

The Photochemical Reaction of Furan with Dimethyl Acetylenedicarboxylate

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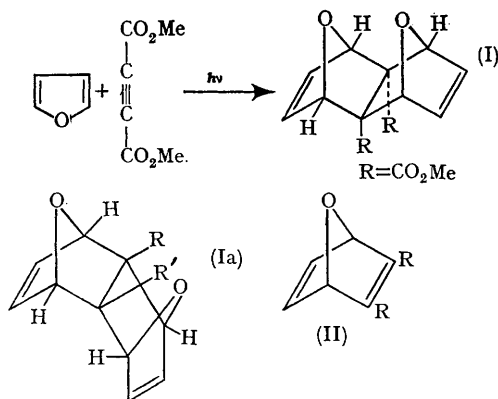
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ADDITION reactions of furan, in the dark, with substrates such as maleic ester, maleic anhydride, maleimide, have been reported¹ to lack stereo-specificity, resulting in the formation of both *exo*- and *endo*-products. We have now examined photochemical (unsensitised) addition of furan to dimethyl acetylenedicarboxylate (DMAD). In view of a recent report² of a mercury photosensitised reaction involving furan, we place on record our own results.

Irradiation of a solution of DMAD (5 g.) in furan (40 ml.) with a 250 w medium-pressure mercury-arc in a quartz vessel (52 hr., room temp.)

produced only two compounds (t.l.c.); (I), crystalline, (0.17 g.), m.p. 156°, and an oil, (II) (0.87 g.), b.p. 137°/2 mm.³ The compound (I) appeared, from mass spectral evidence, to be a 2:1 adduct of furan and DMAD. It had ν_{\max} (CHCl₃) 1740s, 1650w, 830m cm.⁻¹. The n.m.r. (60 Hz) spectrum showed a 4-H triplet at 6.64 p.p.m. (separation, *P*, between outer lines = $J_{12} + J_{13} = 2$ c./sec.), a 4-H triplet at 5.09 p.p.m. ($P J_{12} + J_{13} = 2$ c./sec.)⁵ and a 6-proton singlet centred at 3.66 p.p.m. The nature of the triplets located at 6.64 and 5.09 p.p.m. suggest the isochronous character of the two hydrogen pairs. The spectral data appear to be in accord with the symmetrical dimethyl *exo-exo*-11,12-dioxatetracyclo-[6,2,1,1^{6,9},0^{5,10}]dodeca-2,7-diene-5,10-dicarboxylate (I)[†] or the corresponding *endo-endo* structure (Ia). The proximity of the two double bonds in the *endo-endo* structure (Ia) would suggest the possibility of its closing down to a cage. On further irradiation, however, no such transformation could be realised. We, therefore, tend to believe (I) to be the correct stereochemical representation of the photo-product.

The product (II) which, from mass spectral evidence, is a 1:1 addition compound of furan and DMAD, proved to be dimethyl-7-oxa-norbornadiene-4,5-dicarboxylate from i.r. [ν_{\max} (CHCl₃) 1660m, 1730s cm.⁻¹ and n.m.r., δ 7.18 (t, separation, *P*, between outer lines 2.1 c./sec.); 5.60



[†] The most abundant ion in the mass spectrum of the adduct corresponded to *m/e* 68 (C₄H₄O⁺).

(t, P 2.0 c./sec.); 3.74 p.p.m.; (s); intensity ratio, 1:1:3].

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¹ F. A. L. Anet, *Tetrahedron Letters*, 1962, 1219; M. P. Kanstmann, D. S. Tarbell, and R. L. Autrey, *J. Amer. Chem. Soc.*, 1962, **84**, 4115; H. Kwart and I. Burchuk, *J. Amer. Chem. Soc.*, 1952, **74**, 3094; J. A. Berson and R. Swindler, *J. Amer. Chem. Soc.*, 1953, **75**, 1721.

² R. Srinivasan, *J. Amer. Chem. Soc.*, 1967, **89**, 4812.

³ Compounds A and B may have been formed in the earlier known thermal reactions of furan and DMAD (O. Diels and K. Alder, *Annalen*, 1931, **490**, 243). However, no stereochemical or spectral details of the adducts are available.

⁴ Stanley Seltzer, *J. Amer. Chem. Soc.*, 1965, **87**, 1534, found a value of 1.9 c./sec. as the summation of vicinal and allylic coupling constants in an *exo*-2-methylfuran-maleic anhydride adduct.