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Photochemical Reactions of Aromatic Compounds. XXXVI.[1] The Photoreactions of Anthracene with Some Selected Tertiary Aromatic Amines in Polar Media

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The photoreaction of anthracene with *N,N*-dimethylaniline in acetonitrile gave 9-(*p*-dimethylaminophenyl)-9,10-dihydroanthracene in a good yield, along with 9,10-dihydroanthracene and 9,9′,10,10′-tetrahydro-9,9′-bianthryl. This photoreaction was found to depend on the polarity of the solvent as well as on its protic or aprotic nature. With *N,N*-dimethyl-*m*-toluidine, a similar 1 : 1 adduct was obtained, while the reduced anthracenes were mainly formed in the photoreactions with *N,N*-dimethyl-*o*- and *p*-toluidines. The mechanisms were discussed in terms of the dissociation into the ion radicals as well as their reactivities.

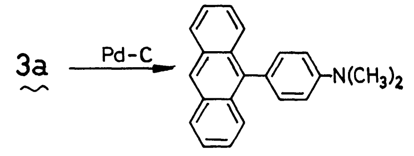
The arene–amine systems are typical electron acceptor-donor pairs for exciplex formation[2] and photochemical electron-transfer reactions.[3] The photoreactions of such systems usually afford adducts of arenes with amines and reduced arenes,[3–7] depending on the structures of the amines as well as on the polarity of solvent. In a previous paper,[4] we reported that the photoreaction of anthracene (A) with *N,N*-dimethylaniline (DMA) in acetonitrile gives mainly 9-(*p*-dimethylaminophenyl)-9,10-dihydroanthracene (**3a**), along with the reduced anthracenes (**1** and **2**) while the irradiation of a benzene solution results in the exclusive dimerization of A. In this paper, we wish to report on the photoreactions of A with some selected tertiary aromatic amines in polar media.

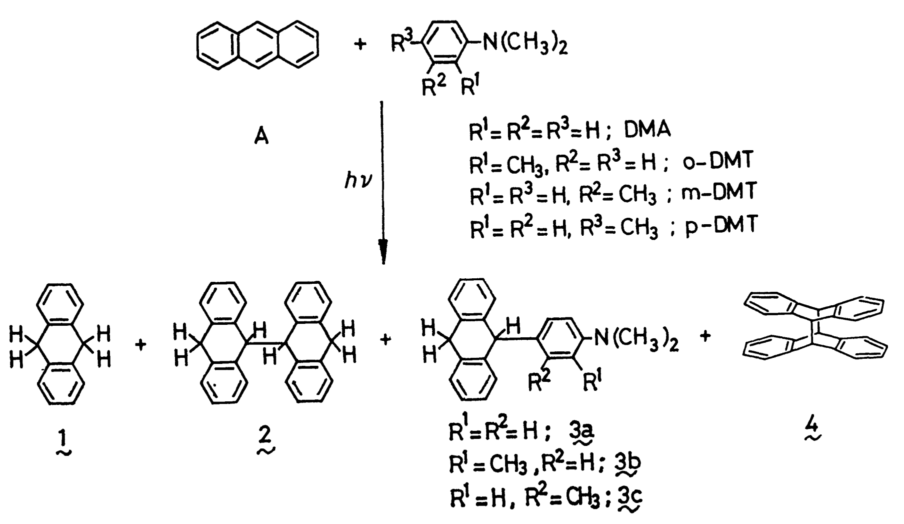
Results

Photoreactions of A with the Tertiary Amines in Acetonitrile. The irradiation was carried out for dry acetonitrile solutions in a Pyrex vessel, using a high-pressure mercury lamp at room temperature. Table 1 lists the isolated yields of the products. The hydrocarbon products (**1**, **2**, and **4**) are known compounds and were unambiguously identified by direct comparison with respective authentic samples. The structures of **3a** and **3c** were indicated by their elemental composition and their spectral properties. For example, the ^{1}H NMR spectrum of **3a** consisted of a sharp singlet at δ 2.75 (N–CH_3), a broad doublet at δ 3.88 (C_{10}–H_2), a broad triplet at δ 5.1 (C_9–H), an A_2B_2 signal at δ 6.7 (p-C_6H_4–), and a multiplet at δ 7.2 (other aromatic protons), strongly supporting the structure assigned. When a *p*-cymene solution of **3a** was refluxed over 5% Pd–C, 9-(*p*-dimethylaminophenyl)anthracene, which is a known compound,[8] was obtained in a 90% yield.

