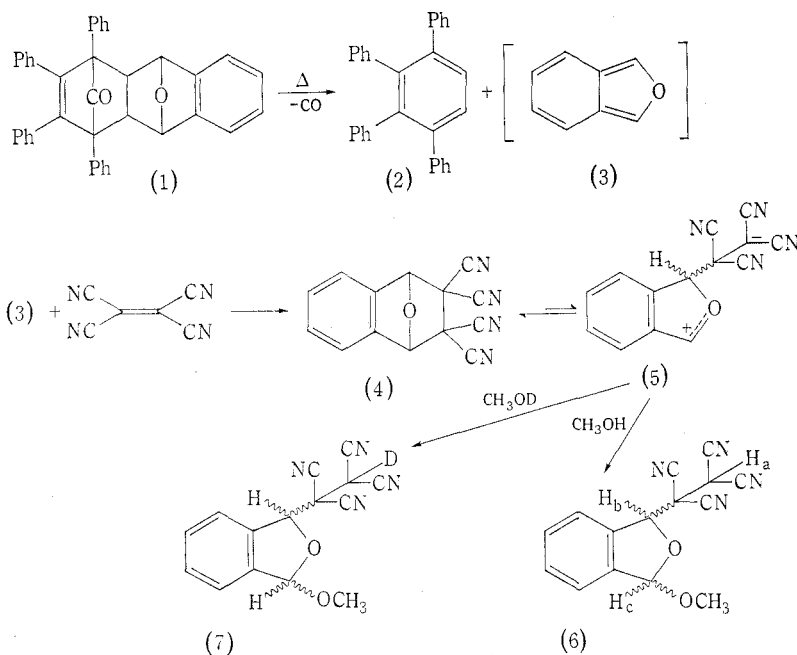


ADDITION OF METHANOL TO THE ISOBENZOFURAN-TETRACYANOETHYLENE DIELS-ALDER ADDUCT

By J. B. BREMNER* and Y. HWA*

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In connection with other studies,¹ a highly reactive dienophile was required to trap isobenzofuran generated photochemically at low temperatures. One of the dienophiles investigated was tetracyanoethylene, and although it was found to be unsuitable for this purpose, its Diels-Alder adduct (4) with isobenzofuran (3) could be prepared by a slight modification of the method² of Fieser and Haddadin.



When the ketone (1) was refluxed in xylene in the presence of tetracyanoethylene the adduct (4) was isolated in good yield. On using Fieser's diglyme-water procedure, however, no adduct could be obtained. The structure of (4) is supported by its elementary analysis and by spectral data, the bridgehead protons appearing at

* Department of Chemistry, University of Tasmania, P.O. Box 252C, Hobart, Tas. 7001.

¹ Hwa, Y., B.Sc. Honours Thesis, University of Tasmania, 1970.

² Fieser, L. F., and Haddadin, M. J., *Can. J. Chem.*, 1965, **43**, 1599.

δ 6.88 (sharp singlet) due to the strong electron-withdrawing effect of the cyano groups.³

An interesting feature of (4) is that on refluxing in methanol it is converted into the substituted phthalan (6). Microanalysis indicated the molecular formula $C_{15}H_{10}N_4O_2$ for (6), and this was confirmed by a molecular ion at m/e 278 in the mass spectrum. The p.m.r. spectrum ($[D_6]$ acetone) shows a three-proton singlet at δ 3.45 (OCH_3), two doublets (J 2 Hz) of one proton each at δ 6.26 and δ 6.56 (H_c and H_b), a multiplet from δ 7.90 to 7.55 (aromatic protons), and an exchangeable one-proton singlet at δ 6.18 (H_a). This proton exchanged rapidly and completely with D_2O , and slowly with $[D_6]$ acetone, the signal integrating for 0.39 of a proton after 5 hr. These results are in keeping with the expected^{4,5} acidity of this proton; tetracyanoethane,⁴ for example, has a pK_a of 3.6.

When (4) was treated with CH_3OD the product (7) (molecular ion at m/e 279) had an identical p.m.r. spectrum in perdeuteroacetone to that of (6), except for the absence of the singlet at δ 6.18. On running the spectrum in acetone, a signal appeared at δ 6.18 which integrated for 0.43 of a proton after 5 hr.

This addition reaction probably proceeds via the dipolar intermediate (5) in equilibrium with (4). A similar nucleophilic addition is observed⁶ with the tetramethoxyallene-tetracyanoethylene adduct, definite spectral evidence being obtained in this case for the intermediacy of a 1,4-dipole.

While the stereochemistry of (6) cannot be assigned⁷ on the basis of the H_b, H_c coupling constant, one might expect the methanol to approach (5) from the opposite side to the bulky tetracyano substituent, affording the *trans* rather than the *cis* isomer.

Experimental

Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Analyses are by the Australian Microanalytical Service, Melbourne. Infrared spectral data refer to Nujol mulls (Perkin-Elmer 221 spectrometer). P.m.r. spectra were performed at 100 MHz with a Jeol JNM-4H-100 spectrometer.

Preparation of 1,2,3,4-Tetrahydro-1,4-epoxynaphthalene-2,2,3,3-tetracarbonitrile (4)

A solution of (1) (400 mg, 0.76 mmol) and tetracyanoethylene (99 mg, 0.77 mmol) in xylene (5 ml) was refluxed for 30 min. The 1,2,3,4-tetrahydro-1,4-epoxynaphthalene-2,2,3,3-tetracarbonitrile (4) (145 mg, 78%), which crystallized from the hot solution on cooling, was collected by filtration. Addition of methanol to the filtrate afforded crystalline 1,2,3,4-tetraphenylbenzene (2) (145 mg, 50%).

An analytical sample of (4), m.p. 180° (dec.), was obtained by recrystallization from acetone-benzene (Found: C, 68.3; H, 2.5; N, 22.9; O, 6.9. $C_{14}H_6N_4O$ requires C, 68.3; H, 2.5; N, 22.8; O, 6.5%). ν_{max} 2250–2255 cm^{-1} (CN^{sa}).

³ Brown, P., and Cookson, R. C., *Tetrahedron*, 1968, **24**, 2551.

⁴ Middleton, W. J., Heckert, R. E., Little, E. L., and Krespan, C. G., *J. Am. chem. Soc.*, 1958, **80**, 2783.

⁵ Rappoport, Z., and Shohamy, E., *J. chem. Soc. (B)*, 1969, 77.

⁶ Hoffmann, R. W., and Schäfer, W., *Angew. Chem.*, 1970, **82**, 700.

⁷ Vaulx, R. L., Jones, F. N., and Hauser, C. R., *J. org. Chem.*, 1964, **29**, 505.

⁸ Bellamy, L. J., "The Infra-red Spectra of Complex Molecules." (a) p. 263; (b) p. 116. Methuen: London 1958.)

Reaction of (4) with Methanol

A solution of (4) (85 mg) in methanol (2 ml) was refluxed for 10 min. On cooling, the precipitated solid was collected by filtration and recrystallized from methanol to afford *1-methoxy-3-(1,1,2,2-tetracyanoethyl)phthalan* (6) (70 mg, 78%) as colourless, chunky needles, m.p. 161° (dec.) (Found: C, 64.7; H, 3.8; N, 20.1; O, 11.4. $C_{15}H_{10}N_4O_2$ requires C, 64.7; H, 3.6; N, 20.1; O, 11.5%). ν_{\max} 2250, 2260vw (CN), 1100s, 1090s (acetal^{8b}), 1019s, and 1004s cm^{-1} (cyclic ether⁷).

The preparation of (7) was carried out in like manner using CH_3OD .

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