Evidence for Stepwise Bond Cleavage in the Transition Metal Promoted Isomerizations of Simple Bicyclo[1,1,0]butanes

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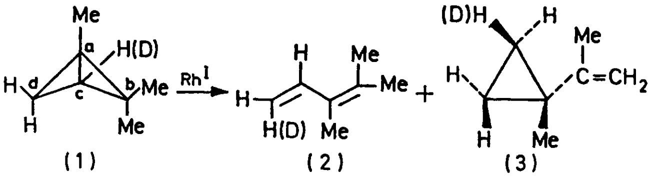
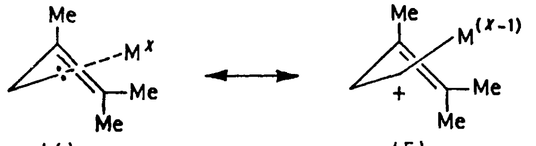
Summary Capture of a carbonium ion type intermediate by nucleophilic solvent in the Rh^I catalysed isomerization of a simple bicyclo[1,1,0]butane provided substantial evidence that the transition metal-catalysed isomerization of these highly-strained bicyclic molecules proceeds *via* a mechanism which involves sequential cleavage of the side and centre bonds of the bicyclo[1,1,0]butane.

NUMEROUS examples of the transition metal-promoted isomerization of derivatives of bicyclo[1,1,0]butane to derivatives of buta-1,3-diene have recently been reported. The use of labelling experiments by Gassman and Williams in the isomerization of (**1**) to (**2**) unequivocally established that the overall process observed in these rearrangements involved cleavage of the a–c and b–c bonds of (**1**).[1] However, the detailed process by which these bonds were cleaved remained a matter of speculation. Several alternate mechanistic proposals have been advanced, including the formation of a transition-metal-complexed carbene–transition metal bonded carbonium ion hybrid,[2] and, in the case of silver ion, both concerted rearrangement[3] and formation of an "argento carbonium ion."[4] Recent work[2,4,5] has led to the abandonment of the proposal of a concerted mechanism in the silver-ion catalysed isomerizations. In addition, intramolecular trapping experiments have established[6] the carbenoid character of the reaction intermediate, supporting the theory that a hybrid of the resonance structures (**4**) and (**5**) was formed. The mechanism whereby this transition metal complexed carbene–transition metal bonded carbonium ion hybrid was formed was not decided. We now present evidence which indicates that the formation of the resonance hybrid represented by (**4**) and (**5**) may involve a stepwise process



in which the b–c bond of (**1**) is initially cleaved by transition metal complexes such as dicarbonylrhodium chloride dimer.

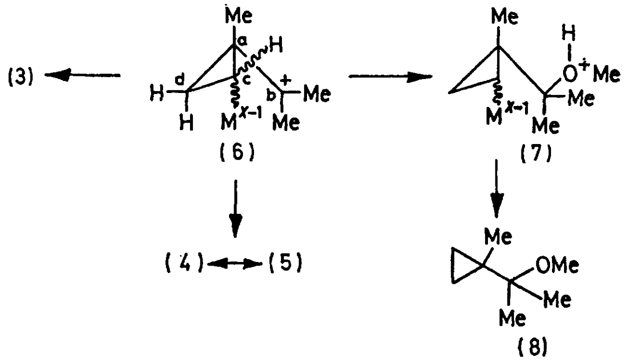
The formation of both (**2**) and (**3**) from (**1**) suggested to us that a common intermediate might be involved as a precursor. If this were correct the precursor of (**2**) and (**3**) would also have to be capable of being transformed into the hybrid represented by (**4**) and (**5**). Intermediate (**6**) would fulfil all of these requirements. Loss of a proton from the methyl group of (**6**) followed by protonolysis of the carbon–metal bond would give (**3**), while shifting of the C^a–C^c bonding electrons would produce (**4**) ↔ (**5**). In order to establish the intermediacy of a species represented by (**6**), we used the relatively strong nucleophilic solvent methanol in the hope of trapping (**6**) prior to rearrangement.



(4) (5)

When 2 mol % of dicarbonylrhodium chloride dimer was added to a methanolic solution of (**1**) at 25° a vigorous reaction ensued which yielded 97% of (**8**) after 1 min. This transformation was qualitatively much faster than the corresponding reactions of (**1**) with the same catalyst in chloroform.

The possible formation of hydrochloric acid from the reaction of the transition metal catalyst with methanol, followed by simple acid-catalysed addition of methanol to (**1**) was eliminated by several control experiments which were performed. We found that in the absence of (**1**), dicarbonylrhodium chloride dimer could be recovered unchanged from methanol after 1 min at 25°. Furthermore, we prepared dicarbonylrhodium acetylacetonate[7] which was rigorously purified.† Use of this catalyst with (**1**) in chloroform gave 58% of (**2**) and 11% of (**3**). In methanol this same catalyst converted (**1**) into (**3**) (13%) and (**8**) (84%). To ensure the complete absence of acid, an amount of sodium methoxide equivalent to 10% of the catalyst was added to the dicarbonylrhodium acetylacetonate. In methanol this basic catalyst system gave the same results with (**1**) as was previously observed in the absence of sodium methoxide. These experiments established that it was the transition metal complex and not protic acid which was responsible for the conversion of (**1**) into (**8**).



The relative clean conversion of (**1**) into (**8**) in the presence of transition metal complexes in methanol supports our contention that the transition metal promoted rearrangement of simple bicyclo[1,1,0]butanes proceeds by a stepwise process which involves initial cleavage of a side bond to yield the most stable cyclopropylcarbinyl cation, such as (**6**). Capture of nucleophilic solvent by (**6**) would produce (**7**) which on proton transfer and cleavage of the carbon–metal bond would yield (**8**).

It should be noted that we cannot rigorously exclude the possibility that different mechanisms might be involved in methanol and acetonitrile or chloroform. However, in the absence of evidence for such a solvent-controlled change in mechanism, we feel that the stepwise process of bond cleavage, deduced from our studies in methanol, can be extrapolated to explain the dicarbonylrhodium chloride dimer-promoted rearrangement of simple bicyclo[1,1,0]butanes in acetonitrile or chloroform to mixtures of buta-1,3-dienes and vinylcyclopropanes.

We are indebted to the National Science Foundation for financial support of this investigation.

(*Received, October 1st, 1971; Com. 1717.*)

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† This catalyst is prepared from dicarbonylrhodium chloride dimer. No contamination by the starting material was found using analytical procedures which would have detected considerably less than 1% impurity.

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