

Reactions of Dichlorine Heptoxide with Alcohols¹

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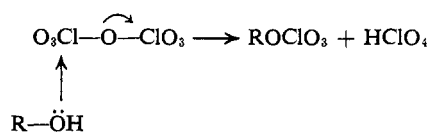
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Abstract: Dichlorine heptoxide in carbon tetrachloride is a general reagent for converting alcohols to alkyl perchlorates. Simple primary alcohols, as well as ethylene glycol, 1,4-butanediol, 2,2,2-trifluoroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol, 2-(2-fluoro-2,2-dinitroethoxy)ethanol, allyl alcohol, and propargyl alcohol gave corresponding unrearranged perchlorates. 2-Propanol gave isopropyl perchlorate. 2-Hexanol and 3-hexanol gave mainly the unrearranged perchlorates, with the corresponding ketones, and in the latter case the isomeric secondary perchlorate as by-products. The sodium salts of perfluoro-*tert*-butyl alcohol, 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol gave the corresponding tertiary perchlorates. The perchlorates, obtained as carbon tetrachloride solutions, could be used directly as alkylating agents. Lithium bromide with tetramethylene diperchlorate, ethylene diperchlorate, pentyl perchlorate, and propargyl perchlorate gave the corresponding bromides. Ethers were prepared by the reactions of pentyl perchlorate with pentanol, isopropyl perchlorate with pentanol, and allyl perchlorate with 2-fluoro-2,2-dinitroethanol. Hexyl perchlorate and dimethyl sulfoxide gave hexaldehyde.

The synthesis of dichlorine heptoxide was first reported by Michael and Conn in 1900 by the reaction of perchloric acid with phosphorus pentoxide.² Several variations of this method were reported³⁻⁷ and the physical^{4,5,7,8} and spectroscopic⁹⁻¹² properties of dichlorine heptoxide were studied extensively. However, the chemical properties of this compound, the anhydride of perchloric acid, are virtually unexplored. The present paper deals with reactions of dichlorine heptoxide with alcohols, and its reactions with other organic and inorganic groups will be described subsequently.

Nucleophilic attack by an alcohol on chlorine in dichlorine heptoxide would yield an alkyl perchlorate. The carbon-oxygen bond is not ruptured in this reaction.



Although methyl perchlorate and ethyl perchlorate have been prepared by several methods,¹³ there is no selective method available for higher aliphatic perchlorates.^{14,15} Because of the low nucleophilicity of the perchlorate

ion,^{16,17} competing rearrangements could be expected in its reactions with carbonium ions or incipient carbonium ions.

Because of the miscibility of dichlorine heptoxide with carbon tetrachloride and the close proximity of the boiling points of the two liquids,³ a carbon tetrachloride solution of dichlorine heptoxide is a convenient preparative reagent. The reagent used in this work was prepared by adding 70% perchloric acid to a suspension of phosphorus pentoxide in carbon tetrachloride, heating under reflux, and then vacuum distilling the solution.

Primary Alcohols. The generality of the synthesis of perchlorates by the reaction of primary alcohols with dichlorine heptoxide is shown by the examples in Table I. Nmr spectra showed that the products were ob-

Table I. Primary Perchlorates

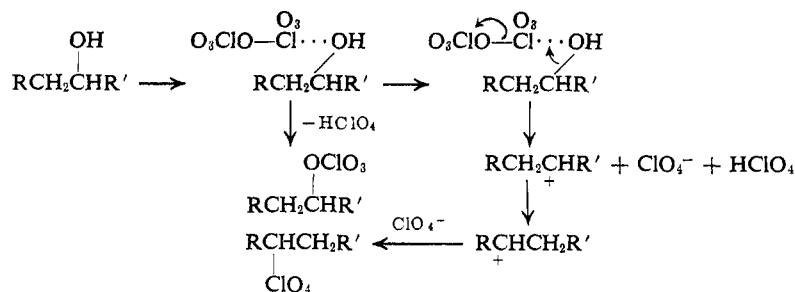
Starting material	Product	Yield, %
CH ₃ OH	CH ₃ OCIO ₃	42
C ₂ H ₅ OH	C ₂ H ₅ OCIO ₃	56
CH ₃ CH ₂ CH ₂ OH	CH ₃ CH ₂ CH ₂ OCIO ₃	73
CH ₃ (CH ₂) ₂ CH ₂ OH	CH ₃ (CH ₂) ₂ CH ₂ OCIO ₃	71
CH ₃ (CH ₂) ₃ CH ₂ OH	CH ₃ (CH ₂) ₃ CH ₂ OCIO ₃	63
CH ₃ (CH ₂) ₄ CH ₂ OH	CH ₃ (CH ₂) ₄ CH ₂ OCIO ₃	58
HOCH ₂ CH ₂ OH	ClO ₃ OCH ₂ CH ₂ OCIO ₃	60
HOCH ₂ (CH ₂) ₂ CH ₂ OH	ClO ₃ OCH ₂ (CH ₂) ₂ CH ₂ OCIO ₃	38
CF ₃ CH ₂ OH	CF ₃ CH ₂ OCIO ₃	55
CH ₃ C(NO ₂) ₂ CH ₂ OH	CH ₃ C(NO ₂) ₂ CH ₂ OCIO ₃	67
FC(NO ₂) ₂ CH ₂ OH	FC(NO ₂) ₂ CH ₂ OCIO ₃	60
FC(NO ₂) ₂ CH ₂ OCH ₂ CH ₂ OH	FC(NO ₂) ₂ CH ₂ OCH ₂ CH ₂ OCIO ₃	43
CH ₂ =CHCH ₂ OH	CH ₂ =CHCH ₂ OCIO ₃	48
HC≡CCH ₂ OH	HC≡CCH ₂ OCIO ₃	43