Table 1. Product distribution in the photoreactions of anthracene with the tertiary aromatic amines in acetonitrile

Amines	Isolated yields/%			
	1	**2**	**3**	**4**
DMA	8	20	70	0
o-DMT	54	32	trace	0
m-DMT	16	25	60	0
p-DMT	72	21	0	0





Scheme 1.

It is notable that the photoreaction with DMA and *m*-DMT mainly gave the adducts (**3a** and **3c**), whereas **1** and **2** are the exclusive products with *o*- and *p*-DMT. In the case of *o*-DMT, the formation of **3b** was indicated by the ^{1}H NMR spectrum of a mixture, which showed a sharp singlet at δ 2.15, a sharp singlet at δ 2.52, a broad doublet at δ 3.87, and a very broad singlet at δ 5.12 in an area ratio of *ca.* 3 : 6 : 2 : 1. However, its formation was too small for an unambiguous determination of the structure to be made. On the other hand, no adduct of A with *p*-DMT was isolated.

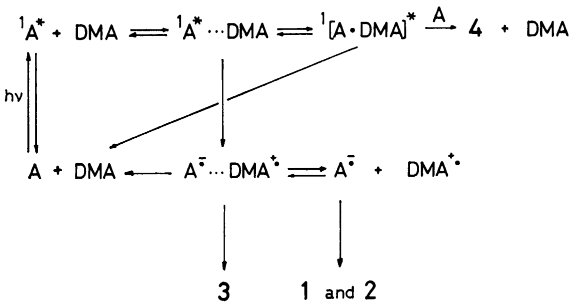
TABLE 2. SOLVENT EFFECT ON THE PHOTOREACTIONS OF ANTHRACENE WITH *N,N*-DIMETHYLANILINE AND *N,N*-DIMETHYL-*p*-TOLUIDINE

Solvents		Isolated yields/%			
		1	2	3	4
DMA	C_6H_6	0	0	0	100
	Et_2O	2	10	trace	85
	EtOH	45	20	30	0
	MeCN	8	20	70	0
p-DMT	EtOH	46	50	—	0
	MeCN-EtOH (9 : 1)	52	47	—	0
	MeCN	72	21	—	0

Solvent Effects on the Photoreactions of A with DMA and p-*DMT*. The photoreaction with DMA depends not only on the polarity of the solvent, but also on its protic or aprotic nature, as is shown in Table 2. The formation of **4** was exclusive in benzene and predominant in diethyl ether, while the combined yields of **1**, **2**, and **3a** were over 90% in such highly polar solvents as acetonitrile and ethanol. The formation of **3a** is favored in acetonitrile, which is a typical, aprotic polar solvent. On the other hand, **1** and **2** are mainly formed in ethanol. Moreover, it was found that the photoreaction with *p*-DMT in acetonitrile affords **1** in a good yield. Ethanol diminished the yields of **1**, though the combined yields of **1** and **2** were invariably high.

Discussion

Aromatic hydrocarbon–tertiary aromatic amine pairs have been extensively investigated as typical exciplex-formation systems and have been well established to dissociate into the ion radicals in polar media.[2,9] Therefore, the observed effect of solvent polarity can be interpreted in terms of a complete electron transfer from DMA to the excited singlet state of A (^{1}A*). Scheme 2 delineates the mechanistic reaction pathways; ^{1}[A·DMA]* and $A^{-\cdot}\cdots DMA^{+\cdot}$ represent the exciplex and the ion pair respectively.

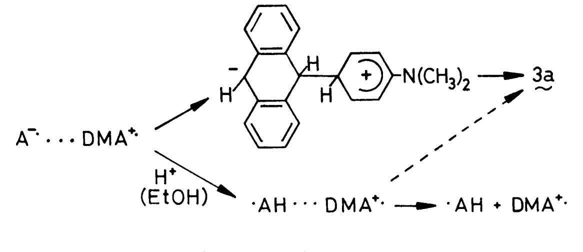


Scheme 2.

