The Formation of Hexachlorocyclopropane by the Addition of Dichlorocarbene to Tetrachloroethylene

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The addition of dihalocarbenes to olefins discovered by Doering and Hoffmann[1] has provided an exceptionally useful and widely used synthesis of dihalocyclopropanes. Studies by Skell[2] and Doering[3] have established that dibromocarbene and dichlorocarbene behave as electrophilic reagents since electron-donating groups on an olefin facilitate addition. Accordingly, a highly negatively substituted olefin would be expected to be quite unreactive[3] toward dihalocarbenes. In particular, it appeared to be of interest to examine the addition of dichlorocarbene to tetrachloroethylene, an olefin which is resistant to electrophilic attack, since the potential adduct, hexachlorocyclopropane, which might prove to be of intrinsic interest, was reported by Stevens[4] to be unavailable by way of chlorination of cyclopropane. To this end, dichlorocarbene was generated in the presence of tetrachloroethylene by treatment of chloroform with strong bases[1] and by the thermal decomposition of sodium trichloroacetate[5] in 1,2-dimethoxyethane. Hexachlorocyclopropane was formed in these reactions, but in low yields (*ca.* 0.2–1%).[6]

The structure of the compound, a white crystalline solid, m.p. 104–104.5°, was established by elemental analysis, which gave an empirical formula of CCl_2, and the determination of the molecular weight cryoscopically and by mass spectrometry. The mass spectrum of C_3Cl_6 does not show any peak due to the molecular ion, but no fragments are formed which have more than three carbon atoms. The most abundant fragment is C_3Cl_5, corresponding to loss of a single chlorine atom. Inasmuch as there can be only two compounds with a molecular formula of C_3Cl_6, namely hexachlorocyclopropane and hexachloropropylene, and the latter is a well known commercially available liquid, it is clear that the solid referred to above is perchlorocyclopropane.

In retrospect, it appears likely that Stevens[4] did prepare hexachlorocyclopropane. He reported that chlorination of 1,1,2,2-tetrachlorocyclopropane for seven days at 63° in the presence of ultraviolet light gave hepta- and octachloropropane as the main products, but also gave a very small amount of a white crystalline solid, m.p. 102–102.5°, which on the basis of elemental analysis he believed to be the then unknown 1,1,1,3,3,3-hexachloropropane.[7] Subsequently, Davis and Whaley[8] have prepared 1,1,1,3,3,3-hexachloropane by chlorination of 1,1,1,3,3-pentachloropropane followed by fractionation to separate the two hexachloropropanes which are formed and have reported that 1,1,1,3,3,3-hexachloropropane is a liquid, b.p. 205°, m.p. −27°. Since all four hexachloropropanes have Raman spectra[9] which are consistent with the assigned structures, we believe that Stevens probably did succeed in preparing hexachlorocyclopropane.

The fact that perchlorocyclopropane was formed at all in the present study, albeit in very low yields, takes on greater significance when one considers that dichlorocarbene apparently fails to react with ethylene[3] (in preference to reaction with *t*-butoxide). Tetrachloroethylene is far less reactive than ethylene in typical electrophilic reactions (*e.g.*, addition of bromine). Thus it is possible that in reacting with tetrachloroethylene, dichlorocarbene may be exhibiting either radical or nucleophilic character.

Experimental

Reaction of Chloroform with Potassium *t*-Butoxide.—Chloroform (36 g.) was added dropwise with stirring over a period of 1 hr. to a mixture of 50.5 g. of potassium *t*-butoxide (freed of alcohol by heating at 140° at 1 mm.) and 325 g. of freshly distilled tetrachloroethylene. The reaction mixture was cooled intermittently with an ice bath. The mixture was stirred at room temperature for an hour and then was poured into water. The organic layer was separated, dried, and the bulk of the tetrachloroethylene was removed by distillation at atmospheric pressure leaving a dark oil, a portion of which distilled at 70–120° (1–2 mm.) leaving a considerable quantity of residual tar. The distillate, shown by gas chromatography to be mainly tetrachloroethylene, was redistilled slowly under reduced pressure, leaving a solid residue. The latter was sublimed five times at 40–50° (0.5 mm.) giving 0.21 g. of hexachlorocyclopropane, m.p. 104.0–104.5°.

