Regioselectivity and the Role of Olefin Co-ordination in Rhodium(I)-catalysed Rearrangement of Vinylcyclopropanes

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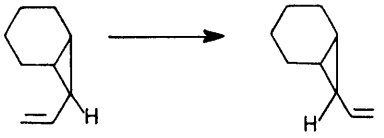
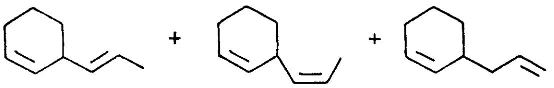
Summary Rearrangement of *syn*- and *anti*-7-vinylbicyclo[4.1.0]heptanes in the presence of di-μ-chloro-tetracarbonyldirhodium(I) exhibits kinetic behaviour and product selectivity which provide good evidence for initial co-ordination of the vinyl group and stereospecific *cis*-β-hydride elimination from a subsequent metallocyclic intermediate.

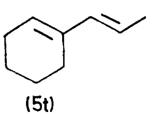
Both *syn*- (**1s**) and *anti*-7-vinylbicyclo[4.1.0]heptane (**1a**)[1] undergo rearrangement with cleavage of the cyclopropane ring in the presence of di-μ-chloro-tetracarbonyldirhodium(I) (**2**) in benzene solution. The *syn* isomer (**1s**) gives (**3**) (40%), (**4t**) (21%), and (**4c**) (19%) while the *anti* isomer (**1a**) gives (**3**) (56%), (**4t**) (39%), and (**4c**) (4%). These products are stable under the reaction conditions. Other isomeric dienes (**5t**), (**5c**), (**6**), and (**7**) are not produced, and are not transformed into (**3**), (**4t**), or (**4c**) under the rearrangement conditions. The rate of disappearance of



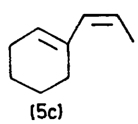
(1s) (1a)



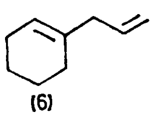
(4t) (4c) (3)



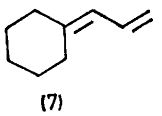
(5t)



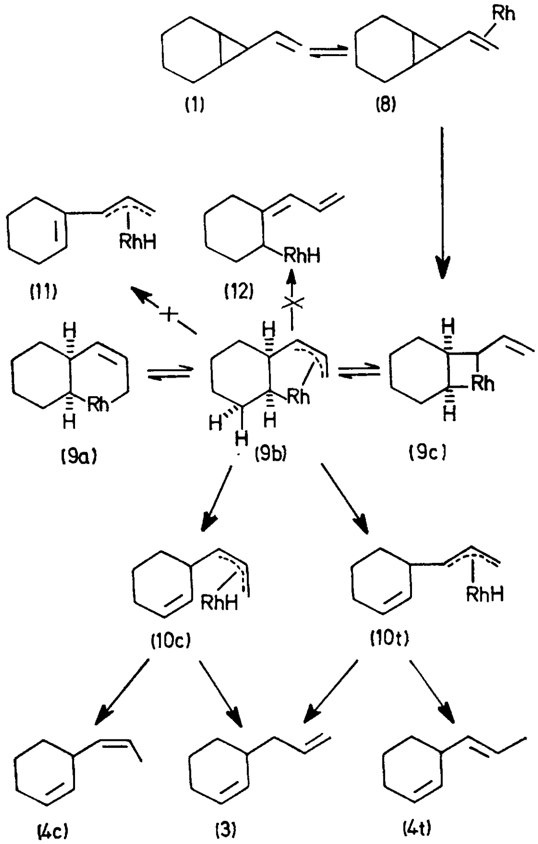
(5c)



(6)



(7)



(**1a**) is about 8 times that of (**1s**). The rearrangement of (**1a**) follows zero-order kinetics for at least 2 half lives, and doubling the catalyst concentration doubles the rate of rearrangement. The kinetic behaviour of (**1s**) is complicated by a competing epimerization which converts (**1s**) into (**1a**). The latter was isolated from the rearrangement of (**1s**).

Conjugated diene products are generally found in the rearrangement of vinyl cyclopropanes catalysed by rhodium(I).[2] The complete absence of such products in the rearrangements of (**1a**) and (**1s**) is thus interesting and significant. This novel product selectivity is readily explained by the stringent stereochemical requirement of *cis*-β-hydride elimination[3] giving allyl rhodium hydride[4] intermediate (**10**) from a metallocyclic intermediate (**9**). The latter arises by oxidative addition to rhodium(I) of a strained C–C σ-bond of the cyclopropyl ring.[2b,4,5] The alternative rhodium hydrides (**11**) and (**12**), which would be the progenitors of (**5t**), (**5c**), (**6**), and (**7**), are not formed since the tertiary hydrogen atom in (**9**) is geometrically precluded from attaining the *syn* periplanar relationship to rhodium(III) required for β-hydride elimination. Furthermore, this simple mechanism, which involves well precedented intermediates, explains all known rhodium-catalysed rearrangements of vinylcyclopropanes.

Clearly, the rearrangement of (**1s**) does not proceed entirely by prior rearrangement to (**1a**) since the product ratios from these two epimers differ.† Some formation of (**3**), (**4c**), and (**4t**) must occur directly from (**1s**). Furthermore, the ratio of isomeric allylrhodium hydrides (**10t**) and (**10c**) produced from (**1a**) and (**1s**) must differ and (**10c**) and (**10t**) are not completely equilibrated under the reaction conditions.

The greater reactivity observed for (**1a**) compared to (**1s**) indicates that the rhodium catalyst co-ordinates initially with the C–C π-bond rather than inserting directly into the strained C–C σ-bond of the cyclopropyl ring. Thus, one face of the cyclopropyl ring in (**1s**) is unsubstituted. Direct insertion by rhodium approaching the cyclopropane from this sterically uncongested face of (**1s**) should occur more readily than direct insertion into the more sterically congested cyclopropane in (**1a**), yet (**1a**) reacts significantly faster than (**1s**). Co-ordination of rhodium by the C–C π-bond of (**1**) prior to oxidative insertion is also supported by the zero-order kinetics at constant catalyst concentration and by the proportionality of rate to total catalyst concentration observed for the disappearance of (**1a**). Formation of the complex (**8**) is thus not rate determining.

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† The product ratios vary slightly during the course of the rearrangements. Examination of these minor changes, now in progress, may lead to a detailed understanding of the relative importance of direct ring cleavage and epimerization of (**1s**).

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