June, 1980] *Bull. Chem. Soc. Jpn.*, *53*, *1683—1688 (1980)*

Photochemical Reactions of Dicyanobenzenes with Aliphatic Amines

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(Received November 22, 1979)

Upon irradiation, *p*-dicyanobenzene reacted with primary, secondary, and tertiary aliphatic amines to give substitution products in which one of the cyano groups was replaced by the amine at α-CH position or by an alkyl group of the amine. *o*-Dicyanobenzene reacted similarly, but the *meta*-isomer did not react under similar conditions. The rates of the fluorescence quenching of *p*-dicyanobenzene with the amines are close to the diffusion-controlled rate, but are somewhat dependent on the ionization potentials of the amines. When the substitution product was irradiated, the corresponding alkylation product was obtained. The mechanisms of these reactions have been investigated by the use of such proton donors as MeOH(MeOD); on the basis of those investigations, new photochemical reactions involving charge-transfer, followed by proton-transfer and then addition-elimination, are proposed, as well as a new type of photo-induced Birch reduction.

Since Bryce-Smith and his co-workers first reported the photoaddition of aliphatic amines to benzene in 1967,[1] a number of photochemical reactions of arenes with amines have been extensively studied. For instance, naphthalene,[2] stilbene[3] and anthracene[4] undergo photoaddition of various amines. It has been well-docummented that these photochemical reactions proceed through exciplexes or solvated radical anion-radical cation pairs.

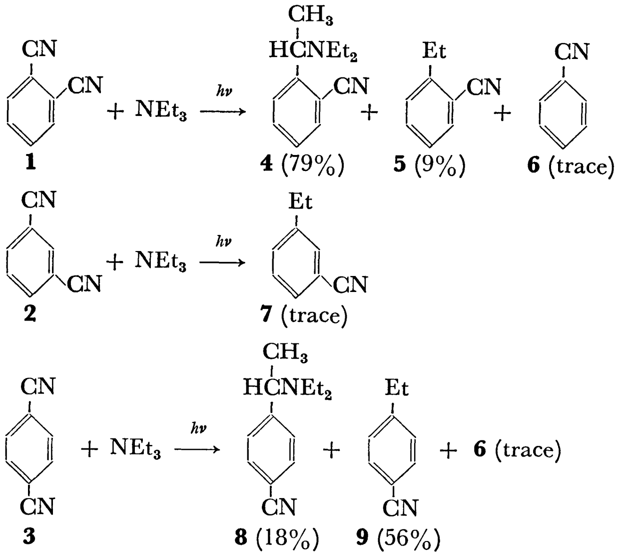
For several years we also have examined the photochemical reactions of charge-transfer complexes and have established several new reactions which proceed through radical anion-radical cation pairs. For instance, on charge-transfer excitation, such typical electron acceptors as tetracyanobenzene (TCNB),[5] tetracyanoquinodimethane (TCNQ),[6] and tetracyanoethylene (TCNE),[7] react with π-donor toluene derivatives, or n-donor ethers, to give substitution or addition products. Here, irradiation within the charge-transfer absorption bands of the system produces a donor radical cation as well as an acceptor radical anion. Subsequent proton-transfer from the donor to the acceptor yields a radical pair, which then couples to lead to an addition product. The energy required for the electron transfer is related to the ionization potential of the donor and the electron affinity of the acceptor according to the Weller equation.[8] It has been shown that the smaller the donor's ionization potentials, and the larger the acceptor's electron affinity, the easier the charge-transfer reaction. In accordance with this, strong donor-acceptor pairs, such as TCNQ or TCNE–amine systems, undergo addition reactions upon only heating,[9] while the reaction of TCNE, TCNQ, or TCNB with aromatic hydrocarbons or ethers takes place only in the excited state, not in the ground state.

Now we have examined photochemical reactions of dicyanobenzenes, relatively weak electron acceptors, with amines, strong electron donors.[10] Since the ultraviolet spectra of dicyanobenzene–amine systems do not exhibit any charge-transfer absorption band, charge-transfer complex formation in the ground state is either absent or very weak. In this case, the electron-transfer reactions do take place upon irradiation.

