g. (0.02 mole) of benzhydrol in 50 ml. of glacial acetic acid was treated with 2.5 ml. of concd. sulfuric acid at room temperature. After 3 hr. the resulting crystals were filtered, washed with water, and recrystallized from *n*-hexane to give 7.5 g. (~100%) of colorless crystals, m.p. 134–134.5°, λ_{max} 284 mμ; ϵ_{max} 2980.

2,6-Di-butyl-4-benzoylphenol (I-C_6H_5CO)—. Aluminum chloride, 13.3 g. (0.1 mole), was added to 40 ml. (0.43 mole) of freshly distilled benzoyl chloride and the flask swirled until complex formation seemed to be complete. Using an ice bath to keep the temperature below 25°, 20.6 g. (0.1 mole) of 2,6-di-*t*-butylphenol was slowly added. The mixture was allowed to stand for an hour in an ice bath, then taken up in benzene, and washed with 4*M* sodium hydroxide. Evaporation of the benzene and recrystallization from petroleum ether (b.p. 90–120°) gave 17 g. (55%) of white crystals, m.p. 124–125°. A mixture melting point with an authentic specimen[18] gave no depression.

2,6-Di-t-butyl-4-acetylphenol (I-CH_3CO)—. At 0°, 3.5 g. (0.25 mole) of aluminum chloride was added to 25 ml. of acetyl chloride and, when solution was complete, 4.12 g. (0.02 mole) of 2,6-di-*t*-butylphenol was slowly added. After 45 minutes the mixture was poured into diluted hydrochloric acid containing cracked ice and then extracted with *n*-hexane. Evaporation of the excess hexane gave 3.2 g. (70%) of white crystals, m.p. 145–148°, recrystallized from *n*-hexane, m.p. 147–148°.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74; MW, 248.35; Found: C, 77.39; H, 9.87; MW, 255 (cryoscopic, benzene).

2,6-Di-t-butyl-4-(α-methoxyethyl)phenol (*I-CH(CH$_3$)OCH$_3$*) was prepared by the addition of methanol to 2,6-di-*t*-butyl-4-ethylidene-2,5-cyclohexadiene-1-one according to the method of Cook and Norcross.[1a] The material was obtained in essentially quantitative yields, m.p. 105–105.5° after recrystallization from acetonitrile-water solutions.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.62; MW, 264.39; Found: C, 77.56; H, 10.18; MW, 261 (cryoscopic, benzene).

B. *Preparation of peroxides.* The peroxides were prepared by oxidizing the phenols with a twofold excess of alkaline potassium ferricyanide solution in oxygen-saturated benzene.[7]

Bis(1,5-di-t-butyl-3-benzoyl-2,4-cyclohexadiene-6-one) peroxide (IV-C_6H_5CO)—. Two grams of I-C_6H_5CO gave 0.22 g. (8%) of the above peroxide, m.p. 132–134° dec. after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{42}H_{50}O_6$: C, 77.51; H, 7.74. Found: C, 77.70; H, 7.68.

The ultraviolet spectrum λ_{max} 262 mμ, ϵ_{max} 23,000; λ_{max} 317 mμ, ϵ_{max} 5000 (cyclohexane) indicates that this peroxide has the structure IV-C_6H_5CO.[19] When 0.1% of the peroxide was added to acrylonitrile and the solution warmed to 70° under a nitrogen atmosphere, polymer started to precipitate within 2 min.

Bis(3,5-di-t-butyl-1-phenyl-2,5-cyclohexadiene-4-one) peroxide (III-$(C_6H_5)_3C$)—. Oxidation of 2 g. of I-C_6H_5 for 8 hr. gave 1.8 g. (87%) of light yellow crystals, m.p. 145–147° dec. after recrystallization from acetonitrile; reported,[1b] m.p. 146–148° dec.

C. *Preparation of dimers.* A mixture of 10 g. of potassium ferricyanide, 2 g. of potassium hydroxide, 75 ml. of water, and 50 ml. of benzene was placed in a flask and flushed with oxygen-free nitrogen. A solution of 0.01 to 0.02 mole of the appropriate phenol (I-Cl, I-Br, I-NO_2) in 25 ml. of benzene was rapidly added and the mixture vigorously stirred for 2 to 5 min. The solutions were separated and the benzene layer dried and taken to dryness in a rotary vacuum drier.

