Photochemical Reactions of Aromatic Compounds. Part 34.[1] Direct Photocyanation of Arenes with Sodium Cyanide in the Presence of Electron Acceptors

By **Masahide Yasuda, Chyongjin Pac,*** and **Hiroshi Sakurai,** The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

Efficient photocyanation of various arenes with sodium cyanide in 9 : 1 acetonitrile–water occurs in the presence of such electron acceptors as *p*-dicyanobenzene, 1-cyanonaphthalene, or 9-cyanophenanthrene. Under nitrogen, photocyanation of phenanthrene, anthracene, naphthalene, and 2,3-dimethylnaphthalene gives both the corresponding hydrocyanation products and the aromatic nitriles, while complex mixtures are formed with other arenes. Under oxygen, a variety of arenes which are electron donors in nature can be efficiently cyanated upon irradiation to give the aromatic nitriles. Cyanation of naphthalene derivatives gives only 1-cyanonaphthalene compounds whereas phenanthrene and anthracene are cyanated at C-9.

THE preparation of aromatic nitriles is usually carried out by substitution of aromatic halides, sulphonates, and diazonium salts with inorganic cyanide salts or by dehydration of oximes and amides.[2] Photosubstitution of aromatic compounds, mainly nitro-, halogeno-, and methoxy-arenes, with cyanide anion [3] can also be used. However, direct cyanation of aromatic hydrocarbons with inorganic salts has been only rarely reported in either thermal or photochemical [4] reactions, except for anodic cyanation.[5] In our previous communication,[6] we reported the efficient photocyanation of some aromatic hydrocarbons with sodium cyanide in the presence of *p*-dicyanobenzene (DCNB), which affords hydrocyanation products (2) and aromatic nitriles (3) [equation (1)]. This reaction seems to be of potential synthetic utility for the preparation of aromatic nitriles.

$$\underset{(1)}{\mathrm{ArH}} + \mathrm{CN^-} \xrightarrow[\mathrm{N_2}]{h\nu/\mathrm{DCNB}} \underset{(2)}{\mathrm{H{-}ArH{-}CN}} + \underset{(3)}{\mathrm{ArCN}} \qquad (1)$$

The photocyanation reaction is apparently initiated by electron transfer from the excited singlet state of ArH (^{1}ArH*) to DCNB, a process which has been estimated to be substantially exothermic,[7] according to calculations using electrochemical redox potentials and excitation energies of ^{1}ArH*.[8] In fact, the formation of the cation radical of pyrene or phenanthrene has been confirmed by means of laser-flash photolysis of the pyrene– or phenanthrene–DCNB–acetonitrile systems.[9,10] The possible reaction pathways of the photocyanation are shown in Scheme 1. Therefore, it can be expected that photocyanation reaction, might occur for reaction systems where the calculated free-energy changes for photochemical electron transfer from arenes to electron acceptors are negative; in other words, arenes which are electron donors in nature may be cyanated by this method. Thus, photocyanation with sodium cyanide in the presence of electron acceptors (A) has now been applied to various arenes. It was found that irradiation under oxygen affords aromatic nitriles in fairly good yields; this then provides a convenient method for the cyanation of arenes [equation (2)].

$$\begin{aligned}
\mathrm{ArH} &\xrightarrow{h\nu} {}^1\mathrm{ArH}^* \\
{}^1\mathrm{ArH}^* + \mathrm{DCNB} &\longrightarrow \mathrm{ArH}^{+\cdot} + \mathrm{DCNB}^{-\cdot} \\
\mathrm{ArH}^{+\cdot} + \mathrm{CN}^- &\longrightarrow {}^{\cdot}\mathrm{ArH{-}CN} \\
{}^{\cdot}\mathrm{ArH{-}CN} + \mathrm{DCNB}^{-\cdot} &\longrightarrow {}^{-}\mathrm{ArH{-}CN} + \mathrm{DCNB} \\
{}^{-}\mathrm{ArH{-}CN} + \mathrm{H}^+ &\longrightarrow \mathrm{H{-}ArH{-}CN} \\
2\,{}^{\cdot}\mathrm{ArH{-}CN} &\longrightarrow \mathrm{H{-}ArH{-}CN} + \mathrm{ArCN} \\
{}^{\cdot}\mathrm{ArH{-}CN} + \mathrm{X} &\longrightarrow \mathrm{ArCN} + \mathrm{Y}
\end{aligned}$$

