# Rhodium(I) Catalysed Rearrangements of Vinyl Epoxides and Oxetans

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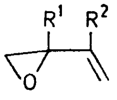
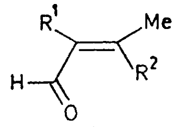
*Summary* $Rh^I$ catalysed rearrangements of vinyl epoxides to $\alpha\beta$-unsaturated aldehydes and cleavage of oxetans to olefins and aldehydes are described and the reactions interpreted in terms of $Rh^I$ acting as a weak Lewis acid.

Recently,[1] we described some rearrangements of cyclo-olefinic epoxides in the presence of $[Rh(CO)_2Cl]_2$. Some further studies are now described. The epoxide (**1a**) rearranged slowly in the cold in the presence of $[Rh(CO)_2Cl]_2$ into the aldehyde (**2a**)[3]. Similarly (**1b**) gave (**2b**) and (**1c**) gave a 2:3 mixture of *cis*- and *trans*-crotonaldehyde.[2] Styrene oxide reacted at room temperature but gave mainly polymer with only a trace amount of an aldehyde. The relative rates of reaction of the epoxides in the presence of $Rh^I$ [styrene oxide > (**1a**) > (**1c**) > (**1b**)] suggests these reactions have carbonium ion character and they are clearly related to the Lewis acid catalysed rearrangements of more complex vinyl epoxides.[4] Ring opening of (**1a**—**c**) by $Rh^I$ could give the normal Lewis-acid dipolar intermediate (**3**) but a $\pi$-allyl intermediate might also be involved. Evidence for the intervention of a $\beta\gamma$-unsaturated aldehyde was obtained by n.m.r. monitoring of the rearrangement of (**1a**) at 80° in $C_6D_6$ when the doublet aldehyde signal ($\tau$ 0·65, $J$ 1·3 Hz) of (**4**) was observed. It was also apparent that the geometrical isomer of (**2a**) was being produced at a faster rate than (**2a**) suggesting that (**2a**) was not directly produced from (**4**) but arose from its geometrical isomer. The $\beta\gamma$-unsaturated aldehyde (**4**) was also observed using $(PhCN)_2PdCl_2$ as the catalyst but a black precipitate, presumably metallic palladium, was also produced suggesting acid catalysis may have been responsible.† The conversion of (**4**) into the corresponding $\alpha\beta$-unsaturated aldehyde could involve a metal catalysed 1,3-hydride shift,[5] or a Lewis acid catalysed conjugation *via* the dienol or its metal complexed equivalent.

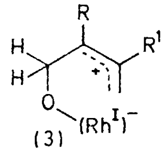
The cleavage of an oxetan into an olefin and a carbonyl compound utilising transition metals has also been studied. Oxetan itself does not fragment to ethylene and formaldehyde (polymer formation is preferred) but a number of substituted oxetans are readily cleaved by catalytic amounts of $[Rh(CO)_2Cl]_2$. In the presence of $Rh^I$ the oxetan (**5**)[6] is cleaved quantitatively to (**6**) (5 h at 35°). Similarly (**7**)[7] gives furan and benzaldehyde (3 h at 35°). Both these reactions are faster when catalysed by $CF_3CO_2H$. However, $[Rh(CO)_2Cl]_2$ gives a cleaner product than $CF_3CO_2H$ for a number of tetracyclic oxetans.‡ *E.g.* (**8**)[8] on heating at 82° for 18 h in the presence of a catalytic amount of $Rh^I$ gave the *endo*-aldehyde (**9**) (82%).§ Similarly the oxetans (**10a**)[8] and (**10b, c**) gave the corresponding *endo*-aldehydes (**11a**—**c**) on heating (85—110°, 2—20 h) in the presence of $Rh^I$ (70—90%).§ Previous attempts to cleave (**10a**) with perchloric acid in methanol gave a mixture of the acetal of



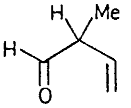
(1) a; $R^1$ = Me, $R^2$ = H
b; $R^1$ = H, $R^2$ = Me
c; $R^1$ = $R^2$ = H



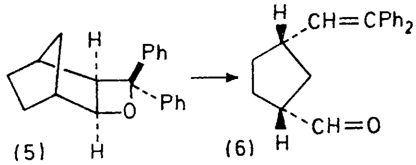
(2) a; $R^1$ = Me, $R^2$ = H
b; $R^1$ = H, $R^2$ = Me



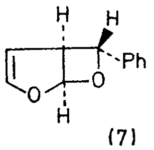
(3)



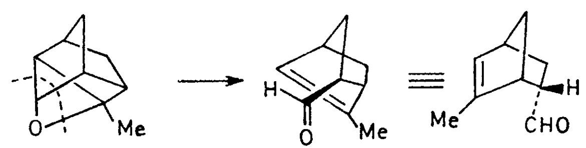
(4)



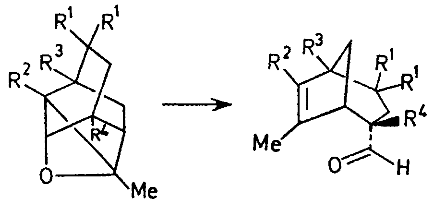
(5) (6)



(7)



(8) (9)



(10) a; $R^1$ = $R^2$ = $R^3$ = $R^4$ = H
b; $R^1$ = $R^2$ = $R^4$ = Me, $R^3$ = H
c; $R^1$ = $R^2$ = H, $R^3$ = Me, $R^4$ = OMe

(11)

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† Rearrangements catalysed by traces of HCl occur at a much slower rate. Reactions carried out under dry conditions showed no decrease in rate of rearrangement. However, $HRh(CO)_2Cl_2$ cannot be ruled out as the catalytically active species. The isomeric dihydrofuran is not an intermediate since 2,5-dihydrohydrofuran is unaffected by $Rh^I$ at 80°.

‡ All new compounds gave satisfactory analytical and spectral data. The oxetans (**10b, c**), were prepared by photocyclisation of the appropriate ketones, which in turn were prepared by Diels–Alder reactions.

§ Yields reported are estimated by n.m.r. Isolated yields were somewhat lower, varying according to the reaction scale, because of polymerisation on work-up.

(**11a**) and an olefinic alcohol.[8] The direction of cleavage of oxetans (**5**), (**8**), and (**10a**—**c**) are correctly predicted by assuming co-ordination of the rhodium to the ether oxygen atom followed by cleavage to give the most stable carbonium ion. The 1,4-dipoles could then collapse directly to the olefinic aldehydes or in the case of (**10a**—**c**) to another intermediate[9] capable of transforming to the olefinic aldehydes. Clearly in (**7**) attack on the more nucleophilic enol-ether is favoured. Other examples of cleavage of oxetanes to carbonyl compounds and olefins by Lewis acids have been reported.[10]

Our results with $Rh^I$ and strained oxygen heterocycles complement recent work[11] on strained alicyclic systems in which Lewis acid catalysis by various metal ions was discussed. We have not detected any acyl rhodium intermediates[12] in these rearrangements.

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