Thermal and Catalysed Rearrangement of Olefinic Epoxides

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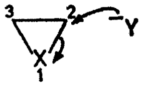
Summary. Some thermal, probably concerted, rearrangements of norbornadiene and hexamethyl Dewar benzene monoepoxides are described and the influence of rhodium-(I) complexes on these rearrangements is reported and discussed.

METAL-ION catalysed rearrangements of alicyclic compounds containing strained σ bonds are of some current interest.[1-4] Evidence favouring stepwise processes[4-6] rather than concerted rearrangements[3] has been reported, and prompted us to extend these studies to strained heterocycles.



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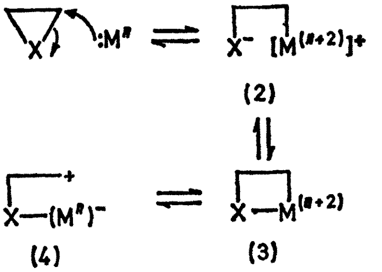

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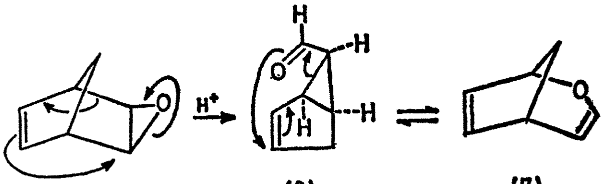
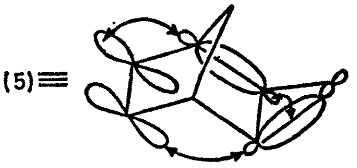


(5) (6) (7)



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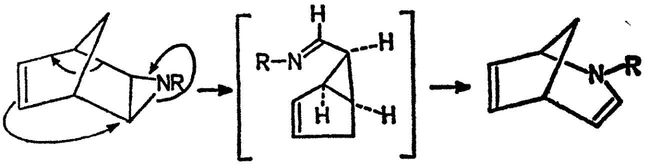
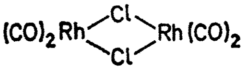


(9) (10) (11)

Three-membered heterocycles (**1**; X=O, NR, or S) undergo ready cleavage of the 1,2-bond by nucleophiles whilst cleavage of the 2,3-bond is comparatively rare. A two-step oxidative-addition[7] (**1** → **2** → **3**) of a metal ion M (oxidation state *n*) would involve nucleophilic attack on the strained ring. Both one- (**1** → **3**) and two-step oxidative-addition processes should favour cleavage of the 1,2-bond whereas in a concerted catalysed process the preferred cleavage should be more dependent on the structure of the molecule (proximity of double bonds *etc.*) A further possibility is initial co-ordination of the metal ion to the heteroatom which could lead directly to (**4**).

Norbornadiene *exo*-epoxide (**5**)[8] has been shown to undergo an acid-catalysed rearrangement to give an equilibrium mixture (ratio 7:3) of aldehyde (**6**) and cyclic ether (**7**).[9] Orbital symmetry considerations suggest that a purely thermal ${}_{\pi}2_a + {}_{\sigma}2_s + {}_{\sigma}2_a$ concerted pathway is also feasible (**8**). When the thermal rearrangement (**5** → **6**, **7**) was studied in base (KOH) washed apparatus at 100° it was found to be complete after 1 h in quantitative yield. A study of the rearrangement at five temperatures by n.m.r. spectroscopy gave the following data: E_A 24·2 kcal mol^{-1} and $\Delta S^{\ddagger}$ −0·2 e.u. We consider this to be a concerted process and draw attention to two related rearrangements (**9** → **11**; R = $PhSO_2$ or CN)[10] which can also be classified as ${}_{\pi}2_a + {}_{\sigma}2_s + {}_{\sigma}2_a$ processes.



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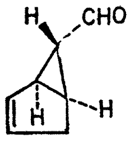

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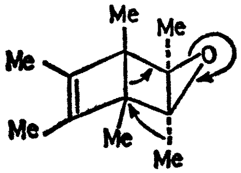

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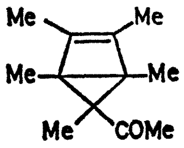

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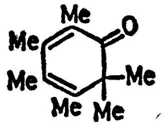

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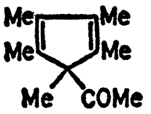

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When the epoxide (**5**) was treated at room temperature with a catalytic amount of tetracarbonyl-μ-dichlorodirhodium (**12**) an immediate and quantitative conversion into (**6** ⇌ **7**) was observed and after heating (**6**, **7**) with (**12**) at 100° for 15 min the epimeric aldehyde (**13**; 66%) could be isolated. The same aldehyde was obtained by base-catalysed epimerisation of (**6**, **7**) and is sterically incapable of equilibrating with (**7**) *via* a Cope rearrangement.

The monoepoxide of hexamethyl Dewar benzene (**14**) was of interest since a ${}_{\pi}2_a + {}_{\sigma}2_s + {}_{\sigma}2_a$ process would lead to a very strained system (**15**). However, when (**14**) was heated at 155° for 15 h rearrangement occurred to give a mixture of the cyclohexadienone (**16**)[11] and the cyclopentadiene ketone (**17**),[12] (total 62%, ratio 2·7: 1) plus two other unidentified components. The possibility of an allowed $_{\sigma}2_{a} + {}_{\sigma}2_{s} + {}_{\sigma}2_{a}$ process for the generation of (**16**) must be considered (**14**, arrows). In contrast, the rearrangement (130°; 3·5 h) of (**14**) in the presence of (**12**) was more specific and gave the cyclopentadiene ketone (**17**; 69% isolated) as the major product. The cyclopentadiene ketone (**17**) has also been isolated as a by-product in the preparation of (**14**).[12] The cyclohexadienone (**16**) was unchanged on heating at 130° in the presence of (**12**) indicating it was not an intermediate in the formation of (**17**).

Although the catalysed rearrangements are explainable in terms of organo-rhodium intermediates [*e.g.* (**3**), (**4**)] we have not detected any organo-rhodium compounds. These studies are being extended to related heterocycles and other metal catalysts and the possible involvement of the carbon monoxide ligands in the rearrangement is being investigated.

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