

digital pH meter fitted with a combination electrode. The pK_a was taken to be equal to neutralization point. The results are listed in Table IV. Three or more titrations were used except where indicated. The precision of the results appears to equal the accuracy normally accepted for glass electrodes, pH meters, and commercial pH standards.

The pK_a 's of *N,N*-Diethylanilines (2). These values were obtained from titration curves of 0.001 *M* solutions of the aniline in a slight excess of HCl titrated with 0.001 *M* NaOH solution. If the amines were insoluble in water (less than 0.001 *M*), but soluble in a 10% (v/v) ethanol-water solution, then the same concentrations were used in that medium. The results are summarized in Table II.

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Registry No.—1a, 121-69-7; 1b, 701-56-4; 1c, 15799-79-8; 1d, 99-97-8; 1e, 121-72-2; 1f, 403-46-3; 1g, 2107-43-9; 1h, 698-69-1; 1i, 6848-13-1; 1j, 586-77-6; 1k, 168-62-0; 1l, 100-23-2; 1m, 619-31-8; 2a, 91-66-7; 2b, 15144-80-6; 2c, 92-18-2; 2d, 613-48-9; 2e, 606-46-2; 2h, 2873-89-4; 2i, 6375-75-3; 2j, 2052-06-4; 2k, 53142-19-1; 2m, 2216-16-2; 3a, 5382-46-2; 3b, 13330-09-1; 3c, 53142-20-4; 3d, 13330-17-1; 3e, 53247-79-3; 3f, 53142-21-5; 3g, 53142-22-6; 3h, 16657-26-4; 3i, 53142-23-7; 3j, 16657-27-5; 3k, 53142-24-8; 3l, 13330-12-6; 3m, 53142-25-9; 4a, 826-42-6; 4b, 53142-26-0; 4c, 53142-27-1; 4d, 53142-28-2; 4e, 53142-29-3; 4h, 22480-56-4; 4i, 53142-30-6; 4j, 53142-31-7; 4k, 53142-32-8; 4l, 24429-84-3; 4m, 53142-33-9; dimethyl sulfate, 77-78-1; diethyl sulfate, 64-67-5; *m*-anisidine, 536-90-3; *m*-nitroaniline, 99-09-2; *m*-toluidine, 108-44-1; *m*-bromoaniline, 591-19-5; *m*-fluoroaniline, 372-19-0; *m*-chloroaniline, 108-42-9; *p*-fluoroaniline, 371-40-4; *p*-anisidine, 104-94-9; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-chloroaniline, 106-47-8; *p*-bromoaniline, 106-40-1.

References and Notes

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- (2) National Science Foundation Cooperative Fellow, 1963-1965. A portion of this work was taken from the Ph.D. dissertation of T.L.K., University of Vermont, 1966. Address correspondence to this author at Ball State University.
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Reactions of Dichlorine Heptoxide and of Acyl Perchlorates with Ethers¹

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Spectral and solubility properties of acyl perchlorates, prepared from silver perchlorate and acid chlorides, are consistent with covalent mixed anhydride structures and not with acylium salts. Acetyl perchlorate in carbon tetrachloride reacted with tetrahydrofuran to give 4-perchloratobutyl acetate and with epoxides to give vicinal acetoxy perchlorates. Isopropyl ether gave isopropyl perchlorate and isopropyl acetate whereas isopropyl pentyl ether gave isopropyl perchlorate and pentyl acetate. Dimethoxymethane gave methyl acetate and methoxymethyl perchlorate. Benzoyl perchlorate and *N,N*-diethylcarbonyl perchlorate reacted with tetrahydrofuran to give the corresponding 4-perchloratobutyl esters. Dichlorine heptoxide in carbon tetrachloride reacted with tetrahydrofuran, trimethylene oxide, and 2,3-butene oxide to give 1,4-butane diperchlorate, 1,3-propane diperchlorate, and 2,3-butane diperchlorate, respectively. Ethyl ether gave ethyl perchlorate and a trace of ethyl acetate. Propyl ether gave propyl perchlorate and isopropyl perchlorate, whereas isopropyl ether gave isopropyl perchlorate and 2,2-diperchloratopropane. Dimethoxymethane and dichlorine heptoxide gave methyl perchlorate and methoxymethyl perchlorate.

Dichlorine heptoxide in carbon tetrachloride was shown recently to be an effective perchlorylating agent for alcohols² and for amines.³ The present paper deals with reactions of this little explored reagent and of related acyl perchlorates with ethers.

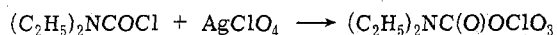
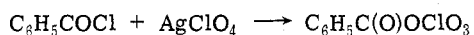
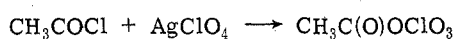
Acyl perchlorates⁴⁻⁶ have been used as acylating agents and are generally assumed⁷ to be perchlorate salts of acylium cations, $\text{RCO}^+\text{ClO}_4^-$. Solubilities in nonpolar solvents and spectral properties, which should readily differentiate between the salt structures and the corresponding covalent mixed anhydrides, RC(O)-OClO_3 , have not been reported.

The present work includes the characterization of acyl perchlorates and their utilization in ether cleavages to prepare alkyl perchlorate derivatives.