1,1'-Dichloro-3,5,3'5'-tetra-t-butyl-bis-2,2',5,5'-cyclohexadiene-4,4'-one (V-Cl)—. Oxidation of 2.6 g. (0.01 mole) of I-Cl as above gave 2.09 g. (77%) of the above dimer V-Cl, recrystallized from ethyl acetate to m.p. 148.5–150°; reported,[12] m.p. 150–151°; λ_{max} 242 mμ, ϵ_{max} 16,600 (cyclohexane).[20]

Anal. Calcd. for $C_{28}H_{40}O_2Cl_2$: C, 70.13; H, 8.41; Cl, 14.79; MW, 479.51; Found: C, 70.48; H, 8.49; Cl, 14.75; MW, 482 (cryoscopic, benzene). Attempted recrystallization from ethanol or shaking a benzene solution with mercury gave quantitative yields of diphenoquinone (VI) as identified by comparison of ultraviolet spectra and mixture melting points with an authentic specimen.[14]

Oxidation of 2.85 g. (0.01 mole) of I-Br as above gave 2.3 g. (81%) of impure yellow crystals which decomposed over a wide temperature range (110° up) and which decomposed on standing, on solution in polar solvents, or on shaking in benzene with mercury to give the diphenoquinone VI. The material showed an ultraviolet max at 242 mμ, ϵ_{max} = ~25,000 and gave a molecular weight (cryoscopic, benzene) of 538. Calculated for V-Br, 570.6.

Very rapid oxidation of I-NO_2 with limiting amounts of ferricyanide gave only the diphenoquinone VI and unchanged I-NO_2. Use of excess ferricyanide led to quantitative yields of VI.

D. *Other oxidations. 2,6-Di-t-butyl-4-benzhydrylidine-2,5-cyclohexadiene-1-one*—. A solution of 3 g. (0.08 mole) of I-$(C_6H_5)_2CH$ in 25 ml. of benzene was stirred with 20 g. (0.06 mole) of potassium ferricyanide and 10 g. (0.25 mole) of sodium hydroxide in 100 ml. water. The solution turned brilliant blue and gradually faded to deep orange. Removal of the benzene and recrystallization of the residue gave 2.6 g. (87%) of orange crystals, m.p. 178.5–179°, λ_{max} 261 mμ, ϵ_{max} 16,700 (cyclohexane).

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.30; H, 8.15. Found: C, 87.40; H, 8.10.

Oxidation of 2,6-di-t-butyl-4-methylmethoxymethylphenol (I-CH(CH$_3$)OCH$_3$) to 2,6-di-t-butyl-4-acetylphenol (I-CH$_3$CO)—. A solution of 730 mg. (0.0027 mole) of I-CH-$(CH_3)OCH_3$ in 20 ml. benzene was oxidized with a solution of 5 g. (0.011 mole) potassium ferricyanide and 1 g. (0.025 mole) of sodium hydroxide in 25 ml. of water. The layers were separated and the benzene layer was washed with water and dried over sodium sulfate. After removal of the benzene 140 mg. (20%) of product was obtained, m.p. 144–147°. Mixed melting point and infrared spectrum showed the sample to be identical with I-CH_3CO.

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[18] T. H. Coffield, A. H. Filbey, G. C. Ecke, and A. J. Kolka, *J. Am. Chem. Soc.* **79**, 5023 (1957).

[19] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.* 3211 (1953).

(20) Reported for V, R = H, λ_{max} 242 mμ, ϵ_{max} = 15,000 ref. 13.