(X = O_2 and/or impurities)

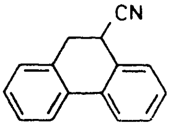
SCHEME 1

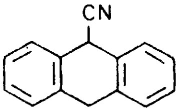
$$\mathrm{ArH} + \mathrm{CN^-} \xrightarrow[\mathrm{O_2}]{h\nu/\mathrm{A}} \mathrm{ArCN} \qquad (2)$$

RESULTS AND DISCUSSION

Solvent.—Very polar solvents are required for dissolution of the sodium cyanide and also for the occurrence of photochemical electron transfer. In our original work,[6] we used a mixture of *NN*-dimethylformamide (DMF) and water as solvent, but it was found that dark reactions take place in this solvent, leading to considerable consumption of DCNB and formation of intractable materials. Therefore, efforts were made to find better solvents in which no dark reactions occur. Hexamethylphosphoric triamide is a poor solvent for the photocyanation since no appreciable photoreaction took place. Although methanol is a good solvent for dissolution of sodium cyanide, control experiments showed that the photocyanation of phenanthrene and naphthalene in methanol or methanol–water was less efficient than that in DMF–water. It was found that 9 : 1 acetonitrile–water is a better solvent since the photocyanation in this solvent is relatively efficient and clean; dark reactions did not occur to any appreciable extent. This solvent system was therefore used throughout the present investigation.

Electron Acceptor.—The electron acceptors investigated were *o*-, *m*-, and *p*-dicyanobenzenes, methyl *p*-cyanobenzoate, 1-cyanonaphthalene (CNN), 9-cyanophenanthrene (CNP), and 9,10-dicyanoanthracene. In the photocyanation of anthracene and naphthalene compounds, CNP was the most efficient; its use improved yields of cyanation products and led to a shortening of irradiation times. Photocyanation of *m*-dimethoxybenzene and mesitylene occurred efficiently when CNN was used. On the other hand, 9,10-dicyanoanthracene, a typical electron acceptor, was not useful because of its rapid consumption during the irradiation and its low solubility in 9 : 1 acetonitrile–water.


(2a)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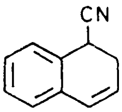
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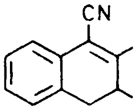
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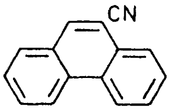
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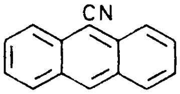
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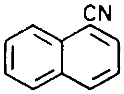
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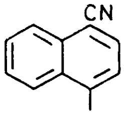
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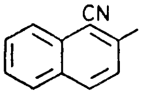
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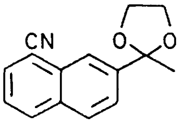
Photocyanation under N_2.—The photocyanation of phenanthrene under N_2 in the presence of DCNB gave 9,10-dihydrophenanthrene-9-carbonitrile (2a) and 9-cyanophenanthrene (3a) in 55 and 16% yields, respectively, with 72% of DCNB being recovered. In the absence of DCNB, formation of the cyanation products was much slower. In the case of anthracene, (2b) and (3b) were obtained in 67% combined yield. Although (2b) could not be purified because of rapid aromatisation to (3b) during recrystallisation, its formation was indicated by the n.m.r. spectrum of a mixture of (2b) and (3b), which showed two singlets at δ 4.3 and 4.7 in a 2 : 1 ratio. The mixture of (2b) and (3b) was quantitatively converted into (3b) by refluxing a *p*-cymene solution in the presence of 5% Pd–C. Similarly, photocyanation of naphthalene (1c) and 2,3-dimethylnaphthalene (1g) gave the corresponding 1-cyanonaphthalene compounds (3c and g) and their dihydro-isomers (2c and g). Although analytically pure (2g) could not be obtained, the structure was inferred from the spectroscopic properties; the n.m.r. spectrum showed a singlet for 2-CH_3 at δ 2.2 and a doublet for 3-CH_3 at δ 1.0, but none for olefinic protons. On the other hand, the other arenes gave complex mixtures upon irradiation under N_2. The results are summarised in Table 1.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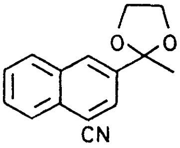
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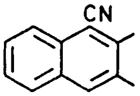
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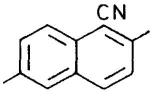
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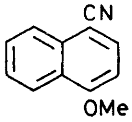
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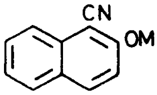
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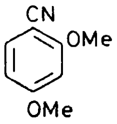
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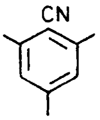

