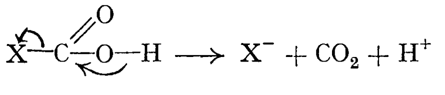
362. *Experiments on the Mechanism of Decarboxylation. Part I. Decomposition of Quinaldinic and* iso*Quinaldinic Acids in the Presence of Compounds containing Carbonyl Groups.*

By P. Dyson and D. Ll. Hammick.

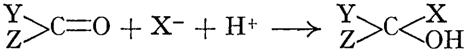
When quinaldinic and *iso*quinaldinic acids are heated with excess of certain aldehydes and ketones (benzaldehyde, anisaldehyde, acetophenone), carbon dioxide is evolved and products are obtained which indicate that the decarboxylation takes place in accordance with the scheme *A* (below), where X is the quinolyl or *iso*quinolyl radical and Y and Z may be aryl, alkyl or hydrogen.

A mechanism for the loss of carbon dioxide from a carboxyl group is



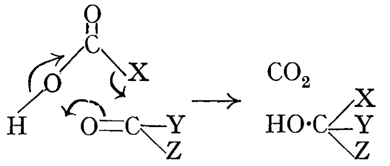
$$X{-}C(=O){-}O{-}H \longrightarrow X^- + CO_2 + H^+$$

if provision can be made in the reacting system for the stabilisation of the free radical X^- and the proton H^+ by subsequent (or simultaneous) reaction. In the preliminary experiments here described, such provision has been made by causing the decarboxylation of quinaldinic and *iso*quinaldinic acids to occur in the presence of excess of substances containing the carbonyl group (benzaldehyde, anisaldehyde and acetophenone), which is known from its reactions, such as the formation of cyanohydrins (Robinson, *J. Soc. Dyers and Colourists*, 1934, 65), to be capable of the electromeric activation process $>C{=}O$. Under such conditions, the above mechanism might be expected to lead to the formation of carbinols, thus :



$$\begin{smallmatrix}Y\\Z\end{smallmatrix}{>}C{=}O + X^- + H^+ \longrightarrow \begin{smallmatrix}Y\\Z\end{smallmatrix}{>}C{<}\begin{smallmatrix}X\\OH\end{smallmatrix}$$

or, in one process,



(*A*)

(for aldehydes, Z = H)

The choice of quinaldinic and *iso*quinaldinic acids for the study of decarboxylation in the presence of carbonyl groups was determined by the fact that their structures are such that decomposition of the type suggested above might be expected to be facilitated by the inductive effect of the $\overset{+\!\rightarrow}{C{=}N}$ linkages in their molecules.

In each case decarboxylation was brought about by boiling the acid in excess of the other reagent. As will be seen in the Experimental part, we have been able to isolate either the carbinol to be expected on the basis of the mechanism suggested above or its ketonic oxidation product. Thus from benzaldehyde we have obtained *phenyl-2-quinolylcarbinol* and *phenyl-1-*iso*quinolylcarbinol*, and from acetophenone and quinaldinic acid we have isolated *phenyl-2-quinolylmethylcarbinol*, $C_9H_6N{\cdot}CPhMe{\cdot}OH$. By the decomposition of quinaldinic acid in boiling anisaldehyde we were unable to obtain the expected anisyl-2-quinolylcarbinol, owing apparently to its ready oxidisability to the corresponding *ketone*, which was the substance actually isolated. The unsubstituted phenyl-2-quinolylcarbinol is less readily oxidised to the ketone, though crystallisation from hydroxylic solvents in the presence of air converts it into phenyl 2-quinolyl ketone, m. p. 107°, identical with an authentic specimen (Besthorn, *Ber.*, 1906, **39**, 2330). It appears to be quite stable in contact with non-polar solvents such as ligroin. The corresponding phenyl-1-*iso*quinolylcarbinol is, on the other hand, comparatively stable in air and can be crystallised from any suitable solvent.

The conclusion we draw from these preliminary experiments is that the decarboxylation mechanism put forward above is in accordance with the facts observed when quinaldinic and *iso*quinaldinic acids are decomposed in certain aldehydes and ketones at their boiling points. Experiments are in hand to ascertain the generality of this type of reaction.

EXPERIMENTAL.

