Hydrolysis of 1 g. (7 mmoles) of the above acetal in aqueous ethanolic hydrochloric acid gave acetaldehyde, isolated as the 2,4-dinitrophenylhydrazone, m.p. 148°.[22]

3-Methyl-2,4-dioxa-7-bicyclo[3.3.1]nonanol.—A suspension of 16.1 g. (0.122 mole) of 1,3,5-cyclohexanetriol,[17] 0.4 g. of mercuric oxide, and 0.3 ml. of boron trifluoride etherate in 1500 ml. of anhydrous tetrahydrofuran was heated to reflux and 12.9 g. (0.15 mole) of freshly distilled vinyl acetate was added very slowly. The mixture was heated for 2 hr. after all of the triol had gone into solution. Aqueous sodium carbonate was added until gas evolution ceased and the organic layer was separated and dried over anhydrous potassium carbonate. Evaporation of the solvent gave a thick viscous liquid from which a small amount of more mobile liquid was separated by extraction with ether and chloroform. This was distilled at a bath temperature of 110° at 0.05 mm.: $\bar{\nu}$ 3425, 1108, and 1093 (with a weak band at 1740 due to acetate impurity). The n.m.r. spectrum showed a quartet (1H) at τ 4.88, a poorly resolved but apparent triplet (2H) at τ 5.63, a singlet (1H) whose position varies between τ 5.9 and 7.5 depending on concentration, a doublet (*ca.* 3H) $J = 5.5$ c.p.s. at τ 8.88 and a group of unresolved peaks between τ 7.0 and 9.0. This product, obtained in less than 2% yield, polymerized before an analysis could be obtained.

2-Ethyl-1,3-dioxane.—A mixture of 19.3 g. (0.33 mole) of freshly distilled propionaldehyde, 95 g. (1.25 moles) of 1,3-propanediol, and 0.5 g. of *p*-toluenesulfonic acid was allowed to stand overnight, and then heated at reflux for 10 hr. After the addition of 300 ml. of methylene chloride and 10 ml. of 10% potassium hydroxide, the organic layer was separated, washed with saturated sodium sulfate solution, and dried. The product was distilled through a 24-in. helix-packed column, b.p. 130.5–131.5°, $n^{20}\text{D}$ 1.4219, giving 18.5 g. (48%) of a clear mobile liquid. Infrared absorption occurred at 1137, 1100, 1003, 973 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 61.87; H, 10.50.

Infrared Spectra.—Routine spectra were obtained using a Perkin-Elmer Model 21 equipped with sodium chloride prism. Spectra were run in carbon tetrachloride solution or neat in a sandwich cell. The C–H stretching frequencies were studied using a Beckman IR-7 equipped with a grating and capable of resolution to ±1 cm.$^{-1}$ in the 2700–3200-cm.$^{-1}$ range. These spectra were run on 10% solutions in carbon tetrachloride except in those cases where the bands proved too strong in a 0.05-mm. cell and more dilute solutions had to be employed.

Proton Magnetic Resonance Spectra.—Spectra were carried out using a Varian A-60 spectrometer. Samples were run in carbon tetrachloride solution and tetramethylsilane was employed as an internal standard.

Acknowledgment.—The authors are indebted to the Petroleum Research Fund for partial support of this work under Grant 814A. Financial support toward the purchase of the Varian A-60 spectrometer by the National Science Foundation is most gratefully acknowledged.

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t-Butyl Hypochlorite Chlorinations of Hydrocarbons. The Role of Chlorinated Solvents[1]

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In the course of a continuing investigation of relationships between reactivity, hyperconjugative stabilization, and activation energies of alkyl radical reactions it became necessary to establish the role of carbon tetrachloride, the usual solvent, in *t*-butyl hypochlorite chlorinations of hydrocarbons.[2] This fairly selective chlorinating agent reacts *via* the chain. Reactions 1–2,