(3l)

Table 1

Photocyanation of arenes under nitrogen [a]

Arene (mmol)	A [b] (mmol)	NaCN (mmol)	Irradn. time/h	Products, yield (%) [c]	Conversion (%)	Recovery of A (%)
Phenanthrene (1a) (6.0)	DCNB (3.0)	(120)	10	(2a) 55; (3a) 16	89	72
	DCNB [d]		8	(2a) [52] [d]; (3a) [11] [d]	(79)	
	d,e		8	(2a) [4] [d]; (3a) [3] [d]	(11)	
Anthracene (1b) (3.6)	DCNB (3.0)	(36)	12	(2b) + (3b) 25	79	0
	CNP (0.9)	(36)	4	(2b) 19 [f]; (3b) 48 [f]	81	0
Naphthalene (1c) (10)	CNP (1.25)	(100)	41	(2c) 44; (3c) 18	94	57
2,3-Dimethylnaphthalene (1g) (10)	CNP (1.25)	(100)	6	(2g) [49]; (3g) [35]	100	71

[a] For solutions in acetonitrile–water (100 ml; 9 : 1 v/v). [b] Electron acceptor: DCNB = *p*-dicyanobenzene, CNP = 9-cyanophenanthrene. [c] Based on arenes unrecovered. Values in parentheses are g.l.c. yields. [d] Control runs for solutions in acetonitrile–water (3 ml; 9 : 1 v/v) of phenanthrene (0.2 mmol) and NaCN (4 mmol) [and DCNB (0.1 mmol)]. Yields are based on phenanthrene used. [e] In the absence of DCNB. [f] The product ratio was determined by n.m.r.

Photocyanation under O_2.—When the irradiation was carried out for oxygen-saturated solutions under O_2, various arenes were efficiently cyanated to give the corresponding aromatic nitriles in fairly good yields, even in cases where irradiation under N_2 gave complex mixtures. The results are shown in Table 2. In the case of anthracene, however, the irradiation of an oxygen-saturated solution gave no definite cyanation products but mainly intractable brownish material. Probably, photo-oxidation of anthracene (and also the products) would prevail.

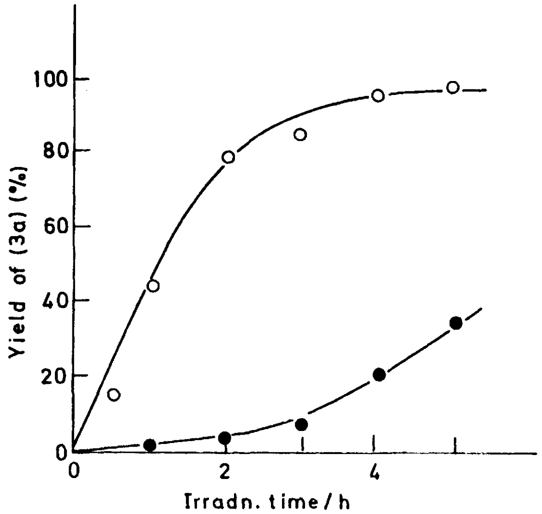
TABLE 2

Photocyanation of arenes under oxygen [a]

Arene [mmol]	A (mmol) [b]	Irradn. time/h	Products, yield (%) [c]	Recovery of A (%)
Phenanthrene (1a) [6.0]	CNP (0.92)	10	(3a) 78 [d]	
Naphthalene (1c) [10]	CNP (1.25)	15	(3c) 65	59
1-Methylnaphthalene (1d) [10]	CNP (1.25)	15	(3d) 64	70
2-Methylnaphthalene (1e) [10]	CNP (1.25)	14	(3e) 63	72
2-Acetonaphthone ethylene glycol acetal (1f) [10]	CNP (1.25)	23	(3f) 51; (3f′) 9	68
2,3-Dimethylnaphthalene (1g) [10]	CNP (1.25)	7	(3g) 63	51
2,6-Dimethylnaphthalene (1h) [10]	CNP (1.25)	10	(3h) 60	23
1-Methoxynaphthalene (1i) [10]	CNP (1.25)	15	(3i) 21; (3c) 35	79
2-Methoxynaphthalene (1j) [10]	CNP (1.25)	10	(3j) 51	53
m-Dimethoxybenzene (1k)	CNN (2.5)	24	(3k) 45	59
Mesitylene (1l) [10]	CNN (2.5)	36	(3l) 14	50

