The Photochemical Reaction of Benzo[*c*]cinnoline. I. The Photoreduction and Subsequent Reactions in Acidified Alcohols

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The photoinduced reaction of benzo[*c*]cinnoline (BCC) in strongly acidic aqueous alcohols, in which BCC exists in a monoprotonated form (BCCH$^+$), was investigated. The initial step of the photoreaction was the hydrogen abstraction, which gave rise to 5,6-dihydroBCCH$^+$, irrespective of the excitation wavelengths and the kind of alcohol (methanol, ethanol, or 2-propanol) used as a solvent. The subsequent reaction occurred upon irradiation by a light longer than 400 nm to afford 2,2′-diaminobiphenyl in ethanol, but not in methanol and 2-propanol. The 1-hydroxyethyl radical formed in the initial photoreduction appeared to participate in this reaction, donating its hydrogen atom to the ground-state 5,6-dihydroBCCH$^+$. On the other hand, ultraviolet irradiation caused the subsequent photoreaction of 5,6-dihydroBCCH$^+$, thus giving carbazole accompanied by the liberation of ammonia.

The photochemistry of a variety of nitrogen heterocyclic compounds has been studied.[1,2] Hitherto, however, little has been known concerning the photochemical behavior of *ortho*-diazines. Chen *et al.*[3] studied the photoreaction of 4-methylcinnoline in ethers, and showed that the 1,4-addition of the ethers occurred. According to Davis and Cohen,[4] benzo[*c*]cinnoline (BCC) undergoes photoreduction to give 5,6-dihydrobenzo[*c*]cinnoline (5,6-dihydroBCC) in benzene containing triethylamine as a hydrogen donor. 5,6-DihydroBCC is very susceptible to oxidation to BCC;[5] hence, it is not isolated. However, in a previous paper[6] it has been found that 5,6-dihydroBCC is fairly stable in a polyvinyl alcohol film, thus permitting the observation of its ultraviolet spectrum, when it is produced photochemically in the film. As has been briefly reported,[7] the ultraviolet irradiation of BCC in strongly acidic aqueous 2-propanol (3.75 M HCl), interestingly, affords carbazole in a fairly high yield. However no carbazole formation is observed when irradiation is carried out on a neutral solution of BCC in 2-propanol.

The purpose of the present paper is to present the experimental results on the photoreaction of BCCH$^+$ in strongly acidic alcohol under nitrogen. Since the photoreaction has been found previously to depend on the excitation wavelengths and on the kind of alcohol used as a solvent (methanol, ethanol, or 2-propanol), particular attention is paid to these points.

Results and Discussion

In an acidic solution stronger than 3 M HCl, BCC exists in the monoprotonated form (BCCH$^+$) and has the absorption spectrum shown in Fig. 1. Although the n-π^* band is at the longest wavelength for BCC,[8] the 420 nm band of BCCH$^+$ is of the π-π^* type. All irradiations were carried out on such strongly acidic solutions of BCC.

Photoreaction of BCC in 2-Propanol and Methanol upon Visible-light Irradiation. A 1.6×10^{-4} M solution of BCCH$^+$ in acidic aqueous 2-propanol was irradiated with visible light longer than 400 nm in an atmosphere of nitrogen at room temperature by using a filter whose percent transmittance is shown in Fig. 1. The spectral change in the solution caused by the irradiation is shown in Fig. 2. The reaction was completed in 180 min of irradiation, giving rise to a compound with absorption bands at 240, 270, and 316 nm. The compound thus produced readily reverted quantitatively to BCC when the irradiated solution was neutralized or bubbled with air, while it was fairly stable in the acidic solution under nitrogen. These facts may indicate that the photoreduction of BCCH$^+$ takes place to give 5,6-dihydroBCC, which is known to be susceptible to oxidation to BCC.[5] The product was identified on the basis of the absorption spectrum. That is to say, as BCC has been found to be photoreduced to 5,6-dihydroBCC in a polyvinyl alcohol film,[6] the absorption spectrum of the acidified film containing 5,6-dihydroBCCH$^+$ was measured. The spectrum thus obtained is almost identical with that of the product under consideration in the acidic solution.

