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HIGH ENERGY HALOGEN CHEMISTRY

Kurt Baum, et al

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HIGH ENERGY HALOGEN CHEMISTRY

A Report on Work Sponsored By

THE OFFICE OF NAVAL RESEARCH

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By

K. Baum, C.D. Beard and V. Grakauskas

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13. ABSTRACT

Propene reacted with dichlorine heptoxide to give propyl perchlorate and 1-chloro-2-propyl perchlorate. 2-Butene gave 3-chloro-2-butyl perchlorate, 2,3-butanediperchlorate, and a compound tentatively identified as 3-keto-2-butyl perchlorate. The 3-chloro-2-butyl perchlorate was formed by a stereospecific trans addition. 1-Hexene gave 1-chloro-2-hexyl perchlorate, 2-chloro-1-hexyl perchlorate, and 1-chloro-2-hexanone. Ethylene glycol, 1,4-butanediol, 2,2,2-trifluoroethanol, allyl alcohol and propargyl alcohol reacted with dichlorine heptoxide to give 1,2-ethanediperchlorate, 1,4-butanediperchlorate, 2,2,2-trifluoroethyl perchlorate, allyl perchlorate and propargyl perchlorate, respectively. Ketones were byproducts in the preparation of perchlorates from secondary alcohols. Tetrahydrofuran, trimethylene oxide and 2-butene oxide and dichlorine heptoxide gave 1,4-butanediperchlorate, 1,3-propanediperchlorate and 2,3-butanediperchlorate, respectively, but terminal epoxides gave mainly polymers. Primary N-perchlorylamines formed alkali metal salts which reacted with chlorine and bromine to give the halo derivatives. The pK_a of N-perchloryl-t-butylamine was 6.82. Alkyl perchlorates reacted with lithium bromide to give alkyl bromides and with alcohols to give ethers. The reaction of alkyl trifluoromethanesulfonates with 2,2-dinitroalcohols was found to be a general synthesis method for 2,2-dinitroalkyl ethers. Fluorammonium trifluoromethanesulfonate showed greater thermal stability than other fluorammonium salts.

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Nuclear magnetic resonance spectra						
Infrared spectra						

CONTENTS

	Page
Introduction	1
Discussion	2
Reactions of Olefins with Dichlorine Heptoxide	2
Reactions of Alcohols with Dichlorine Heptoxide	7
Reactions of Ethers with Dichlorine Heptoxide	10
Reactions of Amines with Dichlorine Heptoxide	11
Reactions of Organometallics with Dichlorine Heptoxide	14
Reactions of Alkyl Perchlorates	14
Fluoronitro Chemistry	16
Experimental Section	17
References	38
Appendix A	
Synthesis of Some Highly Reactive Trifluoromethanesulfonates (Triflates) and Their Reactions with Alcohols	39
Appendix B	
Fluorammonium Trifluoromethanesulfonate	60

INTRODUCTION

The objective of this research program is to explore the synthesis of new functional groupings with potential utility in high energy propellants and explosives. The major emphasis of the research has been on the chemical reactions of dichlorine heptoxide, a broad area of investigation that was initiated in the preceding report period.[1] An investigation of reactions of alkyl trifluoromethanesulfonates with nitroalcohols is included in manuscript form as Appendix A. This work provided model reactions for the perchlorate group, which has reactivity similar to the trifluoromethanesulfonate group, and also provided a general route to ethers of nitroalcohols. The trifluoromethanesulfonate ion also provided a fluorammonium salt more stable than those previously obtained. This salt is described in Appendix B.

DISCUSSION

In the preceding Annual Report on this program[1] a convenient procedure was described for preparing carbon tetrachloride solutions of dichlorine heptoxide. It was found that dichlorine heptoxide reacts with alcohols, even those with electron-withdrawing substituents, to give the corresponding alkyl perchlorates. Tetrahydrofuran and diethyl ether were cleaved by this reagent to give perchlorates, and ketones added dichlorine heptoxide to give gem-diperchlorates. Primary and secondary amines gave perchlorylamines. Olefins also reacted with dichlorine heptoxide, but the products were not identified.

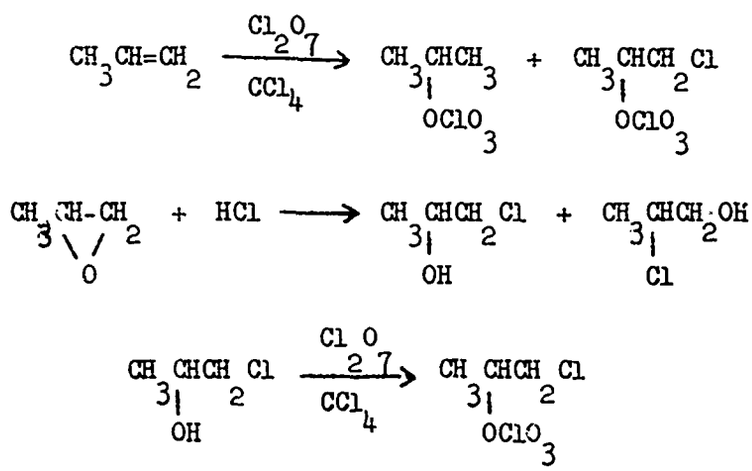
Subsequent work in these areas has included determination of yields and the effects of some reaction variables, product identification, and the examination of other functional groups.

REACTIONS OF OLEFINS WITH DICHLORINE HEPTOXIDE

The reaction of olefins with dichlorine heptoxide is relatively complex, and the simple 1,2-adducts, $>C(OClO_3)C(ClO_3)<$ or $>C(OClO_3)C(OClO_2)<$, were not found. The major products from propene, 2-butene and 1-hexene were identified.

Propene reacted with dichlorine heptoxide in carbon tetrachloride solution, over a 24 hr period, to give a 17% yield of 1-chloro-2-propyl perchlorate and a 32% yield of isopropyl perchlorate. Isopropyl perchlorate was identified by spectral and glpc comparison with authentic material prepared from isopropanol. 1-Chloro-2-propyl perchlorate was identified by elemental analysis and by ir and nmr spectra. The structure was confirmed by preparing

a sample independently. 1-Chloro-2-propanol was prepared from propylene oxide and hydrochloric acid by a previously reported procedure.[2] This alcohol reacted with dichlorine heptoxide to give material identical with that from propene.

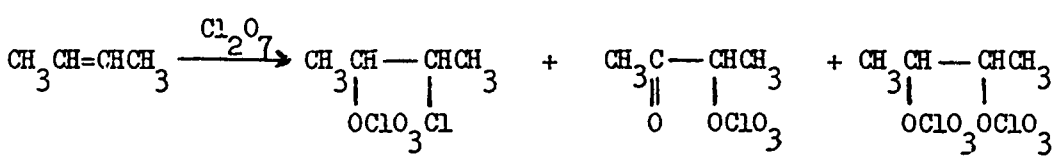


Isopropyl perchlorate could be formed by the reaction of propene with perchloric acid formed during the reaction. Experiments were therefore carried out with anhydrous lithium perchlorate or sodium sulfate in suspension to adsorb perchloric acid as it was liberated. Yields of isopropyl perchlorate were reduced under these conditions, but new products were not obtained and yields of 1-chloro-2-propyl perchlorate remained the same.

2-Butene reacted in 4 hrs with dichlorine heptoxide in carbon tetrachloride. The major product, formed in yields of 26-30% was identified as 3-chloro-2-butyl perchlorate. A methyl ketone, tentatively identified as 3-keto-2-butyl perchlorate, was formed in 2% yield. When the reaction was carried out with added lithium perchlorate, the yield of this ketone was increased to 20%. Another product, obtained as a distillation residue, was identified as 2,3-butanediperchlorate by spectral comparison with a sample

prepared from 2-butene oxide and dichlorine heptoxide.

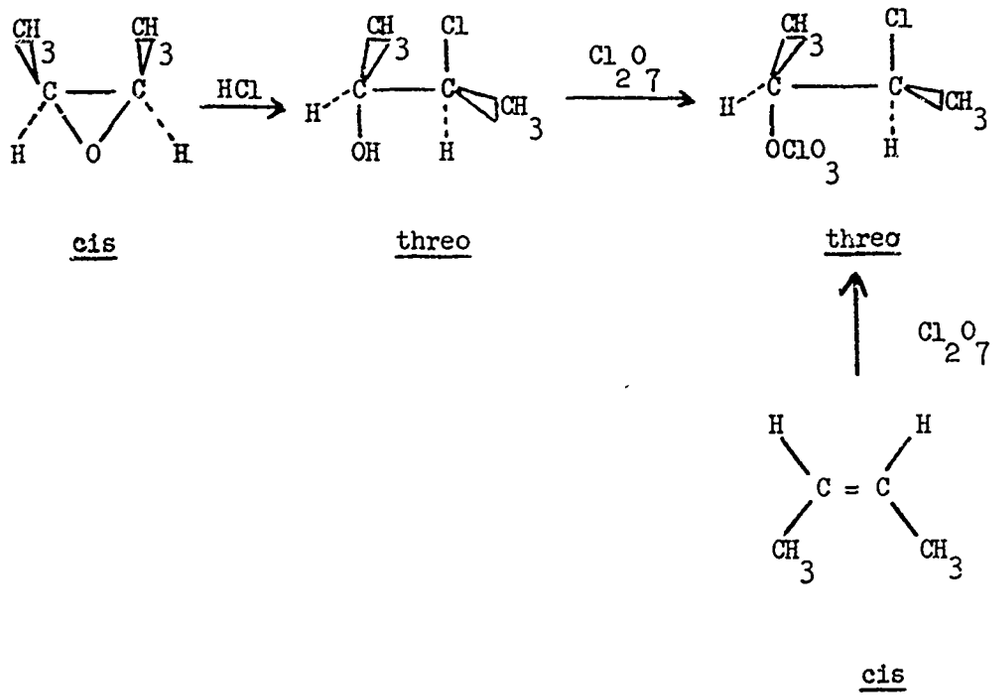
The ketone product showed nmr (δ 1.61 doublet, δ 2.30 singlet and δ 5.12 quintet) and ir (1720, 1020, 1240 and 1270 cm^{-1}) spectra consistent with a structure $CH_3COCHXCH_3$, where X is ClO_4 or ClO_3. Carbon and hydrogen analyses correct for the perchlorate structure were obtained, but analytical data was erratic. Mass spectra gave no informative chlorine-containing fragments; the highest molecular weight peak containing carbon was assignable to the $CH_3CO^{\oplus}$ ion. Attempts will be made to obtain confirmatory evidence by independent synthesis.

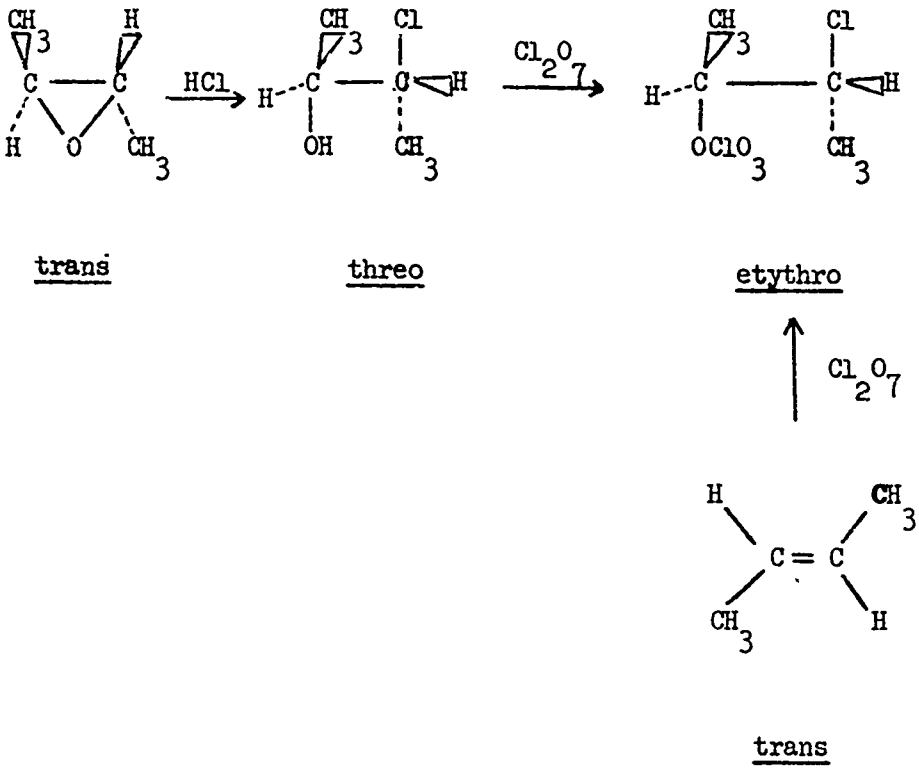


3-Chloro-2-butyl perchlorate was identified by nmr and ir spectra and by elemental analysis. A sample for comparison was prepared by adding hydrochloric acid to 2-butene oxide and treating the resulting chlorohydrin with dichlorine heptoxide. The gas chromatogram of the perchlorate prepared in this way showed two equal closely spaced peaks. The gas chromatogram of the 3-chloro-2-butyl perchlorate obtained from cis-2-butene showed only the lower-retention-time peak and that from trans-2-butene showed only the higher-retention-time peak. Thus the formation of 3-chloro-2-butyl perchlorate involves a stereospecific addition.