[a] For solutions in acetonitrile–water (100 ml; 9 : 1 v/v) of NaCN (100 mmol). [b] Electron acceptor: DCNB = *p*-dicyanobenzene, CNP = 9-cyanophenanthrene, CNN = 1-cyanonaphthalene. [c] Yields based on arene used. [d] Yield based on (1a) and CNP used.

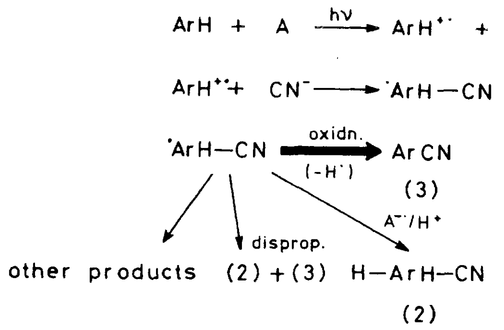
It was again confirmed that the use of electron acceptors is remarkably advantageous in most cases, because of the occurrence of clean and rapid cyanation reactions. For example, the Figure shows that the photocyanation of phenanthrene in the presence of DCNB is much more efficient than when it is absent, and that the photocyanation in the absence of DCNB gradually accelerated with an increase in conversion, probably because of the photosensitisation effect of the product (CNP) formed.



Plots of yield of (3a) *vs.* irradiation time for the photocyanation of (1a) under oxygen in the presence (○) and absence of DCNB (●); solutions in acetonitrile–water of (1a) (0.2 mmol) and NaCN (4 mmol) [and DCNB (0.1 mmol)].

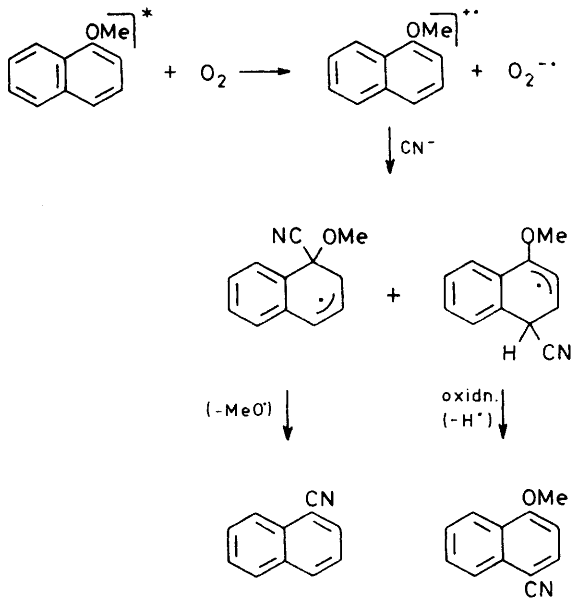
The ensuing reactions of the cyanated radicals, ArH-CN, formed by nucleophilic attack of cyanide anions on the cation radicals of arenes appear to be important in determining whether or not the cyanation proceeds efficiently (Scheme 2). Under N_2, the cyanated radicals are reduced by the anion radical of electron acceptors or undergo disproportionation, dimerisation, and/or polymerisation reactions, depending on their reactivities. Under O_2, however, oxidative aromatisation of the radicals to (3) by O_2 and its related species appears to overcome the other reaction pathways. This might be the reason why the photocyanation is successful under O_2 even in cases where complex mixtures are formed under N_2.