Also, in acidic methanol the visible-light irradiation led to the photoreduction of BCCH$^+$ into 5,6-dihydroBCCH$^+$. The rate of the reaction in the methanol solution was much slower than that in the 2-propanol solution, in agreement with the difference in the ease

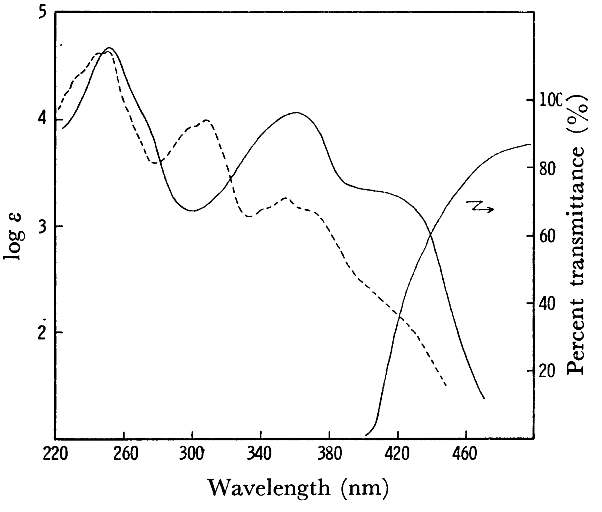


Fig. 1. Absorption spectra of BCC and percent transmittance of a filter used for visible light irradiation.
——: in ethanol, ----: in 4M HCl ethanol-water

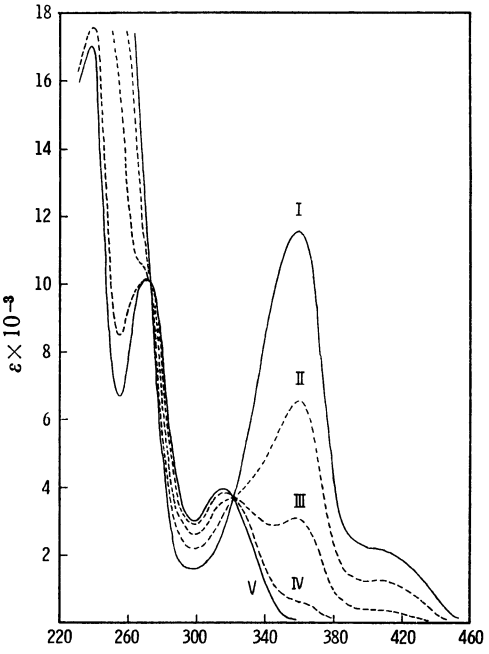


Fig. 2. Spectral change caused by visible light irradiation upon 4M HCl 2-propanol solution.
Initial concentration of BCC: 1.6×10^{-4}M. Irradiation time (min); I: 0, II: 15, III: 30, IV: 60, V: 180.

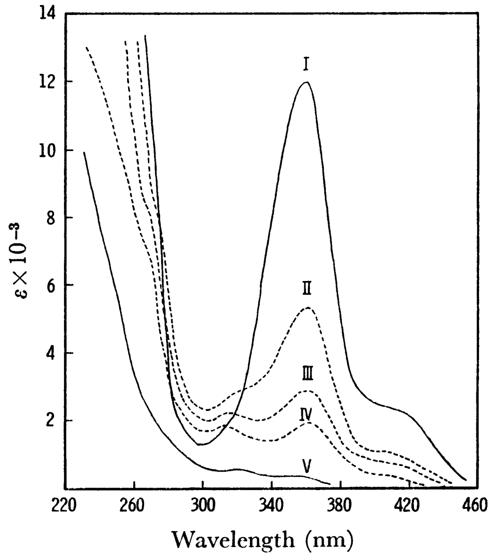


Fig. 3. Spectral change caused by visible light irradiation upon 4N HCl ethanol solution.
Initial concentration of BCC: 1.0×10^{-4}M. Irradiation time (hr); I: 0, II: 1, III: 2, IV: 3, V: 6.