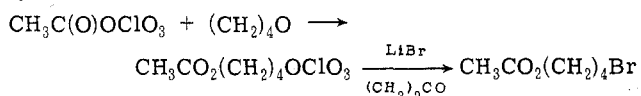
Acetyl chloride was found to react on mixing with a suspension of silver perchlorate in carbon tetrachloride to give a solution of acetyl perchlorate. The yield, determined by nmr, was essentially quantitative. The nmr chemical shift of the compound, δ 2.27, is close to those of acetyl halides and anhydrides, whereas values reported for CH_3CO^+ salts⁸ are approximately δ 4.0. The infrared spectrum of acetyl perchlorate shows a normal carbonyl peak at 1825

cm^{-1} rather than the peak at 2300 cm^{-1} assigned to CH_3CO^+ salts.⁸ Solutions of acetyl perchlorate in methylene chloride, chloroform, and ethylene chloride were also prepared by adding acetyl chloride to suspensions of silver perchlorate in these solvents. The solubility properties and spectra of acetyl perchlorate are thus clearly consistent with the covalent mixed anhydride structure $\text{CH}_3\text{C}(\text{O})\text{OCIO}_3$ and not with the salt structure.

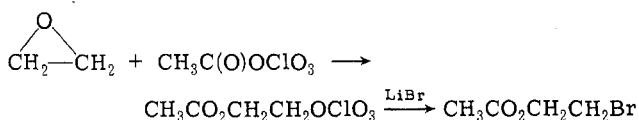
Electron-supplying substituents would increase the likelihood for an acyl perchlorate to exist as an acylium salt. Benzoyl perchlorate and *N,N*-diethylcarbamoyl perchlorate were therefore prepared from the corresponding acid chlorides and silver perchlorate in carbon tetrachloride. The compounds were soluble in carbon tetrachloride, and their spectral properties, described in the Experimental Section, are similar to those of acetyl perchlorate. Thus even an adjacent phenyl or amino group to stabilize positive charge is not sufficient to impart salt-like properties to an acyl perchlorate.



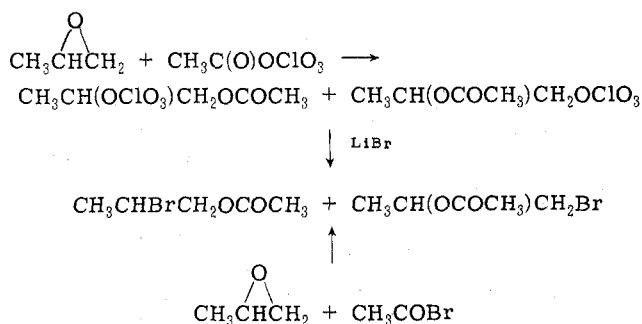
Acyl perchlorates in carbon tetrachloride reacted cleanly with cyclic ethers to give α,ω -acetoxy perchlorates. Thus, acetyl perchlorate in carbon tetrachloride reacted rapidly with tetrahydrofuran at 0° to give a 78% yield of 4-perchloratobutyl acetate, identified by ir and nmr spectra and by conversion to 4-bromobutyl acetate with lithium bromide in acetone. No 1,4-butane diperchlorate or 1,4-diacetoxybutane was formed, which would be expected if acetyl perchlorate equilibrates to dichlorine heptoxide and acetic anhydride.



Epoxides readily added acetyl perchlorate to give vicinal acetoxy perchlorates. Thus, ethylene oxide gave an 89% yield of 2-perchloratoethyl acetate, identified by spectra and by conversion to 2-bromoethyl acetate. Propylene

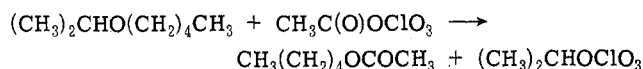
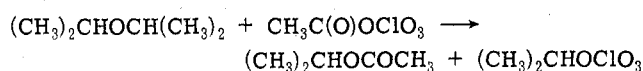


oxide gave an 80% yield of 2-perchlorato-1-propyl acetate and an 8% yield of 1-perchlorato-2-propyl acetate. This mixture reacted with lithium bromide in acetone to give the corresponding acetoxy bromides, which were also prepared independently from acetyl bromide and propylene oxide. Epichlorohydrin similarly gave a mixture of 1-per-

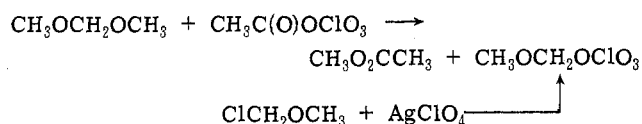


chlorato-3-chloro-2-propyl acetate and 2-perchlorato-3-chloro-1-propyl acetate. 2-Butene oxide gave 3-perchlorato-2-butyl acetate.

Secondary alkyl ethers were also cleaved readily. Thus, isopropyl ether reacted with acetyl perchlorate in carbon tetrachloride to give essentially quantitative yields of isopropyl perchlorate and isopropyl acetate. Similarly, isopropyl pentyl ether gave isopropyl perchlorate and pentyl acetate, with no detectable trace of pentyl perchlorate or isopropyl acetate. Simple primary dialkyl ethers were less readily cleaved by acetyl perchlorate. Ethyl ether, propyl ether, and pentyl ether gave ethyl acetate, propyl acetate, and pentyl acetate, respectively, in yields of 20–25%, but no alkyl perchlorates were detected.

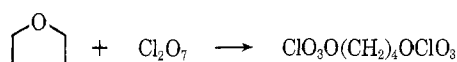


Acetals were also cleaved by acetyl perchlorate. Thus, dimethoxymethane gave methyl acetate and methoxymethyl perchlorate. The latter compound was also synthesized independently from silver perchlorate and chloromethyl methyl ether.



