

A NEW CYCLIZATION REACTION BY TRIS(TRIPHENYLPHOSPHINE)-  
RHODIUM CHLORIDE.<sup>(1)</sup>

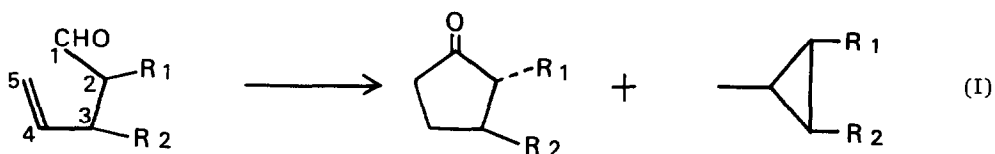
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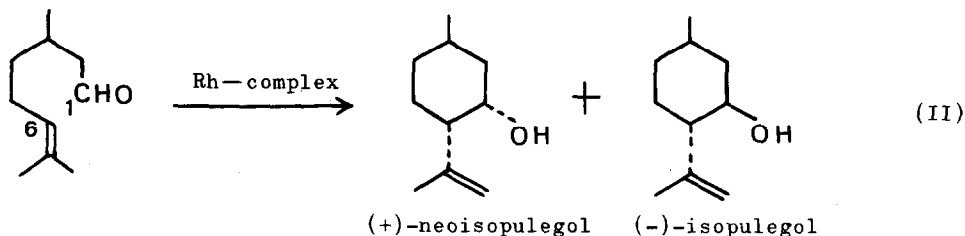
In a previous paper<sup>(2)</sup> we reported a new cyclization reaction (I) involving conversion of various 1-al-4-ene systems by tris(triphenylphosphine)rhodium chloride (rhodium complex) to the cyclopentanone and cyclopropane derivatives under mild conditions.



We now wish to report another type of cyclization reaction (II) by means of the rhodium complex.

Reaction of (+)-citronellal (1 eq.) bearing the 1-al-6-ene system with the rhodium complex (1 eq.) in  $\text{CHCl}_3$ <sup>(3)</sup> at room temperature for 15 hrs., proceeded smoothly without any fade of the original dark-red color, and two spots were observed on TLC at the end of the reaction. The less polar component and more polar one were obtained in the ratio of 3 to 1 by silica gel column chromatography in total yield 55%. By a direct comparison with the standard samples prepared by a known method<sup>(4)</sup>, the less polar one and more polar one were identified as (+)-neoisopulegol and (-)-isopulegol, respectively. It is note-

worthy that, contrary to the ratio of products synthesized according to the known method, (4)(5) (+)-neoisopulegol in which OH and isopropenyl groups are cis configuration, is obtained as a main product in this reaction.



The possible pathway for the formation of cyclopentanone and cyclopropane derivatives from the 1-al-4-ene system proceed presumably via the acyl complex which is generally accepted as the intermediate of the decarbonylation reaction. (6) Since, however, a cyclohexanone derivatives which were expected from the reaction of the 1-al-4-ene system could not be obtained, it seems doubtful that the formation of cyclohexanol derivatives from (+)-citronellal involves the acyl complex as an intermediate. Work designed to learn more about the mechanism of these cyclization reactions is now in progress.

#### Acknowledgement

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#### REFERENCES AND FOOTNOTES.

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- (3) Freshly distilled  $\text{CHCl}_3$ .
- (4) H. Ueda and S. Shimizu, *Bull. Agr.Chem.Soc. Japan*, 24, 402 (1960).
- (5) Treatment of (+)-citronellal with  $\text{SnCl}_4$  in  $\text{CH}_3\text{NO}_2$  afforded also (-)-isopulegol as a main product.
- (6) a) J. Tsuji and K. Ohno, *Synthesis*, 157, (1969).  
b) H. M. Walvorsky and L.E. Allen, *J. Amer. Chem. Soc.*, 93, 5465 (1971).