[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

1,2-Diketo-3-phenylhydrindene[1]

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Few α-diketones derived from hydrindene have been studied and some phenomena observed in connection with these compounds have been incorrectly interpreted. These α-diketones may be conveniently divided into three classes corresponding to the number of activated hydrogen atoms they contain: class A having none, B one and C two.

Representatives of class C have been prepared by Perkin and co-workers.[2] No compounds of class A have been described. Since representatives of these two classes do not enolize and since enolization is the main topic investigated in the present research, a discussion of these types will be deferred for later papers.

In class B, the compounds represented in the accompanying formulas (I, II, III, IV) have been
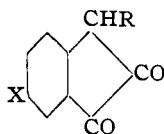
I, R = CH₃, X = H
II, R = CH₃, X = NO₂
III, R = CH₃, X = NHCOC₆H₅
IV, R = CH₂COOH, X = H

investigated by v. Braun and co-workers.[3] These substances, themselves red, are easily soluble in aqueous alkalies, the solutions so obtained being

deep blue or green. Now 1,3-diketo-2-methylhydrindene, a colorless substance, dissolves in aqueous alkalies to give a deep red solution, and this solution has been shown by Hantzsch[4] to contain a salt of the formula (V). Primarily on the basis of this difference in color between (V) and the enolates of his diketones[5] v. Braun postulated the formula (VI) for the latter.
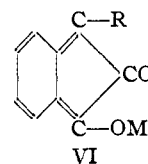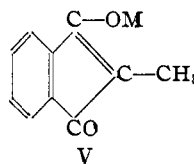

Since the o-quinoid structure is generally unstable,[6] it was decided to investigate this enolate formula more thoroughly. Because of the unattractive physical properties of (I), an undistillable oil, and because of the complications introduced along with the functional groups in the crystalline compounds (II), (III) and (IV), a search was made, ending with 1,2-diketo-3-phenylhydrindene (VII), for a compound not possessing these disadvantages.[7]

(1) Presented at the Cleveland meeting of the American Chemical Society, September, 1934.

(2) Perkin, Roberts and Robinson, J. Chem. Soc., 101, 232 (1912); ibid., 105, 2405 (1914).

(3) V. Braun and Kirschbaum, Ber., 46, 304 (1913); v. Braun and Heider, ibid., 49, 1268 (1916); v. Braun and Fischer, ibid., 64, 1790 (1931).

(4) Hantzsch, Ann., 392, 286 (1912).

(5) Secondary considerations were the observation that (I) reacted with neither bromine nor ferric chloride. These observations are probably erroneous, the physical character of (I) making visual determination of reaction difficult.

(6) Especially unstable is the o-quinomethylene grouping, represented with certainty only by 3,4-benzofuran; cf. Koelsch, THIS JOURNAL, 58, 1331 (1936).

(7) After the present work had been completed, the preparation of diketophenylhydrindene by a different method was carried out by Pfeiffer and de Waal [Ann., 520, 185 (1935)]. Since a different aspect of the chemistry of the diketone was studied by these investigators, little duplication has taken place. Descriptions of the few similar compounds involved in the two researches check closely.

VII

VIII

IX
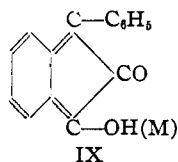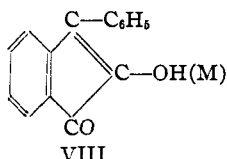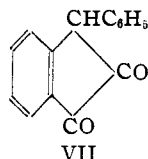
This substance in the crystalline state closely resembles potassium permanganate; like (I) its solutions in organic solvents are red, those in aqueous alkalies deep blue. However, it enolizes to give (VIII) and not (IX). This is clearly shown by the following evidence: the diketone in carbon tetrachloride combines instantly with the calculated amount of bromine; it is mono-phenylated by phenylmagnesium bromide, and the product of this reaction must be (X) and not (XI) since it yields o-dibenzoylbenzene on oxidation. To be noted also is the fact that the blue enolate gives a red O-methyl derivative with dimethyl sulfate.[8]


X

XI
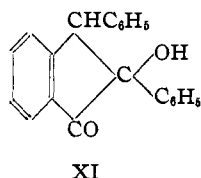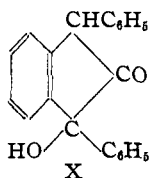
The diketone apparently exists completely in the enolic form: on quantitative treatment with methylmagnesium iodide it reacts with two equivalents of the reagent, liberating one equivalent of gas; and furthermore, as stated above, it combines instantly with the calculated amount of bromine. Also the color of the substance, solid or in solution, indicates that its chromophore is not the α-diketone group (orange) but is the indone nucleus (red). Although the compound gives no color reaction with ferric chloride, this is not evidence against its enolic nature, since it is oxidized immediately by this reagent.

