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PHOTOCHEMICAL REACTIONS OF p-DICYANOBENZENE WITH PRIMARY AND SECONDARY AMINES

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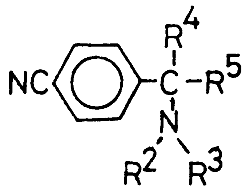
In sharp contrast with the cases of benzene or anthracene-primary or secondary amine systems, photochemical reactions of p-dicyanobenzene with those amines take place at the α-positions instead of the N-H groups of amines via electron-transfer followed by proton-transfer.

It has been demonstrated by Bryce-Smith and his co-workers that photoaddition of primary and secondary amines to benzene occurs at the N-H groups,[1] while that of tertiary amines proceeds at the α-positions through excited charge-transfer complexes.[2] Similar investigations have been reported by Yang in anthracene-amine systems.[3] Very recently Bryce-Smith et al. reported that photoamination of pyridine and chlorobenzene resulted in the formation of α-C- rather than N-substituted products.[4] Their results prompted us to report our findings that, in contrast with the benzene or anthracene-primary or secondary amine system, cyclohexylamine, a primary amine, and diisopropylamine, a secondary amine, react with p-dicyanobenzene(I) upon irradiation at the α-positions instead of the N-H groups.[5]

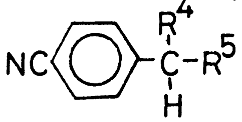
Irradiation of a mixture of I(0.046 M) and cyclohexylamine(2.61 M) in acetonitrile with a medium-pressure mercury arc(100 W) for 13 h gave p-cyclohexylbenzonitrile(IIa) together with a substituted product(IIIa, mp 61-63°C; IR(KBr) 3380 and 3310 cm^{-1}; NMR δ(CCl$_4$) 0.92-2.20(10H, m) 7.59(2H, d, J=9.5 Hz) 7.69(2H, d, J=9.5 Hz); MS(20 eV) 200(M$^+$ 20) 157(100). Found: C, 77.48; H, 8.28; N, 13.87. Calc. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99) in 11 and 10% yields respectively(conversion 39%). Similarly, irradiation of I(0.046 M) in the presence of diisopropylamine(0.87 M) for 9 h gave p-isopropylbenzonitrile(IIb) and a substituted product(IIIb, an oil; IR(neat) 3300 cm^{-1}; NMR δ(CCl$_4$) 0.86(6H, d, J=7 Hz) 1.40(6H, s) 2.69(1H, septet, J=7 Hz) 7.05-7.85(4H, m); MS(20 eV) 202(M$^+$ 4) 187(100) 145(48). The picrate, mp 196-108°C. Found: C, 52.54; H, 4.86; N, 15.90. Calc. for $C_{19}H_{25}N_5O_7$: C, 52.90; H, 4.91; N, 16.23) in 30 and 25% yields respectively(conversion 76%). A small amount of benzonitrile was detected in both reaction mixtures by GC-MS spectrometry but no product corresponding to the adduct of I at the N-H groups of amines has been detected. Identification of IIa and IIb were confirmed by conventional alternative syntheses. Structures IIIa and IIIb were unequivocally identified by MS, NMR and IR data. Products IIa and IIb must have been derived from IIIa and IIIb respectively as in the case of photochemical ethylation of I with triethylamine where irradiation of the substituted product IIIc gave the ethylated product IIc.[6]

The Stern-Volmer treatments of the fluorescence quenching of I with amines in acetonitrile gave nice linear plots with the $k_q\tau$ values of 158, 145, and 126 M^{-1} for the tertiary, secondary and primary amines respectively. Since the τ value of I was evaluated as 18 ns,[7)] the k_q values were caluculated to be $8.8x10^9$, $8.1x10^9$, and $7.0x10^9$ $M^{-1}s^{-1}$ for those amines respectively, which are close to the diffusion rate constant. The trend that amines with lower ionization potential are more efficient quenchers resembles to that of anthracene-amine systems[3)] and of other general electron donor-acceptor systems.[8)] Piperylene(0.01 M) did not quench the reaction of I with diisopropylamine. Neither charge-transfer absorption nor exciplex emission could be observed in these systems. We conclude from these results that, regardless of the type of amines, the photochemical reactions of I with amines proceed through electron-transfer from amines to the excited singlet state of I via encounter complexes or exciplexes as in the cases of amine-aromatic hydrocarbon systems.[9)]

The difference in the reaction features between in benzene-primary or secondary amines and in I-those amines is remarkable. Bryce-Smith suggested that the excited charge-transfer species of a benzene-secondary amine system decay through proton-transfer in which two molecules of the amine participate. In accord with this mechanism methanol accelerates the photochemical reaction of benzene with triethylamine.[2)] By contrast, methanol quenches the photochemical reaction of I with triethylamine,[6)] which indicates that the participation of a proton-transfer step is in a different way from that of the benzene-amine system. Davidson demonstrated that the formation of products from ion pairs is determined by the acidity of suitably placed protons in the photochemical reactions of aromatic hydrocarbons with amines.[10)] Although the exact mechanism to cause the difference in behavior between I and benzene or anthracene is still not completely elucidated, our findings suggest that electron affinity of acceptors or molecularity of excited donor-acceptor complexes plays also an important role for the determination of the reactive site of amines.



(III)
a $R^2=R^3=H$
$R^4=R^5=-(CH_2)_5-$
b $R^2=i\text{-}Pr$, $R^3=H$
$R^4=R^5=Me$
c $R^2=R^3=Et$
$R^4=Me$, $R^5=H$



(II)
a $R^4,R^5=-(CH_2)_5-$
b $R^4=R^5=Me$
c $R^4=H$, $R^5=Me$

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