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THE REACTION OF A NON-PLANAR ENONE WITH ETHANEDIOL

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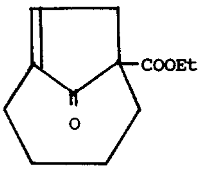
The recently reported synthesis of the non-planar αβ unsaturated ketones I(1) and II(2) prompts us to report the synthesis of a further example of this structural type: bicyclo-[4.3.1]dec-1-en-10-one(III). Sulphuric acid dehydration of IV(3) gave V in good yield but pyrolysis of the benzoate of IV gave a product in 70% yield which proved to be a 1:2 mixture of III and V from which III was obtained by preparative g.l.c.



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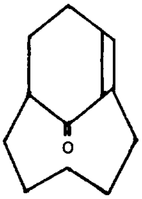

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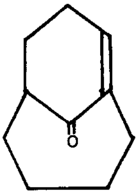

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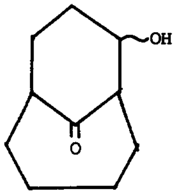

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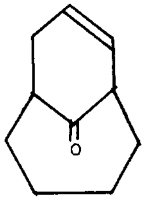

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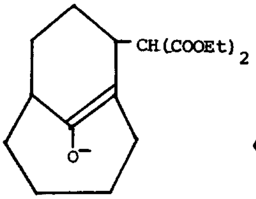

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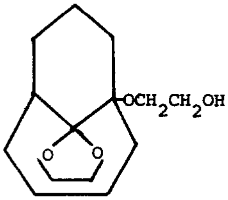
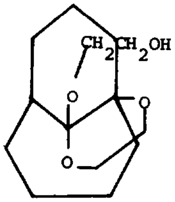


VII

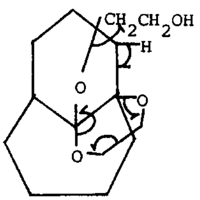


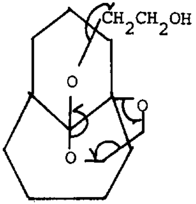
VIII

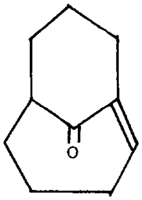
The enone III was stable at room temperature and was solid at 0°. The structure followed from the N.M.R. which showed protons at τ, 5.9 (I H, multiplet) and multiplets centred at τ, 2.4, τ, 2.05 and τ, 1.5. Irradiation of the single proton multiplet at τ 5.9 caused a partial collapse of the τ 2.4 multiplet. The u.v. spectrum (λ max, 238 nm; ε max, 3000), which was similar to the spectra reported for I and II, reflected the incomplete π bond overlap, in III. The i.r. spectrum showed $\upsilon_{C=O}^{max}$ 1710 cm^{-1} and $\upsilon_{C=C}^{max}$ 1640 cm^{-1}. The C=C absorption is dissimilar to that reported for II (λ_{max} 1695 cm^{-1})(2).

Attempted rearrangement of III to V with p-toluene sulphonic acid in benzene or with

H_2SO_4 in ether was very slow and accompanied by some polymerisation. When III was refluxed with ethanediol and benzene in the presence of p-toluene sulphonic acid a viscous liquid was isolated which analysed for $C_{14}H_{24}O_4$. The 100 mHz n.m.r. spectrum showed signals at τ, 5.8 (triplet, 2H); τ, 6.3 (multiplet, 4H); τ, 7.45 (broad singlet, IH disappearing on D_2O exchange); τ, 7.6 (v. broad singlet, 1 H) and an unresolved envelope between τ 8 and τ9. This data is consistent with structures VII and VIII for the product formed from III and ethanediol. The mass spectrum of the compound is, however, more readily explained if VIII is the correct structure. The 70 e.v. spectrum of VIII showed major peaks at m/e 256 (M^+), 226, 195, 151, 150, 123, 122, 105, 93, 89, 88, 81, 80 and the 70 e.v. spectrum of III showed peaks at 150, 122, 93 and 80 suggestive that VIII is fragmenting as shown below. Peaks at 151, 123 and 81 might therefore arise from a protonated form of III. The alternative stereoisomer of VIII would lead, on fragmentation, to IX.







IX

It has been reported that II fails to undergo condensation with diethyl malonate$^{(2)}$ and, similarly III failed to form a condensation product with diethyl malonate. This is not surprising since an expected intermediate in this reaction would be the highly strained VI and the failure of II and III to undergo Michael addition would not necessarily reflect lack of reactivity due to incomplete π bond overlap of the carbonyl and olefinic groupings$^{(2)}$. The first step in the addition of ethanediol to III to give VIII is, therefore, probably the formation of a hemiketal followed by nucleophilic attack at the 1-position of III.

References

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Acknowledgement

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