Results and Discussion

Photochemical Reactions of Dicyanobenzenes with Triethylamine. The irradiation of a mixture of *o*-dicyanobenzene (0.05 M, **1**) and triethylamine (0.5 M) in acetonitrile with a low-pressure mercury arc gave a substitution product (**4**) in 79% yield, together with small amounts of *o*-ethylbenzonitrile (**5**, 9%) and benzonitrile (trace). The quantum yield of the disappearance of the starting material was measured at 0.15 by means of trioxalatoferrate (III) actinometry. Similarly, *p*-dicyanobenzene (**3**) reacted with triethylamine under similar conditions to give the corresponding substitution product (**8**) and *p*-ethylbenzonitrile (**9**) in 18 and 56% yields respectively. A trace amount of benzonitrile was also detected. Again, the quantum yield of disappearance of *p*-dicyanobenzene was 0.15. On the contray, *m*-dicyanobenzene (**2**) was inert under similar conditions: after long irradiation (20 h), only a trace amount of *m*-ethylbenzonitrile (**7**) was detected by gas chromatography-mass spectrometry and a large amount of the starting materials was recovered.

Although the photochemical reactivities of **1** and **3** were similar, their product distributions were different; *i.e.*, in the photochemical reaction of **1**, the substitution product, **4**, was the major one, while the alkylated product, **9**, was the major one in the case of **3**. It is also remarkable that the *meta*-isomer (**2**) has a very low reactivity in comparison with that of the *ortho*- or



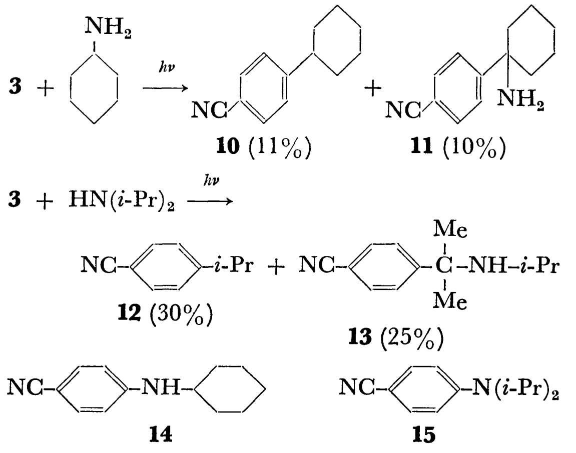
Scheme 1.

para-isomer. The difference in the reactivities of the isomers may suggest that a complication is involved in the reactions.

Reactions analogous to those in Scheme 1, but using tetramethylurea in place of triethylamine, have been reported.[11]

Photochemical Reactions of p-*Dicyanobenzene with Primary and Secondary Amines.* It has been reported that the photoaddition of primary and secondary amines to benzene or the photosubstitution in a difluorobenzene–diethylamine system occurs at the NH group in the amine.[1,12] Similar results have been reported in anthracene-amine systems.[4] We ourselves have found that, in contrast with the benzene or anthracene-primary or secondary amine systems, cyclohexylamine, a primary amine, and diisopropylamine, a secondary amine, reacted with **3** upon irradiation not at the NH group, but at the α-CH instead.[10b] Recently, it has also been reported that the photoamination of pyridine or chlorobenzene resulted in the formation of substitution derivatives at the α-CH position of the amine.[13]

The irradiation of a solution of **3** (0.046 M) and cyclohexylamine (2.6 M) in acetonitrile with a medium-pressure mercury arc for 13 h gave *p*-cyclohexylbenzonitrile (**10**), along with a substitution product (**11**), in 11 and 10% yields respectively. Similarly, the irradiation of **3** in acetonitrile in the presence of diisopropylamine (0.87 M) under similar conditions gave *p*-isopropylbenzonitrile (**12**) and a substitution product (**13**) in 30 and 25% yields respectively. A small amount of benzonitrile was also detected in both reaction mixtures by gas chromatography-mass spectrometry. The reactivities of the amines, however, were very low in comparison with that of triethylamine. The reaction scarcely occured under the same irradiation conditions as those of the aforementioned **3**-triethylamine system. The structures of the alkylated products, **10** and **12** were confirmed by direct comparison with the authentic specimens. Structures of **11** and **13** were assigned to the substitution products on the basis of elementary analyses and spectral investigations; the IR spectrum of **11** shows peaks at 3380 and 3310 cm^{-1}, characteristic of a NH_2 groups, while **13** shows a peak at 3330 cm^{-1} (NH) in the IR spectrum and a singlet 6H peak ($>CMe_2$) at δ 1.40 in the NMR spectrum, indicating that the compounds have structures substituted at the α-CH groups of the amines. Structures **14** and **15** were ruled out by the spectroscopic evidence (see Experimental section). No products corresponding to the adducts of **3** at the NH groups of the amines have been detected.



