[Contribution from the School of Chemistry of the University of Minnesota]

THE REACTIONS AND ENOLIZATION OF CYCLIC DIKETONES. III.[1] 1,2-DIKETO-3,4-DIPHENYLCYCLOPENTENE*

T. A. GEISSMAN and C. F. KOELSCH

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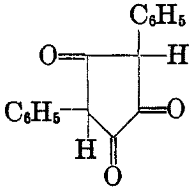
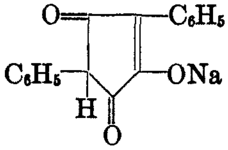
Numerous examples of acyclic α-diketones, cyclic α-diketones containing a saturated ring, and 1,2-diketohydrindenes have been described, but so far no alicyclic analogs of 1,2-diketohydrindenes have been prepared except those containing acyl groups on the carbon atom corresponding to the 3 position in 3-substituted 1,2-diketohydrindenes. The reactivity of such α-diketones is affected by the acyl substitutent, since it forms a part of a β-dicarbonyl system with one of the α-diketone carbonyl groups, in such a way that no comparison can be made between these compounds and the known 1,2-diketohydrindenes containing a substitutent in the 3 position, such as methyl or phenyl.

One of the earliest examples of a substituted diketocyclopentene is oxalyldibenzyl ketone (I) a yellow compound, prepared by Claisen and Ewan.[2] This substance dissolves in one equivalent of alkali with the formation of a yellow salt and in two equivalents of alkali with the formation of a blue salt. The structures of these were written by Claisen and Ewan as (II) and (III).



I



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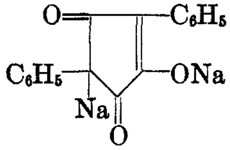

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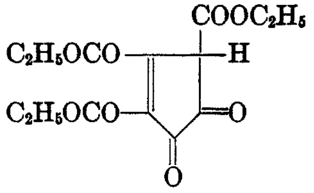
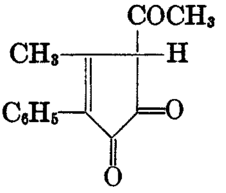


IV



V

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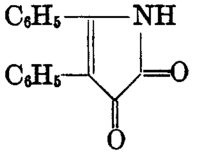
[1] Previous paper in this field, Koelsch and Hochmann, J. Org. Chem., 3, 503 (1938).

* A portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy by T. A. Geissman, May, 1937.

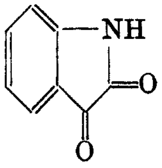
[2] Claisen and Ewan, *Ann.*, **284**, 245 (1895).

Triethyl oxalylaconitate (IV) was prepared later by Ruhemann and Hemmy[3] and acetomethylphenyldiketocyclopentene (V) by Ruhemann and Merriman.[4] These compounds, written as enols by Ruhemann, are red, and they form blue alkali salts.

Ruhemann's final view as to the structures of the blue salts of these compounds and of Claisen and Ewan's triketone, grew out of his study of diketodiphenylpyrroline (VI).[5] This compound is an analog of isatin (VII), and resembles it in many ways. Both substances are red; both dissolve in alkali with the formation of blue salts, the blue color fading in a short time to yellow; and both give phenylhydrazones which are insoluble in acid or in alkali.

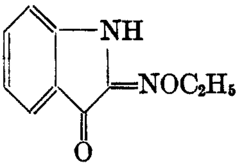


VI

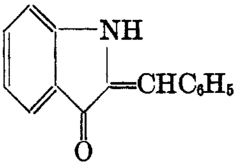


VII

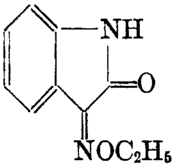
von Baeyer had previously shown[6, 7] that the ethyl ether of isatin α-oxime (VIII) dissolved in alkali with the formation of a blue salt, as did benzylidene indoxyl (IX), while no blue salt was formed from the ether of the β-oxime of isatin (X).



