

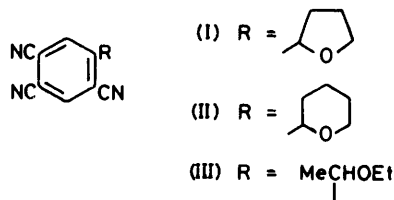
## Photosubstitution of 1,2,4,5-Tetracyanobenzene by Ethers

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Irradiation of a mixture of 1,2,4,5-tetracyanobenzene and diethyl ether, tetrahydrofuran, or tetrahydropyran gave the corresponding substitution product, 1-ethoxy-1-(2,4,5-tricyanophenyl)ethane, tetrahydro-2-(2,4,5-tricyanophenyl)furan, or tetrahydro-2-(2,4,5-tricyanophenyl)pyran. Three possible mechanisms involving electron transfer are discussed.

REACTIONS between radical anion–radical cation pairs produced upon irradiation are currently of considerable interest.<sup>1</sup> 1,2,4,5-Tetracyanobenzene (TCNB) is a typical electron acceptor and readily forms charge-transfer complexes with electron donors.<sup>2</sup> In previous papers we described a substitution reaction of several charge-transfer complexes of TCNB–toluene derivatives on irradiation of their charge-transfer absorption bands.<sup>3</sup> Although spectroscopic investigations on the charge-transfer complexes of TCNB with several ethers have been well documented and ionic photodissociation has been confirmed by flash photolysis,<sup>4</sup> no photochemical reactions of these systems have been reported. In continuing our studies on photochemical reactions of electron donor–acceptor systems, we investigated the TCNB–ether system and found<sup>5</sup> that a new substitution reaction takes place upon irradiation in a similar manner as for TCNB–toluene complexes.<sup>3</sup>

A solution of TCNB ( $7 \times 10^{-2}\text{M}$ ) in tetrahydrofuran (THF) was irradiated with a 10 W low pressure mercury arc for 3.3 h under nitrogen. The product (31%) was isolated by chromatography on silica gel and its structure was determined as tetrahydro-2-(2,4,5-tricyanophenyl)furan (I) on the basis of analytical and spectral data.



The quantum yield of this reaction was measured by the use of a merry-go-round apparatus. Values of 0.19 and 0.023 were obtained on irradiation at 254 and 313 nm, respectively, for consumption of TCNB.

Similarly irradiation of a mixture of TCNB ( $8.3 \times 10^{-3}\text{M}$ ) and tetrahydropyran (THP) (0.7M) in acetonitrile with a low pressure mercury lamp for 4 h under nitrogen gave tetrahydro-2-(2,4,5-tricyanophenyl)pyran (II) in 20% yield. When TCNB ( $2.0 \times 10^{-2}\text{M}$ ) in 1:2 diethyl ether–acetonitrile was irradiated under similar conditions for 3 h, 1-ethoxy-1-(2,4,5-tricyanophenyl)ethane (III) was obtained in 25% yield.

Although we could not observe any charge-transfer absorption band in these systems, Mataga and his co-workers reported that weak charge-transfer absorption

bands were observed in TCNB–2-methyltetrahydrofuran (MTHF) and irradiation of the bands produces a radical cation–radical anion pair from the excited Franck–Condon state.<sup>4a</sup> On the other hand, Achiba and Kimura have demonstrated that TCNB anion is formed bi-photonicly *via* the lowest excited triplet state of the 1:1 TCNB–diethyl ether charge-transfer complex in diether–isopentane glass at 77 K.<sup>4b</sup> Accordingly, the photochemical reactions here mentioned seem to be initiated by electron transfer from the ether to TCNB.

In order to examine a possible radical chain mechanism as proposed in the case of a photoreaction of 7,7,8,8-tetracyanoquinodimethane (TCNQ)–THF,<sup>6</sup> a solution of TCNB (0.5M) and azobisisobutyronitrile (0.05M) in THF was refluxed under nitrogen for 12 h in the dark. A large amount of polymerized material was obtained but the substitution product (I) was not detected and the starting TCNB was mostly recovered (84%). Similarly, in the case of TCNB–THP–acetonitrile the dark reaction with azoisobutyronitrile resulted only in recovery of the starting TCNB (90%). From these results a radical chain mechanism can be excluded for the present reactions.