The mode of addition was determined by using cis-2-butene oxide and trans-2-butene oxide, obtained by preparative gas chromatography from the commercial cis-trans mixture. The isomeric epoxides were then each reacted with hydrochloric acid, and the chlorohydrins were subsequently treated with dichlorine

heptoxide. It was found that cis-2-butene oxide gave the chloroperchlorate with the lower retention time and that trans-2-butene oxide gave the perchlorate with the higher retention time. Lucas and Garner[3] showed that the addition of hydrochloric acid to the 2-butene oxides is stereospecifically a trans addition. The reaction of alcohols with dichlorine heptoxide is presumed to be an electrophilic attack on oxygen and thus should result in retention of configuration at the carbon atom. Therefore, the formation of 3-chloro-2-butyl perchlorate from 2-butene involves a stereospecific trans addition to the double bond.





The reaction of 1-hexene with dichlorine heptoxide also gave chloroperchlorates and a mixture of ketones. Both 1-chloro-2-hexyl perchlorate and 2-chloro-1-hexyl perchlorate were observed, in a ratio of 3:1, in a combined yield of 29%. These compounds were also synthesized for structure proof from 1-chloro-2-hexanol and 2-chloro-1-hexanol, respectively, and Cl_2O_7. A mixture of ketone products was separated from the chloroperchlorates by column chromatography, and the three most abundant products in this mixture were isolated by gas chromatography. One of these was found to be 1-chloro-2-hexanone by comparison with an authentic sample. Spectral properties of the other two suggested that they were ketoperchlorates. One of these showed a singlet in the nmr spectrum at δ 2.30, consistent with an

acetyl group. Some double bond migration is thus indicated. The original reaction mixture also showed an nmr doublet at δ 1.50, indicative of 2-hexyl perchlorate, but the material was decomposed during column chromatography.

$$CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow{Cl_2O_7} CH_3CH_2CH_2CH_2\underset{}{\overset{OClO_3}{\overset{|}{C}}}HCH_2Cl$$

$$+\ CH_3CH_2CH_2CH_2CHClCH_2OClO_3 \ +\ CH_3CH_2CH_2CH_2\underset{O}{\underset{\|}{C}}CH_2Cl \ +\ CH_3CH_2CH_2CH_2\underset{OClO_3}{\underset{|}{C}}HCH_3$$

No reaction was observed within several days at room temperature between dichlorine heptoxide and ethylene, allyl chloride, methyl acrylate, or perfluoro-2-butene.

REACTIONS OF ALCOHOLS WITH DICHLORINE HEPTOXIDE

In the preceding report on this contract,[1] it was demonstrated that the reaction of alcohols with dichlorine heptoxide provides a safe and versatile synthesis method for alkyl perchlorates. Ethanol, isopropanol, pentanol, 2-hexanol, 2-(2-fluoro-2,2-dinitroethoxy)ethanol, 2-fluoro-2,2-dinitroethanol and 2,2-dinitropropanol were converted to the corresponding perchlorates. Subsequent work on this reaction included extension to additional substrates, including difunctional and unsaturated alcohols. Effects of reaction variables on yields were examined.

Perchlorates that were prepared from the corresponding alcohols are shown in Table I. Yields were determined by nmr, using chlorobenzene as a quantitative internal reference.

Table I

Perchlorates from Alcohols

Perchlorates	Yield (%)
$CH_3CH_2OClO_3$	56
$CH_3(CH_2)_3CH_2OClO_3$	63
$CH_3(CH_2)_4CH_2OClO_3$	58
$(CH_3)_2CH\text{-}OClO_3$	48
$CH_3(CH_2)_3\text{-}CH(OClO_3)\text{-}CH_3$	62
$CH_3(CH_2)_2\text{-}CH(OClO_3)\text{-}CH_2CH_3$	53
$F\text{-}C(NO_2)_2\text{-}CH_2OClO_3$	60
$CH_3\text{-}C(NO_2)_2\text{-}CH_2OClO_3$	67
$FC(NO_2)_2CH_2OCH_2CH_2OClO_3$	43
$CF_3CH_2OClO_3$	55
$ClO_3O\text{-}CH_2CH_2CH_2CH_2\text{-}OClO_3$	38
$ClO_3OCH_2\text{-}CH_2OClO_3$	60
$CH_2{=}CH\text{-}CH_2OClO_3$	48
$HC{\equiv}C\text{-}CH_2OClO_3$	43

The reactions were conducted simply by adding the alcohols to carbon tetrachloride solutions of dichlorine heptoxide. A mildly exothermic reaction takes place immediately, and the liberated perchloric acid complexes with unreacted alcohol, removing it from solution. This complex reacts more slowly with dichlorine heptoxide, generally giving optimum yields of perchlorates in 12-18 hrs with simple primary alcohols. Electronegatively substituted alcohols require longer reaction periods, generally 72 hrs.

Acid scavengers were examined with the objective of preventing interaction of liberated perchloric acid with the reactants. Potassium carbonate and pyridine reacted rapidly with dichlorine heptoxide, and gave only low yields of alkyl perchlorates. Potassium fluoride and sodium fluoride reacted slowly with dichlorine heptoxide to give a gas presumably perchloryl fluoride. In the reaction of pentanol with dichlorine heptoxide, the use of these salts resulted in the formation of 20-30% yields of pentyl ether. Sodium sulfate appeared to adsorb alcohol-perchloric acid complex, and yields were not improved with simple alcohols.

However, with chemically sensitive alcohols, such as allyl alcohol and propargyl alcohol sodium sulfate prevented side reactions due to perchloric acid. Allyl perchlorate and propargyl perchlorate were identified by nmr and ir spectra, as well as by displacement reactions described in a later section. Unsuccessful attempts have been reported to prepare allyl perchlorate from allyl halides and silver perchlorate.[4]

Primary diols reacted normally with dichlorine heptoxide; 1,4-butanediol and ethylene glycol gave the corresponding diperchlorates. However, 2,3-butanediol did not give a significant yield of the diperchlorate, probably because of

a competing pinacol rearrangement. This diperchlorate was prepared readily from 2-butene oxide, however.

The reaction of 2,2,2-trifluorcethanol with dichlorine heptoxide gave 2,2,2-trifluoroethyl perchlorate, which was identified by fluorine and proton nmr spectra and ir spectra. This compound was previously stated to be a product of the reaction of perchloryl fluoride with 2,2,2-trifluoroethanol, but no characterization was provided.[5] Trinitroethanol, however, gave no reaction with dichlorine heptoxide, even after prolonged reflux.

In reactions of secondary alcohols with dichlorine heptoxide, a significant side reaction was oxidation to the corresponding ketones. Thus, in the reactions of 2-hexanol and 3-hexanol with dichlorine heptoxide, 2-hexanone and 3-hexanone were isolated along with the corresponding perchlorates. No isomerization was detected in these reactions.

$$CH_3(CH_2)_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow{Cl_2O_7} CH_3(CH_2)_3\underset{\underset{OClO_3}{|}}{C}HCH_3 \;+\; CH_3(CH_2)_3\overset{\overset{O}{\|}}{C}CH_3$$

62% 12%

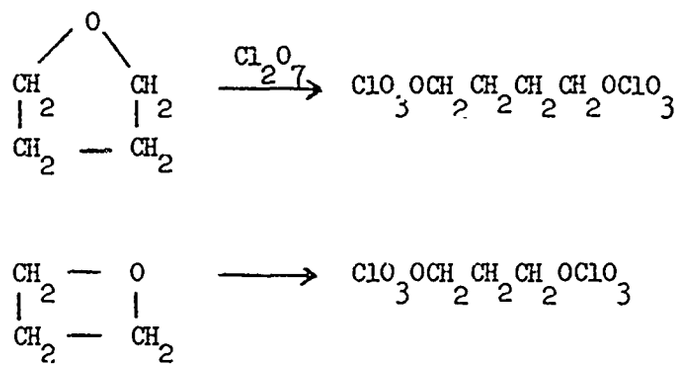
$$CH_3(CH_2)_2\underset{\underset{OH}{|}}{C}HCH_2CH_3 \xrightarrow{Cl_2O_7} CH_3(CH_2)\underset{\underset{OClO_3}{|}}{C}HCH_2CH_3 \;+\; CH_3(CH_2)\overset{\overset{O}{\|}}{C}CH_2CH_3$$

53% 15%

REACTIONS OF ETHERS WITH DICHLORINE HEPTOXIDE

The reaction of tetrahydrofuran with dichlorine heptoxide was shown

in the previous report[1] to give 1,4-butanediperchlorate. The yield of this reaction was subsequently found to be 83%. Trimethylene oxide was also found to react smoothly with dichlorine heptoxide to give 1,3-propanediperchlorate. Although 2-butene oxide gave 2,3-butanediperchlorate readily, less hindered epoxides gave little if any of the desired diperchlorates. Ethylene oxide, propylene oxide and 1-butene oxide gave mainly polymers.



Reactions of open-chain ethers with dichlorine heptoxide are more complex. Diisopropyl ether appeared to give an initial complex with dichlorine heptoxide that subsequently was converted to isopropyl perchlorate and 2,2-diperchloratopropane. The latter was identified by nmr[6] and by conversion to acetone 2,4-dinitrophenylhydrazone. The reaction of pentyl ether gave only 30-40% yields of pentyl perchlorate in 3 days, with 75% of the pentyl ether consumed, and several unidentified compounds were formed.

REACTIONS OF AMINES WITH DICHLORINE HEPTOXIDE

Several secondary amines and one primary amine were reported previously[1] to

give N-perchlorylamines in reactions with dichlorine heptoxide. These reactions were repeated, and yields were determined (Table II).

Chemical properties of primary perchlorylamines were examined. The compounds are acidic and can be extracted from carbon tetrachloride with aqueous sodium hydroxide, and recovered on acidification. Potentiometic titration showed that the pK_a of N-perchloryl-t-butylamine was 6.82.

The halogenation of primary N-perchlorylamines was studied. N-Perchlorylhexylamine reacted with sodium hypochlorite solution to give a product that was stable in carbon tetrachloride solution at room temperature. The compound could not be extracted with sodium hydroxide solution, and its nmr and ir spectra were consistent with the N-perchloryl-N-chlorohexylamine structure.

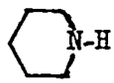
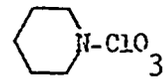
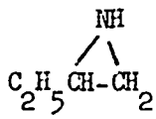
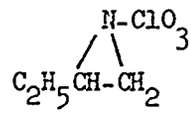
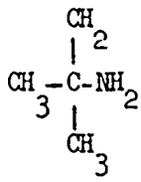
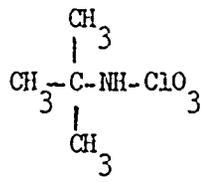
$$CH_3(CH_2)_5NHClO_3 \xrightarrow{NaOCl} CH_3(CH_2)_5\overset{\overset{Cl}{|}}{N}\text{-}ClO_3$$

The reaction of bromine with an aqueous solution of the sodium salt of N-perchloryl-t-butylamine was also carried out. Bromine color was discharged in 20 min at 0°. The product decomposed at room temperature, with liberation of bromine. A rapid nmr scan of a freshly prepared carbon tetrachloride solution of this product showed a singlet at approximately δ 1.5, consistent with the N-perchloryl-N-bromo-t-butylamine structure.

$$(CH_3)_3CNClO_3^{\ominus} \xrightarrow{Br_2} (CH_3)_3C\overset{\overset{Br}{|}}{N}\text{-}ClO_3$$

Table II

Reaction of Amines with Dichlorine Heptoxide

Starting Material	Product	Yield (%)
		73
$(C_2H_5)_2NH$	$(C_2H_5)_2N\text{-}ClO_3$	77
$(C_5H_{11})_2NH$	$(C_5H_{11})_2N\text{-}ClO_3$	81
		83
$CH_3(CH_2)_2CH_2NH_2$	$CH_3(CH_2)_2CH_2NHClO_3$	61
		71
$CH_3(CH_2)_4CH_2NH_2$	$CH_3(CH_2)_4CH_2NH\text{-}ClO_3$	63

Several attempts to fluorinate salts of perchlorylamines in aqueous solution were unsuccessful. No reaction was observed in attempts to alkylate these salts in aqueous solution with dimethyl sulfate or methyl triflate. Attempts to add these salts to methyl acrylate were also unsuccessful.

REACTIONS OF ORGANOMETALLICS WITH DICHLORINE HEPTOXIDE

Reactions of aromatic organometallic compounds with dichlorine heptoxide would be expected to yield aromatic perchloryl compounds. Only diphenylmercury and diphenyltin were examined as yet, but no perchlorylbenzene was detected. The only organic products identified were chlorobenzene and benzoquinone in both cases.

REACTIONS OF ALKYL PERCHLORATES

Although alkyl perchlorates are recognized as powerful alkylating agents,[7] systematic studies of their reactions have not been reported. Most reported alkylations were done in-situ in the presence of silver salts. The convenient and safe preparative methods for alkyl perchlorates based on dichlorine heptoxide make their use as chemical reagents more attractive.

