxymethyl acetate: ^1H NMR ($CDCl_3$) δ 5.17 (s, 2 H, $-COOCH_2-$), 4.66 (d, J_{HF} = 16 Hz, 2 H, $FCCH_2$–), and 2.10 ppm (s, 3 H, CH_3).

Anal. Calcd for $C_5H_7FN_2O_7$: C, 26.56; H, 3.12. Found: C, 27.3; H, 3.14.

Reaction of Fluorodinitroethoxyacetyl Chloride with Aluminum Chloride. Gas was evolved immediately when 0.3 g of anhydrous aluminum chloride was added to 1.0 g (0.047 mol) of fluorodinitroethoxyacetyl chloride. When evolution of gas ceased in ca. 10 min, the mixture was washed with 10 ml of ice water and extracted with 10 ml of methylene chloride. The methylene chloride solution was distilled to give 0.85 g of a colorless liquid, bp 40 °C (0.2 mm), identified as chloromethyl fluorodinitroethyl ether by comparing its physical properties and its ^1H NMR spectrum with those of an authentic sample of the ether.[9] There was no reaction when a 4:1 molar mixture of fluorodinitroethoxyacetyl chloride and stannic chloride