Hexachloroacetone as a Novel Source of Dichlorocarbene

PANKAJA K. KADABA AND JOHN O. EDWARDS

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Edwards, Evans, and Watson[1] carried out an electrometric study on dilute aqueous solutions of

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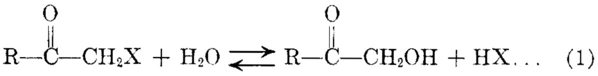
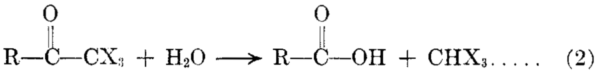
[1] E. G. Edwards, D. P. Evans, and H. B. Watson, *J. Chem. Soc.*, 1942 (1937).

halogenated ketones and discovered the presence of halide ions in the solutions and of chloroform in solutions of hexachloroacetone. They explained these observations as resulting from, not the ionization of ketones, as was thought earlier,[2] but from hydrolyses of two types: an alkyl halide type 1, in the case of mono- and dihalogenated ketones, and a haloform type 11, in the case of polyhalogenated ketones containing the $—CX_3$ group, which involves attack upon the carbonyl carbon. The



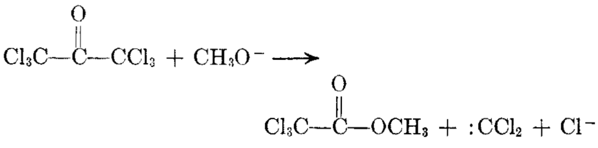
$$R-\overset{O}{\overset{\|}{C}}-CH_2X + H_2O \rightleftarrows R-\overset{O}{\overset{\|}{C}}-CH_2OH + HX\ldots \quad (1)$$



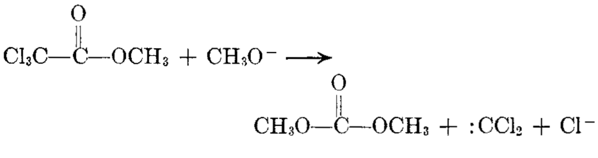
$$R-\overset{O}{\overset{\|}{C}}-CX_3 + H_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + CHX_3\ldots\ldots \quad (2)$$

electron attractive character of the halogen atoms in $R-\overset{O}{\overset{\|}{C}}-CX_3$ render the carbonyl group highly reactive towards nucleophiles, thereby enabling the $—CX_3$ to break away with the electron pair by which it was originally linked to the carbonyl carbon. They found this reaction to be prominent in ketones which have three halogens linked to the same carbon atom, and in hexachloroacetone the carbonyl group is so activated that this change occurs to the almost complete exclusion of reaction 1.

From the results of these authors, hexachloroacetone would be expected to yield dichlorocarbene in a nonprotonic medium in the presence of a base like sodium methoxide. Further, the methyl trichloroacetate[3] formed in the first step would then react with more methoxide to yield more dichlorocarbene in a similar manner. Thus, for every mole



$$Cl_3C-\overset{O}{\overset{\|}{C}}-CCl_3 + CH_3O^- \longrightarrow Cl_3C-\overset{O}{\overset{\|}{C}}-OCH_3 + :CCl_2 + Cl^-$$



$$Cl_3C-\overset{O}{\overset{\|}{C}}-OCH_3 + CH_3O^- \longrightarrow CH_3O-\overset{O}{\overset{\|}{C}}-OCH_3 + :CCl_2 + Cl^-$$

of hexachloroacetone, there could result two moles of dichlorocarbene.

The carbene hypothesis has been tested here by the introduction of carbene acceptors and has indeed been found to be the case. Experiments have been carried out using three acceptors. In the first case, a mixture of benzalaniline in dry petroleum ether containing sodium methoxide was treated with hexachloroacetone and the adduct (1,2-diphenyl-3,3-dichloroethylenimine) was obtained as the sole reaction product in 61% yield. Our product had the same melting point reported by Fields and Sandri[4] and underwent rearrangement to the α-chloro-α-phenylacetanilide. In the second case, a mixture of cyclohexene and sodium methoxide in petroleum ether was treated with hexachloroacetone to yield the expected 7,7-dichlorobicyclo[4.1.0]heptane (dichloronorcarane) in 43% yield based on olefin. There was also obtained a stable, colorless, crystalline solid (10% yield based on hexachloroacetone). Similar results were obtained with 2-methyl-2-butene, the latter also yielding (in addition to 1,1-dichloro-2,2,3-trimethylcyclopropane) the same crystalline compound. The solid melted at 86–87° and contained chlorine. It was insoluble in water but dissolved readily in bases and underwent fast hydrolysis in basic solutions. The solid showed no precipitation with alcoholic silver nitrate and gave a positive carbylamine test. Its infrared spectrum showed a strong absorption at 3525 cm.$^{-1}$ and a weak band at 3225 cm.$^{-1}$ Analysis gave C, 13.98%; H, 0.93% and Cl, 79.65%. All of the above observations are in agreement with the expected behavior of hexachloroisopropyl alcohol; this compound had been synthesized by Geiger, *et. al.*[5] but its chemical properties were not investigated by them. The strongly acidic nature of the hydroxyl group of this compound is explained as due to the presence of two strong electron withdrawing groups on the carbon atom to which the hydroxyl group is attached.

