

Photoinduced Substitution of 1,3,5-Tricyanobenzene by Toluene

Mamoru Ohashi,* Nobuyuki Aoyagi, and Shuzo Yamada

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

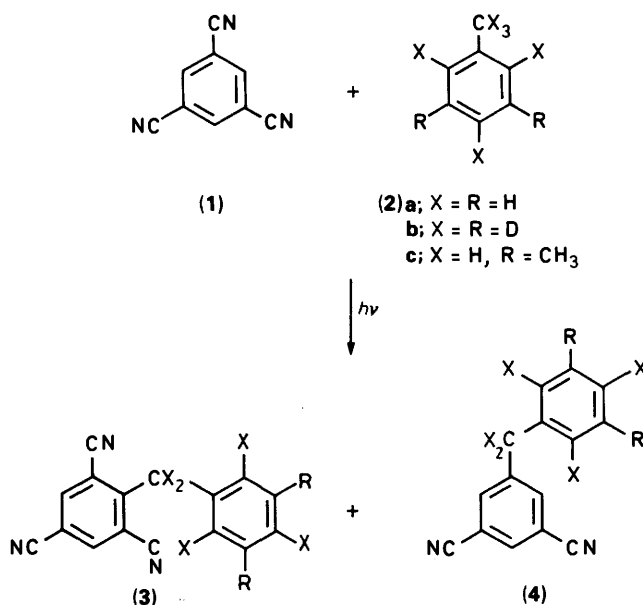
Irradiation of a solution of 1,3,5-tricyanobenzene in acetonitrile in the presence of toluene gives 1-benzyl-3,5-dicyanobenzene and 1-benzyl-3,5,6-tricyanobenzene. In a toluene solution only bibenzyl is obtained. On the basis of results obtained using [$^2\text{H}_8$]toluene (*i.e.* deuterium incorporation only in the benzyl and not in the cyanoaromatic moiety) a series of reactions which involves photoinduced electron-transfer, removal of proton from the radical cation, and then coupling of the radical anion and the radical formed is postulated. It is also suggested that for the coupling reaction to take place then the reduction potential for radical anion to dianion on the cyanoaromatic species might play an important role.

Photoinduced electron-transfer reactions between polycyano- and methylaromatics have attracted considerable interest since we initially investigated the photochemical reactions of tetracyanobenzene (TCNB) in toluene solution.¹ Recently Lewis and Petisce investigated the proton transfer reactions of photogenerated cyanoaromatic-methylaromatic radical ion pairs and demonstrated the occurrence of toluene photo-substitution with *o*- and *p*-dicyanobenzene (DCNB) but not *m*-DCNB.² A difference between the *ortho* and *para* isomers and the *meta* isomer has been reported for the reactions of triethylamine³ and 2,3-dimethylbut-2-ene⁴ with dicyanobenzenes. It is also noteworthy that the photoinduced electron-transfer reaction of a TCNB-toluene system underwent substitution to give 1-benzyl-2,4,5-tricyanobenzene, but that of a *m*-DCNB-toluene system gave only bibenzyl but no substitution product.² Those reports prompted us to investigate the photoinduced electron-transfer reactions of 1,3,5-tricyanobenzene-methylaromatic systems in order to establish a better understanding of this kind of reaction. The photochemical reactions of 1,3,5-tricyanobenzene [TrCB (1)] as an electron acceptor have scarcely been investigated. Only our investigations on TrCB-nitrile,⁵ and TrCB-hexamethyldisilane⁶ systems have been reported. At first we expected that the photoreaction of compound (1) would be similar to that of *m*-DCNB, but it turned out to be different in each case. This paper deals with the photochemical reactions of TrCB-toluene systems and compares them with those of TCNB- and DCNB-toluene systems.

Results and Discussion

Irradiation of TrCB (1) in a toluene (2a)-acetonitrile mixture (1:10) with a 100 W medium-pressure mercury arc for 2 h under nitrogen gave 1-benzyl-2,4,6-tricyanobenzene (3a) and 1-benzyl-3,5-dicyanobenzene (4a) in 33 and 15% yields, respectively; conversion of the starting material was 64%. A trace amount (0.42%) of bibenzyl (5a) was also detected in the reaction mixture. When a similar reaction was carried out in toluene, no substitution products were obtained but bibenzyl (5a) was formed exclusively. This solvent effect may indicate the participation of a polar intermediate in a series of reactions which leads to the substitution products.

