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HIGH ENERGY HALOGEN CHEMISTRY

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By

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

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13. ABSTRACT

Dichlorine heptoxide was shown to be a versatile perchlorylating reagent. Reaction with alcohols provides a general method of synthesizing alkyl perchlorates, including electronegatively substituted examples, such as 2-fluoro-2,2-dinitroethyl perchlorate and 2,2-dinitropropyl perchlorate, which cannot be prepared by standard methods. Secondary amines gave dialkylperchlorylamines, and primary amines gave alkylperchlorylamines, a new class of compounds. The latter gave alkali salts stable in aqueous solution. Ketones gave gem-diperchlorates. Nitronate salts gave oxidative coupling, chlorination and Nef reaction products. Cyclohexene gave a product tentatively identified as 1-chloro-2-perchlorylcyclohexane.

Unsuccessful attempts were made to prepare perchlorylalkanes from silver chlorate and alkyl halides. Bis(2-fluoro-2,2-dinitromethyl)mercury reacted with methyl iodide very slowly to give 1-fluoro-1,1-dinitroethane, but other attempted alkylations of this salt failed. Perchloryl fluoride reacted with 2-fluoro-2,2-dinitroethanol in methanol to give 2-fluoro-2,2-dinitroethyl methyl ether.

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Gem-diperchlorates						
Silver chlorate						
Perchloryl fluoride						
Bis(fluorodinitromethyl)mercury						
Infrared spectra						
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CONTENTS

I. INTRODUCTION

The objective of this research is to explore new functional groupings that might find utility in propellants and explosives. The major emphasis of the program is on the chemistry of organic oxidized halogen derivatives. Some exploratory work was also done on alkylation reactions of heavy metal salts of nitro compounds.

II. CHLORINE HEPTOXIDE CHEMISTRY

A. DISCUSSION

1. Preparation

Dichlorine heptoxide was first synthesized by Michael and Conn in 1900 by the reaction of anhydrous perchloric acid with phosphorous pentoxide[1]. Several modified procedures were later reported[2]; Schmeisser described a convenient preparation using 70% perchloric acid with carbon tetrachloride as a diluent[3]. Although dichlorine heptoxide is generally described as the most stable oxide of chlorine and its physical and spectroscopic properties have been studied extensively[2], its chemical reactions have not been explored. As the anhydride of perchloric acid it would be expected to function as an efficient perchlorylating agent.

Carbon tetrachloride solutions of dichlorine heptoxide were prepared conveniently and safely by a modification of Schmeisser's method. Thus, 70% perchloric acid was added to a suspension of phosphorous pentoxide in carbon tetrachloride at 0°, and the mixture was gradually heated to reflux. Dichlorine heptoxide and carbon tetrachloride, which codistill, were removed under vacuum. Yields were quantitative. The same method was used to prepare solutions of dichlorine heptoxide in deuterochloroform for use in cases where products were insoluble in carbon tetrachloride; the reactions were monitored by nmr.

2. Reaction with Alcohols

Alkyl perchlorates have previously been prepared by the reaction of anhydrous perchloric acid with alcohols or alkenes[4], by reaction of diazoalkanes with 70% perchloric acid[5], and more often by reaction by alkyl iodides with silver perchlorate in hydrocarbon solvents[6]. None of these methods is satisfactory for perchlorates of alcohols bearing electronegative substituents.

The reaction of a solution of dichlorine heptoxide in carbon tetrachloride with a variety of substituted and unsubstituted alcohols gives the corresponding alkyl perchlorates in high yields and thus constitutes a new general synthesis of esters of perchloric acid.

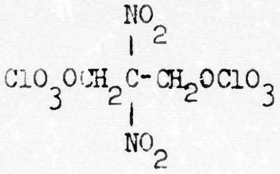
In general, equimolar quantities of alcohol and dichlorine heptoxide in carbon tetrachloride were stirred at room temperature as required. The reactions were conveniently monitored by nmr as hydrogens geminal to $OClO_3$ are deshielded by 0.7 - 1.0 ppm from the starting alcohol (Table 1).

Table 1

Nmr Spectra of alkyl perchlorates prepared from alcohols and dichlorine heptoxide[a] ($R\text{-}CH_2OClO_3$).

Compound	→$CH\text{-}OClO_3$	R
$CH_3CH_2OClO_3$	4.57 q J=7 Hz	CH_3, 1.53 t J=7 Hz
$(CH_3)_2CHOClO_3$	5.15 septet J=6 Hz	CH_3, CH_3, 1.48 d J=6 Hz

Table 1 (cont'd)

Compound	$\geq$CH-OClO$_3$	R
$FC(NO_2)_2CH_2OCH_2CH_2OClO_3$	4.57 m (A_2B_2)	$-OC\underline{H}_2-CH_2-$, 4.00 m (A_2B_2) $FC(NO_2)_2-C\underline{H}_2-C-$, 4.58 d $J_{HF}=17$ H_z
$CH_3(CH_2)_3CH_2OClO_3$	4.50 t J=6.5 H_z	$-CH_2-$, 1.6 broad m CH_3-, 1.05 m
$CH_3(CH_2)_3-CH(OClO_3)CH_3$	4.95 m	$-CH(OClO_3)CH_3$, 1.53 d J=6 H_z $-CH_2-$, 1.5 broad m $\underline{C}H_3-CH_2$, 1.0 m
$FC(NO_2)_2CH_2OClO_3$	5.56 d $J_{HF}=16$ H_z	
$CH_3C(NO_2)_2CH_2OClO_3$	5.43 s	CH_3, 2.33 s
 $ClO_3OCH_2\overset{NO_2}{\underset{NO_2}{C}}-CH_2OClO_3$	5.43 s	

(a) Nmr spectra were measured on a Varian T-60 spectrometer as dilute solutions in carbon tetrachloride. Chemical shifts are reported as ppm relative to TMS as internal standard. Integral ratios were in accord with theory (± 5%).

Simple primary and secondary alcohols reacted rapidly with dichlorine heptoxide and the alcohol were completely consumed after several hours. Thus, 1-pentanol, ethanol, 2-hexanol and isopropanol gave, respectively, 1-pentyl perchlorate, ethyl perchlorate, 2-hexyl perchlorate, and isopropyl perchlorate. The products were identified by comparison of the ir spectra with published data[4,6] and by nmr spectra. In contrast to results reported for the perchloric acid-alcohol reaction isomeric products were not observed[4].