In the case of 1- and 2-methoxynaphthalene, effects of oxygen saturation are notable (Table 3). In either the



SCHEME 2

presence or absence of CNP (electron acceptor), irradiation under O_2 improved the yield of the cyanation product of 2-methoxynaphthalene compared with that obtained under N_2. Moreover, photocyanation of 1-methoxynaphthalene in the absence of CNP under O_2 gave 4-methoxynaphthalene-1-carbonitrile and 1-cyanonaphthalene in the ratio 3 : 4, similar to that for photocyanation in the presence of CNP, while the latter product was much more predominantly formed than the former by irradiation under N_2. These observations suggest that molecular oxygen may act as an electron acceptor towards the excited singlet methoxynaphthalenes; electron transfer from excited singlet aromatic compounds to O_2 has been reported.[11] The formation of 1-cyanonaphthalene under N_2 would arise, at least in part, from the direct nucleophilic attack of cyanide anion on the methoxylated carbon of 1-methoxynaphthalene.



In summary, it is noted that direct efficient cyanation of various arenes with sodium cyanide occurs upon irradiation in the presence of electron acceptors to give cyanation products in fairly good yields. Moreover, favourable effects of oxygen saturation were observed. Thus, the photocyanation described here provides a convenient, useful synthetic tool for the preparation of aromatic nitriles, a method which does not require the use of any such specific reagents as crown ethers,[12] phase-transfer catalysts,[13] or ammonium cyanides,[13] nor require high dilution, even in the case of anthracene.

TABLE 3

Photocyanation of 1- and 2-methoxynaphthalenes[a]

Arene	Irradn. time/h	Products, yield (%)[b]					
		Under O_2				Under N_2	
		CNP					
1-Methoxynaphthalene	12	(3i) 20	(3c) 25	(3i) 12	(3c) 16	(3i) 6	(3c) 28
2-Methoxynaphthalene	14	(3j) 54		(3j) 50		(3j) 17	

[a] For solutions in acetonitrile–water (3 ml; 9 : 1 v/v) of the arenes (0.3 mmol) and NaCN (3 mmol) [and CNP (0.07 mmol)]. [b] G.l.c. yields based on the arenes used.

EXPERIMENTAL

M.p.s were taken on a Yanagimoto hot stage. ^1H N.m.r. spectra were recorded for solutions in CCl_4 with Me_4Si as internal standard at 100 MHz on a JEOL JNM-PS-100

TABLE 4

Characterisation of the nitriles

Compound	M.p. (°C) (lit. m.p.)	^1H N.m.r. (δ) in CCl_4	Found (%) [Calc. (%)]
(2a)	84—85	3.05 (d, 2 H), 3.88 (dd, 1 H), 7.0—7.4 (m, 4 H), 7.5—7.6 (m, 2 H)	C, 87.65; H, 5.2; N, 6.8 [C, 87.77; H, 5.40; N, 6.82]
(2c)	b.p. 93 at 0.1 mmHg	3.5 (m, 2 H), 3.9 (t, 1 H), 5.9 (dt, 1 H), 6.5 (dt, 1 H), 7.3—7.9 (m, 4 H)	C, 85.2; H, 5.6; N, 9.0 [C, 85.13; H, 5.85; N, 9.03]
(2g)	b.p. 70 at 0.01 mmHg	1.0 (d, 3 H,) 2.2 (s, 3 H), 2.4—2.6 (m, 2 H) 2.8—3.1 (m, 1 H), 6.9—7.2 (m, 4 H)	
(3d)	193—194[a] (194)[a,b]	2.7 (s, 3 H), 7.1—7.6 (m, 5 H), 7.9—8.2 (m, 1 H)	
(3e)	84—85 (84.5—85.5)[c]	2.7 (s, 3 H), 7.2—7.9 (m, 5 H), 8.15 (d, 1 H)	
(3f)	80—81	1.68 (s, 3 H), 3.76—4.16 (m, 4 H), 7.44 (t, 1 H), 7.64 (dd, 1 H), 7.76—8.06 (m, 2 H), 8.26 (br, s, 1 H)	C, 75.05; H, 5.35; N, 5.8 [C, 75.30; H, 5. 48; N, 5.85]
(3f′)	85	1.64 (s, 3 H), 3.7—4.16 (m, 4 H), 7.46—7.94 (m, 3 H), 7.96 (d, 1 H), 8.1 (br d, 1 H), 8.2 (br d, 1 H)	C, 75.0; H, 5.4; N, 5.85 [C, 75.30; H, 5.48; N, 5.85]
(3g)	82.5—83.5 (82—83)[d]	2.4 (s, 3 H), 3.6 (s, 3 H), 7.4—7.7 (m, 4 H), 8.0—8.1 (m, 1 H)	
(3h)	88 (86—87)[e]	2.5 (s, 3 H), 2.64 (s, 3 H), 7.2—7.5 (m, 3 H), 7.7 (d, 1 H), 7.95 (d, 1 H)	
(3i)	101—102 (102.5)[f]	4.0 (s, 3 H), 6.5 (d, 1 H), 7.3—7.7 (m, 3 H), 7.8—8.2 (m, 2 H)	
(3j)	96—97 (95—96)[g]	4.0 (s, 3 H), 7.0—8.0 (m, 6 H)	
(3k)	89—90 (89)[h]	3.86 (s, 3 H), 3.9 (s, 3 H), 6.44 (br s, 1 H), 6.50 (dd, 1 H), 7.44 (d, 1 H)	
(31)	51—52 (50—52)[i]	2.2 (s, 3 H), 2.36 (s, 6 H), 6.7 (s, 2 H)	