Displacement reactions also can provide structure proof for perchlorates. The reaction of perchlorates with lithium bromide in acetone was found to be particularly useful in this respect. Thus, 1,4-butanediperchlorate, pentyl perchlorate, 1,2-ethanediperchlorate and propargyl perchlorate gave the corresponding bromides in almost quantitative yield.

$$ClO_3O(CH_2)_4OClO_3 \xrightarrow[CH_3COCH_3]{LiBr} Br(CH_2)_4Br$$

$$CH_3(CH_2)_4OClO_3 \longrightarrow CH_3(CH_2)_4Br$$

$$ClO_3OCH_2CH_2OClO_3 \longrightarrow BrCH_2CH_2Br$$

$$HC{\equiv}CCH_2OClO_3 \longrightarrow HC{\equiv}CCH_2Br$$

Alkyl perchlorates were examined as reagents for preparing ethers from alcohols. Thus allyl perchlorate and 2-fluoro-2,2-dinitroethanol in CCl_4-CH_2Cl_2, in the presence of potassium carbonate, gave a 38% yield of 2-fluoro-2,2-dinitroethyl allyl ether in 48 hrs. Isopropyl perchlorate and pentanol, in the presence of sodium sulfate to remove perchloric acid, gave 25% conversion to isopropyl pentyl ether in 18 hrs, 50% in 72 hrs and 85% in 144 hrs. Pentyl perchlorate and pentanol in the presence of potassium carbonate gave 5% conversion to dipentyl ether in 20 hrs, 25% in 96 hrs and 90% in 192 hrs. Under the same conditions, pentyl triflate gave 90% conversion in 20 hrs. Thus perchlorates are effective alkylating agents under mild conditions, but are somewhat less reactive than triflates (see Appendix A).

Another reaction of perchlorates that was examined briefly is oxidation by dimethyl sulfoxide. Alkyl tosylates are converted to aldehydes by this reagent at 150°.[8] Hexyl perchlorate gave a 55% yield of hexaldehyde

in 24 hrs at room temperature with this reagent.

FLUORONITRO CHEMISTRY

A high-boiling liquid fluorodinitro compound, bis(2-fluoro-2,2-dinitroethyl) methyl orthoformate was prepared by the reaction of 2-fluoro-2,2-dinitroethanol with dichloromethyl methyl ether in the presence of aluminum chloride.

$$FC(NO_2)_2CH_2OH + Cl_2CHOCH_3 \xrightarrow{AlCl_3} (F-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}CH_2O)_2CHOCH_3$$

EXPERIMENTAL SECTION

GENERAL

Dichlorine heptoxide was prepared by the previously described method.[1] A Varian T-60 nmr spectrometer and a Perkin-Elmer 700 ir spectrometer were used for the spectral determination, and a Varian 920 gas chromatograph was used for analytical and preparative glpc. Safety shielding must be used in the isolation of alkyl perchlorates.

REACTION OF PROPENE WITH DICHLORINE HEPTOXIDE

A 25 ml flask containing 2.0 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mol) with a magnetic stirrer was fitted with a stopcock adapter to a Luer joint. Air was removed and 13 ml (0.6 mol) of propene was added with a syringe fitted with a stopcock (Hamilton Co.). The mixture was stirred for 24 hrs. Nmr analysis using chlorobenzene as quantitative internal standard showed a 32% yield of isopropyl perchlorate and a 17% yield of 1-chloro-2-propyl perchlorate. No major impurity was indicated by nmr or glpc analysis. The structure assignments were confirmed by nmr and glpc by adding independently synthesized samples.

An analytical sample of 1-chloro-2-propyl perchlorate was isolated by glpc (5 ft x 1/4 in column of 12% QF-1 on Chromosorb W, 60°); nmr (CCl_4) δ 1.62 (d, 3 H, J = 6 Hz, CH_3), 3.67 (d, 2 H, J = 7 Hz, CH_2) and 5.17 ppm (m, 1 H, CH); ir (CCl_4) 1005, 1230 and 1265 cm^{-1}.

<u>Anal.</u> Calcd for $C_3H_6Cl_2O_4$: C, 20.35; H, 3.41. Found: C, 19.86; H, 2.94.

A similar experiment with 0.5 g of lithium perchlorate added to the reactants gave a 17% yield of 1-chloro-2-propyl perchlorate and a 25% yield of isopropyl perchlorate.

1-CHLORO-2-PROPYL PERCHLORATE

A 2:1 mixture of 1-chloro-2-propanol and 2-chloro-1-propanol was prepared by the reported method.[2] A pure sample of 1-chloro-2-propanol, the major component, was isolated by glpc (8 ft x 3/8 in column of 12% QF-1 on Chromosorb W, 70°).

A mixture of 0.012 ml of 1-chloro-2-propanol and 1 ml of carbon tetrachloride solution of dichlorine heptoxide (0.3 mmol) was stirred for 16 hrs at ambient temperature. The solution was washed with water and dried over sodium sulfate. Comparison by nmr, ir and glpc showed that the product was identical with that of 1-chloro-2-propyl perchlorate from the propylene-dichlorine heptoxide reaction.

REACTION OF CIS-2-BUTENE WITH DICHLORINE HEPTOXIDE

To a 25 ml flask containing 2.0 ml of a carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) was added 13 ml (0.6 mmol) of cis-2-butene. After 4 hrs, nmr analysis (chlorobenzene as quantitative standard) showed a 26-30% yield of 3-chloro-2-butyl perchlorate and a 2% yield of 3-keto-2-butyl perchlorate. Three other singlets were observed in the δ 2.2 - 2.5 region representing a yield of about 15%. No 2-butene was observed. Extending the reaction period to 24 hrs resulted in no change. A 4 hr reaction to which 0.5 g of lithium perchlorate had been added gave the same yield of 3-chloro-

2-butyl perchlorate but the yield of 3-keto-2-butyl perchlorate was increased to 20%.

A larger scale reaction was carried out for isolation and characterization of the products. A 250 ml flask containing 100 ml of a carbon tetrachloride solution of dichlorine heptoxide (30 mmol) and 10 g of lithium perchlorate was cooled to 0° and evacuated to 50 mm, and 672 ml (30 mmol) of cis-2-butene was added with stirring. After 2 hrs, the solution was washed with water, dried over sodium sulfate, and passed through a 2 x 32 cm column of silica gel. The product was eluted with carbon tetrachloride and the eluent was monitored by nmr. The 3-chloro-2-butyl perchlorate was contained in the first 100 ml of eluent. The next 50 ml of eluent contained no product, and the following 250 ml of eluent contained 3-keto-2-butyl perchlorate

Most of the solvent was removed from half of the combined first 100 ml of eluent by vacuum distillation with a Holzmann column. The remaining solvent was removed by vacuum transfer at 5 mm. 3-Chloro-2-butyl perchlorate was collected in 0.03 ml fractions by vacuum transfer to a -78° receiver at 3 to 0.1 mm. One of these samples exploded when it was removed from the apparatus. The residue, approximately 0.05 ml, gave ir and nmr spectra identical with that of 2,3-butanediperchlorate prepared from 2-butene oxide.

3-Chloro-2-butyl perchlorate was characterized by nmr, ir and mass spectra, and by glpc comparison with an independently synthesized sample (see below): nmr (CCl_4) δ 1.55 (d, J = 6 Hz, $CHCl\text{-}\underline{CH}_3$), 1.58 (d, J = 6 Hz, $CHClO_4\underline{CH}_3$) 6 H combined for δ 1.55 and 1.58 peaks, 4.25 (m, 1H, CHCl) and 5.05 (m, 1 H, $CHClO_4$); ir (CCl_4) 1230 and 1265 cm^{-1}. The mass spectrum gave peaks at 127 ($CH_3CHClO_4^{\oplus}$),

175 ($CH_3CHClCHClO_4^{\oplus}$) and the corresponding Cl^{37} peaks, 129, 131, 177 and 179. An analytical sample of 3-keto-2-butyl perchlorate was obtained by gas chromatography after the solution from column chromatography was concentrated to 30 ml by distillation through a Holzmann column; glpc, 5 ft x 1/4 in column of 12% QF-1 on Chromosorb W, 100 cc/min helium, 90°, 10 min retention time; nmr (CCl_4) δ 1.61 (d, 3 H, J = 7 Hz, $\underline{CH_3}CH$), 2.30 (s, 3 H, CH_3CO) and 5.12 ppm (q, 1 H, J = 7 Hz, $\underline{CH}CH_3$); ir (CCl_4) 1720 (C=O), 1020, 1240 and 1270 cm^{-1} (ClO_4). Anal. Calcd for $C_4H_7ClO_5$: C, 28.17; H, 4.13. Found: C, 28.32; H, 4.10.

3-CHLORO-2-BUTYL PERCHLORATE

3-Chloro-2-butanol[9] was prepared as a mixture of diastereomers by the addition of hydrochloric acid to 2-butene oxide (cis-trans mixture). To 2 ml of a carbon tetrachloride solution of dichlorine heptoxide (0.6 mol) was added 0.050 ml of this 3-chloro-2-butanol and the solution was kept at room temperature for 24 hrs. The carbon tetrachloride solution was washed with 1 ml of water and dried over sodium sulfate. The nmr spectrum differed from that of the product obtained from cis-2-butene in that two sets of methyl peaks were present, differing by approximately 1 Hz. Glpc (70°, 5 ft x 1/4 in column of 12% QF-1 on Chromosorb W, 100 cc/min helium) showed two partially overlapping peaks at 15 min and 16 min retention times. Glpc of a mixture of this material with the product from cis-2-butene resulted in increase of the 15 min peak. Similarly, glpc of a mixture with the corresponding material from trans-2-butene (see below) resulted in increase of the 16 min peak.

REACTION OF TRANS-2-BUTENE WITH DICHLORINE HEPTOXIDE

To 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) and 0.2 g of lithium perchlorate was added 13 ml (0.6 mmol) of trans-2-butene. After 2 hrs of stirring, the solution was washed with 1 ml of water and dried over sodium sulfate. The nmr spectrum showed a mixture similar to that obtained from cis-2-butene. The solution was filtered through silica gel to remove 3-keto-2-butyl perchlorate. This solution was used for glpc comparison with the preceding product.

CONFIGURATION ASSIGNMENT OF 3-CHLORO-2-BUTYL PERCHLORATES

Preparative gas chromatography of commercial 2-butene oxide, a mixture of cis and trans isomers (3/8" x 12 ft column of 12% QF-1 on Chromosorb W, 100 cc/min helium, 24°) gave pure trans-2-butene oxide, retention time 20 min, n_D^{20} 1.3741 (reported value[10] n_D^{20} 1.3736) and cis-2-butene oxide, retention time 26 min, n_D^{20} 1.3821 (reported value[10] n_D^{20} 1.3826). To 15 µl of trans-2-butene oxide and to 30 µl of cis-2-butene oxide, each in a gc collection tube, was added 150 µl of concentrated hydrochloric acid at 0° and the mixtures were kept at ambient temperature 1 hr. Each product was extracted with 100 µl of methylene chloride after 150 µl of water was added. The organic layers were separated and solvent was removed at 30 mm. The crude chlorohydrins, 8 µl from trans-2-butene oxide and 20 µl from cis-2-butene oxide, were each added to 1 ml of carbon tetrachloride solution of dichlorine heptoxide (0.3 mmol). After 24 hrs, each reaction mixture was washed with 0.5 ml of water and dried over sodium sulfate. Mixed glpc comparison of these solution with the 3-chloro-2-butyl perchlorates from cis- and trans-2-butene showed that the product from cis-2-butene oxide

was identical with that from cis-2-butene (15 min retention time, 5 ft x 1/4 in column of 12% QF-1 on Chromosorb W, 70°, 100 cc helium/min) and that the product from trans-2-butene was identical with that from trans-2-butene (16 min retention time).

REACTION OF 1-HEXENE WITH DICHLORINE HEPTOXIDE

1-Hexene (2.52 g, 0.03 mol) was added to 100 ml of carbon tetrachloride solution of dichlorine heptoxide (0.03 mol) and the reaction mixture was stirred for 18 hrs at room temperature. The mixture was washed with water, dried and filtered. The solution was chromatographed using carbon tetrachloride and silica gel as described for the 2-butene reaction. The nmr spectra of the early fractions were consistent with a 3:1 mixture of 1-chloro-2-hexyl perchlorate and 2-chloro-1-hexyl perchlorate (compared to independently synthesized samples). No change in spectra was observed after vacuum transfer at 0.01 mm or preparative glpc (5 ft x 1/4" aluminum column packed with 12% QF-1 on 60/80 mesh Chromosorb W, 105°). Mass spectra gave peaks at 118 and 120 ($C_6H_{11}Cl^{\oplus}$) and 169 and 171 ($C_5H_{10}ClO_4^{\oplus}$).

Further elution of the silica gel with methylene chloride-carbon tetrachloride (1:1) gave a ketone fraction. Methylene chloride was removed by distillation through a short column to give a solution suitable for spectral analysis. The nmr spectrum indicated a complex mixture. Notable features were singlets at δ 3.90 and 2.30, a multiplet at 5.01 and a triplet at 2.57. Strong bands in the infrared spectrum at 1710-1720, 1260, 1240, and 1110 cm^{-1} suggested ketone and perchlorate or perchloryl functional groups.

Glpc analysis (above column, 95°) revealed the presence of three major as well as several minor components. The three major components were collected (area ratio 2:2:1). The first of these was identified as 1-chloro-2-hexanone by spectral and glpc comparison with an authentic sample. The second component, in the order of increasing retention times, appeared to be a ketoperchlorate: nmr (CCl_4) δ 5.01 (m), 2.30 (s), 1.46 (m), 0.90 ppm (m); ir (CCl_4) 1715 (C=O), and 1260, 1240, 1130 cm^{-1} ($OClO_3$).

Accurate integral values could not be obtained because of the small sample size available. The singlet at 2.30 ppm suggested an acetyl group. A possible structure would be 2-keto-3-hexyl perchlorate which could arise by isomerization of 1-hexene to 2-hexene and reaction with Cl_2O_7. The third component was obtained only in very small amounts. The ir spectrum suggested a ketone perchlorate: ir (CCl_4) 1715 (C=O), 1260, 1240, and 1120 cm^{-1} ($OClO_3$).

