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PHOTOADDITION OF DIMETHYL ACETYLENEDICARBOXYLATE TO CYCLIC ETHERS

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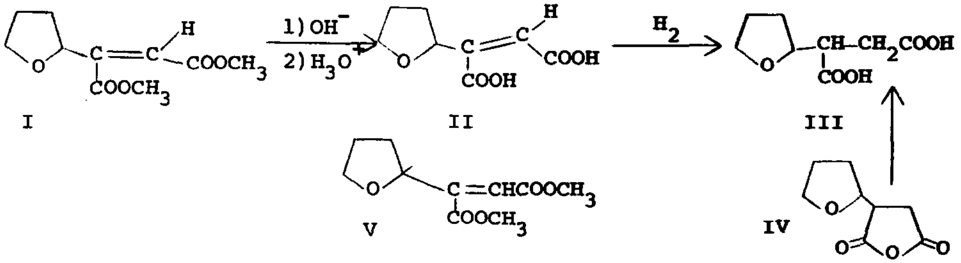
The free radical addition of both aliphatic and alicyclic ethers to a variety of unsaturated substrates has been a subject of recent interest[1,2]. Jacobs and Ecke[3] reported the efficient addition of tetrahydrofuran (THF) and tetrahydro-2-methylfuran to maleic anhydride but failed to observe any reaction with dimethyl acetylenedicarboxylate (DMAD). Our reinvestigation however showed that a 1:1 photoadduct is indeed formed and the findings are reported below.

DMAD in excess THF was irradiated under nitrogen with a 250-W Hanovia lamp through a pyrex filter. After 20 hours the unchanged reactants were distilled under reduced pressure, and the residue was chromatographed on silica gel to give (I) as a colourless liquid[4]. The structure (I) is based on spectroscopic data: m/e 214 (parent ion); λ_{max}(neat) 5.81, 6.04, 9.30, 9.95 μ; δ(CCl_4) 1.7-2.3 (m,4H), 3.68 and 3.73 (singlets, 6H), 5.12 (broad t, J=7 Hz, 1H), and 6.42 (s,1H).



Hydrolysis of (I) afforded a diacid (II)[5], m.p. 112-114°, λ_{max}(EtOH) (log ϵ) 206 (3.96), which on hydrogenation gave (III), m.p. 142-144°. The structure of (III) was established as tetrahydrofurylsuccinic acid by spectroscopic and mixed

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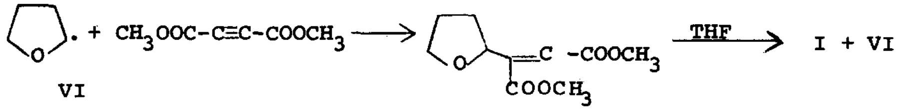
m.p. comparison with an authentic sample, obtained by the hydrolysis of tetrahydrofurylsuccinic anhydride (IV)[3].

The mass spectral fragmentation of the unsaturated acid (II) showed no parent ion but showed a strong ion at M-18 (85%), strongly suggesting cis orientation of the carboxylic groups. This was confirmed by heating (II) at 180° when the melt showed bands in its infrared spectrum ($CHCl_3$) at 5.52 and 5.67μ. The structure of the photoadduct (I) is thus secured as dimethyl tetrahydrofurylmaleate.

Irradiation of DMAD and tetrahydro-2-methylfuran gave a 1:1 adduct (V) (C-2 methyl as a singlet at δ 1.42). No reaction was however observed when DMAD and 1,4-dioxan were irradiated for 24 hours.



VI

VII

The key step in the formation of (I) is considered to involve the formation of the tetrahydrofuryl radical (VI) by the fortuitous presence of a photoinitiator in commercial THF[1,6]. The radical (VI) adds to DMAD to give the vinyl radical (VII), which further reacts with THF to regenerate the radical (VI) and the product (I).

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References

1) I. Rosenthal and D. Elad, Tetrahedron, 23, 3193 (1967), and references cited therein.

2) R. Srinivasan and K.H. Carlough, Can. J. Chem., 45, 3209 (1967).

3) R.L. Jacobs and G.G. Ecke, J. Org. Chem., 28, 3036 (1963).

4) The photoadduct was found to be pure by t.l.c. but v.p.c. showed it ca. 90% pure.

5) Satisfactory elemental analyses and spectral data were obtained for all the new compounds.

6) 1,4-Dioxan and DMAD were found to react when the mixture was irradiated in the presence of acetone.