<div align="center">

TABLE II

NMR SPECTRA OF NEW COMPOUNDS PREPARED

</div>

Compd	Chemical shift (F)^a	Chemical shift (H), τ
CH$_3$O$_2$CCF$_2$CF$_2$CO$_2$NO	41.5, 47.2	6.44^b
CH$_3$O$_2$CCF$_2$CF$_2$CF$_2$CO$_2$NO A B A	41.7(A), 47.5(B)	6.45^b
CH$_3$O$_2$CCF$_2$CF$_2$NO	40.2, 43.3	6.83^b

CH$_3$O$_2$CCF$_2$CF$_2$CF$_2$NO
  A C A
  B   B
	38.9(A,B), 42.9(A,B), 48.9(C)	6.88^b

(CH$_3$O$_2$CCF$_2$CF$_2$)$_2$NOCF$_2$CF$_2$CO$_2$CH$_3$
   C B   A C
   D   D
	12.7(A), 19.8(B), 39.5(C,D),
	43.1(C,D)
		6.24^b

(CH$_3$O$_2$CCF$_2$CF$_2$CF$_2$)$_2$NOCF$_2$CF$_2$CF$_2$CO$_2$CH$_3$
   D E B   A F D
        C
	10.2(A), 14.9(B,C), 17.3(B,C),
	40.0(D), 42.1(E), 45.8(F)
		6.22^b

(HO$_2$CCF$_2$CF$_2$CF$_2$)$_2$NOCF$_2$CF$_2$CF$_2$COOH
   D E B   A F D
      C|
	9.5(A), 15.9(B,C), 17.7(B,C),
	39.8(D), 43.2(E), 46.9(F)
		. . .

(H$_2$NOCCF$_2$CF$_2$CF$_2$)$_2$NOCF$_2$CF$_2$CF$_2$CONH$_2$
   D E B   A F D
       C
	8.7(A), 14.9(B,C), 17.3(B,C),
	40.0 (D), 42.1 (E), 45.8 (F)
		2.36^b

(NCCF$_2$CF$_2$CF$_2$)$_2$NOCF$_2$CF$_2$CF$_2$CN
   D E B   A F D
       C
	9.7(A), 14.5(B,C), 19.4(B,C),
	28.2(D), 43.1(E), 47.3(F)
		3.40^c

^{a} Parts per million upfield from trifluoroacetic acid. ^{b} Acetaldehyde reference. ^{c} Tetramethylsilane reference.

chloride showed that the mixture contained 10.5% KCl. All attempts to obtain compound VII free from KCl by extraction, recrystallization, or sublimation were unsuccessful.

The melting point of the tricarboxylic acid was found by differential scanning calorimetry to be 220°.

Tris(3-carbamylperfluoropropyl)hydroxylamine (VIII).—Ethyl ether (150 ml) and [CH$_3$O$_2$C(CF$_2$)$_3$]$_2$NO(CF$_2$)$_3$CO$_2$CH$_3$ (VI) (113.5 g, 0.173 mol) were placed in a 250-ml flask and cooled in ice water. Ammonia was bubbled into the solution with rapid stirring until uptake of ammonia ceased. Ether was removed under vacuum and the residue was ground to a powder and dried in a vacuum oven at 50° to give 65 g (72% conversion) of a white solid, mp 157–160°. Infrared and nmr analysis were consistent with the structure [H$_2$NOC(CF$_2$)$_3$]$_2$NO(CF$_2$)$_3$CONH$_2$.

Anal. Calcd for C$_{12}$H$_6$F$_{18}$N$_4$O$_4$: C, 23.50; H, 0.98; F, 55.90; N, 9.15. Found: C, 23.59; H, 1.03; F, 55.54; N, 9.19.

Tris(3-cyanoperfluoropropyl)hydroxylamine (IX).—A 250-ml flask containing thoroughly mixed P$_2$O$_5$ (150 g) and the triamide (VIII) (72.6 g, 0.119 mol) from the preceding reaction was heated to 200° under vacuum. A liquid product distilled from the flask and was caught in a cold trap. Distillation gave 21.7 g (33% conversion) of [NC(CF$_2$)$_3$]$_2$NO(CF$_2$)$_3$CN boiling at 110–115° (60 mm). Infrared and nmr analysis were consistent with the assigned structure.

