September, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***54***, *2829—2830 (1981)* 2829

The Photochemical Reaction of Benzo[*c*]cinnoline. IV. Comments on the Mechanism of 2,2′-Diaminobiphenyl Formation

Hiroyasu INOUE,* Yukimi HIROSHIMA, Toshihiko SAKAI,
Tadamitsu SAKURAI, and Norio FUKUDA
Department of Applied Chemistry, Faculty of Technology, Kanagawa University,
Kanagawa-ku, Yokohama 221

(Received November 20, 1980)

Synopsis. In order to determine the mechanism of 2,2′-diaminobiphenyl formation from benzo[*c*]cinnoline, effect of aldehyde on the reaction was examined. It is proposed that ethanal, which was generated from ethanol in the initial photoreduction, formed an adduct with 5,6-dihydrobenzo[*c*]cinnoline, and that the resulting adduct participated in the subsequent photo-induced 2,2′-diaminobiphenyl formation.

Photochemical reactions of benzo[*c*]cinnoline (hereafter referred to as BCC) show a dependence on excitation wavelengths and solvents. In a previous paper,[1)] BCC found to give 2,2′-diaminobiphenyl (referred to as DAB) under irradiation of light of wavelength longer than 400 nm in an acidic aqueous ethanol. In the DAB formation, 5,6-dihydroBCC, which is monoprotonated in the acidic solution, is initially produced as an intermediate. On the other hand, when 2-propanol is used in the place of ethanol, the visible light irradiation does not afford DAB, although the photoreduction to 5,6-dihydroBCC occurs.[2)] Therefore, there is a distinct difference in the DAB formation between these alcohols. Such solvent dependence is a problem to be solved.

Protonated 5,6-dihydroBCC itself can not be excited electronically by visible light; it has been shown that the excitation of 5,6-dihydroBCC with ultraviolet light causes the photoelimination to afford carbazole in an acidic 2-propanol as well as in an acidic ethanol.[3)] The present paper is concerned with the mechanism of the photo-induced DAB formation from 5,6-dihydroBCC.

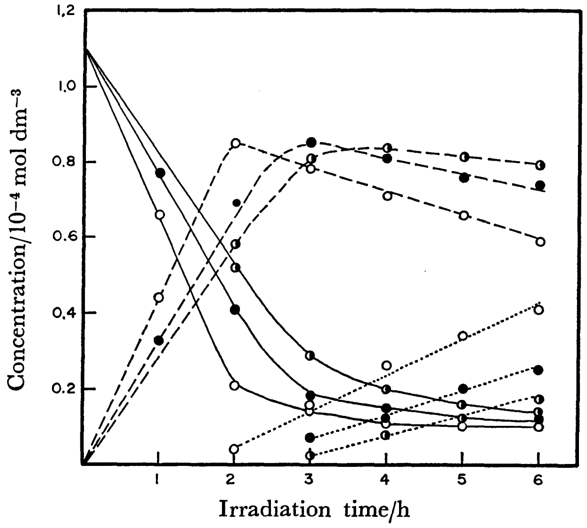


Fig. 1. Rate of the reaction under the visible light irradiation upon a 3.6 mol dm^{-3} HCl ethanol solution of BCC (1.1×10^{-4} mol dm^{-3}).
Concentrations of BCC(——), 5,6-dihydroBCC(- - -), and DAB(……). Relative light intensity; ○: 3.1; ●: 1.6; ◑: 1.0.

Experimental

BCC and 2-propanol were the same as those used previously.[2)] Aldehydes used here were ethanal, propanal, butanal, and 2-methylpropanal and were purified by distillation.

A 500 W high pressure mercury arc lamp (Ushio USH-500), with a glass filter (Corning CS-3—73), which cut off light of wavelength shorter than 400 nm, was used as a visible light source. The quantitative conversion of BCC (5.0×10^{-5} mol dm^{-3}) into 5,6-dihydroBCC was attained by the visible light irradiation for 3 h upon an acidic (4 mol dm^{-3} HCl) 2-propanol solution of BCC. In order to examine the effects of some added compounds, further irradiation were carried out in the same manner after the addition of additives into the reactant solution. All irradiations were carried out at room temperature under nitrogen. The intensity of incident light was determined by actinometry, using a potassium trioxalatoferrate(III) solution.

Results and Discussion

Figure 1 shows the rates of reaction under the visible light irradiation upon a 3.6 mol dm^{-3} HCl aqueous ethanol solution of BCC (1.1×10^{-4} mol dm^{-3}). The concentrations of BCC, 5,6-dihydroBCC, and 2,2′-diaminobiphenyl were determined spectrophotometrically as reported earlier.[1)] The DAB formation was initiated after about 80% of the initial amount of BCC was converted into 5,6-dihydroBCC, irrespective of light intensities. Moreover, as seen from Fig. 1, the amount of DAB produced is related linearly to the irradiation time, and is dependent on light intensities. Since 5,6-dihydroBCC itself has no absorption in the visible region, these results suggest that a certain species, which can be excited electronically with the visible light, may play an essential role in the subsequent DAB formation.

