

To check this supposition the reaction mixture was treated at 0°C with an equivalent amount of ${}^3\text{HCl}$, followed by fractionation of the solution. By radio-GLC (20% Carbowax on Chromosorb W at 55°C) labelled ethyl formate was shown to be present in the distillate with the expected specific activity. This means that the hitherto unknown formate anion is actually formed during the reaction. Its formation may be favoured by resonance stabilization. Excess of Li-compounds favours both the formation of ethyl formate anion and the conversion into aldehyde. Excess of formate increases the yield of aldehyde to some extent, but simultaneously depletes the α -anion of the acid.

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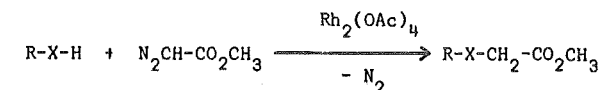
TRANSITION METAL CATALYSED REACTIONS OF DIAZOCOMPOUNDS - PART III
A ONE-STEP SYNTHESIS OF SUBSTITUTED FURANES AND ESTERS.

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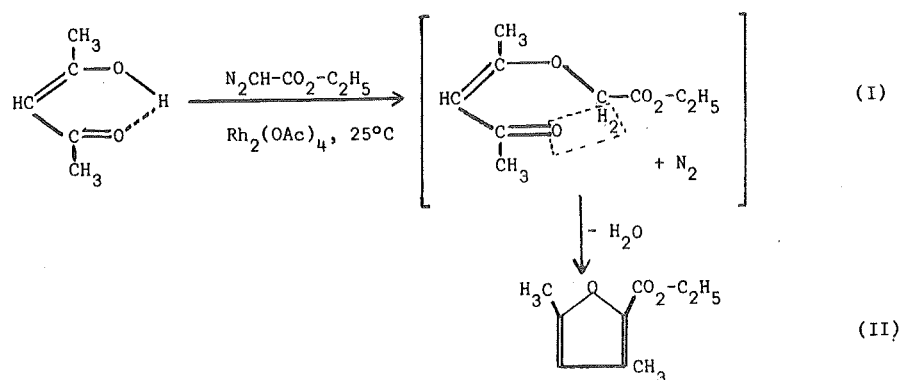
The important influence of copper in the reactions of diazoalkanes with various substrates is well-known (1). Since the role of copper can be tentatively attributed to its coordinating abilities, we have investigated several reactions of diazocompounds catalysed by different transition metal complexes. 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 :



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) :



(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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COUROUPITINE A, A NEW ALKALOID FROM COUROUPITA GUIANENSIS

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Couroupita guianensis Aubl. is commonly known as cannon ball tree as its fruit resembles a cannon ball. Some chemical works have already been done on the fruits¹, flowers² and the stem bark³, but no alkaloidal constituent has yet been isolated from any part of the plant. During the course of our investigation on matured fruits we have been able to isolate two alkaloids; the present communication deals with the structure elucidation of one of them designated as Couroupitine A. Various spectrometric data together with biogenetic consideration led us to suggest structure (I) for this compound.

Petroleum extract of dried and powdered fruits on repeated chromatographic purification followed by crystallisation from MeOH- $CHCl_3$ mixture yielded couroupitine A as yellow needles, m.p. 265-66°, $[\alpha]_D^{25} \pm 0^\circ$ ($CHCl_3$) and gave a molecular ion peak at m/e 248, confirming the molecular formula $C_{15}H_{18}O_2N_2$ assigned on the basis of elementary analysis. The UV spectrum exhibited λ_{max}^{EtOH} 225, 251 and 315 nm (inflection) (log ϵ 4.46, 4.68 and 4.04 respectively) characteristic of a pseudo indoxyl skeleton⁴. The IR spectrum (nujol) showed bands at 1725 (5-ring ketone in conjugation with aromatic ring), 1680, 1310 (amide I and amide III bands), 1519, 1550, 760 (phenyl) and 1350 cm^{-1} (C-N stretching). The NMR spectrum (100 MHz, $CDCl_3$, TMS) did not show the presence of any saturated aliphatic proton, instead it indicated the aromatic character of all the 8 protons. The doublet centred at δ 8.61 was assigned to H_a present in proximity with the N atom in the pyridine ring. The H_b and H_c appeared as a sextet centred at δ 7.51. Thus as it would be expected the three protons