Benzoyl perchlorate and *N,N*-diethylcarbamoyl perchlorate also reacted with tetrahydrofuran to give 4-perchloratobutyl benzoate and 4-perchloratobutyl *N,N*-diethylcarbamate, respectively. Reaction of these products with lithium bromide gave the corresponding 4-bromobutyl esters. The acyl perchlorates also gave high yields of the corresponding methyl esters on addition of methanol.

Reactions of ethers with dichlorine heptoxide were studied using the standard 0.3 *M* reagent in carbon tetrachloride described previously.² Tetrahydrofuran was cleaved rapidly by this reagent to give an 83% yield of 1,4-butane diperchlorate. Trimethylene oxide gave 1,3-propanedipерchlorate in 55% yield.

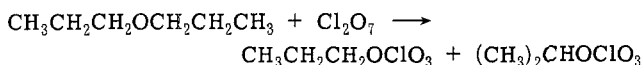


Epoxides also reacted with dichlorine heptoxide. An excess of dichlorine heptoxide reacted with 2-butene oxide to give a 30% yield of 2,3-butane diperchlorate, but stoichiometric mixtures of the reagents gave a mixture of products, which appeared to contain oligomers. Regardless of the ratio of reactants, ethylene oxide, propylene oxide, and epichlorohydrin gave complex mixtures which showed perchlorate bands in their ir spectra.

Simple aliphatic ethers were also cleaved with dichlorine heptoxide. The reaction of ethyl ether, monitored by nmr, was found to be rapid initially, yielding 33% ethyl perchlorate. The formation of ethyl perchlorate then became progressively slower; the yield was 53% in 2 hr, 59% in 18 hr, and 67% in 66 hr. Apparently perchloric acid, formed in a side reaction, reduces the rate by complexing with unreacted ether. An acidic hydrogen appeared at δ 15.5–16.0, accompanied by a downfield shift of 0.28 ppm for the methylene hydrogens of ether. A 2–3% yield of ethyl acetate was also formed.

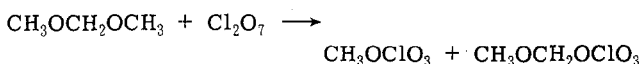
A similar effect was observed in the reaction of propyl ether with dichlorine heptoxide. In 15 hr, a 49% yield of

propyl perchlorate was obtained, as well as a 13% yield of isopropyl perchlorate.

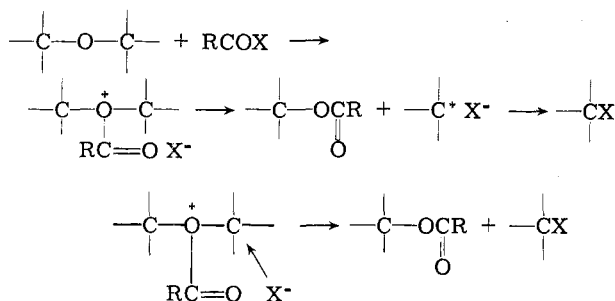


Isopropyl ether was also cleaved by dichlorine heptoxide in carbon tetrachloride to give a 10% yield of isopropyl perchlorate, but the major product was 2,2-diperchloratopropane, identified spectrally and by conversion to the 2,4-dinitrophenylhydrazone.⁹ Isopropyl pentyl ether also gave this compound as well as low yields of isopropyl perchlorate and pentyl perchlorate.

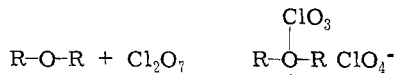
Dimethoxymethane was cleaved by dichlorine heptoxide to give a 78% yield of methoxymethyl perchlorate and an 86% yield of methyl perchlorate in 5 days.



Ether cleavages by acylium ions and related species are generally assumed to take place through oxonium ion intermediates.¹⁰⁻¹² Cleavage of the intermediates may take place by a spectrum of mechanisms ranging from SN1 to SN2, depending on the carbonium ion stability of the substrate fragment and the strength of the nucleophile, as well as steric factors.



Lewis acid catalyzed cleavages of secondary and tertiary ethers by acid halides appear to go by an SN1 type mechanism whereas primary ethers give SN2 type products. Mechanisms of cleavages by mixed sulfonic carboxylic anhydrides are shifted toward the SN1 end of the mechanistic spectrum because of the weak nucleophilic properties of sulfonate anions.¹² This shift would be expected to be more pronounced for acyl perchlorates. A similar mechanism for cleavages by dichlorine heptoxide would involve a perchloroxyoxonium ion intermediate.



This strongly electron-withdrawing group on the oxonium ion should further enhance the tendency toward an SN1-like cleavage. The formation of a significant amount of isopropyl perchlorate from propyl ether and dichlorine heptoxide is thus noteworthy, since isopropyl derivatives were not found in the reaction of propyl ether with acetyl tosylate.¹²

The formation of oxidation products from dichlorine heptoxide, particularly with isopropyl ethers, is also consistent with a perchloroxyoxonium ion intermediate, which has similarities to intermediates proposed for the oxidation of ethers by bromine¹³ and of alcohols by chromic acid.¹⁴ Direct oxidation by dichlorine heptoxide cannot be ruled out, however.

Although alkyl perchlorates are sensitive explosives as neat materials, they are insensitive when sufficiently diluted in an inert solvent and have been shown to function as potent alkylating agents in solution.² The acyl perchlorate

and dichlorine heptoxide reagents used in this work were prepared as dilute solutions. With reasonable precautions, the methods provide practical means of introducing functionalized alkoxy moieties in synthesis.

