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Preliminary communication

The chemistry of bent bonds
XXXVIII*. The intermolecular trapping of a rhodium complexed carbene

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The mechanism of the transition metal complex promoted rearrangement of derivatives of bicyclo[1.1.0]butane has been the subject of many recent discussions[2-4]. In general, our proposal of the intermediacy of a transition metal complexed carbene–transition metal bonded carbonium ion[5] has received substantial support. Of particular importance have been the recent low temperature NMR studies of Masamune's[3] and Dauben's[4] groups. Both of these groups have chosen to interpret their NMR data in terms of the intermediacy of either a transition metal complexed carbene or in terms of its resonance form, the transition metal bonded carbonium ion. In addition, Noyori has recently demonstrated[6] that when these rearrangements are promoted by nickel(0), in the form of bis(acrylonitrile)nickel, an intermediate complex was formed which could react with olefinic solvent to yield cyclopropane derivatives. This cyclopropyl ring formation can be interpreted in terms of the intermolecular capture of a nickel(0) complexed carbene intermediate. The extensive use of rhodium(I) in the transition metal complex promoted rearrangement of derivatives of bicyclo[1.1.0]butane[2] raises the question of whether an analogous intermolecular capture of an intermediate rhodium(I) complexed carbene might occur under the proper conditions. We now wish to report that we have successfully carried out such an intermolecular trapping experiment.

The initial indication that trapping experiments of the type described above, might be possible in rhodium(I) complex promoted rearrangements of derivatives of bicyclo[1.1.0]butane came from the observation that the rearrangement of bicyclo[1.1.0]-butane (I)** and 1-methylbicyclo[1.1.0]butane (II)*** in the presence of norbornadiene-rhodium chloride dimer produced substantial amounts of 1,4,7-octatriene (III) and 2,7-dimethyl-1,4,7-octatriene (IV), respectively. In a typical experiment, one mg of nor-

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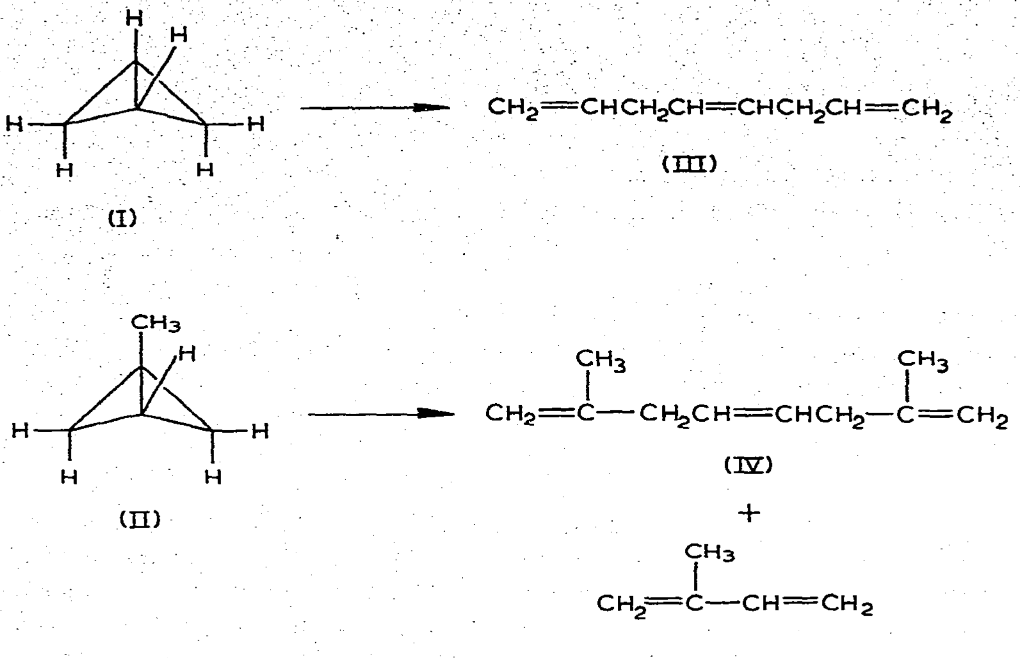
*For part XXXVII see ref. 1.