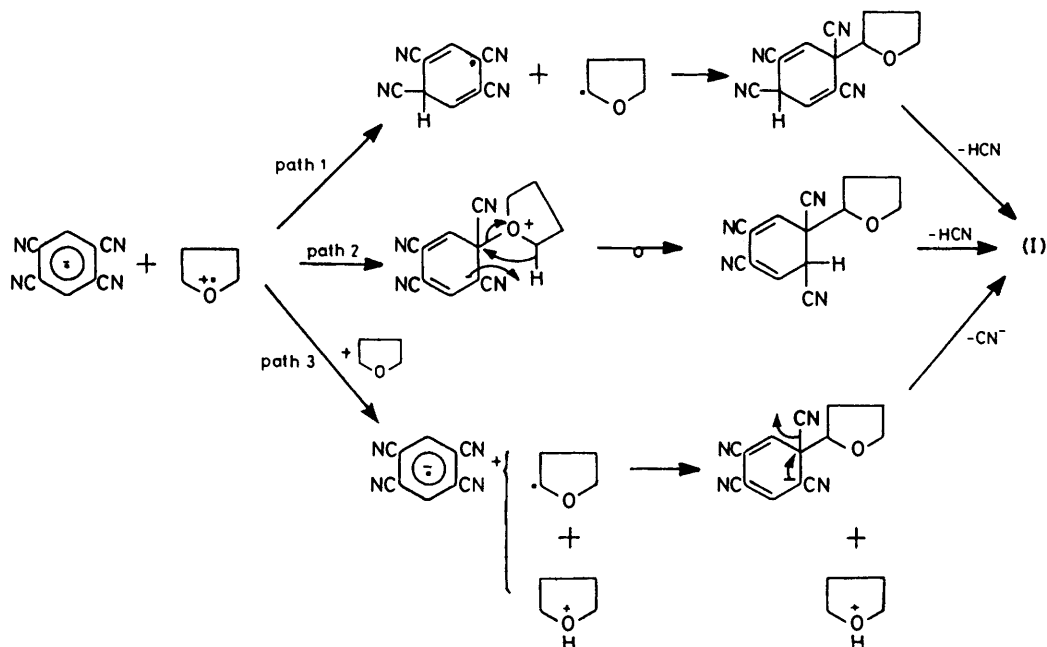
Although the critical step of the reaction seems to be electron transfer from the ether to TCNB to produce the radical anion–radical cation pair, three possible processes are conceivable for the succeeding reactions as shown in the Scheme for the reaction of TCNB with THF. Path I is analogous to the generally accepted mechanism which proceeds through charge-transfer exciplexes as shown in the cases of 1,2-di-4-pyridylethylene–ethers,<sup>7</sup> tetrahalogenophthalonitrile–ethers,<sup>8</sup> and dimethyl acetylenedicarboxylate–THF<sup>9</sup> systems. It has been suggested, however, by Bryce-Smith *et al.*<sup>10</sup> and by ourselves<sup>11</sup> that the participation of a proton transfer step in this mechanism would be affected by the addition of a proton donor such as trifluoroacetic acid (TFA) or methanol. Thus we examined the effects of TFA on the reaction.

The relative yield (I) upon irradiation of the TCNB–THF system decreased in the presence of 0.4 and 0.8M-TFA to 80 and 70%, respectively. In the TCNB–THP system the yield of (II) was little affected by the addition of TFA (0.1M). These results are in contrast with those for TCNB–toluene in which the photosubstitution was almost completely quenched by 0.5M-TFA,<sup>3</sup> and TCNQ–toluene in which the photoaddition was accelerated about ten-fold by 0.5M-TFA.<sup>11</sup> The insensitivity of the

reaction to TFA suggests that path 1 is not adequate for the present reaction.

Path 2 is analogous to the mechanism proposed by Bryce-Smith *et al.* in the photoreaction of the benzene-diethyl ether system.<sup>10</sup> The first step after electron transfer is radical coupling to produce a zwitterion which is somewhat analogous to the intermediate in the photoaddition of benzene to maleic anhydride.<sup>12</sup> The second step involves an intramolecular proton transfer followed by Stevens rearrangement of an oxonium analogue. In connection with the photoaddition of benzene-maleic anhydride, however, Bryce-Smith *et al.* have indicated