VIII



IX



X

The interpretation placed on these facts by Ruhemann[5,8] was that since replacement of the α-keto oxygen did not interfere with the formation of a blue salt while that of the β-keto oxygen did, the metal must be attached to the β-keto oxygen, so that the structure of the blue salt of

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[3] Ruhemann and hemmy, *J. Chem. Soc.*, **71**, 334 (1897).

[4] Ruhemann and Merriman, *ibid.*, **87**, 1383 (1905).

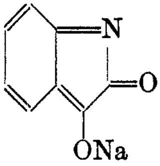
[5] Ruhemann, *ibid.*, **95**, 984 (1909).

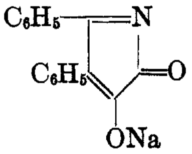
[6] v. Baeyer, *Ber.*, **16**, 2192 (1883).

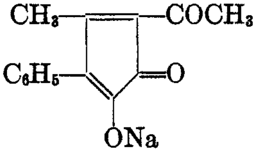
[7] Heller, "Sammlung chem. und chemisch-tech. Vorträge." Ferdinand Enke, Stuttgart, **1931**, New Series, Vol. **5**, pp. 49–62.

[8] Ruhemann, *J. Chem. Soc.*, **97**, 1438 (1910).

isatin itself would be (XI) and by analogy that of the blue salt of diketodiphenylpyrroline, (XII)

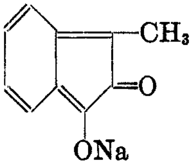

XI

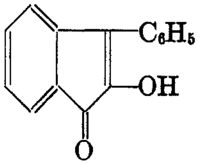

XII

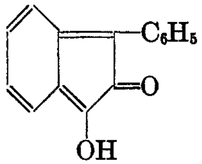

XIII

Analogous structures, for example XIII were assigned to the blue salts of the carbocyclic compounds, V, I, and IV.

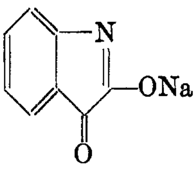
Ruhemann's deduction of an *o*-quinoid structure for the blue salt of isatin led v. Braun[9] to postulate the structure XIV for the blue salts of 3-methyl-1,2-diketohydrindene. But this is probably incorrect, since it has been shown[10] that 3-phenyl-1,2-diketohydrindene enolizes to give XV and not XVI.

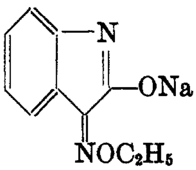

XIV

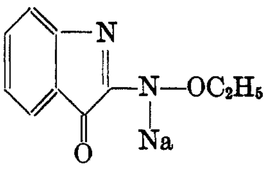

XV


XVI

Indeed the evidence for the *o*-quinoid structure of the blue salts of isatin itself is not as conclusive as it at first appears. Whether the salt formation takes place as in XI or as in XVII, the chromophore is a crossed conjugated system. That a blue salt is not formed from isatin β-oxime ether is probably due to replacement of the carbonyl oxygen by the oximino grouping as indicated in formula XVIII, while the blue color of the salt of the α-oxime ether (XIX) is due to the intact carbonyl group.


XVII


XVIII


XIX

That replacement of a carbonyl oxygen in such a system does strongly affect color may be illustrated by diphenylindone and its oxime, which are deep red and yellow respectively.

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[9] v. Braun and co-workers. *Ber.*, **46**, 3041 (1912); **49**, 1268 (1916); **64**, 1790 (1931).

[10] Koelsch, *J. Am. Chem. Soc.*, **58**, 1321 (1936).

The question which this formulation of the enolates of isatin raises as to the structure of diketodiphenylpyrroline salts will be the subject of future communications from this laboratory.†

Isatin, diketodiphenylpyrroline, and the cyclopentene derivative (V) are all red compounds, all form blue salts in alkali, all give phenylhydrazones which are not soluble in acid or alkali; and all give phenazines when treated with *o*-phenylenediamine. But the two heterocyclic compounds yield yellow phenazines while that derived from the compound (V) is purple. These and other similarities on the one hand, and differences on the other, between compounds containing an isatin ring and compounds of which the cyclopentene (V) is a representative, led Ruhemann to consider studying the properties of a compound containing an intact methylene group adjacent to the diketone grouping, for example 1,2-diketohydrindene.