tained in high purity and secondary perchlorate isomers were clearly absent. This reaction thus provides a convenient source of simple primary alkyl perchlorates. The reaction was also applied to two α,ω-diols, ethylene glycol, and 1,4-butanediol, to give the corresponding diperchlorates. Alcohols with electron-withdrawing substituents likewise reacted with dichlorine heptoxide;

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(17) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **80**, 459 (1958).

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- (6) V. Ya. Rosolovskii, A. A. Zinov'ev, and V. A. Prokhorov, *Zh. Neorg. Khim.*, **5**, 2148 (1960).
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- (8) E. Colocchia, R. V. Figini, and H. J. Schumacher, *Angew. Chem.*, **68**, 492 (1956).
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- (10) R. Savoie and P. A. Giguere, *Can. J. Chem.*, **40**, 991 (1962).
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- (12) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **42**, 2496 (1964).
- (13) J. Meyer and W. Spormann, *Z. Anorg. Chem.*, **228**, 341 (1936).
- (14) G. Radell, J. W. Connolly, and A. J. Raymond, *J. Amer. Chem. Soc.*, **83**, 704 (1960), reported the synthesis of several primary alkyl perchlorates from alkyl iodides and silver perchlorate, but the detection of isomerization would have been unlikely since nmr was not available. Our repetition of their procedures yielded mixtures containing mainly secondary isomers. This work will be reported elsewhere.
- (15) D. M. Hoffman, *J. Org. Chem.*, **36**, 1716 (1971), reported the preparation of mixtures of secondary perchlorates by the reaction of perchloric acid and sulfuric acid with olefins.



2,2,2-trifluoroethanol, 2,2-dinitropropanol, 2-fluoro-2,2-dinitroethanol, and 2-(2-fluoro-2,2-dinitroethoxy)ethanol were converted to the corresponding perchlorates. Even unsaturated alcohols were found to be amenable to this reaction, and allyl perchlorate and propargyl perchlorate were prepared from allyl alcohol and propargyl alcohol, respectively. Unsuccessful attempts to prepare allyl perchlorate have been reported.¹⁸

Simple alkyl perchlorates were prepared by treating the alcohol with the theoretical amount of 0.3 *M* solution of dichlorine heptoxide in carbon tetrachloride for 18 hr. Longer reaction times were generally used with electronegatively substituted alcohols, and in some cases methylene chloride was added to enhance solubility. The unsaturated alcohols were treated with the reagent for 0.5 hr at 0°. Side reactions due to the reaction liberated by perchloric acid with the double and triple bonds were prevented by adding sodium sulfate to the reaction mixtures to adsorb the acid.

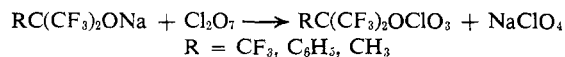
Secondary Alcohols. Isopropyl perchlorate was obtained in 48% yield from 2-propanol and dichlorine heptoxide by following the general procedure used for simple primary alcohols. 2-Hexanol and 3-hexanol gave 2-hexyl perchlorate and 3-hexyl perchlorate in yields of 62 and 53%, respectively. Some oxidation and, at least in the latter case, some rearrangement were also observed. Thus, in the 2-hexanol reaction, 2-hexanone was obtained in 8% yield. No 3-hexyl perchlorate was observed, but the limit of detection by nmr is about 10% because of overlapping peaks of the two perchlorates. In the 3-hexanol reaction, a 9% yield of 3-hexanone was obtained, as well as a 6% yield of 2-hexyl perchlorate, which is readily observed by its methyl doublet at δ 1.48. The perchlorates did not interconvert under the reaction conditions.

The oxidation of the alcohols to ketones could take place through cyclic complexes similar to those that have been postulated for chromate oxidations.^{19,20} The formation of isomeric perchlorates suggests that the initial alcohol complex undergoes carbon-oxygen bond cleavage in competition with the loss of perchloric acid. Hydride shift in the resulting carbonium ion or incipient carbonium ion or elimination-addition would lead to the isomeric perchlorate.

