Tetrahedron Letters No.43, pp. 3829-3832, 1969. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMICAL ADDITION OF AROMATIC AMINES TO ANTHRACENE

Chyongjin Pac and Hiroshi Sakurai

The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka, Japan

(Received in Japan 5 July 1969; received in UK for publication 18 August 1969)

Spectroscopic investigations have been widely carried out on excited charge-transfer complexes (ex-CT),$^{1)}$ which form only in an electronically excited state, especially on those between N,N-dialkylanilines and aromatic hydrocarbons.$^{2)}$ As a series of our investigation on chemical behavior of ex-CT,$^{3)}$ the photochemical reaction of anthracene with aromatic amines was carried out.

An acetonitrile solution of dimethylaniline (DMA) containing solid anthracene in the bottom of the reaction vessel was irradiated through a glass filter by a high pressure mercury arc, untill the solid anthracene completely disappeared. After removal of the solvent and an excess of DMA, usual treatment of a solid residue gave a small amount of anthracene photodimer (I), 5 - 10% of 9,10-dihydroanthracene (II), 10 - 20% of 9,10,9',10'-tetrahydro-9,9'-bianthryl (III), and 60 - 65% of 9-(p-dimethylaminophenyl)-9,10-dihydroanthracene (IV).

The hydrocarbon products were known materials, the structure of which were unambiguiously determined by direct comparison of the spectral and physical data with those of the respective authentic samples.

The adduct IV (m.p. 138 - 139.5 °C) was shown to be an 1:1-adduct by the elemental analyses and the mass spectra (m/e 299 (M^+), 178 (M - DMA) and 121 (M - anthracene)). The infrared absorption spectra had charactristic absorption bands of tertiary aromatic amine at 1320 cm^{-1} and of para-disubstituted benzene ring at 820 cm^{-1}. An acetonitrile solution of IV showed a longest absorption maximum at 306 nm (ϵ 2.6 x 10^3) which was very similar to that of p-toluidine (λ_{max} 307 nm, ϵ 2 x 10^3).

The structure assignment of IV was mainly based on nmr data. The nmr spectra (60 MHz) consisted of a sharp singlet at τ 7.25 (6H, N-CH$_3$), a doublet at τ 6.12 (2H, J = 2 Hz, the methylene protons on 10-position), a triplet at τ 4.9 (1H, J = 2 Hz, the methine proton on 9-position), an AB quartet in a ratio of about 1 : 2 : 2 : 1 at the middle point of τ 3.3 (4H, $J_{a,b}$ = 9 Hz, the protons of *p*-dimethylaminophenyl ring) and a multiplet centered at τ 2.8 (8H, the aromatic protons of 9,10-dihydroanthracene skeleton). That the methylene group coupled with the methine group was confirmed by a spin decoupling technique. The small coupling canstant (2 Hz) might suggest a long range coupling. The AB quartet was typical of a *para*-disubstituted benzene ring.4) Thus all of the spectral data gave a strong support to the structure assignment.

A chemical support was also obtained. Treatment of the adduct IV with palladium-charcoal in boiling p-cymene gave a yellow green crystal, 9-(*p*-dimethylaminophenyl)-anthracene (m.p. 256 °C, lit.,5) 258 °C), which was independently prepared from 9-anthrone and *p*-lithio-N,N-dimethylaniline.

In contrast, when benzene was used as solvent, anthracene photodimer was obtained in ca 90% yield, while none or trace of IV could be detected.

For mechanistic elucidation, the formation of the hydrocarbons II and III was important, since they could be expected to be derived from anthracene radical anion. On the basis of this expectation, the photochemical reaction in the presence of deuterium oxide was undertaken, and there were obtained 9,10-dideuterio-9,10-dihydroanthracene (V), 10,10'-dideuterio-9,10,9',10'-tetrahydro-9,9'-bianthryl (VI) and 10-deuterio-9-(*p*-dimethylaminophenyl)-9,10-dihydroanthracene (VII). Deutrium incorporation in these products V - VII was established by nmr spectroscopic measurements. The nmr spectra of VII showed a moderate broad singlet at τ 5 (1H) and two broad singlets at τ 6.15 and τ 6.28 with equal intensity having a combined area corresponding to one proton. The latter two signals might be ascribed to a difference in chemical shift due to two isomers having the deuterium either *cis* or *trans* to the *p*-dimethylaminophenyl group.

