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A THERMAL TETRAMER OF DIMETHYL ACETYLENEDICARBOXYLATE

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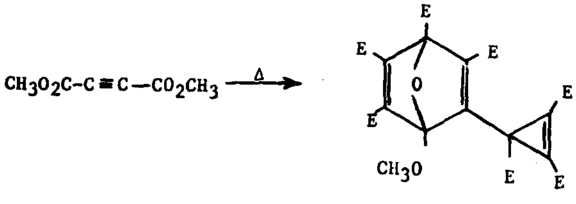
In the course of studying some chemistry of dimethyl acetylenedicarboxylate we have observed that aged samples of this ester or samples that have been heated at 120° for several hours contain approximately 25% of a viscous material. Trituration of this material with methanol affords a white crystalline solid, $C_{24}H_{24}O_{16}$ (C,50.67;H,4.13; mol. wt. 568) m.p. 109-111° (recrysallized from MeOH), in yields as high as 15%. The ultraviolet spectrum, λ_{max}^{EtOH} 220 mμ (ε 15,500); 232 shoulder (ε 12,600), suggests the presence of three non-conjugated carbomethoxylated double bonds. In the infrared spectrum weak double bond absorption is observed at 1635 and 1655 cm^{-1} and a strong, somewhat broadened carbonyl ester absorption is centered at 1735 cm^{-1}. In addition a medium intensity absorption occurs at 1875 cm^{-1} indicating the presence of a disubstituted (dicarbomethoxy) cyclopropene double bond (1). The n.m.r. spectrum exhibited <u>seven</u> peaks at τ=6.06(3H),6.10(6H),6.12(3H),6.20(3H),6.25(3H), 6.31(3H), and 6.38(3H) attributable to the methoxy protons. We believe these data (2) are consistent with the structure I. A possible route to I could occur *via* II, the 1,3-dipolar adduct of dimethyl acetylenedicarboxylate with itself. Chemical evidence for the intermediacy of II in the formation of 2-methoxy-3,4,5-tricarbomethoxyfuran has been put forward (3).



(E=-CO$_2$CH$_3$)

I.

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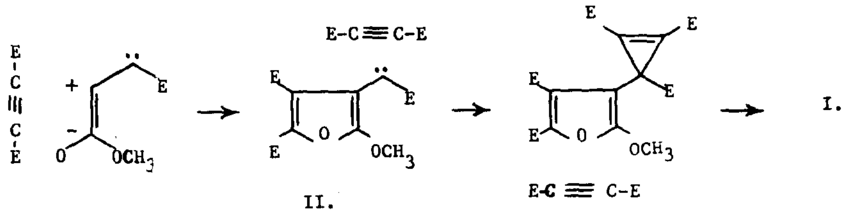
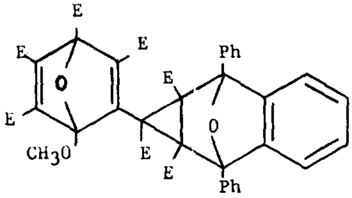
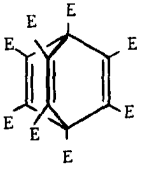
The carbenoid addition of II to a third molecule of acetylenic ester and a Diels-Alder addition of a fourth molecule of acetylenic ester to the furan system would yield I.



Chemical transformations of I, with one exception, have been unrewarding. While hydrogenation, bromination and reactions with aqueous acids and bases (I is particularly sensitive to the latter) rapidly extinguish the 1875 cm^{-1} cyclopropene absorptions, only intractable products result. However, I rapidly adds (in less then 20 min. at room temperature) in a mildly exothermic reaction to the **diene** diphenylisobenzofuran, forming in 75% yield the Diels-Alder adduct III, $C_{44}H_{38}O_{17}$ (C,63.05;H,4.54) m.p. 224-225° (recrystallized from MeOH). In the double bond stretching region of the I.R. III shows only carbonyl absorption as a broad peak centered at 1730 cm^{-1}and C=C absorption at 1650 cm^{-1}. The n.m.r. spectrum of III consists of an aromatic complex from 2.0 to 3.2 (14H) and eight singlets at τ=6.06(3H),6.16(3H),6.23(3H),6.28(3H),6.43(3H),6.55(3H),6.70(3H) and 7.46(3H) due to



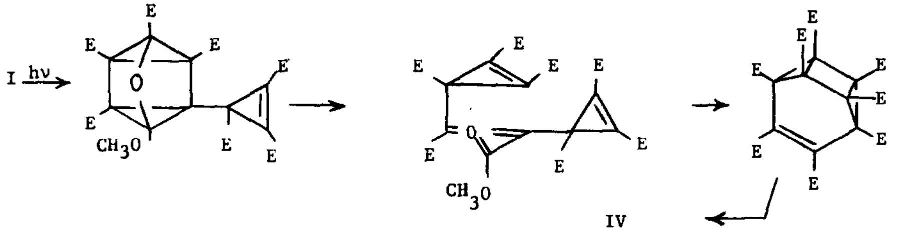
III.



IV.

presence of eight different CH_3-O- protons in this highly unsymmetrical molecular environment.

Photoisomerization of I affords a new tetramer, $C_{24}H_{24}O_{16}$ (C,50.88;H,4.03; mol.wt. 568) m.p. 162-163° (recrystallized from MeOH). On the basis of the following spectral information we have tentatively assigned the structure IV to this tetramer. The I.R. spectrum of IV has an ester carbonyl absorption at 1730 cm^{-1} and a C = C absorption at 1610 cm^{-1}. The U.V. spectrum, λ_{max}^{EtOH} 222 mμ (ε 12,300) 230 shoulder (ε 11,800), is very similar to that of I. The n.m.r. spectrum exhibits two methoxy absorptions at τ6.21 (18H) and 6.26(6H). A possible pathway to IV from I is suggested in the following sequence of photochemical and thermal reactions:



A second minor product isolated from this photochemical reaction appears to be an oxygen adduct of one of these tetramers, $C_{24}H_{24}O_{18}$ (C,48.17;H,4.17) m.p. 176-177°.

References

(1) G. L. Closs, "Advances in Alicyclic Chemistry", Vol. I, H.Hart and G. J. Karabatsos, Ed., Academic Press., New York, 1966, p. 75.

(2) Molecular weights were determined from MS-9 mass spectometer data. Melting points are corrected. Ultraviolet spectra were recorded on a Cary-14. Infrared spectra were obtained on a P.E. -21,-237 or an IR-9. Proton magnetic resonance spectra were obtained on an A-60 using $DCCl_3$ as solvent and T.M.S. as internal standard. Photochemical reaction were carried out in quartz equipment using Hanovia 450 watt high pressure lamp.

(3) E. Winterfelt and G. Giesler, Angew. Chem., 78, 588 (1966).