Ruhemann's attempt to prepare this substance was unsuccessful, although it led to the discovery of triketohydrindene.[8] 1,2-Diketohydrindene was first prepared by Perkin, Roberts, and Robinson,[11] and later these investigators and others[12] prepared various derivatives of 1,2-diketohydrindene containing substituents in the benzene ring. These derivatives, like the parent substance, are all yellow, but for the most part their properties have not been studied in detail.

So far as chemical behavior is concerned, unsubstituted (except in the benzene ring) 1,2-diketohydrindenes have two structural features of special interest: the carbonyl groups and the methylene group.

1,2-Diketohydrindene reacts[11] with the usual carbonyl reagents, forming an oxime when treated with hydroxylamine, an osazone with phenylhydrazine, and a quinoxaline with *o*-phenylenediamine. The greater reactivity of the carbonyl group adjacent to the methylene group is shown by the fact that oximation of the diketone leads to the formation of the same compound as that obtained by the nitrosation of hydrindone-1; that is, 2-isonitrosohydrindone-1. The diketone reacts with hydrogen cyanide and with sodium bisulfite with the formation of colorless addition compounds. Perkin and co-workers observed that solutions of the diketone in methanol or ethanol are nearly colorless while in non-hydroxylic

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† It is recognized that in these salts the metal is ionically bound to the organic part of the molecule and that accordingly the latter may have several forms through resonance. Nevertheless it is believed that inferences drawn from color, preferential reactivity of one carbonyl group, or other properties may indicate which of the forms represents a preferred structure; certainly they are allowable from a pragmatic standpoint.

[11] PERKIN, ROBERTS, AND ROBINSON, *J. Chem. Soc.*, **101**, 232 (1912); **105**, 2405 (1914).

[12] CHAKRAVARTI AND SWAMINATHAN, *J. Indian Chem. Soc.*, **11**, 101 (1934).

solvents the solutions are deep yellow. This behavior points to the formation of acetals, but no acetal has been isolated in this laboratory or by Perkin. Upon evaporation of the alcohol from a solution of the diketone in methanol or ethanol, the solution remains nearly colorless until the solvent has been largely removed. On removal of the last of the solvent, the diketone crystallizes unchanged. The compound is cleaved in the usual way by hydrogen peroxide, the expected homophthalic acid being formed.

1,2-Diketohydrindene dissolves in 5 per cent. sodium hydroxide[11] to give at first a colorless solution which becomes brownish-red, then brownish-yellow. Acidification at that point precipitates a colorless substance. If the alkaline solution is boiled a color change through violet to red is observed. In sodium carbonate, or very dilute sodium hydroxide solution the compound dissolves with an olive-green color which on standing becomes greenish-blue, and on boiling becomes an intense blue.

1,2-Diketohydrindene does not react with bromine[1] except in boiling acetic acid, and then not readily in the absence of a catalyst such as hydrobromic acid. Depending on the amount of bromine used, a dibromo or an unstable monobromo substitution product is formed. This behavior indicates that the compound exists entirely in the keto form, and support for this view is found in absorption spectrum measurements.

The open-chain analog of 1,2-diketohydrindene, phenylbenzylglyoxal, has been studied by Dufraisse and Moureu and by Kohler and Barnes.[13] This substance may be obtained in three forms, two of them stereoisomeric modifications of the enol, and one the diketone. The ketonic and both enolic forms liberate methane when treated with methylmagnesium iodide, the latter yielding 93 per cent. of the theoretical amount, and the former 50 per cent., indicating an enolizing action of the Grignard reagent. No tendency of the diketone to form acetals has been noted.

Whether the marked differences in the characters of 1,2-diketohydrindene and phenylbenzylglyoxal are the result of the effects arising from the presence of the benzene ring in the former, or simply as an effect of the double bond connecting the methylene and carbonyl groups, can be ascertained by a study of a compound containing the double bond in the same position but not as a part of a benzene ring.

The experimental part of the present paper and the following discussion are devoted to a description of the preparation and properties of such a compound, 3,4-diphenylcyclopentenedione-1,2 (XXIII).

