

Reactions of Lone Pair Electron Donors with Unsaturated Electrophiles.

III. Addition of Tetrahydrofuran to Dimethyl Maleate¹

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In a previous paper,² it was shown that tetrahydrofuran (THF) and oxetane add thermally and photochemically to dimethyl acetylenedicarboxylate in a free radical chain reaction. Here, the radical chain was presumed to be initiated by electron and proton transfer from the ether to the electrophile. Furthermore, it is known that THF adds to maleic anhydride and diethyl maleate to give α -substituted tetrahydrofurans (*1*) initiated by dibenzoyl peroxide³ or by direct³⁻⁶ or sensitized irradiation.⁵

In the present study it was found that THF adds thermally to dimethyl maleate in the presence of oxygen to give the adducts *1* and *2* even though initiators such as dibenzoyl peroxide are absent. Typically, oxygen was bubbled for a few minutes through a solution of dimethyl maleate in a 3–10 fold excess of THF.⁶ This mixture was then kept at 120 °C in a sealed pyrex tube for 12 h. The adducts (*1* and *2*) were isolated by evaporation of excess THF under reduced pressure followed by vacuum-distillation (*1*: b.p. 0.05 mmHg 90–100 °C, *2*: b.p. 0.05 mmHg 160–180 °C). The yields of the adducts *1* and *2* are 75 % and 25 %, respectively. The structures of *1* and *2* were determined by their spectral properties (IR, NMR, mass spectra). *Analyses*: *1*, Found: C 55.27; H 7.31. Calc. for C₁₀H₁₆O₅: C 55.54; H 7.46. *2*, Found: C 52.96; H 6.55. Calc. for C₁₆H₂₄O₈: C 53.33; H 6.71. NMR (CDCl₃) *2*: δ 1.85 (m, 4 H), 2.5–3.1 (m, 6 H), 3.70 (two s, 12 H), 4.0 (m, 2 H). Alkaline hydrolysis of *1* gave its corresponding acid (as compared with an authentic sample⁶).⁷

This reaction does not take place in the absence of oxygen. Furthermore, small amounts of a free radical scavenger such as *p*-dinitrobenzene⁸ completely inhibit the reaction; in both cases the maleate is virtually completely

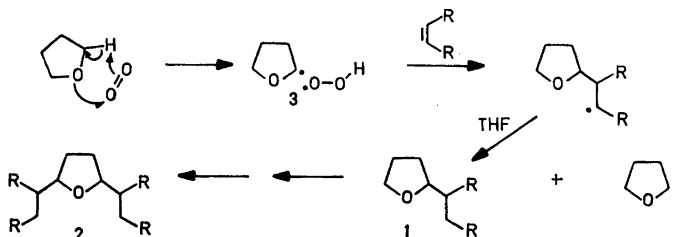
recovered. When the reaction is initiated with dibenzoyl peroxide at lower temperatures, only a moderate yield of *1* is formed and no formation of the adduct *2* is detected.

The effect of *p*-dinitrobenzene suggests that *1* and *2* are formed in a free radical chain reaction, and decomposition of THF peroxide formed by reaction of the dissolved oxygen with THF may be responsible for the radical initiation. Alternatively, and in consonance with what has been suggested for a related system,³ THF radicals may be generated directly by a possibly concerted electron and proton transfer from the ether oxygen and α -position, respectively, to the electrophilic oxygen as indicated in Scheme 1. Diffusion of the radical pair *3* would then generate a free radical chain reaction. Abstraction of the hydroperoxy radical hydrogen by a chain-carrying radical would account for termination of the chain and the apparently catalytic action of oxygen.

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- The THF was assured to be dry and peroxide free. For details of purification procedures, see, Ref. 2.
- The acid obtained from hydrolysis of the adduct *2* is not crystalline and could not be obtained in a pure state.
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Scheme 1.