Scheme 2.

Mechanism for the Substitution Reactions. When the reaction of **1** with triethylamine was carried out in CH_2Cl_2, the reaction did not proceed; this suggested that the reaction takes place *via* a dipolar intermediates. Methanol also quenched the reaction. This behavior is similar to the case of the photo-induced substitution of TCNB–toluene systems, implying the participation of a proton-transfer process.[5a,b] When the reaction of **3** with triethylamine was carried out with oxygen bubbling through the mixture, **8** and **9** were not detected as products in the reaction mixture, but a trace amount (<1%) of *p*-cyanobenzamide was obtained instead, along with a large amount of the recovered starting materials. The quenching action of oxygen suggests that the reaction proceeds through a triplet state or an ion-radical intermediate. 1,3-Pentadiene (0.01 M), however, failed to quench the reaction. In order to clarify the multiplicity of the reactive state, fluorescence quenching experiments were performed.

The results of the Stern-Volmer treatments of the fluorescence quenching of **3** with the amines are summarized in Table 1. The kq values obtained are close to the diffusion-rate constant. The trend for amines with lower ionization potentials to be more efficient quenchers resembles that to be found in anthracene–amine systems and other general electron donor–acceptor systems.[4] Neither charge-transfer absorption nor exciplex emission was observed in these systems. The fluorescence of *o*-dicyanobenzene (**1**) was similarly quenched by triethylamine with a $k_q\tau$ value of 133 M^{-1}. It may be concluded from these experiments that the reactive species is a singlet state of the dicyanobenzene and that the primary photochemical step must be electron-transfer from the amine to the aromatics, as is usual in arene–amine systems.

The mechanisms of the fluorescence quenching of arenes by amines are probably the same in these systems, but those of the subsequent substitution differ. For instance, while the quenching of anthracene fluorescence by secondary amines and by tertiary amines proceeds *via* the same mechanism, the photochemical reactions of anthracene with secondary amines proceed *via* a different mechanism from that with a tertiary amine.[4] Concerning the molecularities of these reactions, it has been suggested that the excited charge-transfer species of a benzene–secondary amine system decay through proton-transfer in which two molecule of the amine participate,[1] while the photo-induced reaction of anthracene with *N*,*N*-dimethylaniline takes place *via* a triple exciplex.[4] It has also been demonstrated that

$$\mathrm{Ar} + \mathrm{R_2NH} \rightleftarrows \text{exciplex} \longrightarrow$$
$$\mathrm{ArH}\cdot + \mathrm{R_2N}\cdot \longrightarrow \mathrm{H\text{-}Ar\text{-}NR_2}$$
$$\mathrm{Ar} + \mathrm{R_3N} \rightleftarrows \text{exciplex} \longrightarrow \mathrm{Ar}^{\overline{\cdot}} + \mathrm{R_3N}^{\dot{+}} \longrightarrow$$
$$\mathrm{ArH}\cdot + \mathrm{R_2N\text{-}\dot{C}R'R''} \longrightarrow \mathrm{H\text{-}Ar\text{-}C(R'R'')NR_2}$$

Scheme 3.

TABLE 1. FLUORESCENCE QUENCHING OF **3** WITH AMINES

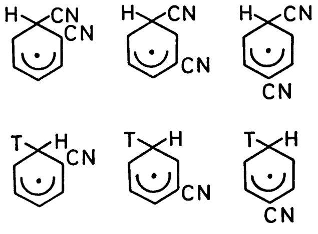
Amine	Solvent	k_q (M^{-1})[a]	k_q $(\times 10^9\ M^{-1}\ s^{-1})$[a]	Concn of **3** $(\times 10^{-4}\ M)$	*Ip* (eV)
a) Triethylamine	MeCN	158	8.8	2.18	7.50
b) Triethylamine	CH_2Cl_2	116	6.4	9.97	75.0
c) Diisopropylamine	MeCN	145	8.1	1.09	7.73
d) Cyclohexylamine	MeCN	126	7.0	2.18	8.86

a) The k_q values were calculated, based on τ being 18 ns.[15] See Fig. 1 for the amine-concentration range. Exciting light at 283 nm. Fluorescence at 394 nm.