Anhydracetone benzil (XX)[14] was reduced to diphenylcyclopentenone

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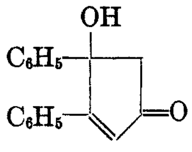
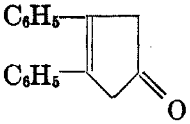
[13] DUFRAISSE AND MOUREU, *Bull. soc. chim.*, **41**, 1607 (1927); KOHLER AND BARNES, *J. Am. Chem. Soc.*, **56**, 211 (1934).

[14] JAPP AND KNOX, *J. Chem. Soc.*, **87**, 673 (1905).

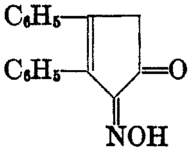
(XXI).[15] Nitrosation of this ketone led to the expected isonitroso compound (XXII) which was then hydrolyzed in the presence of formaldehyde as an hydroxylamine acceptor, giving the diketone (XXIII).



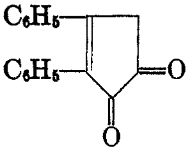
XX



XXI



XXII



XXIII

The diketone (XXIII) is yellow, like 1,2-diketohydrindene, but has an orange tinge. Its solutions in non-polar solvents are yellow, but in thin layers are distinctly pink-tinged by transmitted light.

The compound resembles 1,2-diketohydrindene in most ways, so far as the latter has been investigated. Treated with hydroxylamine it forms a mono-oxime (XXIV). It gives a colorless phenazine (XXV) with phenylenediamine, and is readily cleaved by alkaline hydrogen peroxide to the corresponding glutaconic acid, isolated as its anhydride (XXVI).

Bromine has no effect on the diketone in the cold or in boiling carbon tetrachloride. In boiling acetic acid, however, bromination proceeds smoothly to yield the monobromo compound (XXVII) or the dibromo compound (XXVIII). There is an appreciable period of induction before bromination proceeds, but the subsequent reaction is rapid.

The diketone is insoluble in aqueous alkali in the cold, and on boiling decomposition occurs. Its solution in alcohol becomes greenish yellow on the addition of a drop of alkali. There is no color reaction with ferric chloride.

These facts show clearly that the diketone exists in the keto form and indicate that it has little or no more tendency to react in the enol form than a simple monoketone with two α-hydrogen atoms.

The superior reactivity of the carbonyl group adjacent to the methylene group is shown by the fact that it is preferentially oximated by hydroxylamine with the formation of an isonitrosocyclopentenone (XXIV) different from, but isomeric with, the isonitroso compound (XXII) from which the diketone is prepared. An even more striking example of the pronounced reactivity of this carbonyl group is found in the ease with which the diketone forms an acetal. When a methyl-alcoholic solution of the diketone containing a trace of acid is boiled, the color fades to a pale

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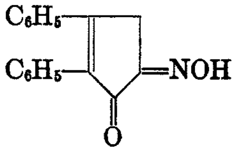
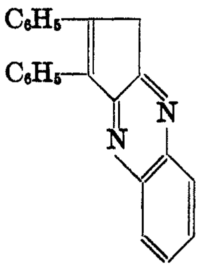
[15] Japp and Lander, *ibid.*, **71**, 131 (1897).

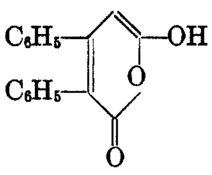
yellow and from the resulting solution there is obtained a colorless crystalline substance, the acetal (XXIX).



