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REARRANGEMENTS OF OXO-DICYCLOPENTADIENES

R.C. Cookson, J. Hudec and R.O. Williams
The University, Southampton.

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IN the account[1] of their beautiful experiments on the rearrangement of asymmetric hydroxydicyclopentadienes, Woodward and Katz mentioned that Oppenauer oxidation of the syn-8-alcohol (I) in boiling benzene yielded the 1-ketone (II). This observation suggested to us either that the thermal isomerisation of the 8-ketone (III) was much faster than that of the alcohols (which are stable in boiling benzene), or that it was catalysed by the electrophilic aluminium t-butoxide.

We have now prepared the 8-ketone (III), m.p. 63-64° (with rearrangement to the 1-ketone), ν_{max} 1780 cm $^{-1}$, λ_{max} 278 mμ, ε 25, by oxidation of the alcohol (I) with chromic oxide in pyridine. It is stable in the crystalline state or in solution in cyclohexane at 20°, but a trace of boron trifluoride in the cyclohexane causes rapid rearrangement to the 1-ketone (II). Hydrogen chloride also strongly catalyses

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[1] R.B. Woodward and T.J. Katz, Tetrahedron 5, 70 (1959).

the rearrangement in dioxan at room temperature. In fact it proceeds slowly even in neutral ethanol at 20°.

The equilibrium lies entirely on the side of the 1-ketone (II) probably because of a combination of the greater strain associated with a trigonal than with a tetrahedral atom at C-8[2] and the conjugation in the 1-ketone (II). The much faster rearrangement of the 8-ketone than of the 8-alcohol, especially in polar solvents, is understandable in terms of the transition state leading to Woodward and Katz's intermediate (IV), which in this case will have considerable dipolar character. The catalysis by Lewis and proton acids, and even by hydrogen-bonding solvents, is also to be expected from consideration of the polarised transition state leading to (IV): the essential bond-breaking is symbolised in formula (V) (which omits for simplicity the other electronic and nuclear displacements, already discussed for the general case by Woodward and Katz). Yates and Eaton[3] have recently described catalysis of the rearrangement of the tetrachloro-derivative of (III) by aluminium chloride. The apparently greater sensitivity to acid of the 8-ketone (III) than of its tetrachloro-derivative[3] may be partly due to the greater basicity of its carbonyl group.

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[2] W.G. Woods, R.A. Carboni and J.D. Roberts, J. Amer. Chem. Soc. 78, 5653 (1956).

[3] P. Yates and P. Eaton, Tetrahedron Letters No. 11, 5 (1960).

Ultraviolet irradiation of the 1-ketone (II) gave the isomer (VI), m.p. 124-126°, ν_{max} 1760 cm $^{-1}$, λ_{max} 297 mμ, ε 13. The symmetry of the cage (VI) is such that its cracking amounts to a simple competition (in this particular system) between the ability of an α-carbonyl and an α-methylene group to promote cleavage of a cyclobutane ring.

In our flow apparatus the cage was stable up to 425°, but at 450° it underwent clean pyrolysis. No product could be detected that was not also present in the pyrolysate of the 1- and 8-ketones, so that the cage must crack only in the two ways that simultaneously break two cyclobutane rings (horizontal planes in VI), not in either direction that initially breaks only one cyclobutane ring (vertical planes in VI). Cyclopentadiene and dihydroindene[4] (VII) were formed in all cases, characterised, inter alia, by their respective adducts with benzoquinone, m.p. 73-74°, and maleic anhydride, m.p. 142-143°. The ratio of the areas of the peaks for cyclopentadiene and dihydroindene on gas chromatograms of the pyrolysates from the 1-ketone (II), the cage (VI) and the 8-ketone (III) were respectively 1 : 1.7, 1 : 3.7 and 1 : 5.85. Clearly at high temperatures in the absence of acid and in the gas phase the 8-ketone (III) loses carbon monoxide faster than it rearranges to the 1-ketone (II). The cage shows no tendency

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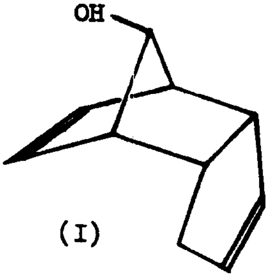
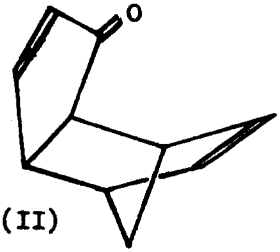
[4] K. Alder and F.H. Flock, Ber. 87, 1916 (1954).

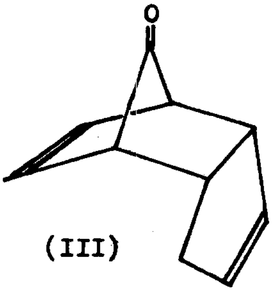
to break next the carbonyl group (to give II) in preference to the methylene group (to give III).



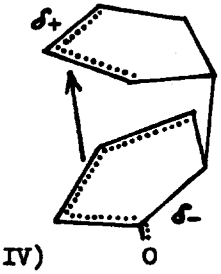
(I)



(II)



(III)



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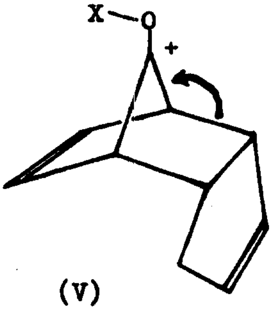
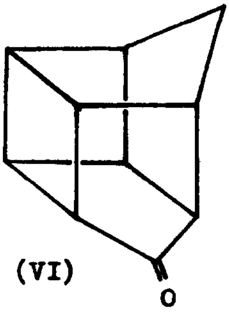
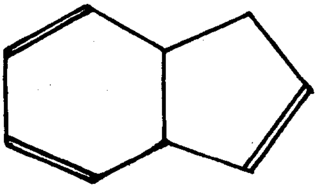


(V)



(VI)



(VII)