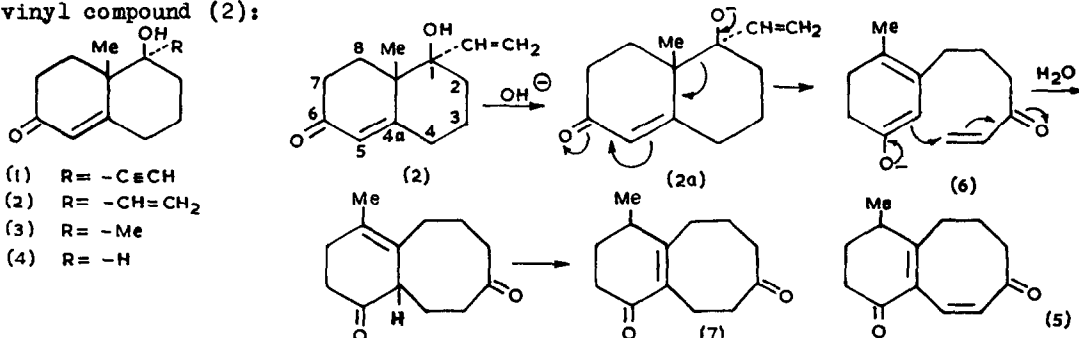


ON THE MECHANISM OF THE BASE CATALYSED REARRANGEMENTS OF SOME
BICYCLIC- δ -HYDROXY- α,β -ENONES¹

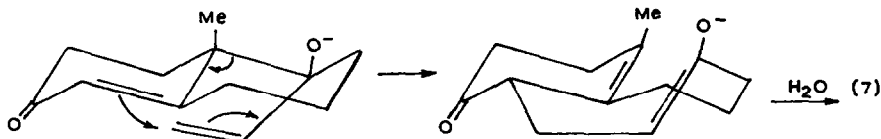
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Bicyclic- δ -hydroxy- α,β -enones (1) to (4) have been shown to rearrange in the presence of bases, acids and also photochemically.^{2,3,4,5} The mechanism that has been suggested for the base catalysed reaction is illustrated with the vinyl compound (2):



A Cope-type mechanism has also been envisaged for the formation of ring enlarged dione (7) from (2).

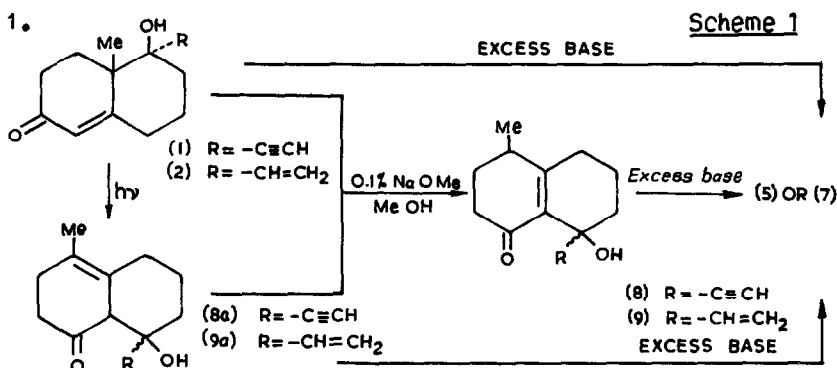


None of the intermediates postulated in either mechanism have, however, been isolated.

It has now been found that when the enone (1) is treated with catalytic amounts of 0.1% solution of sodium methoxide in methanol, a crystalline product (8) can be isolated in 10% yield in addition to unreacted starting material and the dione (5). The product (8) after purification by preparative t.l.c. has m.p. 101-102°, analyses for C₁₃H₁₆O₂ and has the following light absorptions: $\lambda_{\text{KBr max}}$ 2.95, 3.075 and 6.125 μ ; $\lambda_{\text{EtOH max}}$ 245 m μ (ϵ , 11,880); NMR absorptions at δ 1.1-1.3 (>CH-CH₂ doublet), δ 1.5-2.5 (-C≡CH and methylenes) and δ 5.3-5.4 (-OH, singlet). The compound is labile and rapidly isomerises when heated with base at 60°, as revealed by t.l.c. analysis of crude product and also by isolation.