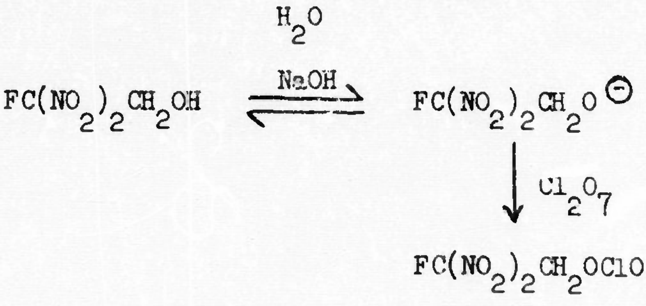
As is generally the case in reactions of alcohols with electrophilic reagents, electron-withdrawing substituents were found to lower the reaction rate. Nevertheless, perchlorates derived from nitro alcohols could be prepared and isolated conveniently by this reaction. Thus 2-fluoro-2.2-dinitroethanol required four days for 90% conversion to 2-fluoro-2,2-dinitroethyl perchlorate at room temperature. The low reaction rate is attributable in part to the low solubility of 2-fluoro-2,2-dinitroethanol in the reaction solvent, carbon tetrachloride. Unreacted alcohol and the byproduct, perchloric acid, were removed by extracting the solution with water, and the perchlorate was hydrolytically stable under these conditions. The perchlorate, which distilled at room temperature at 0.05 mm, is a colorless oil. It was identified by elemental analysis and nmr spectra. Its density at 25° is 1.704.

$$FC(NO_2)_2CH_2OH + Cl_2O_7 \xrightarrow{CCl_4} FC(NO_2)_2CH_2OClO_3 + HClO_4$$

Under the same conditions, 2,2-dinitropropanol reacted completely in 48 hrs to give 2,2-dinitropropyl perchlorate. This material was also unaffected by aqueous extraction to remove perchloric acid. It was vacuum transferred at 0.03 mm, and was identified by elemental analysis as well as ir and nmr spectra. Its density was found to be 1.601.

Similarly, 2,2-dinitro-1,3-propanediol reacted with dichlorine heptoxide. After four days, the nmr spectrum of the solution was consistent with the diperchlorate contaminated with 5-10% of the monoperchlorate of the alcohol. This impurity was removed by filtration through acidic alumina. The product was a colorless non-volatile oil which gave the expected ir and nmr spectra for 2,2-dinitro-1,3-propane diperchlorate. However consistent elemental analyses could not be obtained. 2-(Fluorodinitroethoxy)ethanol[7] showed intermediate reactivity, giving complete conversion to the perchlorate in 20 hrs. Attempts to prepare a perchlorate from trinitroethanol were unsuccessful. No reaction took place in 5 days at room temperature or 3 hrs at the reflux temperature of carbon tetrachloride.

Dichlorine heptoxide reacts sufficiently slowly with water that perchlorates can be prepared even in aqueous solutions. Rates of reaction of electronegatively substituted alcohols can be greatly enhanced under these conditions by the addition of base. Thus, 2-fluoro-2,2-dinitroethanol was converted to the perchlorate in minutes at 0° in aqueous alkaline solution.

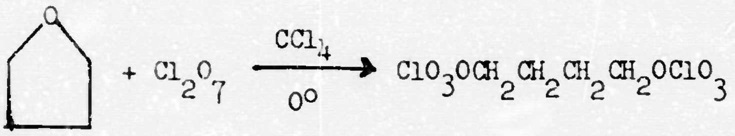


$$\begin{tikzcd} FC(NO_2)_2CH_2OH \arrow[r, shift left, "H_2O \; NaOH"] & FC(NO_2)_2CH_2O^{\ominus} \arrow[l, shift left] \arrow[d, "Cl_2O_7"] \\ & FC(NO_2)_2CH_2OClO_3 \end{tikzcd}$$

3. Reaction with Ethers

The cleavage of ethers with dichlorine heptoxide was investigated as an alternative method for synthesizing alkyl perchlorates. This method has the potential advantage of complete utilization of dichlorine heptoxide without the simultaneous formation of perchloric acid.

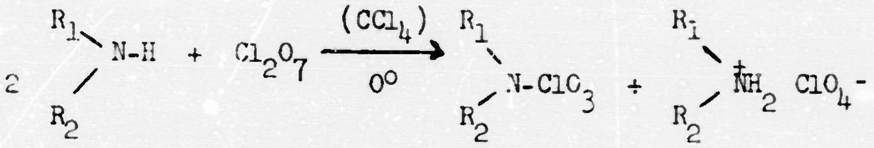
Tetrahydrofuran was found to react exothermically with dichlorine heptoxide to give 1,4-butanediperchlorate quantitatively. The product was identified by ir and nmr spectra.



Diethyl ether also reacted with dichlorine heptoxide under these conditions but the reaction was relatively slow; it did not go to completion in 18 hrs. This reaction has not yet been investigated extensively.

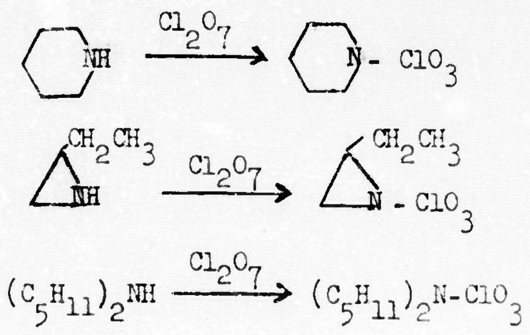
4. Reaction with Amines

Perchloryl fluoride reacts with aqueous or anhydrous ammonia to give a mixture of NH_4F and NH_4NHClO_3[8] from which other salts of perchlorylamide (NH_2ClO_3) can be prepared by metathesis reactions in aqueous solution. Amines, however, generally give complex oxidation and N-fluorination products, rather than perchlorylation[9]. The synthesis of N-perchlorylpiperidine in 66% yield from $FClO_3$ and aqueous piperidine is an exception and this compound is the only such derivative previously characterized[10]. Reactions of dichlorine heptoxide with amines were investigated on this program with the objective of providing a more general route to N-ClO_3 compounds so their stability can be assessed. Dichlorine heptoxide in carbon tetrachloride was found to react rapidly at 0° with two equivalents of primary or secondary amines to give nearly quantitative yields of the N-perchloryl derivatives as shown in the following equation.



Solutions of the products in carbon tetrachloride are obtained by acidification of the reaction mixtures with dilute sulfuric acid which effectively removes salts and traces of unreacted amines. Advantage can also be taken of the relatively slow rate of hydrolysis of dichlorine heptoxide protected by a nonpolar solvent. N-Perchlorylamines are conveniently prepared by dropwise addition of dichlorine heptoxide in carbon tetrachloride to an aqueous solution of excess amine followed by acidification and separation of organic and aqueous layers.

