

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

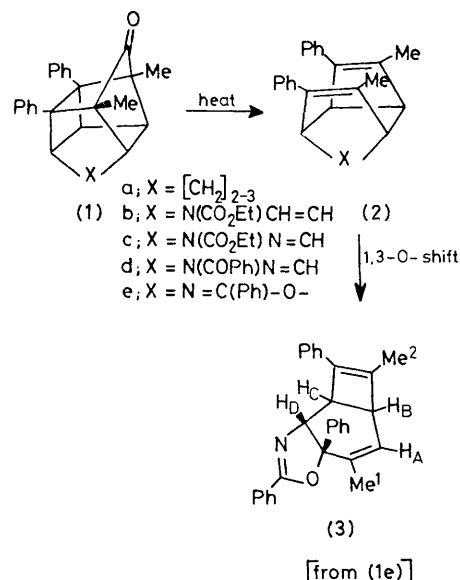
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Summary In the thermal decarbonylation of cage ketones of type (1), the presence of an oxygen-containing bridge or a hydroxy-substituent resulted in an unusual rearrangement and cleavage reaction, *e.g.* the conversions of (1e) into (3) and (4) into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

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).

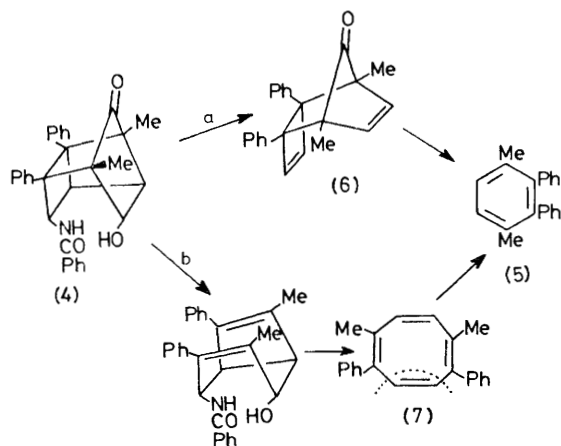
We have synthesized several cage ketones (1b—e) by the reported method;³ those possessing nitrogen bridges (1b—d), upon pyrolysis using a conventional flow method, underwent ready decarbonylation at 320 °C to give the expected dienes (2b—d, m.p. 108—109 °C, 200—201 °C, and 195—196 °C, respectively) in 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 (CDCl₃): δ 1.73 (Me¹, dd, *J* 1.5 and 1.5 Hz), 2.00 (Me², 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

† Satisfactory elemental analyses were obtained for all new compounds.

accommodated by structure (3). This structure also agrees with n.o.e. experiments (H_A -Me², 8%; H_A -Me¹, 18%; and H_B -Me², 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≡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≡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.

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