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DECARBONYLATION OF ALLYLIC ALCOHOLS USING RHODIUM(I) COMPLEXES

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Recent studies of the reactions of tris(triphenylphosphine)rhodium chloride [$(Ph_3P)_3RhCl$] (1) with organic compounds have revealed its potential as a catalyst and reagent for a variety of synthetically important transformations.[1] The ability of this complex to abstract carbon monoxide,[2,3,4] sulfur dioxide[5] and nitrogen[6] from organic compounds has no parallel in organic chemistry.

We wish to report the decarbonylation of allylic alcohols with 1 in nitrile solvents.[7] The reaction can be expressed as follows.

$$\begin{array}{ll} \underset{\mathbf{1}}{(Ph_3P)_3RhCl} + RCH{=}CHCH_2OH \rightarrow & RCH_2CH_3 \text{ (major)} \\ & RCH{=}CH_2 \text{ (minor)} \\ & Ph_3P + \underset{\mathbf{2}}{(Ph_3P)_2RhCOCl} \end{array}$$

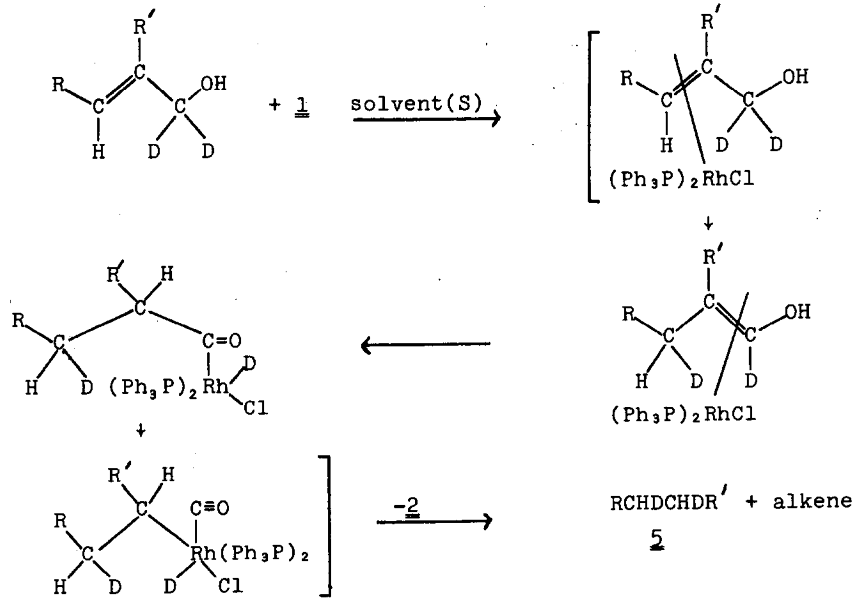
The decarbonylation proceeds at 110-150° in acetonitrile or benzonitrile. During the course of the reaction the solution turns from dark red to yellow indicating the formation of 2 which precipitates from the solution upon cooling. Triphenylphosphine can be isolated by column chromatography and detected by g.l.p.c. The present study was carried out on a microscale in sealed tubes at 145-155° for 12 hrs. The volatile products were detected and identified by g.l.p.c. Among the allylic alcohols reacted were cis-but-2-ene-1,4-diol, which gave a 89% yield of 1-propanol as the only detectable product derived from the diol. Cinnamyl alcohol gave both ethyl benzene (76%) and styrene (4%). Likewise α-methyl cinnamyl alcohol gave phenyl propane (67%) and 1-phenylpropene (20%). The reaction was extended to Δ^3-cyclohexene methanol which gave cyclohexane and cyclohexene but in greatly reduced yields (>10%). The reaction of 3-phenylpropyn-1-ol gave styrene, ethyl benzene and phenyl acetylene again in low yields.

Since in nitrile solvents the complex 1 is solvated[2] as 3, the present reaction most probably involves initial catalyzed allylic isomerization of the unsaturated alcohol via coordination of the π C-C bond with the three-coordinate species, 3. Subsequent decarbonylation of the aldehyde tautomer of the enol thus produced should parallel that observed in the reactions of $(Ph_3P)_3RhCl$ with aldehydes.[2]

$$\underset{1}{(Ph_3P)_3RhCl} \xrightleftharpoons{\text{solvent(S)}} \underset{3}{(Ph_3P)_2RhClS} + Ph_3P$$

The deuterium labelling pattern shown in Scheme 1 predicted by this sequence was indeed observed in the reaction of dideutero-α-methyl cinnamyl alcohol (4; R = Ph, R′ = CH_3) to give dideutero phenylpropane (5; R = Ph, R′ = CH_3). Since the decarbonylation of aldehydes is known to proceed in an intramolecular and stereospecific fashion[9] the production of both erythro and threo 5 from stereochemically pure 4 indicates that if the reaction proceeds as shown the initial allylic isomerization and enol tautomerization are not

Scheme 1



stereospecific (i.e. the tautomerization of the enol to the aldehyde produces both *erythro* and *threo* aldehydes).[10] The predominant intramolecularity of the present reaction was indicated by the concurrent decarbonylation of **4** and cinnamyl alcohol. Mass spectral analysis of the products revealed the dideuterophenyl propane (**5**) obtained contained over 90% of the deuterium which was originally in **4** whereas the ethyl benzene obtained from cinnamyl alcohol contained a maximum of 10% deuterium.

Investigations into the reaction of **1** with related unsaturated oxygenated organic compounds is continuing.

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(7) The use of nitrile solvents prevents the dimerization of **1** under the reaction conditions (ref. 2).

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(9) Decarbonylation of aldehydes attached to benzylic carbons with **1** proceeds with 94% retention of configuration and quantitative retention of deuterium label. H.M. Walborsky and L.E. Allen, *Tetrahedron Letters*, 823 (1970).

(10) Comparison of the n.m.r. spectrum of a sample of **5** derived from **4** and **1** with that of a sample of *threo*-**5** prepared by catalytic deuteration of *trans*-1-phenylprop-1-ene revealed differences attributable to the presence of *erythro* **5** in the former.