

Photo-substitution of 1,2,4,5-Tetracyanobenzene by Toluene

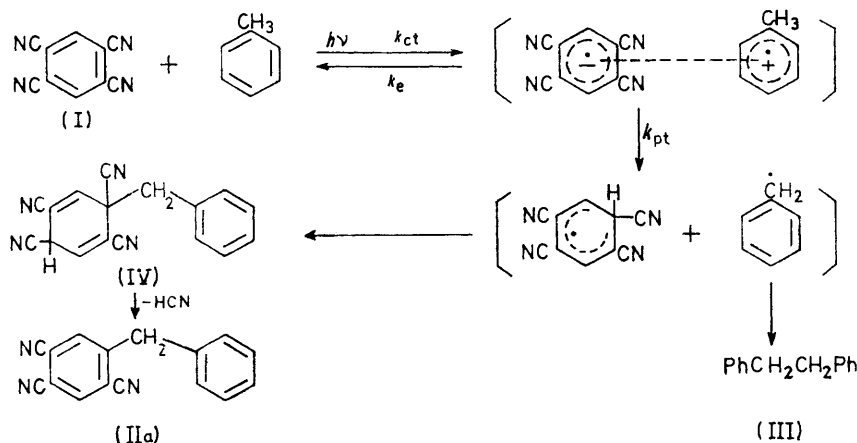
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A novel photo-induced reaction involving charge-transfer excitation is described. Irradiation of a solution of 1,2,4,5-tetracyanobenzene in toluene with a medium-pressure mercury arc gave 1-benzyl-2,4,5-tricyanobenzene with a small amount of bibenzyl. Irradiation at the frequency of a charge-transfer band of the 1,2,4,5-tetracyanobenzene-mesitylene system with acetone-filtered u.v. light gave the analogous product, indicating that the reaction proceeds through a charge-transfer mechanism. The reaction was quenched in the presence of trifluoroacetic acid. The structure of the intermediate was deduced on the basis of results obtained by using [α - $^3\text{H}_3$]toluene. Substituted toluenes underwent the same type of reaction; the effect of substituents on product yields is discussed.

STUDIES on the interaction between a radical anion-radical cation pair produced upon irradiation seem to be fruitful for devising novel photochemical reactions. For instance, Bryce-Smith and his co-workers have reported that photoadditions of maleic anhydride,¹ ethers,² and amines³ to benzene proceed through a charge-transfer (CT) mechanism; Cohen and his co-workers have demonstrated that the photoreduction of aromatic ketones by amines involves a charge-transfer process;⁴ and Wagner and Leavitt have suggested the

1-benzyl-2,4,5-tricyanobenzene (IIa) in 68% yield, along with a small amount of bibenzyl (III). Since the CT band (314.5 nm) of the TCNB-toluene complex is too close to the absorption band of TCNB (314 nm) for specific irradiation at the CT band frequency, we carried out a similar experiment using the mesitylene-TCNB complex, in order to demonstrate that the reaction is in fact produced by the irradiation at the CT band frequency. The CT band of the TCNB-mesitylene complex is at 353.4 nm,⁴ and selective irradiation in this



SCHEME

occurrence of a new type of charge-transfer process in the photoreduction of 2,2,2-trifluoroacetophenone by alkylbenzenes.⁵

Although spectroscopic investigations⁶ on the charge-transfer complexes of 1,2,4,5-tetracyanobenzene (TCNB) with aromatic nuclei have been well documented, no photochemical reactions of these systems have been reported. We have studied the photoreactions of several TCNB-substituted toluene complexes and now report a novel substitution reaction.⁷

Irradiation of TCNB (I) in toluene with a medium-pressure mercury arc for 10 h at room temperature gave

¹ D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47; D. Bryce-Smith, R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561.

² D. Bryce-Smith and G. B. Cox, *Chem. Comm.*, 1971, 915.

³ D. Bryce-Smith, M. T. Clark, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.

