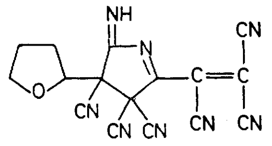
Photoaddition of the Charge-transfer Complexes of Tetracyanoethylene–Ether Systems

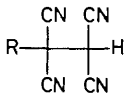
By MAMORU OHASHI,* SHUJI SUWA, and YASUSHI OSAWA
(*Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo* 182, *Japan*)

Summary Irradiation of the charge-transfer bands of the tetracyanoethylene–tetrahydrofuran, –tetrahydropyran, and –diethyl ether systems gave the corresponding 1 : 1 adducts.

IN 1963 Diekmann observed that irradiation of tetracyanoethylene (TCNE) in tetrahydrofuran (THF) gave the 2 : 1 adduct (I) and proposed a mechanism with the 1 : 1 adduct (II) as the primary intermediate, followed by ionic addition of TCNE to (II).[1] We now report, however, that on irradiation of the charge-transfer band of this system the 1 : 1 adduct (II) could be isolated in reasonable yield, but the thermal reaction of this adduct with TCNE in THF led to recovery of starting materials and (I) was not obtained.

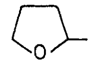


(I)

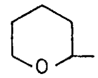


$R-C(CN)_2-C(CN)_2-H$

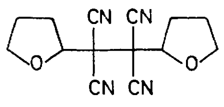
(II) R =



(IV) R =

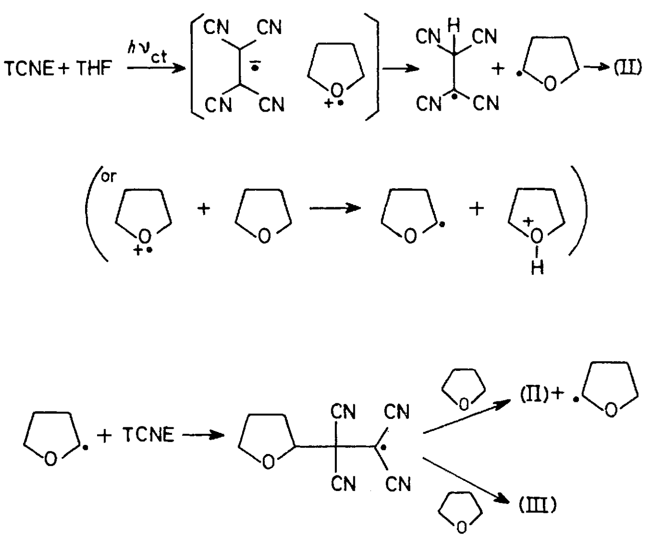


(V) R = EtOCH(Me)-



(III)

On irradiation of TCNE (0·135 M) in THF with a Pyrex-filtered medium-pressure mercury arc for 1 h, (II), m.p. 87—88 °C, and the 1 : 2 adduct (III), m.p. 119—121 °C, were isolated in 37 and 3% yields respectively. These compounds were identified unambiguously by analytical and spectroscopic data, in particular the in beam electron impact mass spectra[2] showed $M+1$ peaks at m/e 201 and 271 for (II) and (III), respectively. Irradiation of a similar mixture with a low-pressure mercury arc also gave (II) and (III) in 32 and 3% yields, respectively, demonstrating that the reaction does not depend on the wavelength of incident light.



SCHEME

When a solution of (II) and TCNE in THF was refluxed for 5 h, starting materials were recovered (83 and 88%, respectively), and we have not so far isolated (I) from any photochemical or thermal reaction products.

Since the charge-transfer band of this system lies in the 300—350 nm region[3] and since excitation of this band yields a TCNE radical anion–THF radical cation pair,[4] the reaction must proceed through electron-transfer from THF to TCNE. The resulting THF radical cation may produce a THF radical through proton transfer to the TCNE radical anion or to a neighbouring THF molecule.[5] Subsequent radical coupling or radical chain reactions would produce the 1 : 1 adduct (II). The formation of the 1 : 2 adduct (III) clearly indicates the participation of a radical route. Thus the mechanism in the Scheme is proposed for the formation of (II) and (III).

This type of reaction is general in TCNE-ether systems. Irradiation of a solution of TCNE (0·134 M) in tetrahydropyran with a Pyrex-filtered medium-pressure mercury arc for 1 h gave the corresponding 1 : 1 adduct (IV), m.p. 58—60 °C, in 18% yield.† Similarly, irradiation of a mixture of TCNE and diethyl ether in acetonitrile (ether : acetonitrile 1 : 2) under similar conditions gave the corresponding 1 : 1 adduct (V) in 37% yield.† In these cases no 1 : 2 adducts analogous to (III) have been isolated. These photochemical reactions of the TCNE–ether systems are of a similar type to the benzene–diethyl ether,[6] tetracyanobenzene–THF,[7] tetracyanoquinodimethane–THF,[1] and tetrahalogenophthalonitrile–ether[8] systems.

(*Received*, 29*th July* 1977; *Com.* 786.)

---

† Identified by mass spectrometric, n.m.r., i.r., and analytical data.

[1] J. Diekmann and C. J. Pederson, *J. Org. Chem.*, 1963, **28**, 2879.
[2] M. Ohashi, K. Tsujimoto, and A. Yasuda, *Chem. Letters*, 1976, 439.
[3] R. Vars, L. A. Tipp, and L. W. Pickett, *J. Phys. Chem.*, 1962, **66**, 1754.
[4] Y. Achiba, S. Katsumata, and K. Kimura, *Chem. Phys. Letters*, 1972, **13**, 213.
[5] Y. Achiba and K. Kimura, *Chem. Phys. Letters*, 1976, **39**, 515.
[6] D. Bryce-Smith and B. G. Cox, *Chem. Comm.*, 1971, 915.
[7] M. Ohashi and K. Tsujimoto, *Chem. Letters*, 1975, 829.
[8] K. Al-Fakhri and A. C. Pratt, *J.C.S. Chem. Comm.*, 1976, 484.