A doublet was observed at 1.50 ppm in the original reaction mixture (8-10%) and may be due to 2-hexyl perchlorate which apparently does not survive the chromatographic conditions.

Using chlorobenzene as internal standard 85% of the total 1-hexene used could be accounted for. The yield of the isomeric chloroperchlorates was 29%. Nmr integration of a fraction purified by column chromatography indicated a mixture of 1-chloro-2-hexyl perchlorate and 2-chloro-1-hexyl perchlorate in the ratio 3:1. The yields of the two major ketone products were about 4% each.

1-CHLORO-2-HEXANOL AND 2-CHLORO-1-HEXANOL

To a solution of 0.5 g (.005 mol) of 1-hexene oxide in 10 ml of methylene

chloride was added 10 ml of concentrated hydrochloric acid at 0° with stirring. The reaction mixture was stirred for an additional 30 min and the methylene chloride solution was washed with water and dried over sodium sulfate. Evaporation of solvent and vacuum transfer of the residue at 0.001 mm gave 0.476 g (70%) of a mixture of 1,2-hexene chlorohydrins. The individual isomers were collected by glpc (12 ft x 3/8 in aluminum column packed with 12% QF-1 on 60/80 mesh Chromosorb W at 105°) and the first compound eluted was identified as 1-chloro-2-hexanol: nmr (CCl_4) δ 3.63 (m, 2 H, CH_2Cl), 3.50 (m, 1 H, $\underline{CH}$-O), 2.27 (s, 1 H, OH, exchangeable with D_2O), 1.42 (m, 6 H, $-CH_2-$), and 0.90 ppm (m, 3 H, CH_3).

Anal. Calcd for $C_6H_{13}ClO$: C, 52.75; H, 9.66. Found: C, 52.74; H, 9.60.

The second glpc component was 2-chloro-1-hexanol: nmr (CCl_4) δ 3.90 (m, 2 H, $-CH_2O$), 3.63 (m, 1 H, =CHCl), 1.97 (s, 1 H, OH, exchangeable with D_2O), 1.20 (m, 6 H, CH_2), and 0.95 ppm (m, 3 H, CH_3).

Anal. Calcd for $C_6H_{13}ClO$: C, 52.75; H, 9.66. Found: C, 52.65; H, 9.72.

The ratio of isomers was 1.5:1.

1-CHLORO-2-HEXANONE

A stock solution of Jones reagent was prepared from 5 g of CrO_3, 10 ml of water, and 8 g of concentrated sulfuric acid. Jones reagent was added dropwise over a 15 min period of 0.25 g (0.00183 mol) of 1-chloro-2-hexanol, dissolved in 10 ml of acetone, until the orange color persisted. Excess reagent was destroyed by dropwise addition of isopropanol after 2 hrs. The solution was filtered, diluted with 50 ml of water, and extracted with three

10 ml portion of methylene chloride. Evaporation of the methylene chloride gave 0.212 g (85%) of crude chloroketone. An analytical sample was obtained by glpc (12 ft x 3/8 in, 12% QF-1 on Chromosorb W, 110°): nmr (CCl_4) δ 3.95 (s, 2 H, $\overset{O}{\overset{\|}{C}}$-$CH_2Cl$), 2.58 (t, 2 H, J = 6 Hz, $\underline{CH_2}$-$\overset{O}{\overset{\|}{C}}$-$CH_2Cl$), 1.48 (m, 4 H, CH_2), and 0.95 ppm (m, 3 H, CH_3); ir (CCl_4) 1720 cm^{-1} (C=O).

<u>Anal</u>. Calcd for $C_6H_{11}ClO$: C, 53.54; H, 8.24; Cl, 26.34. Found: C, 53.70; H, 8.52; Cl, 26.54.

2-CHLORO-1-HEXYL PERCHLORATE

2-Chloro-1-hexanol (0.082 g, 0.6 mmol) was added to 2 ml of dichlorine heptoxide-carbon tetrachloride solution (0.6 mmol). The mixture was stirred for 18 hrs at room temperature and then was washed with water, dried over sodium sulfate and filtered through silica gel to remove a slight yellow coloration. The resulting colorless solution contained 2-chloro-1-hexyl perchlorate in high purity: nmr (CCl_4) δ 4.57 (m, 2 H, CH_2OClO_3), 4.10 (m, 1 H, =CH-Cl), 1.55 (broad m, CH_2), and 0.98 ppm (m, 3 H, CH_3); ir (CCl_4) 1265, 1245, 1025 cm^{-1} ($OClO_3$).

REACTION OF A MIXTURE OF 1-CHLORO-2-HEXANOL AND 2-CHLORO-1-HEXANOL WITH DICHLORINE HEPTOXIDE

A mixture of chlorohydrins obtained from 1-hexene oxide, .082 g (0.6 mmol) was added to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) and the reaction mixture was stirred for 18 hrs at room temperature. The solution was washed with water, dried over sodium sulfate, and filtered through silica gel to give an equal mixture of the chloroperchlorates:

nmr (CCl_4) δ 4.93 (m, $-\underset{OClO_3}{\underset{|}{CH}}-CH_2Cl$), 4.70 (m, , $\underset{Cl}{\underset{|}{CH}}-CH_2OClO_3$), 4.07 (m, $\underset{Cl}{\underset{|}{CH}}-CH_2OClO_3$), 3.73 (d, J = 5 Hz, $\underset{OClO_3}{\underset{|}{CH}}-CH_2Cl$), 2.1-1.1 (broad m, $-CH_2-$), and 0.97 ppm (m).

The ratio of the downfield peaks was as expected for a 1:1 mixture of chloroperchlorates. The individual bands for 2-chloro-1-hexyl perchlorate were superimposable with peaks at 4.70 and 4.07 ppm and peaks for crude 1-chloro-2-hexyl perchlorate matched those at 4.93 and 3.73 ppm.

The use of pure 1-chloro-2-hexanol in this procedure gave a 1.4:1 mixture of 1-chloro-2-hexanone and 1-chloro-2-hexyl perchlorate. This experiment was repeated three times using different ratios of Cl_2O_7. The oxidation product, 1-chloro-2-hexanone was always the major product.

GENERAL PROCEDURE FOR REACTIONS OF ALCOHOLS WITH DICHLORINE HEPTOXIDE

The alcohol (0.6 mmol) was added by syringe to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) at 0° with stirring. The mixture was stirred 18 hrs at room temperature and then was washed with water and dried over magnesium sulfate. The solution was examined by ir and nmr spectroscopy, and yields were determined by nmr using chlorobenzene as a quantitative internal standard. The ir spectra, unless other data is given, showed characteristic perchlorate bands at 1260, 1240 and 1040 cm^{-1}.

ETHYL PERCHLORATE

The yield was 56%; nmr (CCl_4) δ 4.57 (q, 2 H, J = 6.5 Hz, CH_2) and 1.53 ppm (t, 3 H, J = 6.5 Hz, CH_3).

HEXYL PERCHLORATE

The yield was 58% and the ir spectrum was identical with the published spectrum;[11] nmr (CCl_4) δ 4.67 (t, 2 H, J = 6 Hz, $-CH_2OClO_3$), 1.83 (m, 2 H, $\underline{CH_2}CH_2OClO_3$), 1.52 (broad m, 6 H, $-CH_2-$) and 0.93 ppm (m, 3 H, CH_2).

PENTYL PERCHLORATE

The yield was 63%; nmr (CCl_4) δ 4.52 (t, 2 H, J = 6 Hz, CH_2-OClO_3), 1.82 (m, 2 H, $\underline{CH_2}CH_2OClO_3$), 1.45 (m, 4 H, $-CH_2CH_2-$) and 0.95 ppm (m, 3 H, CH_3).

ISOPROPYL PERCHLORATE

The yield of isopropyl perchlorate was 48%, and an oil insoluble in carbon tetrachloride was also formed, which gave acetone on addition of water. Nmr (CCl_4) δ 5.10 (septet, 1 H, J = 6 Hz, $CH-OClO_3$) and 1.58 ppm (d, 6 H, J = 6 Hz, CH_3).

2-HEXYL PERCHLORATE

2-Hexanol (0.061 g, 0.6 mmol) was added to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) and the mixture was stirred for 3 hrs at ambient temperature. The solution became greenish-yellow and some oil separated. The mixture was stirred with 1 ml of water and the carbon tetrachloride layer was separated and dried. Nmr analysis showed a 62% yield of 2-hexyl perchlorate and an 8.5% yield of 2-hexanone. The presence of 2-hexanone was confirmed by ir and glpc comparison with an authentic sample. No 3-hexyl perchlorate was detected; nmr of 2-hexyl perchlorate (CCl_4) δ 4.85 (m, 1 H, $CH-OClO_3$), 1.57 (broad m, 6 H, $-CH_2-$), 1.48 (d, 3 H, J = 6 Hz, $CH_3-CH-OClO_3$)

and 0.93 ppm (m, 3 H, CH_3).

3-HEXYL PERCHLORATE

The above procedure using 3-hexanol gave a 53% yield of 3-hexyl perchlorate and a 9.4% yield of 3-hexanone. No 2-hexyl perchlorate was detected. Nmr of 3-hexyl perchlorate (CCl_4) δ 4.85 (m, 1 H, $CHOClO_3$), 1.57 (broad m, $-CH_2-$) and 1.03 ppm (m, 6 H, CH_3).

2,2,2-TRIFLUOROETHYL PERCHLORATE

2,2,2-Trifluoroethanol (0.150 g, 1.5 mmol) was added to 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) and the mixture was stirred for 48 hrs. The solution was washed with water and dried. Analysis by nmr showed a 55% yield of 2,2,2-trifluoroethyl perchlorate; proton nmr (CCl_4) δ 4.80 (q, J_{HF} = 8 Hz); fluorine nmr (CCl_4) ϕ 91.0 ppm (t, J_{HF} = 8 Hz).

2-(2-FLUORO-2,2-DINITROETHOXY)ETHYL PERCHLORATE

2-(2-Fluoro-2,2-dinitroethoxy)ethanol (0.118 g, 0.6 mmol) was added to 2.5 ml of carbon tetrachloride solution of dichlorine heptoxide (0.75 mmol) and the mixture was stirred for 18 hrs. The carbon tetrachloride solution was washed with water and dried over magnesium sulfate. Nmr analysis showed a 43% yield of 2-(2-fluoro-2,2-dinitroethoxy)ethyl perchlorate; nmr (CCl_4) δ 4.57 (A_2B_2 pattern, 2 H, CH_2-$OClO_3$), 4.00 (m, 2 H, O-$\underline{CH_2}CH_2$) and 4.58 ppm (d, 2 H, J_{HF} = 17 Hz, $FCCH_2$).

1,2-ETHANEDIPERCHLORATE

Ethylene glycol (0.186 g, 3 mmol) was added to 20 ml of carbon tetrachloride solution of dichlorine heptoxide (6 mmol) and 20 ml of methylene chloride, and the mixture was stirred 18 hrs at ambient temperature. The solution was washed with water, dried, and concentrated to 2 ml. The product was isolated by preparative glpc (5 ft x 1/4 in column of 12% QF-1 on 60/80 Chromosorb W, 120°). The yield determined by nmr in a separate experiment at 1/10 of this scale (methylene chloride omitted) was 60%; nmr ($CDCl_3$) δ 4.83 ppm (s).

1,4-BUTANEDIPERCHLORATE

1,4-Butanediol (0.054 g, 0.6 mmol) was added to 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) and the mixture was stirred for 18 hrs, washed with water and dried. The product (38% yield) was identical with that obtained from tetrahydrofuran.

ALLYL PERCHLORATE

Allyl alcohol (0.035 g, 0.6 mmol) was added to 2.5 ml of carbon tetrachloride solution of dichlorine heptoxide (0.75 mmol) and 0.2 g of sodium sulfate at 0° with stirring. After 30 min, the solution was washed with ice water, and dried over sodium sulfate. Nmr analysis showed only allyl perchlorate (48% yield); nmr (CCl_4) δ 3.90 (ABC multiplet, 3 H, CH_2=CH-) and 4.93 ppm (m, 2 H, =C-CH_2-$OClO_3$); ir (CCl_4) 1620 (C=C), 1260, 1240 and 1030 cm^{-1} (-$OClO_3$).

PROPARGYL PERCHLORATE

Propargyl alcohol (0.084 g, 1.5 mmol) was reacted with 5 ml of carbon tetra-

chloride solution of dichlorine heptoxide (1.5 mmol) and 0.5 g of sodium sulfate by the above procedure to give a 43% yield of propargyl perchlorate: nmr (CCl_4) δ 5.10 (d, 2 H, J = 2 Hz, $\equiv C-CH_2OClO_3$) and 2.72 ppm (t, 1 H, J = 2 Hz, HC≡C; ir (CCl_4) 3320, 2160 (HC≡C) and 1280, 1245 and 1045 cm^{-1} ($OClO_3$).

1,4-BUTANEDIPERCHLORATE

Tetrahydrofuran (0.043 g, 0.6 mmol) was added with magnetic stirring to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol at 0°. An exothermic reaction took place, and after 15 min, the solution was washed with water and dried over sodium sulfate. Nmr showed only 1,4-butanediperchlorate (63% yield using chlorobenzene as a quantative standard: nmr (CCl_4) δ 4.60 (m, 4 H, $-CH_2-OClO_3$) and 3.70 ppm (m, 4 H, $-CH_2CH_2-$); ir (CCl_4) 1260, 1240 and 1030 cm^{-1} ($OClO_3$).