Experimental Section

Nmr spectra were recorded with a Varian T-60 spectrometer and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. A Varian 920 gas chromatograph with a 5 ft \times 0.25 in. column of 12% QF-1 on chromosorb W was used for glpc separations.

Caution! Neat alkyl perchlorates are sensitive explosives, and the previously noted² precautions should be observed. Similar safeguards should be observed with acyl perchlorates.

Acetyl Perchlorate. Acetyl chloride (0.0785 g, 1 mmol) was added in two portions to a stirred suspension of 0.3 g (1.5 mmol) of silver perchlorate in 4 ml of carbon tetrachloride at 0°. The reaction mixture was stirred for 30 min and filtered to give a colorless solution which fumed in moist air. The yield was 96%, determined by nmr using ethylene chloride as internal standard. Solutions of acetyl perchlorate were stable for several days at room temperature. The same procedure was used to prepare acetyl perchlorate solutions in methylene chloride, chloroform, and ethylene chloride. Nmr (CCl₄) δ 2.27 ppm (s); ir (CCl₄) 1825 (vs), 1370 (w), 1285 (vs), 1160 (m), 1040 (s), 1095 cm⁻¹ (m).

Reaction of Acetyl Perchlorate with Methanol. Excess methanol (1 ml) was added with stirring to 1 mmol of acetyl perchlorate in 4 ml of carbon tetrachloride at 0°. The mixture was stirred for 30 min, washed with water, and dried. Nmr and ir spectra showed only methyl acetate obtained in 90% yield.

Reaction of Acetyl Perchlorate with Tetrahydrofuran. Tetrahydrofuran (0.072 g, 1 mmol) was added to 1 mmol of acetyl perchlorate in 4 ml of carbon tetrachloride with stirring at 0°. The reaction mixture was stirred for 30 min, washed with water, and dried. The only product in the carbon tetrachloride layer was 4-perchloratobutyl acetate in 78% yield (chlorobenzene as internal nmr standard): nmr (CCl₄) δ 4.52 (t, 2 H, $J = 6$ Hz, CH₂OCIO₃), 4.38 (t, 2 H, $J = 6$ Hz, CH₂OAc), 2.02 (s, 3 H, CH₃CO), 1.88 ppm (m, 4 H, CH₂CH₂); ir (CCl₄) 1740 (C=O), 1280, 1240, 1040 cm⁻¹ (OCIO₃).

The solution of 4-perchloratobutyl acetate was added dropwise at room temperature to 5 ml of a 10% solution of lithium bromide in acetone. After 30 min, the reaction mixture was washed with water and dried. Evaporation of solvent gave 0.146 g (75%) of 4-bromobutyl acetate: nmr (CCl₄) δ 4.02 (t, 2 H, $J = 6$ Hz, CH₂OAc), 3.37 (t, 2 H, $J = 6$ Hz, CH₂Br), 2.00 (s, 3 H, CH₃CO), 1.87 ppm (m, 4 H, CH₂CH₂); ir (CCl₄) 1740, 1240 cm⁻¹ (COO).

Anal. Calcd for C₆H₁₁BrO₂: C, 36.92; H, 5.64; Br, 40.99. Found: C, 36.69; H, 5.38; Br, 40.88.

Reaction of Acetyl Perchlorate with Isopropyl Ether. Isopropyl ether (0.102 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in 4 ml of carbon tetrachloride with stirring at 0°. Nmr spectra indicated completion of reaction in less than 10 min. The reaction mixture was washed with water and dried. Isopropyl perchlorate² and isopropyl acetate were obtained in 97% yield, identified by comparison with authentic samples by ir and nmr.

Reaction of Acetyl Perchlorate with Isopropyl Pentyl Ether. By the above procedure, acetyl perchlorate and isopropyl pentyl ether gave isopropyl perchlorate and *n*-pentyl acetate in 95 \pm 5% yield. Pentyl perchlorate and isopropyl acetate were not observed. Control experiments indicated that 1-2% of these components would have been detected.

Reaction of Acetyl Perchlorate with Primary Ethers. The appropriate primary ether (1 mmol) was added to 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0°. The solution immediately became yellow-orange and some insoluble material was formed. The only products observed either before or after treatment with water were the *n*-alkyl acetate (20-25% yield) and starting material (45-50%). Thus, ethyl acetate, propyl acetate, and pentyl acetate were obtained from ethyl, propyl, and pentyl ethers, respectively. Increasing the reaction time to 48 hr did not improve the yield and a dark tarry residue was deposited. In no case was any alkyl perchlorate detected.

Reaction of Acetyl Perchlorate with Ethylene Oxide. Ethylene oxide (0.088 g, 2 mmol) was added at 0° with stirring to a solution of 2 mmol of acetyl perchlorate in 10 ml of CCl₄. The reaction mixture was stirred for 30 min, washed with water, and dried. The nmr spectrum of the solution showed an 89% yield of 2-perchlora-

toethyl acetate (C_6H_5Cl as quantitative standard): nmr (CCl_4) δ 4.60 (m, 2 H, A_2B_2 , CH_2OCIO_3), 4.27 (m, 2 H, A_2B_2 , CH_2OAc)? 2.10 ppm (s, 3 H, CH_3COO); ir (CCl_4) 1750 (COO), 1285, 1240, 1040 cm^{-1} ($OCIO_3$). Treatment of the CCl_4 solution with an excess of 10% lithium bromide in acetone gave 2-bromoethyl acetate (81%): nmr (CCl_4) δ 4.22 (t, 2 H, $J = 6.5$ Hz, CH_2OAc), 3.37 (t, 2 H, $J = 6.5$ Hz, CH_2Br), 2.00 ppm (s, 3 H, CH_3COO). The infrared spectrum was identical with that of an authentic sample.

