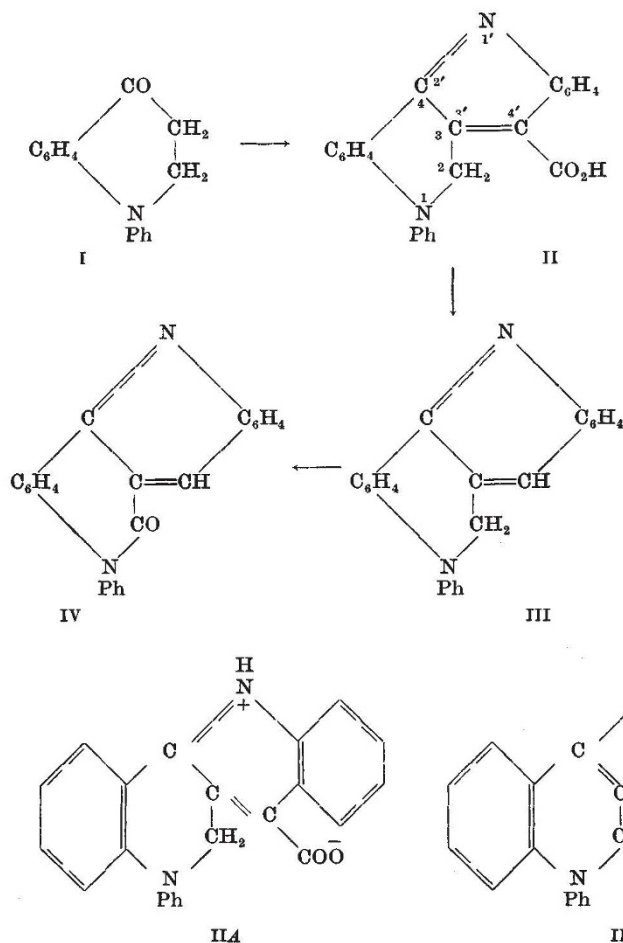


LETTERS TO THE EDITORS

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Structure and Colour in the 1:2-Dihydroquinolino(3':2':3:4)quinolines

THE preparation of 4-keto-1-phenyl-1:2:3:4-tetrahydroquinoline (I) has recently been described by Cookson and Mann¹, who showed that the phenyl-hydrazone of this ketone, when boiled with alcoholic hydrogen chloride, underwent indolization and dehydrogenation to give 1-phenyl- ψ -indolo(3':2':3:4)-quinoline. This yellow base gives colourless salts with acids, and further work has now confirmed the



structures suggested by the above workers for the base and its salts.

When the quinolone (I) is subjected to the Pfitzinger reaction, the products obtained show some very interesting features. If the quinolone (I) is boiled with isatin in sodium hydroxide solution, subsequent acidification gives 4'-carboxy-1-phenyl-1:2-dihydroquinolino(3':2':3:4)quinoline (II) as deep red needles. An alcoholic solution of this compound has the properties of an indicator, for the addition of an excess of alkali causes the colour of the solution to change to bright yellow, while subsequent acidification restores the deep red colour. The potassium salt can

readily be isolated as bright yellow needles. If the acid (II) is heated in a vacuum, decarboxylation occurs, and 1-phenyl-1:2-dihydroquinolino(3':2':3:4)-quinoline (III) distils. This base forms bright yellow crystals, but its hydrochloride forms deep garnet-red crystals.

Now the formal structure (II) does not account for the deep red colour of this acid. It is clear, however, from the above evidence that the free acid must exist as a zwitter-ion, which would be a resonance hybrid of the three canonical forms (IIA), (IIB) and (IIC) and hence certainly coloured. The potassium salt, on the other hand, would necessarily have a structure of type (II), in which this resonance could not occur, and one would expect it to be much paler in colour. The decarboxylated base, however, has the structure shown in (III), and thus has also a yellow colour. Salt formation by proton addition gives a cation which again is a resonance hybrid of three canonical forms precisely similar to (IIA), (IIB) and (IIC), with, of course, the $-\text{COO}^-$ group replaced by hydrogen; and hence these salts in turn have a deep red colour similar to that of the free acid (II).

The base (III) shows one remarkable reaction. If the powdered crystals are heated at 120° in a stream of air, oxidation readily occurs with the formation of 1-phenyl-2-keto-1:2-dihydroquinolino(3':2':3:4)quinoline (IV). This compound, which forms cream-coloured crystals, can also be obtained by oxidizing the base (III) with a cold acetone solution of potassium permanganate, but not with hydrogen peroxide. The keto-base (IV) forms yellow salts, in marked distinction to the deep red salts of the base (III). This is not unexpected, because although the cation of these yellow salts might also be a resonance hybrid of three canonical forms similar in general type to (IIA), (IIB) and (IIC), the contribution by the third form, having a positive charge on the phenyl-nitrogen atom, must now be very small, and the colour correspondingly less intense.

The structure of the keto-base (IV) has been indicated by its chemical properties, but placed

beyond reasonable doubt by an infra-red spectroscopic investigation kindly undertaken by Dr. G. B. B. M. Sutherland.

The investigation of the compounds produced by the Fischer indolization and the Pfitzinger reaction when applied to a number of analogous cyclic ketoamines, for example, 4-keto-julolidine, has also been undertaken and will be described later.

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May 19.

¹J. Chem. Soc., 67 (1949).