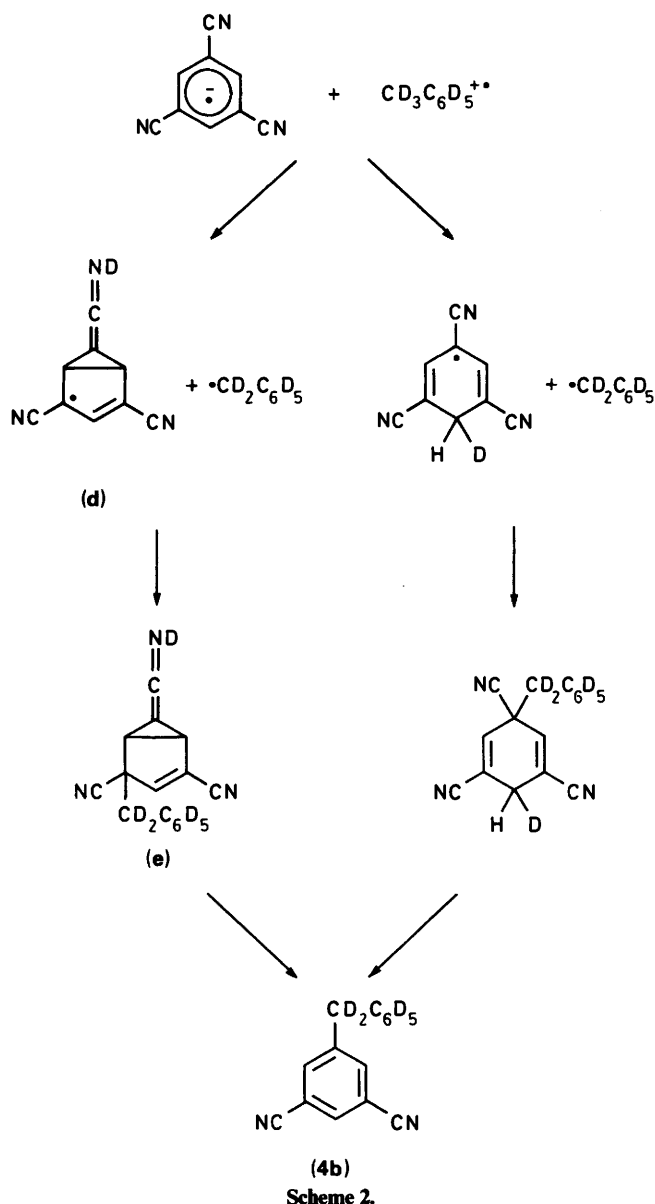
When [$^2\text{H}_8$]toluene (2b) was used in place of toluene, similar products (3b) and (4b) were obtained, in which deuterium was incorporated only in the benzyl moiety and not in the cyanoaromatic moiety. Furthermore, the mass spectra of



Scheme 1.

starting and recovered TrCB indicate that the relative abundance of m/z 154($M + 1$) to m/z 153(M) is 13.5% for the recovered TrCB, compared with 11.4% for the starting material, which means that only *ca.* 2% of the TrCB was deuteriated in the reaction. This result excludes the proton-transfer mechanism initially proposed for the TCNB-toluene system¹ in which proton transfer from the radical cation to the radical anion was assumed. If such proton transfer occurs, deuterium should be incorporated at the C-2 or C-4 position of (4b) at least in part, as shown in Scheme 2. If protonation occurred at the CN group of the TrCB radical anion, as we assumed in the case of the TrCB-isobutyronitrile system,⁵ the intermediate which leads to (4c) would be (e) or (d) which seems unreasonable. A concerted reaction, involving proton transfer to the nitrogen atom of the aryl nitrile group, with simultaneous addition of the benzyl group, may avoid the unlikely intermediate radical (d) but not the succeeding neutral intermediate (e) which is also unlikely.