Reaction of Acetyl Perchlorate with Propylene Oxide. Propylene oxide (0.058 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate at 0° with stirring. After 30 min, the reaction mixture was washed with water and dried. Nmr spectra showed two compounds identified as 2-perchlorato-1-propyl acetate (80% yield) and 1-perchlorato-2-propyl acetate (8% yield): nmr (CCl_4) of 2-perchlorato-1-propyl acetate, δ 5.17 (m, 1 H, $CHOCIO_3$), 4.13 (m, 2 H, CH_2OAc), 2.07 (s, 3 H, $OCOCCH_3$), 1.52 ppm (d, 3 H, $J = 7$ Hz, CH_3CH); nmr of 1-perchlorato-2-propyl acetate; δ 5.10 (m, $CHOAc$), 4.48 (m, CH_2OCIO_3), 2.07 (s, CH_3COO), 1.33 ppm (d, $J = 6$ Hz, CH_3CH). The ir spectrum of the mixture had a strong carbonyl band at 1755 cm^{-1} and perchlorate bands at 1280, 1240, and 1040 cm^{-1} .

The mixture of isomers in carbon tetrachloride was added dropwise to 5 ml of 10% bromide in acetone at room temperature. A mixture of 2-bromopropyl acetate (95%) and 1-bromo-2-propyl acetate (5%) was obtained. The structures were assigned by comparison of nmr and ir spectra with those of an independently prepared mixture described below.

Reaction of Acetyl Bromide with Propylene Oxide. Propylene oxide (2.90 g, 0.05 mol) dissolved in 10 ml of carbon tetrachloride was added dropwise (1 hr) to a solution of 6.15 (0.05 mol) of acetyl bromide in 50 ml of carbon tetrachloride with a catalytic quantity of zinc bromide. The reaction mixture was then stirred for 1 hr, washed with water, and dried. Evaporation of the solvent and distillation of the residual oil gave 6.55 g (72%) of a mixture of bromo acetates, bp $54-58^\circ$ (10 mm). The ratio of 1-bromo-2-propyl acetate to 2-bromo-1-propyl acetate was 2:1. Nmr (CCl_4) of 1-bromo-2-propyl acetate δ 4.87 (septet, 1 H, $CHOAc$), 3.32 (d, 2 H, $J = 5$ Hz, CH_2Br), 1.32 ppm (d, 3 H, $J = 6$ Hz, CH_3CH); 1-bromo-2-propyl acetate nmr (CCl_4) δ 4.05 (m, 3 H, $CHBr$, and CH_2OAc), 1.65 ppm (d, 3 H, $J = 6.5$ Hz, CH_3).

Anal. Calcd for $C_5H_9BrO_2$: C, 33.17; H, 5.01; Br, 44.13. Found: C, 33.11; H, 4.98; Br, 44.16.

Reaction of Acetyl Perchlorate with Epichlorohydrin. Epichlorohydrin (0.0925 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0° . After 30 min the reaction mixture was washed with water and dried. The nmr spectrum showed 1-perchlorato-3-chloro-2-propyl acetate and 2-perchlorato-3-chloro-1-propyl acetate in the ratio 1.4:1. The total yield was 93% using chlorobenzene as a quantitative nmr standard: 1-perchlorato-3-chloro-2-propyl acetate nmr (CCl_4) δ 5.10 (m, 1 H, $CHOAc$), 4.68 (d, 2 H, $J = 5$ Hz, CH_2OCIO_3), 3.65 (d, 2 H, $J = 6$ Hz, CH_2Cl), 2.13 ppm (s, 3 H, CH_3COO); 1-perchlorato-2-chloro-1-propyl acetate nmr (CCl_4) δ 5.20 (m, 1 H, $CHOCIO_3$), 4.37 (m, 2 H, CH_2OAc), 3.78 (d, 2 H, $J = 6$ Hz, CH_2Cl), 2.08 ppm (s, 3 H, CH_3COO). The infrared spectrum of the mixture of products showed strong bands at 1755 ($C=O$) and 1280, 1240, 1050 cm^{-1} ($OCIO_3$).

The solution was added dropwise to 5 ml of a 10% solution of lithium bromide in acetone with stirring at room temperature. The reaction mixture was washed with water and dried. Evaporation of solvent gave 0.186 g (87%) of a mixture of 1-bromo-3-chloro-2-propyl acetate and 2-bromo-3-chloro-1-propyl acetate.

Reaction of Acetyl Perchlorate with 2-Butene Oxide. 2-Butene oxide (0.072 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate with stirring at 0° . After 30 min the solution was washed with water and dried to give a carbon tetrachloride solution of 3-perchlorato-2-butyl acetate in 73% yield: nmr (CCl_4) δ 4.92 (m, 2 H, $CHOAc$, $CHOCIO_3$), 2.03 (s, 3 H, CH_3COO), 1.48 (d, 3 H, $J = 6.5$ Hz, $CH_3CHOCIO_3$), 1.28 ppm (d, 3 H, $J = 7$ Hz, CH_3CHOAc); ir (CCl_4) 1745 ($C=O$), 1280, 1240, 1040 cm^{-1} ($OCIO_3$).