Tertiary Alcohols. Tertiary perchlorates have not been reported previously, other than trityl derivatives, which have properties of carbonium ion salts.²¹ The covalent character of tertiary perchlorates would be expected to increase with the degree of electron-with-

drawing substitution. The reactivity of tertiary alcohols toward dichlorine heptoxide, however, would decrease with electron-withdrawing substituents, and steric hindrance would also reduce their reactivity.

tert-Butyl alcohol was found to react on mixing with dichlorine heptoxide in carbon tetrachloride, but a complex intractable mixture was obtained. Three fluorine-substituted tertiary alcohols were also examined, perfluoro-*tert*-butyl alcohol, 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, and 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol. These alcohols did not give perchlorates with dichlorine heptoxide within several days. The alkoxides, however, readily gave the corresponding perchlorates. The fluorine nmr spectra of the crude carbon tetrachloride solutions showed only the perchlorates and the starting alcohols. The alcohols were removed from the solutions by washing with 1 *N* sodium hydroxide without affecting the perchlorates. The phenyl derivative was isolated by preparative glpc and the others, which could not readily be separated from the solvent, were characterized spectrally.



Characterization and Reactions of Perchlorates. The dichlorine heptoxide-alcohol reaction provides alkyl perchlorates as insensitive solutions in carbon tetrachloride. They can be utilized as chemical reagents in this form without the necessity of handling the neat materials, which are generally sensitive explosives. Two examples, 2,2-dinitropropyl perchlorate and 2-fluoro-2,2-dinitroethyl perchlorate, were isolated by vacuum transfer and combustion analyses were obtained. A procedure requiring less tedious manipulation was used with 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propyl perchlorate; a weighed sample, isolated by glpc, was diluted with solvent and analyzed for H and F by nmr integration against quantitative reference standards. The structural assignment of allyl perchlorate was confirmed by an alternative synthesis from allyl bromide and silver perchlorate in carbon tetrachloride.

Nmr and ir spectra of the perchlorates are described in the Experimental Section. Nmr chemical shifts and coupling data, as well as area ratios, are in agreement with the structures. It is noteworthy that hydrogens on the carbon atoms bearing a perchlorate group were consistently deshielded by 0.7 to 1.0 ppm relative to the corresponding hydrogens of the starting alcohols. The ir spectra show characteristic perchlorate bands. Perhaloalkyl perchlorate bands at 1295–1320 (doublet) and 997–1036 cm^{-1} have been assigned to the $\text{Cl}=\text{O}$ antisymmetric and symmetric stretching vibrations, respectively.²² The observed spectra show strong bands

(18) H. Burton and D. A. Munday, *J. Chem. Soc.*, 1456 (1954).

(19) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1964.

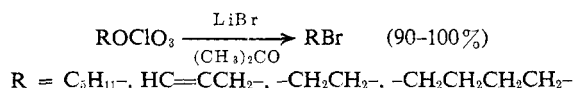
(20) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(21) K. M. Harmon, H. J. Dauben, and L. R. Honnen, *J. Org. Chem.*, 25, 1442 (1960).

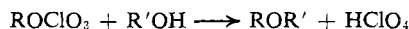
(22) C. J. Schack, D. Pilipovich, and J. F. Hon, *Inorg. Chem.*, 12, 897 (1973).

in these regions, with shifts to lower frequency for substrates not as highly electron withdrawing. Bands in the C–O stretch region are also apparent.

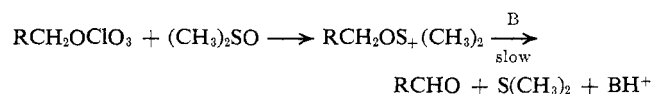
Some reactions utilizing alkyl perchlorates in carbon tetrachloride were investigated to provide additional structure proof as well as to demonstrate synthetic utility of the reagents. Mixing the carbon tetrachloride solutions with a 10% solution of lithium bromide in acetone gave the corresponding bromides in yields of 90–100%. Pentyl perchlorate, propargyl perchlorate, ethylene dperchlorate, and tetramethylene dperchlorate were used in this reaction.



Solutions of perchlorates in carbon tetrachloride, as obtained from the dichlorine heptoxide reaction, can be used directly as alkylating agents for the preparation of ethers under mild conditions. Thus, pentyl perchlorate and pentanol in the presence of potassium carbonate gave a 90% yield of dipentyl ether in 8 days at room temperature. Similarly, isopropyl perchlorate and pentanol gave an 85% yield of isopropyl pentyl ether in 6 days, with sodium sulfate used to adsorb liberated perchloric acid. Allyl perchlorate and 2-fluoro-2,2-dinitroethanol in the presence of potassium carbonate gave a 79% yield of allyl 2-fluoro-2,2-dinitroethyl ether in 48 hr. This reaction constitutes a versatile synthetic procedure for the preparation of ethers under neutral or mildly basic conditions in a nonpolar solvent.



The perchlorate reagents can also be used for the preparation of aldehydes using dimethyl sulfoxide. A solution of hexyl perchlorate in carbon tetrachloride was treated with dimethyl sulfoxide and sodium bicarbonate. An initially exothermic reaction took place with complete consumption of the perchlorate followed by the slow formation of hexaldehyde, with a 95% yield in 24 hr. The reaction parallels that of hexyl 4-nitrobenzenesulfonate.²³



Although a few organic perchlorates have been known for many years, the utilization of this class of compounds has been hampered by the lack of selective and safe synthetic methods. The reaction of alcohols with dichlorine heptoxide in carbon tetrachloride provides the first general route to primary, secondary, and tertiary perchlorates. The solutions obtained can be used directly as synthetic reagents.

