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PHOTOREACTION OF 1,2,4,5-TETRACYANOBENZENE WITH TETRAHYDROFURAN

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Irradiation of 1,2,4,5-tetracyanobenzene in tetrahydrofuran underwent photosubstitution to give tetrahydro-2-(2,4,5-tricyanophenyl)furan. The reaction is scarecely affected by trifluoroacetic acid and hence it appears to belong to a novel class of photoelectrophilic substitution.

Recently reported photosubstitution of 1,2,4,5-tetracyanobenzene (TCNB) in toluene[1)] and photoaddition of toluene to 7,7,8,8-tetracyanoquinodimethane (TCNQ)[2)] seem to involve electron-transfer followed by proton-transfer. These reactions are affected by an addition of a proton donor such as trifluoroacetic acid (TFA) or methanol. Thus, by TFA the photosubstitution is quenched, while the photoaddition is accellerated. Bryce-Smith et al. have indicated that the use of proton donors can be used as a mechanistic probe for a proton-transfer step.[3,4)] We now report that the photoreaction of TCNB with tetrahydrofuran (THF) is scarecely affected by TFA and appears to belong to a novel class of photoelectrophilic substitution.[5)]

A solution of TCNB in THF (0.07 M) was irradiated by means of a 10 W low pressure mercury lamp for 3.3h under nitrogen. The product was isolated by chromatography on silica gel and identified as tetrahydro-2-(2,4,5-tricyanophenyl)furan (I), mp 145.5 °C in 31% yield, on the basis of the following analytical and spectral data; λ_{max}^{MeOH} 308($3.9\text{x}10^3$) 297($3.4\text{x}10^3$) 247($1.6\text{x}10^4$) nm, ν_{max}^{KBr} 2220 1070 920 cm^{-1}, δ in $CDCl_3$ 8.09(s, 1H) 8.01(s, 1H) 5.35(t, 1H, J=7 Hz) 4.15(q, 2H, J=6 Hz) 2.80-1.50(m, 4H), MS m/e 223(M^+ 9) 180(38) 42(100). Anal. Found: C, 69.70; H, 3.88; N, 18.61%. Calcd. for $C_{13}H_9N_3O$: C, 69.94; H, 4.06; N, 18.83%.

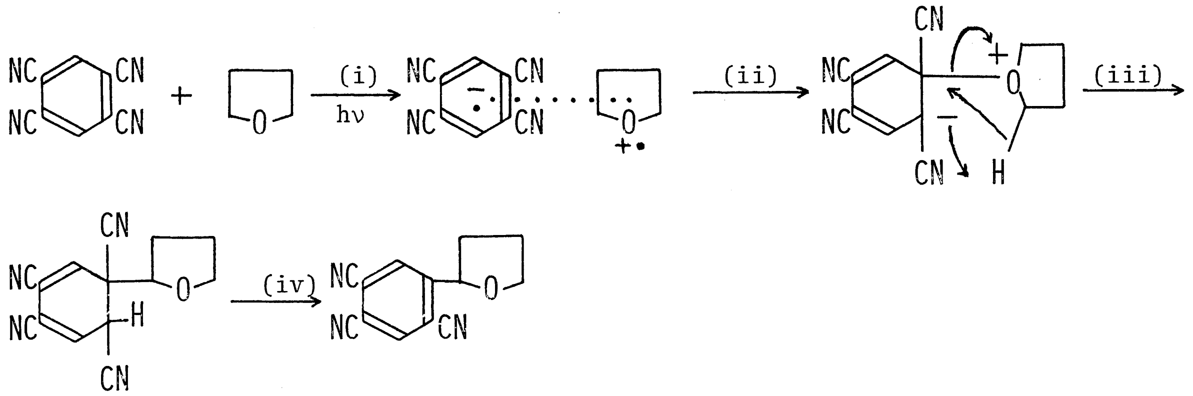
The quantum yield of the reaction was estimated by using the ferrioxalate actinometry from disappearance of the absorption of TCNB at 317 nm. The values 0.19 and 0.023 were obtained on irradiation at 254 and 313 nm respectively.

In order to elucidate the reaction mechanism the effect of TFA was examined.

The yields of I upon irradiation of a TCNB-THF (0.08 M) solution decreased in the presence of 0.4 and 0.8 M TFA to 0.8 and 0.7, respectively in comparison with the case without TFA. This result is in sharp contrast to the case of the TCNB-toluene system in which the photosubstitution was almost completely quenched by 0.5 M TFA.1) This means that a proton-transfer step in the case of TCNB-THF is not rate-determining.

When a solution of TCNB (0.5 M) and azobisisobutyronitrile (0.05 M) in THF was refluxed under nitrogen for 12 h in the dark, a large amount of polymerized materials was obtained but I was not detected on TLC and the starting TCNB was mostly recovered (84%). From this result a radical chain mechanism for the photoreaction was excluded.

Since Mataga et al. have shown that irradiation of the charge-transfer band of TCNB-2-methyltetrahydrofuran (MTHF) produces a radical cation radical anion pair from the excited Franck-Condon state,6) the photoreaction here mentioned must be initiated by electron transfer from THF to TCNB.7) On the above mentioned results we propose the following mechanism (Scheme*). Step (ii) is somewhat analogous to the photoaddition of benzene-maleic anhydride3) and so is step (iii) to the 1,4-photoaddition of diethyl ether to benzene.8)



*Scheme; (i) electron-transfer (ii) radical coupling (iii) an intramolecular hydrogen rearrangement followed by the Stevens rearrangement of an oxonium analogue (iv) elimination of hydrogen cyanide.

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7) Irradiation of TCNB in MTHF gave a mixture of products. The NMR spectra indicated that cis- and trans-tetrahydro-2-methyl-5-(2,4,5-tricyanophenyl)- and tetrahydro-2-methyl-2-(2,4,5-tricyanophenyl)furan were produced in nearly same amounts.
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