the reactions of arene with secondary amines seem to proceed through exciplexes in which hydrogen transfer, followed by radical coupling, takes place; consequently, the 1,2- or 1,4-addition of the NH group in the amine results (Scheme 3).[3,4] Unlike the case of secondary amines, electron-transfer from the amine to the arene occurs in an arene–tertiary amine systems to form a pair of solvated radical ions, which then collapse to radicals *via* proton-transfer and subsequently couple to give the addition product at the α-CH bond of the amine to the arene. These mechanisms are shown in Scheme 3. A full electron-transfer is necessary to render the α-CH bond sufficiently acidic for proton-transfer to occur.[3]

In view of those investigations, two possible mechanisms are conceivable. One is that, since the electron affinity of **3** is larger than that of benzene, electron-transfer from the amine to the aromatics must be easier than in the hydrocarbon–amine systems and the pair of radical ions can be produced even by using the secondary or primary amine as an electron donor. Subsequent proton-transfer occurs predominantly from the α-CH position rather than from the NH group, though the acidities of the α-CH and the NH group of diisopropylamine or cyclohexylamine radical cation have not yet been determined. A similar hydrogen-transfer from the α-CH position has been observed in the photochemical reactions of ketones with primary amines.[14] The other is that, as is the case with a secondary amine–arene system, hydrogen-transfer from the NH group occurs in the exciplex or the radical ion pair, with the resulting radicals coupling to give an unstable *N*-addition product (**16**) as an intermediate. If the elimination of HCN occurs, an *N*-substitution product, **14** or **15**, will be produced. On the other hand, if the elimination of the amine takes place, the starting materials will be recovered, with the photochemical reactions working as radiationless decay processes of the excited species. This is probably the actual case. This mechanism accounts for the low reactivities of the primary and the secondary amines in comparison with those of triethylamine. The quenching of the reaction of **3** with triethylamine by methanol is also accounted for by a similar mechanism; methanol protonates the anion radical in the exciplex or the ion pair to give the neutral radical, from which the back transfer of an electron to the cation radical, followed by deprotonation, then gives the starting materials again.

Although the reduction potential of *m*-dicyanobenzene (−2.17 V) is similar to those of the *o*- or *p*-isomers (−2.12 and −1.97 V respectively),[15] the fact that the meta-isomer has much less reactivity than the *ortho*- and *para*-isomers is remarkable. In order to account for this fact, we assume that a proton from the radical cation transfers to the *ipso*-position of the dicyano compounds, and that the resulting radical is stabilized by conjugation with the cyano group in the *ortho*- and *para*-isomers, but not in the *meta*-isomer. Since the proton-transfer step is supposed to determine the rate for these reactions,[6] the stabilization of the radical intermediate may control the reactivity of the acceptor employed. A similar trend has been reported in the light-induced hydrogen isotope exchange in benzonitrile, where the exchange occurred mainly at the para(89.8%) and ortho(10%) positions, but scarcely at all at the meta(0.2%) position, in the benzonitrile–triethylamine–tritiated water system.[16] It was concluded from those results that the stability of the inter mediate radical is in the order of $I_p > I_o > I_m$, which is in accord with our assumption (Scheme 4).



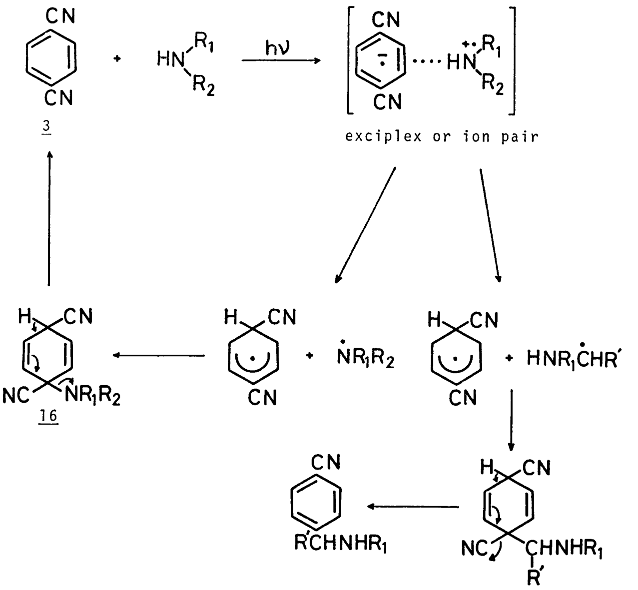
(I_o) (I_m) (I_p)

Scheme 4.

