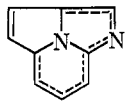
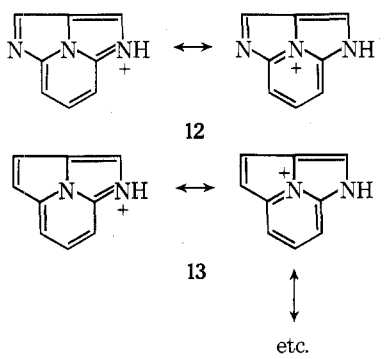


11

tive whose ^1H NMR spectrum (see Table I) clearly identifies it as the 4-bromo derivative (**10**). This is, of course, in agreement with the results of electrophilic substitution studies on cycl[3.2.2]azine and on its 2-aza derivative.[2]

Methylation of compound **4**, as expected, affords a *N*-methyl quaternary salt (**8**) (see Table I). The ^1H NMR spectrum of this compound is essentially superimposable upon that of the parent compound **4** in aqueous acid. The intriguing result is that the 1-azacyl[3.2.2]azine (**4**) is stable to aqueous acid, in contrast to the great acid lability of the 1,4-diaza analogue **2**.

If we consider the monoprotonated forms of compounds **2** and **4** (structures **12** and **13**), as being initially formed, the acid



12

13

etc.

lability of the HC=N– bond, an imine in **12**, as compared to the –CH=CH– bond in **13**, is understandable. Thus, the hydrolytic instability of the protonated diazacyl[3.2.2]azine (**12**) as compared to the monoazacycl[3.2.2]azine (**13**) is readily explained.

Experimental Section[8]

4-Formyl-1-azacycl[3.2.2]azine (6). To a stirred solution of 45 ml of 2 M BuLi (0.908 mol) in 20 ml of sodium-dried tetrahydrofuran (THF) was added tetramethylethylenediamine (TMEDA, 10.53 g, 0.0908 mol) under a N_2 atmosphere and at −15 °C. 5-Methylimidazo[1,2-*a*]pyridine (5.00 g, 0.0379 mol) in 30 ml of dried THF was then added to the solution. After 1 min, a solution of dry dimethylformamide (5.52 g, 0.0758 mol) in 30 ml of THF was added all at once. The resulting blue-green solution was stirred for an additional 30 min, after which time 100 ml of water was added to the reaction mixture. The mixture was extracted with $CHCl_3$ (3 × 150 ml), the combined extracts were dried over anhydrous Na_2CO_3 and filtered, and the solvent was evaporated in vacuo. The resulting brown solid was chromatographed over Al_2O_3 (grade III) and eluted with benzene. Evaporation of the solvent afforded a yellow solid which was recrystallized from chloroform to yield 0.580 g (9%), mp 210–212 °C. Anal. Calcd for $C_{10}H_6N_2O$: C, 70.59; H, 3.52; N, 16.47. Found: C, 70.35; H, 3.40; N, 16.22.

1-Azacycl[3.2.2]azine-4-carboxylic Acid (7). To a solution of 4-formyl-1-azacycl[3.2.2]azine (0.10 g, 0.588 mmol) in 10 ml of acetone was added 5 ml of water. Solid $KMnO_4$ (220 mg, 1.4 mmol) was added all at once, and the resulting solution was stirred for 1 h. The solution was treated with a small amount of solid $NaHSO_3$ and filtered through a Celite pad. The filtrate was evaporated in vacuo to approximately 5 ml and carefully acidified with 2 N HCl. The white precipitate was filtered and dried to yield 85 mg (75%) of 1-azacycl[3.2.2]azine-4-carboxylic acid, which decomposes at its melting point (318–320 °C).

