Thermal Reactions of Cage Ketones Possessing an Oxygen-containing Bridge or a Hydroxy-substituent

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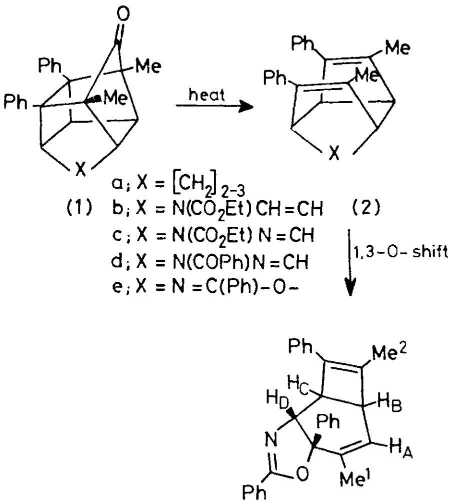
Summary In the thermal decarbonylation of cage ketones of type (**1**), the presence of an oxygen-containing bridge or a hydroxy-substituent resulted in an unusual rearrangement and cleavage reaction, *e.g.* the conversions of (**1e**) into (**3**) and (**4**) into (**5**).



(1) (2)

a; X = $[CH_2]_{2-3}$
b; X = $N(CO_2Et)CH{=}CH$
c; X = $N(CO_2Et)N{=}CH$
d; X = $N(COPh)N{=}CH$
e; X = $N{=}C(Ph){-}O{-}$

(3)

[from (1e)]

STUDIES on strained cage compounds have received considerable attention and yielded some novel results in recent years.[1] Previously we reported the thermally induced decarbonylation of the cage ketones (**1a**).[2] Here we discuss other unusual examples of thermal reactions of cage ketones, in particular the behaviour of the ketones (**1e**) and (**4**).

We have synthesized several cage ketones (**1b**—**e**) by the reported method;[3] those possessing nitrogen bridges (**1b**—**d**), upon pyrolysis using a conventional flow method, underwent ready decarbonylation at 320 °C to give the expected dienes (**2b**—**d**, m.p. 108—109 °C, 200—201 °C, and 195—196 °C, respectively) in quantitative yields.† The structures of the dienes (**2b**—**d**) were established on the basis of spectral and chemical data.[2] In contrast the cage ketone (**1e**) containing an oxygen bridge, upon heating at 400 °C under the same conditions, afforded the diene (**3**), m.p. 164—165 °C, in 56% yield, instead of the expected diene (**2e**). The structure of (**3**) was deduced on the basis of the following n.m.r. data ($CDCl_3$): δ 1·73 (Me^1, dd, J 1·5 and 1·5 Hz), 2·00 (Me^2, dd, J 2·5 and 1·5 Hz), 3·32 (H_B, dddd, J 5·2, 4·5, 1·5, and 1·5 Hz), 4·01 (H_C, ddd, J 4·5, 2·5 and 1·1 Hz), 4·61 (H_D, d, J 1·1 Hz) 6·11 (H_A, dd, J 5·2 and 1·5 Hz), 7·0—7·5 (13H, m), and 8·0—8·1 (2H, m). The fact that the two methyl signals as well as the olefinic proton signal appear as double-doublets, and that the coupling constants J_{AB} and J_{CD} are distinctly different is inconsistent with structure (**2e**), but can be reasonably

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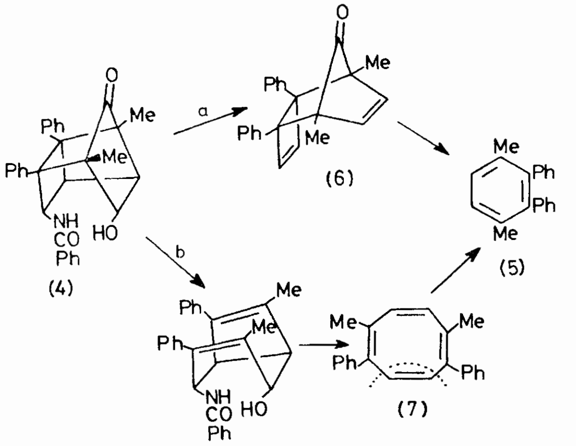
† Satisfactory elemental analyses were obtained for all new compounds.

accommodated by structure (**3**). This structure also agrees with n.o.e. experiments (H_A–Me^2, 8%; H_A–Me^1, 18%; and H_B–Me^2, 10%). The formation of (**3**) can be explained by an easy 1,3-oxygen shift from the assumed primary product (**2e**).[4]



Scheme

For comparison, the cage ketone (**4**), obtained by hydrolysis of (**1e**),[3] was pyrolysed at 350 °C, and the unexpected product (**5**) was obtained in 74% yield. The structure of (**5**) was established by direct comparison with an authentic sample.[5] The formation of (**5**) from (**4**) formally requires elimination of CO, PhCONHOH, and $HC\equiv CH$, PhCONHOH elimination being the first step in path a, and CO elimination the first step in path b in the Scheme. Elimination of $HC\equiv CH$ from the cyclo-octatetraene (**7**) in path b, or from its bicyclic valence isomer (**6**) after loss of CO in path a would lead to the product (**5**). However, path b may be ruled out because cyclo-octatetraenes are generally in equilibrium with bicyclo[4.2.0]octatrienes having maximum substitution on the cyclobutene double bond.[6] The bicyclo-octatriene derived from (**7**) would not lead to the product (**5**). It follows that ketones of type (**1**) possessing oxygen substitution in their skeleton may undergo unusual thermal reactions as secondary processes.

(*Received*, 9*th May* 1977; *Com.* **439**.)

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