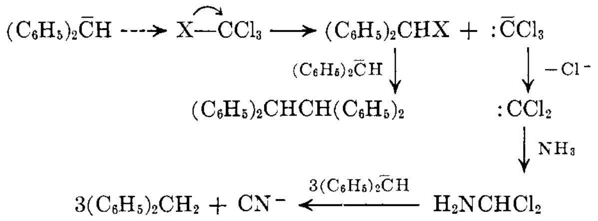
Mechanism of Reaction of Potassium Diphenylmethide with Carbon Tetrachloride[1]

WILLIAM G. KOFRON AND CHARLES R. HAUSER

Department of Chemistry, Duke University, Durham, North Carolina

Received October 22, 1962

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., $n^{25}\text{D}$ 1.5932, which gave an infrared spectrum identical with that of an authentic sample ($n^{25}\text{D}$ 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.

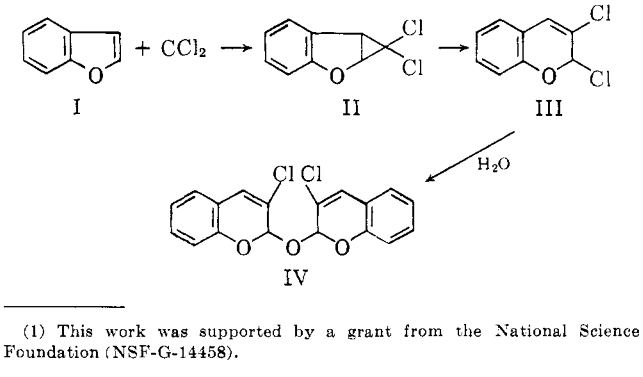
The Reaction of Dichlorocarbene with Benzofuran and Benzothiophene[1]

WILLIAM E. PARHAM, CHARLES G. FRITZ, ROBERT W. SOEDER, AND R. M. DODSON

Department of Chemistry, University of Minnesota, Minneapolis 14, Minnesota

Received September 10, 1962

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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(1) This work was supported by a grant from the National Science Foundation (NSF-G-14458).