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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(8) (a) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962); (b) M. Anbar, S. Guttman, and R. Rein, *ibid.*, **81**, 1816 (1959).

1,2-Dichlorotetracyanoethane

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Contribution No. 976 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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

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(5) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *ibid.*, **82**, 6132 (1960).

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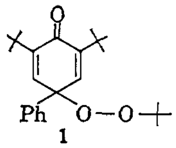
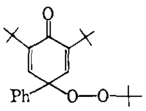
(1) E. R. Altwicker, C. D. Cook, and D. L. Marks, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963, p. 26Q.

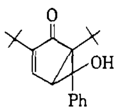


1

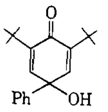
One product isolated from the reaction mixture was thought to be **2** (on the basis of spectral data). This was shown to be incorrect later, but it prompted the investigation of **3**[2] as a possible precursor to **2**. The photolysis of **3** itself is of interest since (a) it is a dienone with bulky *ortho* substituents, (b) in view of the work of Yang[3] it would be of importance to establish whether the methyl hydrogens participate in intramolecular H-transfer to give cyclobutanol derivatives, and (c) **3** is an example of a cross-conjugated dienone having groups other than carbon attached directly in the 4-position.[4]



1

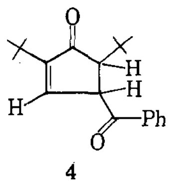


2



3

The photolysis of **3** (0.5% solutions in dioxane containing a small amount of water) was carried out in Pyrex with a Hanovia utility lamp at 22 ± 2° until most of **3** had been consumed. Column chromatography and fractional crystallization gave a crystalline solid **4**, m.p. 157.0–158.2°, isomeric with **3**, $C_{20}H_{26}O_2$. The ultraviolet spectrum (in methanol) of **4** showed absorption at 318 mμ (ϵ 249) and strong end absorption at 223 mμ (cyclopentenone), as well as absorption at 328 (249), 277 (1440), and 243 (22,400) (benzoyl group); strong infrared bands were observed at 1691 (conjugated carbonyl), 1681 (benzoyl–carbonyl), and 1007 cm.$^{-1}$, as well as aromatic bands constituent with monosubstitution. The n.m.r. spectrum showed peaks at τ 8.99 and 8.84 (*t*-butyl groups), a doublet ($J = 2.5$ c.p.s.) centered at 7.05 (tertiary H), a triplet at 5.48 (PhCO–CH), a doublet ($J = 3$ c.p.s.) at 2.88 (O=C—C=C—H), and aromatic peaks in the 2.46–1.92 region. Peak areas were in the approximate ratios of 9:9:1:1:1:5. Compound **4** formed a mono-2,4-dinitrophenyl hydrazone (sharp carbonyl absorption at 1691 cm.$^{-1}$), m.p. 166.0–167.4°, $C_{26}H_{30}N_4O_5$. These data established the structure of **4** as a cyclopentenone derivative. The yield of **4** was about 20%. A second crystalline compound, m.p. 110.8–11.6°, also isomeric with **3**, was isolated in very low yield; sufficient material for full characterization has not been accumulated.



4

No evidence for **2** or other fractions containing hydroxyl absorption has been obtained. The occurrence of **2** as an intermediate would have been of interest, since it could give rise to **4** *via* a cyclopropanol ring opening of the type observed by DePuy,[5] although DePuy has recently reported[6] that this reaction is probably not free radical in nature. By employing the polar concept of product control in photochemical reactions,[7] the rearrangement of **3** to **4** *via* **2** can be rationalized. The generality of the reaction is under exploration.

Experimental[8]

The starting material **3** was prepared according to Müller, *et al.*,[2] m.p. 140.2–141.0°. Eastman White Label dioxane was passed over alumina just before use. The solution (containing *ca.* 5% water) was flushed 30 min. with oxygen-free N_2 before irradiation commenced. The course of the reaction was followed by thin layer chromatography (silica gel G). When most or all of **3** had been consumed, the solvent was removed by vacuum distillation at about 30°. The viscous residue was treated with hexane (or cyclohexane) to give a small crop of **4** or was taken up in ether, dried, and, after removal of the ether, chromatographed on Woelm III neutral alumina from hexane. Two recrystallizations of the first fraction from hexane–chloroform gave **4**, m.p. 157.0–158.2°; yields varied somewhat (10–25%) depending on work-up.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.40; H, 8.78. Found: C, 80.28; H, 8.47; mol. wt., 298.4 (Rast, 251). Calcd. for $C_{26}H_{30}N_4O_5$: C, 65.22; H, 6.32; N, 11.70. Found: C, 65.14; H, 6.49; N, 11.57.

Acknowledgment.—The authors wish to thank Dr. Michael Gianni for his help with the n.m.r. spectrum and the Petroleum Research Fund (Grant 1156-A4) for financial assistance.

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(8) All melting points are uncorrected. Analyses are by Galbraith Laboratories, Knoxville 21, Tenn. The n.m.r. spectrum was obtained on a Varian A-60 (using tetramethylsilane as internal standard).

The Structure of 1,3-Naphthalenediol Anion

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Although the ketone form of phenols is frequently postulated to explain certain of their reactions, direct observations of such ketone–enol interconversions are scarce. Among the few examples of the presence of the ketone form are the partial isomerization of 1,4-naphthalenediols in the molten state[2,3] and the equili-

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(1) To whom inquiries should be addressed.

(2) D. B. Bruce and R. H. Thomson, *J. Chem. Soc.*, 2759 (1952).

(3) *Cf.* also the existence of leucoquinizarin, a 1,4-naphthalenediol, in the ketone form: S. M. Bloom and R. F. Hutton, *Tetrahedron Letters*, 1993 (1963).