In a benzene solution, ^{1}A* forms the exciplex with DMA at the diffusion-controlled limit without any dissociation into the ion radicals.[9] Saltiel and his coworkers have demonstrated that the photodimerization of A in benzene in the presence of DMA proceeds *via* an interaction of the exciplex with A, probably involving a termolecular exciplex, ^{1}[A·A·DMA]*.[10] This mechanism holds for the present photoreaction in benzene since ^{1}A* is completely quenched by DMA under the conditions employed.

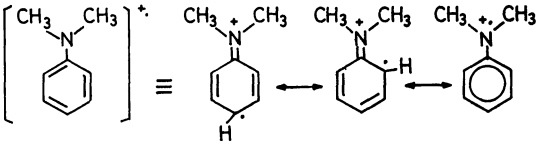
Although the photodimerization is still dominant in diethyl ether, the formation of **1** and **2** is notable, perhaps suggesting the occurrence of a partial dissociation into the ion radicals in this solvent; the pyrene–DMA pair is known to dissociate into the ion radicals upon the photoexcitation in moderately polar solvents.[11] In acetonitrile and ethanol, the ionic-dissociation process evidently overcomes the exciplex formation as well as other chemical and physical pathways from the exciplex, thus leading to the complete lack of the photodimerization. In other words, the photoreactions in these solvents are closely related with the chemistry of the ion radicals.

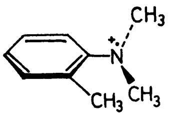
In this regard, it should be noted that the formation of **3a** is more favored in acetonitrile than in ethanol. Since ethanol is a good proton donor for anion radicals, the free anion radical of A and probably also $A^{-\cdot}$ in the ion pair are easily protonated in ethanol.[12] On the other hand, such a rapid protonation of $A^{-\cdot}$ can not be expected in acetonitrile, since possible proton donors in this solvent may be impurities involving water. This argument may lead to the conclusion that the ion pair is a precursor of the formation of **3a**; a radical-coupling reaction between $A^{-\cdot}$ and $DMA^{+\cdot}$ may compete with the charge neutralization between them. The protonation of $A^{-\cdot}$ in the ion pair should result in the loss of the Coulombic force binding the ion pair. As a result, the radical pair, $\cdot AH\cdots DMA^{+\cdot}$, will rapidly diffuse out from the solvent cage, thus making a radical-coupling reaction less possible.



Although a similar mechanism operates for the formation of **3b** and **3c**, the photoreaction with *o*-DMT clearly indicates that the structures of the aromatic amines also affect the reaction courses from the ion pair. It is well known that DMA has a coplanar structure between the dimethylamino group and the benzene ring in the solid state;[13] the structure in solution would again be coplanar, or almost so. This might also be true for *m*-DMT and *p*-DMT. Therefore, odd electrons of the cation radicals would populate the benzene ring, perhaps largely at the ortho and para positions. Thus, the cation radical of DMA and *m*-DMT can undergo the radical-coupling reaction with $A^{-}\cdot$ at the para position, where the steric hindrance is much less.

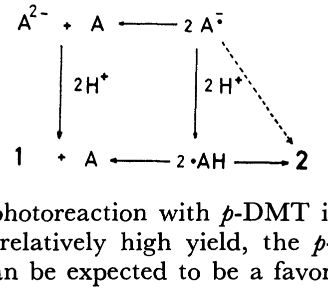
On the other hand, coplanarity seems to be largely lost in the case of *o*-DMT because of steric hindrance by the ortho methyl group. Therefore, the spin density of odd electrons on the benzene ring of *o*-DMT$^{+}\cdot$ would be much lower than that of the cation radicals of DMA and *m*-DMT, leading to a lower reactivity of *o*-DMT$^{+}\cdot$ at the benzene ring toward the radical-coupling reaction.