Reaction of Acetyl Perchlorate with Dimethoxymethane. Dimethoxymethane (0.076 g, 1 mmol) was added to a solution of 1 mmol of acetyl perchlorate in carbon tetrachloride with stirring at 0° . After 15 min, nmr showed the disappearance of the starting materials and the formation of methyl acetate (95%) and methoxymethyl perchlorate (83%). The yields were determined by nmr using chloroform as a quantitative standard. Washing with water and filtration of the solution through silica gel to remove formaldehyde polymer gave a solution of methyl acetate (78%) identified by

comparison of spectral and gas chromatographic parameters with those of an authentic sample.

Reaction of Chloromethyl Methyl Ether with Silver Perchlorate. Chloromethyl methyl ether (0.0805 g, 1 mmol) was added to a stirred suspension of 0.30 g (1.5 mmol) of silver perchlorate in 4 ml of carbon tetrachloride. After 30 min, nmr spectra indicated that starting material was consumed, and methoxymethyl perchlorate, identical with the material above, was formed in 81% yield. Solutions fumed in moist air: nmr (CCl_4) δ 5.57 (s, 2 H, CH_2), 3.67 ppm (s, 3 H, CH_3); ir (CCl_4) 1280, 1260, 1050 cm^{-1} ($OCIO_3$).

Benzoyl Perchlorate. Benzoyl chloride (0.703 g, 5 mmol) in 5 ml of carbon tetrachloride, was added dropwise at 0° with stirring to 1.45 g (7 mmol) of silver perchlorate suspended in 10 ml of carbon tetrachloride. Stirring was continued for 2 hr. Filtration under anhydrous conditions gave a colorless solution of benzoyl perchlorate which fumed in moist air. The yield was 98% using cyclohexane as quantitative internal nmr standard: nmr (CCl_4) δ 7.4-8.1 (m, Ar); ir (CCl_4) 3080 (w), 1780 (vs), 1590 (m), 1450 (m), 1280 (vs), 1225 (s), 1180 (m), 1050 (s), 950 cm^{-1} (vs).

Reaction of Benzoyl Perchlorate with Methanol. Excess methanol (0.96 g, 30 mmol) was added to 5 mmol of benzoyl perchlorate in carbon tetrachloride prepared as above. The reaction mixture was stirred for 10 min, washed with water, and dried. The only product was methyl benzoate (95%).

Reaction of Benzoyl Perchlorate with Isopropyl Ether. Isopropyl ether (0.50 g, 5 mmol) was added to 5 mmol of benzoyl perchlorate in carbon tetrachloride at room temperature. After 3 hr the reaction, monitored by nmr, was complete and gave isopropyl perchlorate and isopropyl benzoate each in 98% yield (ethylene chloride as quantitative internal nmr standard). The structure of the products was confirmed by comparison of nmr and ir spectra with those of authentic isopropyl perchlorate and isopropyl benzoate.

Reaction of Benzoyl Perchlorate with Tetrahydrofuran. A solution of 0.36 g (5 mmol) of tetrahydrofuran in 2 ml of carbon tetrachloride was added dropwise with stirring to 5 mmol of benzoyl perchlorate in carbon tetrachloride at 0° . After 30 min the reaction mixture was washed with water and dried. Nmr spectra of the carbon tetrachloride solution showed 4-perchloratobutyl benzoate (83%) contaminated by a small quantity of polymeric materials showing a broad band in the ether region (3.50 ppm). Filtration through a short column of silica gel removed the latter: nmr (CCl_4) δ 7.2-8 (m, 5 H, Ar), 4.57 (m, 2 H, CH_2OCIO_3), 4.32 (m, 2 H, $CH_2OCOC_6H_5$), 1.95 ppm (broad m, 4 H, CH_2CH_2); ir (CCl_4) 1735 ($C=O$), 195, 1260 cm^{-1} ($OCIO_3$).

The carbon tetrachloride solution was added dropwise at room temperature to 20 ml of a 10% solution of lithium bromide in acetone. The reaction mixture was stirred for 30 min, washed with water, and dried. Evaporation of solvent gave 0.905 g (71%) of 4-bromobutyl benzoate: nmr (CCl_4) δ 7.1-7.8 (m, 5 H, Ar), 4.20 (m, 2 H, $CH_2OCOC_6H_5$), 3.33 (m, 2 H, CH_2Br), 1.93 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 1720 cm^{-1} ($C=O$).

Anal. Calcd for $C_{11}H_{13}BrO_2$: C, 51.40; H, 5.10; Br, 31.10. Found: C, 51.42; H, 4.93; Br, 31.20.

***N,N*-Diethylcarbamoyl Perchlorate.** Diethylcarbamoyl chloride (0.675 g, 5 mmol) dissolved in 5 ml of carbon tetrachloride was added dropwise with stirring, over a 10-min period, to 1.20 g (6 mmol) of silver perchlorate suspended in 15 ml of carbon tetrachloride at 0° . The reaction mixture was stirred for 30 min and 10 ml of carbon tetrachloride was added to give a solution of *N,N*-diethylcarbamoyl perchlorate in 82% yield (ethylene chloride as quantitative nmr standard): nmr (CCl_4) δ 3.33 (q, 4 H, $J = 7$ Hz, NCH_2), 1.25 ppm (t, 6 H, $J = 7$ Hz, CH_3); ir (CCl_4) 2960 (m), 1782 (vs), 1480 (m), 1460 (m), 1420 (m), 1390 (m), 1370 (w), 1320 (w), 1280 (vs), 1220 (m), 1140 (s), 1100 (s), 1050 (s), 1020 (m), 960 (w), 900 cm^{-1} (s).