1-Azacycl[3.2.2]azine (4). In a 10-ml distillation flask fitted with a short path condenser was placed a mixture of 1-azacycl[3.2.2]azine-4-carboxylic acid (0.350 g, 1.88 mmol) and Cu powder (400 mg). The flask and its contents were heated with a flame until a greenish liquid collected on the walls of the flask and condenser. The liquid was collected by dissolving it in $CHCl_3$. The $CHCl_3$ solution was placed on a short (5 cm) alumina column (grade III) and eluted with $CHCl_3$. Evaporation of the $CHCl_3$ eluent afforded 1-azacycl[3.2.2]azine (205 mg, 77%) as a low-melting solid. The picrate of compound **4** was obtained, mp 218–220 °C, and was analyzed. Anal. Calcd for $C_{15}H_9N_5O_7$: C, 48.52; H, 2.42; N, 18.87. Found: C, 48.42; H, 2.20; N, 18.35.

***N*$_1$-Methyl-1-azacycl[3.2.2]azinium Iodide (8).** To a solution of 1-azacycl[3.2.2]azine (50 mg, 0.35 mmol) in 10 ml of reagent-grade acetone was added 0.5 ml of CH_3I. The resulting solution was allowed to stand at room temperature for 15 h. The crystalline precipitate was collected and washed with 5 ml of cold reagent-grade acetone to yield *N*$_1$-methyl-1-azacycl[3.2.2]azinium iodide (85 mg, 84%) as a brick-red solid, mp 142–144 °C. Anal. Calcd for $C_{10}H_9N_2I$: C, 42.24; H, 3.16; N, 9.86. Found: C, 42.05; H, 2.89; N, 9.50.

4-Bromo-1-azacycl[3.2.2]azine (10). To a solution of 1-azacycl[3.2.2]azine (100 mg, 0.70 mmol) in 10 ml of $CHCl_3$ was added *N*-bromosuccinimide (0.310 mg, 1.75 mmol). The resulting solution was stirred for 5 h at room temperature and filtered, and the filtrate was evaporated to dryness. The residue was placed on a short (5 cm) alumina column (grade III) and eluted with benzene. Evaporation of the benzene afforded a yellow solid which was sublimed to yield 95 mg (62.1%) of 4-bromo-1-azacycl[3.2.2]azine, mp 81–82 °C. Anal. Calcd for $C_9H_5N_2Br$: C, 48.87; H, 2.26; N, 12.67. Found: C, 48.51; H, 2.05; N, 12.48.

Registry No.—**1**, 209-81-4; **2**, 10558-77-7; **3**, 54384-90-6; **4**, 209-83-6; **4** picrate, 58374-91-7; **5**, 933-69-7; **6**, 58374-92-8; **7**, 58374-93-9; **8**, 58374-94-0; **10**, 58374-95-1.

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(7) The electron densities given are exclusive of the $1s^2$ electrons.
(8) The ^1H NMR spectra were obtained with a Varian HA-100 spectrometer. Elemental analyses were done by Atlantic Microlab, Inc., Atlanta, Ga.

Reactions of Dichlorine Heptoxide with Olefins[1]

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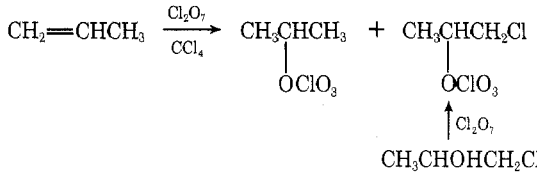
Dichlorine heptoxide in carbon tetrachloride is a conveniently accessible perchlorylation reagent, and its reactions with alcohols,[2] amines,[3] ethers,[4] and alkyl iodides[5] have been described. As a continuation of this study of the utility of the reagent the present investigation deals with its reactions with olefins.

Propene was found to react with dichlorine heptoxide in carbon tetrachloride to give isopropyl perchlorate (32%) and 1-chloro-2-propyl perchlorate (17%). The yields of these impact sensitive materials were determined by NMR using a quantitative internal standard. Isopropyl perchlorate was identified by spectral comparison with an authentic sample.[2] A sample of 1-chloro-2-propyl perchlorate was isolated and analyzed, and the compound was also synthesized independently from 1-chloro-2-propanol and dichlorine heptoxide.