Anal. Calcd. for C_3Cl_6: C, 14.46; Cl, 85.54; mol. wt., 249. *Found:* C, 14.46; Cl, 85.69; mol. wt., 241.[10]

In solution (carbon disulfide and carbon tetrachloride), perchlorocyclopropane shows prominent bands in the infrared at 850 (s), 905 (m), and 930 (w) cm.$^{-1}$. Mass spectrum was measured on a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer with a heated inlet system (140°) at an ionizing potential of 70 v. The mass number of the largest isotopic peak of each monopositive carbon-containing fragment is given as a percentage of the largest peak in the spectrum. Normal isotopic distribution of Cl^{35} and Cl^{37} was observed within each fragment (thus all fragments listed contain only Cl^{35} except the last three each of which contains one Cl^{37}).

Fragment, mass number (percentage): CCl, 47 (35.4); C_2Cl, 59 (6.4); C_3Cl, 71 (30.3); CCl_2, 82 (22.2); C_2Cl_2, 94 (12.2); C_3Cl_2, 106 (15.4); CCl_3, 117 (26.4); C_2Cl_3, 129 (4.4); C_3Cl_3, 141 (16.8); C_2Cl_4, 166 (12.8); C_3Cl_4, 178 (0.9); C_3Cl_5, 213 (100.0).

Use of Sodium Hydride.—Methyl alcohol (9.6 g., 0.30 mole) was added dropwise with stirring over a period of 9.5 hr. at room temperature to a mixture of 298 g. of tetrachloroethylene, 7.2 g. (0.30 mole) of sodium hydride, and 44.6 g. (0.37 mole) of chloroform. The mixture was processed as above to give 0.42 g. of hexachlorocyclopropane. When the methyl alcohol was omitted (reflux, 40 hr.) or replaced by *t*-butyl alcohol (60°, 11 hr.), only a trace of this product was isolated.

Use of Sodium Trichloroacetate.—A mixture of 18.5 g. of sodium trichloroacetate, 80 g. of tetrachloroethylene, and 150 ml. of 1,2-dimethoxyethane was refluxed 24 hr. After processing in the usual way, the mixture was concentrated by distillation and and both distillate and residue were analyzed by gas chromatog-

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

(2) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(3) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(4) P. G. Stevens, *ibid.*, **68**, 620 (1946).

(5) W. M. Wagner, *Proc. Chem. Soc.* (London), 229 (1959).

(6) (a) Since this work was completed, the formation of hexachlorocyclopropane by similar means (chloroform and fused potassium hydroxide at 105°), but in higher yields (5–10%), has been reported by S. W. Tobey and R. C. West, Abstracts of Papers presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, p. 95Q; (b) after submission of this manuscript we learned that E. K. Field and S. Meyerson have also prepared this compound and measured its mass spectrum.

(7) Analysis indicated 0.53% hydrogen, a value in between the required values of 0.00 for hexachlorocyclopropane and 0.80 for hexachloropropane.

(8) H. W. Davis and A. M. Whaley, *J. Am. Chem. Soc.*, **73**, 2361 (1951).

(9) H. Gerding and H. G. Haring, *Rec. trav. chim.*, **74**, 841 (1955).

(10) Determined by Dr. C. M. Starks by freezing point lowering of benzene solutions.

raphy which indicated formation of *ca.* 1% of hexachlorocylopropane (t_R = 6.6).[11] The chromatograms showed peaks due to several other minor components, one of which was collected (t_R = 2.7) and found to have a strong band at 1763 cm.$^{-1}$ but which was not characterized further.

In a similar experiment, the gas evolved during the reflux period was collected and analyzed by infrared spectroscopy which indicated that the sample consisted of carbon dioxide that did not contain more than a small amount (< 5%) of carbon monoxide. This result apparently precludes significant reaction of dichlorocarbene with trichloroacetate ion to give, over-all, carbon monoxide, trichloroacetyl chloride, and chloride ion by a reaction path formally similar to that described[12] for the reaction of dichlorocarbene with alkoxide ions. In other control experiments it was found that the thermal decomposition of sodium trichloroacetate in 1,2-dimethoxyethane did not produce significant quantities of materials with retention times greater than that of the solvent.

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(11) Retention time relative to tetrachloroethylene, t_R = 1.00; 1,2-dimethoxyethane, t_R = 0.33 on silicone oil at 150°.

(12) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

Addition Reactions of *m*- and *p*-Nitronitrosobenzene[1]

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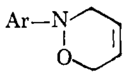
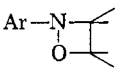
The addition reactions of aromatic nitroso compounds to conjugated dienes are well known.[2] The reaction products I, dihydroöxazines, generally are isolated in high yields. Side products of the reaction have not been reported.

o-Nitronitrosobenzene[2] conforms to this pattern, but for the reaction of *m*- or *p*-nitrosobenzene with 2,3-dimethyl-1,3-butadiene, we have found two reaction products. One of these reaction products was found to be the expected adduct I. The second reaction product II showed an elemental analysis and molecular weight corresponding to an adduct consisting of one mole of diene and two moles of nitroso compound.