1,3-PROPANEDIPERCHLORATE

A solution of 0.087 g (1.5 mmol) of trimethylene oxide in 2 ml of carbon tetrachloride was added dropwise with stirring to 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) at 0°. After 30 min, the solution was washed with water, dried over sodium sulfate and filtered through silica gel to remove some polymeric material. Nmr showed that the solution contained only 1,3-propanediperchlorate (55% yield using chlorobenzene as quantitative standard); nmr (CCl_4) δ 4.63 (t, 4 H, J = 6 Hz, $-CH_2OClO_3$) and 2.28 ppm (quintet, 2 H, J = 6 Hz, $CH_2CH_2CH_2$); ir (CCl_4) 1230, 1270, 1290, 1010, and 1030 cm^{-}($-OClO_3$).

REACTION OF DIISOPROPYL ETHER WITH DICHLORINE HEPTOXIDE

Diisopropyl ether (0.061 g, 0.6 mmol) was added to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) at room temperature with stirring. After 5 min the solution became greenish-yellow, and after 10-15 min a colorless oil separated. The nmr spectrum of the oil in $CDCl_3$ consisted of a sharp singlet at δ 2.69, attributable to $(CH_3)_2C(OClO_3)_2$.[6] Addition of water and 2,4-dinitrophenylhydrazine reagent gave acetone 2,4-dinitrophenylhydrazone, identical with an authentic sample. The nmr spectrum of the carbon tetrachloride solution showed no starting material.

A similar experiment with the reaction time extended to 48 hrs gave a 20% yield of isopropyl perchlorate in the carbon tetrachloride layer.

N-PERCHLORYLDIETHYLAMINE

Diethylamine (0.22 g, 3 mmol) was added to 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) with stirring at 0°. After 15 min of stirring at 0-5°, 5 ml of 1N HCl was added, and the organic layer was washed with water and dried. The yield of N-perchloryldiethylamine (nmr) in solution was 77%; nmr (CCl_4) δ 3.47 (m, 4 H, $(CH_2)_2N$) and 1.37 ppm (t, 6 H, J = 6 Hz, CH_3); ir (CCl_4) 1255, 1200 and 1000 cm^{-1} (N-ClO_3).

N-PERCHLORYL-t-BUTYLAMINE

A solution of 0.224 g (.003 mol) of t-butylamine in 1 ml of carbon tetrachloride was added dropwise with stirring at -20° (dry ice- CCl_4 slush bath) to 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) over a period

of 15 min. The reaction mixture was then stirred with 10 ml of 1N HCl. The organic layer was dried over molecular sieves and filtered. Evaporation of solvent from an aliquot left a colorless oil which was vacuum transferred at 0.02 mm to give an analytical sample: nmr (CCl_4) δ 7.10 (broad, 1 H, $\underline{N}HClO_3$; disappears on shaking with D_2O), and 1.32 ppm (s, 9 H, $(CH_3)_3C$-); ir (CCl_4) 3280 (N-H), 1245, 1190, and 1005 cm^{-1} (N-ClO_3). The yield (nmr) was 71%.

Anal. Calcd for $C_4H_{10}NClO_3$: C, 30.86; H, 6.46; N, 9.64; Cl, 22.87. Found: C, 29.62; H, 6.47; N, 8.22; Cl, 22.62.

Potentiometric titration gave an equivalent weight of 151 ± 4 (calcd 155) and a pK_a of 6.82 ± .03.

N-PERCHLORYLHEXYLAMINE

The reaction of 0.303 g (3 mol) of hexylamine with dichlorine heptoxide by the above procedure gave a 63% yield of N-perchlorylhexylamine: nmr (CCl_4) δ 6.73 (m, 1 H, $NHClO_3$: removed by shaking with D_2O), 3.42 (m, 2 H, CH_2NHClO_3), 1.40 (m, 8 H, -CH_2-), and 0.93 ppm (m, 3 H, -CH_3); ir (CCl_4) 3290 ($\underline{N}H$-ClO_3), 1210, 1020 (N-ClO_3).

CHLORINATION OF N-PERCHLORYLHEXYLAMINE

A carbon tetrachloride solution of N-perchlorylhexylamine (1.5 mmol) was shaken for 5 min with 5 ml of 5% aqueous sodium hypochlorite, and the organic layer was dried. Spectra of the solution were consistent with the N-perchloryl-N-chlorohexylamine structure: nmr (CCl_4) δ 3.70 (t, 2 H, J = 6 Hz, -$CH_2NClClO_3$), 1.40 (broad m, 8 H, -CH_2-), and 0.90 (m, 3 H, CH_3); ir (CCl_4) 1240, 1210, 1010 cm^{-1}.

The nmr and ir spectra showed no evidence of N-H. The material could not be extracted with 1 N sodium hydroxide.

BROMINATION OF N-PERCHLORYL-t-BUTYLAMINE

To an aqueous solution of the sodium salt of N-perchloryl-t-butylamine, described above, was added 0.240 g (1.5 mmol) of bromine, dropwise, with stirring at 0°. The bromine color was discharged over a period of 20 min and the product was extracted with 5 ml of carbon tetrachloride to give a colorless solution. Exothermic decomposition with liberation of bromine took place when the carbon tetrachloride solution was allowed to warm to room temperature. Rapid nmr scan of a cold, freshly prepared solution showed a singlet at approximately δ 1.5.

REACTION OF N-PERCHLORYL-t-BUTYLAMINE WITH SODIUM HYDROXIDE

Carbon tetrachloride solution of N-perchloryl-t-butylamine, prepared as above, was extracted with 4 ml of 1.0 N sodium hydroxide in a separatory funnel. The carbon tetrachloride layer showed no nmr signals. Acidification of the aqueous layer with 4.5 ml of 1.0 N HCl and extraction with 5 ml of CCl_4 gave the starting material with no change in ir and nmr spectra. This technique could be applied to N-perchlorylbutyl amine and N-perchlorylhexyl amine in the same way.

REACTION OF DICHLORINE HEPTOXIDE WITH DIPHENYLMERCURY

To a stirred and cooled solution of 1.77 g (5 mmol) of diphenylmercury in 50 ml of carbon tetrachloride was added dropwise (4-5 min) at 22-24° 17 ml of a solution of dichlorine heptoxide (5.1 mmol) in carbon tetrachloride. A mildly

exothermic reaction took place and in a few minutes the reaction mixture began to deposit a gray solid. The mixture was stirred for 20 min and filtered. The filtrate contained a 4:1 mixture of chlorobenzene and p-benzoquinone, identified by spectral and glpc comparison with authentic samples.

REACTION OF DICHLORINE HEPTOXIDE WITH TETRAPHENYLTIN

The reaction of dichlorine heptoxide with one equivalent of tetraphenyltin following the above procedure also yielded a mixture of chlorobenzene and p-benzoquinone.

REACTION OF HEXYL PERCHLORATE WITH DIMETHYL SULFOXIDE

To a solution of hexyl perchlorate prepared from 0.306 g (3 mmol) of hexanol and 10 ml of carbon tetrachloride solution of dichlorine heptoxide (3 mmol) was added 5 ml of anhydrous dimethyl sulfoxide and 0.5 g (6 mmol) of sodium bicarbonate. An initial exothermic reaction took place and nmr examination of the solution indicated immediate consumption of perchlorate and slow formation of hexaldehyde. After 24 hrs the mixture was washed several times with water, dried, and analyzed by nmr. The only products detected were hexaldehyde (55% yield based on hexyl alcohol) and dimethylsulfide. The dimethyl sulfide could be removed in vacuo to give pure aldehyde.

REACTION OF PERCHLORATES WITH LITHIUM BROMIDE

A solution of butane-1,4-diperchlorate prepared from 0.176 g (2.4 mmol) of tetrahydrofuran and 8 ml of carbon tetrachloride solution of dichlorine heptoxide (2.4 mmol) was added dropwise with stirring at 0° to 8 ml of 10% lithium

bromide in acetone. The mixture was stirred for 45 min at ambient temperature, washed with water, dried and stripped of solvent to give 0.404 g of 1,4-dibromobutane (78% yield based on tetrahydrofuran, 94% based on 1,4-butanediperchlorate). 1,4-Dibromobutane was identified by comparison of nmr and ir spectra and glpc retention time with those of an authentic sample.

The same procedure using pentyl perchlorate, 1,2-ethanediperchlorate and propargyl perchlorate gave 90-100% yields of the corresponding bromides, identified by comparison with authentic samples.

REACTION OF ALLYL PERCHLORATE WITH 2-FLUORO-2,2-DINITROETHANOL

To a solution of allyl perchlorate prepared from 0.087 g (1.5 mmol) of allyl alcohol and 5 ml of carbon tetrachloride solution of dichlorine heptoxide (1.5 mmol) was added 5 ml of methylene chloride, 0.30 g (2 mmol) of 2-fluoro-2,2-dinitroethanol and .69 g (5 mmol) of anhydrous potassium carbonate. The reaction mixture was stirred for 48 hrs. The solution was washed with water and with 5% sodium hydroxide, dried over sodium sulfate, and solvent was removed to give 0.11 g (38% based on allyl alcohol) of 2-fluoro-2,2-dinitroethyl allyl ether, identical with an authentic sample.[12]

REACTION OF ISOPROPYL PERCHLORATE WITH PENTYL ALCOHOL

To a solution of 0.3 mmol of isopropyl perchlorate in 2 ml of carbon tetrachloride was added 0.026 g (0.3 mmol) of pentanol and 0.142 g (1 mmol) of sodium sulfate. The progress of the reaction was monitored by nmr. The perchlorate was 25% converted to isopropyl pentyl ether in 18 hrs, 50% in 72 hrs and 85% in 144 hrs.

REACTION OF PENTYL PERCHLORATE WITH PENTANOL

To a solution of pentyl perchlorate (0.6 mmol) prepared from 0.069 g (0.9 mmol) of pentanol and 3 ml of carbon tetrachloride solution of dichlorine heptoxide (0.9 mmol) (after water washing and drying) was added 0.053 g (0.6 mmol) of pentanol and 0.276 g (2 mmol) of potassium carbonate. The disappearance of perchlorate and formation of ether was monitored by nmr. The perchlorate was 5% converted to dipentyl ether in 20 hrs, 25% converted in 96 hrs, and 90% converted in 192 hrs.

A similar mixture, with 0.6 mmol of pentyl triflate used in place of pentyl perchlorate, was prepared. Nmr indicated that the reaction was 90% completed in 20 hrs and 100% completed in 26 hrs.

BIS(2-FLUORO-2,2-DINITROETHYL)METHYL ORTHOFORMATE

Aluminum chloride (0.5 g) was added to a solution of 5.7 g (.05 mol) of dichloromethyl methyl ether and 15.4 g (0.1 mol) of 2-fluoro-2,3-dinitroethanol in 250 ml of methylene chloride. The reaction mixture was refluxed with stirring for 3 hrs and then was stirred at room temperature for 18 hrs. The reaction mixture was poured onto ice water. The organic layer was washed three times with 5% sodium hydroxide solution, dried, filtered, and stripped of solvent to give 10.5 g (60%) of the product as a pale yellow oil. Chromatography through a short column of silica gel (CH_2Cl_2-CCl_4 as eluent) removed color and traces of impurities to give the analytical sample. Purification could also be accomplished by distillation in a molecular still (105-110° bath temperature, at 0.001 mm). Nmr ($CDCl_3$) δ 5.28 (s, 1 H, CH), 4.62 (d, 2 H,

J_{HF} = 16 Hz, $FC(NO_2)_2$-CH_2-), and 3.38 ppm (s, 3 H, OCH_3); density, 1.542.

<u>Anal</u>. Calcd for $C_6H_8F_2N_4O_{11}$: C, 20.57; H, 2.30; N, 16.00. Found: C, 20.25; H, 1.82; N, 15.86.

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Appendix A

SYNTHESIS OF SOME HIGHLY REACTIVE TRIFLUOROMETHANESULFONATES (TRIFLATES) AND THEIR REACTIONS WITH ALCOHOLS[1]

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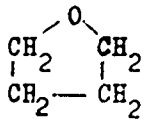
Abstract: Some exceptionally reactive trifluoromethanesulfonate esters were prepared and their reactions with poorly nucleophilic alcohols were studied. Allyl triflate, propargyl triflate, pentyl triflate, 2-(2-fluoro-2,2-dinitroethoxy)ethyl triflate, and 1,2,3-propane tritriflate were prepared from the alcohols using triflic anhydride and pyridine. 1,4-Butane ditriflate was formed from tetrahydrofuran and triflic anhydride. These triflates in chlorinated hydrocarbon solvents reacted with 2-fluoro-2,2-dinitroethanol or 2,2,2-trifluoroethanol in the presence of potassium carbonate to give the ethers without skeletal rearrangement. 1,2,3-Propane tritriflate underwent monosubstitution and elimination to yield 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate. When sodium sulfate was used instead of potassium carbonate to scavenge triflic acid, pentyl triflate and 2,2-dinitropropanol gave a mixture of the 1-, 2- and 3-pentyl ethers. Isopropyl and allyl triflates gave the corresponding ethers of β-dinitroalcohols and of 2,2,2-trinitroethanol, as well as of pentanol; these ether syntheses were carried out at ambient temperature, in inert solvents, under neutral conditions.

