To check this supposition the reaction mixture was treated at 0°C with an equivalent amount of \( \text{HCl} \), followed by fractionation of the solution. By radio-GLC (20% Carbowax on Chromosorb W at 30°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 stabilisation. 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 \( \alpha \)-anion of the acid.

REFERENCES


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 diazoalkanes catalysed by different transition metal complexes. Even under very mild conditions, especially 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 carbonylcarbene in various polar \( \pi \)-bonds following the general scheme:

\[
\begin{align*}
\text{Rh}_2(\text{OAc})_4 & \rightarrow R-X-H + \text{H}_2 \rightarrow \text{Rh}_2(\text{OAc})_4 + \text{R}-\text{CH}_2\text{CO}_2\text{H} \\
\text{R}-\text{CH}_2\text{CO}_2\text{H} + \text{H}_2 & \rightarrow \text{R}-\text{CH}_2\text{CO}_2\text{H}
\end{align*}
\]

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 acetylacetone with ethyl diazoacetate (diazocatalyst molar ratio > 500) which allows the fast one-step synthesis of 3,5-dimethyl-2-furoic acid ethyl ester (II) in 88 % yield at room temperature, most probably by cyclisation of the intermediate ester (I):
COOURPITINE A, A NEW ALKALOID FROM COOURPITA GUIANENSIS

A. E. Sen, S. B. Mahato and N. L. Datta

Indian Institute of Experimental Medicine, Calcutta-32, India.

(Received 22 December 1974; accepted for publication 11 January 1975)

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 fruits\(^1\), flowers\(^2\) and the stem bark\(^3\), but no alcaloidal 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 biogenic 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\(^\circ\), \(\log \epsilon_\lambda^\text{max} = 4.66\) and gave a molecular ion peak at \(m/e = 248\), confirming the molecular formula \(C_{19}H_{21}O_2\) assigned on the basis of elementary analysis. The UV spectrum exhibited \(\log \epsilon_\lambda^\text{max} = 225, 251\) and 315 nm (inflection) \((\log \epsilon = 4.46, 4.66\) and 4.04 respectively\) characteristic of a pseudo indoxyl skeleton\(^4\). The IR spectrum (Nujol) showed bands at 1725 (S-ring ketone in conjugation with aromatic ring), 1680, 1510 (amide I and amide III bands), 1519, 1550, 760 (phenyl) and 1350 \(\text{cm}^{-1}\) (CON stretching). The NMR spectrum (100 MHz, CDCl\(_3\), TM). 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 \(\delta 6.61\) was assigned to \(H_8\) present in proximity with the \(N\) atom in the pyridine ring. The \(H_8\) and \(H_9\) appeared as a sextet centred at \(\delta 7.51\). Thus as it would be expected the three protons...