Tetrahedron Letters No.11, pp. 823-824, 1970. Pergamon Press. Printed in Great Britain.

# A STEREOSELECTIVE DECARBONYLATION OF ALDEHYDES[1]

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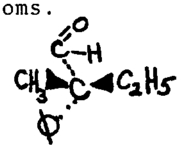
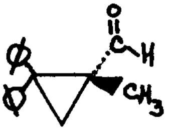
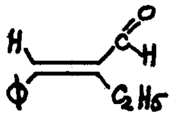
(Received in USA 4 November 1969; received in UK for publication 2 February 1970)

Although there are a number of methods available for the decarbonylation of aldehydes[2] none of them are stereoselective. In connection with another problem, it became necessary for us to find a stereospecific method for the removal of carbon monoxide from a molecule. It was the work of Tsuji and Ohno[3,4] on the use of rhodium complexes that seemed to hold the most promise. We would like to report, at this time, our results on the stereochemistry of the decarbonylation of aldehydes in which the carbonyl group is directly attached to a cyclopropyl as well as trigonally and tetrahedrally hybridized carbon atoms.


(-)-(*R*)-**1**


(+)-(*R*)-**2**


(*E*)-**3**

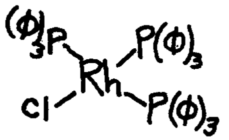

**4**

Table I. Decarbonylation of Aldehydes

| R-CHO | Amt,g. | Complex(g) | Solvent | Temp. | Time,hr. | R-H(g) | Config.,% |
|---|---|---|---|---|---|---|---|
| **1** | 0.66 | **4**(1.86) | benzonitrile | 110° | 2 | 0.14 | 93, ret. |
| **2** | 0.72 | **4**(1.86) | xylene | reflux | 12 | 0.29 | 94, ret. |
| **3** | 1.72 | **4**(2.77) | benzene | reflux | 0.5 | 0.53 | 100, *Z* |
| **3** | 7.85 | **5**(0.37)[a] | neat | 125°/30mm | 2 | 3.60 | 75,*Z*,25,*E*[b] |

(a) $RhCl(CO)(\phi_3P)_2$ (b) The hydrocarbon mixture was converted to a 50:50 mixture of *E* and *Z* isomers by heating under reaction conditions for 2 hours.

As can be seen from Table I, the decarbonylation proceeds with a high degree of stereoselectivity and with overall retention of configuration. The reaction of (-)-(R)-1 leads to the formation of (+)-(S)-2-phenylbutane with 86% retention of optical activity (93% retention of configuration) and (+)-(R)-2 yields (+)-(S)-1-methyl-2,2-diphenylcyclopropane with 88% retention of optical activity (94% retention of configuration). During the course of this study, Tsuji and Ohno reported the decarbonylation of aldehyde 3 with essentially the same results that we obtained. The small amount of E-isomer that the Japanese workers report can be accounted for by the isomerization of product under the reaction conditions (Table I).

The stereochemical results are pertinent to the mechanism of the reaction and provides support for the mechanism proposed[4] and has the effect of eliminating from consideration, the intervention of radical or carbonium ion intermediates. Moreover, it indicates that a carbanion must be abstracting the proton from the rhodium complex in an almost concerted fashion.

We have also demonstrated that when the C-1 deuterated aldehyde 2 is decarbonylated, 100% of the deuterium is found in the hydrocarbon formed. This result provides evidence for the intramolecular nature of the reaction. Furthermore, since C-1 deuterated aldehydes can be made readily and cheaply,[5] this provides a good means of preparing deuterated hydrocarbons.

## References

1. The support of this work by grants from the National Science Foundation and Public Health Service Research Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

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