The high reactivity of the trifluoromethanesulfonate (triflate) group in solvolysis and displacement reactions has been the subject of a number of recent investigations. Thus, methyl and ethyl triflates were reported to undergo solvolysis more than 10^4 times as fast as the corresponding tosylates[2,3]. The use of the triflate leaving group in otherwise unreactive polycyclic systems has extended the range of solvolysis reactions[4-6], and vinyl triflates have been used extensively in studies of vinyl cations[7-10]. No attempts have been reported, however, to prepare a triflate ester more reactive than the ethyl derivative. Such extremely reactive alkylating agents would be expected to extend the range of weakly nucleophilic reagents that can be alkylated. In the present investigation, triflates with a wide range of reactivities were prepared and their synthetic utility was examined in reactions with electronegatively substituted alcohols.

The triflates prepared in this work are shown in Table I. Most of these compounds were synthesized from the corresponding alcohols by the commonly used[4] triflic anhydride-pyridine method. Methylene chloride or carbon tetrachloride were used as solvents. Methyl triflate, because of its low boiling point, was prepared conveniently, from dimethyl sulfate and a procedure previously used for the corresponding fluorosulfonate[11]. The reaction of tetrahydrofuran with triflic anhydride gave 1,4-butane ditriflate, a reaction similar to ring openings with mixed sulfonic-carboxylic anhydrides[12]. This ditriflate and 1,2,3-propane triflate, prepared from glycerol, are the first reported polyfunctional examples.

TABLE I. PREPARATION OF TRIFLATES

Starting Material	Product	Yield(%)
$\underline{n}$-$C_5H_{11}OH$	$\underline{n}$-$C_5H_{11}OSO_2CF_3$	85
$(CH_3)_2CHOH$	$(CH_3)_2CHOSO_2CF_3$	82
$CH_2{=}CHCH_2OH$	$CH_2{=}CHCH_2OSO_2CF_3$	75
$HC{\equiv}CCH_2OH$	$HC{\equiv}CCH_2OSO_2CF_3$	80
$FC(NO_2)_2CH_2OH$	$FC(NO_2)_2CH_2OSO_2CF_3$	42
$FC(NO_2)_2CH_2OCH_2CH_2OH$	$FC(NO_2)_2CH_2OCH_2CH_2OSO_2CF_3$	87
	$CF_3SO_2O(CH_2)_4OSO_2CF_3$	73
$CH_2(OH)CH(OH)CH_2OH$	$CH_2(OSO_2CF_3)CH(OSO_2CF_3)CH_2OSO_2CF_3$	98
$(CH_3)_2SO_4$	$CH_3OSO_2CF_3$	81

Allyl triflate, propargyl triflate, and isopropyl triflate were not sufficiently stable for elemental analysis and were characterized by spectral data, described in the Experimental Section. Even pentyl triflate gave only partially acceptable analytical data, and these compounds were generally used as freshly prepared solutions for alkylations. Allyl triflate in carbon tetrachloride solution was completely decomposed in 3 days at ambient temperature. Electron-withdrawing substituents, such as nitro groups or additional triflate groups in the molecule improved stability; neat 2-fluoro-2,2-dinitroethyl triflate was unchanged after several months at room temperature.

The reactivity of triflates with alcohols of low nucleophilicity was examined using 2,2,2-trinitroethanol, 2,2-dinitro-1,3-propanediol, 2,2-dinitropropanol and 2-fluoro-2,2-dinitroethanol. With the exception of low yields of methyl ethers of 2,2-dinitropropanol and 2,2-dinitropropanediol prepared by heating the alcohols with dimethyl sulfate[13], these alcohols have not been alkylated under neutral or acidic conditions. In the presence of base, nitronate salts are formed by loss of formaldehyde[14]. With aqueous base, 2-fluoro-2,2-dinitroethanol is the only one of the above alcohols with a sufficient equilibrium concentration of alkoxide ion to react with alkyl sulfates, allyl halides or epoxides[13].

Reactions of nitroalcohols with triflates were generally conducted in chlorinated hydrocarbon solvents. To avoid side reactions due to liberated triflic acid, anhydrous potassium carbonate or sodium sulfate was added as a heterogeneous acid scavenger. 2,2,2-Trinitroethanol, 2,2-dinitropropanol and 2,2-dinitropropanediol could not be alkylated in

the presence of potassium carbonate because deformylation took place.

In the presence of potassium carbonate, 2-fluoro-2,2-dinitroethanol reacted at ambient temperature with pentyl triflate, allyl triflate, propargyl triflate, 1,4-butane ditriflate and with 2-(2-fluoro-2,2-dinitroethoxy)ethyl triflate to give the corresponding 2-fluoro-2,2-dinitroethyl ethers in yields of 43 to 75%.

$$ROSO_2CF_3 + FC(NO_2)_2CH_2OH \xrightarrow{K_2CO_3} ROCH_2CF(NO_2)_2$$

$$R = C_5H_{11}-;\ CH_2{=}CHCH_2-;\ HC{\equiv}CCH_2-;\ -CH_2CH_2CH_2CH_2-;\ FC(NO_2)_2CH_2OCH_2CH_2-$$

Application of the same reaction conditions to 2,2,2-trifluoroethanol and pentyl triflate gave an 86% yield of pentyl 2,2,2-trifluoroethyl ether.

$$CH_3(CH_2)_4OSO_2CF_3 + CF_3CH_2OH \xrightarrow{K_2CO_3} CH_3(CH_2)_4OCH_2CF_3$$

The reaction of 2-fluoro-2,2-dinitroethanol with 1,2,3-propane tritriflate in the presence of potassium carbonate resulted in displacement of a terminal triflate group followed by rapid elimination of triflic acid to give 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate. No other products were observed when the reaction was not carried tc completion. Under the same experimental conditions, 1,2,3-propane tritriflate was stable and did not undergo elimination. When sodium sulfate was used in place of

potassium carbonate no reaction took place.

$$CF_3SO_3CH_2CH(CF_3SO_3)CH_2(CF_3SO_3) \xrightarrow[\substack{K_2CO_3 \\ CHCl_3}]{FC(NO_2)_2CH_2OH}$$

$$[FC(NO_2)_2CH_2OCH_2CH(CF_3SO_3)CH_2(CF_3SO_3)] \xrightarrow{-CF_3SO_3H}$$

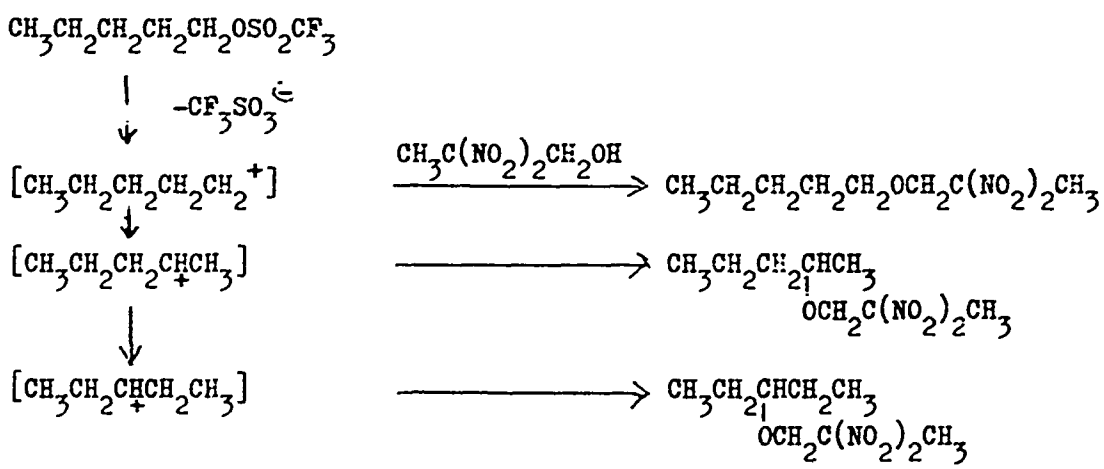
$$FC(NO_2)_2CH_2OCH_2\text{-}\underset{\substack{| \\ OSO_2CF_3}}{CH}{=}CH_2$$

The reaction of 2-fluoro-2,2-dinitroethyl triflate with 2-fluoro-2,2-dinitroethanol in the presence of potassium carbonate was also attempted. No fluorodinitroethyl ether was formed and the triflate was decomposed. This reaction appears similar to that of 2-fluoro-2,2-dinitroethyl tosylate with alkoxides, which was reported to result in elimination of nitrous acid[15].

Under the same experimental conditions that produced a 75% yield of 2-fluoro-2,2-dinitroethyl pentyl ether from 2-fluoro-2,2-dinitroethanol and and pentyl triflate, no product was observed when sodium sulfate was substituted for potassium carbonate. Potassium carbonate functioned not only as a scavenger for triflic acid, but also as a heterogeneous base catalyst, and reactions using sodium sulfate required more forcing conditions.

Pentyl triflate and 2,2-dinitropropanol reacted in refluxing 1,2-dichloroethane, with sodium sulfate as the acid scavenger, to give a 38% yield of 2,2-dinitropropyl pentyl ethers. This product consisted of 33.5% 1-pentyl ether, 58.8% 2-pentyl ether and 7.6% 3-pentyl ether.

The potassium carbonate catalyzed reactions of 2-fluoro-2,2-dinitroethanol and pentyl triflate, on the other hand, gave no detectable secondary ethers. The reaction in the presence of sodium sulfate thus has the characteristics of a carbonium ion reaction, even with a relatively non-polar solvent.



At ambient temperature isopropyl triflate in the presence of sodium sulfate reacted with 2-fluoro-2,2-dinitroethanol, 2,2-dinitro-propanol and 2,2,2-trinitroethanol to give the corresponding isopropyl ethers in yields of 75, 67, and 37%, respectively. Methylene chloride or chloroform was used as solvent, and the reactions were allowed to proceed for 12 hrs.

$$(CH_3)_2CHOSO_2CF_3 \quad + \quad XC(NO_2)_2CH_2OH \longrightarrow (CH_3)_2CHOCH_2C(NO_2)_2X$$

$$X = F,\ CH_3,\ NO_2.$$

Pentanol was also reacted with isopropyl triflate under the same conditions to give a 52% yield of isopropyl pentyl ether in 1 hr.

Allyl triflate was reacted similarly with 2,2-dinitropropanol, 2,2,2-trinitroethanol, and 2,2-dinitro-1,3-propanediol to give allyl 2,2-dinitropropyl ether, allyl 2,2,2-trinitroethyl ether, and 2,2-dinitro-1,3-diallyloxypropane in yields of 53, 33, and 28%, respectively. In the latter case, no attempt was made to isolate the monoallyl ether which was undoubtedly also present.

In contrast to the reactivity of isopropyl triflate and allyl triflate with 2,2,2-trinitroethanol, methyl triflate gave no methyl 2,2,2-trinitroethyl ether when the reagents were heated in refluxing 1,2-dichloroethane for 45 hrs.

Thus, isopropyl triflate and allyl triflate react with a variety of alcohols, including some of the least nucleophilic known, at ambient temperature and neutral conditions in an inert solvent. These new alkylating agents, which are conveniently accessible synthetic reagents, should be extremely useful for chemically labile and thermally sensitive substrates, as well as those of very low nucleophilicity.

EXPERIMENTAL SECTION

General. Explosive properties of polynitro ethers described below have not been investigated. Adequate safety shielding should be used in all operations. 2-Fluoro-2,2-dinitroethanol is a severe skin irritant and contact should be avoided.

Proton and fluorine nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane and trichlorofluoromethane as the respective internal standards. Gas chromatographic separations were carried out on a Varian 920 instrument using a 12 ft x 3/8 in aluminum column packed with 12% QF-1 on 60/80 mesh Chromosorb W. Infrared spectra were obtained with a Perkin-Elmer 700 instrument.

Trifluoromethanesulfonic Anhydride. The published procedure[16] was used with the exception that the amount of phosphorous pentoxide was reduced by 50%. The yield was 73%, bp 82-84°. Analysis by fluorine nmr of the singlets at Ø 76.7 ppm for the anhydride and Ø 72.8 ppm for the acid indicated less than 1% of trifluoromethanesulfonic acid as an impurity.

Methyl Triflate. Trifluoromethanesulfonic acid (50 g, 0.030 mol) was added with stirring to 45.5 g (0.36 mol) of dimethyl sulfate. Distillation through a short Vigreux column gave 42.2 g (81%) of methyl triflate, bp 98-99°, nmr (CCl_4) δ4.22 ppm (s) (reported* bp 97°).

1,4-Butane Ditriflate. A solution of 2.16 g (.030 mol) of tetrahydrofuran in 100 ml of methylene chloride was added dropwise to a solution of 9.90 g (.030 mol) of trifluoromethanesulfonic anhydride in 100 ml of methylene chloride at -78°. The reaction mixture was allowed to warm to

room temperature, and was washed with water and dried over sodium sulfate. Evaporation of solvent and recrystallization of the residue from methylene chloride gave 7.75 g (73%) of colorless crystals, mp 35-37°; proton nmr ($CDCl_3$) δ 4.63 (m, 4 H, $-C\underline{H}_2-O$), and 2.03 ppm (m, 4 H, $C\underline{H}_2-CH_2O$); fluorine nmr ϕ 75.1 ppm (s); ir (CCl_4) 1403, 1200, 1138, and 920 cm^{-1} (OSO_2CF_3).

<u>Anal</u>. Calcd for $C_8H_8F_6O_6S_2$: C, 20.34; H, 2.27. Found: C, 20.30; H, 1.90.