Comparison of 1,2-diketo-3-phenylhydrindene, more properly 2-hydroxy-3-phenylindone, with its β-diketonic isomer and of these with their open chained analogs (Table I) indicates that in the cases of both α and β-diketones of class B, a greater

(8) It is also of interest in this connection that the red 2-p-hydroxyphenyl-3-phenylindone forms a deep purple sodium salt. Postulation of o-quinoidation in this case necessitates the assumption of a considerable, and therefore improbable, shifting of the aromatic double bonds.

tendency toward enolization is found in the cyclic compounds. That the reverse is true for diketones of class C will be shown in a later paper.

Certain derivatives of 1,2-diketo-3-phenylhydrindene obtained through the replacement of the enolizable hydrogen indicate a considerable reactivity of one of the carbonyl groups. The bromo compound (XII) reacts readily with alcohols giving colorless ether–acetals of the probable structures (XIII).

XII

XIII

XIV
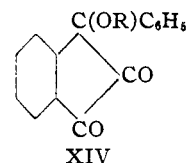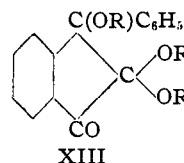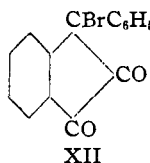
By appropriate treatment, these compounds can be converted into the alkoxy diketones (XIV), whose colors are strikingly different from those of open chain diketones and also from that of the enol (VIII).

Experimental

2-Isonitroso-3-phenylhydrindone.—To a solution of 75 g. of 3-phenylhydrindone in 450 ml. of 95% alcohol is added 75 ml. of butyl nitrite and 10 ml. of concd. hydrochloric acid. The mixture is warmed to 55° for one hour, and after twelve hours at room temperature, the isonitroso compound is removed. The product so obtained (55 g.) is quite pure; crystallization from ethyl acetate–petroleum ether yields faintly yellow prisms that melt at 198–203° with decomposition. The compound gives a yellow-orange solution in aqueous sodium hydroxide.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 76.0; H, 4.64. Found: C, 75.8; H, 4.73.
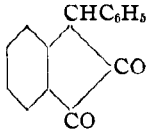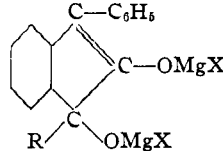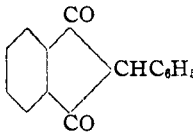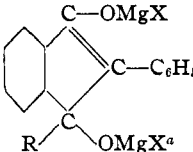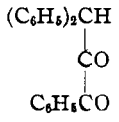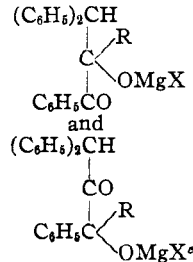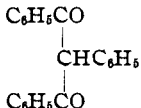
In alkaline solution with methyl sulfate the above oxime yields its methyl ether, which forms pale tan plates that melt at 148–149° after crystallization from alcohol.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.4; H, 5.18. Found: C, 76.4; H, 5.26.

1,2-Diketo-3-phenylhydrindene (VII).—The maximum yield of the diketone if its monoxime is hydrolyzed in the presence of the usual formaldehyde is 20%, and the product so obtained is difficult to purify. (Optimum conditions developed from many experiments: a mixture of 1 g. of oxime, 10 ml. of 40% formaldehyde, 5 ml. of acetic acid, 5 ml. of water, and 1 ml. of concd. hydrochloric acid is heated at 80–85° for ten minutes.)

The use of pyruvic acid as a hydroxylamine acceptor[9] is very advantageous. A mixture of 50 g. of the oxime, 50 ml. of pyruvic acid, 300 ml. of water, 300 ml. of acetic acid and 50 ml. of concd. hydrochloric acid is boiled for thirty minutes. On standing the solution deposits 29 g. of diketone, and an additional 2.5 g. may be obtained from the mother liquors. In larger runs one-half the proportional amount of pyruvic acid may be used with only a slight reduction in yield. Crystallized from benzene–petroleum

(9) Suggested by Dr. P. D. Bartlett.