Solutions of N-perchlorylpiperidine, N-perchloryl-2-ethylaziridine, and N-perchloryldiamylamine in carbon tetrachloride were prepared as outlined above and the products identified by spectral and analytical methods. Infrared spectroscopy is particularly useful. Strong bands were always observed near 1220, 1190, and 1000 cm^{-1} characteristic of the $N-ClO_3$ group. The absence of N-H absorption was noted.



N-Perchlorylpiperidine was identified by comparison of the ir spectrum with that of an authentic sample. Evaporation of the solvent from a small portion of the reaction mixture from 2-ethylaziridine gave N-perchloryl-2-ethylaziridine as a colorless oil which could be vacuum transferred at 0.05 mm to provide an analytical sample. Correct C,H,N, and Cl analyses together with the spectral data permits unequivocal assignment of structure.

Primary N-perchlorylamines can be obtained in solution exactly as outlined for the secondary derivatives. The presence of the $NHClO_3$ group was readily confirmed by the nmr and ir spectra. Evaporation of the solvent from N-perchloryl-n-butylamine gave a colorless oil which decomposed spontaneously when air was admitted to the system. In contrast, N-perchloryl-*t*-butylamine, which does not contain hydrogens adjacent to the $NHClO_3$ group, gave a colorless oil which could be vacuum transferred and identified by elemental analysis.

Preliminary investigations indicate that these compounds can be extracted with dilute sodium hydroxide and recovered after acidification. Chemical reactions for the salts of primary N-perchloryl amines have not yet been investigated.

$$R\text{-}NHClO_3 \xrightarrow{NaOH} R\text{-}NClO_3^{\ominus}$$

5. Reaction with Ketones

gem-Diperchlorates have been prepared by the reaction of ketones with solutions of anhydrous perchloric acid in chloroform or methylene chloride[11]. A disadvantage of this method is that a mole of water is liberated which extracts perchloric acid from the organic solvent and can also shift the equilibrium of the perchlorate formation reaction. Dichlorine heptoxide should also react with ketones, but without the formation of water.

$$R_2C = O + Cl_2O_7 \longrightarrow R_2C(OClO_3)_2$$

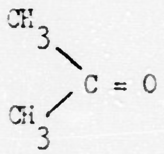
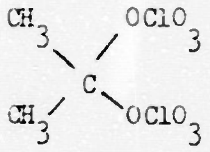
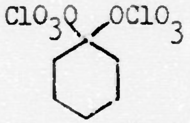
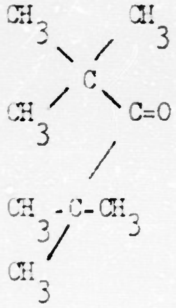
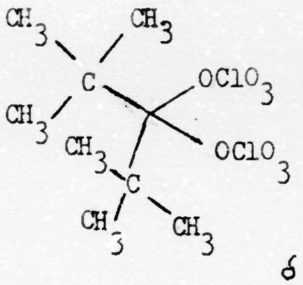
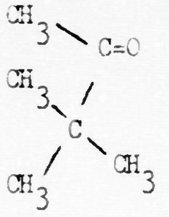
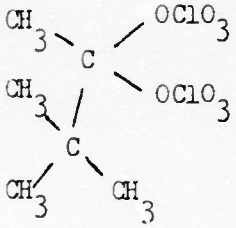
$$R_2C=O + 2HClO_4 \longrightarrow RC(OClO_3)_2 + H_2O$$

Ketones were found to react rapidly with dichlorine heptoxide in carbon tetrachloride, but the products were insoluble in this solvent. Deuterochloroform was a more satisfactory reaction solvent for spectral identification of the products. Thus acetone gave a quantitative yield of 2,2-diperchloratopropane, identical with the compound obtained from perchloric acid. In the same way, the corresponding gem-diperchlorates were obtained from cyclohexanone, methyl t-butyl ketone and di-t-butyl ketone. In each case, the chemical shifts of hydrogens α to the carbon bearing the perchlorate groups were greater than those of the corresponding ketones by 0.41 to 0.46 units, and the β hydrogens were shifted by 0.13 to 0.17 units (Table 2). The formation of the diperchlorate from di-t-butyl ketone indicates that the reaction is not sensitive to steric factors.

Unsuccessful attempts were made to displace the perchlorate groups of 2,2-diperchloratopropane with inorganic anions. Silver nitrate, sodium nitrite, sodium chloride and potassium carbonate all regenerated acetone, suggesting that nucleophilic attack was on chlorine rather than carbon. Triethylsilane, however, reduced the diperchlorate to isopropyl

Table 2

gem-Diperchlorates

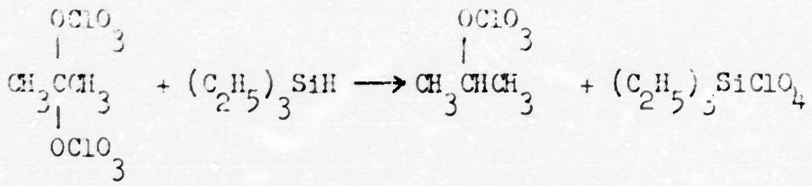
Starting Materials	Products	a	b
 δ 2.17	 2.58	0.41	-
 δ 2.27 (m, 4H) δ 1.80 (m, 6H)	 2.73 (m, 4H) 1.93 (m, 6H)	0.46	0.13
 δ 1.23	 δ 1.40	-	0.17
 δ 2.05 (s, 3H) δ 1.12 (s, 9H)	 2.48 (s, 3H) 1.28 (s, 9H)	0.43	0.16

---

a. Difference in chemical shift between alpha hydrogens of gem-diperchlorate and those of the corresponding ketone.

b. Difference in chemical shift between beta hydrogens of gem-diperchlorate and those of the corresponding ketone.

perchlorate.

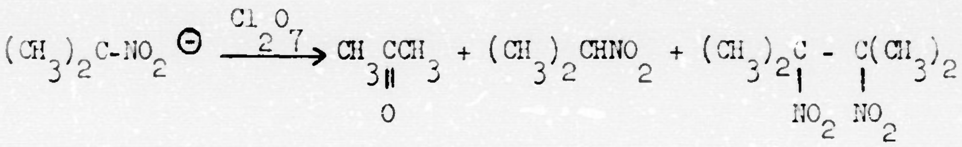


$$CH_3\underset{OClO_3}{\overset{OClO_3}{C}}CH_3 + (C_2H_5)_3SiH \longrightarrow CH_3\overset{OClO_3}{C}HCH_3 + (C_2H_5)_3SiClO_4$$

6. Reaction with Nitronate Ions

Reactions of nitronate salts with dichlorine heptoxide were examined with the objective of preparing perchlorylnitroalkanes.