Anal. Calcd for C$_{12}$F$_{18}$N$_4$O: C, 25.82; F, 61.28; N, 10.04. Found: C, 25.68; F, 61.12; N, 10.16.

Hydrolysis of Methyl 4-Nitrosoperfluorobutyrate.—Methyl 4-nitrosoperfluorobutyrate (10 g, 0.042 mol) was placed in an erlenmeyer flask containing distilled water (60 ml) and a magnetic stirring bar. The aqueous layer gradually acquired a blue color as the ester hydrolyzed. After 5 days the lower, organic layer was no longer present. The product, 4-nitrosoperfluorobutyric acid (7.0 g, 75% conversion), was isolated by salting out with sodium chloride.

Registry No.—I, 16005-34-8; II, 16005-35-9; III, 7660-01-7; IV, 16031-01-9; V, 16031-02-0; VI, 16005-37-1; VII, 16005-24-6; VIII, 16005-25-7; IX, 16005-26-8.

A Superior Method for Preparing Sulfinyl Chlorides[1a]
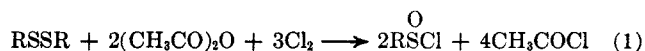
IRWIN B. DOUGLASS[1b] AND RICHARD V. NORTON

Department of Chemistry, University of Maine, Orono, Maine 04473

Previous papers from this laboratory have reported that sulfinyl chlorides can be prepared by the solvolysis of organosulfur trichlorides[2] or by the action of chlorine on a mixture of disulfide and glacial acetic acid.[3] Both of these methods have the disadvantage that a large volume of hydrogen chloride is produced in the reaction.

We have recently observed that if an anhydrous mixture of an alkyl or aryl disulfide and acetic anhydride is chlorinated at 0° to −10° the disulfide is smoothly converted into the corresponding sulfinyl chloride and the anhydride is converted into acetyl chloride. The over-all reaction is shown in eq 1. The

$$\text{RSSR} + 2(\text{CH}_3\text{CO})_2\text{O} + 3\text{Cl}_2 \longrightarrow 2\overset{\text{O}}{\text{RSCl}} + 4\text{CH}_3\text{COCl} \quad (1)$$

end point of the chlorination is indicated by the disappearance of the colored sulfenyl chloride formed by the reaction shown in eq 2. The other sequential steps are

$$\text{RSSR} + \text{Cl}_2 \longrightarrow 2\text{RSCl} \quad (2)$$

shown in eq 3 and 4. Reaction 4 is noteworthy in that

$$\text{RSCl} + \text{Cl}_2 \longrightarrow \text{RSCl}_3 \quad (3)$$

$$\text{RSCl}_3 + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow \text{RSOCl} + 2\text{CH}_3\text{COCl} \quad (4)$$

(1) (a) Taken in part from the Ph.D. Thesis of R. V. Norton, University of Maine, Orono, Maine, 1967; (b) to whom inquiries should be sent.
(2) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).
(3) I. B. Douglass, B. S. Farah, and E. G. Thomas, *ibid.*, **26**, 1996 (1961).

it represents the first solvolytic decomposition of an organosulfur trichloride by a reagent not containing a hydroxyl group.[4]

Reaction 4 appears to be more temperature dependent than reaction 2 or 3. If the chlorination is carried out at too low a temperature ($< -20°$) the organosulfur trichloride formed in eq 3 separates as white crystals which may cause the entire reaction mixture to solidify. At 0° to $-10°$, however, the solid trichloride is not observed and the reaction proceeds smoothly to completion as a one-phase system.

As pointed out previously,[3] an excess of disulfide or the solvolytic reagent should be avoided. Any excess of the disulfide, at the end of the reaction, will be in the form of the organosulfur trichloride which will decompose during work-up into the corresponding sulfenyl chloride or the α-chlorosulfenyl chloride.

