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THE STRUCTURE OF THE MALEIC ANHYDRIDE ADDUCTS OF ETHYL ACETOACETATE AND ACETYLACETONE

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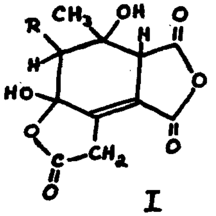
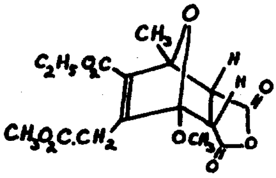
The reaction of maleic anhydride with ethyl acetoacetate or acetylacetone gives rise to 2:1 adducts, which have been assigned the structures (Ia) and (Ib) respectively[1]. The novel mode of reaction of maleic anhydride which had to be postulated to account for the formation of these adducts has led us to re-examine the problem.

The infrared spectra of both adducts confirmed the presence of a saturated five-membered anhydride ring (1875 and 1790 cm.$^{-1}$) and showed additional carbonyl absorption (ca. 1710 cm.$^{-1}$). The broad absorption between 2,400 and 3,300 cm.$^{-1}$ was consistent with the presence of carboxyl and hydrogen-bonded hydroxyl groups. The limited solubility of these adducts prevented examination of their N.M.R. spectra. However, treatment of the ethyl acetoacetate adduct with excess ethereal diazomethane yielded a dimethyl derivative, m.p. 115.5 - 117° (Found: C,53.84; H, 4.76.



I



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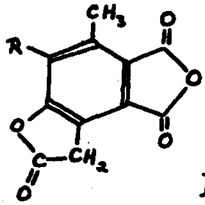
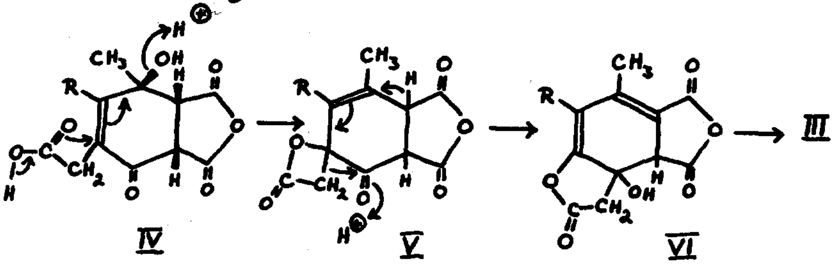
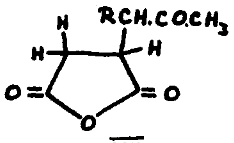


III

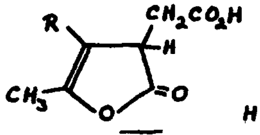
(a) R = $CO_2C_2H_5$

(b) R = $CO.CH_3$

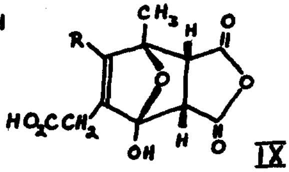




VII



VIII



IX

$C_{16}H_{18}O_9$ requires: C, 54.23; H, 5.13%). The N.M.R. spectrum[2] of this compound was remarkably simple and excluded any structure corresponding to (Ia). In fact consideration of the wide variety of structures logically derivable from maleic anhydride and ethyl acetoacetate shows that only one of these (II) is in accord with the observed spectrum[3]. In addition to confirming the absence of hydroxyl groups, characteristic absorptions for the ester methyl ($\tau = 6.27$) and ethyl ($\tau = 8.68$, $J = 7.0$ and $\tau = 5.74$, $J = 7.3$) groups were observed. As anticipated for (II) the methylene group shows a singlet at 6.94τ, the methoxyl a singlet at 5.97τ and the methyl group a singlet at 8.22τ. The observed β shift to lower field is as expected for the system $CH_3 - \overset{|}{\underset{|}{C}} - O - C$. Finally a quadruplet centred at $\tau = 6.37$ ($J = 3$ cps.) indicates by the very low intensity of the outer lines the presence of two adjacent hydrogen atoms in similar environments. The latter suggests the depicted endo configuration although this cannot be confirmed in the absence of the exo adduct[4].

The principal evidence[1] for structures (Ia) and (Ib) was supplied by degradation to p-xylenol of the compounds (IIIa) and (IIIb), obtained by dehydration of the original adducts with concentrated sulphuric acid. This degradative sequence has been confirmed and the structures of the intermediates involved found to be in agreement with their infrared and N.M.R. spectra. The revised structures of these adducts implies that a rearrangement must have accompanied the 'dehydration' of the adducts to (IIIa and b). A rational mechanism could proceed, from IV via V and VI as shown. In accord with the previous investigation attempts to obtain other significant degradation products from these adducts have met with little success.

The adducts are envisaged as being formed through Michael addition of ethyl acetoacetate, or acetylacetone, to maleic anhydride giving (VII), followed by intramolecular acylation with formation of the furanone (VIII). Subsequent Diels-Alder addition of a second molecule of maleic anhydride to the 2-hydroxyfuran tautomer of (VIII), or the equivalent Michael addition, gives the adduct (IX) which may also be formulated as (IV).

REFERENCES

1. E. Berner, *J. Chem. Soc.*, 1052 (1946).

2. We are greatly indebted to Dr. J. H. Pryce, Alderley Park, for providing the N.M.R. spectra.

3. This structure was independently suggested to us by Mr. B. Tuck.

4. P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, *86*, 1171 (1964).