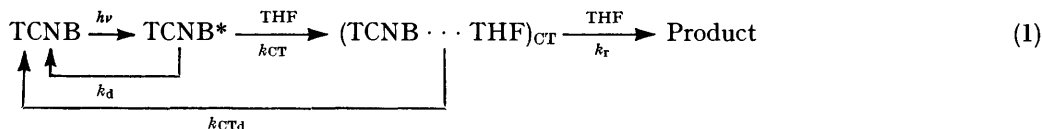
possibility of path 3 in which the THF radical cation produced by photoinduced electron transfer reacts quickly with the neighbouring THF molecule to give a THF radical and an oxonium ion as shown in the Scheme. The resulting THF radical then reacts with TCNB radical anion to give an anion from which the cyanide ion is eliminated to give product (I). Since this mechanism involves neither the proton-transfer step between the radical cation and the radical anion nor the zwitterion intermediate, path 3 would be little affected by the addition of TFA and seemed to be very attractive.



SCHEME

that the use of a proton donor such as TFA strongly influences the course of photochemical reactions which involve dipole intermediates.<sup>12</sup> These authors have also

However, when the reaction was analysed kinetically, path 3 could be differentiated clearly from the other paths in terms of the order of THF concentration.



shown that the photochemical addition of benzene to diethyl ether takes place only in the presence of TFA. Those results seem to suggest that the insensitivity of the present reaction to a proton donor is not consistent with a mechanism involving a zwitterion intermediate, although we proposed path 2 in a preliminary communication.<sup>5</sup>

Recently Achiba and Kimura have shown that in tetracyanoethylene (TCNE)-MTHF an initially photo-induced cation radical reacts with the nearest MTHF molecule forming a more stable cation which prevents the ion pair from engaging in geminate recombination.<sup>4b</sup> Referring to their observation, we have examined the

Reaction (1) was assumed for path 3. The steady state assumption for the concentrations of TCNB\* and (TCNB  $\cdots$  THF)<sub>CT</sub> made the resulting equation (2) simpler;  $\phi$  is the quantum yield of the consumption of TCNB.

$$1/\phi \propto (1 + k_d/k_{CT}[\text{THF}])(1 + k_{CTd}/k_r[\text{THF}]) \quad (2)$$

It was found that plots of  $1/\phi$  versus  $1/[\text{THF}]$  gave a linear relationship for THF concentrations between  $0.75 \times 10^{-3}$  and  $6.75 \times 10^{-3}$  M. This suggests that path 3 is wrong for this reaction. On the other hand, we can easily get the following linear relationship for

paths 1 and 2, which is in accord with the experimental observations:  $1/\phi \propto (1 + k_{CTA}/k_r)(1 + k_d/k_{CT}[THF])$ .

As a consequence the present reaction seems to proceed through path 1 or 2 in spite of the fact that it was little affected by the proton donor.

#### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are not corrected. U.v. spectra were recorded with a Hitachi 124 spectrophotometer. I.r. spectra were recorded with a JASCO IRA-1 grating spectrophotometer. N.m.r. spectra were measured with a Hitachi R-20B or R-24 instrument. Mass spectra were recorded with a Hitachi RMU-6MG spectrometer. G.l.c. analyses were performed with a Shimadzu GC-3BF instrument with flame ionization detection.

**Irradiation of TCNB in THF.**—A solution of TCNB (205 mg) in THF (167 ml) was irradiated for 3.3 h with a 10 W low pressure mercury arc under nitrogen. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with chloroform gave a solid which was crystallized from benzene-hexane (1 : 1) to give *tetrahydro-2-(2,4,5-tricyanophenyl)furan* (I) (78 mg, 31%), m.p. 145.5 °C,  $\lambda_{\max}$ (MeOH) 308 ( $\epsilon$   $3.9 \times 10^3$ ), 297 ( $3.4 \times 10^3$ ), and 247 ( $1.6 \times 10^4$ ) nm,  $\nu_{\max}$ (KBr) 2200, 1070, and 920  $\text{cm}^{-1}$ ,  $\delta$ (CDCl<sub>3</sub>) 8.09 (1 H, s), 8.01 (1 H, s), 5.35 (1 H, t, *J* 7 Hz), 4.15 (2 H, q, *J* 6 Hz), and 2.80–1.50 (4 H, m), *m/e* 223 (*M*<sup>+</sup>, 9%), 180 (38), and 42 (100) (Found: C, 69.7; H, 3.9; N, 18.6. C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O requires C, 69.9; H, 4.05; N, 18.8%).

