

Palladium(II)-catalysed Isomerization of Bicyclobutanes

By M. SAKAI, H. YAMAGUCHI, and S. MASAMUNE*

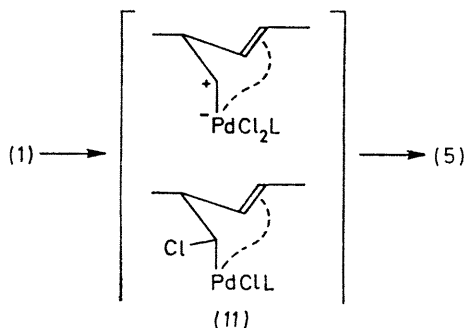
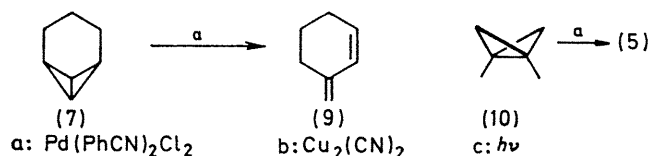
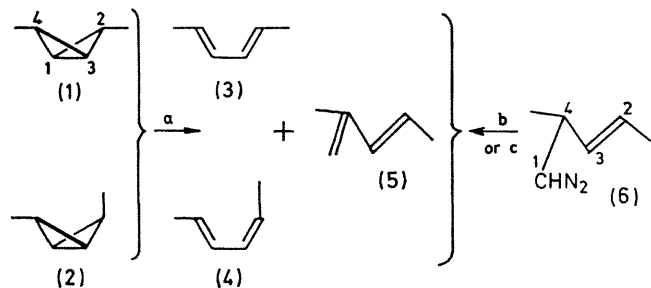
(Department of Chemistry, University of Alberta, Edmonton 7, Alberta, Canada)

Summary Two isomerizations of bicyclobutanes, one catalysed by Pd^{II} and the other by Ag^I are found to be different in both product distribution and substituent effect on the course of reaction.

RECENTLY we have demonstrated that the Ag^I-catalysed rearrangement of *exo,exo*- and *exo,endo*-2,4-dimethylbicyclobutanes (**1** and **2**) is largely stereospecific and provides

trans,trans- and *cis,trans*-hexa-1,3-dienes (**3** and **4**), respectively.¹ In view of recent reports that both Ag^I and Pd^{II} effect the same rearrangement of cubane into cuneane,² and that the two reactions are suggested to proceed through the same mechanism,³ we have extended our study to the Pd^{II}-catalysed rearrangement. We report that (i) the two metal ions behave in a different manner towards the bicyclobutane system, as shown in the product distribution of the isomerization and (ii) the position and stereochemistry of substituents on bicyclobutane delicately affect the mode of isomerization.

Bicyclobutanes (**1**) and (**2**) (*ca.* 0.2 M) in chloroform were smoothly isomerized at room temperature in the presence of a catalytic amount of bisbenzotriendedichloropalladium. (**1**) and (**2**) provided 2-methylpenta-1,3-diene (**5**) as a major product in addition to (**3**) and (**4**),† in contrast to the corresponding Ag^I-bicyclobutane reaction which afforded only hexa-1,3-dienes, (**3**) and (**4**). Results, with those of Ag^I for comparison, are summarized in the Table.



Product distribution (%) of metal-catalysed reaction of 2,4-dimethylbicyclobutanes at 26°

Catalyst	(3)	(4)	(5)	Total yield
Pd ^{II} (1)	37 ^a	16 ^a	47	95
Pd ^{II} (2)	51 ^a	24 ^a	24	70
Rh ^I (1)	75	3	22	78
Rh ^I (2)	60	8	32	98
Ag ^I (1)	78	22	0	89
Ag ^I (ref. 1) (2)	5	95	0	99

* Control experiments to examine the stability of the products under the isomerization conditions showed that only in the case of Pd^{II}, (**3**) and (**4**) were equilibrated to afford a *ca.* 2 : 1 mixture as shown.

It was previously observed that tricyclo[4,1,0,0²,7]-heptane (**7**)^{1,4} underwent Ag^I-catalysed rearrangement to provide cyclohepta-1,3-diene (**8**). Treatment of (**7**) with a catalytic amount of Pd^{II} in chloroform at room temperature provided an entirely different product, 3-methylenecyclohexene (**9**) (90%) (confirmed by comparison with an authentic sample independently synthesized) and no (**8**). Similarly, 1,3-dimethylbicyclobutane (**10**), isomeric with (**1**) and (**2**), underwent an equally specific rearrangement to afford (**5**) (*ca.* 80%) as the sole C₆-compound. The four

† In a similar fashion, [Rh(CO)₂Cl]₂, HgBr₂, and Cu₂Cl₂ all effect non-stereospecific rearrangements to provide a mixture of dimethylbutadienes including (**5**) as one of the major products; the [Rh(CO)₂Cl]₂ results are included in the Table.

examples (**1**, **2**, **7**, **10**) demonstrate that the course of the Pd^{II} isomerization is sensitive to the position and stereochemistry of alkyl substituents on bicyclobutane.

The various products can be classified into two groups; (i) those (**5** and **9**) resulting from a formal C-1,2 and C-1,3 bond cleavage of bicyclobutane and (ii) those (**3** and **4**) from a C-1,2 and C-3,4 bond cleavage. Formation of group (i) products is most simply rationalized by involving a carbenoid type intermediate⁵ and in fact Cu₂(CN)₂-catalysed decomposition of diazo-compound (**6**) provided (**5**) as a major product together with (**1**), (**2**), (**3**), and (**4**).¹ In addition, similar results were obtained upon photolysis of (**6**) in pentane at *ca.* -50°, (**3**), (**4**), and (**5**) being major products. Since the generation of carbenes and related species from halogenomethylmetal compounds [*e.g.*, phenyl-(bromodichloromethyl)mercury in the presence of olefins] is well known,⁶ the involvement of a similar intermediate in the present reaction is, at least, energetically feasible. Structures (**11**) are suggested for plausible Pd^{II}-complex intermediates leading to the carbenoid species. If the carbenoid mechanism is operative in the Pd^{II} reaction, one would readily accept a 1,2-hydrogen shift to the carbenoid centre (C₁) to form (**5**) [from (**1**), (**2**), and (**10**)] and (**9**) from (**7**).

The route leading to group (ii) compounds (**3** and **4**) requires a more elaborate explanation. These hexadienes could be derived from the carbenoid intermediate considered above as the precursor to (**5**) by either a methyl migration or a *net* vinyl migration. While this type of methyl migration is scarcely recorded and thus unlikely in the present case, the vinyl migration has numerous precedents⁷ and could be the formal result of a stepwise process involving interaction of the carbene centre with the double bond. Alternatively, (**3**) and (**4**) could arise from a pathway not involving a carbene but rather heterolytic cleavage of the C-1,2 bond followed by a cyclopropyl-carbinyl-allylcarbinyl type rearrangement.

While the overall product distribution is influenced by several competing factors, it is clear that hydrogen migration is required for group (i) compound formation. It would be of interest to see if group (ii) compounds would dominate in the case where this migration is completely blocked by alkyl substitution.

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⁶ *E.g.*, D. Seyforth, J. Y. P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1967, **89**, 4953.

⁷ *E.g.*, see D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 1964, 323; G. L. Closs and R. B. Larrabee, *ibid.*, 1965, 287.