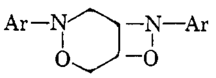
Aromatic nitroso compounds have been reported to react smoothly with suitably substituted alkenes,[3] yielding oxazetidines III. Product II, therefore, might be the result of the normal 1,4-addition of nitroso compound to diene, followed by a 1,2-addition of the nitroso compound to the dihydroöxazine, yielding compound IV or its isomer.



I



III



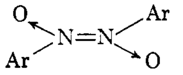
IV

In order to test this hypothesis, we attempted to treat the normal 1,4-adduct of *p*-nitronitrosobenzene and 2,3-dimethyl-1,3-butadiene with the equivalent amount of *p*-nitronitrosobenzene. We were unable to detect a reaction with the aid of infrared spectra. Unsuccessful attempts were also made to prepare an oxazetidine from *p*-nitronitrosobenzene and the following alkenes: cyclohexene, cyclopentene, isobutylene, *cis*- and *trans*-2-butene.

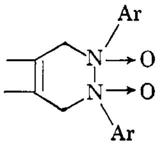
Considering the evidence, this hypothesis concerning the structure of product II was then rejected. It was also considered unlikely that the conjugated diene would add two moles of the nitroso compound in a 1,2-fashion.

It is well established that many aromatic nitroso compounds are in a state of equilibrium between monomer and dimer in solution.[4] The monomeric state is generally favored by electron-donating groups. The electron-withdrawing nitro group will cause a considerable fraction of the nitronitrosobenzenes to be in the dimeric state V. It is also well known that electron-poor azo groups are excellent dienophiles in Diels–Alder reactions.[5]

The formation of the products II may then be accounted for by a reaction between the diene and the electron-poor N=N group of the dimeric nitronitrosobenzene, to form a tetrahydro-1,2-diazine-N,N-dioxide VI.



V



VI

Steric hindrance may explain the failure of *o*-nitronitrosobenzene to give an adduct of this type, while the low yield of this adduct for *m*-nitronitrosobenzene may be ascribed to the decreased resonance effect.

The infrared absorption band at about 1050 cm.$^{-1}$ associated with the oxazine ring,[2] was absent from the spectra of products II. Although the spectra of a small number of tertiary amine oxides have been reported[6], we have not been able to assign bands in the 970–950-cm.$^{-1}$ region unequivocally to the amine oxide. The insolubility of products II in suitable solvents ruled out the determination of an nuclear magnetic resonance spectrum.

Conclusive evidence for the assertion that products II have structure VI was furnished by the deoxygenation of the N,N-dioxide IIa by Ochai's method,[7] employing phosphorus trichloride as the deoxygenation agent. The known substance 4,5-dimethyl-1,2-bis-(*p*-nitrophenyl)-1,2,3,6-tetrahydropyridazine[8] was obtained as the deoxygenation product.

Experimental[9]

***m*-Nitronitrosobenzene,** m.p. 89–90°, and ***p*-nitronitrosobenzene,** m.p. 118°, were prepared by oxidation with Caro's acid from the corresponding amines.[10]

Adducts of *p*-Nitronitrosobenzene.—*p*-Nitronitrosobenzene, 0.50 g. (3.3 mmoles), and 2,3-dimethyl-1,3-butadiene, 0.37 g. (4.5 mmoles), were dissolved in 20 ml. of nitromethane at 0°. The green color of the solution, caused by the monomeric nitroso compound, changed in about 15 min. to orange, indicating the

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(1) This work was supported by the Petroleum Research Fund; it was presented at the 14th Southeastern Regional Meeting, Gatlinburg, Tenn., November 3, 1962.

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(3) C. K. Ingold and J. D. Weaver, *J. Chem. Soc.*, **125**, 1146 (1924).

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(5) A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).

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(7) E. Ochai, *J. Org. Chem.*, **18**, 550 (1953).

(8) P. Baranger, J. Levisalles, and M. Vuidart, *Compt. rend.*, **236**, 1365 (1953).

(9) All melting points are uncorrected. Analysis by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra measured in potassium bromide with a Beckman IR-5.

(10) E. Bamberger and E. Huebner, *Ber.*, **36**, 3803 (1903).