TABLE I

Compound	Action with			Grignard prod.	Color (solid)	Structure
	Br₂	FeCl₃	NaOH aq.			
(CHC₆H₅ / CO / CO structure)	Reacts rapidly	Oxidized	Stable salt formed	(C—C₆H₅ / C—OMgX / R—C—OMgX structure)	Red-violet	Enolic
(CO / CHC₆H₅ / CO structure)	Reacts slowly	No color	Stable salt	(C—OMgX / C—C₆H₅ / R—C—OMgXᵃ structure)	White	Ketonic; some enol in polar solventsᵇ
(C₆H₅)₂CH / CO / C₆H₅CO	Reactsᶜ	Transient color; oxidizedᶜ	Unstable salt formed: benzilic rearrangementᶜ	(C₆H₅)₂CH—C(R)(OMgX) / C₆H₅CO and (C₆H₅)₂CH / CO / C₆H₅C(R)(OMgX)ᶜ	Yellowᶜ	16% enol in CH₃OHᶜ
C₆H₅CO / CHC₆H₅ / C₆H₅CO	Reacts (?)ᵈ	No color (?) forms no Cu derivativeᶜ	Unstable salt formed; cleavageᶜ	Cleavage or addition:ᶜ no gas with CH₃MgIᶠ	Colorlessᵈ yellowᵍ	Ketonicᶜ

ᵃ Unpublished data. Compare ref. 7. ᵇ Ref. 5. ᶜ Kohler and Weiner, THIS JOURNAL, **56**, 434 (1934); corrected in accordance with a private communication from Professor Kohler. ᵈ Marshall, *J. Chem. Soc.*, **107**, 520 (1915). ᶜ Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931). ᶠ Kohler, Stone and Fuson, *ibid.*, **49**, 3181 (1927). ᵍ De Neufville and v. Pechmann, *Ber.*, **23**, 3377 (1890).

ether, the diketone forms violet black needles; from dilute acetic acid, red violet plates. Both forms melt at 140–147°. The diketone decomposes and liquefies on standing in air; the decomposition is complete after about three months.

Anal. Calcd. for C₁₅H₁₀O₂: C, 81.0; H, 4.51. Found: C, 81.0; H, 4.58.

Solutions of the compound in organic solvents, polar or non-polar, are dark red. It is readily soluble in cold aqueous sodium hydroxide or in warm carbonate, giving deep blue solutions from which the diketone is precipitated by acids. The solutions in alkali lose their color on long (*ca.* ten minutes) boiling, acidification then giving a small amount of diphenylmethane-*o*,*α*-dicarboxylic acid together with unworkable oils.

Oxidation.—To a solution of 0.5 g. of the diketone in 10 ml. of 0.5 N sodium hydroxide is added 5 ml. of 3% hydrogen peroxide. After the mixture has become colorless (two minutes) it is acidified. The product, diphenylmethane-*o*,*α*-dicarboxylic acid, forms fine white needles from ethyl acetate–benzene that melt at 171–172° with gas evolution.

Anal. Calcd. for C₁₅H₁₂O₄: C, 70.3; H, 4.7. Found: C, 70.1; H, 4.8.

Quinoxaline Formation.—The diketone is condensed with *o*-phenylenediamine in alcohol in the usual way. The product forms colorless needles that melt to a blue liquid at 169–172°.

Anal. Calcd. for C₂₁H₁₄N₂: C, 85.6; H, 4.76. Found: C, 85.3; H, 4.82.

Reaction with Ferric Chloride.—The color of an alcoholic solution of the diketone (0.5 g.) rapidly fades when ferric chloride (0.8 g. of FeCl₃ + 6H₂O) in alcohol is added. The orange-pink crystalline precipitate (0.45 g.) contains only a trace of iron, and is insoluble in all solvents other than hot nitrobenzene, by which it is altered. It darkens at 180° and melts at 200–205° with gas evolution.

Anal. Calcd. for C₃₀H₁₈O₄: C, 81.4; H, 4.1. Found: C, 80.9; H, 4.36.

Bromination.—The diketone (5 g.) in chloroform (30 ml.) is treated with 3.75 g. of bromine in carbon tetrachloride. The halogen is absorbed immediately and hydrogen bromide is given off. The solvents are removed under reduced pressure, and the residue is crystallized from ether–petroleum ether. There is obtained 4.9 g. of 1,2-diketo-3-bromo-3-phenylhydrindone (XII) which forms orange-brown prisms that melt at 77–79°.

Anal. Calcd. for C₁₅H₉O₂Br: C, 59.9; H, 3.0. Found: C, 60.1; H, 3.0.

Methylation.—A solution of 28 g. of the diketone in 150 ml. of N sodium hydroxide is treated with 15 ml. of methyl sulfate, and the mixture is stirred vigorously for thirty minutes. The solid is filtered and crystallized from methanol, when it is obtained in the form of red prisms and needles (18 g.) that melt at 67–68°. Although it can be distilled without decomposition at 20 mm., the 2-methoxy-

3-phenylindone rapidly (three days) decomposes on standing in air, giving off an odor of formaldehyde and leaving a red resin.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.2; H, 5.1. Found: C, 80.6; H, 5.1.