⁴ S. G. Cohen, A. Parola, and G. H. Parson, *Chem. Rev.*, 1973, **73**, 141, and references cited therein.

region was made feasible by using an acetone filter, which removes irradiation below 340 nm. Irradiation of TCNB in mesitylene under these conditions gave 1,2,4-tricyano-5-(3,5-dimethylbenzyl)benzene (IIb) as the sole product in 93% yield. This result demonstrates that the substitution reaction proceeds *via* the charge-transfer complex, and we suggest that it takes place by a proton transfer mechanism in the excited state as shown in the Scheme.

In order to verify the mechanism we carried out detailed mechanistic studies. If the proton transfer step participates in the reaction, it is expected that the

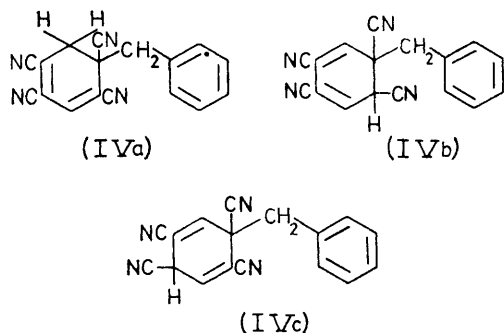
⁵ P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, 1970, **92**, 5806; 1973, **95**, 3669.

⁶ T. Kobayashi, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1971, **44**, 2603; H. Masuhara, M. Shimada, and N. Mataga, *ibid.*, 1970, **43**, 3316.

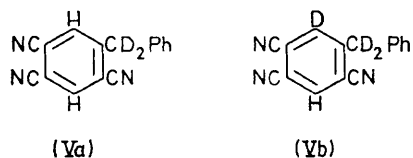
⁷ Preliminary communication, A. Yoshino, M. Ohashi, and T. Yonezawa, *Chem. Comm.*, 1971, 9.

presence of another proton source such as a protic acid would influence the outcome. In fact when the reaction was carried out in the presence of trifluoroacetic acid, the starting material was largely recovered (90%). Bryce-Smith and his co-workers have reported on the influence of trifluoroacetic acid in the photoreactions of benzene-maleic anhydride and benzene-triethylamine CT complexes.¹⁻³ Irradiation of benzene-maleic anhydride gave a 1:2 adduct, but in the presence of trifluoroacetic acid this product was totally suppressed and a new 1:1 adduct, phenylsuccinic anhydride, was obtained. A zwitterionic intermediate was suggested. In the case of the benzene-triethylamine CT complex, the presence of trifluoroacetic acid greatly accelerated the reaction and a mechanism involving a benzene-triethylamine-trifluoroacetic acid complex was suggested. However, the trifluoroacetic acid in our case neither gives a new product nor increases the reaction rate; instead the reaction is quenched. We therefore suggest that proton transfer from the cation radical to the anion radical is the first step (Scheme). Details of the action of trifluoroacetic acid in the system have not been clarified, but it seems reasonable that the acid protonates the anion radical in the CT excited state.³ Back transfer of an electron from the resulting neutral radical to the cation radical, followed by deprotonation, would then give back starting material, as observed.

Structure of the Intermediate.—Three possible structures (IVa-c) are considered for the intermediate.



Several attempts at trapping by Diels-Alder adduct formation were unsuccessful, and we therefore studied the substitution reaction with [α -²H₃]toluene instead of toluene. If the intermediate was (IVa), both (Va) and (Vb) would be expected as products. The n.m.r. and



mass spectra of the product indicated the presence of (Va) only; no evidence for the formation of (Vb) was obtained, and thus the intermediate is not (IVa). In view of Bryce-Smith's finding that 1,4-addition of an

⁸ S. G. Cohen and G. H. Parson, *J. Amer. Chem. Soc.*, 1970, **92**, 7603.

amine to benzene appears to be a non-concerted process,³ we conclude that the most reasonable structure for the intermediate is (IVc).

