Rhodium(I) Catalysed Rearrangements of Cyclo-octatetraene Epoxide and Bicyclo[6,1,0]nonatrienes

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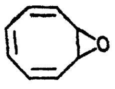
Summary. Ring contraction of cyclo-octatetraene epoxide to cycloheptatriene-7-aldehyde occurs at $-50°$ in the presence of rhodium(I) and further rearrangement occurs at higher temperatures, whilst in the carbon series bicyclo[6,1,0]nonatriene and its 9,9-dimethyl derivative undergo stereospecific rearrangement, in the presence of rhodium(I), to the corresponding *cis*-8,9-dihydroindenes.

CYCLO-OCTATETRAENE EPOXIDE (**1**) undergoes thermal rearrangement[1] (**1** → **2** → **3**) with difficulty (400°) and although acid catalysis induces rearrangement (**1** → **4** → **3**) under much milder conditions,[2] it did not prove possible to isolate the intermediate (**4**) other than as a derivative. As an extension of our previous work on epoxides[3] we have studied the reaction of (**1**) with the Rh complex (**5**). At $-50°$ an immediate, quantitative, isomerisation (**1** → **4**) occurs and on slowly warming from $-50°$ to $+50°$ (monitoring by n.m.r. spectroscopy) the conversion of (**4**) into (**3**) is seen to involve an intermediate not containing a formyl group (disappearance of formyl proton in n.m.r.). The conversion (**4** → **3**) does not require Rh^I and proceeds slowly even at 0°. Isolation of (**4**), λ_{max}(CHCl$_3$) 263·5 nm, ϵ_{max} 3140; ν(C=O) 1725 cm^{-1}; τ(CDCl$_3$) 0·3 (s, 1H), 3·3—3·8 (m, 4H), 4·75 (m, 2H), and 7·33 (t, 1H), and keeping in the presence of deuterium oxide gave mono-deuteriated (**3**) with the deuterium located specifically in the methylene group, implicating the enol (**6**) as an intermediate. A reasonable path for the conversion (**4** → **3**) is the disrotatory closure of (**4**) to the bicyclic *exo*-aldehyde (**7**) followed by an orbital symmetry allowed H-shift (**7**, arrows) generating the enol (**6**) directly. The rearrangement of (**1**) involves cleavage of the C–O bond and can be rationalised by an oxidative-addition type mechanism.[3] The possible involvement of the valence tautomer (**8**) in the rearrangement cannot be ruled out.[4]

Thermal rearrangements in the related hydrocarbon series, the bicyclo[6,1,0]nonatrienes, have attracted much attention[5,6] due to their tendency to rearrange to the corresponding *cis*-8,9-dihydroindenes rather than the *trans*-8,9-dihydroindenes as predicted from orbital symmetry considerations.[7] Only one report[8] of a rearrangement of bicyclononatrienes in the presence of a metal has appeared (non-catalytic) and this involved conversion of the molybdenum complex (**9**) into (**10**) at 125° *i.e.* formal cleavage of the C–C bond equivalent to the C–O bond in (**1**). When the bicyclononatriene (**11**; R = H) was allowed to stand with a catalytic amount of (**5**) at 35° for 2 h smooth essentially quantitative conversion occurred into the *cis*-8,9-dihydroindene (**12**; R = H) uncontaminated with any *trans*-isomer (g.l.c.) but containing a trace (<0·5%) of an unidentified product. The *cis*-8,9-dihydroindene (**12**; R = H) was identified by comparison with an authentic sample. This catalysed process proceeds under milder conditions than the thermal (90°) rearrangement and is more specific. The thermal process gives a mixture of *cis*- and *trans*-dihydroindenes (9 : 1).[9] In contrast to the molybdenum complex the Rh^I catalysed process would appear to involve cleavage of the other C–C bond of the cyclopropane fragment.



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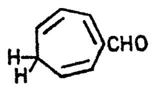

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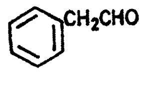

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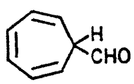

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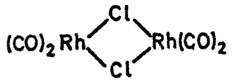

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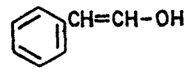

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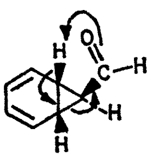

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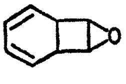

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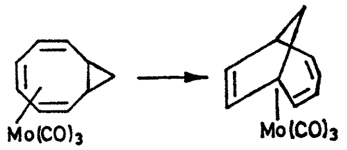

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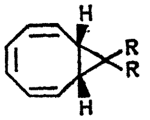

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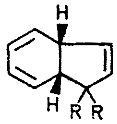

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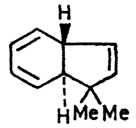

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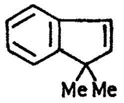

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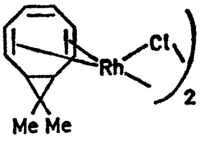
A remarkable difference in stereochemistry is observed when the 9,9-dimethylbicyclononatriene (**11**; R = Me) is heated in the presence of Rh^I. Whereas heating (**11**; R = Me) at 151° gives the *trans*-dihydroindene (**13**) plus two other products arising from (**13**)[11] we find that heating (**11**; R = Me) at 140° for 30 min in the presence of a catalytic amount of (**5**) gives a mixture consisting of 80% *cis*-dihydroindene (**12**; R = Me) ($J_{8,9}$ 12 Hz, centred at τ 6·35 and 7·45), 2% *trans*-(**13**), 8% (**11**; R = Me) and three other components (total 10%) one of which is the indene (**14**; 2%). The mechanism of this rearrangement is under investigation and preliminary results indicate the complex (**15**) is not a catalyst for the rearrangement of (**11**; R = Me). The complex (**15**; 82%), m.p. 232—232·5°, is readily prepared from (**11**; R = Me) and (**5**) in n-hexane, τ ($CDCl_3$) 4·37 (br s, 2H), 5·7 (q of AB, 4H) 7·27 (br s, 3H), 8·87 (s, 3H), and 9·3 (br s, 2H).



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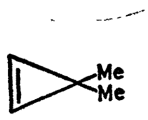

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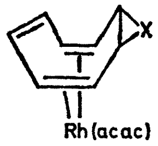

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Other metal catalysts are being investigated and preliminary findings show that the rearrangement of (**1**) to (**3**) is incomplete after two days at room temperature in the presence of silver nitrate whereas silver borofluoride effects rapid conversion at 0°. In contrast both silver borofluoride and boron trifluoride etherate react with (**11**; R = Me) on heating (140° and 100°, respectively) with formation of benzene. The fate of the remainder of the molecule is under investigation but we have been unable to detect any dimethylcyclopropene (**16**). Finally, (**1**) and (**11**; R = H or Me) form stable π-complexes (**17**; X = O, CH_2, or CMe_2), in good yield, with $Rh(CO)_2(acac)$.[10]

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