Mechanism of Reaction of Potassium Diphenylmethide with Carbon Tetrachloride[1]

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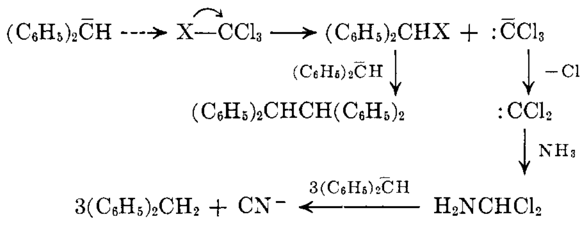
Recently[2] carbon tetrachloride and bromotrichloromethane were shown to react with potassium diphenylmethide in liquid ammonia to form tetraphenylethane, diphenylmethane, and cyanide ion. These products were assumed to arise through an initial displacement on halogen by diphenylmethide ion to form benzhydryl halide and trichlorocarbanion, which undergo further reactions as indicated in Scheme A.



Scheme A

That the trichlorocarbanion was an intermediate was supported by the isolation of its decomposition product, dichlorocarbene, as an adduct with cyclohexene when the reaction was carried out in this solvent.[2] However, the trichlorocarbanion did not necessarily arise by the displacement on halogen indicated in Scheme A. It might have arisen through two consecutive displacements on carbon by diphenylmethide ion. The first displacement would have occurred at the carbon of the carbon tetrahalide to form I, and the second would have taken place at the benzhydryl carbon of I. The latter reaction also would have afforded tetraphenylethane, one of the products obtained.

$$\underset{\text{I}}{(C_6H_5)_2CH—CCl_3} \qquad \underset{\text{II}}{(C_6H_5)_2C{=}CCl_2}$$

We have now shown that I is not an intermediate in the reaction of the carbon tetrahalide with potassium diphenylmethide in liquid ammonia. Thus an authentic sample of I afforded only a little tetraphenylethane and no cyanide ion with this reagent under similar conditions. Instead I underwent dehydrohalogenation to give II and diphenylmethane.

More significantly, we have isolated intermediate benzhydryl chloride, which would be one of the two initial products from the displacement on halogen. This was accomplished by adding a solution of potassium diphenylmethide in liquid ammonia to excess carbon tetrachloride. Benzhydryl chloride is known[3] to react with diphenylmethide ion in liquid ammonia to form tetraphenylethane. Therefore the displacement on halogen shown in Scheme A may now be considered established.

Experimental[4]

Dehydrohalogenation of I with Diphenylmethide Ion.—To a stirred solution of 0.0183 mole of potassium diphenylmethide[2] in 150 ml. of liquid ammonia was added 5.22 g. (0.0183 mole) of 1,1-diphenyl-2,2,2-trichloroethane (I) in 100 ml. of ether. The red-orange color of the reagent was discharged. The ammonia was evaporated, and water and methylene chloride were added. The mixture was filtered and the layers were separated. The aqueous layer did not give a Prussian blue test for cyanide ion. The methylene chloride solution was concentrated, diluted with hexane, and chilled. The resulting precipitate was removed by filtration and recrystallized from ethanol to give 1.43 g. (31%)[5] of 1,1-dichloro-2,2-diphenylethylene (II), m.p. 78°. The melting point was not depressed on admixture with authentic III (m.p. 78°), prepared by dehydrohalogenation of I with ethanolic potassium hydroxide.[6] The methylene chloride–hexane filtrate obtained above was fractionally distilled to give 2.61 g. (85%) of diphenylmethane, b.p. 80–82° at 0.5 mm. Only a 3% yield of tetraphenylethane could be isolated from the reaction product.

Isolation of Benzhydryl Chloride from Diphenylmethide Ion and Carbon Tetrachloride.—To a stirred solution of 32 g. (0.21 mole) of freshly distilled carbon tetrachloride in 60 ml. of dry ether was added a solution of 0.05 mole of potassium diphenylmethide[2] in 300 ml. of liquid ammonia (inverse addition procedure). The ammonia was evaporated and water was added. The resulting mixture was filtered and the two layers were separated. The aqueous layer contained 0.012 mole of cyanide ion.[7] The organic layer was dried over Drierite and concentrated. The residual oil was shown by v.p.c. to contain 4.2 g. (50%) of diphenylmethane and 4.3 g. (42%) of benzhydryl chloride (chlorodiphenylmethane). Distillation afforded a sample of benzhydryl chloride, b.p. 102° at 0.5 mm., $n^{25}\mathrm{D}$ 1.5932, which gave an infrared spectrum identical with that of an authentic sample ($n^{25}\mathrm{D}$ 1.5933).