An excess of acetic anhydride, like an excess of acetic acid, will react with the sulfinyl chloride in the presence of chlorine to form the sulfonyl chloride and acetyl chloride (eq 5).

$$RSOCl + (CH_3CO)_2O + Cl_2 \longrightarrow RSO_2Cl + 2CH_3COCl \quad (5)$$
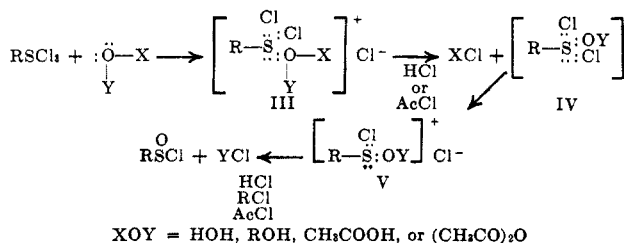
In isolating the sulfinyl chloride we have found it desirable to remove the acetyl chloride under the reduced pressure of a water pump, collecting it in a vessel of adequate capacity cooled to the temperature of Dry Ice. Some sulfinyl chloride codistils with the acetyl chloride and might be recovered by redistillation, but since the yield is above 85% without recovery, this step is usually omitted. By avoiding the long-continued heating of the reaction mixture to remove acetyl chlo-

---

(4) The mechanism by which the solvolysis of organosulfur trichlorides takes place presents interesting considerations. The structure of the organosulfur trichlorides is unknown; it can be formulated as covalent (I), in which a ten-electron shell for sulfur is assumed, or as ionic (II), in which the valence shell contains a normal octet. The crystallinity and low solubility of the

$$R - \overset{Cl}{\underset{Cl}{\overset{|}{S}}} \colon Cl \qquad\qquad \left[R - \overset{Cl}{\underset{\cdot\cdot}{S}} \colon Cl \right]^{+} Cl^{-}$$
$$\quad I \qquad\qquad\qquad\qquad II$$

organosulfur trichlorides in solvents like methylene chloride lends some support to the ionic structure.

The solvolysis would appear to be a nucleophilic attack at sulfur by an oxygen in water, an alcohol, acetic acid, or acetic anhydride. (Neither ethyl ether nor ethyl acetate will react in this way.) If the organosulfur trichloride exists in the covalent state the nucleophilic attack can be considered as taking place by displacement of a chloride ion to give an ionic intermediate (III) having a ten-electron shell. (Nucleophilic attack without displacement of chloride ion would have the unlikely result of producing a complex with a twelve-electron shell.) If the organosulfur trichloride is in the ionic form, nucleophilic attack at sulfur would produce the same addition complex III. One can postulate that the sequence of events in the solvolysis follows a course as indicated below.

$$RSCl_3 + \colon\overset{\cdot\cdot}{\underset{Y}{O}} - X \longrightarrow \left[R - \overset{Cl}{\underset{Y}{\overset{\colon Cl}{S}}} \colon \overset{}{O} - X \right]^{+} Cl^{-} \xrightarrow[\substack{HCl \\ or \\ AcCl}]{} XCl + \left[R - \overset{Cl}{\underset{\cdot\cdot}{\overset{\colon OY}{S}}} \colon Cl \right]^{+}$$
$$\qquad\qquad\qquad\qquad III \qquad\qquad\qquad\qquad\qquad\qquad IV$$

$$\underset{RSCl}{\overset{O}{\parallel}} + YCl \longleftarrow \left[R - \overset{Cl}{\underset{\cdot\cdot}{S}} \colon OY \right]^{+} Cl^{-}$$
$$\substack{HCl \\ RCl \\ AcCl} \qquad\qquad V$$

XOY = HOH, ROH, CH₃COOH, or (CH₃CO)₂O

Loss of XCl (HCl or CH₃COCl) from ionic complex III would give the neutral complex IV having a ten-electron shell. Separation of a chloride ion would give the ionic complex V having an octet valence shell. Finally, nucleophilic attack by chloride ion on Y would yield the sulfinyl chloride and YCl (HCl, RCl, or CH₃COCl).

