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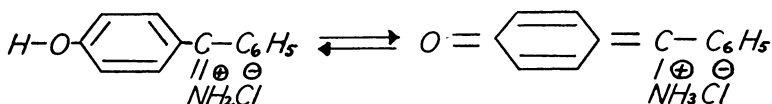
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ABSORPTION SPECTRA OF KETIMINES WITH REFERENCE TO KETIMINE-ENAMINE TAUTOMERISM

J. B. CULBERTSON

The first reported preparation (Hoesch, 1915, 1917) of diphenyl ketimine salts in which hydroxy groups were 2- and 4- positions indicated that these compounds were unusually stable toward hydrolysis to the corresponding ketones and ammonium chloride. Subsequent studies (Culbertson, 1927, 1931) have suggested that the resistance of these phenolic ketimine salts toward hydrolysis was due to a ketimine-enamine tautomerism, or resonance, resulting in masking the ordinary reactivity of the imine ($>N-H$) group toward reaction with water. The proposed tautomerism may be represented as follows:



This involves a change from a benzoid-imine to a quinoid-amine structure, the latter being unhydrolyzable. Or, a resonance of the positive ion may be the stabilizing factor here. The situation is quite similar to that for auramine. The great stability of this dye toward hydrolysis to Michler's ketone, the fact that its most intense color is produced in acid solution, and spectroscopic studies have been cited in support of a quinoid-amine structure. Nevertheless, that it does have a measurable rate (Holmes and Darling, 1924) of hydrolysis indicates the presence of the benzoid-imine form in tautomeric equilibrium with the quinoid-amine. Comparative velocities of hydrolysis, colors of the free bases and salts, solubilities in various solvents, and other properties have rather uniformly suggested this tautomerism for the 2- and 4- hydroxydiphenyl ketimines. Most striking is the fact that the 2- and the 4- hydroxydiphenyl ketimine hydrochlorides are hydrolyzed much more slowly, while the 3- hydroxy compound more rapidly, than the unsubstituted diphenyl ketimine hydrochloride.

Absorption spectra in the ultra-violet have furnished additional evidence for some structure in the 2- and 4-hydroxydiphenyl ketimines different from that of the 3-hydroxy- and other diphenyl ketimines. Twelve variously substituted diphenyl ketimines have been included in this study. Absolute methyl or ethyl alcohols were used as solvents. Complete absorption in the ultra-violet was observed for all of these ketimines at 10-fold dilutions down to 0.0001 M. where selective absorption appeared. Consequently all observations were made at this concentration. In every case where a benzoid-imine quinoid-amine structure would appear possible there has been a distinct absorption band in the near ultra-violet (320 to 330 millimicrons), whereas for the others absorption was more remote in the ultra violet (250 to 270 millimicrons).

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