Since the pK_a value of the toluene radical cation is estimated to be -10 in acetonitrile,⁷ deprotonation from the radical cation should be very favourable. When a mixture of (1)



(25 mg) and di-*t*-butyl peroxide (12 mg) in toluene 0.5 ml was heated at 135 °C for 22 h, a large amount of bibenzyl was formed but little (3a) and (4a) were detected on GC/MS analysis of the reaction mixture. This result eliminates the possibility that the benzyl radical may attack the neutral TrCB molecule. From these results we conclude that the reaction proceeds through the attack of benzyl radical on the TrCB radical anion. According to this mechanism the intermediate anion must lose hydride ion to form (3a) (see Scheme 4). An explanation for this unlikely reaction is that protonation to the intermediate anion gives a dihydro derivative which may be oxidized by air during the isolation procedure. A similar reaction mechanism has been proposed in the case of photoinduced electron-transfer reactions of dicyanobenzene-alkene systems by Arnold *et al.*⁴ However, this proposal does not deny the protonation mechanism assumed in the photoinduced substitution of the TCNB-toluene system.²

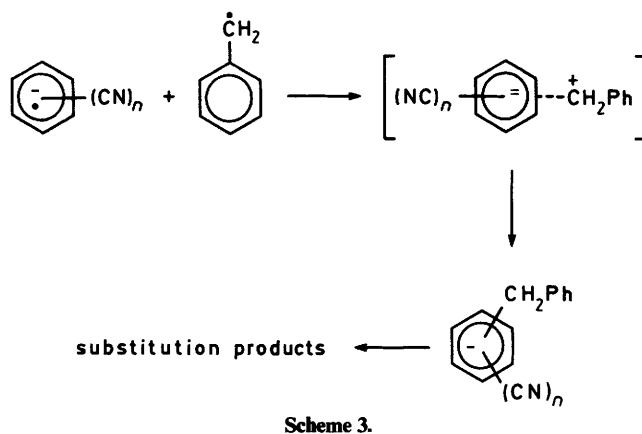
When mesitylene (2c) was used in place of toluene, a weak charge-transfer absorption band was observed at 300–340 nm. Similar irradiation of TrCB in acetonitrile in the presence of (2c) gave the dimethyl analogues (3c) and (4c) in 30 and 24%,

yields respectively. A small amount of 3,3',5,5'-tetramethylbibenzyl (16%) was obtained.

Since the TrCB-toluene system shows no charge-transfer absorption band and since the fluorescence of TrCB was quenched by (2a) [$k_q\tau$, 413 dm³ mol⁻¹; ΔG (calculated by the Rehm-Weller equation), -87 kJ mol⁻¹] the initial step of the reaction must be electron-transfer in the excited state. In the presence of methanol (1 mol dm⁻³) in acetonitrile the reaction was accelerated ($\times 4$) but the product ratio (3a):(4a) did not change.

It is generally accepted that a radical or radical cation attacks the position of highest spin density in the radical anion. All the photoinduced electron-transfer reactions of *o*-, *m*-, and *p*-DCNB, TCNB, and dicyanonaphthalene (DCN)⁸ so far studied obey this rule.⁶ Thus the substitution reaction of TrCB with (2) takes place predominantly at the C-2 position of the TrCB radical anion, but the C-1 position was also attacked. Although this behaviour is the same as that observed in the case of TrCB-tetramethyldisilane,⁶ a series of complex reactions may participate in the processes which lead to the final product from the intermediate anion; these processes are still obscure.

Since TrCB undergoes substitution but *m*-DCNB does not, the *meta*-dicyano grouping, which cannot stabilize the anion radical by means of resonance stabilization with the second cyano group, must not be important for the substitution to take place. Lewis suggested the requirement for the kinetic acidity of the radical cation and the kinetic basicity of the radical anion in order that proton-transfer within the radical ion pairs might take place.² However, in our case the toluene radical cation seems to readily lose a proton to give the benzyl radical prior to coupling of the radical ion pairs. Substitution would then occur between the radical anion of the cyanoaromatic and benzyl radicals. We suggest that for reaction of the radical anion with benzyl radical to occur in competition with dimerization of the benzyl radical, partial electron-transfer from the radical to the radical anion may take place, as shown in Scheme 3.