Effects of aldehyde and ketone on the reaction were examined, because these compounds were generally produced from primary and secondary alcohols, respectively, in photo-induced hydrogen abstraction reactions by substrates.[4,5)] When ethanal was added into an acidic 2-propanol solution of 5,6-dihydroBCC prepared previously[2)] and the irradiation was allowed to continue, the DAB formation was observed without the induction period. On the other hand, acetone was shown to have no effect on the reaction. Therefore, the solvent dependence of the photo-induced DAB formation can be interpreted in terms of the

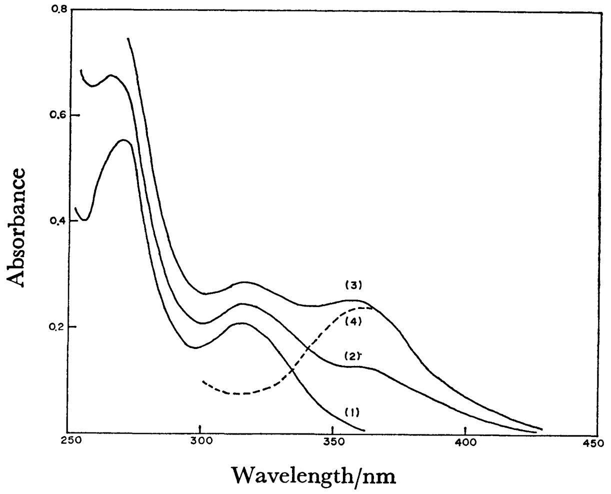
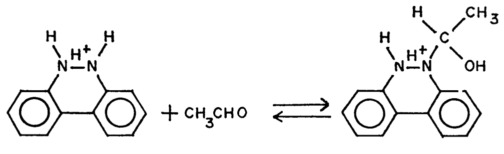


Fig. 2. Spectral change caused by the addition of butanal into an acidic 2-propanol solution of 5,6-dihydroBCC(5.0×10^{-5} mol dm^{-3}).
Concentration of butanal; (1): 0 mol dm^{-3}, (2): 2.2×10^{-3} mol dm^{-3}, (3): 8.9×10^{-3} mol dm^{-3}, (4): difference spectrum (3)—(1).

difference of the products from alcohols in the initial photoreduction.

Figure 2 shows the spectral change caused by the addition of butanal into an acidic 2-propanol solution of 5,6-dihydroBCC. As seen from this figure, a new absorption band appears around 360 nm on the addition of the aldehyde, thus indicating that there is interaction between 5,6-dihydroBCC and the aldehyde giving a certain species. The resulting species can absorb the irradiation light. On the other hand, no spectral change was observed when acetone was added.

The species formed is so unstable that it gives BCC quantitatively after being allowed to stand for several hours under nitrogen, although 5,6-dihydroBCC itself is relatively stable in the acidic solution. Here it should be noted that this aldehyde is known to form an adduct with amine, and the resulting adduct (carbinolamine) is usually unstable.[6–8] In the present case, therefore, the following equilibrium can be considered to be established, and the adduct may participate in the DAB formation through the visible light absorption. The adduct converts spontaneously to BCC, as described above. This conversion may be expected to be accompanied by the generation of a primary alcohol, RCH_2OH. In order to detect the alcohol generated from the adduct, an acidic tetrahydrofuran solution of 5,6-dihydroBCC in concentration of 1.2×10^{-1} mol dm^{-3} was prepared using $LiAlH_4$ as reported earlier.[2] Propanal was added into the 5,6-dihydroBCC solution to form the adduct,[9] and then the solution was allowed to stand for enough time for the conversion of the adduct to BCC. Gas chromatography showed that propanol was present in the tetrahydrofuran solution.



5*H*-6-(1-Hydroxyethyl)-benzo[*c*]cinnoline

Table 1. Equilibrium constants (*K*) of the adduct formation and rates of the conversion of BCC into DAB[a)]

Aldehyde[b)]	*K*/mol dm^{-3} at 21 °C	DAB produced (%)
Ethanal	322	67
Butanal	243	39
Propanal	110	31
2-Methylpropanal	25	14

a) Initial concentration of BCC: 2.0×10^{-5} mol dm^{-3}, Irradiation time: 30 min. b) Concentration of aldehyde: 4.0×10^{-4} mol dm^{-3}.

For several aldehydes the same new absorption band was observed around 360 nm. The alkyl groups in the aldehydes did not affect the position of the band. The equilibrium constants for the adduct formation were determined by applying the Benesi-Hildebrand equation.[10] The results are presented in Table 1, in which the rates of the DAB formation are also shown. The equilibrium constant is dependent on the alkyl groups in the aldehydes. The observed correlation between the equilibrium constant and the product yield indicates that the carbinolamine adduct serves as a precursor of DAB.

References

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9) The absorption spectrum of the adduct thus obtained is similar to the difference spectrum shown in Fig. 2(4).

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