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UNUSUAL ADDUCTS OF METHYL ACETYLENEDICARBOXYLATE AND OLEFINS

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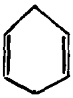
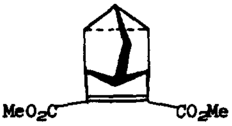
As a continuation of our work on Diels-Alder adducts with methyl acetylenedicarboxylate(1) we have investigated the reactions of the diester with norbornadiene (I) and with 1,4-cyclohexadiene (II). The 1:1 norbornadiene adduct, obtained in up to 50% yield by refluxing an intimate, equimolar mixture of diene and ester for 12 hours, proved to be identical with that (III) reported as product of a reaction of the two substances in the presence of a special nickel catalyst(2)

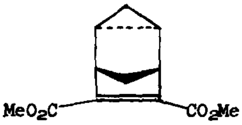
I



II



III



IV

Anticipating 1,4-cyclohexadiene to undergo an addition process similar to that of norbornadiene, hence leading to IV, an intimate, equimolar mixture of II and methyl acetylenedicarboxylate was refluxed for 48 hours. However, two products neither of which possessed structure IV were isolated. The preponderant product was a 1:1 adduct, $C_{12}H_{14}O_4$, b.p. 170°|20 mm.*, while the minor product was a curious $C_{11}H_{12}O_8$ substance, m.p. 117-118°.

Saponification of the C_{12} diester yielded an acid, $C_{10}H_{10}O_4$, m.p. 230° (dec.), whose ultraviolet spectrum ($\lambda_{max.}^{EtOH}$ 208 mµ; log ε 3.73)

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*Satisfactory elemental analyses and correct mass spectral molecular weights were obtained for all the compounds reported.

and conversion to a dihydro product, m.p. 265-268°, showed it to be monoolefinic. The proton magnetic resonance spectrum of the ester* and double resonance data led directly to the structure of the adduct. The two ester methyl singlets appeared at 3.35 and 3.41 p.p.m. Two olefinic hydrogen multiplets, centered at 5.62 and 5.92 p.p.m., revealed shapes characteristic of a $CH_A-CH_B=CH_C-CH_D$ arrangement within a six-membered ring ($J_{AB}=5.5$ c.p.s., $J_{BC}=8.2$ c.p.s., $J_{AC}=J_{BD}=1.7$ c.p.s., $J_{CD}=7.0$ c.p.s.). A doublet($J=5.0$ c.p.s.) at 3.20 p.p.m., the signal of the most deshielded alicyclic hydrogen, could be assigned to the hydrogen on the α carbon of an ester (H_E) and shown to be coupled with H_A or H_D whose combined complex signal appeared at 2.25-2.65 p.p.m. The highest field hydrogen (H_F), a doublet at 0.68 p.p.m., could be shown to be an ordinary alicylic hydrogen strongly shielded by the double bond rather than one associated with a cyclopropane ring in view of its large coupling constant ($J=11.5$ c.p.s.) and a large downfield shift of its signal on hydrogenation; H_F in the dihydro compound appears in a featureless group of methylene and methine protons between 1.1 and 2.4 p.p.m. The size of its J value indicated it to be part of a methylene group. Its gem neighbor (H_G) (multiplet at 1.44 p.p.m.) was coupled with two further hydrogens, one of which was an allylic hydrogen while the other was the remaining hydrogen (H_H) (multiplet at 1.79 p.p.m. $J_{GH}=2.5$ c.p.s.) which, in turn, was coupled with the other allylic hy-

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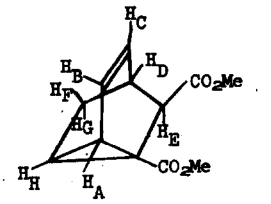
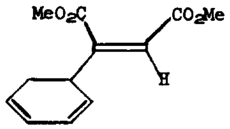
* The proton magnetic resonance spectra was run in deuterobenzene solution with TMS as internal standard on a Varian HA-100 spectrometer.

drogen. These data limit the structure of the 1,4-cyclohexadiene adduct to V. The stereochemistry of the carbomethoxymethine site is as depicted since models indicate that the epimeric form should have $J_{DE}\sim 0$[**] whereas J_{DE} found was 5.0 c.p.s. This stereochemistry is also revealed by the absence of any significant change in chemical shift of H_E (3.12 p.p.m.) in the dihydro compound[*]. The presence of the cyclopropane ring in V is revealed by characteristic infrared cyclopropyl hydrogen absorptions: a fundamental stretching vibration at 3062 cm.$^{-1}$, a first overtone at 5999 cm.$^{-1}$ and a second overtone at 8827 cm.$^{-1}$ (3).