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

$$R\cdot + (CH_3)_3COCl \longrightarrow RCl + (CH_3)_3CO\cdot \qquad (2)$$

carried out in nonpolar solvents, proceed cleanly and in high yields. Fluorocarbons, excess hydrocarbon substrate, and carbon tetrachloride have been used as solvents, the last being the most common. Although products and yields are substantially the same in all these solvents, there exists the possibility that in carbon tetrachloride the sequence 3–4 can become a part of the radical chain reaction. The possibility that

$$R\cdot + ClCCl_3 \longrightarrow RCl + \cdot CCl_3 \qquad (3)$$

$$CCl_3 + (CH_3)_3COCl^* \longrightarrow Cl^*CCl_3 + (CH_3)_3CO\cdot \qquad (4)$$

reaction 5 may also occur can be ruled out on the basis of

$$\cdot CCl_3 + RH \longrightarrow HCCl_3 + R\cdot \qquad (5)$$

the report that the relative reactivities of a series of hydrocarbons do not vary significantly with changes in solvent.[3] The absence of any significant amounts of chloroform among the products is inconclusive in view of the considerable selectivity of the trichloromethyl radical.[4] Sequence 3–4 is suggested by the well-known use of polyhalomethanes as chlorinating agents.[5]

The chlorination of toluene, 2,3-dimethylbutane, and 2,2-dimethylpropane (neopentane) in carbon tetrachloride and the possible involvement of the solvent was investigated by the use of *t*-butyl hypochlorite labeled with chlorine-36, a β-emitter. In all cases the activity was found exclusively, within experimental error, in the alkyl chloride product indicating that reactions 3–4 do not occur to any significant extent. Even when the hypochlorite was added dropwise as a dilute solution in carbon tetrachloride to a carbon tetrachloride solution of the hydrocarbon, no activity could be detected in the carbon tetrachloride.

In the case of toluene, the absence of any involvement of the solvent is not unexpected in view of the results of Walling and Padwa who, in a similar reaction with *t*-butyl hypochlorite and toluene in bromotrichloromethane solvent, did not obtain more than a 3% yield of bromotoluene.[6] A reactive alkyl radical (cyclobutyl), however, was reported to react 97% with the solvent to give alkyl bromide, upon dropwise addition of hypochlorite. In our case the failure of even the reactive primary radical neopentyl to react with approximately a 500-fold excess on the average of carbon tetrachloride over hypochlorite indicates a large difference in activation energy for abstraction of bromine *vs.* chlorine from halomethanes. An activation energy of about 13 kcal./mole for abstraction of chlo-

(1) Research was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); (b) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963).

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(4) B. P. McGrath and J. M. Tedder, *Bull. soc. chim. Belges*, **71**, 772 (1962).

(5) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 390; (b) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).

(6) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

rine from carbon tetrachloride by the methyl radical can be estimated.[7]

It appears that, in the usual *t*-butyl hypochlorite chlorinations in carbon tetrachloride, the solvent is not involved in the chain reaction sequence. Studies of activation energies of reactions of alkyl radicals derived from or in the presence of hypochlorites can be carried out in carbon tetrachloride without any doubt as to the origin of the chlorine atom in the alkyl halide product.

Experimental

***t*-Butyl hypochlorite-Cl^{36}** was prepared essentially as in ref. 2a. Chlorine was bubbled through 200 ml. of carbon tetrachloride until the solution became 2.015 *N* by iodometric titration; 48 g. of mercuric oxide (yellow) was added and stirring was continued for 17 hr. with tap water cooling. The solids were filtered and the organic layer was extracted with 160 ml. of cold distilled water. After one washing with 20 ml. of carbon tetrachloride, titration showed the water layer to be 1.93 *N* in hypochlorous acid. *t*-Butyl alcohol (3.7 g.) in 71.3 ml. of carbon tetrachloride and all of the hypochlorous acid solution were mixed and stirred for 3 hr. with ice cooling. The organic layer was separated, washed with 5 ml. of water, 10 ml. of 5% sodium carbonate, and 5 ml. of water, and dried with anhydrous magnesium sulfate. The entire preparation was carried out in subdued light or in the dark. Titration showed that the carbon tetrachloride solution was 0.965 *M* in *t*-butyl hypochlorite, for a 96.5% yield based on the alcohol.