The potassium salt of 2-nitropropane gave three products in the reaction with dichlorine heptoxide in carbon tetrachloride: 2-nitropropane, acetone, and 2,3-dimethyl-2,3-dinitropropane. The same products, along with 2-fluoro-2,2-nitropropane were reported as a result of the reaction of perchloryl fluoride with salts of 2-nitropropane[12].



$$(CH_3)_2C\text{-}NO_2^{\ominus} \xrightarrow{Cl_2O_7} CH_3\underset{\underset{O}{\|}}{C}CH_3 + (CH_3)_2CHNO_2 + (CH_3)_2\underset{NO_2}{C} - \underset{NO_2}{C}(CH_3)_2$$

Salts of 1,1-dinitroalkanes also failed to give perchloryl derivatives. The potassium salts of 1,1-dinitroethane and 1,1-dinitrobutane yielded only the corresponding dinitroalkanes and 1-chloro-1,1-dinitroalkanes. Transitory blue colors of the solutions suggest that nitroso intermediates were involved. The sodium salt of nitroethane yielded only acetic acid.

$$R\text{-}C(NO_2)_2^{\ominus} \xrightarrow{Cl_2O_7} R\text{-}C(NO_2)_2Cl + RC(NO_2)_2H$$

$$CH_3CHNO_2^{\ominus} \longrightarrow CH_3\ CO_2H$$

It appears that attack on the oxygens of the nitro groups and oxidation predominates in these reactions. Lower oxides of chlorine, which would result from oxidation-reduction reactions, disproportionate readily to give hypochlorous acid or chlorine which would chlorinate the dinitro anions.

7. Reaction with Unsaturated Compounds

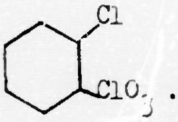
Perchlorybenzenes have been prepared by the reaction of aromatic compounds with perchloryl fluoride catalyzed by aluminum chloride[13]. Reactive olefins, such as vinyl ethers, also react with perchloryl fluoride but yield fluorine-containing products rather than perchloryl compounds[14].

A study was initiated of reactions of aromatic compounds and of olefins with dichlorine heptoxide. The olefin reaction is of particular interest as a potential source of perchlorylalkanes, an unknown class of compounds.

Benzene reacted vigorously with a solution of dichlorine heptoxide in carbon tetrachloride, but only dark, insoluble tars were formed, with no detectable trace of perchlorylbenzene. In the presence of the Lewis acid catalysts, aluminum chloride or zinc chloride, similar results were obtained. To determine whether traces of perchloric acid catalyze this reaction, sodium sulfate, potassium fluoride, or sodium carbonate was added as a scavenger. No reaction occurred under these conditions. Nitrobenzene did not react with dichlorine heptoxide, whereas chlorobenzene gave tars slowly and anisole gave the same type of tarry material even in the presence of potassium fluoride.

Cyclohexene gave dark insoluble tars with the Cl_2O_7-CCl_4

reagent, but when the reaction was repeated with potassium fluoride present, a colorless solution was formed. Molecular distillation gave a small amount of a material with elemental analysis consistent with the structure,



. The infrared spectrum showed strong bands at 1225 and 1260 cm^{-1}, attributable to $-ClO_3$, and the nmr spectrum was typical of 1,2-disubstituted cyclohexanes.

B. EXPERIMENTAL

1. Dichlorine Heptoxide

To a suspension of 50 g (0.35 mol) of phosphorous pentoxide in 100 ml of carbon tetrachloride, 8.2 g (0.0603 mol) of 70% perchloric acid was added dropwise, with efficient stirring, over a period of 2 hrs at 0°. The reaction mixture was allowed to stand at room temperature overnight and then was heated at reflux for 90 min. The mixture was cooled to room temperature, and the product was vacuum transferred to a -70° receiver at 60 mm. The distillate consisted of 93 ml (149 g) of very pale yellow liquid which contained 0.00030 moles of dichlorine heptoxide per ml of solution, 93% yield (titration after stirring for 45 min with 1N sodium hydroxide). The nmr spectrum showed that no perchloric acid was present.

Using deuterochloroform rather than carbon tetrachloride as the solvent in the above procedure gave the same results.

2. Pentyl perchlorate

1-Pentanol (0.0006 mole, 0.052 g) was added to two ml of dichlorine heptoxide in carbon tetrachloride (0.0006 mol) with magnetic stirring and ice cooling. Stirring was continued for two hours and then the reaction mixture was quenched with ice water. The carbon tetrachloride layer was dried over sodium sulfate and analyzed by nmr (Table 1) and ir. The ir spectrum was very similar to that published for n-hexyl perchlorate[6] with strong bonds at 1260 and 1240 cm^{-1} characteristic of covalent perchlorates. No OH absorbtion was present.

3. 2-Fluoro-2,2-dinitroethyl Perchlorate

a. 2-Fluoro-2,2-dinitroethanol (0.51 g, 0.00325 mole) was added to 15 ml of dichlorine heptoxide-carbon tetrachloride solution (0.0045 mole) and stirred for our days at which time nmr indicated the reaction was 90-95% completed. The reaction mixture was quenched with ice and the organic layer was dried over sodium sulfate. Excess alcohol was completely removed by this treatment. Evaporation of solvent (60 mm) from an aliquot left a colorless oil which could be vacuum transferred at 0.05 mm to give the analytical sample: nmr (CCl_4) δ 5.56 (d, J_{HF} = 15 Hz); $d^{25°}$= 1.704.

Anal. Calcd for $C_2H_2ClFN_2O_8$: C, 10.16; H, 0.85; F, 8.03. Found: C, 10.17; H, 0.52; F, 8.51.

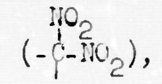
b. 2-Fluoro-2,2-dinitroethanol (0.345 g, large excess) was added to 1 ml of 1.00 N NaOH (0.001 mol) with stirring at 0°. To this mixture was added 4 ml of dichlorine heptoxide-carbon tetrachloride solution (.0012 mol) in several portions. The yellow color presumably due to fluorodinitromethyl anion faded in three minutes indicating completion of reaction. Dilution with water and separation of layers gave a carbon tetrachloride solution of 2-fluoro-2,2-dinitroethyl perchlorate identical to the material above.