The reduction of hexachloroacetone to form hexachloroisopropyl alcohol occurred exclusively in the reactions wherein olefins were present. This indicated that either the olefin itself, or its dichlorocarbene adduct, is involved in the reduction. However, a mixture of dichloronorcarane and hexachloroacetone in dry petroleum ether containing sodium methoxide, under conditions identical with earlier experiments, failed to yield the alcohol. Also, no reduction was observed (either by isolation or by infrared analysis) when an excess of cyclohexene was treated with hexachloroacetone in the absence of sodium methoxide. The reaction is highly interesting and further investigations should be carried out on the chemistry of this reduction.

The yields obtained with hexachloroacetone as carbene source were not as large as with ethyl trichloroacetate[3] as carbene source. However, hexachloroacetone certainly is a dichlorocarbene source of ready availability at low price and might be desirable as a source of dichlorocarbene for large scale preparations.

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(3) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(4) E. K. Fields and J. M. Sandri, *Chem. & Ind.* (*London*), 1216 (1959).

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EXPERIMENTAL

1,2-Diphenyl-3,3-dichloroethylenimine Hexachloroacetone (97%, technical grade, Baker and Adams) (26 g., 0.1 mole), was added with stirring under dry nitrogen, over 1 hr. to a mixture of commercial sodium methoxide (5.4 g., 0.1 mole) (Matheson, Coleman, and Bell) and benzalaniline[6] (9 g., 0.05 mole) in dry petroleum ether (b.p. 37–39°) (200 ml., treated to remove any unsaturation present), cooled in an ice bath. Stirring was continued for 5–6 hr. under nitrogen, with the reaction mixture cooled in ice and water. The flask was then stoppered and kept overnight. It was then filtered and the residue separately treated with water, to remove inorganic materials; the desired product remained, 5 g., m.p. 95–98°. From the petroleum ether solution was obtained another 3 g. of product, m.p. 95–98° (total yield, 61%). Careful crystallization of a sample from petroleum ether gave creamy white crystals, m.p. 98–99° (reported,[4] m.p. 98–99°), identical with the product obtained by using ethyltrichloroacetate[3] in place of hexachloroacetone.

The compound has a characteristic unpleasant odor and precipitates silver chloride from an alcoholic solution of silver nitrate. It undergoes rearrangement in water; the reaction is very slow at room temperature but is complete in 30 min. at 100°, to give α-chloro-α-phenylacetanilide in quantitative yields. The amide was crystallized from acetone–petroleum ether mixture to give colorless crystals, m.p. 148–149° (reported,[4] m.p. 146–148°).

7,7-Dichlorobicyclo[4.1.0]heptane (dichloronorcarane). The reaction was carried out in essentially the same manner as before. It was then poured into cold water, extracted with ether, the ether extracts dried over anhydrous sodium sulphate, and concentrated. The residue was distilled through a short fractionating column and the dichloronorcarane collected at 78–79.5°/15 mm. (reported[7] b.p. 78–79°/15 mm.).

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.9; H, 6.1; Cl, 43.0. Found: C, 50.80; H, 5.95; Cl, 43.23.