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[1] Supported by the National Science Foundation.

[2] C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

[3] C. R. Hauser and P. J. Hamrick, *J. Am. Chem. Soc.*, **79**, 3142 (1957).

[4] Melting points are uncorrected.

[5] This yield might be improved by employing the inverse addition procedure, since II can react further with the reagent to form 1,1,3,3-tetraphenylallene; this reaction is being studied.

[6] A. Baeyer, *Ber.*, **6**, 220 (1873).

[7] F. Charlot and D. Bezier, "Quantitative Inorganic Analysis," transl. by R. C. Murray, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 380.

The Reaction of Dichlorocarbene with Benzofuran and Benzothiophene[1]

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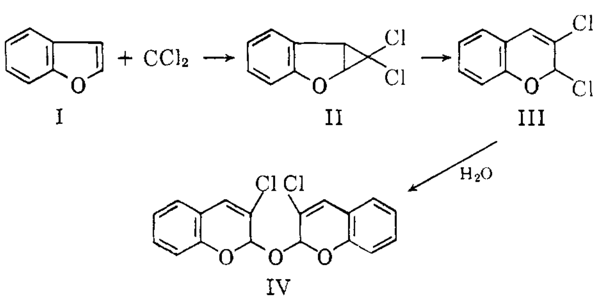
Benzofuran reacts with dichlorocarbene in hexane to form an adduct which is converted into bis[3-chloro-2(3-chromenyl)] ether (IV, m.p. 181–182°, 14.9% yield) by hydrolysis with water.



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Evidence related to the structure of the ether IV was obtained in the following way. The product had the molecular formula $C_{18}H_{12}Cl_2O_3$, and the ultraviolet spectrum suggested olefinic unsaturation conjugated to a benzene ring. The nuclear magnetic resonance spectrum showed peaks at 3.75, 3.09, 2.79, and 2.60 τ (see Experimental), and no absorption in the 5.94- or 7.95-τ region expected for the cyclopropyl ether II.[2] The ether reacted readily with 2,4-dinitrophenylhydrazine reagent to give a hydrazone with the composition calculated for the expected derivative of 2-chloro-3-(2-hydroxyphenyl)propenal.

The ether IV is thought to form as shown in the equations I $\rightarrow$ II $\rightarrow$ III $\rightarrow$ IV. The product, II and/or III, formed prior to addition of water, decomposed upon attempted distillation of chromatography upon alumina. The facile ring expansion of II to III, which occurred either spontaneously in hexane or rapidly upon addition of water, was not unexpected in view of the behavior of related compounds. The corresponding cyclopropane derived from indene[3] underwent ring expansion to give chloronaphthalene when it was dissolved in polar solvents such as alcohol, and the corresponding cyclopropanes derived from dichlorocarbene and 1- or 2-methoxynaphthalene underwent ring expansion[4] in nonpolar solvents at temperatures below 32°.

Although dichlorocarbene does not add appreciably to benzene, the observed addition to benzofuran was expected in view of: (a) the greater nucleophilic character of furan relative to benzene and (b) the known effects of strongly electron-donating substituents as evidenced by the reaction of dichlorocarbene with methoxy-substituted aromatics.[4]

Benzothiophene does not react appreciably with dichlorocarbene even when the latter is in 100% excess. A 92% recovery of aromatic was noted. This observation is consistent with the fact that oxygen can normally[5] enrich the electron density of an attached double bond by utilizing its unshared p-orbital electrons more effectively than can sulfur, and with the greater nucleophilic character of furan relative to thiophene; however, one cannot discount at this time further deactivation of benzothiophene by complex formation between the sulfur atom and dichlorocarbene.[6]

Experimental

Bis[3-chloro-2(3-chromenyl)] Ether (IV).—Ethyl trichloroacetate (53.6 g., 0.281 mole) was added all at once to a cold (ice bath) mixture, under nitrogen, of benzofuran (27.5 g., 0.233 mole), sodium methoxide (16.1 g., 0.298 mole), and pure hexane (200 ml.). The violet color which developed rapidly disappeared. The mixture was kept cold for 6 hr., then allowed to come to room temperature overnight. The resulting solution was divided in two equal parts. Attempts at purification of one part by vacuum distillation and by chromatography on alumina were unsuccessful. In each case decomposition was noted.