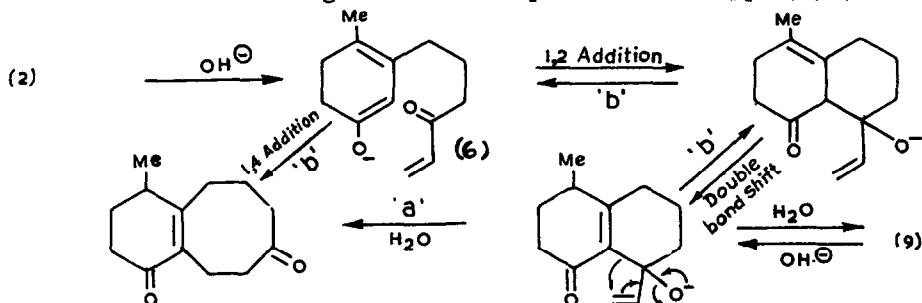
The vinyl compound (2) also when treated with dilute base at room temperature furnishes a pale yellow liquid product (9) in 15% yield, after purification by t.l.c., in addition to the dione (7). This product is homogeneous on t.l.c., has a mass peak at 206 and analyses for $C_{13}H_{18}O_2$. It has the following characteristic absorptions: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.95, 6.05 and 6.15 μ ; $\lambda_{\text{max}}^{\text{EtOH}}$ 241 m μ (ϵ , 9,852); NMR absorptions at δ 1.1-1.3 ($>\text{CH}-\text{CH}_3$, doublet), δ 1.6-2.6 ($-\text{OH}$ and methylenes, multiplet), δ 4.8-5.2 and 5.9-6.3 (vinyl protons). This compound also is labile, capable of isolation only under strictly controlled conditions and rapidly isomerising to the dione (7) above room temperature in the presence of base. The spectral absorptions leave no doubt that the above two products have the rearranged structures (8) and (9) respectively, even though their stereochemistry is uncertain.

The crystalline photoproducts (8a) and (9a) reported by us recently,⁶ on similar treatment with dilute base at room temperature give the compounds (8) and (9) respectively as shown by t.l.c., whereas at 60° or above, they isomerise to the diones (5) and (7) smoothly. The above transformations are shown in Scheme 1.

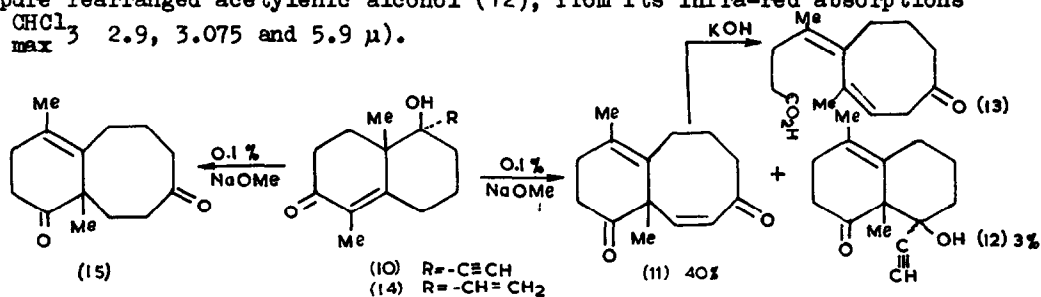


Compounds (8) and (9) can be intermediates or side products in the formation of cyclooctenones (5) and (7). Qualitative t.l.c., analysis of mixtures of compounds (8a), (9a), (8) and (9) with base reveal that they isomerise to the diones (5) and (7) faster than the isomers (1) and (2) and do so cleanly without formation of any trace of compounds (1) and (2) or other products. A concerted one-step conversion of compounds (1) and (2) to compounds (5) and (7) seems therefore unlikely. A concerted Cope-type conversion of compounds (1) and (2) to compounds (8) and (9) seems unlikely also, in view of the unfavourable transoid location of carbon atoms 1 and 5. Products (8) and (9) result probably from protonation under kinetic control after an internal 1,2-addition in the reactive species of the type (6). Hydrogen bonding between the oxygen atoms at the peri position in (8) and (9) and less crowding in the vicinity of the $-\text{OH}$ bearing carbon in (8) and (9) as compared to (1) and (2) probably provide the driving force for this 1,2-addition. Compounds (8) and (9) have the

