

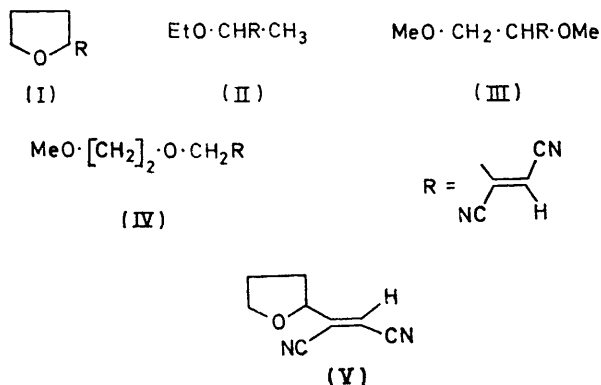
Reaction between Dicyanoacetylene and Ether Solvents

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Dicyanoacetylene forms 1:1 adducts with tetrahydrofuran, diethyl ether, and 1,2-dimethoxyethane.

WHEN attempting to use dicyanoacetylene in ether solution it was found that there was a reaction between the acetylene and the solvent. Further investigation showed that when dicyanoacetylene is refluxed in tetrahydrofuran a 37% yield of the adduct (I) is obtained, diethyl ether gives a 41% yield of adduct (II), and 1,2-dimethoxyethane a 12% yield of a 1:1 mixture of (III) and (IV). Several attempts to induce a reaction with 1,4-dioxan gave only traces of adduct. The products probably have the fumaronitrile stereochemistry shown. Heating or u.v. irradiation (*cis-trans* isomerisation) of the tetrahydrofuran adduct gave an

isomer (V). As expected this was considerably more polar than (I) and showed a larger allylic coupling constant in the n.m.r. spectrum.¹



Additions of olefins^{2,3} and acetylenes^{1,4} to ethers have been reported before but most require u.v. irradiation or heating with a radical initiator. They are thought to involve a radical-chain process and the stereochemistry of the dicyanoacetylene reaction¹ and the low selectivity of attack on 1,2-dimethoxyethane are in keeping with this. The unusual property of dicyanoacetylene, only shared with 7,7,8,8-tetracyano-*p*-quinodimethane and tetracyanoethylene,² is the ease with which it reacts. Whilst it is difficult to exclude the possibility of initiation by peroxide impurities, the ease of reaction may be related to the fact that dicyanoacetylene, like the cyanoethylenes, forms charge-transfer complexes with ethers.⁵

EXPERIMENTAL

N.m.r. spectra were determined on a Varian A60A instrument and u.v. spectra on a Unicam SP 800 spectrometer. Ether solvents were distilled from lithium aluminium hydride before use.

¹ P. Singh, *J. Org. Chem.*, 1972, **37**, 836.

² J. Diekmann and C. J. Pedersen, *J. Org. Chem.*, 1963, **28**, 2879.

³ R. L. Jacobs and G. G. Ecke, *J. Org. Chem.*, 1963, **28**, 3036; I. Rosenthal and D. Elad, *Tetrahedron*, 1967, **23**, 3193; T. M. Patrick, U.S.P. 2,628,238/1953 (*Chem. Abs.*, 1954, **48**, 711e) and related patents; V. G. Glukhovtsev, G. I. Nikishin, S. S. Spektor, S. V. Zakharova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 1065 (*Chem. Abs.*, 1968, **69**, 96,359x) and other papers by these authors.

(*Tetrahydrofuran-2-yl*)fumarionitrile.—Dicyanoacetylene (967 mg) was prepared by the method of Blomquist and Winslow⁶ and trapped at -78° . Tetrahydrofuran (40 cm³) was added. The initially pink solution became green on warming and after refluxing for 16 h was black. Evaporation under reduced pressure and chromatography on silica (eluting with 1:1 pentane-ether) followed by bulb distillation (120° at 15 mmHg) gave the *adduct* (I) as a water-white liquid (685 mg, 37%) (Found: C, 64.7; H, 5.7; N, 18.7. C₈H₈N₂O requires C, 64.9; H, 5.4; N, 18.9%), λ_{\max} (EtOH) 225 (ϵ 23,000) and 255sh nm (2600),⁷ τ (CDCl₃) 3.96 (1H, d, J 1 Hz, C=CH), 5.12br (1H, dt, J 7 and 1 Hz, >CH·O), 5.8—6.2 (2H, m, CH₂·O), and 7.5—8.2 (4H, m, CH₂·CH₂).

Thermal or photochemical isomerisation of the product gave a mixture which on chromatography on silica gel (eluting with 1:1 pentane-ether) followed by bulb distillation (120° at 15 mmHg) gave (*tetrahydrofuran-2-yl*)-maleonitrile (V) (Found: C, 64.6; H, 5.8%), τ (CDCl₃) 3.73 (1H, d, J 2.5 Hz, C=CH), 5.4br (1H, dt, J 6 and 2.5 Hz, >CH·O), 5.9—6.15 (2H, m, CH₂·O), and 7.7—8.2 (4H, m, CH₂·CH₂).

(1-Ethoxyethyl)fumarionitrile.—In a similar manner dicyanoacetylene (474 mg) and diethyl ether (25 cm³) gave the *adduct* (II) (385 mg, 41%) (Found: C, 63.8; H, 7.1; N, 18.3. C₈H₁₀N₂O requires C, 64.0; H, 6.7; N, 18.6%), τ (CDCl₃) 3.91 (1H, d, J 0.8 Hz, C=CH), 5.52 (1H, dq, J 6 and 0.8 Hz, >CH·O), 6.48 (2H, q, J 7 Hz, CH₂·O), 8.56 (3H, d, J 6 Hz, CH₃·CH), and 8.78 (3H, t, J 7 Hz, CH₃·CH₂).

Adducts with Dimethoxyethane.—In a similar manner the initially blue solution of dicyanoacetylene (360 mg) in 1,2-dimethoxyethane (20 cm³) gave (1,2-dimethoxyethyl)-fumarionitrile (III) (48 mg, 6%) (Found: C, 58.0; H, 6.1; N, 17.3. C₈H₁₀N₂O₂ requires C, 57.8; H, 6.1; N, 16.9%), τ (CDCl₃) 3.73 (1H, d, J 0.8 Hz, C=CH), 5.58 (1H, approx. dt, J 5 and 0.8 Hz, O·CH·CH₂), 6.25—6.35 (2H, ABX, CH₂), and 6.54 and 6.59 (each 3H, s, CH₃O); and [(2-methoxyethoxy)methyl]fumarionitrile (IV) (57 mg, 6%) (Found: C, 57.8; H, 6.1%), τ (CDCl₃) 3.91 (1H, t, J 1.1 Hz, C=CH), 5.54 (2H, d, J 1.1 Hz, CH₂·O), 6.2—6.5 (4H, m, O·CH₂·CH₂·O), and 6.61 (3H, s, CH₃O).

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⁴ R. Srinivasan and K. H. Carlough, *Canad. J. Chem.*, 1967, **45**, 3209.

⁵ D. F. Iften and M. Calvin, *J. Chem. Phys.*, 1965, **42**, 3760.

⁶ A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, 1945, **10**, 149.

⁷ R. L. Webb, S. Frank, and W. C. Schneider, *J. Amer. Chem. Soc.*, 1955, **77**, 3491.