Experimental Section

Caution: Neat alkyl perchlorates should be handled only with adequate protective devices. Samples for elemental analysis were obtained by distilling minimum quantities of solution behind safety shields, using rods or tongs to manipulate stopcocks and distillates. The explosive nature of methyl perchlorate and ethyl perchlorate was described graphically by Meyer and Spormann.¹³ Carbon tetrachloride solutions in the concentrations used in this work, however, could not be detonated in a qualitative hammer test. The carbon tetrachloride–dichlorine heptoxide reagent was also not detonated. No explosions occurred in any of the alcohol reactions studied. Nevertheless, care must be exercised to avoid pro-

ducing anhydrous perchloric acid by prolonged exposure to atmospheric water vapor, and, of course, to prevent evaporation of solvent. Safety shields should always be used, and insoluble by-products should be handled with caution.

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

Dichlorine Heptoxide. To a suspension of 50 g (0.35 mol) of phosphorus pentoxide in 100 ml of carbon tetrachloride, 5.1 ml (0.0603 mol) of 70% perchloric acid was added dropwise with stirring over a 2-hr period. The mixture was cooled with an ice bath during the addition. The bath was removed and stirring was continued for 2 hr. The mixture was then heated under reflux for 1.5 hr. The phosphorus pentoxide gradually became a sponge-like mass and stirring was then discontinued. The mixture was cooled to room temperature and the carbon tetrachloride and dichlorine heptoxide were codistilled into a Dry Ice cooled receiver at 60–20 mm. The distillate consisted of 93 ml (149 g) of a pale yellow liquid which was found to contain 0.30 mmol of dichlorine heptoxide per milliliter of solution (93% yield) by titration after stirring for 45 min with 1 *N* sodium hydroxide. The nmr spectrum showed no perchloric acid.

Although this procedure was repeated more than ten times without incident, the use of safety shielding is recommended. The same procedure was used to prepare a solution of dichlorine heptoxide in chloroform-*d*, a reagent useful for following, by nmr, reactions of alcohols with low solubility in carbon tetrachloride. Particular caution should be observed in extending the reaction to other solvents; explosions occurred during refluxing when ethylene dichloride or cyclohexane were used. It is noteworthy that in these attempts the characteristic swelling of the phosphorus pentoxide particles did not take place.

Reaction of Alcohols with Dichlorine Heptoxide. General Procedure. The alcohol (0.6 mmol) was added to 2 ml of carbon tetrachloride solution of dichlorine heptoxide (0.6 mmol) at 0° with stirring. The mixture was stirred 18 hr at room temperature and then was washed with water and dried over magnesium sulfate. Yields were determined by nmr, using chlorobenzene as a quantitative internal standard.

Methyl Perchlorate. This compound was obtained in 42% yield: nmr (CCl_4) δ 4.22 ppm (s); ir (CCl_4) 1280 (vs), 1250 (vs), 1045 (s), 965 (s), and 700 cm^{-1} (s).

Ethyl Perchlorate. This compound was obtained in 56% yield: nmr (CCl_4) δ 4.57 (q, 2 H, $J = 6.5$ Hz, CH_2OClO_3) and 1.53 ppm (t, 3 H, $J = 6.5$ Hz, CH_3); ir (CCl_4) 1275 (vs), 1240 (vs), 1045 (s), 1000 (s), 880 (s), 720 cm^{-1} (s).

Propyl Perchlorate. This compound was obtained in 73% yield: nmr (CCl_4) δ 4.45 (t, 2 H, $J = 6$ Hz, CH_2OClO_3), 1.87 (septet, 2 H, CH_2), and 1.80 ppm (t, 3 H, $J = 7$ Hz, CH_3); ir (CCl_4) 1275 (vs), 1240 (vs), 1040 (s), 850 (s), 820 (s), 715 cm^{-1} (s).

Butyl Perchlorate. This compound was obtained in 71% yield: nmr (CCl_4) δ 4.40 (t, 2 H, $J = 6$ Hz, CH_2OClO_3), 2.19 (broad m, 4 H, CH_2CH_2), and 0.98 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1140 (m), 1040 (s), 1240 (vs), 980 (m), 940 (s), 860 (m), 720 cm^{-1} (s).

Pentyl Perchlorate. This compound was obtained in 63% yield: nmr (CCl_4) δ 4.52 (t, 2 H, $J = 6.5$ Hz, CH_2OClO_3), 2.00 (m, 2 H, $\text{CH}_2\text{CH}_2\text{OClO}_3$), 1.45 (m, 4 H, CH_2), and 0.95 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1245 (vs), 1140 (m), 1045 (s), 960 (s), 940 (m), 890 (s), 720 cm^{-1} (s).