cis-2-Butene reacted with dichlorine heptoxide to give 3-chloro-2-butyl perchlorate (30%), 3-keto-2-butyl perchlorate (2%), and 2,3-butane diperchlorate (5%). When the reaction

was repeated with added lithium perchlorate in suspension, the yield of 3-keto-2-butyl perchlorate was increased to 20%, but the other products were unaffected. The 2,3-butane diperchlorate was identified spectrally by comparison with the compound prepared from 2-butene oxide and dichlorine heptoxide.[4] The other products were isolated by GLC and characterized. The isolation of 3-keto-2-butyl perchlorate is particularly noteworthy in that it is the first reported example of a carbonyl compound with a covalent perchlorate group.

$$\begin{matrix} CH_3 & CH_3 \\ | & | \\ HC{=}CH \end{matrix} \xrightarrow{Cl_2O_7} CH_3CH(OClO_3)CH(OClO_3)CH_3 + CH_3CHClCH(OClO_3)CH_3 + CH_3\overset{\overset{O}{\|}}{C}CH(OClO_3)CH_3$$

trans-2-Butene gave the same product mixture that *cis*-2-butene did, with the exception of the stereochemistry of the 3-chloro-2-butyl perchlorate. This product from the two olefins was distinguishable by GLC, and in each case only one isomer was observed. Structural assignments were made by synthesizing 3-chloro-2-butyl perchlorate from dichlorine heptoxide and 3-chloro-2-butanol of known configuration. Lucas and Garner[6] showed that the addition of hydrochloric acid to the 2-butene oxides is stereospecifically a trans addition; *cis*-2-butene oxide gives *threo*-3-chloro-2-butanol and *trans*-2-butene oxide gives *erythro*-3-chloro-2-butanol. The reaction of dichlorine heptoxide with alcohols should not affect the carbon stereochemistry. It was found that the 3-chloro-2-butyl perchlorate thus prepared from *cis*-2-butene oxide was identical with that obtained from *cis*-2-butene and dichlorine heptoxide, and that from *trans*-2-butene oxide was identical with the *trans*-2-butene product. Thus, the formation of 3-chloro-2-butyl perchlorate from 2-butene and dichlorine heptoxide is a trans addition.

A completely substituted olefin, 2,3-dimethyl-2-butene, was also examined. A product insoluble in carbon tetrachloride was obtained that was identified as a mixture of 2,2-diperchloratopropane and 2,2-dimethyl-3,3-diperchloratobutane. The former was prepared previously from acetone and perchloric acid,[7] and the latter was characterized by the proximity of the NMR chemical shift of the methyl adjacent to the perchlorates to that of 2,2-diperchloratopropane. Treating the mixture in methylene chloride with sodium bicarbonate gave acetone and pinacolone.

$$(CH_3)_2C{=}C(CH_3)_2 \xrightarrow{Cl_2O_7} (CH_3)_2C(OClO_3)_2 + CH_3C(OClO_3)_2C(CH_3)_3$$

Both 2,2-diperchloratopropane and 2,2-dimethyl-3,3-diperchloratobutane were prepared, in yields of 70 and 52%, respectively, from the ketones and dichlorine heptoxide in carbon tetrachloride. This reaction is more convenient and provides higher yields than the anhydrous perchloric acid method[7] for preparing *gem*-diperchlorates.

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

Electronegatively substituted olefins were unreactive with dichlorine heptoxide in carbon tetrachloride. Thus, 1,1-difluoroethylene and allyl chloride gave only trace amounts of 1,1-difluoroethyl perchlorate and 1-chloro-2-propyl perchlorate, respectively, the perchloric acid adducts, apparently resulting from the spurious introduction of water. The yields of these perchlorates were increased to 76 and 91%, respectively by introducing water into the reaction mixture. Under these conditions, propene gave a 65% yield of isopropyl perchlorate and a 10% yield of 1-chloro-2-propyl perchlorate. Ethylene was also unreactive with dichlorine heptoxide, but with water added, a 63% yield of ethyl perchlorate was obtained. The addition of water to the dichlorine heptoxide solution is an experimentally convenient source of small amounts of anhydrous perchloric acid for additions to olefins under mild conditions.