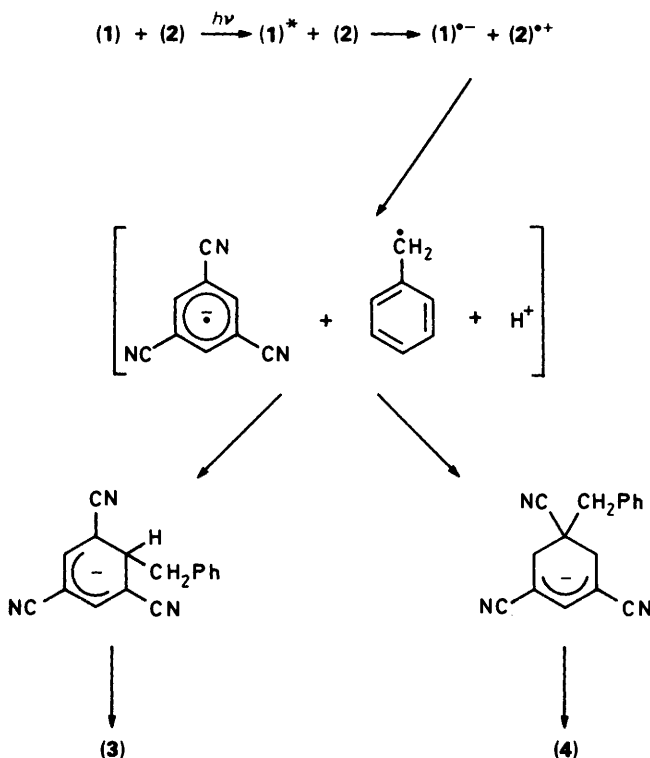
The participation may occur only when the reduction potential of the radical anion to dianion and the oxidation potential of the benzyl radical to benzyl cation (E_3^{ox} 0.40 V in acetonitrile⁹) are low. Table 1 shows voltammetric results of the first and second reduction potentials of DCNB and TrCB by Sertel *et al.*¹⁰ From these results it is clear that the differences between the first and second reduction potentials of *o*-, *p*-DCNB and TrCB are relatively small and that substitution occurs, while the difference for *m*-DCNB is large and substitution does not occur. Our suggestion is that in general the kinetic acidity (electron-accepting ability) of the radical anion, or the difference between the first and second reduction potential of the radical anion, may play an important role in

Table 1. Voltammetric results for the first and second reduction potentials of cyanobenzene derivatives.^a

	$-E_1^1/V$	$-E_2^2/V$	$\Delta E/V$
<i>o</i> -DCNB	1.66	2.46	0.80
<i>p</i> -DCNB	1.58	2.31	0.73
<i>m</i> -DCNB	1.83	—	—
TrCN	1.38	2.65	1.27

^a In MeCN, 0.1 mol dm⁻³ TBAP, Ag/AgCl (ref. 10).

coupling of the radical anion and radical. On the basis of these results, the mechanism described in Scheme 4 is proposed for this substitution reaction.

**Scheme 4.**

Experimental

General Procedure.—TLC was performed with silica gel 60 PF254 (Merck). IR spectra were determined on a JASCO IRA-1 spectrometer. ¹H NMR spectra were recorded on JEOL GX-270 (270 MHz) and Hitachi R-24 (60 MHz) spectrometers. Mass spectra (70 eV, EI) were measured with Hitachi M-80B, RMU-6MG and Shimadzu QP-1000 GC/MS instruments. UV spectra were recorded with a Hitachi 320 spectrophotometer. Fluorescence spectra were recorded with a Hitachi 204 spectrometer. Gas chromatography was carried out with Shimadzu GC-8A with FID and with TCD instruments.

Tricyanobenzene was synthesized according to the literature procedure.¹¹ Photoreactions were carried out with a SEN SL-100W medium-pressure mercury arc.

Photochemical Reaction of 1,3,5-Tricyanobenzene (1) with Toluene.—A solution of (1) (112 mg) and toluene (8 ml) in acetonitrile (80 ml) was irradiated, using a 100 W medium-pressure mercury lamp, under nitrogen for 2 h. Solvent was

Table 2. Quenching of the fluorescence of TrCB with toluene.^a

[Toluene]/mol dm ⁻³	<i>I</i> ₀ / <i>I</i>
0	1.00
5.76 × 10 ⁻⁴	1.28
1.44 × 10 ⁻³	1.65
2.88 × 10 ⁻³	2.14
5.76 × 10 ⁻³	2.95

^a [TrCB], 3.1 × 10⁻⁴ mol dm⁻³ in acetonitrile. Excitation at 280 nm.