**For the preparation of I see ref. 7.

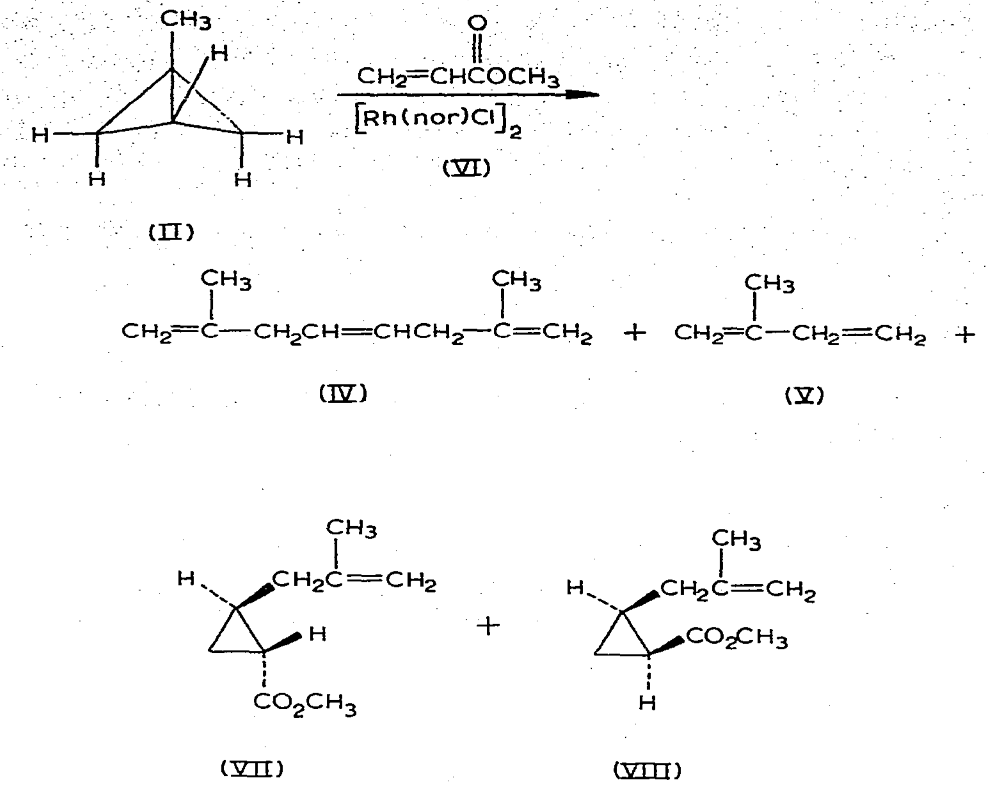
***The synthesis of II involved monomethylation of I according to the general procedure of Closs and Closs[8].



bornadiene rhodium chloride dimer (VI) in 50 μl of deuteriochloroform was added to a solution of ca. 50 mg of I in 0.3 ml of deuteriochloroform. An immediate exothermic reaction ensued which resulted in the formation of 65% of III. Collection of III by preparative VPC gave a sample which was identified on the basis of its IR, NMR, and mass spectral data. Infrared maxima at 910 and 990 cm^{-1} indicated the presence of the terminal monosubstituted vinyl groups while the absorption at 970 cm^{-1} was consistent with an internal *trans*-disubstituted double bond[9]. The NMR spectrum showed the four allylic protons as a broad singlet at τ 7.20, the four terminal methylene protons as a multiplet at τ 5.2–4.8, and the remaining four vinyl hydrogens as a singlet at τ 4.59 superimposed on a multiplet centered at τ 4.4; exact mass mol. wt., found: 108.0941; calcd.: 108.0939.

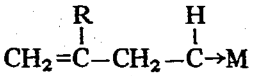
Similar treatment of a solution of 100 μl of II in 150 μl of $CDCl_3$ with a solution of 1.0 mg of VI in 150 μl of deuteriochloroform gave an exothermic reaction, which resulted in the complete rearrangement of II in less than 5 min. This led to the formation of isoprene (V) in 10% yield and IV (68% yield). The structure of IV was established on the basis of its IR absorption: 890 cm^{-1} (1,1-disubstituted vinyl group)[9] and 965 cm^{-1} (*trans*-1,2-disubstituted double bond);[9] NMR maxima: τ 8.33 (s, 6H, CH_3), 7.45–7.17 (m, 4H, allylic CH_2), 5.32 (s, 4H, terminal methylene), and 4.70–4.40 (m, 2H, non-terminal olefinic hydrogens); and exact mass mol. wt., found: 136.1249; calcd: 136.1252.

The formation of III and IV, and the interpretation of these results in terms of the dimerization of a Rh^I complexed carbene has some precedence in the formation of tetraphenylethylene from rhodium complexed diphenylcarbene[10]. In view of the apparent



carbenoid character of our intermediate it was decided to attempt to trap this species in an intermolecular manner★. Addition of 3 mg of VI to 180 mg of II in 380 mg of methyl acrylate resulted in an immediate exothermic reaction. After 5 min, no 1-methylbicyclo-[1.1.0]butane (II) remained. NMR spectroscopy indicated the presence of four products, IV, V, VII and VIII, in the ratio of 25/37/8/30, respectively. The structures of VII and VIII were assigned on the basis of NMR and IR spectral data and elemental analysis. NMR spectral comparison of VII and VIII with analogous compounds, previously reported in the literature[6], confirmed the stereochemical assignments of VII and VIII.

The formation of the dimers, III and IV, and the isolation of the cyclopropane derivatives VII and VIII strongly supports the contention that the rearrangement of derivatives of bicyclo[1.1.0]butane promoted by rhodium(I) complexes involves the intermediacy of a metal complexed carbenoid species of general formula IX where M represents a transition metal with its associated ligands and R represents hydrogen in the rearrangement



$$CH_2{=}\overset{R}{\overset{|}{C}}{-}CH_2{-}\overset{H}{\overset{|}{C}}{\rightarrow}M$$

(IX)

★ Intramolecular trapping experiments have previously been reported[11].

of I and methyl in the isomerization of II. The failure of this intermediate to add to electron-rich olefins and the facility with which it is trapped by electron-deficient olefins to form cyclopropane derivatives implies that this carbenoid species is nucleophilic rather than electrophilic. This indicates that in those cases represented by the general formula IX, there exists extensive back donation of electrons from M to the divalent carbon to give an electron-rich carbenoid.

We are currently investigating the synthetic and mechanistic implications of this concept.

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