The oily residue left behind in the distillation flask, on cooling solidified to give hexachloroisopropyl alcohol which crystallized from hexane to give colorless, stout crystals, m.p. 86–87° (reported[5] m.p. 87–87.5°).

Anal. Calcd. for $C_3H_2OCl_6$: C, 13.50; H, 0.76; Cl, 79.75. Found: C, 13.98; H, 0.93; Cl, 79.65.

Four experiments with variation in reactant concentrations gave yields of dichloronorcarane ranging from 34 to 43%. Yields of hexachloroisopropyl alcohol varied from 3% to 10%; the higher values were obtained with short reaction times and with equimolar amounts of hexachloroacetone and sodium methoxide.

1,1-Dichloro-2,2,3-trimethylcyclopropane. Hexachloroacetone (53.0 g., 0.2 mole) was added with stirring over 1.5 hr. under dry nitrogen, to a cold mixture of sodium methoxide (10.8 g., 0.2 mole) and 2-methyl-2-butene (150 ml., excess). The mixture was stirred for 3.5 hr. and worked up in the same manner as above. Fractional distillation yielded the product (b.p. 144°)[7] mixed with small amounts of methyltrichloroacetate (b.p. 154°). The ester was destroyed by refluxing with a 15% aqueous solution of potassium hydroxide (50 ml.) for 15 min., and 1,1-dichloro-2,2,3-trimethylcyclopropane distilled at 69.5°/55 mm., yield 7 g. (23%), (reported[7] b.p. 69–70°/55 mm.).

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 46.93; H, 6.66; Cl, 46.60.

From the residue was obtained hexachloroisopropyl alcohol, 4.0 g., m.p. 86–87°, identical in properties with that obtained in the reaction using cyclohexene.

Reaction media. After the above data were obtained, Dr. Francis T. Smyth found that more consistent yields could be obtained if 5 ml. of methanol were added to the petroleum ether solvent.

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(7) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.,* **76,** 6162 (1954).

Hexachloroacetone as a Source of Dichlorocarbene

F. W. GRANT AND W. B. CASSIE

February 18, 1960

Since the original observation of Doering and Hoffman[1] that cyclopropane derivatives are formed by the reaction of chloroform, olefins, and potassium *t*-butoxide, a number of attempts have been made to increase the efficiency of this conversion by varying the base[2,3] and the chlorinated species.[3] Recently, Parham and Schweizer[3] have developed an elegant procedure based on ethyl trichloroacetate as the progenitor of the dichlorocarbene intermediate in this reaction. Yields of cyclohexene adduct of up to 79%, based on trichloroacetate, were obtained using sodium methoxide as the base.

The reaction of sodium methoxide with hexachloroacetone presents a mechanistically similar situation where the latter reagent has the advantage of offering two equivalents of dichlorocarbene per molecule. Preliminary experiments carried out with cyclohexene as the carbene acceptor have resulted in a 59% yield of 2,2-dichlorobicyclo[4.1.0]heptane based on the indicated stoichiometry.

$$Cl_3CCOCCl_3 \xrightarrow{OR^-} :CCl_2 + Cl^- + Cl_3CCOOR$$

$$Cl_3CCOOR \xrightarrow{OR^-} :CCl_2 + Cl^- + CO(OR)_2$$

EXPERIMENTAL[4]

2,2-Dichlorobicyclo[4.1.0]heptane. Sodium (5.75 g., 0.25 g.-atoms) was added in portions to 30 ml. of anhydrous methanol. Excess methanol was removed by heating and flushing with dry nitrogen. Hexachloroacetone[5] (26.5 g., 0.10 mole) was added dropwise with stirring to a mixture of the sodium methoxide and 82.0 g. (1.0 mole) of cyclohexene at 0–5°. Stirring was continued for 5 hr. at this temperature

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(1) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.,* **76,** 6162 (1954).

(2) H. E. Winberg, *J. Org. Chem.,* **24,** 264 (1959).

(3) W. E. Parham and E. E. Schweizer, *J. Org. Chem.,* **24,** 1733 (1959).

(4) Boiling points are uncorrected.

(5) We wish to thank the General Chemical Division of Allied Chemical Corporation for a sample of this material.