On the basis of these results, we propose the following mechanism, in which the two processes involved in the hydrogen-transfer step compete with each other. Hydrogen- or proton-transfer from the NH group probably results in the recovery of the starting materials, while proton-transfer from the α-CH position gives the substitution products, as is shown in Scheme 5.

Mechanism of the Formation of Alkylated Products. To identify the route to the alkylated products, the substitution product, **4**, was irradiated in acetonitrile under nitrogen with a low-pressure mercury arc; the alkylated product, **5**, was thus obtained in a good yield. Triethylamine added to the system slightly increased (1.4 times) the yield of the product, while methanol slightly decreased it (0.7 times). From these results, it is clear that the alkylated products have been derived from the corresponding substitution products through a new photo-induced reductive cleavage of the benzylic C–N bond.

Although many studies have been reported on the photolytic solvolysis of benzyl acetate,[17] alcohols,[18] ammonium salts,[19] halides[20] and sulfonium salts,[21] the photo-induced reductive cleavage of benzylic C–O or C–N bonds by electron donor has scarcely been examined at all.[22] Recently it was reported that



Scheme 5.

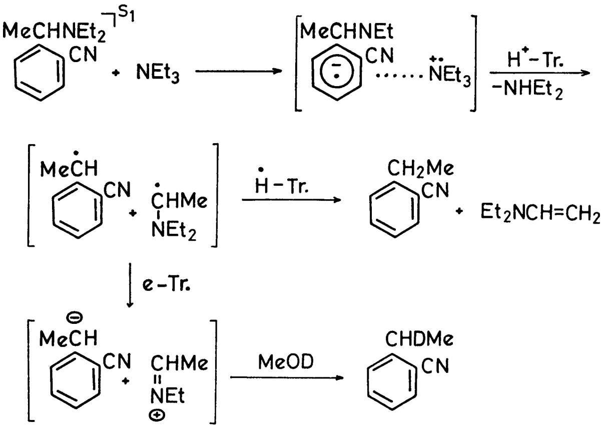
photo-induced intramolecular charge-transfer gives rise to the cleavage of benzylic C–O bonds through a carbonium-ion mechanism.[17)]

In our case, the intramolecular charge-transfer excitation from the amino group to the aromatic moiety is negligible, because the absorption spectrum of **4** is identical to that of *o*-tolunitrile. The emission spectrum of **4**, however, exhibits a broad weak band at 350—400 nm, along with a strong band at 316 nm. The former may be assigned to the fluorescence from the excited singlet state of the intramolecular charge-transfer configuration. The Stern-Volmer treatments of the quenching of both emission bands by triethylamine gave linear plots with a $k_q\tau$ value of 163 M^{-1}. Here again, a charge-transfer interaction between the singlet state of **4** and triethylamine is conceivable.

When the reaction was carried out in MeOD in place of acetonitrile, 0.51 atoms of deuterium were incorporated in the product, **5**, indicating that a proton-transfer step participated in the reaction process. A similar deuterium incorporation (0.55 atoms) was obtained in the case of the acetonitrile–MeOD–triethylamine system. The NMR spectrum of the deuterated **5** indicated that the incorporated deuterium was located mainly in the benzylic methylene group. The irradiation of **5** under similar conditions showed that no significant incorporation of deuterium by H–D exchange occurred.