Hexyl Perchlorate. This compound was obtained in 58% yield: nmr (CCl_4) δ 4.50 (t, 2 H, $J = 6$ Hz, CH_2OClO_3), 1.82 (m, 2 H, $\text{CH}_2\text{CH}_2\text{OClO}_3$), 1.42 (m, 6 H, CH_2), and 0.92 ppm (m, 3 H, CH_3); ir (CCl_4) 1280 (vs), 1245 (vs), 1050 (s), 990 (m), 950 (s), 915 (s), 720 cm^{-1} (s).

Ethylene Dperchlorate. Ethylene glycol (0.0186 g, 0.3 mmol) was added to a solution of 0.6 mmol of dichlorine heptoxide in 4 ml of carbon tetrachloride and the mixture was stirred 18 hr at ambient temperature. Nmr analysis, using chlorobenzene as a quantitative standard, showed a 60% yield of ethylene dperchlorate. In a larger scale reaction, 0.186 g (3 mmol) of ethylene glycol was added to a mixture of 20 ml of methylene chloride and 20 ml of a 0.3 *M* solution of dichlorine heptoxide in carbon tetrachloride. This homogeneous solution was stirred for 18 hr at ambient temperature, washed with water, dried, and concentrated under vacuum to a volume of 2 ml. Ethylene dperchlorate was isolated by preparative glpc at 120°: nmr (CDCl_3) δ 4.83 ppm (s); ir (CDCl_3) 2990 (w), 1460 (w), 1285 (vs), 1250 (vs), 1060 (m), 1020 (s), and 980 cm^{-1} (m).

(23) H. Snyder, P. L. Gendler, and H. Chang, *Synthesis*, 655 (1971).

Tetramethylene Diperchlorate. 1,4-Butanediol (0.054 g, 0.6 mmol) was added to 5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride and the mixture was stirred for 18 hr at ambient temperature. The organic layer was used with water and dried over magnesium sulfate. The yield of tetramethylene diperchlorate was 38%: nmr (CCl_4) δ 4.60 (m, 4 H, CH_2OCIO_3) and 3.70 ppm (m, 4 H, CH_2CH_2); ir (CCl_4) 3000 (m), 1475 (m), 1460 (m), 1390 (w), 1280 (vs), 1245 (vs), 1045 (s), 930 (s), and 700 cm^{-1} (s).

2,2,2-Trifluoroethyl Perchlorate. 2,2,2-Trifluoroethanol (0.150 g, 1.5 mmol) was added to 5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride at room temperature and the mixture was stirred for 48 hr. The solution was washed with water and dried. The yield of 2,2,2-trifluoroethyl perchlorate was 55%: proton nmr (CCl_4) δ 4.80 (q, $J_{\text{HF}} = 8$ Hz); fluorine nmr (CCl_4) $\phi + 91$ ppm (t, $J_{\text{HF}} = 8$ Hz); ir (CCl_4) 1440 (w), 1400 (m), 1280 (vs), 1245 (vs), 1180 (vs), 1030 (s), 1005 (s), 985 (m), and 860 cm^{-1} (m).

2,2-Dinitropropyl Perchlorate. 2,2-Dinitropropanol (0.45 g, 3.0 mmol) was added to 10 ml of 0.3 *M* solution of dichlorine heptoxide in carbon tetrachloride and the mixture was stirred for 48 hr. The reaction mixture was quenched with ice and the organic layer was separated and dried over sodium sulfate. The yield (nmr) was 67%. Evaporation of solvent from an aliquot gave a colorless oil which was vacuum transferred at 0.03 mm to a -78° receiver: nmr (CCl_4) δ 5.32 (s, 2 H, CH_2OCIO_3), and 2.32 ppm (s, 3 H, CH_3); ir (CCl_4) 3005 (w), 2950 (m), 2800 (w), 1590 (vs), 1425 (m), 1280 (vs), 1245 (vs), 1120 (m), 1040 (s), 1010 (s), 980 (s), and 840 cm^{-1} (m); $d(25^\circ) = 1.601$.

Anal. Calcd for $\text{C}_3\text{H}_5\text{ClN}_2\text{O}_8$: C, 15.48; H, 2.18; Cl, 15.25; N, 12.05. Found: C, 16.40; H, 1.92; Cl, 15.36; N, 11.68.

2-Fluoro-2,2-dinitroethyl Perchlorate. 2-Fluoro-2,2-dinitroethanol (0.51 g, 3.25 mmol) was added to 15 ml of a 0.3 *M* solution of dichlorine heptoxide in carbon tetrachloride at room temperature, and the mixture was stirred for 96 hr. The reaction mixture was quenched with ice and the organic layer was separated and dried over sodium sulfate. The yield was 60%. Evaporation of solvent (60 mm) from an aliquot left a colorless oil which was vacuum transferred at 0.05 mm to a -78° receiver: nmr (CCl_4) δ 5.56 ppm (d, $J_{\text{HF}} = 15$ Hz); ir (CCl_4) 3005 (w), 2950 (m), 2800 (w), 1590 (vs), 1425 (m), 1280 (vs), 1245 (vs), 1120 (m), 1040 (s), 1010 (s), 980 (s), and 840 cm^{-1} (m); $d(25^\circ) = 1.704$.