Water (100 ml.) was added to the second portion and the resulting mixture was stirred for 3 days at room temperature.[7] The organic layer was separated, dried, and the solvent was removed. The residue was triturated with petroleum ether (b.p. 30–60°), and the solid thus obtained was recrystallized from benzene. There was obtained 3 g. (14.9%) of IV which decomposed at 181–182° with elimination of hydrogen chloride.

Anal. Calcd. for $C_{18}H_{12}Cl_2O_3$: C, 62.35; H, 3.46; Cl, 20.43; mol. wt., 347. Found: C, 62.60; H, 3.68; Cl, 20.89; mol. wt. (Rast), 313.

Infrared (KBr pellet) spectrum: 3068 w, 1638 m, 1606 m, 1575 w, 1489 s, 1460 s, 1206 s, 1194 s, 1124 s, 1083 s, 1008 vs, 962 vs, 925 vs, 756 vs cm.$^{-1}$.

Ultraviolet spectrum (in absolute ether): λ_{max} 263.2 (ϵ 27,200), 273 (ϵ 25,700), and 297 mμ (ϵ 6500).

The nuclear magnetic resonance spectrum of IV as a 10% solution in deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as a reference gave: 3.75 τ, singlet assigned to hydrogens alpha to the ether oxygen (calcd.[8] 3.73), 3.09 τ, finely split doublet assigned to the benzyl hydrogen, and 2.79 and 2.60 τ, complex splitting assigned to the aromatic hydrogens.

The 2,4-dinitrophenylhydrazone of 2-chloro-3-(2-hydroxyphenyl)propenal was obtained from IV and the usual reagent. The product was purified by recrystallization from ethyl acetate (m.p. with decomposition 257.5–260°, yield <50%).

Anal. Calcd. for $C_{15}H_{11}ClN_4O_5$: C, 49.66; H, 3.04; N, 15.45. Found: C, 49.59; H, 3.24; N, 15.51.

The reaction of benzothiophene and dichlorocarbene was attempted using the same conditions described above for benzofuran. Benzothiophene (m.p. 29–31°) was recovered (92% recovery).

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(2) W. E. Parham and L. D. Huestis, *J. Am. Chem. Soc.*, **84**, 813 (1962).

(3) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *ibid.*, **78**, 1437 (1956).

(4) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *ibid.*, **83**, 603 (1961).

(5) It has been suggested that this situation may not obtain in furan relative to thiophene due, primarily, to steric factors; *cf.* M. M. Kreevoy, *ibid.*, **80**, 5543 (1958).

(6) W. E. Parham and R. Koncos, *ibid.*, **83**, 4034 (1961).

(7) In an earlier experiment the mixture was merely extracted with water; the yield of IV was essentially the same.

(8) D. P. Daily and J. N. Schoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

The Reaction of Carbanilides with Sodium Hypochlorite[1]

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Treatment of carbanilide (Ia) with three moles of sodium hypochlorite has been reported by Rosnati[2] to yield 1-phenyl-2-hydroxybenzimidazole (the enol form of IIa). Rosnati also cyclized a number of symmetrically substituted carbanilides (*e.g.*, 4,4′-dimethyl-; 4,4′-dichloro-; 4,4′-dimethoxy-) and demonstrated that the N,N′-dialkylated carbanilides (I. R_3, R_4 = CH_3; R_1, R_2, R_3, R_4 = H) and 2,2′,4,4′,6,6′-hexamethylcarbanilide are inert to alkaline hypochlorite. Because of its biological interest, we deemed it advisable to investigate the behavior of 3,4,4′-trichlorocarbanilide (Ib)[3] upon hypochlorite treatment. Because of the asymmetry involved, ring closure could occur in several directions. Rosnati's work with symmetrical carbanilides does not provide sufficient information for predicting the course of the cyclization.

To obtain a reference compound for our work, we repeated Rosnati's experiment with Ia. Following Rosnati's directions,[2] Ia, when treated with three moles

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(1) Presented before the Division of Organic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) L. Rosnati, *Gazz. chim. ital.*, **86**, 275 (1956).

(3) D. J. Beaver, D. P. Roman, and P. J. Stoffel, *J. Am. Chem. Soc.*, **79**, 1236 (1957); D. J. Beaver and P. J. Stoffel, U. S. Patent 2,818,390 (December 31, 1957).