Barltrop has shown that the photo-induced Birch reduction of naphthalene by triethylamine in the presence of D_2O resulted in the formation of a dihydro product in which 1.6 atoms were deuterated. He concluded that the naphthalene radical anion produced by photoinduced electron-transfer picks up the deuterium and that the resulting deuterated radical is reduced in two parallel paths, *i.e.*, one proceeding by means of electron-transfer, followed by deuterium-transfer giving a dideuterated product, and the other involving hydrogen-atom transfer.[2b)]

Referring to those observations, we propose a reduction-elimination mechanism for the present unique reduction. The reaction probably proceeds through an excimer of **4** or an exciplex between **4** and triethylamine when the amine is present in the system. Electron-transfer, followed by proton-transfer in the excited donor-acceptor system, gives a radical intermediate with the ejection of diethylamine, from which two parallel paths, as in the case of the naphthalene–triethylamine system, proceed; hydrogen-transfer, and electron-transfer followed by proton-transfer. Scheme 6 represents the possible mechanism for the photochemical reaction of **4** with triethylamine in the presence of MeOD. The intramolecular charge-transfer excitation may only result in an increase of the radiation-less decay; it may be that no chemical reactions proceed from this configuration.[23)]



Scheme 6.

Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO model IRA-1 instrument, while UV spectra were obtained with a Hitachi 124 spectrophotometer. ^1H NMR spectra were recorded with Hitachi R-24 and R-20B instruments, with tetramethylsilane as the internal standard. Mass spectra were recorded with a Hitachi RMU-6MG single-focusing instrument equipped with a direct/in-beam ion source; ionizing energy, 70 or 20 eV, source temperature, *ca.* 200 °C. Fluorescence spectra were measured with a Hitachi 204 fluorescence spectrophotometer. Irradiations for photochemical reactions were carried out with a low-pressure mercury lamp(Ushio ULO-6DQ, 6 W) or with a medium-pressure mercury lamp(Ushio UM-102, 100W). A merry-goround spparatus (Taika-Kogyo MGR) was used for the actinometry.

The dicyanobenzenes, purchased from the Tokyo Kasei Co., were recrystallized from benzene. The amines, purchased from the Wako-Junyaku Co., were reagent-grade and were distilled befor use.

Photochemical Reactions of o-*Dicyanobenzene with Triethylamine.* A solution of *o*-dicyanobenzene (955 mg, 7.5 mmol) in acetonitrile (70 ml) in the presence of triethylamine (7 g, 70 mmol) was irradiated with a low-pressure mercury lamp (6 W) for 16 h under nitrogen. The solvent was then evaporated *in vacuo*, and the residue was chromatographed on silica gel (Wako C-200) to give **4** (657 mg, 79%), **5** (50 mg, 9%), **6** (trace, detected by gas chromatography-mass spectrometry, identified by a mass spectral comparison with an authentic sample), and the starting material (534 mg).

o-*[1-(Diethylamino)ethyl]benzonitrile (4).* Bp 70 °C (17 mg Hg); IR (liq) 2230 cm^{-1}; NMR (CCl$_4$) δ 0.96 (t, 6, J=7.0 Hz), 1.32 (d, 3, J=7.0 Hz), 2.58 (q, 4, J=7.0 Hz), 4.14 (q, 1, J=7.0 Hz), 7.06—7.77 (m, 4); mass spectrum, 70 eV, m/z (rel. intensity) 204 (14), 187 (100), 159 (3), 130 (36), 103 (3), 72 (4), 58 (48), mass spectrum calcd for $C_{13}H_{18}N_2$: m/z 202.1470, found: 202.1455.

o-*Ethylbenzonitrile (5).*[24] Identified by direct comparison with the authentic specimen synthesized according to the Bissell[25] and Newman[26] methods.

Photochemical Reaction of m-*Dicyanobenzene with Triethylamine.* A solution of *m*-dicyanobenzene (1.02 g, 5.63 mmol) and triethylamine (11 g, 1.09 mmol) in acetonitrile (170 ml) was irradiated for 20 h under similar conditions. A usual work-up gave a trace amount of *m*-ethylbenzonitrile[24] [3 mg, mass spectrum, 20 eV, m/z (rel. intensity) 132 (12), 131 (47), 130 (9), 117 (17), 116 (100), 104 (15), 103 (20), 89 (12)]. The retention time of this compound in the gas chromatography-mass spectrometry was different from those of **5** and **9**.

