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Photolysis of Tetraphenylcyclobutadienenickel Bromide

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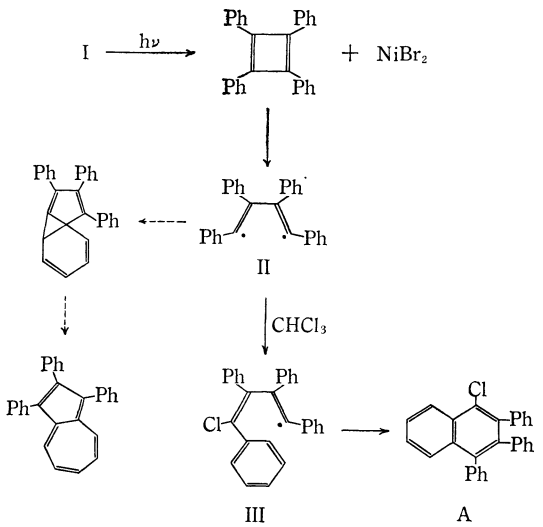
Thermal behavior of some cyclobutadiene-metal complexes has been well studied.[1] Much less is known, however, about the photochemical reaction of the complexes except for the results of the photolysis of cyclobutadieneiron tricarbonyl by Masamune *et al.*[2] An interesting point in such a reaction is the photochemical behavior of the unstable cyclobutadiene-ligands which are liberated by photodecomposition. Therefore, we have investigated the photolysis of tetraphenylcyclobutadienenickel bromide (I).

The complex I was prepared from 1,1-dimethyl-2,3,4,5-tetraphenylstannole by Freedman's method.[3] The irradiation of I was carried out in a chloroform solution under a nitrogen atmosphere at 10—16°C for 12 hr by using a 500 W high pressure mercury lamp.[4] After irradiation, the insoluble material which resulted from the reaction was filtered off and characterized as nickel bromide. Thus it can be considered that in the reaction the complex I is decomposed by light, thus liberating tetraphenylcyclobutadiene. After the solvent had been evaporated *in vacuo*, the reaction products were separated by alumina-column chromatography. Elution with petroleum ether and recrystallization gave colorless needles (A). The other products were a large quantity of a tarry matrial and an uncharacterized complex. The compound A was found to be 1-chloro-2,3,4-triphenylnaphthalene by an elemental analysis, a molecular-weight determination, and a study of its spectroscopic data. The structure of A was further confirmed by converting it to 1,2,3-triphenylnaphthalene[5] by treatment with metal lithium and then methanol.

The photochemical reaction of diphenylacetylene in *n*-hexane has previously been reported to give 1,2,3-triphenylnaphthalene and 1,2,3-triphenylazulene *via* a tetraphenylcyclobutadiene intermediate.[6] In contrast to this reaction, interestingly, only a chlorinated naphthalene was obtained in our reaction, not azulene. Accordingly, a chlorine atom must be abstracted from the solvent in one stage of the reaction. Therefore, we propose the following reaction scheme including the diradical intermediate (II). The diradical II abstracts the chlorine atom more easily to afford the monoradical III than II rearranges itself intramolecularly since no azulene is formed in this reaction.[7]



Thus, it can be said that this may depend upon the ease with which the chlorine atom is abstracted from the solvent. In fact, when (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin bromide was irradiated in benzene, only 1,2,3-tri-

1) As leading references for the reaction of cyclobutadienemetal complexes; see a) P. M. Maitlis, "Advances in Organometallic Chemistry," Vol. 4, Academic Press, New York, N. Y. (1966), p. 95. b) M. P. Cava and M. J. Mitchell," Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y. (1967), p. 88.

2) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz and H. E. Gunning, *Chem. Commun.*, **1967**, 497.

3) H. H. Freedman, *J. Amer. Chem. Soc.*, **83**, 2194, 2195 (1961).

4) At intervals of about 3 hr, the wall of the internal, water-cooled high-pressure mercury arc lamp (Eikosha Co. Ltd., Oyodo-ku Osaka model PIH-500S), which had been coated with a tarry material during the reaction, was washed with hydrochloric acid.

5) L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, **63**, 1184 (1941).

6) G. Buchi, C. W. Perry and E. W. Robb, *J. Org. Chem.*, **27**, 5106 (1962).

7) Very recently such an intermolecular naphthalene formation has been reported for the dimerization of phenylpropiolic acid by H. W. Whitlock, Jr., E-M. Wu and B. J. Whitlock in *J. Org. Chem.*, **34**, 1857 (1969).

phenylazulene was formed,[8] whereas in chloroform only the naphthalene A was obtained.[9]

Experimental

Irradiation of Tetraphenylcyclobutadienenickel Bromide (I). A solution of 2.43 g (4.23 mmol) of I[3] in 1 liter of chloroform, agitated by the bubbling of nitrogen gas, was irradiated with a 500 W high pressure mercury lamp, and then the reaction vessel was cooled with ice water. The reaction was followed by studying the ultraviolet spectrum. After the solution had been irradiated for 12 hr, the characteristic ultraviolet peak near 300 mμ, present in I, disappeared. The nickel bromide (*ca.* 718 mg, 3.29 mmol) which appeared during the irradiation was filtered off, and the chloroform was evaporated *in vacuo*. Into the residue, there was added petroleum ether, and then the undissolved amorphous material was filtered off. The filtrate was chromatographed on a column of alumina (48 g). Elution with petroleum ether (55 m*l*) gave pale yellow crystals (133 mg), which were then further chromatographed and recrystallized from petroleum ether. We thus obtained 76 mg (0.19 mmol) of 1-chloro-2,3,4-triphenylnaphthalene (A) as colorless crystals, mp 187—188°C. IR (Nujol): 1070, 1028, 883, 763, 700, and 645 cm^{-1}. UV: λ_{max}^{EtOH} 238 (log ε=4.79), 270[sh] (4.20), and 297 mμ (4.04). NMR (CCl_4): multiplet at τ 1.65—1.70 (1H), multiplets centered at τ 2.55 (3H), 2.97 (11H), and 3.27 (4H). Its UV and NMR spectra were very similar to those of 2,3,4-triphenyl-1-naphthol.[11]

Found: C, 85.38; H, 4.87; Cl, 9.01%. Calcd for $C_{28}H_{19}Cl$: C, 86.03; H, 4.89; Cl, 9.07%.

Reduction of A with Lithium, 1,2,3-Triphenylnaphthalene. A solution of 58 mg of A in 10 m*l* of dry ether was refluxed with stirring in the presence of 10 mg of clean lithium shavings. A purple-brown lithium compound was formed after 8 hr, after which the reflux was continued for an additional 3 hr. The excess lithium was decomposed with methanol, and then the mixture was poured into water. The organic layer was extracted with ether, dried over anhydrous sodium sulfate, and concentrated. The residue was chromatographed on a column of alumina (3.9 g). Elution with petroleum ether (40 m*l*) gave 45 mg of 1,2,3-triphenylnaphthalene (mp 153—156°C (from ethanol-benzene)). The IR spectrum of this compound was superimposable upon that of an authentic material prepared from diphenylacetylene and lithium,[5] and a mixed melting point was undepressed.

8) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962). This reaction has been reported to proceed *via* a tetraphenylcyclobutadiene-like intermediate.

9) Unfortunately, the complex I could not be irradiated in benzene since I is quite insoluble in this solvent.

10) Petroleum ether refers to a fraction with a bp of 40—60°C, the melting points are uncorrected.

11) N. Obata and I. Moritani, This Bulletin, **39**, 1975 (1966).