4. 2,2-Dinitropropyl Perchlorate

2,2-Dinitropropanol (0.45 g, 0.0030 mol) was added to 10 ml of dichlorine heptoxide-carbon tetrachloride solution and the mixture was stirred for 48 hrs at which time the reaction was complete. The solution was washed with ice water and dried. Solvent was removed from an aliquot giving the colorless perchlorate which was subsequently vacuum transferred (0.03 mm) to a dry ice cooled receiver: nmr (CCl_4) δ5.32 (s, 2H, $\overset{|}{\underset{|}{C}}-\underline{CH_2}OClO_3$) and 2.32 ppm (s, 3H, CH_3); ir (CCl_4) 1570(s) ($NO_2-\overset{|}{\underset{|}{C}}-NO_2$) and 1280(s), 1240(s), 975(m) cm^{-1} ($OClO_3$); $d^{25^\circ} = 1.601$.

Anal. Calcd for $C_3H_5ClN_2O_8$: C, 15.48; H, 2.13; Cl, 15.25; N, 12.05. Found: C, 16.40; H, 1.92; Cl, 15.36; N, 11.68.

5. 2,2-Dinitro-1,3-Propane diperchlorate

2,2-Dinitro-1,3-propanediol (0.199 g, 0.0012 mole) was added to 8 ml of dichlorine heptoxide-carbon tetrachloride solution (0.0024 mol) and the mixture was stirred for **four** days. Nmr indicated that the major product was the diperchlorate, but was contaminated with 5-10% of an impurity which appeared to be the monoperchlorate. Aqueous extraction did not remove this compound but purification was accomplished by filtration through acidic alumina. Removal of solvent left a colorless oil (~30% yield): nmr (CCl_4) δ5.43 ppm (s); ir (CCl_4) 1570(s)  ($-\overset{NO_2}{\underset{|}{C}}-NO_2$), and 1280, 7240, 970 cm^{-1} ($C-OClO_3$). An acceptable elemental analysis has not yet been obtained.

Anal. Calcd for $C_3H_4Cl_2N_2O_{12}$: C, 10.89; H, 1.22; N, 8.46. Found: C, 13.33; H, 1.05; N, 7.28.

6. Reaction of Tetrahydrofuran with Dichlorine Heptoxide

Tetrahydrofuran (0.043 g, 0.0006 mol) was added to 2 ml of an ice cooled solution of dichlorine heptoxide in carbon tetrachloride (0.0006 mol) with magnetic stirring. A vigorous exothermic reaction occurred. Nmr analysis of the slightly yellow solution confirmed the disappearance of the tetrahydrofuran multiplets at δ 3.75 and 1.85 and revealed new multiplets at δ 4.60 (m, 4H) and 3.70 (m, 4H) which are attributed to 1,4-butanediol diperchlorate. The nmr spectrum was unchanged by aqueous extraction. Addition of excess tetrahydrofuran gave separate nmr peaks as expected ruling out complexes or "oxonium" type compounds. Work is in progress to further characterize this material.

7. Reaction of Diethyl ether with Dichlorine Heptoxide

Diethyl ether (0.044 g, 0.0006 mol) was added to 2 ml (0.0006 mol) of dichlorine heptoxide-carbon tetrachloride solution as outlined above. Nmr analysis after two hours revealed a pair of triplets and a pair of quartets. The downfield quartet was centered at 4.57 ppm superimposable with that of ethyl perchlorate prepared from ethanol. The other quartet corresponded to diethyl ether. The pair of triplets were somewhat overlapping, but chemical shifts were consistent with a mixture of ethyl perchlorate and diethyl ether. The ratio of perchlorate to ether was 1.4:1 after 2 hrs and 3:1 after 18 hours. Strong ir bands at 1220 and 1190 cm^{-1} after aqueous extraction were identical to those of ethyl perchlorate prepared by alternative methods.

8. Reaction of Benzene with Dichlorine Heptoxide

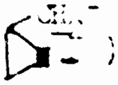
Four ml of a solution of dichlorine heptoxide was added dropwise to 2 ml of dry benzene with stirring and cooling. An exothermic reaction took place and a dark material deposited on the sides of the flask which was insoluble in carbon tetrachloride, chloroform, and water. Broad absorbtions were noted in the ir spectrum. The organic layer was washed with water, dried and filtered. Evaporation gave no trace of perchlorylbenzene. Repetition of this procedure with added scavengers for strong acid (e.g. sodium sulfate, potassium carbonate, potassium fluoride) suppressed reaction completely. Variation of modes of mixing of reagents as well as stoichiometric ratios gave similar results. Friedel Crafts catalysts such as aluminum chloride or zinc chloride gave the same black material. In the case of aluminum chloride a small quantity of chlorobenzene was obtained.

9. N-Perchlorylpiperidine

a. Piperidine (0.104 g, 0.0012 mol) was added to 2 ml of dichlorine heptoxide-carbon tetrachloride solution (0.0006 mol) with cooling and stirring. A yellow precipitate separated immediately and after five minutes the reaction mixture was quenched with dilute sulfuric acid, washed with water, dried over 5A molecular sieves and filtered. The ir spectrum was identical with the published[10] spectrum of N-perchlorylpiperidine: nmr (CCl_4) δ 3.42 (m, 4H), and 1.85 ppm (broad m, 6H); ir (CCl_4) 1230, 1195, 1035, and 990 cm^{-1} ($N\text{-}ClO_3$).

b. Piperidine (0.208 g, 0.0024 mol) was added to 10 ml of water with stirring and cooling and 4 ml (0.0012 mol) of dichlorine heptoxide-carbon tetrachloride was added in portions. After five min the mixture was acidified and treated as above. Yields (nmr) are nearly quantitative in both procedures.

10. N-Perchloryl-2-ethylaziridine

2-Ethylaziridine (0.182 g, .0024 mol) was added to 10 ml of water and 4 ml (0.0012 mol) of dichlorine heptoxide-carbon tetrachloride solution was added in several portions. After five min the reaction mixture was acidified with dilute sulfuric acid and the organic layer was washed with water and dried over molecular sieves. Evaporation of solvent from a portion left a colorless oil which was vacuum transferred at 0.05 mm to give the analytical sample: nmr (CCl_4) δ 2.85 (broad m, 3H, N-ClO$_3$), 1.67 (m, 2H, ), and 1.30 ppm (m, 3H, $-CH_3$); ir (CCl_4) 1220, 1190, and [illegible] cm^{-1} ($>N-ClO_3$).

Anal. Calcd for $C_4H_8NClO_3$: C, 31.28; H, 5.25; Cl, 23.08; N, 9.12. Found: C, 30.76; H, 4.81; Cl, 23.57; N, 8.06.

11. N-Perchloryldiamylamine

The procedure was that outlined for 2-ethylaziridine. Spectral data are as follows: nmr (CCl_4) δ 3.27 (m, 4H, $-CH_2-N-ClO_3$); 1.47 (broad m, 12H, $-CH_2-$), and 0.93 ppm (m, 6H, $-CH_3$); ir (CCl_4) 1225, 1190, and [illegible] cm^{-1} ($N-ClO_3$).