*Quinaldinic Acid and Benzaldehyde. Preparation of Phenyl-*2-*quinolylcarbinol and of Phenyl* 2-*Quinolyl Ketone.*—Quinaldinic acid (5 g.) was boiled with freshly distilled benzaldehyde (40 g.) in a 100 c.c. flask fitted with an air condenser until carbon dioxide was no longer evolved (2—3 hours). The mixture was poured into water, acidified with hydrochloric acid, and separated from the excess of benzaldehyde. After extraction with ether to remove traces of aldehyde and other impurities, the acid solution was made alkaline with sodium hydroxide. The oil that separated was taken up in ether and dried with anhydrous sodium sulphate. The oil remaining after the removal of the ether was dissolved in light petroleum (b. p. 40—60°) and left overnight in the ice chest. The colourless crystals (2·2 g.) that separated were recrystallised from light petroleum (b. p. 49—60°); m. p. 50—60°. Yield, 33% (Found: C, 81·8; H, 5·3. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5%).

The above reaction, carried out in a stream of nitrogen, gave a yield of 42%.

All attempts to prepare derivatives of this *carbinol* failed owing to the readiness with which it is oxidised to phenyl 2-quinolyl ketone (2-benzoylquinoline).

Quinaldinic Acid and Anisaldehyde. Preparation of Anisyl 2-*Quinolyl Ketone.*—Quinaldinic acid (5 g.) was refluxed for 3 hours with freshly distilled anisaldehyde (40 g.); evolution of carbon dioxide had then ceased. The product was worked up exactly as above for the reaction with benzaldehyde. Instead, however, of the corresponding carbinol we obtained *anisyl* 2-*quinolyl ketone* (0·72 g.), which formed colourless needles, m. p. 78°, after two recrystallisations from light petroleum (b. p. 40—60°); yield, 10%. The yield was increased to 30% (1·5 g. of the ketone from 5 g. of quinaldinic acid) by carrying out the reaction in a stream of nitrogen (Found: C, 77·8; H, 4·9. $C_{17}H_{13}O_2N$ requires C, 77·6; H, 4·9%). The 2 : 4-*dinitrophenylhydrazone* had m. p. 242° (Found: C, 62·6; H, 4·0. $C_{23}H_{17}O_5N_5$ requires C, 62·3; H, 3·8%). The picrate, precipitated from ethereal solution and recrystallised from water, had m. p. 165°. The oxime was prepared by refluxing 0·263 g. of the ketone (1 mol.), 0·08 g. of hydroxylamine hydrochloride (1·1 mols.), and 0·1 g. (1·25 mols.) of anhydrous sodium acetate in 10 c.c. of 50% aqueous alcohol for 2½ hours. It separated on dilution with water and was crystallised first from aqueous alcohol and finally from benzene; m. p. 145°.

*Quinaldinic Acid and Acetophenone. Preparation of Phenyl-*2-*quinolylmethylcarbinol.*—Quinaldinic acid (5 g.) was refluxed for 3 hours with freshly distilled benzophenone (40 g.), and the product worked up as before. The *carbinol* separated as colourless crystals from the ethereal extract and was recrystallised from light petroleum (b. p. 40—60°). Yield, 1·58 g. (32%); m. p. 100° (Found: C, 81·5; H, 6·1; N, 5·6. $C_{17}H_{15}ON$ requires C, 81·6; H, 6·0; N, 5·6%). The picrate, obtained from ethereal solution and recrystallised twice from water, had m. p. 169° (decomp.).

iso*Quinaldinic Acid and Benzaldehyde. Preparation of Phenyl-*1-iso*quinolylcarbinol and Phenyl* 1-iso*Quinolyl Ketone.*—*iso*Quinaldinic acid (2 g.) was refluxed with freshly distilled benzaldehyde (10 g.), evolution of carbon dioxide ceasing after 2 hours. The product, worked up as in the preceding experiments, separated from the ethereal extract as an oil which solidified on standing (1·14 g.; yield 57%); it had m. p. 106° after two recrystallisations from light petroleum (b. p. 40—60°) (Found: C, 81·9; H, 5·7; N, 6·1. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%). The *benzoyl* derivative, obtained by shaking the carbinol (0·14 g.) and benzoyl chloride (0·11 g.) in 5 c.c. of 2N-sodium hydroxide for 3 hours, had m. p. 158—159° after recrystallisation from 50% aqueous alcohol (Found: C, 80·8; H, 5·2. $C_{23}H_{17}O_2N$ requires C, 81·4; H, 5·0%).

A solution of the carbinol (0·23 g.) in 5 c.c. of 50% aqueous acetic acid containing 0·1 g. of potassium dichromate was kept at room temperature with occasional shaking for 24 hours. The ketone separated on dilution with water and after drying was crystallised from light petroleum (b.p. 40—60°); m. p. 76—77° (Kaufmann, *Ber.*, 1914, **47**, 2935) (Found: C, 82·7; H, 5·0. Calc. for $C_{16}H_{11}ON$: C, 82·4; H, 4·7%).

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