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TRANSITION METAL CATALYSED REACTIONS OF DIAZOCOMPOUNDS - PART III
A ONE-STEP SYNTHESIS OF SUBSTITUTED FURANES AND ESTERS.

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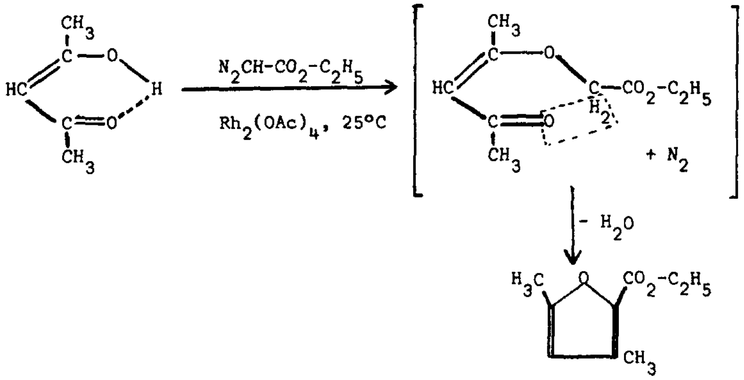
The important influence of copper in the reactions of diazoalkanes with various substrates is well-known (1). Since the role of copper can be tentatively attributed to its coordinating abilities, we have investigated several reactions of diazocompounds catalysed by different transition metal complexes. Even under very mild conditions, specially with palladium and rhodium salts, much better yields and selectivities are obtained (2) and sometimes new reaction pathways are observed (3) with all the characteristic features of coordination-controlled mechanisms.

After the nearly quantitative reaction of diazoacetic esters with alcohols including the competitive reaction between nucleophiles, (2b), we now wish to report an interesting extension of the rhodium (II)-catalysed insertion of carbomethoxycarbene in various polar X-H bonds following the general scheme :

$$\text{R-X-H} \ + \ \text{N}_2\text{CH-CO}_2\text{CH}_3 \xrightarrow[-\ \text{N}_2]{\text{Rh}_2(\text{OAc})_4} \text{R-X-CH}_2\text{-CO}_2\text{CH}_3$$

With phenol, thiophenol and the isomeric butyl mercaptans, the reactions are rather specific and yields are good (respectively 90, 92 and 70 % yield) at room temperature, whereas aniline reacts at 80°C to give 70 % of the insertion product. These reactions have been carried out either neat or in solution (benzene or ethylene glycol dimethyl ether).

Special attention should be devoted to the reaction of acetyl-acetone with ethyl diazoacetate (diazo/catalyst molar ratio : 600) which allows the fast one-step synthesis of 3,5-dimethyl-2-furoic acid ethyl ester (II) in 68 % yield at room temperature, most probably by cyclisation of the intermediate ester (I) :



(I)

(II)

(II) was identified by analytical data and its physical properties. Found : C : 64,10 % ; H : 7,04 % ; m/e = 168. Calculated for $C_9H_{12}O_2$: C : 64,27 % ; H : 7,19 % ; m/e = 168. Its I.R. spectrum (CCl_4) exhibits strong bands at 3,35, 5,85, 6,24, 6,46 and 11,60 microns and its U.V. spectrum at 268 nm. in the same solvent. N.M.R. absorptions (CCl_4) occur as expected at 1,35 (3 H), 2,26 (3 H), 2,30 (3 H), 4,25 (2 H) and 5,88 (1 H) p.p.m. from T.M.S.

These results stress again the great interest of transition metal complexes in organic synthesis ; mechanistic and preparative implications of these results are under investigation in our laboratory.

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