12. N-Perchlorylbutylamine

n-Butyl amine (0.176 g, 0.0024 mol) was stirred with 10 ml of water and 4 ml of dichlorine heptoxide-carbon tetrachloride was added in portions. Stirring was continued for five min and then the solution was acidified with dilute sulfuric acid. The organic layer was dried over 5A molecular sieves, and was analyzed by ir and nmr. Evaporation of solvent from a portion gave a colorless oil which decomposed vigorously when air was admitted to the system. This instability has so far precluded elemental analysis: nmr (CCl_4) δ 5.77 (broad, 1H, N-H, disappears on addition of D_2O), 3.40 (t, 2H, CH_2-$NHClO_3$), 1.53 (m, 4H, $-CH_2CH_2-$), and 0.97 ppm (m, 3H, $-CH_3$); ir (CCl_4) 3270 ($\overset{H}{\overset{|}{N}}$-$ClO_3$), and 1240, 1200, 1020 cm^{-1} (N-ClO_3).

13. N-Perchloryl-t-butylamine

t-Butylamine (0.003 mol, 0.224 g) was added in four portions to a solution of dichlorine heptoxide in carbon tetrachloride (5 ml, 0.0015 mol) with stirring and cooling in a dry ice-carbon tetrachloride bath (≃20°). The mixture was stirred for ten min and then was acidified with dilute sulfuric acid. The organic layer was washed with water, dried over molecular sieves, and filtered. Evaporation of solvent from a portion left a colorless oil which was vacuum transferred at 0.02 mm to provide an analytical sample: nmr (CCl_4) δ 7.10 (broad, 1H,-NH-ClO_3), disappears upon shaking with D_2O), and 1.32 ppm (s, 9H, t-butyl); ir (CCl_4) 3280 (m),(NH), 1245 (s) 1190 (vs), and 1005 (s) cm^{-1} (N-ClO_3).

Anal. Calcd for $C_4H_{10}NClO_3$: C, 30.86; H, 6.46; N, 9.04. Found: C, 29.01; H, 6.44; N, 8.09.

14. Reaction of Dichlorine Heptoxide with Urethane

Urethane (0.216 g, 0.0024 mol) was added to 4 ml of dichlorine heptoxide-carbon tetrachloride solution (.0012 mol) and stirred for three hours. A viscous oil separated. The only product soluble in carbon tetrachloride, both before and after aqueous work-up, was ethyl perchlorate identified by comparison of nmr and ir spectra with an authentic sample. Experiments in aqueous solution gave no product soluble in carbon tetrachloride.

15. 2,2-Diperchloratopropane

Spectroquality acetone (0.034 g, 0.0006 mol) was added by syringe to 2 ml of dichlorine heptoxide-chloroform-d solution ($\simeq$0.0006 mol). After 15 min, nmr and ir spectra were identical with those reported[11]. No evidence for impurities was found and the yield was quantitative.

16. Reaction of 2,2-Diperchloratopropane with Inorganic Anions

Treatment of a solution of the diperchlorate in $CDCl_3$ (see above) with silver nitrate, sodium nitrite, sodium chlorate, sodium chloride, and potassium carbonate all regenerated acetone.

17. Reaction of 2,2-Diperchloratopropane with Triethylsilane

Reaction of 0.0006 mol of diperchlorate in $CDCl_3$ with triethylsilane (0.070 g, 0.0006 mol) for one hr gave a high yield of isopropyl perchlorate (identified by comparison of the nmr with an authentic sample).

18. Reaction of Dichlorine Heptoxide with the Potassium Salt of 2-Nitropropane

The potassium salt of 2-nitropropane (0.10 g, 0.0008 mol) was added to 0.0006 mol of dichlorine heptoxide in 2 ml of carbon tetrachloride. A blue solution formed, but the color faded in about an hour. The nmr spectrum showed that the products in solution consisted of 58 mol % acetone (δ 2.1), 29% 2-nitropropane (d, δ 1.5) and 9% 2,3-dimethyl-2,3-dinitrobutane (δ 1.7). Assignments were confirmed by the addition of authentic samples.

19. Reaction if Dichlorine Heptoxide with 1,1-Dinitroethane

1,1-Dinitroethane (0.07 g, 0.0006 mol) was added to 1 ml of a 1 *N* potassium hydroxide solution in methanol. Solvent was removed and the salt was dried for 1 hr at 1 mm. Carbon tetrachloride (0.5 ml) was added to desensitize the salt and then a solution of 0.0006 mol of dichlorine heptoxide in 2 ml of carbon tetrachloride was added at 0°. A blue solution formed. After 3 hrs at room temperature, the yellow salt of 1,1-dinitroethane was consumed, and the blue color of the solution faded. The nmr spectrum of the solution showed 70% 1,1-dinitroethane, and 30% 1-chloro-1,1-dinitroethane. Filtration through neutral alumima removed the dinitroethane, and the ir spectrum of the solution was identical with that of authentic 1-chloro-1,1-dinitroethane.

20. Reaction of Dichlorine Heptoxide with 1,1-Dinitrobutane

The above procedure using the potassium salt of 1,1-dinitrobutane gave only 1,1-dinitrobutane and 1-chloro-1,1-dinitrobutane.

21. Reaction of Dichlorine Heptoxide with Nitroethane

The sodium salt of nitroethane was prepared by heating 6 g of nitroethane (0.08 mol), 3.2 g (.08 mol) of sodium hydroxide and 30 ml of methanol for 2 hrs at 50°. The salt was filtered, washed with ether, and dried under vacuum. To a suspension of 3.45 g (0.0345 mol) of the salt in 25 ml of carbon tetrachloride at 0°, 0.038 mol of dichlorine heptoxide in 125 ml of carbon tetrachloride was added. The mixture was stirred for 1 hr at 0° and then warmed to ambient temperature. The nmr spectrum of the resulting solution showed only nitroethane and acetic acid.

22. Reaction of Dichlorine Heptoxide with Cyclohexene

Cyclohexene (0.75 g, 0.009 mol) was added dropwise at 0° to a stirred suspension of 2 g of potassium fluoride in a solution of 0.01 mol of dichlorine heptoxide in 35 ml of carbon tetrachloride. A colorless solution resulted. The solvent was distilled off at 100 mm.

The material darkened on attempted distillation at 50°. Molecular distillation at 0.005 mm, -70° coldfinger, yielded 0.05 ml of colorless liquid.

Anal. Calcd for $C_6H_{10}Cl_2O_3$: C, 35.82; H, 4.97. Found: C, 36.74; H, 4.66.

