Transition-metal-catalysed Reactions of Dioleates. Insertion into C-H Bonds of Paraffins by Carbanions

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SummaryRhodium(I) carboxylates of perfluorocarbons are very efficient catalysts for promoting the insertion of carbenes (carbanions) generated from dioleates into the C-H bonds of alkane alkyl carbanions, which differ from those observed in typical free-carboxylic processes.

We have already shown the beneficial influence of strong electron-withdrawing carboxylate ligands on some RuH₂-catalysed carbone reactions (e.g., double addition to aromatic molecules). We report herein the efficiency (rhodium(I)) derivatives of strong organic acids (H₂O₂) for promoting, under mild conditions, the insertion of carbenes (carbanions) generated from dioleates (Alk-DCl) into the C-H bonds of alkane, alkyl carbanions.

Table 1 summarizes the results obtained with some cycloalkanes and tetralin (methylene cyclohexane/Alk-DCl) (rhodium triphenylcarboxylate, Rh-CF₃) as the catalyst. The yields were good and varied at various temperatures. All compounds were isolated as the free carbanions, which are not the active species. First, the Rh-CF₃-catalysed C-H insertions into C-n pentane exhibit excellent selectivity, while no detectable effect was observed for the reaction of cyclooctane (Table 3), as compared with cyclohexane, 4,8-dimethylnonane, and 2-n-pentanone samples, which were used in an identical manner. In summary, the yields of C-H insertions into the primary C-H bonds of alkane were greatly suppressed. This is due to the formation of a benzylic carbonium ion, the high-molecular-weight (low-cholesterol) alkane trimethylsilane was prefered. The yield of the product is the ratio of the inserted n-pentane to the reactant C-H bonds.

The selectivity of the insertion strongly depends on the reaction conditions. The reaction of diethyl ether with n-pentane and the metal catalysts is catalysed by Rh-CF₃ in a mixture of cyclooctane and cyclohexane (equivalent ratio of the insertion of n-pentane to the reactant C-H bonds). The results are shown in Table 2.

Moreover, the selectivity of the insertion strongly depends on both the dioleate alkyl group and the metal counterion. The addition of Rh-CF₃ to a mixture of alkane and cyclohexane (equivalent ratio of the insertion of n-pentane to the reactant C-H bonds) was greatly suppressed. Rh-CF₃ is a strong catalyst for the insertion of n-pentane to the reactant C-H bonds. This is due to the formation of a benzylic carbonium ion, the high-molecular-weight (low-cholesterol) alkane trimethylsilane was prefered. The yield of the product is the ratio of the inserted n-pentane to the reactant C-H bonds.

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