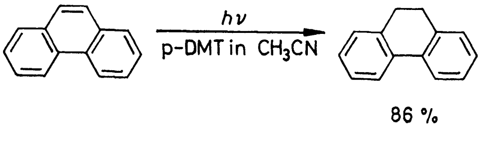


In the case of *p*-DMT$^{+}\cdot$, the para position is blocked by the methyl group and the ortho position is sterically hindered for the radical-coupling reaction. In the cases of *o*- and *p*-DMT, therefore, the escape of the ion radicals from the solvent cage would predominate.

The formation of **1** and **2** evidently arises from the disproportionation and dimerization of $A^{-}\cdot$ and/or $\cdot AH$. In protic media, the precursor is certainly $\cdot AH$, whereas both ($A^{-}\cdot$) and ($\cdot AH$) exist in acetonitrile. In the photoreaction with *p*-DMT, as a solvent acetonitrile is more suitable for the formation of **1** than is ethanol. It should be noted that the presence of 10 vol% ethanol in acetonitrile lowered the yields of **1**. Therefore, it may be suggested that $A^{-}\cdot$ predominantly undergo disproportionation, whereas both disproportionation and dimerization occur with $\cdot AH$ in a *ca.* 1 : 1 ratio.



Since the photoreaction with *p*-DMT in acetonitrile gave **1** in a relatively high yield, the *p*-DMT–acetonitrile pair can be expected to be a favorable reaction system for the photo-Birch reduction of aromatic hydrocarbons. Therefore, the photo-Birch reduction of phenanthrene was attempted, using the *p*-DMT–acetonitrile system; 9,10-dihydrophenanthrene was thus obtained in an 86% yield.



Experimental

The melting points were determined on a Yanagimoto hot stage and are uncorrected. The ^{1}H NMR spectra were measured on a JEOL JNM-PS-100 spectrometer, with tetramethylsilane as the internal standard. The IR spectra were taken on a Shimadzu IR-400 spectrometer, and the mass spectra, on a Hitachi RMU-6E. The UV spectra were measured on a Hitachi 124 spectrometer. The GLC was carried out on a Shimadzu GC-3BF apparatus using a column of SE-30 (5% on Celite 545, 0.75 m).

Materials. Spectral-grade acetonitrile was distilled three times over P_2O_5 and then twice over CaH_2 before use. The ethanol was distilled over CaH_2 and then over C_2H_5ONa before use. The diethyl ether was distilled over $LiAlH_4$. The benzene was washed three times with concentrated sulfuric acid, with a saturated sodium hydrogencarbonate solution, and three times with water, and was then distilled over P_2O_5. The tertiary aromatic amines (Tokyo Kasei) were distilled *in vacuo* before use. The anthracene (Nakarai Chemicals) was recrystallized five times from a mixture of benzene–ethanol and then sublimed. The phenanthrene was recrystallized three times from ethanol and then sublimed.

Photoreaction of Anthracene with the Amines. General Procedure: The experimental procedures used for the irradiation and isolation of the products were essentially identical in all the runs. A solution (150 ml) containing anthracene (0.5 g, 2.8 mmol) and an amine (5 g, 37 mmol) in a Pyrex vessel was bubbled with a nitrogen stream for 20 min and then irradiated with an Eikosha PIH-300 high-pressure mercury lamp under cooling with water. Except in the case of the benzene solution, the anthracene was not completely dissolved before the irradiation. The progress of the reaction was followed by GLC, and it was confirmed that the irradiation for 24 h resulted in the complete consumption of anthracene. During the irradiation, solids different from anthracene were precipitated except for a few cases where the yields of **2** or **4** are low (see Tables 1 and 2). The filtration of the solids gave **2** or **4**. After the removal of the solvent from the filtrate, vacuum distillation gave the starting amine (4—4.5 g). The remaining semisolids were dissolved into a minimal volume of benzene and then chromatographed on silica gel (Merck, 70—230 mesh). Elution with hexane and then with 10% benzene in hexane gave a mixture of **1** and **2**, to which hot hexane was then added; the filtration of the insoluble solids gave **2** while the evaporation of the filtrate left almost pure **1**. Further elution with a 1 : 1 benzene–hexane mixture gave **3a**—**c**. Tables 1 and 2 summarize the isolated yields of the photoproducts.

