

A CONTRIBUTION TO THE STUDIES OF ELIMINATION  
REACTIONS OF MANNICH BASES, USING POLAROGRAPHIC METHOD

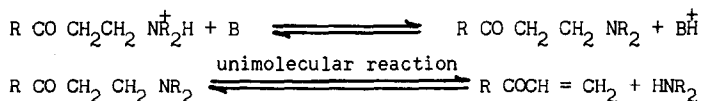
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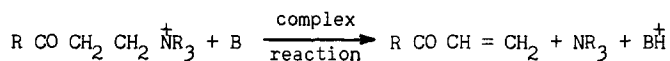
DURING the study of the mechanism of alkylation by Mannich bases, the elimination reaction of 2-piperidinomethylcyclopentanone and of  $\omega$ -piperidino-propiophenone and its methiodide was studied. The polarographic method enabled us to follow the change of concentration with time of both the Mannich base and the resulting  $\alpha$ ,  $\beta$ -unsaturated ketone from their separated waves. The reaction products were identified by paper and thin layer (alumina) chromatography.

As anticipated the reversible elimination reaction of Mannich bases proceeds by a different mechanism to the irreversible process observed with the corresponding quaternary salt. The isolated elimination reactions were compared by measuring the initial reaction velocities, thus eliminating the effect of the consecutive inactivation of the unstable  $\alpha$ ,  $\beta$ -unsaturated ketone which is formed. With increasing pH-value, the measured rate constant of the initial reaction follows the course of a dissociation curve in the case of Mannich bases, but increases steadily for the methiodide. The elimination reaction of Mannich bases is thus not acid-base catalysed, but the elimination step is preceded by a dissociation equilibrium:



This view is substantiated by the coincidence of the potentiometrically measured pK-value with the pH-value at which the rate constant reaches the half of its maximum value, by the slope of the pH-dependence of the rate constant corresponding to a transfer of one proton and finally by the absence of any dependence of the measured rate constant on the type and concentration of the buffer used. The small influence of the ionic strength is also in accordance with the unimolecular rate determining step.

On the other hand, the quaternary salts undergo a generally base catalysed reaction of the type



This is manifested (in addition to the difference in the pH-dependence) by the dependence of the measured initial rate constants on capacity and kind of the buffer. The slopes of the linear relationships between rate constants and buffer capacity at given pH-values do not correspond to a simple Brønsted equation. It is thus assumed that a more complicated mechanism than E2 is operating.

A similar behaviour was observed for the elimination reaction of the 6-methylthio-cyclohept-2-en-one, the intermediate in the elimination reaction of thioanalogue of tropinone. Further studies on elimination reactions, Michael addition and the total alkylation reactions of Mannich bases are in progress.