Substituent Effects.—Irradiation of TCNB in substituted toluenes (*m*-xylene, *m*-chloro-, *p*-chloro- and *p*-fluoro-toluene, and *m*-toluonitrile) afforded similar photoproducts (IIc-g). Under similar conditions *p*-xylene afforded 1,5-dicyano-2,4-bis-(*p*-methylbenzyl)-benzene (IIh) instead of the expected product, 1,2,4-tricyano-5-(*p*-methylbenzyl)benzene. Table 1 gives the product yields. The greatest yield was obtained in the case of *m*-xylene; both electronegative and electro-positive substituents reduced the reactivity resulting in lower yields. *p*-Methoxy- and *p*-amino-toluene did not react with TCNB upon irradiation; the rate of back electron transfer (k_e) is possibly larger than that of proton transfer (k_{pt}) in these charge-transfer complexes, thus leading only to self-quenching. These results are in broad agreement with those of Cohen and Parson for the photoreduction of fluorenone by dimethylaniline,⁸ which suggests that the charge-transfer mechanism here is reasonable.

TABLE 1
Products of the photoreaction

Subst. toluene	Product			Yield (%)
	R ¹	R ²	R ³	
Toluene (IIa)	H	H	H	68
Mesitylene (IIb)	Me	H	Me	(93) *
<i>m</i> -Xylene (IIc)	Me	H	H	91
<i>p</i> -Chlorotoluene (IId)	H	Cl	H	54
<i>m</i> -Chlorotoluene (IIe)	Cl	H	H	27
<i>p</i> -Fluorotoluene (IIf)	H	F	H	42
<i>m</i> -Toluonitrile (IIg)	CN	H	H	37

* Yield in the case of specific CT excitation based on the consumed amount of TCNB.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Hitachi 215 spectrometer and u.v. spectra with a Hitachi EPS-4T recording spectrophotometer. N.m.r. spectra were measured with a JEOL JNM-3H60 or a Varian HR-220 instrument. Mass spectra were recorded with a JEOLCO-01 spectrometer. G.l.c. analyses were performed with a Shimadzu GC-4A PTF instrument with flame-ionization detectors. TCNB was prepared as described previously.⁹

Irradiation of TCNB in Toluene.—A solution of TCNB (I) (480 mg) in toluene (350 ml) was irradiated for 10 h with a 200 W medium-pressure mercury arc under nitrogen. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with methylene chloride afforded a pale yellow oil (45 mg) which soon crystallized and was identified as bibenzyl (III) by comparison of its i.r. spectrum with that of an authentic sample. Further elution gave a pale yellow solid. Recrystallization from benzene gave needles of 1-benzyl-

⁹ E. A. Lawton and D. D. McRitchie, *J. Org. Chem.*, 1959, **24**, 26.

TABLE 2

<i>m/e</i>	(IIa) Intensity	Product from [α - $^2\text{H}_3$]toluene		Natural abundance (calc. for $\text{C}_{16}\text{H}_9\text{N}_3$)	
		<i>m/e</i>	Intensity	<i>m/e</i>	Intensity
243	100	245	100	243	100
244	19.8	246	18.8	244	18.6
245	2.0	247	1.8	245	1.6

2,4,5-tricyanobenzene (IIa) (68%), m.p. 137°, ν_{max} (KBr) 2250, 1600, 1500, and 900 cm^{-1} , τ (CDCl_3) 1.89 (1H, s), 2.16 (1H, s), 2.60 (5H, m), and 5.62 (2H, s), *m/e* 243 (M^+) (Found: C, 79.1; H, 4.0; N, 16.9. $\text{C}_{16}\text{H}_9\text{N}_3$ requires C, 79.0; H, 3.75; N, 17.3%). Further elution afforded unchanged TCNB (95 mg).

nitrogen. The solvent was evaporated off *in vacuo* to leave a brown oil which was chromatographed on silica gel. Elution with methylene chloride afforded a yellow oil (200 mg) whose i.r. spectrum exhibited no CN band but a strong absorption at 1800 cm^{-1} (CF_3CO). The structure of this product was not further investigated. Further elution gave unchanged TCNB (540 mg).