ride at atmospheric pressure, as previously recommended, the tendency of the sulfinyl chloride to disproportionate[5] can be largely avoided (eq 6). Although

$$2RSOCl \longrightarrow RSCl + RSO_2Cl \quad (6)$$

we previously reported the purification of benzenesulfinyl chloride, C_6H_5SOCl, by distillation,[3] it is now our belief that *aromatic sulfinyl chlorides should not be distilled.* Unless the distillation is carried out at low pressure (< 2 mm) benzenesulfinyl chloride darkens and decomposes without distilling. An attempt to distil *p*-toluenesulfinyl chloride in our laboratory led to an explosion. There are no indications, however, that any hazard exists if distillation is avoided and the preparation is carried out at the moderate temperatures described in the Experimental Section. Due caution, nevertheless, should be observed in scaling up the reaction.

It might be well to repeat the earlier warning,[5] that *alkanesulfinyl chlorides should not be stored for long periods in sealed containers* at room temperature. Disproportionation and subsequent decomposition of the alkanesulfenyl chloride formed liberates gases which may develop high pressure within the container. Under refrigeration we have found that alkanesulfinyl chlorides can be stored for several months without appreciable decomposition. Moisture must be rigidly excluded, however, for an unusual reaction producing methanesulfonyl chloride and methyl methanethiolsulfonate occurs when methanesulfinyl chloride reacts with less than an equimolar quantity of water.[6]

Experimental Section

The Preparation of Methanesulfinyl Chloride.—Freshly distilled methyl disulfide (23.55 g, 0.25 mol) and acetic anhydride (51.05 g, 0.5 mol) were placed in a three-neck flask fitted with a stirrer, a chlorine inlet tube, and an outlet tube connected to a calcium chloride tube. After cooling the flask and contents in a Dry Ice bath, chlorine was passed in at such a rate that the temperature was held between 0 and $-10°$. At first the mixture turned yellow, then reddish as methanesulfenyl chloride accumulated but gradually the color faded and the solution became colorless when the stoichiometric quantity of chlorine had been added. At this point, in one preparation, the reaction mixture weighed 127.6 g. (The calculated weight of 0.5 mol of methanesulfinyl chloride and 1.0 mol of acetyl chloride is 127.8 g.)

The reaction mixture was transferred to a distilling flask attached to an 18-in. Vigreux column and connected, through a trap cooled in an acetone–Dry Ice bath, to a water pump. At 15 mm the mixture boiled below 0° and held near this temperature until most of the acetyl chloride had distilled. The pot temperature then gradually rose and finally the methanesulfinyl chloride distilled at 47–48° (15 mm) as a nearly colorless liquid with n^{25}D 1.5000 (lit.[2] n^{25}D 1.5038). Its nmr spectrum showed a single peak at δ 3.33 ppm with no sign of a signal at 3.64 ppm, the frequency characteristic of methanesulfonyl chloride. The yield was 41–42 g (83–86%).

The Conversion of Methanesulfinyl Chloride into Methanesulfonyl Chloride.—Chlorine was passed into a cold ($-50°$) mixture of methanesulfinyl chloride (11.1 g, 0.113 mol) and acetic anhydride (11.5 g, 0.113 mol), contained in a large test tube, until 8.0 g (0.113 mol) had dissolved. The color of chlorine did not appear to diminish over several hours and when the mixture was removed from the cold bath and allowed to warm to $-10°$, chlorine gas tended to escape. The mixture was finally set aside in the cold bath and allowed to stand for 48 hr during which time the bath slowly came to room temperature and the color dis-

---

(5) I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

(6) R. V. Norton, G. M. Beverly, and I. B. Douglass, *ibid.*, **32**, 3645 (1967).

appeared. Nmr analysis of the reaction mixture and integration of the spectrum indicated a composition consisting of 32.7 mol % of methanesulfonyl chloride, 2.0 mol % of unchanged methanesulfinyl chloride, 61.3 mol % of acetyl chloride, 1.4 mol % of acetic anhydride, and 2.0 mol % of acetic acid. The results suggested some loss of chlorine and some diffusion of moisture into the mixture during the period of standing.