On the basis of the results obtained, the following mechanism was tentatively proposed.

$$D \quad + \quad A \xrightarrow{h\nu} (D^{+}\text{-}A^{-})$$

$$\begin{tikzcd}
(D^{+}\text{-}A^{-}) \arrow[r] & (D^{+}\text{---}\ A^{-}) \arrow[r, "H_2O \text{ or } D_2O"] \arrow[dr] & IV \text{ or } VII \\
 & & D^{+} \quad + \quad A^{-}
\end{tikzcd}$$

$$2\ A^{-} \longrightarrow {}^{-}A\text{-}A^{-} \xrightarrow{H_2O \text{ or } D_2O} III \text{ or } VI$$

$$A^{-} \xrightarrow{H_2O \text{ or } D_2O} AH \text{ or } AD$$

$$AH \text{ or } AD \quad + \quad A^{-} \longrightarrow A \quad + \quad AH^{-} \text{ or } AD^{-} \xrightarrow{H_2O \text{ or } D_2O} II \text{ or } V$$

D = dimethylaniline, A = anthracene

Since the glass filter cuts off only the light below about 310 nm, it can not be concluded which is the photo-excited species, D or A. Although mechanistic details cannot be drawn at the present stage, a charge-transfer character of the reactions is evident. In connection with spectral data on the ex-CT between DMA and excited anthracene,[2)] it is of interest to note that anthracene photodimer was the exclusive product in the photolysis of a benzene solution. Weller showed that in toluene emission from the ex-CT stoichiometrically appeared with disappearence of fluorescence from anthracene as concentration of DMA increased, while an acetonitrile solution exhibited only quenching of fluorescence from anthracene.[2)] Since the formation of the ex-CT may compete with that of anthracene photodimer, one can interprete the photodimer formation in the photo- reaction in benzene by assuming the exclusive decay of the ex-CT to ground state molecules. On the other hand, in acetonitrile the ex-CT leads to a solvent shared ion pair, which in turn gives rise to bond formation to afford IV (or VII) or dissociates into free ion radicals, since a highly polar solvent fascilitates electron-transfer.[2, 6)] For the formation of II (or V) and III (or VI), the mechanism suggested by Winkler and Winkler[7)] was chosen. In order to determine mechanistic details, we are now intending to carry out spectroscopic and kinetical investigations.

The photochemical addition of the other aromatic amines such as aniline and N,N-dimethyl-*m*-toluidine to anthracene was observed as well, and 1:1-adducts were obtained in ca 20% and 60% yields, respectively. In the case of N,N-dimethyl-*o*-toluidine, the yield of 1:1-adduct was low (ca 5%), while anthracene photodimer was obtained in 70% yield. On the other hand, II and III were yielded as the major products in respective yields of 50% and 30% by the photoreaction of anthracene with N,N-dimethyl-*p*-toluidine.

References

1) Various nomenclatures on such a species were proposed such as heteropolar excimer, mixed excimer, exciplex and so on.

2) A. Weller, Pure Appl. Chem., **16**, 115 (1968); N. Mataga and K. Ezumi, Bull. Cem. Soc. Japan, **40**, 1355 (1967).

3) C. Pac and H. Sakurai, Tetrahedron Letters, 1865 (1968); Kogyo Kagaku Zasshi, **72**, 230 (1969); Tetrahedron Letters, to be published.

4) J. W. Emsley, J. Feeney and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. II, p. 771. Pergamon Press, London (1966).

5) E. de Barnett, J. W. Cook and M. A. Matthews, Rec. Trav. Chim., **44**, 217 (1925).

6) H. Leonhardt and A. Weller, Ber. Bunsenges. Physik. Chem., **67**, 791 (1963); K. Kaneta and M. Koizumi, Bull. Chem. Soc. Japan, **40**, 2254 (1967).

7) H. J. S. Winkler and H. Winkler, J. Org. Chem., **32**, 1695 (1967).