necessary geometry for a concerted conversion to (5) and (7); their faster rearrangements to (5) and (7) as compared to the rearrangements of (1) and (2) may be due to this favourable geometry for a concerted reaction (mechanism 'a') or due to increased rate of fragmentation to species of the type (6) (mechanism 'b')

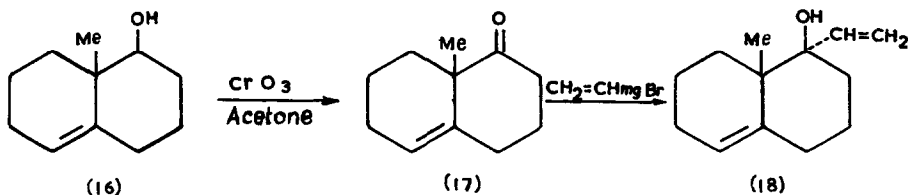


The C_5 -substituted hydroxy enone (10)⁷ on similar treatment with dilute base furnishes after preparative t.l.c., the ring enlarged dione (11) in 40% yield as a liquid and another liquid byproduct (3% yield) believed to be impure rearranged acetylenic alcohol (12), from its infra-red absorptions ($\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.9, 3.075 and 5.9 μ).



The dione (11) analyses for $\text{C}_{14}\text{H}_{18}\text{O}_2$ composition and has the expected light absorptions: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.875, 6.0 and 6.175 μ ; $\lambda_{\text{max}}^{\text{EtOH}}$ 224 μ (ϵ 3,310); NMR absorptions at δ 1.3 (>CH_3 , singlet) δ 1.6-1.7 ($=\text{CH}_3$, singlet) δ 1.9-2.6 (methylenes, multiplet) and δ 5.6 (>C=C< , singlet). The dione (11) is easily cleaved by treatment with strong alkali to the known acid (13).⁷ In contrast to (2), treatment of (14) with dilute base furnishes only the rearranged dione (15)⁷ in addition to a minor product, not yet identified. Apparently, with substitution at the key C_5 -atom, products of the type (12) are more reactive.

The 6-deoxy compound (18) synthesised from the known octalenol (16)⁹ as indicated, is unaffected by treatment with base confirming the vital role played by the conjugated carbonyl function in the fragmentation of the alkoxides of the type (2a).



The bicyclic ketone (17) is a liquid (b.p.100–110°/1 mm) having $\text{C}_{11}\text{H}_{16}\text{O}$ composition and gives a semicarbazone m.p.217–218° (EtOH) with expected analytical values. The ketone (17) has $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.9 μ and proton absorptions at δ 5.3–5.4 (—H singlet), δ 1.3–2.2 (methylenes, multiplet) and δ 1.2 ($\rightarrow\text{CH}_3$, singlet). The vinyl alcohol (18), purified by preparative t.l.c., is also a liquid which analyses for $\text{C}_{11}\text{H}_{20}\text{O}$ and shows characteristic absorptions: $\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.9, 6.1, 10.05 and 11.1 μ and NMR: δ 5.0–6.5 (vinyl and olefinic), δ 1.3–2.0 (methylenes and —OH) and δ 1.2 ($\rightarrow\text{CH}_3$, singlet). This alcohol (18) is stable to temperatures upto 240° in contrast to the enone (2), which is known to undergo rearrangement thermally also to (7).⁷ Evidently, the conjugated carbonyl also plays an important role in the thermal rearrangement of (2).

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