Analysis of the possible mechanism of the reaction between methyl acetylenedicarboxylate and 1,4-cyclohexadiene accounts readily for structure V of the adduct. If it be assumed that the primary reaction is a concerted four-center cyclic process involving the acetylene with C_1 and C_3-H of the diene, methyl 2,4-cyclohexadienylmaleate (VI) would be the anticipated product (4). Since the latter possesses both diene and dienophile components, its further reaction in an internal Diels-Alder manner can be expected (5)



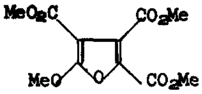
V



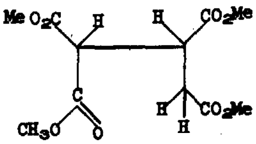
VI

[**] Models show this dihedral angle to be approximately 90°. The symmetrically disposed J_{DF}= 0 whereas J_{DG}=5.0 c.p.s.

[*] The spectrum was run in deuterochloroform solution with TMS as an internal standard on a Varian A-60 spectrometer.



VII



VIII

The minor product of the reaction of methyl acetylenedicarboxylate and II could be shown to be methyl 5-methoxy-2,3,4-furantricarboxylate (VII) by its ultraviolet spectrum ($\lambda_{max.}$ 276 mμ.; log ε 4.18), by the dissimilarity of the four methyl signals (3.04, 3.78, 3.93 and 4.25 p.p.m.)* in its p.m.r. spectrum and by its conversion to methyl propane-1,1,2,3-tetracarboxylate VIII on hydrogenation over platinum in acetic acid. An authentic sample of VIII was prepared by the procedure(6) described for the tetraethyl ester. The closest reported model for the ultraviolet spectrum of VII is ethyl 2,3,4,5-furantetracarboxylate ($\lambda_{max.}$ 259 mμ.; log ε 4.09(7)).

While the origin of this unusual product (VII) is obscure, the outline of a possible mechanism for its formation can be advanced (vide infra)** It requires the trapping of intermediate VI (or the fumarate analog) by methyl acetylenedicarboxylate in a Diels-Alder reaction reminiscent of acrolein dimerization(8), bond reorganization of the adduct, and final extrusion of the hydrocarbon moiety as cycloheptatriene or iso-

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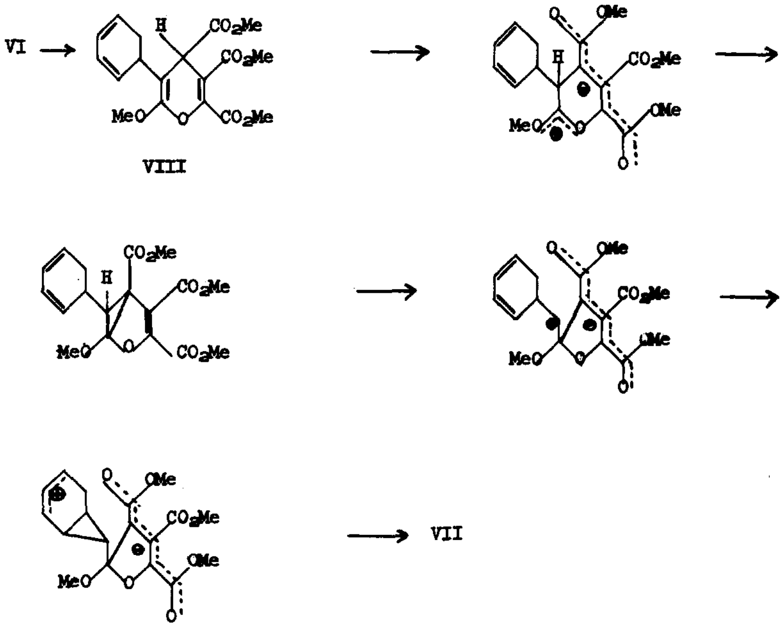
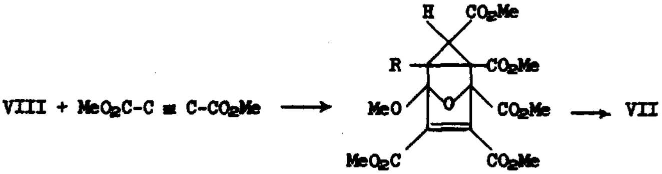
* The spectrum was run in deuterochloroform solution with TMS as internal standard on a Varian A-60 spectrometer.

** While polar intermediates are depicted, radical analogs are equally plausible at this time.

mers thereof. We have found that the co-pyrolysis of methyl acetylenedicarboxylate with methyl fumarate (although not with methyl maleate) yields the same furan derivative (VII), thus pointing to the probable involvement of a fumarate in the formation of VII from II and methyl acetylenedicarboxylate originally observed.



Professor Thomas Katz has suggested the following attractive alternate mechanism for the formation of the furan also utilizing the intermediate VIII.



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