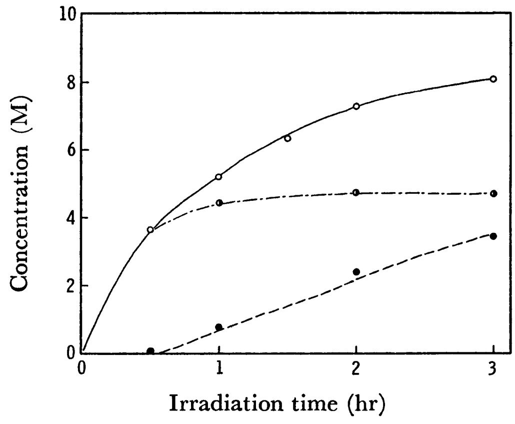


Fig. 4. Rate of the reaction upon visible light irradiation upon 4M HCl ethanol solution.
Initial concentration of BCC: 1.0×10^{-4}M. ○: BCCH$^+$ reacted, ◑: 5,6-dihydroBCCH$^+$ produced, ●: 2,2′-diaminobiphenyl produced

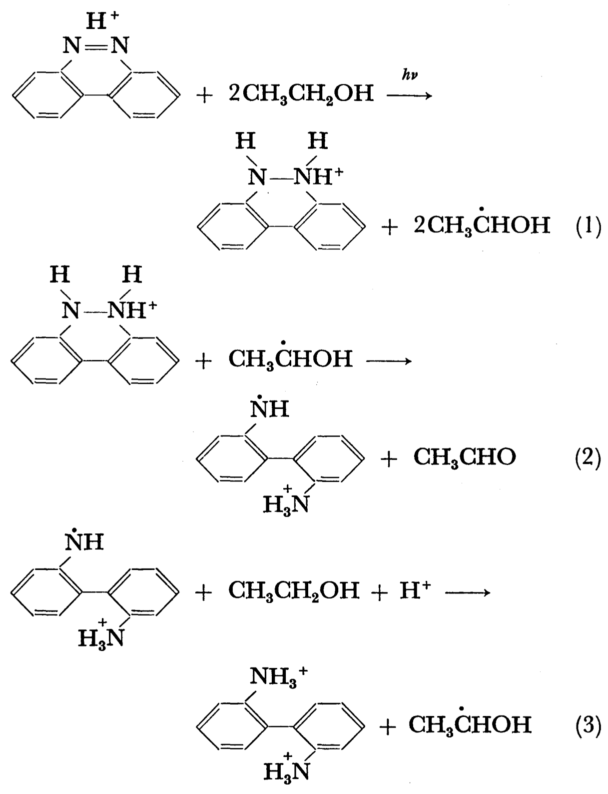
of photochemical hydrogen abstraction from primary and secondary alcohols.

Judging from the absorption spectrum (Curve V in Fig. 2), 5,6-dihydroBCC seems to be protonated at one of the two nitrogen atoms in the acidic solution. In the methanol and 2-propanol solutions, no subsequent reaction was observed.

Photoreaction of BCC in Ethanol upon Visible-light Irradiation. Figure 3 shows the spectral change in an acidic ethanol solution of BCCH$^+$ (1.0×10^{-4} M) caused by irradiation with visible light longer than 400 nm. As may be seen from this figure, 5,6-dihydroBCCH$^+$ is formed in the initial stage of the reaction; subsequently, the absorption bands of 5,6-dihydroBCCH$^+$ decrease in intensity with prolonged irradiation, giving rise to a compound with a tail of a band in the short-wavelength region. When the irradiated solution was neutralized, the absorption band appeared at 294 nm. Therefore, it is evident that the initially produced 5,6-dihydroBCCH$^+$ takes part in the subsequent reaction. The final product was isolated in the preparative experiments; it was identified as 2,2′-diaminobiphenyl.

By the analysis of the absorption spectra,[9] the changes in the concentrations of BCC, 5,6-dihydroBCC, and 2,2′-diaminobiphenyl with the lapse of irradiation time were determined; the results are presented in Fig. 4. As can be seen from this figure, during the first period of 30 min the formation of 2,2′-diaminobiphenyl is not observed, although the photoreduction of BCCH$^+$ occurs to give 5,6-dihydroBCCH$^+$ rapidly. This implies that the conversion of 5,6-dihydroBCCH$^+$ into 2,2′-diaminobiphenyl is initiated after a certain amount of 5,6-dihydroBCCH$^+$ is produced. The yield of 2,2′-diaminobiphenyl in relation to the BCC used initially was 34% upon irradiation for 3 hr.