Although the reaction was slow in going to completion an attempt to separate, as quickly as possible, excess chlorine from a mixture of sulfinyl chloride and acetic anhydride resulted in forming an appreciable amount of sulfonyl chloride. Chlorine (9.0 g, 0.127 mol) was dissolved in a mixture of methanesulfinyl chloride (9.9 g 0.1 mol) and acetic anhydride (10.2 g, 0.1 mol) held at a temperature below $-20°$. The mixture was quickly transferred to a distilling apparatus and subjected to the reduced pressure (15 mm) of a water pump. At first the pot temperature dropped from -20 to $-30°$ as the chlorine vaporized. Gentle heat was applied and when the pot temperature reached 10° the colorless residue was removed and a sample was taken for nmr analysis. Although the nmr spectrum of the original mixture had shown only two peaks, characteristic of methanesulfinyl chloride and acetic anhydride, the final mixture showed four peaks: δ 3.64 (CH_3SO_2Cl), 3.33 (CH_3SOCl), 2.64 (CH_3COCl), and 2.17 ppm (($CH_3CO)_2O$.[7] Integration indicated that 8% of the methanesulfinyl chloride had been converted into the sulfonyl chloride.

The Preparation of Ethanesulfinyl Chloride.—Employing a procedure similar to that described for methanesulfinyl chloride, a mixture of ethyl disulfide (12.2 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was chlorinated to the greenish yellow of excess chlorine and then distilled at reduced pressure. When the excess chlorine had been removed the remaining liquid was completely colorless. Removal of acetyl chloride and distillation gave 19.5 g (86% yield) of faintly colored ethanesulfinyl chloride boiling 66–67.5° (27 mm) and having n^{30}D 1.4903 (lit.[3] n^{25}D 1.4954). The acetyl chloride collected weighed 31.5 g (Calcd 31.4 g) and was yellow from excess chlorine. Addition of cyclohexene readily discharged the color.

The Preparation of Butanesulfinyl Chloride.—A mixture of *n*-butyl disulfide (17.7 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was chlorinated at $-10°$ to a faint color of excess chlorine. Heating under reduced pressure until the pot temperature reached 50° gave a faintly colored product which had n^{31}D 1.477 (lit.[2] n^{25}D 1.4849). The nmr spectrum showed a small peak indicating the presence of acetyl chloride. Reheating to a pot temperature of 95° (25 mm) caused further darkening of the product but the nmr spectrum showed no peak for acetyl chloride. The yield after the second heating was 26.2 g (93%).

The Preparation of Benzenesulfinyl Chloride.—A mixture of freshly recrystallized phenyl disulfide (21.8 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was cooled to $-10°$ and chlorinated. Although the disulfide did not dissolve in the anhydride, chlorination converted it rapidly into the sulfenyl chloride and caused the mixture to liquefy. The reaction mixture never became completely colorless as more chlorine was added but addition was terminated when a greenish yellow color indicated an excess of chlorine. After removing the acetyl chloride and excess chlorine at reduced pressure the residue in the pot was heated to 50° (15 mm) and held at this temperature until boiling ceased. The pale amber product (32.0 g, theoretical yield 32.4 g) had n^{30}D 1.600 (lit.[3] n^{25}D 1.6062) and readily solidified when stored in Dry Ice. A portion, frozen in a capillary, melted at *ca.* 2°.

In an early experiment, after removing the acetyl chloride at reduced pressure, the residue was heated to 135° (15 mm) but no benzenesulfinyl chloride would distil. The contents of the pot began to darken and further heating was discontinued because a previous attempt to distil *p*-toluenesulfinyl chloride in our laboratory had led to an explosion.

Registry No.—Methanesulfinyl chloride, 676-85-7; ethanesulfinyl chloride, 1718-44-1; butanesulfinyl chloride, 13455-88-4; benzenesulfinyl chloride, 4972-29-6.

(7) The nmr spectra were recorded on a Varian A60 nmr spectrometer.