$$CH_2{=}CF_2 \xrightarrow[CCl_4]{Cl_2O_7,H_2O} CH_3CF_2OClO_3$$

$$CH_2{=}CHCH_2Cl \longrightarrow CH_3CH(OClO_3)CH_2Cl$$

$$CH_2{=}CHCH_3 \longrightarrow (CH_3)_2CHOClO_3 + CH_3CH(OClO_3)CH_2Cl$$

$$CH_2{=}CH_2 \longrightarrow CH_3CH_2OClO_3$$

A yellow gas soluble in carbon tetrachloride that causes NMR signal broadening, presumably chlorine dioxide, was generally observed in the olefin–dichlorine heptoxide reaction mixtures. This compound would be formed when dichlorine heptoxide functions as an oxidizing agent; oxidation products have been observed previously in dichlorine heptoxide reactions.[4,5] Chlorine dioxide has been reported[8] to react with olefins to give 2-chloro alcohols formed by trans additions, as well as epoxides and other oxidation products. This compound provides a possible route to the observed products from 2-butene, although other mechanisms are possible. The formation of the diperchlorate from the epoxide has been reported previously.[4] The oxidation reactions also provide water, leading to perchloric acid adducts. The products from 2,3-dimethyl-2-butene are also attributable to oxidation reactions. Pinacolone would be obtained by the pinacol rearrangement of the epoxide or glycol, and acetone would be formed by an oxidative cleavage similar to the well-known reactions of periodic acid.

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 chromatograph was used for GLC determinations.

Dichlorine heptoxide was utilized as a 0.3 M reagent in carbon tetrachloride, prepared by the previously described method[2]. *Caution:* alkyl perchlorates are sensitive explosives if not diluted with solvent, and previously noted precautions should be observed.[2]

Reaction of Propene with Dichlorine Heptoxide. Dichlorine heptoxide in carbon tetrachloride (2 ml, 0.6 mmol) was placed in a 25-ml flask with a magnetic stirrer and fitted with a stopcock syringe adapter. Air was partially removed by syringe and 3 ml (0.6 mmol) of propene was added. The mixture was stirred for 24 h. A yellow gas soluble in carbon tetrachloride, presumably ClO_2, was removed by a brief application of vacuum. NMR analysis of the carbon tetrachloride solution showed isopropyl perchlorate (32% yield) and 1-chloro-2-propyl perchlorate (17%). Isopropyl perchlorate was identified by comparison with an authentic sample.[2] An analytical sample of 1-chloro-2-propyl perchlorate was isolated by GLC (5 ft × 0.25 in. column of 12% QF-1 on Chromosorb W, 60 °C): NMR (CCl_4) δ 1.62 (d, 3 H, J = 6 Hz, CH_3), 3.67 (d, 2 H, J = 7 Hz, CH_2) and 5.17 (m, 1 H, CH); ir (CCl_4) 1005, 1230, and 1265 cm^{-1}.

Anal. Calcd for $C_3H_6Cl_2O_4$: C, 20.37; H, 3.42. Found: C, 20.08; H, 3.11.

1-Chloro-2-propyl Perchlorate. A 2:1 mixture of 1-chloro-2-propanol and 2-chloro-1-propanol was prepared from propylene oxide and hydrochloric acid by the reported method.[9] A sample of 1-chloro-2-propanol, the major component, was isolated by GLC (8 ft × 0.375 in. column of 12% QF-1 on Chromosorb W, 70 °C). The compound (0.012 ml) was stirred with 1 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride for 16 h. The solution was washed with water and dried over sodium sulfate. The product was identical (NMR, ir, and GLC) with the product from propene.

Reaction of *cis*-2-Butene with Dichlorine Heptoxide. Dichlorine heptoxide (0.6 mmol) and *cis*-2-butene (0.6 mmol) were allowed to react for 4 h by the procedure used with propene. Analysis by NMR based on methyl signals showed 0.18 mmol (30%) of 3-chloro-2-butyl perchlorate and 0.012 mmol (2%) of 3-keto-2-butyl perchlorate. A similar reaction with 0.5 g of lithium perchlorate added gave the same yield of 3-chloro-2-butyl perchlorate but 0.12 mmol (20%) of 3-keto-2-butyl perchlorate.