Anal. Calcd for $\text{C}_2\text{H}_2\text{ClF}_2\text{N}_2\text{O}_8$: C, 10.16; H, 0.85; F, 8.03. Found: C, 10.17; H, 0.52; F, 8.51.

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 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride at room temperature, and the mixture was stirred for 18 hr. The carbon tetrachloride layer was washed with water and was dried over magnesium sulfate. Nmr analysis indicated a 43% yield: nmr (CCl_4) δ 4.57 (A_2B_2 multiplet, 2 H, CH_2OCIO_3), 4.58 (d, 2 H, $J_{\text{HF}} = 17$ Hz, FCCH_2O), and 4.00 ppm (A_2B_2 , 2 H, $\text{OCH}_2\text{CH}_2\text{OCIO}_3$); ir (CCl_4) 2950 (m), 1600 (vs), 1460 (m), 1355 (w), 1320 (s), 1285 (vs), 1245 (vs), 1160 (s), 1050 (s), 1015 (s), 885 (m), 855 (m), and 710 cm^{-1} (s).

Allyl Perchlorate. Allyl alcohol (0.035 g, 0.6 mmol) was added to 2.5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride 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. Allyl perchlorate was obtained in 48% yield: nmr (CCl_4) δ 5.73 (ABC multiplet, 3 H, $\text{CH}_2=\text{CH}$), and 4.93 ppm (m, 2 H, CH_2OCIO_3); ir (CCl_4) 1640 (w), 1430 (w), 1280 (vs), 1240 (vs), 1050 (s), 1000 (w), 950 (s), 940 (m), 900 (m), and 720 cm^{-1} (s).

Allyl perchlorate was also prepared independently from silver perchlorate and allyl bromide in carbon tetrachloride and had spectral properties identical with the material prepared above.

Propargyl Perchlorate. A mixture of 0.084 g (1.5 mmol) of propargyl alcohol, 5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride, and 0.5 g of sodium sulfate was stirred for 30 min at 0° . The carbon tetrachloride layer was washed with ice-water and dried over magnesium sulfate. The yield of propargyl perchlorate was 43%: nmr (CCl_4) δ 5.10 (d, 2 H, $J = 2$ Hz, $\text{C}\equiv\text{CCH}_2\text{OCIO}_3$) and 2.72 ppm (t, 1 H, $J = 2$ Hz, $\text{HC}\equiv\text{C}$); ir (CCl_4) 3325 (m), 2960 (w), 2260 (w), 1460 (m), 1350 (w), 1330 (w), 1280 (vs), 1250 (vs), 1040 (s), 980 (m), 940 (s), 905 (s), and 690 cm^{-1} (s).

Isopropyl Perchlorate. This compound was obtained in 48% yield by the general procedure: nmr (CCl_4) δ 5.10 (septet, 1 H, $J = 6$ Hz, CHOCIO_3), and 1.58 ppm (d, 6 H, $J = 6$ Hz, CH_3); ir (CCl_4) 2990 (m), 1470 (m), 1395 (m), 1385 (m), 1275 (vs), 1240 (vs), 1115 (m), 1035 (s), 900 (s), and 720 cm^{-1} (s).

2-Hexyl Perchlorate. 2-Hexanol (0.061 g, 0.6 mmol) was added to 2 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride and

the solution was stirred for 3 hr at ambient temperature. The solution became greenish-yellow and some oil separated. The reaction mixture was stirred with water and the carbon tetrachloride layer was separated and dried. Nmr analysis showed a 62% yield of 2-hexyl perchlorate and an 8% yield of 2-hexanone. The identity of 2-hexanone was established by spectral and glpc comparison with an authentic sample. 3-Hexyl perchlorate was not observed within the limits of detection by nmr, estimated to be about 10% because of overlap. The spectral properties of 2-hexyl perchlorate are: nmr (CCl_4) δ 4.85 (m, 1 H, CHOCIO_3), 1.57 (broad m, 6 H, $-\text{CH}_2-$), 1.48 (d, 3 H, $J = 6$ Hz, $\text{CH}_3\text{CH}(\text{OCIO}_3)$), and 0.93 ppm (m, 3 H, CH_3); ir (CCl_4) (mixture) 2980 (s), 2910 (m), 1715 (m), 1470 (m), 1395 (m), 1310 (m), 1275 (vs), 1240 (vs), 1190 (w), 1050 (s), 910 (w), and 720 cm^{-1} (s).

3-Hexyl Perchlorate. By the above procedure, 3-hexanol gave a 53% yield of 3-hexyl perchlorate, a 9% yield of 3-hexanone, and a 6% yield of 3-hexyl perchlorate (doublet at 1.48). The spectra for 3-hexyl perchlorate are as follows: nmr (CCl_4) δ 4.85 (m, 1 H, CHOCIO_3), 1.57 (broad m, 6 H, CH_2), and 1.03 ppm (m, 6 H, CH_3); ir (CCl_4) (mixture) 2980 (s), 2920 (m), 1710 (m), 1470 (m), 1400 (w), 1280 (vs), 1250 (vs), 1050 (s), 910 (m), 880 (m), and 730 cm^{-1} (s).