Photochemical Reaction of p-*Dicyanobenzene with Triethylamine.* A solution of *p*-dicyanobenzene (744 mg, 5.81 mmol) and triethylamine (9.0 g, 89.1 mmol) in acetonitrile (170 ml) was irradiated with a low-pressure mercury arc (6 W) for 6 h under nitrogen. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel to give **8** (138 mg, 18%), **9** (282 mg, 56%), **6** (trace), and the starting material (257 mg).

p-*[1-(Diethylamino)ethyl]benzonitrile (8).* IR (liq) 2220 cm^{-1}; NMR (CCl$_4$) δ 0.95 (t, 6, J=7.0 Hz), 1.27 (d, 3, J=7 Hz), 2.49 (q, 4, J=7.0 Hz), 3.83 (q, 1, J=7.0 Hz), 7.04—7.91 (m, 4); mass spectrum, 70 eV, m/z (rel. intensity) 202 (20), 187 (100), 173 (9), 130 (21), 116 (5), 103 (21); mass spectrum calcd for $C_{13}H_{18}N_2$: m/z 202.1470, Found: 202.1476.

p-*Ethylbenzonitrile (9).*[24] Identified by direct comparison with the authentic specimen synthesized according to the Bissell[25] and Newman[26] methods.

Photochemical Reaction of p-*Dicyanobenzene with Cyclohexylamine.* A mixture of *p*-dicyanobenzene (501 mg, 3.91 mmol) and cyclohexylamine (21.7 g, 219 mmol) in acetonitrile (60 ml) was irradiated with a medium-pressure mercure arc (100 W) for 13.5 h under nitrogen. A usual work-up gave pale yellow crystals **11** (31 mg, 10%), an oil **10** (32 mg, 11%), **6** (trace), and the starting material (305 mg).

p-*(1-Aminocyclohexyl)benzonitrile (11).* Mp 61—63 °C (from benzene–cyclohexane); IR (KBr) 3380, 3310, 2230, 1605 cm^{-1}; NMR (CCl$_4$) δ 0.90—2.20 (m, 10), 7.59 (d, 2, J=9.5 Hz), 7.69 (d, 2, J=9.5 Hz); mass spectrum, 20 eV, m/z (rel. intensity) 200 (20), 184 (2), 171 (8), 157 (100), 144 (6), 129 (6), 116 (3), 103 (1). Found: C, 77.48; H, 8.28; N, 13.87%. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99%.

p-*Cyclohexylbenzonitrile (10).* IR (liq) 2215 cm^{-1}; NMR (CCl$_4$) δ 0.80—3.20 (m, 11), 7.20 (d, 2, J=9.0 Hz), 7.46 (d, 2, J=9.0 Hz); mass spectrum, 20 eV, m/z (rel. intensity) 185 (59), 159 (9), 143 (13), 129 (100), 117 (15), 116 (12), 103 (3), 102 (3). The structure was identified by a direct comparison of the spectra with those of the authentic specimen synthesized as follows: cyclohexylbenzene (25 g, 156 mmol) was treated with bromine (26 g, 163 mmol) in the presence of iodine (1.7 g, 6.5 mmol) according to Bissell's method[25] to give *p*-bromocyclohexylbenzene[10 g, 27%, bp 85 °C (1 mmHg)], which was then treated with copper (I) cyanide (4.0 g, 44.6 mmol) in pyridine (10 ml) according to Newman's method[25] to give **10** (1.9 g).

Photochemical Reaction of p-*Dicyanobenzene with Diisopropylamine.* A solution of *p*-dicyanobenzene (1.00 g, 7.81 mmol) and diisopropylamine (15 g, 149 mmol) in acetonitrile (150 ml) was irradiated with a medium-pressure mercury arc (100 W) for 9 h under nitrogen. A work-up in the usual manner gave an oil **12** (258 mg, 30%), an other oil **13** (294 mg, 25%), **6** (trace), and the recovered starting material (241 mg).

p-*(1-Isopropylamino-1-methylethyl)benzonitrile (13).* IR (liq) 3330, 2230 cm^{-1}; NMR (CCl$_4$) δ 0.86 (d, 6, J=6.5 Hz), 1.40 (s, 6), 2.69 (sep, 1, J=6.5 Hz), 7.05—7.85 (m, 4); mass spectrum, 20 eV, m/z (rel. intensity) 202 (4), 187 (100), 173 (2), 159 (3), 145 (48), 144 (22), 130 (4), 116 (9), 104 (3), 100 (8), 44 (31). Picrate, mp 196—199 °C (dec from ethanol). Found: C, 52.54; H, 4.86; N, 15.90%. Calcd for $C_{19}H_{25}N_5O_7$: C, 52.90; H, 4.91; N, 16.23%.