evaporated under reduced pressure and the products were separated by repeated column and thin layer chromatography to yield compounds (3g) and (4a). 1-Benzyl-2,4,6-tricyanobenzene (3a): amorphous solid, *m/z* 244 (19), 243 (*M*⁺, 100), 215 (19), 51 (24), and 39 (19); (Found: [*M* - H - HCN]⁺, 215.0598. C₁₅H₇N₂ requires: 215.0608). An accurate mass measurement of the molecular ion could not be determined due to peak overlapping with PFK. δ_H(270 MHz, CDCl₃) 8.12 (2 H, s), 7.33 (5 H, m, Ph), and 4.49 (2 H, s). 1-Benzyl-3,5-dicyanobenzene (4a): amorphous solid, *m/z* 219 (17), 218 (*M*⁺, 100), 217 (54), 190 (23), 91 (45), 65 (20), 51 (32), and 39 (32) (Found: *M*⁺, 218.0872. C₁₅H₁₀N₂ requires: *M*⁺, 218.0843); δ_H(270 MHz, CDCl₃) 7.78 (1 H, t, *J* 1.46 Hz), 7.68 (2 H, dt, *J* 1.46, and 0.7 Hz), 7.4–7.12 (5 H, m) and 4.06 (2 H, s). The yields of (3a) and (4a) were obtained by quantitative analysis by means of GC chromatography with *o*-terphenyl as internal standard.

A solution of (1) (10 mg) and toluene (0.2 ml) in acetonitrile (13 ml) was similarly irradiated for 3 h. GC analysis showed that the solution contained (1), 2.37 × 10⁻⁵ mol; (3a), 1.39 × 10⁻⁵ mol; (4a), 6.17 × 10⁻⁶ mol; and (5c), 2.78 × 10⁻⁸ mol, which corresponds to yields (3a) 33%; (4a) 15%; and (5a) 0.4%, respectively [total conversion of (1), 64%].

Compound (1) (22 mg) was similarly irradiated in the presence of [²H₈]toluene (99%; 0.25 ml) in acetonitrile (2.5 ml) under argon by means of a 100 W medium-pressure mercury arc for 4 h. The products were separated by TLC to give (3b): *m/z* 251 (20), 250 (100), 220 (11), and 98 (5); δ_H(270 MHz, CDCl₃) 8.12 s; and (4b): *m/z* 226 (22), 225 (100), 224 (28), 223 (27), 196 (14), 195 (14), 149 (14), and 98 (15); δ_H(270 MHz, CDCl₃) 7.78 (1 H, t, *J* 1.47 Hz) and 7.68 (2 H, d, *J* 1.47 Hz).

Photochemical Reaction of (1) with Mesitylene.—A solution of (1) (10 mg) and (2c) (1 ml) in acetonitrile (10 ml) was irradiated externally with a 100 W medium-pressure mercury lamp for 3 h under nitrogen. After evaporation of the solvent and excess (2c) under reduced pressure (80 °C, 20 mmHg) the products were separated by TLC to give compounds (3c) and (4c). 3,5'-Dimethylbenzyl-2,4,6-tricyanobenzene (3c) (2.9 mg, 30%), amorphous solid, *m/z* 272 (10), 271 (*M*⁺, 57), 270 (100), 256 (23), 105 (17), and 77 (13) (Found: *M*⁺, 271.1085. C₁₈H₁₃N₃ requires: *M*⁺, 271.1108) δ_H(270 MHz, CDCl₃) 8.11 (2 H, s), 6.91 (3 H, s), 4.41 (2 H, s), and 2.28 (6 H, s). 3,5'-Dimethylbenzyl-3,5-dicyanobenzene (4c) (2.1 mg, 24%), amorphous solid, *m/z* 247 (20), 246 (*M*⁺, 93), 245 (14), 232 (21), 231 (100), 216 (14), 215 (19), 105 (41), and 91 (11) (Found: *M*⁺, 246.1180. C₁₇H₁₄N₂ requires: *M*⁺, 246.1156) δ_H(270 MHz, CDCl₃) 7.77 (1 H, t, *J* 1.35 Hz), 7.68 (2 H, dt, *J* 1.35 and 0.68 Hz), 6.93 (1 H, s), 6.75 (2 H, s), 3.96 (2 H, s) and 2.30 (6 H, s). TrCB (4.4 mg, 44%) and 3,3',5,5'-tetramethylbibenzyl (1.3 mg, 16%) were also shown to be present in the reaction mixture.

Quenching of the Fluorescence of TrCB with Toluene.—The intensity of fluorescence of TrCB (λ_{max} 310 nm) depends on the concentration of toluene added. The results are summarized in Table 2.

Acknowledgements

The present study was partially supported by Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan.

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Paper 9/03871J

Received 11th September 1989

Accepted 16th November 1989