<u>Pentyl Triflate</u>. A solution of 1.76 g (0.020 mol) of pentanol and 1.58 g (0.020 mol) of pyridine in 5 ml of methylene chloride was added, dropwise with stirring, over a 45 min period, to a solution of 6.60 g (0.023 mol) of triflic anhydride in 20 ml of methylene chloride at 0°. After 15 min, the solution was washed with water, dried over sodium sulfate and distilled to give 3.74 g (85%) of pentyl triflate, bp 53-54° (1 mm); proton nmr ($CDCl_3$) δ 4.55 (t, 2 H, $-CH_2O$), 1.85 (m, 2 H, $C\underline{H}_2-CH_2O$), 1.45 (m, 4 H, $-CH_2-$), and 1.27 ppm (t, 3 H, $-CH_3$); fluorine nmr ϕ 75.3 ppm (s, OSO_2CF_3); ir (CCl_4) 1425, 1200, 1140, and 930 cm^{-1} (OSO_2CF_3).

<u>Anal</u>. Calcd for $C_5H_{11}F_3O_3S$: C, 32.72; H, 5.03; F, 25.90. Found: C, 31.55; H, 4.71; F, 25.44.

<u>Isopropyl Triflate</u>. A solution of 2.7 g (0.045 mol) of isopropyl alcohol and 3.6 g (0.045 mol) of pyridine in 15 ml of carbon tetrachloride was added dropwise with stirring at 0° to 12.7 g (0.045 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. Nmr analysis of the colorless solution indicated a 90±5% yield of isopropyl triflate. In another experiment using methylene chloride as solvent, the organic layer was washed with water, dried, and concentrated. The residue could be vacuum transferred at ambient temperature (5 mm) to give a colorless liquid which

darkened rapidly at room temperature. The compound decomposed suddenly on attempted vacuum distillation at 50°. Proton nmr (CCl_4) δ 5.16 (septet, J=7 Hz, 1 H, CH), and 1.50 ppm (d, 6 H, J=7 Hz, CH_3); fluorine nmr ϕ 76.7 (s).

Allyl Triflate. A solution of 1.31 g (0.0234 mol) of allyl alcohol and 1.84 g (0.0234 mol) of pyridine in 5 ml of carbon tetrachloride was added dropwise (15 min) with stirring at 0° to a solution of 7.75 g (0.0234 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. Insoluble pyridine salt was removed by filtration through sodium sulfate. The resulting colorless solution was analyzed by ir and nmr and used directly for alkylation reactions. Quantitative nmr analysis (chlorobenzene as internal standard) of aliquots indicated yields of 75±5%. Impurities could not be detected by nmr or ir analysis: proton nmr (CCl_4) δ 6.03 (m, 1 H, -CH=), 5.43 (m, 2 H, $=CH_2$), and 4.92 ppm (m, 2 H, $-CH_2O$); fluorine nmr ϕ 77.6 ppm (s); ir (CCl_4) 1625 (C=C), 1405, 1240, 1190, and 1140 cm^{-1} (OSO_2CF_3).

Propargyl Triflate. A solution of 1.33 g (0.0241 mol) of propargyl alcohol and 1.88 g (0.024 mol) of pyridine in 5 ml of carbon tetrachloride was added dropwise at 0° with stirring to 7.87 g (0.028 mol) of trifluoromethanesulfonic anhydride in 25 ml of carbon tetrachloride. The solution was filtered through sodium sulfate and used directly for alkylation reactions. The yield (nmr) was 80±5%: proton nmr (CCl_4) δ 5.05 (d, 2 H, J= 2 Hz, $C\equiv C-CH_2O$), and 2.77 ppm (t, 1 H, J= 2 Hz, C≡C-H); fluorine nmr ϕ 75.9 ppm (s, OSO_2CF_3); ir (CCl_4) 3290, 2145 (C≡C-H), and 1410, 1210, 1140 cm^{-1} (OSO_2CF_3).

2-(2-Fluoro-2,2-dinitroethoxy)ethyl Triflate. A solution of 20.6 g (0.104 mol) of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether[13] and 8.22 g (0.108 mol) of pyridine in 50 ml of methylene chloride was added dropwise

over a period of 45 min with stirring to a solution of 29.3 g (0.104 mol) of trifluoromethanesulfonic anhydride in 100 ml of methylene chloride at 0°. After 15 min the mixture was washed with water and dried over sodium sulfate. Evaporation of solvent left a pale yellow oil, which was filtered through silica gel to give 29.1 g (87%) of the triflate: proton nmr ($CDCl_3$) δ4.70 (d, 2 H, J_{HF}= 17 Hz; F$\overset{|}{C}$-$\underline{CH}_2$-O) 4.68 (m, 2 H, $OCH_2\underline{CH}_2$-OTr), and 4.05 ppm (m, 2 H, $O\underline{CH}_2$-CH_2OTr); fluorine nmr: ϕ 110.9 (t, 1 F, J_{HF}= 17 Hz, $\underline{F}$-$\overset{|}{C}CH_2$- and 75.4 ppm (s, 3 F, CF_3SO_3O): ir (CCl_4) 1585 (NO_2), 1310, 1210, 1140 cm^{-1} (OSO_2CF_3).

<u>Anal</u>. Calcd for $C_5H_6F_4N_2O_8$: C, 18.18, H, 1.83; N, 8.48. Found: C, 18.65; H, 1.82; N, 8.16.

<u>1,2,3-Propane Tritriflate</u>. A mixture of 6.14 g (0.067 mol) of glycerol and 16.9 g (0.214 mol) of pyridine was added to a solution of 60.0 g (0.213 mol) of trifluoromethanesulfonic anhydride in 150 ml of methylene chloride over a 30 min period at 0°. Filtration through silica gel and removal of solvent gave a 32 g (98% yield) of analytically pure 1,2,3-propane tritriflate, mp 22-23° (from carbon tetrachloride): proton nmr ($CDCl_3$) δ5.17 (m, 1 H, CH), and 4.67 ppm (d, J= 2.7Hz, 4 H, CH_2O); fluorine nmr ϕ 74.67 (s, 6 F, $CH_2OSO_2CF_3$), and 74.87 ppm (s, 3 F, CH-OSO_2CF_3).

<u>Anal</u>. Calcd for $C_6H_5S_3F_9O_3$: C, 14.76; H, 1.03; F, 35.04. Found: C, 14.60; H, 0.86; F, 35.10.

<u>2-Fluoro-2,2-dinitroethyl Triflate</u>. By the above procedure 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 7.9 g (0.10 mol) of pyridine were reacted with 28.2 g (0.10 mol) of trifluoromethanesulfonic anhydride. The crude product was filtered through silica gel and then was distilled to give 12.0 g (42%) of the triflate, bp 36-38° (0.5 mm): proton nmr (CCl_4) δ 5.38 ppm

(d, J_{HF}= 14 Hz); fluorine nmr ϕ 81.0 (s, 3 F, OSO_2CF_3), and 111.0 ppm (t, 1 F, J_{HF}= 14 Hz, F-$\overset{|}{C}$$CH_2$); ir ($CCl_4$) 1590. 1425, 1300, 1220, 1135, and 1000 cm^{-1} (OSO_2CF_3).

Anal. Calcd for $C_3H_2F_4N_2O$: C, 12.56; H, 0.71. Found: C, 12.43; H, 0.61.

1,2-Bis(2-fluoro-2,2-dinitroethoxy)ethane. To a stirred solution of 16.5 g (0.050 mol)of 2(2-fluoro-2,2-dinitroethoxy)ethyl triflate and 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol in 100 ml of methylene chloride was added 34.5 g (0.25 mol) of anhydrous potassium carbonate. Stirring was continued for 16 hrs and then the reaction mixture was added to ice water and the organic phase was washed with 5% aqueous sodium hydroxide solution and dried over sodium sulfate. Removal of solvent gave 13.03 g (78%) of 1,2-bis-(2-fluoro-2,2-dinitroethoxy)ethane, bp 117-119° (0.01 mm) which solidified on standing at 0°: mp 28-29°; d^{25} 1.539; nmr ($CDCl_3$) δ4.57 (d, 4 H, J_{HF}= 16 Hz, F$\overset{|}{C}$-CH_2O), and 3.80 ppm (s, 4 H, OCH_2CH_2O); ir ($CDCl_3$) 1590, 1310 and 1120 cm^{-1} (C-O-C).

Anal. Calcd for $C_6H_8F_2N_4O_{10}$: C, 12.56; H, 2.41; N, 16.76. Found: C, 21.19; H, 2.20; N, 16.46.

2-Fluoro-2,2-dinitroethyl Pentyl Ether. The reaction of 2.20 g (0.010 mol) of pentyl triflate and 1.54 g (0.010 mol) of 2-fluoro-2,2-dinitroethanol by the above procedure gave 1.64 g (73%) 2-fluoro-2,2-dinitroethyl pentyl ether, bp 46-48° (0.04 mm): nmr (CCl_4) δ4.43 (d, 2 H, J_{HF}= 17 HZ, F$\overset{|}{C}$-C$\underline{H}_2$O), 3.90 (t, 2 H, J= 6 Hz, OC$\underline{H}_2$), 1.27 (broad m, 6 H, $-CH_2-$), and 0.87 ppm (m, 3 H, CH_3); ir (CCl_4) 1590, 1305 (NO_2) and 1120 cm^{-1} (C-O-C).

Anal. Calcd for $C_7H_{13}FN_2O_5$: C, 37.49; H, 5.84. Found: C, 37.78; H, 5.46.

Allyl 2-Fluoro-2,2-dinitroethyl Ether. By the same procedure a solution of 0.03 mol of allyl triflate in carbon tetrachloride (described above) was reacted with 5.39 g (0.035 mol) of 2-fluoro-2,2-dinitroethanol and 13.8 g (0.10 mol) of potassium carbonate in 50 ml of methylene chloride for 3 hrs to give 2.75 g (47%) of allyl 2-fluoro-2,2-dinitroethyl ether, bp 34-35° (0.2 mm), which had ir and nmr spectra identical with those of an authentic sample.[13]

2-Fluoro-2,2-dinitroethyl Propargyl Ether. By the above procedure, 0.0238 mol of propargyl triflate solution, 4.59 g (0.0298 mol) of 2-fluoro-2,2-dinitroethanol and 10 g (0.07 mol) of potassium carbonate in 30 ml of methylene chloride (12 hrs) gave 1.93 g (43%) of 2-fluoro-2,2-dinitroethyl propargyl ether, bp 32-34° (0.1 mm), which had ir and nmr spectra identical with those of an authentic sample.[13]

1,4 Bis-(2-fluoro-2,2-dinitroethoxy)butane. A mixture of 3.54 g (0.10 mol) 1,4-butane ditriflate, 6.16 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol and 23 g (0.167 mol) of potassium carbonate was stirred 18 hrs at ambient temperature. The mixture was diluted with water and the product was extracted with methylene chloride, dried over sodium sulfate, stripped of solvent and purified by column chromatography on silica gel to give 2.71 g (75%) of 1,4-bis(2-fluoro-2,2-dinitroethoxy)butane, a colorless oil: proton nmr ($CDCl_3$) δ 4.52 (d, 4 H, J_{HF}= 18 Hz, $F\overset{|}{C}CH_2O$), 3.63 (m, 4 H, $OC\underline{H}_2$-C), and 1.63 ppm (m, 4 H, $-C\underline{H}_2$-C-O); fluorine nmr ϕ 112.6 (t, J_{HF}= 18 Hz); ir (CCl_4) 1590, 1315 (NO_2).

Anal. Calcd for $C_8H_{14}F_2N_4O_{10}$: C, 26.52; H, 3.34; N, 15.46. Found: C, 26.82; H, 3.24; N, 14.93.

Reaction of 2-Fluoro-2,2-dinitroethanol and 1,2,3-Propane Tritriflate. To a stirred solution of 5.0 g (0.0124 mol) of 1,2,3-propane tritriflate and 5.3 g (0.0344 mol) of 2-fluoro-2,2-dinitroethanol in 15 ml of chloroform was added to 5.5 g (0.040 mol) of potassium carbonate and the mixture was stirred for 16 hrs. The mixture was added to 100 ml of ice water and the product was extracted with 50 ml of methylene chloride, and dried over sodium sulfate. Distillation gave 2.6 g (61%) of 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate, bp 83° (0.2 mm); proton nmr ($CDCl_3$) δ 5.31 (AB quartet, 2 H, CH_2=), 4.77 (d, 2 H, J_{HF}= 18 HZ, $F\overset{|}{\underset{|}{C}}CH_2$), and 4.25 ppm (s, 2 H, $-CH_2O$); fluorine nmr ϕ 111.2 (t, 1 F, $F\overset{|}{\underset{|}{C}}$), and 74.8 ppm (s, 3 F, (OSO_2CF_3).

Anal. Calcd for $C_6H_6F_4N_2SO_8$: C, 12.06; H, 1.76. Found: C, 21.35; H, 1.88.

Pentyl 2,2,2-Trifluoroethyl Ether. A mixture of 2.20 g (0.010 mol) of pentyl triflate, 1.10 g (0.010 mol) of 2,2,2-trifluoroethanol, 4.14 g (0.030 mol) of potassium carbonate and 15 ml of methylene chloride was stirred for 48 hrs. The mixture was washed with water, dried over sodium sulfate and stripped of solvent. Vacuum transfer of the residue gave 1.46 g (86%) of pentyl 2,2,2-trifluoroethyl ether. An analytical sample was isolated by glpc: nmr (CCl_4) δ 3.73 (q, 2 H, J_{HF}= 8 Hz, OCH_2CF_3), 3.57 (t, 3 H, J= 6 Hz, $O-\underline{CH_2}CH_2$), 1.92-1.08 (m, 6 H, $-CH_2-$) and 0.95 ppm (m, 3 H, CH_3).