p-*Isopropylbenzonitrile (12).*[24] The structure was confirmed by a direct comparison of the spectra with those of the authentic material, synthesized by alternative method; the bromination of cumene (20 g, 167 mmol) with bromine (27 g, 169 mmol) and iodine (3.4 g, 13.4 mmol) according to the method in the literature[25] gave the bromide (18 g, 54%), which was then treated with copper(I) cyanide (10 g, 112 mmol) in pyridine (15 ml) for 22 h under nitrogen according to Newman's method[26] to give **12** (2.0 g, 16%).

Photochemical Reaction of p-*Dicyanobenzene with Triethylamine under Oxygen.* A solution of *p*-dicyanobenzene (720 mg, 5.63 mmol) and triethylamine (12 g, 119 mmol) in acetonitrile (120 ml) was irradiated with a low-pressure mercury arc (6 W) for 17 h. Oxygen was bubbled through the solution during the course of irradiation. A work-up in the usual manner gave *p*-cyanobenzamide (3 mg, 1%); colorless crystals; mp 224—226 °C (lit,[27] 224 °C).

Solvent Dependency of the Photochemical Reaction of 1 with Triethylamine. Each solution of **1** (90 mg, 0.703 mmol) and triethylamine (1 ml), dissolved in 10 ml of acetonitrile, methanol, or dichloromethane, was irradiated by means of a merry-go-round apparatus with a low-pressure mercury arc (10 W) for 22 h. The relative yields of the product, **4**, were estimated by means of gas chromatography (Degs 1.5% on Diasolid ZF 80-100), using 2-methoxynaphthalene as the internal standard. The complete quenchig of the reaction in methanol and in dichloromethane was determined.

Quantum Yields of the Disappearance of 3 in the Photochemical Reaction of 3 with Triethylamine. A solution of **3** (80 mg, 0.625 mmol) and triethylamine (1.0 g, 9.91 mmol) in acetonitrile (10 ml) was irradiated by means of a merry-go-round apparatus with a low-pressure mercury arc (10 W) for 6 h. The amount of unreacted **3** was then determined by means of gas chromatography, the conversion of **3** was found to be less than 10%. Trioxalatoferrate(III) actinometry was used (1.15×10^{16} quanta/s) to determine the quantum yields of the consumption of **1** and **3**, they were both 0.15.

Photochemical Reaction of 4. Various solutions (Table 2) of **4**, isolated and purified by vacuum distillation, were irradiated by means of a merry-go-round apparatus with a low-pressure mercury arc (10 W) for 3.5 h. The yields of **5** was then determined by means of gas chromatography.

Table 2. Relative yields of **5** in the photolysis of **4** under different conditions

	4(mg)	CH_3CN (ml)	NEt_3 (ml)	MeOH (ml)	Yield
a	24.5	5.0	—	—	1.0
b	24.5	4.7	0.3	—	1.4
c	24.7	4.0	0.3	0.7	0.65

The results are summarized in Table 2.

Photochemical Reaction of 4 in the Presence of MeOD. **4** (80 mg) was irradiated under various conditions (Table 3) by means of a merry-go-round apparatus with a low-pressure mercury arc (10 W) for 20 h. The solvent was then removed, and the residue was chromatographed on silica gel to give **5**. The isotopic purity of each specimen was determined by mass spectrometry. The results are summarized in Table **3**. The methanol-d_1 was purchased from the Wakenyaku Co., its isotopic purity was better than 99%.

TABLE 3. DEUTERIUM INCORPORATION OF **5**

	CH_3CN (ml)	MeOD (ml)	NEt_3 (ml)	D-incorporation(%)
a	—	12	—	51
b	—	11	1	53
c	11	1	—	40
d[a)]	10	1	1	55

a) In the case of d), the NMR spectrum exhibited the following peaks of the relative intensities: δ 7.30 (m, 4.0H), 2.84(q, 1.4H), and 1.25(t, and d, 3.2H).

This work was supported by a Grant-in-Aid for Scientific Research of the Ministry of Education (No. 247018).

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