The infrared spectrum showed a strong doublet at 1225 and 1260 cm^{-1}.

III. REACTIONS OF CHLORATES

A. DISCUSSION

The chlorate ion could potentially function as an ambident anion in alkylation reactions. Attack of an alkylating agent at an oxygen atom of chlorate would give an organic chlorate, and attack at chlorine would give a perchlorylalkane.

$$R^{\oplus} + ClO_3^{\ominus} \longrightarrow R\text{-}OClO_2 \quad \text{or} \quad R\text{-}ClO_3$$

A literature search revealed only one reported example of this reaction, the preparation of triphenylmethyl chlorate from chlorotriphenylmethane and silver chlorate in carbon tetrachloride[15]. The chlorate was reported to be soluble in carbon tetrachloride, but no spectral or analytical data was given.

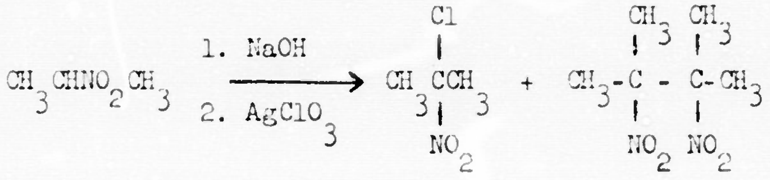
This reaction was repeated under the reported conditions and the nmr spectrum of the carbon tetrachloride solution showed an equimolar mixture of benzophenone and triphenylmethanol, with only minor amounts of other unidentified materials. Triphenylmethanol crystallized on concentration of the solvent and was identified by mixed melting point with an authentic sample. The benzophenone, isolated by distillation, contained a trace amount of a material that oxidized potassium iodide. The same products also were obtained when methylene chloride, 1,1,3-trichlorotrifluoromethane or acetonitrile were used as solvent, or when bromotriphenylmethane or sodium chlorate were used instead of the chloro compound or the silver salt, respectively.

Reactions of alkyl halides with silver chlorate were also complex. Suspensions of silver chlorate in halocarbon solvents were used, as well as solutions in acetonitrile. Acetonitrile took part in the reactions, yielding nitrogen-containing materials with spectra indicating $R\text{-}N{=}C(X)CH_3$ structures. Analytically pure compounds were not isolated, however, t-Butyl chloride and suspensions of silver chlorate in methylene chloride gave t-butanol and an orange-yellow gas, presumably chlorine dioxide. Alkyl iodides gave complex products that liberated elemental iodine even after the inorganic salts were removed and the organic materials were treated with sodium thiosulfate. Cyclohexyl iodide and silver chlorate in ether yielded a small amount of a white solid which analyzed as bicyclohexyl iodide.

These complex reactions suggest that carbonium ion attack on chlorate ion takes place mainly on the oxygens, to give alkyl chlorates as the initial intermediates. These can undergo homolytic cleavage to give chlorine dioxide and alkoxy radicals, which can take part in hydrogen abstractions, fragmentation reactions and rearrangements.

Brief attempts were made to prepare perchloryl bromide by reacting bromine with silver chlorate. In aqueous solution, the reaction gave hypobromous acid, identified by addition to cyclohexene to give 2-bromocyclohexanol. The reaction also was attempted in benzene, which might be perchlorylated by the product. Only bromobenzene was isolated. Control experiments to determine whether bromine (possibly silver catalyzed) or another intermediate was the brominating agent did not give unequivocal results. Bromine did not react with benzene under these conditions but in the presence of silver oxide it did react, but at a much slower rate.

An attempt was also made to utilize silver chlorate as a chlorylating agent in the same way that silver nitrite functions as a nitrating agent in the oxidative nitration reaction[16]. Only two products were formed from the salts of 2-nitropropane; 2-chloro-2-nitropropane and 2,3-dimethyl-2,3-dinitropropane.



$$CH_3CHNO_2CH_3 \xrightarrow[2.\ AgClO_3]{1.\ NaOH} CH_3\overset{Cl}{\underset{NO_2}{C}}CH_3 + CH_3-\overset{CH_3}{\underset{NO_2}{C}}-\overset{CH_3}{\underset{NO_2}{C}}-CH_3$$

Salts of 2-nitropropane are oxidized to 2,3-dimethyl-2,3-dinitropropane by a variety of oxidizing agents. Any acid-liberating reaction would give chloric acid which disproportionates to give chlorinating agents.

B. EXPERIMENTAL

1. Reaction of Chlorotriphenylmethane with Silver Chlorate

A suspension of 2.5 g of silver chlorate in a solution of 2.5 g of chlorotriphenylmethane in 30 ml of carbon tetrachloride was stirred at ambient temperature for 18 hrs. The nmr spectrum of the carbon tetrachloride solution showed an equimolar amount of triphenylmethanol and benzophenone. Triphenylmethanol precipitated when the solution was concentrated, and was characterized by mixed mp with an authentic sample. Benzophenone was further characterized by its infrared spectrum. Benzophenone isolated by molecular distillation from the mixture contained a small amount of oxidizing material, giving an iodometric titer of 0.64 meq/g.

Similar results were obtained using methylene chloride, 1,1,3-trichlorotrifluoroethane or acetonitrile as solvent. Bromotriphenylmethane gave the same products as chlorotriphenylmethane. The same products also were formed when bromotriphenylmethane was reacted with sodium chlorate and with silver bromate.

2. Reaction of Iodocyclohexane with Silver Chlorate

A suspension of 2.0 g (0.0104 mol) of silver chlorate in a solution of 2.0 g (0.0095 mol) of iodocyclohexane in 5 ml of ether was stirred for 20 hrs. The solution was filtered and the solids were washed with five 10 ml portions of ether. Iodine color in the filtrate was pronounced. Removal of the solvent and addition of methylene chloride gave 0.1 g of a white solid, mp 148°, phase change (granules to needles) at $130\text{-}135^\circ$.

Anal. Calcd for $C_{12}H_{21}I$: C, 49.3: H, 72: Found: C, 49.13; H, 6.81.

The methylene chloride solution was treated with 0.1 *N* sodium thiosulfate to remove iodine, but iodine color rapidly reappeared when the solvent was removed. The nmr spectrum was complex.

3. Reaction of Bromine with Silver Chlorate

a. In Benzene

Bromine (0.8 g, 0.005 mol) was added to a suspension of 1.91 g (0.01 mol) of silver chlorate in 10 ml of benzene at 0° with stirring. After 3 hrs at room temperature, the bromine color had disappeared. Filtration and removal of the excess benzene gave 0.9 g (57% yield) of bromobenzene, bp 52° (19 mm), identified by its nmr spectrum.