The oxime of the methyl ether, obtained with hydroxylamine hydrochloride and sodium acetate in alcohol, forms orange prisms that melt to a red liquid at 184–186° and are stable in air.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.4; H, 5.2. Found: C, 76.0; H, 5.2.

With phenylmagnesium bromide, the methyl ether gives a colorless carbinol which could not be obtained crystalline and could not be converted into a solid methyl ether, but whose solution in acetic acid is colored red-violet by a trace of sulfuric acid.

2-Methoxy-3-phenylindone (15 g.) is reduced when its solution in acetic acid (150 ml.) is treated with zinc dust (15 g.). The solution becomes warm and its color rapidly disappears. The product, 2-methoxy-3-phenylhydrindone, is precipitated by water, distilled at 20 mm. and crystallized from methanol, when it forms colorless prisms that melt at 96–98°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.7; H, 6.0.

Reaction with Grignard Reagents.—Quantitative examination of its behavior in the Grignard machine[10] shows that 1,2-diketo-3-phenylhydrindene reacts with two equivalents of methylmagnesium iodide, liberating one equivalent of gas.

With an excess of phenylmagnesium bromide, the diketone yields 1,3-diphenyl-1-hydroxy-2-ketohydrindene (X), which from ethanol forms white plates that melt at 195–200° with decomposition.

Anal. Calcd. for $C_{21}H_{16}O_2$: C. 83.9; H, 5.3. Found: C, 83.1; H, 5.3.

Oxidized with chromic acid in acetic acid, this hydroxy ketone yields o-dibenzoylbenzene (mixed m. p.) nearly quantitatively.

Reduced with hydriodic acid in acetic acid, the hydroxy ketone is converted into 1,3-diphenyl-2-ketohydrindene, which, from acetic acid, forms white needles that melt with decomposition at 169°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.6; H, 5.6. Found: C, 88.0; H, 5.7.

With benzylmagnesium chloride, diketophenylhydrindene yields 1-benzyl-1-hydroxy-2-keto-3-phenylhydrindene, white needles that melt at 155–157°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.7. Found: C, 84.1; H, 6.1.

Reactions of the Bromo Compound (XII) with Alcohols.—A solution of the crude bromo compound from 5 g. of diketophenylhydrindene in methanol is distilled to a

(10) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

small volume, the methanol is replaced, and the resulting solution is cooled. There is deposited 5 g. of 2,2,3-trimethoxy-3-phenylhydrindone (XIII, R = CH_3), which forms colorless prisms that melt at 102–103°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.4; H, 6.0. Found: C, 71.9; H, 6.0.

The trimethoxy compound does not react with o-phenylenediamine in alcohol even on warming, but the addition of a trace of hydrochloric acid to the mixture causes the immediate precipitation of the quinoxaline of 1,2-diketo-3-methoxy-3-phenylhydrindene.

Anal. Calcd. for $C_{22}H_{16}ON_2$: C, 81.4; H, 4.94; OCH_3, 9.6. Found: C, 81.3; H, 4.96; OCH_3, 9.3.

The trimethoxy compound (0.5 g.) forms a faintly pink solution in acetic acid (8 ml.) which becomes deep crimson on the addition of a drop of sulfuric acid. Dilution with water causes the separation of a crystalline precipitate which can be separated by extraction with cold benzene into a soluble orange compound and a colorless insoluble substance. The orange compound melts at 86–87° and is the methoxy diketone (XIV, R = CH_3).

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.3; H, 4.8.

The colorless substance is a hydrate of the methoxy diketone, since at its melting point (115–120°, gas evolution) it is converted into the latter.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.2; H, 5.2. Found: C, 71.2; H, 5.3.

With ethanol, the bromo compound (XII) yields 2,2,3-tri-ethoxy-3-phenylhydrindone (XIII, R = C_2H_5), which forms white plates that melt at 89–90°. This compound is much more easily soluble than its trimethoxy analog, and its quantitative isolation is more difficult.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.0; H, 7.06. Found: C, 74.0; H, 7.09.

Treatment of the triethoxy compound with acetic acid-sulfuric acid converts it into the ethoxy diketone (XIV, R = C_2H_5), which from benzene forms cerise plates that melt at 102–103°. No benzene insoluble substance (hydrate) is formed.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.6; H, 5.26. Found: C, 76.4; H, 5.28.

Summary

It is shown that 1,2-diketo-3-phenylhydrindene exists in the enolic form, and that this enolization does not involve o-quinoidation. When enolization is prevented by the replacement of the enolizable hydrogen by alkoxyl, one of the diketonic carbonyl groups becomes active enough to form an acetal.