Irradiation of TCNB in [α - $^2\text{H}_3$]Toluene.—A solution of TCNB (50 mg) in [α - $^2\text{H}_3$]toluene¹⁰ (15 ml) was irradiated with a medium-pressure mercury arc through a Pyrex filter for 3 h. The solvent was removed and the residue was chromatographed on silica gel. Elution with benzene gave needles (60 mg) whose n.m.r. spectrum lacked a

TABLE 3

Spectral and physical properties of the photoproducts (IIc—g)

	Yield [mg (%)]	M.p. (°C)	ν_{max} (KBr)/ cm^{-1}	τ (MeCN)	M^+
(IIc)	134 (91)	138	2250, 1610, 1490, 910	1.72 (1H, s), 2.09 (1H, s), 2.96 (4H, m), 5.74 (2H, s), 7.62 (3H, s)	257
(IId)	85 (54)	95	2250, 1500, 1090, 1010	1.72 (1H, s), 2.10 (1H, s), 2.72 (4H, m), 5.73 (2H, s)	277
(IIe)	43 (27)	96	2250, 1600, 1500, 780, 700, 670	1.59 (1H, s), 2.00 (1H, s), 2.69 (4H, m), 5.69 (2H, s)	277
(IIf)	62 (42)	96	2249, 1600, 1510, 830, 790	1.47 (1H, s), 1.82 (1H, s), 2.40 (4H, m), 5.59 (2H, s)	261
(IIg)	56 (37)	175	2250, 1600, 1490, 790, 680	1.41 (1H, s), 1.70 (1H, s), 2.27 (4H, m), 5.45 (2H, s) *	268

* In $(\text{CD}_3)_2\text{CO}$.

Irradiation of TCNB in Mesitylene through an Acetone Filter.—A solution of TCNB (350 mg) in mesitylene (70 ml) was irradiated through an acetone filter with a 100 W medium-pressure mercury arc under nitrogen. The solution was evaporated to ca. 5 ml under reduced pressure. The crystals which separated were identified as unchanged TCNB (204 mg). The solution was evaporated further and the brown solid obtained was chromatographed on silica gel. Elution with methylene chloride gave 1,2,4-tricyano-5-(3,5-dimethylbenzyl)benzene (IIb) as needles (90 mg), m.p. 179°, ν_{max} (KBr) 2250, 1600, 1500, 920, and 820 cm^{-1} , τ (CDCl_3) 2.05 (1H, s), 2.45 (1H, s), 3.10 (1H, s), 3.45 (2H, s), 5.84 (2H, s), and 7.70 (6H, s), *m/e* 271 (M^+) (Found: C, 78.9; H, 4.8; N, 16.2. $\text{C}_{18}\text{H}_{13}\text{N}_3$ requires C, 79.7; H, 4.85; N, 15.5%). Further elution afforded unchanged TCNB (85 mg).

Irradiation of TCNB in Toluene in the Presence of Trifluoroacetic Acid.—A solution of TCNB (600 mg) and trifluoroacetic acid (20 g) in toluene (350 ml) was irradiated for 10 h with a 200 W medium-pressure mercury arc under

signal at τ 5.62 but showed the expected resonances at τ 1.89 and 2.16 [*cf.* (IIa)]. The relative intensities of the peaks in the molecular ion region of its mass spectrum are summarized in Table 2.

Irradiation of TCNB in Substituted Toluenes.—General procedure. A 0.022M-solution of TCNB (100 mg) in the substituted toluene was irradiated with a 200 W medium-pressure mercury arc through a Pyrex filter for 10 h under nitrogen. The solvent was removed and the residue was chromatographed on silica gel. The yields and structures of the products are summarized in Table 1 and the physical and spectral properties in Table 3.

The reaction in *p*-xylene gave 1,5-dicyano-2,4-bis-(*p*-methylbenzyl)benzene (IIh) (62 mg, 42%), m.p. 105–108°, ν_{max} (KBr) 2230, 1600, 1500, and 800 cm^{-1} , τ (CDCl_3) 1.88 (1H, s), 2.30 (1H, s), 2.70 (8H, m), 5.76 (1H, s), and 7.63 (6H, s), *m/e* 336.157 (M^+).

[4/1575 Received, 29th July, 1974]

¹⁰ R. Renaud and L. C. Leitch, *Canad. J. Chem.*, 1956, **34**, 98.