Portions of the hypochlorite solution were labeled with chlorine-36 immediately before use since autoradiolysis may be fairly fast with hypochlorites. In a typical preparation 5.0 ml. of the hypochlorite solution was shaken in a separatory funnel with 4.0 ml. of a 1.6 *N* aqueous solution of HCl containing 80 μc. of chlorine-36. The exchange was fast[8] and equilibration was complete after 15 min. Titration showed that autoradiolysis is insignificant for 15 min. in the dark.

Reactions of *t*-Butyl Hypochlorite-Cl^{36}.—In a typical experiment 3.82 g. (29.8 mmoles) of carbon tetrachloride and 1.36 g. (18.9 mmoles) of neopentane were placed in an ice bath and 3.77 ml. of labeled hypochlorite solution (3.8 mmoles of hypochlorite and 36.1 mmoles of carbon tetrachloride) was added dropwise over 2 hr. with vigorous stirring and irradiation from a 300-w. incandescent lamp. The products were analyzed by gas–liquid chromatography with a Loenco Model 70 Hi-Flex coupled with an on-line ionization chamber and a Cary 31 vibrating reed electrometer for simultaneous detection of the activity. All the activity was found under the neopentyl chloride mass peak. The experimental error in the activity determination was 5%.

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1,2-Dichlorotetracyanoethane

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The exceptionally electrophilic character of the double bond in tetracyanoethylene is illustrated by its facile condensation with amines,[1] alcohols,[2] and electron-rich aromatic[3] compounds and by the ease with which it takes up an electron to form an anion radical.[4] Another illustration has now been found in its chlorination to 1,2-dichlorotetracyanoethylene. This chlorination, like that of tricyanoethylene[5] and tetracyanoquinodimethan,[6] is catalyzed by chloride ion. Evidently a chloro carbanion is an intermediate rather than a chlorocarbonium ion as in the chlorination of most alkenes.

$$(NC)_2C{=}C(CN)_2 + Cl^- \longrightarrow [(NC)_2CClC(CN)_2^-] \xrightarrow{Cl_2} (NC)_2CClCCl(CN)_2 + Cl^-$$

The chlorination is most conveniently carried out in acetonitrile at 0°, where no catalyst is needed. However, in methylene chloride the chlorination proceeds at a negligible rate until a trace of tetramethylammonium chloride is added, whereupon chlorination is rapid.

1,2-Dichlorotetracyanoethane is a colorless, crystalline compound that sublimes at 100° (6 mm.) with no apparent loss of chlorine. Positive chlorine is shown by liberation of iodine from sodium iodide solution. With excess N,N-dimethylaniline, 1,2-dichlorotetracyanoethane reacts to give N,N-dimethyl-*p*-tricyanovinylaniline.[7] This must arise by initial chlorination of the N,N-dimethylaniline with formation of tetracyanoethylene, which then reacts with the excess N,N-dimethylaniline. Heating 1,2-dichlorotetracyanoethane with cyclohexene or 1-hexene gave rise to tetracyanoethylene. The chlorinated products were not isolated.

Experimental

1,2-Dichlorotetracyanoethane.—A solution of 31.5 g. (0.44 mole) of chlorine in 100 ml. of acetonitrile was stirred in a 500-ml., three-necked flask equipped with a Dry Ice condenser and dropping funnel and immersed in an ice bath. A solution of 55 g. (0.43 mole) of tetracyanoethylene in 300 ml. of acetonitrile was added rapidly through the dropping funnel. The mixture was stirred for 1 hr., and a crystalline precipitate of 1,2-dichlorotetracyanoethane was separated by filtration. It was recrystallized from benzene: yield 57 g. (66%), m.p. 160–162°. An analytical sample was prepared by sublimation at 100° (6 mm.), followed by recrystallization from benzene: m.p. 164–165°.

Anal. Calcd. for $C_6N_4Cl_2$: C, 36.2; N, 28.1; Cl, 35.7. Found: C, 36.2; N, 27.4; Cl, 35.3.

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The Photorearrangement of 2,6-Di-*t*-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadien-1-one

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In connection with our work on the thermal decomposition of the peroxide **1**,[1] we became interested in the photo reactions of **1** (and related peroxides).

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