It should be noted that 5,6-dihydroBCCH$^+$ has no absorption in the visible region longer than 400 nm, as is shown in Fig. 2. Therefore, it can be said that the ground-state 5,6-dihydroBCCH$^+$ is probably involved in the subsequent reaction. Nevertheless, this reaction did not take place without continued irradiation even after a sufficient concentration of 5,6-dihydroBCCH$^+$ was reached. In view of this and the fact that 5,6-dihydroBCCH$^+$ fails to take part in this reaction in the 2-propanol and methanol solutions, the disproportionation between the 5,6-dihydroBCCH$^+$ molecules can be ruled out as the mechanism of the reaction. Moreover, the ground-state 5,6-dihydroBCCH$^+$ can not abstract a hydrogen atom from acetaldehyde as well as ethanol; a hydrogen donor participating in the conversion should be a transient species generated in the initial photoreduction of BCCH$^+$. That is to say, the 1-hydroxyethyl radical, $\mathrm{CH_3\dot{C}HOH}$, is considered to play an essential role in furthering the reaction. Consequently, the mechanism of the 2,2′-diaminobiphenyl formation, which explains the results presented here, can be visualized as is shown in Scheme 1.



Scheme 1.

The conversion is initiated by the hydrogen abstraction of 5,6-dihydroBCCH$^+$ from the 1-hydroxyethyl radical (Reaction (2)). This reaction does not proceed until a certain amount of 5,6-dihydroBCCH$^+$ is formed, because a relatively short-lived species, $\mathrm{CH_3\dot{C}HOH}$, takes part in the reaction. This is the reason for the appearance of the induction period between the first formation of 5,6-dihydroBCCH$^+$ and that of 2,2′-diaminobiphenyl. The successive reproduction of the radical, $\mathrm{CH_3\dot{C}HOH}$, is performed in Reaction (3).

The observed solvent dependence of the reaction can be attributed to the different reactivities of the radicals resulting from alcohols in the initial photoreduction. In the cases of 2-propanol and methanol solutions, the resulting radicals are the 1-hydroxy-2-propyl, $\mathrm{(CH_3)_2\dot{C}OH}$, and the 1-hydroxymethyl, $\mathrm{\dot{C}H_2OH}$, radicals respectively; these radicals apparently have no ability to donate a hydrogen to 5,6-dihydroBCCH$^+$ under the present experimental conditions, probably because other decay processes occur more rapidly than does the hydrogen donation to 5,6-dihydroBCCH$^+$. However, it is a problem to be settled from what such a difference arises.

Photoreaction of BCC upon Ultraviolet Irradiation. In the case of ultraviolet irradiation by light shorter than 380 nm, the main product was carbazole, regardless of the kind of alcohol used here. Figure 5 shows the spectral change of a 1.0×10^{-4} M solution of BCCH$^+$ in acidic 2-propanol upon ultraviolet irradiation by means of a high-pressure mercury lamp. Irradiation for 3 hr resulted in the conversion of BCCH$^+$ into carbazole in about a 92% yield. Although the absorption bands of 5,6-dihydroBCCH$^+$ are apparently not observed in the course of the reaction, as can be seen from Fig. 5, the following fact clearly indicates that this is an intermediate product in the carbazole formation also: when the ultraviolet irradiation was carried out upon a 2-propanol solution in which BCCH$^+$ has previously been photoreduced to 5,6-dihydroBCCH$^+$ with the visible-light irradiation, as has been described above, carbazole was produced much faster than in the case of the ultraviolet irradiation of the BCCH$^+$ solution. The rate of the reactions in these different irradiation manners are compared in Fig. 6.