**Irradiation of TCNB in Acetonitrile in the Presence of THP.**—A solution of TCNB (200 mg) in acetonitrile (160 ml) in the presence of THP (10 ml) was irradiated for 4 h with a 10 W low pressure mercury lamp under nitrogen. The solvent was removed *in vacuo* and the brown residue was chromatographed on silica gel. Elution with chloroform gave *tetrahydro-2-(2,4,5-tricyanophenyl)pyran* (II) as needles (23 mg), m.p. 136 °C (from isopropyl alcohol),  $\lambda_{\max}$ (MeOH) 307, 296, and 249 nm,  $\nu_{\max}$ (KBr) 2240  $\text{cm}^{-1}$ ,  $\delta$ (CDCl<sub>3</sub>) 8.20 (1 H, s), 8.05 (1 H, s), 4.75 (1 H, d, *J* 10 Hz), 4.22 (1 H, m), 3.9–3.4 (1 H, m), and 1.1–2.1 (6 H, m), *m/e* 237 (*M*<sup>+</sup>) (Found: C, 70.4; H, 4.15; N, 17.7. C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O requires C, 70.9; H, 4.65; N, 17.7%). Further elution afforded unchanged TCNB (69 mg).

**Irradiation of TCNB in 1 : 2 Diethyl Ether-Acetonitrile.**—A mixture of TCNB (459 mg), diethyl ether (50 ml), and acetonitrile (100 ml) was irradiated for 3 h with a 10 W low pressure mercury arc under nitrogen. Removal of the solvent gave an oil which was chromatographed on silica gel. Elution with chloroform gave *1-ethoxy-1-(2,4,5-tricyanophenyl)ethane* (III) as needles (99 mg), m.p. 101–102 °C (from isopropyl alcohol),  $\lambda_{\max}$ (MeOH) 306 ( $\epsilon$   $3.8 \times 10^3$ ), 295 ( $3.1 \times 10^3$ ), and 248 ( $1.8 \times 10^4$ ) nm,  $\nu_{\max}$ (KBr) 2240 and 1200  $\text{cm}^{-1}$ ,  $\delta$ (CDCl<sub>3</sub>) 8.08 (1 H, s), 8.00 (1 H, s), 4.86 (1 H, q, *J* 8 Hz), 3.50 (2 H, q, *J* 7 Hz), 1.60 (3 H, d, *J* 8 Hz), and 1.31 (3 H, t, *J* 7 Hz), *m/e* 210 (*M* – CH<sub>3</sub>) and 181 (100%) (Found: C, 69.4; H, 4.85; N, 18.7. C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O requires C, 69.3; H, 4.8; N, 18.7%). Further elution afforded unchanged TCNB (140 mg).

**Quantum Yield Measurements.**—Quantum yields for disappearance of TCNB were obtained by irradiating samples in a merry-go-round apparatus and measuring changes in the intensity of the absorption band at 317 nm of TCNB. Chemical actinometry (potassium ferrioxalate<sup>13</sup>) was used to monitor the lamp emission and light absorption

of the irradiated solutions. To isolate the mercury emission line at 313 nm, the standard filters were used with a 100 W medium pressure mercury arc.<sup>14</sup>

**Reaction of TCNB with Azoisobutyronitrile (AIBN).**—A solution of TCNB (43 mg) and AIBN (4.6 mg) in THF (5 ml) was refluxed for 12 h under nitrogen. The solvent was removed *in vacuo* and the residue was examined by preparative t.l.c. (silica gel). Polymerized materials (65 mg), unchanged TCNB (36 mg), and no trace of (I) were obtained.

Similarly, a mixture of TCNB (48 mg), THP (10 ml), AIBN (5.7 mg), and acetonitrile (10 ml) was refluxed for 8 h under nitrogen. Removal of the solvent *in vacuo* and t.l.c. on silica gel gave unchanged TCNB (43 mg).

**Quenching Experiments using TFA.**—Solutions of TCNB in THF containing various amounts of TFA were irradiated by means of a merry-go-round apparatus and the relative yields of (I) were estimated from the n.m.r. spectra using durenene as an internal standard. Similarly, the effects of TFA on the yields of (II) were also examined. The results were summarized in the Table.

System	Concentration of TFA(M)	Relative yield of product
TCNB (0.08M)-THF	0.0	(I) 1.0
	0.4	0.8
	0.8	0.7
TCNB (0.015M)-THP-MeCN	0.0	(II) 1.0
	0.05	1.1
	0.08	1.0
	0.12	0.7

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