

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-Cl³⁶ 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 μ c. of chlorine-36. The exchange was fast⁸ and equilibration was complete after 15 min. Titration showed that autoradiolysis is insignificant for 15 min. in the dark.

Reactions of *t*-Butyl Hypochlorite-Cl³⁶.—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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Received May 28, 1964

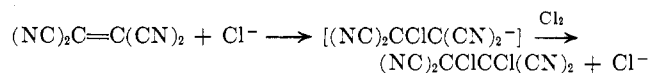
The exceptionally electrophilic character of the double bond in tetracyanoethylene is illustrated by its facile condensation with amines,¹ alcohols,² and electron-rich aromatic³ compounds and by the ease with

(1) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

(2) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

(3) J. R. Roland and B. C. McKusick, *ibid.*, **83**, 1652 (1961).

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 tricyanoethylene⁵ and tetracyanoquinodimethane,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.



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 C₆N₄Cl₂: 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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Received February 27, 1964

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).

(1) E. R. Altwickler, C. D. Cook, and D. L. Marks, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963, p. 26Q.