Perfluoro-tert-butyl Perchlorate. Perfluoro-tert-butyl alcohol (0.354 g, 1.5 mmol) was added to 0.30 ml of 5 *N* sodium hydroxide and the salt was dried for 5 hr at 0.1 mm. The residue was stirred for 18 hr with 5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride. Fluorine nmr analysis of the solution, using hexafluorobenzene as a quantitative internal standard, showed a 33% yield of perfluoro-tert-butyl perchlorate, ϕ 68.20, and a 56% yield of perfluoro-tert-butyl alcohol, ϕ 74.61. The perfluoro-tert-butyl alcohol was removed by washing the carbon tetrachloride solution with 1 *N* sodium hydroxide solution: ir (CCl_4) 1295 (vs), 1275 (vs), 1230 (m), 1095 (s), 1040 (s), and 995 (s) cm^{-1} . The glpc retention time of the material was too close to that of carbon tetrachloride to allow facile preparative isolation.

1,1,1,3,3,3-Hexafluoro-2-phenyl-2-propyl Perchlorate. Sodium hydride (0.115 g, 4.6 mmol) was added to a solution of 0.7355 g (3.01 mmol) of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, in 3 ml of carbon tetrachloride and the mixture was heated briefly to 50° . The mixture was cooled to 0° and 10 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride was added. The reaction mixture was stirred for 1 hr at ambient temperature and then for 30 min after 1 ml of water was added. The carbon tetrachloride layer was dried over sodium sulfate. Fluorine nmr, using hexafluorobenzene as a quantitative internal standard, showed a 50% yield of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propyl perchlorate, ϕ 69.33, and a 29% yield of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, ϕ 76.04. The alcohol was removed by extracting the carbon tetrachloride solution with 1 *N* sodium hydroxide. An analytical sample of the perchlorate was obtained by preparative glpc (20 min retention time, 80° , 60 ml He/min): proton nmr, δ 7.68 (sym m); ir (CCl_4) 1290 (vs), 1235 (vs), 1200 (s), 1170 (m), 1000 (m) and 980 (m) cm^{-1} . Elemental analyses for hydrogen and fluorine were obtained by nmr integration of a weighed sample using 1,2-dichloroethane and hexafluorobenzene, respectively, as standards.

Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_6\text{ClO}_4$: H, 1.41; F, 34.90. Found: H, 1.41; F, 34.43.

1,1,1,3,3,3-Hexafluoro-2-methyl-2-propyl Perchlorate. Sodium hydride (0.0251 g, 1.05 mmol) was added to 0.1707 g (0.938 mmol) of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol and the mixture was heated to 50° . Dichlorine heptoxide in carbon tetrachloride (3.5 ml, 1.05 mmol) was added at 0° and the mixture was stirred 18 hr at ambient temperature. The solution was stirred 30 min with 1 ml of water and was dried over sodium sulfate. Nmr analysis showed a 15% yield of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propyl perchlorate and an 83% yield of the alcohol. The latter was removed by washing with 1 *N* sodium hydroxide: proton nmr (CCl_4) δ 2.17 ppm (broad s); fluorine nmr, ϕ 76.86 ppm (s); ir (CCl_4) 1290 (vs), 1260 (s), 1230 (vs), 1190 (m), 1140 (m), 1120 (m), 1090 (s) and 1030 (s) cm^{-1} .

Reaction of Perchlorates with Lithium Bromide. A solution of 2.0 mmol of tetramethylene diperchlorate in 8 ml of carbon tetrachloride was added dropwise with stirring at 0° to 8 ml of 10% lithium bromide in acetone. The solution was stirred at ambient temperature for 45 min, washed with water, dried, and stripped of solvent to give 0.404 g (94%) of 1,4-dibromobutane, identified by spectral and glpc comparison with an authentic sample. The same procedure using pentyl perchlorate, ethylene diperchlorate, and propargyl perchlorate gave 90–100% yields of the corresponding bromides.

Reaction of Pentyl Perchlorate with Pentanol. Pentanol (0.053 g, 0.6 mmol) and potassium carbonate (0.276 g, 2 mmol) were added to a solution of 0.6 mmol of pentyl perchlorate in 3 ml of carbon tetrachloride and the mixture was stirred at ambient temperature. Dipentyl ether was formed in 5% yield in 20 hr, 25% in 4 days, and 90% in 8 days. The reaction was monitored by nmr, and the product was identified by glpc comparison with an authentic sample.

Reaction of Isopropyl Perchlorate with Pentanol. Pentanol (0.026 g, 0.3 mmol) and sodium sulfate (0.142 g, 1 mmol) were added to a solution of 0.3 mmol of isopropyl perchlorate in 2 ml of carbon tetrachloride and the mixture was stirred. Isopropyl pentyl ether was formed in 25% yield in 18 hr, 50% in 3 days, and 85% in 6 days.

