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Photochemical Reactions of Aromatic Compounds. XVII.[1] The Photocyclization of *N*-(*o*-Chlorobenzyl)aniline

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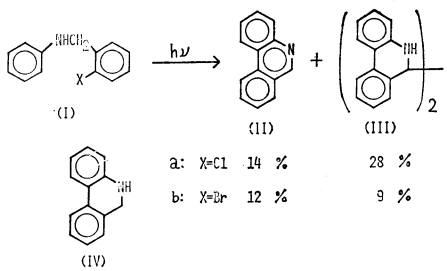
The dehydrohalogenative photocyclization has been shown to be of potential use for the synthesis of some alkaloids.[2] However, the starting halides are limited to iodides and bromides, and difficulties have been generally encountered in the case of chlorides. In the previous papers,[3] we have reported the photoinduced reduction of halobenzenes with *N*,*N*-dimethylaniline, which affords the dehalogenative adducts in the maximum yield in the case of chlorobenzene. Therefore, *N*-(*o*-chlorobenzyl)aniline (Ia) can be expected to undergo an intramolecular dehydrohalogenative photocyclization and we did obtain the cyclized products (II) and (III) in moderate yields.

Irradiation was carried out for an acetonitrile–water (9: 1) solution of *N*-(*o*-halobenzyl)anilines (Ia—b) in the presence of sodium hydroxide through a Pyrex glass by a high pressure mercury arc. Phenanthridine (II)[4] and 5,5′,6,6′-tetrahydro-6,6′-biphenanthridyl (III)[4] were isolated from the reaction mixture by column chromatography on silica gel.



In the present photoreactions, the primary product can be expected to be 9,10-dihydrophenanthridine (IV), but it could not be isolated. However, when the photoreactions were monitored by the UV spectra, the

1) Part XVI: K. Mizuno, C. Pac, and H. Sakurai, *Chem. Commun.*, **1973**, 219.

2) T. Kametani and K. Fukumoto, *Account. Chem. Res.*, **5**, 212 (1972).

3) a) T. Tosa, C. Pac, and H. Sakurai, *Tetrahedron Lett.*, **1969**, 3635. b) C. Pac, T. Tosa, and H. Sakurai, This Bulletin, **45**, 1169 (1972).

4) J. J. Eisch and R. M. Thompson, *J. Org. Chem.*, **27**, 4171 (1962).

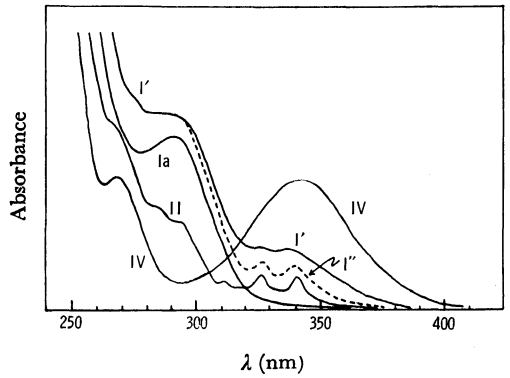


Fig. 1. The UV spectra in acetonitrile solutions: Ia (1.1×10^{-3} M of Ia); I' (after irradiation of Ia at 313 nm in a degassed solution); I'' (after irradiation of I' at 366 nm after I' was air-saturated; II (phenanthridine); IV (9,10-dihydrophenanthridine). The absorption intensities are in arbitrary unit.

characteristic broad absorption maximum of IV at 342 nm appeared by the irradiation of Ia at 313 nm (Fig. 1). Further irradiation of the solution resulted in the decrease of the broad absorbtion band with the appearance of the bands similar to II at 326 and 342 nm. In fact, IV was found to be quantitatively oxidized into II by the treatment of column chromatography on silica gel and easily photolyzed into II and an unknown dimeric material (V), though III was not detected. The structure of V has not been determined, since it is insoluble in usual organic solvents. Therefore, it is suggested that the primary product IV might be oxidized into II during the work-up procedures and also photolyzed into II and the other products during the irradiation. On the other hand, the formation of III cannot be rigorously interpreted at present.

Although Ogata and Takagi have reported the photorearrangement of *N*-(*p*-chlorobenzyl)-*p*-toluidine,[5] the rearranged products, *o*-amino-*o*-chlorodiphenylmethane and *p*-amino-*o*-chlorodiphenylmethane, could not be obtained in appreciable amounts.

5) Y. Ogata and K. Takagi, This Bulletin, **44**, 2186 (1971).

Experimental

All the melting points and boiling points are uncorrected. Spectroscopic analyses of the organic products were carried out as follows; the IR spectra using a high Hitachi EPI-S2 spectrophotometer, the UV spectra using a Hitachi RMU-6E spectrometer. The acetonitrile was purified as uasul. The aniline, *o*-chlorobenzyl chloride and *o*-bromotoluene were distilled under nitrogen stream *in vacuo* before use.

The Preparation of The Starting Halides, Ia and Ib. Ia was obtained from aniline and *o*-chlorobenzylchloride according to the method described for the preparation of *N*-benzylaniline[6]: bp 160—163 °C/4 mmHg; ν_{max}^{KBr} 3380 cm^{-1} (N–H);. $\lambda_{max}^{C_2H_5OH}$ (ε) 296 (1090) and 246 nm (21010); Found: C, 71.36; H, 5.01; N, 6.37; Cl, 16.45%. Calcd for $C_{13}H_{12}NCl$: C, 71.26; H, 5.56; N, 6.43; Cl, 16.28%.

In a similar way, Ib was obtained from aniline and *o*-bromobenzyl bromide prepared by the bromination of *o*-bromotoluene with *N*-bromosuccinimide: bp 184—189 °C/7 mmHg; ν_{max}^{KBr} 3393 cm^{-1} (N–H); $\lambda_{max}^{CH_3CN}$ (ε) 293 (2470) and 244 nm (12820). Found: C, 59.63; H, 4.72; N, 5.12; Br, 30.78%. Calcd for $C_{13}H_{12}NBr$: C, 59.54; H, 4.58; N, 5.34; Br, 30.53%.

Irradiation of Ia and Ib. A solution of (Ia) (1 g) and sodium hydroxide (0.2 g) in 200 ml of acetonitrile–water (9: 1) was irradiated through a Pyrex glass under a nitrogen atmosphere at room temperature by a high-pressure mercury arc for 30 hr. After removal of the solvent *in vacuo*, the residue was dissolved in 200 ml of ether, washed by water and dried over magnesium sulfate. After removal of the ether, the residue was subjected to column chromatography on silica gel. Benzene eluted III (0.23 g) which was recrystallized from benzene–hexane: mp (dec.) 183—184 °C (lit,[4] 175—185 °C), ν_{max}^{KBr} (KBr disk) 3240 cm^{-1} (N–H); *m/e* 360 (M^+) and 180. Found: C, 87.02; H, 5.51; N, 7.69%. Calcd for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59; N, 7.77%.

Benzene containing 10% of ether eluted 0.04 g of II, which was recrystallized from hexane: mp 105.5—106.5 °C (lit,[4] 105—106 °C). Found: C, 87.41; H, 4.83; N, 7.74%. Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82%.

Further elution gave brownish tarry materials, the sublimation of which afforded 0.075 g of II.

In a similar way, irradiation of Ib afforded II (0.08 g) and III (0.06 g).

6) F. G. Willson and T. S. Wheeler, "Organic Syntheses," Coll. Vol. I, p. 102 (1941).