[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ENOLIZATION OF 1,2-DIKETOHYDRINDENE AND OF 1,2-DIKETO-3-PHENYLHYDRINDENE*

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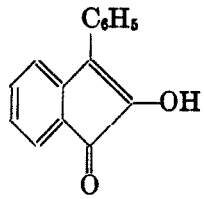
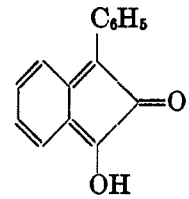
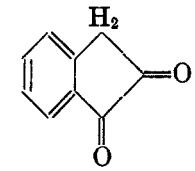
In a previous paper[1] chemical evidence was presented which indicated that 1,2-diketo-3-phenylhydrindene is completely enolic and that the enolic form has structure I rather than II. Evidence for the structure of this compound and for that of its unsubstituted analog, 1,2-diketohydrindene, III, based on ultraviolet absorption measurements is now brought forward.



I



II



III

The absorption curves of the compounds investigated, given in Figures 1 and 2, fall into two distinct classes. In one of these the maxima (with the exception of that for diphenylindone) are close to 2500Å, while in the other they are close to 2730Å; also, the absorption of the former class is considerably the stronger.

Since the optical properties of 1,2-diketo-3-phenyl-hydrindene[1] (curve 4) are similar to those of 2-methoxy-3-phenylindone[1] (curve 5) and 2,3-diphenylindone[2] (curve 7), the enolic structure I of this compound is indicated.

The absorption of 1,2-diketohydrindene[3] (curve 6) however, places it in a class with 3-methyl-3-phenyl-[4] (curve 1), 3-hydroxy-3-phenyl-[4] (curve 2), and 3,3-dimethyl-1,2-diketohydrindene[4] (curve 3), compounds which

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[1] KOELSCH, *J. Am. Chem. Soc.*, **58**, 1321 (1936).

[2] Prepared by the action of phenylmagnesium bromide on 2-phenylindandione-1,3. Compare KOELSCH, *J. Am. Chem. Soc.*, **58**, 1328 (1936).

[3] PERKIN, ROBERTS, AND ROBINSON, *J. Chem. Soc.*, **101**, 232 (1912).

[4] Preparation to be described in a future paper from this laboratory.

must have the diketonic structure. The chemical behavior of the unsubstituted diketone also indicates that it is completely ketonic. The compound dissolves in aqueous alkali without the formation of a blue color, and the solution so obtained does not give back the diketone on acidification.[3] Also, the diketone is quite resistant to the action of bromine, even in hot acetic acid, although a dibromo substitution product can be obtained under the proper conditions.

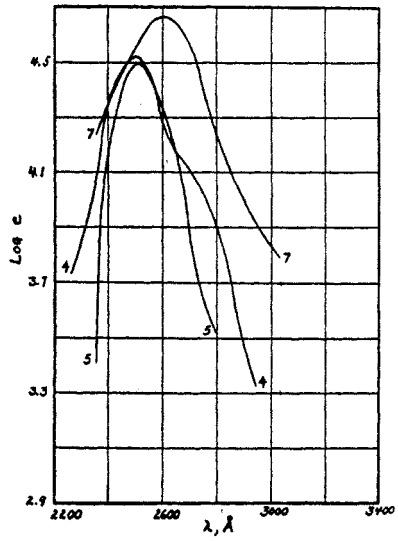

FIG. 1

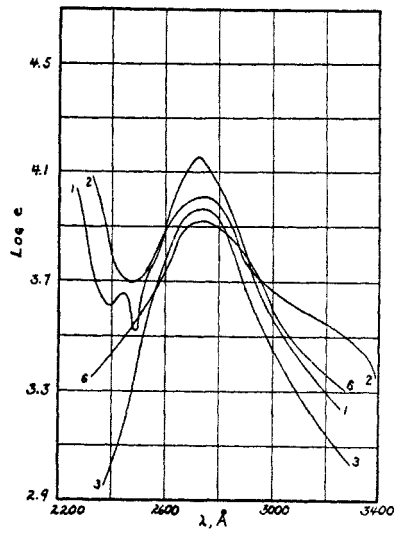

FIG. 2

FIGURE 1.—ABSORPTION CURVES OF INDENONES

Curve 4 = 1,2-Diketo-3-phenylhydrindene. Curve 5 = 2-Methoxy-3-phenylindone. Curve 7 = 2,3-Diphenylindone.

FIGURE 2.—ABSORPTION CURVES OF DIKETONIC SUBSTANCES

Curve 1 = 1,2-Diketo-3-methyl-3-phenylhydrindene. Curve 2 = 1,2-Diketo-3-hydroxy-3-phenylhydrindene. Curve 3 = 1,2-Diketo-3,3-dimethylhydrindene. Curve 6 = 1,2-Diketohydrindene.

EXPERIMENTAL

The compounds used were prepared by methods described in the reference given. Special attention was paid to the purity of the substances, and those compounds which are unstable, 1,2-diketo-3-phenylhydrindene and its enol ether, were prepared immediately before the optical measurements were made.

The absorption curves were determined photographically by means of a Judd-Lewis photometer and a Hilger quartz spectrograph using a hydrogen arc as a light source. Cyclohexene was used throughout as a solvent. In Figures 1 and 2 the logarithm of the molar extinction coefficient is plotted as a function of wave-length in Ångstroms.

Bromination of 1,2-diketohydrindene.—1,2-Diketohydrindene (1 g.) can be boiled

with bromine (2.3 g.) in acetic acid (20 ml.) without change, but it reacts when a little sodium acetate or a few drops of hydrobromic acid is added. The dibromodiketone separates on cooling, and after recrystallization from acetic acid it forms orange plates (1.1 g.) that melt at 141–142°.

Anal. Calc'd for $C_9H_4Br_2O_2$: C, 35.5; H, 1.3.
Found: C, 35.8; H, 1.9.

The bromine is removed completely (0.132 g. subst. gave 0.159 g. AgBr; calc'd 0.163 g.) when the dibromo compound is boiled with alcoholic silver nitrate for one minute. Hence both bromine atoms are in the alicyclic ring.

SUMMARY

The ultraviolet absorption of 1, 2-diketo-3-phenylhydrindene indicates that it exists in the enolic form, while that of 1, 2-diketohydrindene indicates that this compound is ketonic. The chemical behaviors of these substances are consistent with these structures.