Anal. Calcd for $C_7H_{13}F_3O$: C, 49.40; H, 7.70. Found: C, 49.42; H, 7.73.

Allyl 2,2,2-Trinitroethyl Ether. A solution of (0.030 mol) of allyl triflate in carbon tetrachloride was added to 5.5 g (0.030 mol) of 2,2,2-tri-

nitroethanol, 100 ml of methylene chloride, and 5 g of sodium sulfate, and the mixture was stirred for 48 hrs. The mixture was washed with water, dried over sodium sulfate and solvent was removed under vacuum. Column chromatography of the dark residue on silica gel gave 1.72 g (33%) of allyl 2,2,2-trinitroethyl ether, a pale yellow oil. nmr ($CDCl_3$) δ 5.83 (m, 1 H, -CH=C); 5.30 (m, 2 H, $=CH_2$); 4.67 (s, 2 H, CH_2-$C(NO_2)_3$), and 4.20 ppm (m, 2 H, OCH_2C=C); ir (CCl_4) 1630 (C=C); 1590, 1300 (NO_2), and 1120 cm^{-1} (-O-).

Anal. Calcd for $C_5H_7N_3O_7$; C, 27.15; H, 3.19; N, 19.00. Found: C, 27.26; H, 3.25; N, 18.88.

Allyl 2,2-Dinitropropyl Ether. Substitution of 2,2-dinitropropanol for 2,2,2-trinitroethanol in the preceding experiment gave after chromatography, 2.36 g (53%) of allyl 2,2-dinitropropyl ether, a colorless oil: nmr (CCl_4) δ 5.63 (m, 1 H, -CH=C), 5.23 (m, 2 H, $=CH_2$), 4.20 ppm (s, 2 H, $(NO_2)_2C$-CH_2-O), 4.03 (m, 2 H, OCH_2C=), and 2.17 ppm (s, 3 H, CH_3-$C(NO_2)_2$): ir (CCl_4) 1630 (C=C), 1580, 1320 (NO_2), and 1100 cm^{-1} (-O-C).

Anal. Calcd for $C_6H_{10}N_2O_5$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.58; H, 5.27; N, 14.98.

2,2-Dinitro-1,3-diallyloxypropane. By the above procedure, 1.83 g (0.011 mol) of 2,2-dinitro-1,3-propanediol was reacted with (0.022 mol) of allyl triflate for 48 hrs. The crude solution was washed with 5% sodium hydroxide to remove starting material and monoalkylation product. Chromatography of silica gel gave 0.755 g (28%) of the diallyl ether; nmr (CCl_4) δ 5.77 (m, 2 H, CH=C), 5.43 (m, 4 H, $=CH_2$), 4.27 (s, 4 H, $OCH_2C(NO_2)_2$), and 4.03 ppm (m, 4 H, OCH_2C); ir (CCl_4) 1625 (C=C), 1582, 1320 (NO_2), and 1095 cm^{-1} (C-O-C).

Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.89; H, 5.73; H, 11.38. Found: C, 43.34; H, 5.69; N, 11.29.

Reaction of 2,2-dinitropropanol with Pentyl Triflate. A mixture of 4.0 g (0.0182 mol) of pentyl triflate and 4.1 g (0.0273 mol) of 2,2-dinitropropanol, 5 g of sodium sulfate, and 50 ml of 1,2-dichloroethane was refluxed for 6 hrs. The mixture was washed with water and with 5% sodium hydroxide, dried over sodium sulfate, stripped of solvent and chromatographed on silica gel to give 1.52 g (38%) of a mixture of three 2,2-dinitropropyl pentyl ethers (glpc area ratio 0.13:1:0.57 in the order of retention times).

The major component was 2,2-dinitropropyl 2-pentyl ether: nmr (CCl_4) δ 5.87 (s 2 H, $C(NO_2)_2$-CH_2-O), 3.50 (m, 1 H, O-$\dot{C}H$-), 2.17 (s, 3 H, $CH_3C(NO_2)_2$-), 1.40 (broad m, 4 H, CH_2), 1.15 (d, 3 H, J= 6 Hz, CH_3-$\dot{C}H$-O), and 0.90 ppm (m, 3 H, CH_3); ir (CCl_4) 1560, 1320 cm^{-1} (NO_2).

Anal. Calcd for $C_8H_{16}N_2O_5$: C, 43.62; H, 7.32. Found: C, 43.21; H, 7.20.

The third component identified as 2,2-dinitropropyl 1-pentyl ether: nmr (CCl_4) δ 4.17 (s, 2 H, $C(NO_2)_2$-CH_2), 3.50 (t, 2 H, J= 6 Hz, OCH_2-), 2.15 (s, 3 H, $CH_3C(NO_2)_2$) 1.37 (broad m, 6 H, CH_2) and 0.90 (m, 3 H, CH_3); ir (CCl_4) 1560, 1320, and 1110 cm^{-1} (C-O-C)

Anal. Calcd for $C_8H_{16}N_2O_5$: C. 43.62; H, 7.32; N, 12.72. Found: C, 43.53; H, 7.04; N, 13.02.

The least abundant component was not isolated in sufficient quantity for elemental analysis, but the nmr spectrum indicated that the compound was 2,2-dinitropropyl 3-pentyl ether: nmr (CCl_4) δ 4.20 (s, 2 H, $-CH_2C(NO_2)_2-$), 3.47 (m, H, $CH_2\underline{C}HCH_2$), 2.17 (s, 3 H, $C(NO_2)_2-CH_3$), and 1.7-0.7 (broad m, 10 H).

2-Fluoro-2,2-dinitroethyl Isopropyl Ether. A mixture of 1.54 g (0.010 mol) of 2-fluoro-2,2-dinitroethanol, 1.92 g (0.010 mol) of isopropyl triflate, 3 g of sodium sulfate and 3 ml chloroform was stirred for 12 hours at ambient temperature. The solution was washed with water and with 5% sodium hydroxide, dried and distilled to give 1.45 g (74%) of 2-fluoro-2,2-dinitroethyl isopropyl ether, bp 52° (0.4 mm): proton nmr (CCl_4) δ 4.38 (d, 2 H, J_{HF}= 18 Hz, CH_2), 3.37 (septet, 1 H, J= 7 Hz, CH_2) 1.11 (d, 6 H, J= 7 Hz, CH_3); fluorine nmr ϕ 111.5 ppm (t, J_{HF}= 18 Hz).

Anal. Calcd for $C_5H_9FN_2O_5$: C, 30.61; H, 4.62. Found: C, 30.86; H, 4.65.

2,2-Dinitropropyl Isopropyl Ether. By the above procedure, using methylene chloride as solvent, 7.70 g (0.05 mol) of 2,2-dinitropropanol and (0.040 mol) of isopropyl triflate (12 hrs) gave 5.14 g (67%) of 2,2-dinitropropyl isopropyl ether, bp 45-47° (0.07 mm): nmr (CCl_4) δ 4.13 (s, 2 H, $C(NO_2)_2$-CH_2O), 3.62 (septet, 1 H, J= 6 Hz), 2.13 (s, 3 H, $CH_3C(NO_2)_2$), and 1.15 ppm (d, 6 H, J= 6 Hz, $(CH_3)_2C$); ir (CCl_4) 1560, 1320 (NO_2): and 1110 cm^{-1} (C-O-C)

Anal. Calcd for $C_6H_{12}N_2O_5$: C, 37.49; H, 6.30. Found: C, 37.62; H, 6.36.

Isopropyl 2,2,2-Trinitroethyl Ether. Isopropyl triflate (0.040 mol) and 2,2,2-trinitroethanol (9.05 g, 0.050 mol) were reacted by the above procedure, except that washing with sodium hydroxide solution was omitted and the crude product was passed through a short column of silica gel to give isopropyl 2,2,2-trinitroethyl ether in 38% yield. The analytical sample was distilled in a molecular still at 0.1 mm, bath temperature 50°:

nmr (CCl_4) δ4.60 (s, 2 H, CH_2), 3.80 (septet, 1 H, J= 7 Hz, CH), and 1.25 ppm (d, 6 H, J= 6 Hz, CH_3); ir (CCl_4) 1565, 1315 (NO_2), and 1120 cm^{-1} (C-O-C).

Anal. Calcd for $C_5H_9N_3O_7$: C, 26.91; H, 4.06. Found: C, 27.30; H, 4.29.

Reaction of Isopropyl Triflate with Pentanol. A mixture of 0.44 g (0.0050 mol) of pentanol, 0.95 g (0.0050 mol) of isopropyl triflate, 1.0 g of sodium sulfate and 10 ml of methylene chloride was stirred for 1 hr. The mixture was washed with 30 ml of water, dried and stripped of solvent. Vacuum transfer of the residue gave 0.57 g of a mixture containing 60% isopropyl pentyl ether (52% conversion) and 40% 1-pentanol, separated by glpc and compared with authentic samples. A reference sample of isopropyl pentyl ether was prepared by the reported method[19]: bp 131-132°; nmr (CCl_4) δ3.40 (septet, 1 H, J= 6 Hz, (CHO), 3.27 (t, 2 H, J= 6 Hz, $-CH_2O$), 1.37 (m, 6 H, $-CH_2-$), 1.08 (d, 6 H, J= 6 Hz, $(CH_3)_2C$), and 0.90 ppm (m, 3 H, $-CH_3$).

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Appendix B

Fluorammonium Trifluoromethanesulfonate[1]

Of the three possible fluorine-substituted ammonia derivatives, NH_2F, NHF_2 and NF_3, fluoramine has not been characterized.[2] Two salts of this unknown base, the perchlorate and the methanesulfonate, however, were synthesized indirectly[3] by the reaction of alkyl fluorocarbamates[4] with the corresponding acids:

$$NHFCO_2R + 2HX \longrightarrow NH_3F^+X^- + CO_2 + RX$$

$$R = C_2H_5,\ \underline{i}\text{-}C_3H_7;\ X = ClO_4^-,\ CH_3SO_3^-$$

Only very strong acids give fluorammonium salts in this reaction. Weaker mineral acids such as, for example, hydrogen chloride decompose fluorocarbamates.

The two above fluorammonium salts were found to be relatively unstable. They decomposed readily in the presence of atmospheric moisture, etched glass, and after a few months decomposed even when stored in fluorocarbon or passivated nickel containers. Both salts melted with decomposition at 104-105° and this temperature appeared to signify the stability limits of the fluorammonium ion.

The apparent dependence of stability of fluorammonium salts on the acid strength suggested to us that trifluoromethanesulfonic acid (triflic acid[5]), the strongest simple protic acid known[6], might provide a more stable salt.

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Fluorammonium triflate was obtained quantitatively by the reaction of propyl fluorocarbamate[4] with two moles triflic acid:

$$NHFCO_2CH(CH_3)_2 + 2CF_3SO_3H \xrightarrow[25^\circ]{CH_2Cl_2} NH_3F^+CF_3SO_3^- + CO_2 + (CH_3)_2CHOSO_2CF_3$$

The mildly exothermic reaction was completed in a matter of minutes at room temperature.

Fluorammonium triflate is by far less susceptible to the atmospheric moisture than the two other fluorammonium salts, and a dry-box was not needed for the preparation and isolation of the salt. On prolonged exposure to the atmospheric moisture the salt decomposed gradually over a period of several hours. Whereas fluorammonium perchlorate etches glass rapidly[3], fluorammonium triflate does not attack glass.

Fluorammonium triflate was characterized by elemental analysis and fluorine nmr spectrum. The spectrum exhibited two singlets at ϕ 78.75 and 126.80 (3:1 area ratio) assigned to CF_3 and NH_3F^+ fluorines, respectively. Fluorammonium triflate melts at 164-5° (corr.) with partial decomposition and thus is more stable than fluorammonium perchlorate and the methanesulfonate, both of which melt with complete decomposition at 104-105°.

Fluorammonium triflate is soluble in many organic solvents such as simple esters and nitriles. Its solutions are much more stable than those of fluorammonium perchlorate[3]. A 10-15% solution of the salt in ethyl acetate was stored in glass for several months without noticeable decomposition.

Experimental

To a stirred solution of 6.0 g (0.04 mol) of triflic acid in 70 ml of methylene chloride was added dropwise at 22-27° over a period of 5 min with

cooling (water-bath) 2.42 g (0.02 mol) of isopropyl N-fluorocarbamate[4]. The reaction mixture was stirred until the evolution of carbon dioxide ceased (10-15 min). The salt was collected in a sintered glass funnel and washed with four 10 ml portions of methylene chloride. The material was dried in a vacuum desiccator to give 3.7 g (100% yield) of fluoroammonium triflate, a white crystalline solid mp[7] 164-5° (partial decomposition).

Anal. Calcd for $NH_3FCF_3SO_3$: C, 6.49; H, 1.63; N, 7.57; F, 41.07. Found: C, 6.75; H, 1.26; N, 7.45; F, 39.8.

Fluorine nmr (in ethyl acetate; CCl_3F as internal reference): ϕ 78.75 (s, 1 F, NH_3F^+). Proton nmr (ethyl acetate): δ 11.47 (s, NH_3F^+).

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7. The melting point was recorded on the Fisher-Johns melting point apparatus.