Reaction of Allyl Perchlorate with 2-Fluoro-2,2-dinitroethanol. To a solution of 0.72 mmol of allyl perchlorate in 5 ml of carbon tetrachloride was added 5 ml of methylene chloride, 0.30 g (2 mmol) of 2-fluoro-2,2-dinitroethanol,²⁴ and 0.69 g (5 mmol) of potassium

carbonate. The mixture was stirred for 48 hr. The solution was washed with water and with 5% sodium hydroxide and dried over sodium sulfate, and the solvent was removed to give 0.11 g (79%) of allyl 2-fluoro-2,2-dinitroethyl ether, identical with an authentic sample.²⁵

Reaction of Hexyl Perchlorate with Dimethyl Sulfoxide. Dimethyl sulfoxide (5 ml) and 0.5 g (6 mmol) of sodium bicarbonate were added to a solution of 1.74 mmol of hexyl perchlorate in 10 ml of carbon tetrachloride. An initially exothermic reaction took place, and nmr spectra showed the immediate consumption of perchlorate and slow formation of hexaldehyde. After 24 hr the mixture was washed with water and dried. The only products detected by nmr were hexaldehyde (95% yield) and dimethyl sulfide. Vacuum distillation gave pure hexaldehyde.

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Reactions of Dichlorine Heptoxide with Amines¹

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



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Abstract: Dichlorine heptoxide in carbon tetrachloride reacts as a perchlorylating agent with secondary and primary amines. Piperidine, diethylamine, dipentylamine, and 2-ethylaziridine gave *N*-perchlorylpiperidine, *N*-perchloryldiethylamine, *N*-perchloryldipentylamine, and *N*-perchloryl-2-ethylaziridine, respectively. Hexylamine, butylamine, propylamine, isopropylamine, and *tert*-butylamine gave *N*-perchlorylhexylamine, *N*-perchlorylbutylamine, *N*-perchlorylpropylamine, *N*-perchlorylisopropylamine, and *N*-perchloryl-*tert*-butylamine, respectively. The primary perchlorylamines are acidic and form sodium salts with aqueous sodium hydroxide; the ionization constant of *N*-perchloryl-*tert*-butylamine is 1.51×10^{-7} . The salts of *N*-perchlorylhexylamine and *N*-perchlorylbutylamine were chlorinated with sodium hypochlorite. In carbon tetrachloride solution, primary alkyl *N*-perchlorylamines and the *N*-chloro derivatives give the corresponding carboxylic acids at ambient temperature, whereas *N*-perchlorylisopropylamine gives acetone and *N*-perchloryl-*tert*-butylamine is unchanged.

Only two compounds with nitrogen-bonded perchloryl groups have been reported, the ammonium salt of perchlorylamide² and *N*-perchlorylpiperidine,³ which were prepared by reactions of perchloryl fluoride with ammonia and with piperidine. Attempts to extend this reaction to other amines gave only oxidation and fluorination products,⁴ and perchloryl fluoride was recently used as the reagent of choice for the fluorination of an amine.⁵ The function of dichlorine heptoxide in carbon tetrachloride solution as an effective and convenient perchlorylating agent for alcohols⁶ suggested that its reaction with amines might provide a practical route to perchlorylamines.

Dichlorine heptoxide in carbon tetrachloride reacted with secondary amines to give high yields of perchlorylamines, as shown in Table I. Two moles of amine were used per mole of dichlorine heptoxide, with one functioning as a base, and the reactions were complete on mixing the reagents. The perchlorylamines were obtained as carbon tetrachloride solutions, with no

Table I. Perchlorylamines from Amines and Dichlorine Heptoxide

Starting material	Product	Yield, %
		73
(C ₂ H ₅) ₂ NH	(C ₂ H ₅) ₂ NClO ₃	77
(C ₅ H ₁₁) ₂ NH	(C ₅ H ₁₁)NClO ₃	81
		
C ₂ H ₅ CH—CH ₂	C ₂ H ₅ CH—CH ₂	83
CH ₃ (CH ₂) ₄ CH ₂ NH ₂	CH ₃ (CH ₂) ₄ CH ₂ NHClO ₃	63
CH ₃ (CH ₂) ₃ CH ₂ NH ₂	CH ₃ (CH ₂) ₃ CH ₂ NHClO ₃	61
CH ₃ CH ₂ CH ₂ NH ₂	CH ₃ CH ₂ CH ₂ NHClO ₃	61
(CH ₃) ₃ CHNH ₂	(CH ₃) ₃ CHNHClO ₃	60
(CH ₃) ₃ CNH ₂	(CH ₃) ₃ CNHClO ₃	71

impurities detectable by nmr. Thus piperidine, diethylamine, and dipentylamine gave *N*-perchlorylpiperidine, *N*-perchloryldiethylamine, and *N*-perchloryldipentylamine, respectively. This reaction was even applicable to the preparation of a strained molecule such as *N*-perchloryl-2-ethylaziridine.



Primary amines reacted similarly to give the corresponding perchlorylamines. Thus, hexylamine, butylamine, and propylamine, as well as isopropylamine

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