Photoreaction of Tetrahalogenophthalonitriles with Ethers

By KHALID AL-FAKHRI and ALBERT C. PRATT*

(*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester* M60 1QD)

Summary Irradiation of tetrachloro- or tetrafluorophthalonitrile in tetrahydrofuran or diethyl ether results in halogen replacement to give the corresponding α-aryl ether; an electron-transfer mechanism is proposed.

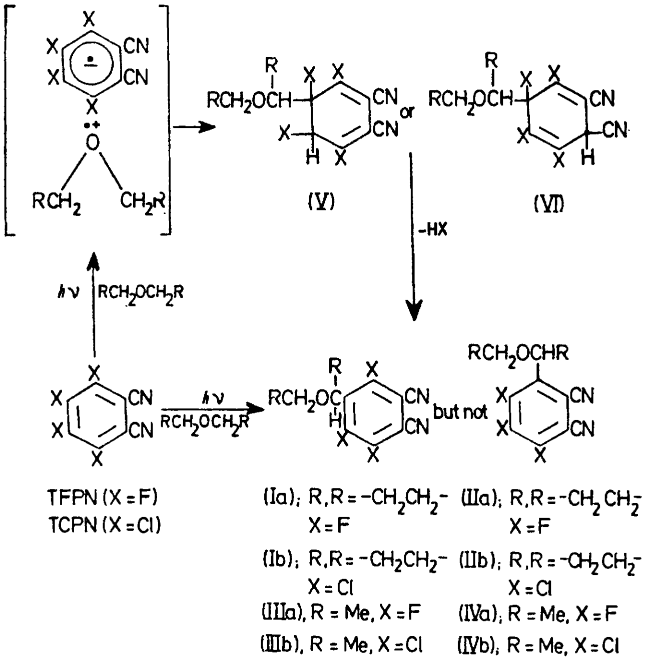
PHOTOCHEMICAL reactions involving electron-transfer followed by proton-transfer have been proposed to explain the addition of tertiary amines to benzene,[1] the photoaddition of toluene to 7,7,8,8-tetracyanoquinodimethane,[2] and the photosubstitution of 1,2,4,5-tetracyanobenzene in toluene.[3] We have discovered a new photosubstitution reaction which results in replacement of an aromatic halogen substituent by an α-alkoxyalkyl group and possibly belongs to this category of excited state reactions.

Irradiation† of tetrafluorophthalonitrile (TFPN) in tetrahydrofuran (THF) gave a single product. The ^{19}F

---

† Pyrex-filtered light from a Hanovia 250 W medium-pressure mercury vapour lamp was used in the reactions reported.

n.m.r. spectrum of the photoproduct,‡ m.p. 64—66 °C, showed three multiplets centred at 28·6, 45·0, and 52·0 p.p.m. upfield from trifluoroacetic acid as external reference; the ^{1}H n.m.r. spectrum was typical of that expected for a 2-substituted tetrahydrofuran. This evidence is consistent with the structure (Ia) and eliminates the alternative structure (IIa) from consideration. In diethyl ether, TFPN yielded the corresponding photoproduct (IIIa) as an oil.‡ The ^{19}F n.m.r. spectrum was inconsistent with the assignment of structure (IVa) to this compound.



SCHEME

Tetrachlorophthalonitrile (TCPN) was similarly converted in THF or diethyl ether into a single solid α-aryl substituted ether in each case.‡ By analogy with the replacement of the 4-fluoro substituent of TFPN, the products obtained from TCPN are almost certainly the 4-substituted compounds (Ib) and (IIIb), rather than the 3-substituted compounds (IIb) and (IVb).

Since trihalogenophthalonitriles or substituted biphenyls were not formed in these reactions, and since both TCPN and TFPN were stable to irradiation in dichloromethane and ethanol, simple aryl–halogen bond fission leading to aryl radicals is an unlikely consequence of excitation of TCPN and TFPN under these conditions. The reaction mechanism does not involve excitation of ground state charge-transfer complexes, since new bands were not observed in the u.v. absorption spectra of TCPN or TFPN when the solvent was changed from hexane to diethyl ether or THF.

The most likely mechanism would appear to be one involving electron transfer from the ether to excited TCPN or TFPN to give a radical anion–radical cation pair (Scheme). Subsequent proton transfer and ether–aryl bond formation would lead to the intermediate (V) or (VI) which would aromatise to the observed product by loss of hydrogen halide. This mechanism finds analogy in the literature, for example in the 1,4-addition of triethylamine to benzene[1] and the photosubstitution of 1,2,4,5-tetracyanobenzene in THF,[4] and intermediates (V) and (VI) have precedent in the 1 : 1 adduct isolated from the photoreaction of benzene with diethyl ether.[5]

(*Received*, 12*th April* 1976; *Com.* 394.)

---

‡ Satisfactory analytical and spectroscopic data were obtained for all new compounds.

[1] D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.
[2] K. Yamasaki, T. Yonezawa, and M. Ohashi, *J.C.S. Perkin I*, 1975, 93.
[3] K. Yamasaki, T. Yonezawa, and M. Ohashi, *J.C.S. Perkin I*, 1975, 735.
[4] M. Ohashi and K. Tsujimoto, *Chem. Letters*, 1975, 829.
[5] D. Bryce-Smith and G. B. Cox, *Chem. Comm.*, 1971, 915.