Reaction of *N,N*-Diethylcarbamoyl Perchlorate with Methanol. Excess methanol (0.96 g, 0.03 mol) was added to a solution of *N,N*-diethylcarbamoyl perchlorate in carbon tetrachloride, prepared as above, with stirring at 0° . The reaction mixture was stirred for 30 min, washed with water, and dried. Evaporation of solvent gave 0.517 g (96%) of methyl *N,N*-diethylcarbamate identified by spectral comparison with an authentic sample described below.

Methyl *N,N*-Diethylcarbamate. Methyl chloroformate (9.45 g, 0.1 mol) was added dropwise with stirring at $0-5^\circ$ to a solution of 7.3 g (0.1 mol) of diethylamine and 3.9 g (0.1 mol) of sodium hydroxide in 25 ml of water. The reaction mixture was stirred for 30 min and extracted with methylene chloride and distilled to give 10.3 g (79%) of methyl *N,N*-diethylcarbamate, bp $66-68^\circ$ (26 mm):

nmr (CCl₄) δ 3.57, (s, 3 H, OCH₃), 3.17 (q, 4 H, J = 7 Hz, NCH₂); 1.10 ppm (t, 6 H, J = 7 Hz, CH₃); ir (CCl₄) 1700, 1280, 1180 cm⁻¹ (OCN).

Reaction of *N,N*-Diethylcarbamoyl Perchlorate with Tetrahydrofuran. A solution of 0.36 g (5 mmol) of tetrahydrofuran in 3 ml of carbon tetrachloride was added dropwise with stirring at 0° to a solution of *N,N*-diethylcarbamoyl perchlorate prepared as above. After 30 min the solution was washed with water and dried to give a solution of 4-perchloratobutyl *N,N*-diethylcarbamate (75% yield by nmr, chlorobenzene quantitative standard): nmr (CCl₄) δ 4.52 (t, 2 H, J = 6 Hz, CH₂OClO₃), 4.00 (t, J = 6 Hz, 2 H, CH₂OCON), 3.18 (q, 4 H, J = 6.5 Hz, CH₂N), 1.83 (m, 4 H, CH₂CH₂), 1.12 ppm (t, 6 H, J = 6.5 Hz, CH₃); ir (CCl₄) 1695 (OCN), 1280, 1040 cm⁻¹ (OClO₃).

The carbon tetrachloride solution of the product was added to 20 ml of a 10% solution of lithium bromide in acetone. After 30 min, the reaction mixture was washed with water and dried. Evaporation of solvent gave 0.176 g (70%) of 4-bromobutyl *N,N*-diethylcarbamate as a pale yellow oil. An analytical sample was collected by glpc using a 6 ft \times 1/4 in. aluminum column packed with 10% QF-1 on 60-80 mesh chromosorb W at 150°: nmr (CCl₄) δ 3.97 (t, 2 H, J = 6 Hz, CH₂OCON), 3.33 (t, 2 H, J = 6 Hz, CH₂Br), 3.17 (q, 4 H, J = 7 Hz, NCH₂), 1.83 (m, 4 H, CH₂CH₂), 1.10 ppm (t, 6 H, J = 7 Hz, NCH₂CH₃); ir (CCl₄) 1695, 1180 cm⁻¹ (OCN).

Anal. Calcd for C₉H₁₈BrNO₂: C, 42.86; H, 7.2; Br, 31.69; N, 5.6. Found: C, 42.56; H, 6.87; Br, 31.58; N, 5.74.

Reaction of Ethyl Ether with Dichlorine Heptoxide. Ethyl ether (0.0888 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride² at room temperature. Aliquots were removed periodically, washed with water, dried, and analyzed by nmr for ethyl perchlorate² (per cent yield) and ethyl ether (per cent recovery) respectively as follows: 10 min, 33, 57; 2 hr, 53, 37; 18 hr, 59, 26; 66 hr, 67, 18. Ethyl acetate was also formed, with a yield of 2-3% in 66 hr. A small acid signal also appeared (before water treatment of the aliquots) at δ 15.5-16.0 as the reaction progressed, and its formation was accompanied by a downfield shift of 0.28 ppm for the methylene hydrogens of ethyl ether.

Reaction of Propyl Ether with Dichlorine Heptoxide. Propyl ether (0.1224 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and the reaction was followed by nmr, as in the preceding example. In 15 hr, the spectrum showed propyl perchlorate² (49% yield), isopropyl perchlorate² (13%), and propyl ether (33%); in 66 hr, no significant further changes took place. An acid signal (δ 15.9) and downfield shift of the α -hydrogen signal of propyl ether were observed before water treatment of the samples. In a control experiment, no reaction was observed between propyl perchlorate and propyl ether under the same conditions.

Reaction of Tetrahydrofuran with Dichlorine Heptoxide. Tetrahydrofuran (0.176 g, 2.4 mmol) in 1 ml of carbon tetrachloride was added dropwise with stirring at 0° to 8 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. After 15 min, the solution was washed with water and dried over magnesium sulfate to give a solution of 1,4-butane diperchlorate² (83% yield using chlorobenzene as quantitative nmr standard). No other products were detected by nmr or ir.

