Rhodium(1) 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 cycloolefinic 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 π -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 (τ 0.65, $J \cdot 1 \cdot 3 \text{ Hz}$ 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 β_{γ} -unsaturated aldehyde (4) was also observed using (PhCN)₂PdCl₂ 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 CF₃CO₂H. However, $[Rh(CO)_2Cl]_2$ gives a cleaner product than CF₃CO₂H 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 $(85-110^\circ, 2-20 h)$ in the presence of





 $[\]dagger$ 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)₂Cl₂ cannot be ruled out as the catalytically active species. The isomeric di-hydrofuran 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.

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(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 intermediate⁹ 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 RhI and strained oxygen heterocycles complement recent work¹¹ on strained alicyclic systems in which Lewis acid catalysis by various metal ions was discussed. We have not detected any acyl rhodium intermediates¹² in these rearrangements.

(Received, 20th December 1971; Com. 2155.)

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