Sufficient products for identification were obtained by adding 30 mmol of *cis*-2-butene to a mixture of 100 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and 10 g of lithium perchlorate at 0 °C. After 2 h of stirring at ambient temperature, the solution was washed with water, dried over sodium sulfate, and passed through a 2 × 32 cm slurry-packed column of silica gel. The product was eluted with carbon tetrachloride and the eluent was monitored by NMR. The 3-chloro-2-butyl perchlorate was contained in the first 100 ml of eluent. The next 50 ml contained no product, and the following 250 ml contained 3-keto-2-butyl perchlorate. The solutions of both compounds were concentrated to 25 ml by vacuum distillation with a Holzmann column, and analytical samples were isolated by GLC. The solution containing the 3-chloro-2-butyl perchlorate was distilled at ambient temperature into a −78 °C receiver at 20–0.1 mm. The residue, dissolved in carbon tetrachloride, was shown by NMR to contain 1.5 mmol (5%) of 2,3-butane diperchlorate.[4] 3-Chloro-2-butyl perchlorate was isolated from the distillate by GLC using a 5 ft × 0.25 in. column of 12% QF-1 on Chromosorb W, 100 ml/min helium, 70 °C, 15 min: NMR (CCl_4) δ 1.55 (d, 3 H, J = 6 Hz, $CHClCH_3$), 1.58 (d, 3 H, J = 6 Hz, $CHClO_4CH_3$), 4.25 (m, 1 H, CHCl), and 5.05 (m, 1 H, $CHClO_4$); ir (CCl_4) 1230 and 1265 cm^{-1}; the mass spectrum showed peaks at m/e 63, 65 (C_2H_4Cl), 91, 93 (C_4H_8Cl), 127, 129 ($C_2H_4ClO_4$), and 175, 177, 179 ($C_3H_5Cl_2O_4$).

A sample of 3-keto-2-butyl perchlorate was isolated from its carbon tetrachloride solution by GLC (5 ft × 0.25 in. column of 12% QF-1 on Chromosorb W, 100 ml/min He, 90 °C, 10 min retention time): NMR (CCl_4) δ 1.61 (d, 3 H, J = 7 Hz, CH_3CH), 2.30 (s, 3 H, CH_3CO), and 5.12 (q, 1 H, J = 7 Hz, $CHCH_3$); ir (CCl_4) 1720 (C=O), 1020, 1240, and 1270 cm^{-1} (ClO_4).

Anal. Calcd for $C_4H_7ClO_5$: C, 28.17; H, 4.13. Found: C, 28.32; H, 4.10.

Reaction of *trans*-2-Butene with Dichlorine Heptoxide. The reaction of *trans*-2-butene with dichlorine heptoxide proceeded in the same manner as that of *cis*-2-butene, and the product mixtures were indistinguishable with the exception of the stereochemistry of the 3-chloro-2-butyl perchlorate. Its GC retention time was 16 min, compared to 15 min for the product from *cis*-2-butene described above.

3-Chloro-2-butyl Perchlorates. Preparative GLC of commercial 2-butene oxide, a mixture of cis and trans isomers (0.375 in. × 12 ft column of 12% QF-1 on Chromosorb W, 100 ml/min He, 24 °C) gave *trans*-2-butene oxide, retention time 20 min, $n^{20}D$ 1.3741 (reported[10] $n^{20}D$ 1.3736), and *cis*-2-butene oxide, retention time 26 min, $n^{20}D$ 1.3821 (reported[10] $n^{20}D$ 1.3826). To 0.015 ml of *trans*-2-butene oxide and to 0.030 ml of *cis*-2-butene oxide, each in a GC collection tube, was added 0.15 ml of concentrated hydrochloric acid at 0 °C, and the mixtures were kept at ambient temperature for 1 h. Each product was extracted with 0.1 ml of methylene chloride after 0.15 ml of water was added. The crude chlorohydrins, 0.008 ml from *trans*-2-butene oxide and 0.02 ml from *cis*-2-butene oxide, were each added to 1 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. After 24 h, each reaction mixture was washed with 0.5 ml of water and dried over sodium sulfate. NMR showed only 3-chloro-2-butyl perchlorate. Mixed GLC showed that the product from *cis*-2-butene oxide was identical with that from *cis*-2-butene and dichlorine heptoxide, and the product from *trans*-2-butene oxide was identical with that from *trans*-2-butene and dichlorine heptoxide.