Reaction of Trimethylene Oxide with Dichlorine Heptoxide. 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 0.3 M dichlorine heptoxide in carbon tetrachloride at 0°. After 30 min, the solution was washed with water, dried over sodium sulfate, and filtered through silica gel to remove small quantities of polymeric material. The nmr spectrum of the resulting solution showed only 1,3-propane diperchlorate (55% yield using chlorobenzene as quantitative standard): nmr (CCl₄) δ 4.63 (t, 4 H, J = 6 Hz, CH₂OClO₃), 2.28 ppm (quintet, 2 H, J = 6 Hz, C-CH₂-C); ir (CCl₄) 1290, 1270, 1230, 1010, 1030 cm⁻¹ (OClO₃).

Reaction of Isopropyl Pentyl Ether with Dichlorine Heptoxide. Isopropyl pentyl ether (0.078 g, 0.6 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide solution in carbon tetrachloride for 18 hr at room temperature. A small quantity of a colorless oil separated, soluble in CDCl₃, which was identified as 2,2-diperchloratopropane by nmr.⁹ The carbon tetrachloride layer was washed with water and dried. Nmr showed a 22% yield of isopropyl perchlorate, 11% pentyl perchlorate, and 18% isopropyl pentyl ether.

Reaction of Dimethoxymethane with Dichlorine Heptoxide. Dimethoxymethane (0.091 g, 1.2 mmol) was added to 4 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. The reaction, followed by nmr, was complete in 5 days to give methyl perchlorate (86%) and methoxymethyl perchlorate (78%).

Reaction of Isopropyl Ether with Dichlorine Heptoxide. Isopropyl ether (0.061 g, 0.6 mmol) was added to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride with stirring at 0°. In 5 min, the solution became pale yellow-green, and after 10-15 min, a colorless oil separated and the solution became colorless. The solution contained isopropyl perchlorate (10% yield by nmr) and isopropyl ether (25%). The oil was identified as 2,2-diperchloratopropane:⁹ nmr (CDCl₃) δ 2.60 ppm (s). In another experiment, water and 2,4-dinitrophenylhydrazine reagent were added to the crude product mixture to give 0.086 g (60%) of acetone 2,4-dinitrophenylhydrazone.

Reaction of Epoxides with Dichlorine Heptoxide. 2-Butene oxide (0.0353 g, 0.49 mmol) was added with stirring to 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at 0°. The solution was stirred 24 hr at ambient temperature. The solution was separated from a dark insoluble oil, washed with water, and dried over sodium sulfate. Spectra were consistent with the 2,3-butane diperchlorate structure (30% yield by nmr): nmr (CCl₄) δ 1.58 (d, 6 H, J = 6 Hz, CH₃), 5 ppm (m, 2 H, CH); ir (CCl₄) 1280, 1240, 1040 cm⁻¹ (ClO₄).

Equimolar amounts of 2-butene oxide and dichlorine heptoxide by this procedure gave a mixture with two additional methyl doublets.

Ethylene oxide, propylene oxide, and epichlorohydrin reacted on mixing with dichlorine heptoxide, but nmr spectra indicated complex mixtures. The ir spectra showed strong perchlorate bands at approximately 1280, 1240, and 1020 cm⁻¹.

Registry No.—Acetyl perchlorate, 2889-74-9; acetyl chloride, 75-36-5; silver perchlorate, 7783-93-9; methanol, 67-56-1; tetrahydrofuran, 109-99-9; 4-perchloratobutyl acetate, 53209-91-9; 4-bromobutyl acetate, 4753-59-7; isopropyl ether, 108-20-3; isopropyl pentyl ether, 5756-37-6; ethylene oxide, 75-21-8; 2-perchloratoethyl acetate, 53209-92-0; 2-bromoethyl acetate, 927-68-4; propylene oxide, 75-56-9; 2-perchlorato-1-propyl acetate, 53209-93-1; 1-perchlorato-2-propyl acetate, 53209-94-2; 1-bromo-2-propyl acetate, 10299-39-5; 2-bromo-1-propyl acetate, 592-19-8; epichlorohydrin, 106-89-8; 1-perchlorato-3-chloro-2-propyl acetate, 53209-95-3; 1-perchlorato-2-chloro-1-propyl acetate, 53209-96-4; 2-butene oxide, 3266-23-7; 3-perchlorato-2-butyl acetate, 53209-97-5; dimethoxymethane, 109-87-5; chloromethyl methyl ether, 107-30-2; methoxymethyl perchlorate, 17810-45-6; benzoyl perchlorate, 53209-98-6; benzoyl chloride, 98-88-4; 4-perchloratobutyl benzoate, 53209-99-7; 4-bromobutyl benzoate, 36978-34-4; *N,N*-diethylcarbamoyl perchlorate, 53210-00-7; diethylcarbamoyl chloride, 88-10-8; *N,N*-diethyl methylcarbamate, 4652-44-2; methyl chloroformate, 79-22-1; diethylamine, 109-89-7; 4-perchloratobutyl *N,N*-diethylcarbamate, 53210-01-8; *N,N*-diethyl 4-bromobutylcarbamate, 53210-02-9; ethyl ether, 60-29-7; dichlorine heptoxide, 10294-48-1; propyl ether, 111-43-3; trimethylene oxide, 503-30-0; 1,3-propane diperchlorate, 53210-03-0; 2,2-diperchloratopropane, 28078-46-8; 2,3-butane diperchlorate, 53210-04-1.

References and Notes

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