[a] M.p. of 4-Methylnaphthalene-1-carboxamide. [b] R. C. Fuson, B. C. McKusick, and F. W. Spangler, *J. Am. Chem. Soc.*, 1945, **67**, 597. [c] R. C. Fuson, C. H. McKeever, and L. C. Behr, *J. Am. Chem. Soc.*, 1941, **63**, 2774. [d] P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc.* (*C*), 1968, 2506. [e] P. H. Gore and M. Yusuf, *J. Chem. Soc.* (*C*), 1971, 2586. [f] A. Fischer, M. A. Riddolls, and J. Vaughan, *J. Chem. Soc.* (*B*), 1966, 106. [g] R. C. Fuson and D. H. Chadwick, *J. Org. Chem.*, 1948, **13**, 484. [h] G. Lohaus, *Chem. Ber.*, 1967, **100**, 2719. [i] R. C. Fuson and J. J. Denton, *J. Am. Chem. Soc.*, 1941, **63**, 654.

spectrometer or at 60 MHz on a JEOL JNM-60 spectrometer, i.r. spectra for solutions in CCl_4 on a Shimadzu IR-400, mass spectra on a Hitachi RMU-6E spectrometer, and g.l.c.–mass spectra on a Hitachi RMU-4 spectrometer. G.l.c. was carried out on a Shimadzu GC-3BF dual-column instrument with flame-ionisation detectors. Columns used were 75 cm × 4 mm of 5% SE-30 on Celite 545, 5% Ucon Oil LB-550X on Celite 545, and 10% PEG-20M on Shimalite W.

Spectral grade acetonitrile was used without further purification. All the arenes and *p*-dicyanobenzene were used as received (Tokyo Kasei). 1-Cyanonaphthalene (Tokyo Kasei) was chromatographed on silica gel and then distilled *in vacuo*. 9-Cyanophenanthrene was prepared according to the literature method [14] and recrystallised from methanol.

General Procedure for Photocyanation under N_2.—To a solution of sodium cyanide (36—120 mmol) in water (10 ml) was added acetonitrile (90 ml) containing the arene (3.6—10 mmol) and the electron acceptor (0.9—3 mmol). In the case of anthracene, 150 ml of the acetonitrile solution was used. The solution was introduced into a Pyrex vessel, N_2 was bubbled through for 20 min, and the solution was irradiated with an Eikosha PIH-300 high-pressure mercury lamp under cooling with water. The progress of the reaction was followed by g.l.c. To the irradiated solution was added brine (50 ml) and then diethyl ether (500 ml). After vigorous shaking, the ethereal layer was separated, washed three times with water, dried ($MgSO_4$), and then evaporated. The residue was chromatographed on silica gel (Merk, Art 7734, 70—230 mesh), using hexane and 10—30% benzene in hexane as the eluants. The results are summarised in Table 1.

General Procedures for Photocyanation under O_2.—A gentle stream of pure oxygen was bubbled through a solution in acetonitrile–water (100 ml) of the arene (6—10 mmol), the electron acceptor (0.92—5.0 mmol), and sodium cyanide (100 mmol) in a Pyrex vessel. The reaction vessel was then connected to a balloon filled with pure oxygen and the solution was irradiated under cooling with water. After the arenes had been completely consumed, the photolysates were extracted with diethyl ether and treated in a manner similar to the work-up described above. In some cases, the products and electron acceptors were isolated without the use of column chromatography. The results are summarised in Table 2.

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