Michael-Type Additions with 2,2-Dimethyl-1,3-dinitropropane
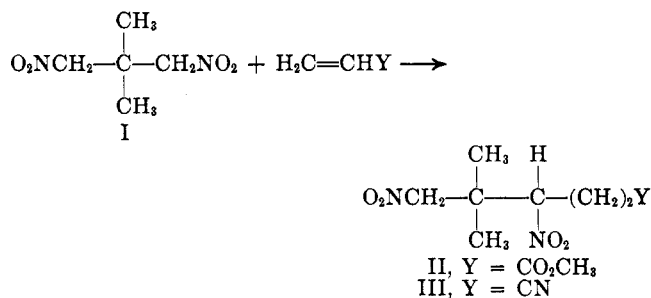
HENRY FEUER, ADEL F. HALASA, AND MELVIN AUERBACH

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

The Michael-type reaction of α,ω-dinitroalkanes with compounds containing activated double bonds has been found to afford exclusively di- or tetra-adducts.[1-4] On the other hand, Michael additions with 2,2-dimethyl-1,3-dinitropropane (I) led to mono- and diadducts depending on the acceptors and reaction conditions.

The reaction of compound I with such acceptors as methyl acrylate and acrylonitrile afforded only the monoadducts methyl 4,6-dinitro-5,5-dimethylhexanoate (II) and 4,6-dinitro-5,5-dimethylhexanenitrile (III), respectively. The identity of compounds II and III was established by infrared and nmr spectra and by correct elemental analyses.
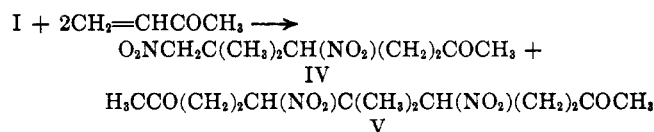
Compounds II and III were the only products obtained when I and a large excess of the acceptors were employed in such solvents as ethanol or THF at 40–45° in the presence of catalytic amounts of base and when reaction times were extended up to 72 hr.

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{O}_2\text{NCH}_2\text{—C—CH}_2\text{NO}_2 + \text{H}_2\text{C=CHY} \longrightarrow \\
| \\
\text{CH}_3 \\
\text{I}
\end{array}
$$

$$
\begin{array}{c}
\text{CH}_3 \quad \text{H} \\
| \qquad | \\
\text{O}_2\text{NCH}_2\text{—C——C—(CH}_2)_2\text{Y} \\
| \qquad | \\
\text{CH}_3 \quad \text{NO}_2 \\
\text{II, Y = CO}_2\text{CH}_3 \\
\text{III, Y = CN}
\end{array}
$$

The reaction of I with 2 equiv of methyl vinyl ketone in 95% ethanol in the presence of catalytic amounts of sodium hydroxide at 40–45° for 36–48 hr gave a mixture consisting of about 40% monoadduct, 5,7-dinitro-6,6-dimethyl-2-heptanone (IV), and 10% diadduct, 5,7-dinitro-6,6-dimethyl-2,10-undecanedione (V).

Only compound IV was obtained in 48% yield when THF was employed as the solvent under otherwise similar reaction conditions.

The addition of I to 4 equiv of methyl vinyl ketone (95% ethanol, sodium hydroxide) produced, after 24 hr, only monoadduct IV and, after 48 hr, only diadduct V. The latter was also obtained when compound IV was treated with methyl vinyl ketone.

I + 2CH$_2$=CHCOCH$_3$ ⟶

  O$_2$NCH$_2$C(CH$_3$)$_2$CH(NO$_2$)(CH$_2$)$_2$COCH$_3$ +
                    IV

  H$_3$CCO(CH$_2$)$_2$CH(NO$_2$)C(CH$_3$)$_2$CH(NO$_2$)(CH$_2$)$_2$COCH$_3$
                    V

(1) H. Feuer and C. N. Aquilar, *J. Org. Chem.*, **16**, 161 (1951).
(2) H. Feuer and R. Harmetz, *ibid.*, **26**, 1061 (1961).
(3) For a general discussion of Michael reactions reference is made to E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).
(4) For a thorough survey of Michael reactions concerning polynitro compounds, see P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).