The **1** (mp 108 °C) was recrystallized from methanol and was identical to commercially available 9,10-dihydroanthracene (Tokyo Kasei) in all respects. The **2** (mp 245—246 °C) was recrystallized from benzene and identified as 9,9′,10,10′-tetrahydro-9,9′-bianthryl by direct comparison with an authentic sample prepared according to the known method.[14]

The **3a** was recrystallized from a benzene–ethanol mixture; mp 148—149.5 °C; UV (CH_3CN): $\lambda(\varepsilon)=266$ (2.3×10^{4}) and 306 nm (2.6×10^{3}); IR (KBr): 3000 (w), 2900 (w), 1610, 1520, 1470, 1450, 1350, 1230, 1200, 1190, 1160, 1060, 1040, 945, 865, 830, 800, 735, and 710 cm^{-1}; MS: 299 (M^{+}, 36%), 178 (40%), and 121 (100%); ^{1}H NMR ($CDCl_3$): δ 2.75 (s, 6H), 3.88 (br d, $J=2$ Hz, 2H), 5.10 (br t, $J=2$ Hz, 1H), 6.45—7.05 (A_2B_2q, $J=9$ Hz, 4H), and 7.06—7.40 (m, 8H); Found: C, 88.52; H, 7.12; N, 4.44%. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68%.

The **3c** had a mp of 134—135.5 °C (from benzene–ethanol);

UV (CH_3CN): $\lambda(\varepsilon)=263$ (2.3×10^4) and 306 nm (2.6×10^3); IR (KBr): 3030 (w), 3000 (w), 2900—2820 (br, w), 2790, 1605, 1560, 1510, 1470, 1440, 1420, 1360, 1290, 1225, 1200, 1170, 1125, 1095, 1060, 960, 840, 830 (sh), 810, 800, 760, and 740 cm^{-1}; MS: 313 (M^+, 50%), 178 (43%), and 135 (100%); ^1H NMR ($CDCl_3$): δ 2.03 (s, 3H), 2.90 (s, 6H), 4.08 (br d, $J=3$ Hz, 2H), 5.20 (br t, $J=3$ Hz, 1H), 6.45—6.60 (m, 1H), 6.62 (br s, 1H), 6.90—7.41 (m, 9H); Found: C, 88.30; H, 7.41; N, 4.48%. Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47%.

Aromatization of **3a** *to 9-(*p*-Dimethylaminophenyl) anthracene.* A *p*-cymene solution (4 ml) containing **3a** (0.1 g) and 5% Pd–C (0.1 g) was bubbled with a nitrogen stream for 20 min and then refluxed for 1.5 h. After the filtration of the Pd–C, evaporation left yellow-green solids (90 mg). Recrystallization from benzene gave pure 9-(*p*-dimethylaminophenyl)-anthracene; mp 252—253 °C (lit,[8] 258 °C); Found: C, 88.62; H, 6.40; N, 4.83%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%.

Photo-Birch Reduction of Phenanthrene with p*-DMT.* An acetonitrile solution (150 ml) containing phenanthrene (0.5 g, 2.8 mmol) and *p*-DMT (5 g, 37 mmol) was irradiated for 24 h; the complete consumption of phenanthrene was confirmed by GLC. After the removal of the solvent, 200 ml of diethyl ether was added to the remaining oil. The ether solution was washed with 150 ml of dilute hydrochloric acid (1 mol dm^{-3}) and three times with brine, and then dried ($MgSO_4$). The evaporation of the ether left an oil, which was then distilled *in vacuo* to give an oil (432 mg, bp 183—184 °C/25 mmHg†). This oil, which was confirmed by GLC to consist of only one component, was identical to commercially available 9,10-dihydrophenanthrene in all respects. To the hydrochloric acid solution sodium hydrogencarbonate was added until the solution became alkaline to litmus. The oil separated was extracted with three 50-ml portions of diethyl ether. The ether layer was dried ($MgSO_4$), evaporated, and then distilled *in vacuo* to give 4.0 g of *p*-DMT.

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† 1 mmHg=133.322 Pa.

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