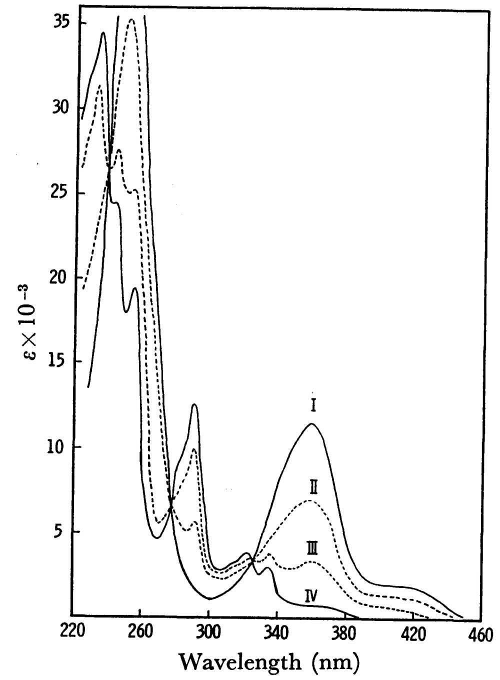


Fig. 5. Spectral change caused by ultraviolet irradiation upon 4M HCl 2-propanol solution.
Initial concentration of BCC: 1.0×10^{-4}M. Irradiation time (hr); I: 0, II: 1, III: 2, IV: 3

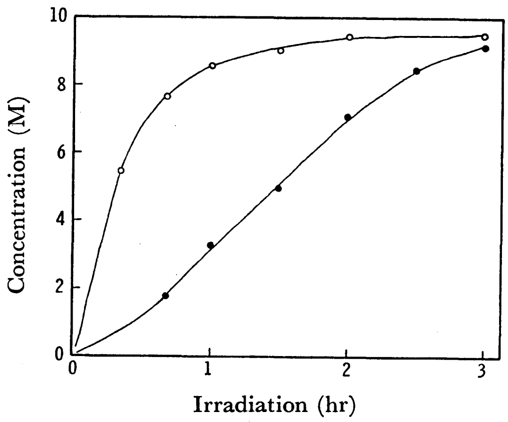
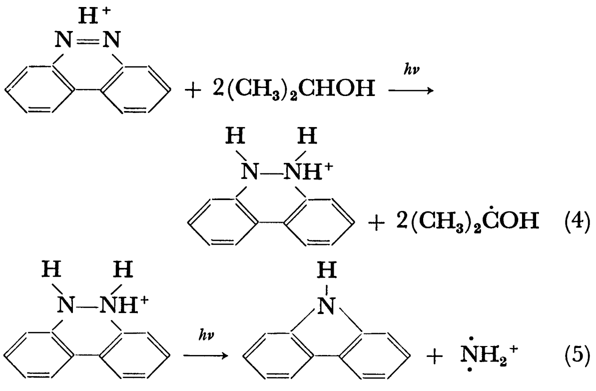


Fig. 6. Rate of the carbazole formation.
●: from BCCH$^+$, ○: from 5,6-dihydro BCCH$^+$

Consequently, 5,6-dihydroBCCH$^+$ is an intermediate product in the formations of both 2,2′-diaminobiphenyl and carbazole. However, in the case of the latter, the intermediate is considered to participate in the reaction through an excited state, judging from its absorption spectrum (Fig. 2).

It was found that the carbazole formation was attended by the liberation of ammonia. The ammonium ion was detected in the irradiated solution by the Nesler test. Therefore, we may expect that carbazole is produced by photoinduced disproportionation between the excited and ground-state 5,6-dihydroBCCH$^+$ molecules. However, this pausible mechanism can be ruled out, in view of the fact that carbazole is produced in an acidified polyvinyl alcohol film containing the substrate in a concentration of about 10^{-3} M, in which the substrate seems to be very difficult to diffuse. In addition, it is evident that the protonation of 5,6-dihydroBCC is essential for the carbazole formation. In fact, ultraviolet irradiation upon a polyvinyl alcohol film containing 5,6-dihydroBCC not being protonated does not lead to the formation of carbazole.

At the present time, it is considered that carbazole is produced by the photoinduced elimination of an imino radical ($\dot{N}H$) from 5,6-dihydroBCCH$^+$, and that the resulting radical gives ammonia. The mechanism of the reaction proposed is shown in Scheme 2.



Scheme 2.

Experimental

The ultraviolet absorption spectra were measured with a Shimadzu Spectrophotometer, UV-200, using 1 cm quartz cells. The infrared absorption spectra were recorded on a Hitachi Infrared Spectrophotometer, EPI-G3, in a KBr disk.