Reaction of 2,3-Dimethyl-2-butene with Dichlorine Heptoxide. 2,3-Dimethyl-2-butene (0.0708 g, 0.84 mmol) was added to 15 ml of 0.3 M dichlorine heptoxide at −10 °C. The mixture was kept at −10 °C for 18 h in order to allow the product to separate, although the reaction appeared to be substantially complete in 1 h. The liquid product, lighter than carbon tetrachloride, was separated. The NMR spectrum ($CDCl_3$) showed only prominent peaks assigned to 2,2-diperchloratopropane[7] and to 2,2-dimethyl-3,3-diperchloratobutane. Quantitative NMR using chloroform as a standard and CD_3NO_2 as solvent because of higher product solubility showed 0.195 mmol (11.6% based on 2 mol per mole olefin) of 2,2-diperchloratopropane and 0.195 mmol (23%) of 2,2-dimethyl-3,3-diperchloratobutane.

Reaction of Ketones with Dichlorine Heptoxide. Acetone (0.044 ml, 0.60 mmol) was added to 3 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at −5 °C. A separate liquid phase formed immediately, NMR ($CDCl_3$) δ 2.59 (s), identical with that reported for 2,2-diperchloratopropane.[7] The yield, 70%, was determined by quantitative NMR allowing a similar reaction mixture to stand for 18 h at −20 °C, removing the carbon tetrachloride by syringe, and dissolving the product in 1 ml of CD_3NO_2: δ 2.61.

By the same procedure, pinacolone gave 2,2-dimethyl-3,3-diperchloratobutane (52%): NMR ($CDCl_3$) δ 1.28 (s, 9 H), 2.48 (s, 3 H); NMR (CD_3NO_2) δ 1.33 (s, 9 H), 2.67 (s, 3 H).

Reactions of Olefins with Perchloric Acid. Water (0.0080 g, 0.44 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride for 30 min in a 25-ml flask fitted with a syringe valve. The flask was evacuated partially and 0.6 mmol of 1,1-difluoroethylene was added by syringe. NMR analysis using chlorobenzene as a quantitative reference showed only 1,1-difluoroethyl perchlorate (0.46 mmol, 76%): ^1H NMR (CCl_4) δ 1.95 (t, J = 14 Hz); fluorine NMR φ 69.52 (q, J = 14 Hz); ir (CCl_4) 1390 (m), 1280 (vs), 1200 (s), 1150 (s), 1130 (s), 1030 (s), 970 (s), and 920 cm^{-1} (s).

By this procedure, propene gave isopropyl perchlorate (65%) and 1-chloro-2-propyl perchlorate (10%) in 24 h.

Allyl chloride gave 1-chloro-2-propyl perchlorate (91%) in 24 h by this procedure.

Ethylene gave ethyl perchlorate[2] (63%) in 24 h.

Registry No.—Cl_2O_7, 10294-48-1; propene, 115-07-1; 1-chloro-2-propyl perchlorate, 58426-27-0; 1-chloro-2-propanol, 127-00-4; *cis*-2-butene, 590-18-1; 3-chloro-2-butyl perchlorate, 58426-28-1; 3-keto-2-butyl perchlorate, 58426-29-2; *trans*-2-butene, 624-64-6; *trans*-2-butene oxide, 21490-63-1; *cis*-2-butene oxide, 1758-33-4; 2,3-dimethyl-2-butene, 563-79-1; acetone, 67-64-1; pinacolone, 75-97-8; 2,2-dimethyl-3,3-diperchloratobutene, 58426-30-5; 1,1-difluoroethylene, 75-38-7; 1,1-difluoroethyl perchlorate, 58426-31-6; allyl chloride, 107-05-1; ethylene, 74-85-1; 2,2-diperchloratopropane, 28078-46-8; ethyl perchlorate, 22750-93-2; isopropyl perchlorate, 52936-33-1.

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