A solution of bromine in benzene, for comparison, did not decolorize in one week. A mixture of 1.16 g (0.01 eq) of silver oxide, 10 ml of benzene and 0.4 g (0.0025 mol) of bromine required 48 hrs for loss of bromine color. The latter reaction yielded 0.20 g of isolated bromobenzene.

b. In Water

Bromine (1.6 g, 0.01 mol) was added dropwise with stirring to a solution of 1.91 g (0.01 mol) of silver chlorate in 20 ml of water. Silver bromide precipitated immediately. The precipitate was filtered and air dried to yield 1.85 g (98% yield) of silver bromide. One third of the aqueous solution was vacuum distilled into a -80° receiver. Cyclohexene reacted instantly with this distillate to give 2-bromocyclohexanol, distilled in a molecular still at 50° (0.01 mm).

Anal. Calcd for $C_6H_{11}BrO$: C, 40.24; H, 6.19. Found: C, 40.72; H, 6.51.

4. Reaction of Silver Chlorate with 2-Nitropropane

2-Nitropropane (0.89 g, 0.01 mol) was dissolved in 11 ml of 1*N* sodium hydroxide with stirring at 50°. A solution of 3.8 g (0.02 mol) of silver chlorate in 30 ml of water was added dropwise sith stirring at 0° over a 15 min period. The mixture was stirred 1 hr at room temperature and was then extracted with methylene chloride. The methylene chloride solution, which contained suspended silver, was stripped under aspirator and ether was added. Filtration gave a clear solution, which was dried and stripped of solvent. The nmr spectrum of the residue showed only two products, 2,3-dimethyl-2,3-dinitrobutane (δ 1.7) and 2-chloro-2,2-nitropropane in a mol ratio of 4.5:1. Authentic samples of both compounds were added to the mixture to show identity.

IV. FLUORONITRO CHEMISTRY

A. DISCUSSION

1. Bis(fluorodinitromethyl)mercury

Bis(fluorodinitromethyl)mercury was recently synthesized[17], but except for halogenation, little work has been reported on its reactions. On the basis of the reactivity of bis(trinitroethyl)mercury with a variety of alkylating agents[18] this mercurial appeared to be a promising intermediate in the synthesis of other fluorodinitromethyl derivatives.

The preparation of bis(fluorodinitromethyl)mercury was simplified. In the original synthesis[17], mercuric oxide and fluorodinitromethane were reacted in wet diethyl ether for several days to give the compound. We found that using freshly precipitated mercuric oxide this reaction can be completed in a matter of minutes in water or methanol.

Bis(fluorodinitromethyl)mercury was found to be less reactive than anticipated in alkylation reactions. It did not react with allyl bromide, benzyl chloride or benzyl bromide at ambient temperatures. At higher temperatures (50-80°) these reactions yielded only tarry, unidentifiable products.

A suspension of the mercurial in methyl iodide was allowed to stand for several weeks before mercuric iodide began to deposit. Another six weeks were required to complete the reaction. 1-Fluoro-1,1-dinitroethane was obtained in 80% yield and the compound was identified by its reported nmr spectra:

$$Hg\left[CF(NO_2)_2\right]_2 + CH_3I \longrightarrow CH_3CF(NO_2)_2 + HgI_2$$

2. Reaction of Perchloryl Fluoride with 2-Fluoro-2,2-dinitroethanol

Before 2-fluoro-2,2-dinitroethyl perchlorate was obtained in the reaction of 2-fluoro-2,2-dinitroethanol with dichlorine heptoxide, several attempts were made to synthesize the compound by reacting the alcohol with perchloryl fluoride:

$$FC(NO_2)_2CH_2OH + FClO_3 \longrightarrow FC(NO_2)_2CH_2OClO_3 + HF$$

2-Fluoro-2,2-dinitroethanol did not react with perchloryl fluoride in carbon tetrachloride or dimethylformamide solution in the presence of equimolar amounts of pyridine. In methanolic sodium hydroxide, the reaction yielded fluorodinitroethyl methyl ether, identified by its reported[20] nmr spectra:

$$FC(NO_2)_2CH_2OH + FClO_3 \xrightarrow[CH_3OH]{NaOH} CH_3OCH_2CF(NO_2)_2 + NaClO_3$$

This product could be formed either from 2-fluoro-2,2-dinitroethyl perchlorate and methanol or from methyl perchlorate and 2-fluoro-2,2-dinitroethanol. This work was discontinued when 2-fluoro-2,2-dinitroethyl perchlorate was prepared from dichlorine heptoxide.

B. EXPERIMENTAL

1. Bis(fluorodinitromethyl)mercury

To a solution of 12.4 g (0.1 mol) of fluorodinitromethane in 150 ml of methylene chloride was added 10.8 g (0.05 mol) of yellow mercuric oxide and the mixture was stirred at 25° for three days. During this period mercuric oxide gradually disappeared and some bis(fluorodinitromethyl)mercury precipitated. The mixture was warmed to 40° and filtered. Bis(fluorodinitromethyl)mercury crystallized at 0° and was washed with cold methylene chloride to yield 16.7 g (75% yield) mp 145-6° (reported[17] mp 147°).

This material was obtained quantitatively by reacting freshly precipitated mercuric oxide with fluorodinitromethane (same amounts as above) in 75 ml of water. The reaction was completed in a few minutes. The clear solution was evaporated to dryness and the salt was crystallized from methylene chloride.

Similarly, the product was obtained quantitatively by reacting fluorodinitromethane with yellow mercuric oxide (same amounts as above) in 40 ml of methanol. The reaction was completed in 45 minutes.

2. 1-Fluoro-1,1-dinitroethane

A suspension of 1.1 g (0.0025 mol) of bis(fluorodinitromethyl)mercury in 4.0 ml of methyl iodide was allowed to stand at ambient temperature for 8 weeks. Red mercuric iodide gradually deposited and was filtered. Removal of excess of methyl iodide gave 0.28 g, (80% yield) of 1-fluoro-1,1-dinitroethane. Its proton spectrum was identifical with that reported[19].

3. 2-Fluoro-2,2-dinitroethyl Methyl Ether

Perchloryl fluoride was bubbled slowly into a solution of 1.0 g (0.025 mol) of sodium hydroxide and 3.9 g (0.025 mol) of 2-fluoro-2,2-dinitroethanol in 70 ml of methanol until the solution became neutral (45 min). The solution was evaporated and the residue was extracted to give 1.0 g of

2-fluoro-2,2-dinitroethyl methyl ether, bp 47° (5mm), lit[21] bp 47-48° (4mm). The proton nmr spectrum was identical with that reported[20].

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