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TRANSITION METAL CATALYSED REACTIONS OF DIAZOCOMPOUNDS - II

INSERTION IN THE HYDROXYLIC BOND

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Since the pioneer work of Meerwein and co-workers on the reaction between methylene and 2-propanol (1) and of Yates on the copper-catalysed decomposition of diazoketones in alcohols and phenols (2), insertion of various carbenes and carbenoids in hydroxylic bonds has been largely investigated In the course of our study of the transition metal-catalysed (3) reactions of diazoalkanes, we have already succeeded in demonstrating the feasibility of a selective and quantitative cyclopropanation of olefins in the presence of palladium salts with some degree of stereocontrol (4).
We are now able to report an homogeneous rhodium-catalysed insertion of ethyl diazoacetate (EDA) in the hydroxylic bond of alcohols, water and weak acids :

$$R-O-H + N_2CHCO_2CH_2CH_3 \xrightarrow[\text{Catalyst}]{25^\circ\ C} R-O-CH_2CO_2CH_2CH_3 + N_2$$

These reactions are nearly quantitative at room temperature, even with very low catalyst concentrations. In each case, the balance in mainly constituted of ethyl maleate and fumarate resulting from the formal dimerization of the corresponding carbene. Some of our results are summarized in the following table.

Catalyst	$\frac{\text{EDA}}{\text{Catalyst}}$	R	% Yield
$Rh_2(OAc)_4$	600	C_2H_5 -	88
$Rh_2(OAc)_4$	600	$(CH_3)_2CH$ -	83
$Rh_2(OAc)_4$	600	$(CH_3)_3C$ -	82
$Rh_2(OAc)_4$	600	H -	80
$Rh_2(OAc)_4$	600	CH_3CO -	93
Rh $Cl_3 \cdot 3\ H_2O$	125	C_2H_5-	64
Rh $Cl_3 \cdot 3\ H_2O$	125	$(CH_3)_3C$ -	58
Rh $Cl(PPh_3)_3$	125	C_2H_5 -	49

Reactions were carried out using the corresponding alcohol as solvent (50 cc) and adding at a constant rate 5.10^{-2} mol. of EDA in 4 h. with a dropping funnel. All the products obtained were identified by their physical properties.

As shown in the table, ethoxycarbonylcarbene is inserted with equal efficiency in the hydroxylic bond of ethanol and t-butanol. However, competitive reactions with equimolecular mixtures of alcohols gave the following relative reactivities of OH bond toward attack by the carbethoxycarbene produced by this catalytic way :
ethanol 2.12, propan-2-ol 1.20, and t-butanol 1.00. This is also the order of decreasing acidity of the alcohols as well as the order of increasing steric hindrance.

Photolysis of diazomethane in the same alcohols give a similar order of reactivity (5) : however, by-products resulting from C - H insertion are also formed which are not found in the present catalytic reactions.

The specificity and generality of our system is to be compared also with the cupric chloride-catalysed decomposition of EDA in various alcohols which afforded OH insertion products only in low yields (6). Thermal and photolytic activation as well as acid catalysis led again to the same lack of specificity and generality (7, 8, 9).

On the other hand, the determining influence of the transition metal (probably through initial formation of an EDA-metal complex) is also reflected in the first-order dependance on the rhodium concentration found by spectroscopic and volumetric measurements.

Further work is in progress to better define mechanistic and preparative aspects of this method. For instance, methylation of alcohols by gaseous diazomethane seems to be particularly promising. However, the most interesting development will be probably the formal extension of the Sandmeyer reaction to aliphatic diazocompounds, since first studies with aqueous solutions of NaCl, KBr and KI show an important competition between the nucleophilic anions and the hydroxyl group to yield the corresponding halogenoacetates.

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