Materials. The BCC was prepared from 2,2′-dinitrobiphenyl according to the method of Badger *et al.*;[10] it was purified by repeated recrystallizations from benzene, by treatment with active charcoal, and finally by recrystallization from ethanol; mp 155 °C (lit,[10] 156 °C). 2,2′-Diaminobiphenyl was prepared by the reduction of 2,2′-dinitrobiphenyl with zinc in HCl aqueous ethanol; it was purified by repeated recrystallizations from aqueous ethanol; mp 78.5 °C (lit,[10] 78.5 °C). The polyvinyl alcohol film was prepared from commercially available powder (mean degree of polymerization: 1500).

Irradiation. The irradiation by visible-light longer than 400 nm was carried out by means of a 500 W super-high-pressure mercury arc lamp (Ushio USH-500) and a Corning glass filter CS-3-73 (transmittance percentage shown in Fig. 1). The ultraviolet irradiation was carried out by means of a 450 W high-pressure mercury arc lamp (Ushio UM-452). In the preparative experiment with ultraviolet irradiation, a solution was placed in a 500 ml cylindrical Pyrex vessel, and a high-pressure immersion mercury arc lamp was used as the light source. All the irradiations were carried out at room temperature; the solution of BCCH$^+$ was flushed with nitrogen passed through a pyrogallol solution for 30 min prior to irradiation and continued throughout the irradiation. For the reaction in the polyvinyl alcohol film, the sample film was prepared by the method described elsewhere.[11]

Photoreaction of BCC in Acidic Ethanol upon Visible-light Irradiation. A 2×10^{-3} M solution of BCCH$^+$ in 100 ml of 3.75 M HCl aqueous ethanol was irradiated with visible light longer than 400 nm for 20 hr. After irradiation, the solution was neutralized with an NaOH aqueous solution. The neutral solution was then extracted with diethyl ether. These procedures were carried out for five runs, after which the ethereal solutions were combined. After the solvent has then been evaporated to dryness, the crystalline solid thus obtained was subjected to silica-gel thin-layer chromatography, using a mixture of benzene, cyclohexane, and acetic acid (1: 1: 1) as the developing solvent. The R_f value for the main product was 0.27. The product thus obtained was further purified by recrystallization from aqueous ethanol; it was identified as 2,2′-diaminobiphenyl; mp 77.0—77.5 °C. Found: C, 77.2; H, 6.6; N, 14.6%. Calcd for $C_{12}H_{12}N_2$: C, 78.2; H, 6.6; N, 15.2%. The UV and IR spectra of the product were identical with those of the authentic sample.

Photoreaction of BCC in Acidic 2-Propanol upon Ultraviolet Irradiation. BCC (120 mg) dissolved in 400 ml of 3.75 M HCl aqueous 2-propanol in a Pyrex vessel was irradiated with a high-pressure immersion mercury arc lamp (Ushio UM-102) for 2 hr. The solvent was then removed by evaporation under reduced pressure to afford a crystalline solid, which was subsequently washed with water. The product thus obtained was dissolved in a mixed solvent of benzene, *n*-hexane, and 2-propanol (2: 2: 1) and chromatographed on a silica gel column, using the same solvent as the eluent. Final purification was accomplished by recrystallization from ethanol. The product was identified as carbazole; mp 246—247 °C. Found: C, 87.0; H, 5.2%. Calcd for $C_{12}H_9N$: C, 86.2; H, 5.4%. The UV and IR spectra of the product were identical with those of commercially available carbazole.

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9) Both 5,6-dihydroBCCH$^+$ and diprotonated 2,2′-diaminobiphenyl have no absorption at 400 nm, so the reaction

is followed by monitoring the absorbances at 400 nm.

$$\mathrm{BCCH^+ \ reacted \ (mol)} = \frac{A_o - A_I}{A_o} \times C_o$$

$$\mathrm{5,6\text{-}DihydroBCCH^+ \ produced \ (mol)} = \frac{A_s - A_I}{A_o} \times C_o$$

$$\mathrm{2,2'\text{-}Diaminobiphenyl \ produced \ (mol)} = \frac{A_o - A_s}{A_o} \times C_o$$

where A_O, A_I, and A_S denote the absorbances before irradiation, immediately after irradiation, and after irradiation followed by oxygen bubbling into solution respectively, and C_O is an initial amount of BCCH+ used.

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