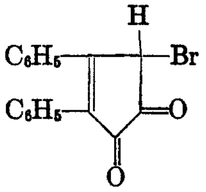
XXIV



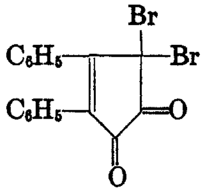
XXV



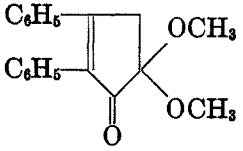
XXVI



XXVII



XXVIII



XXIX

That acetal formation takes place on the carbonyl group indicated was shown in two ways. Treatment of the acetal with benzaldehyde in alcoholic alkali produced no change, the compound being recovered. If acetal formation had taken place on the carbonyl group adjacent to the double bond, the methylene group would be activated by the remaining carbonyl group and benzal formation would be expected. This is negative evidence, however, and more conclusive proof was obtained by treating the acetal with phenylmagnesium bromide. The resulting carbinol (XXX) when boiled with acetic acid containing a trace of sulfuric acid underwent hydrolysis and dehydration with the formation of a colorless compound (XXXI). Although the structure of this compound was not rigidly proved, there is little doubt that it has the structure shown and arises as a result of the dimerization of 2,3,4-triphenylcyclopentadienone, since the same substance is obtained when the carbinol (XXXII)[16] is dehydrated in the same manner. Support for the suggested structure (XXXI) is found in the work of Allen and Spanagel[17] on the dehydration of anhydracetone benzil and in the observations of Dilthey and Schommer[18] on the reversible dimerization of 1,2,4-triphenylcyclopentadienone.

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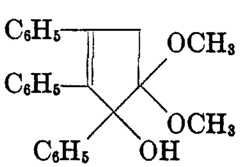
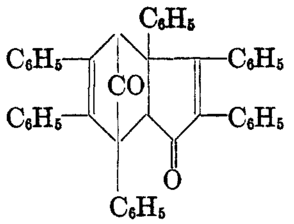
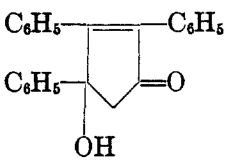
[16] Koelsch and Geissman, J. Org. Chem., **3**, 480 (1938).

[17] Allen and Spanagel, *J. Am. Chem. Soc.*, **54**, 4338 (1932).

[18] Dilthey and Schommer, *J. prakt. Chem.*, **136**, 293 (1933).


XXX


XXXI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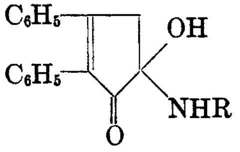
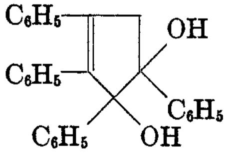
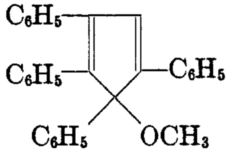
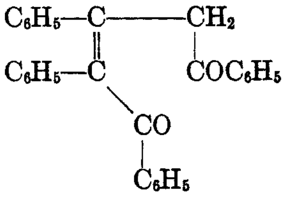
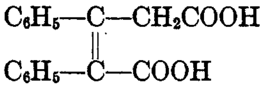

XXXIII


XXXIV

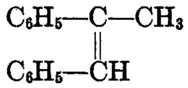

XXXV


XXXVI



$$\begin{array}{l} C_6H_5\text{—}C\text{—}CH_2COOH \\ \qquad\;\; \| \\ C_6H_5\text{—}C\text{—}COOH \end{array}$$

XXXVII



$$\begin{array}{l} C_6H_5\text{—}C\text{—}CH_3 \\ \qquad\;\; \| \\ C_6H_5\text{—}CH \end{array}$$

XXXVIII

Further evidence for the reactivity of the carbonyl group is found in the reaction of the diketone with aniline and with *p*-toluidine. In ether suspension at room temperature these amines are added, structure XXXIII being suggested for the unstable products by analogy with oximation and acetal formation.

The distinctly ketonic character of the diketone (XXIII) is demonstrated further by its reaction with phenylmagnesium bromide. Two moles of the Grignard reagent add with the formation of a glycol (XXXIV).

This glycol is simultaneously dehydrated and etherified in methanol by a trace of sulfuric acid, with the formation of the methyl ether (XXXV).[19] In acetic acid containing a drop of sulfuric acid dehydration and oxidation occur, leading to the formation, in poor yield, of the known tetraphenylcyclopentadienone.[20] Rigid proof for the structure of the glycol was

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[19] The position of the double bonds and of the methoxyl group in this compound are uncertain. Compare KOELSCH, *J. Am. Chem. Soc.*, **56**, 1337 (1934).

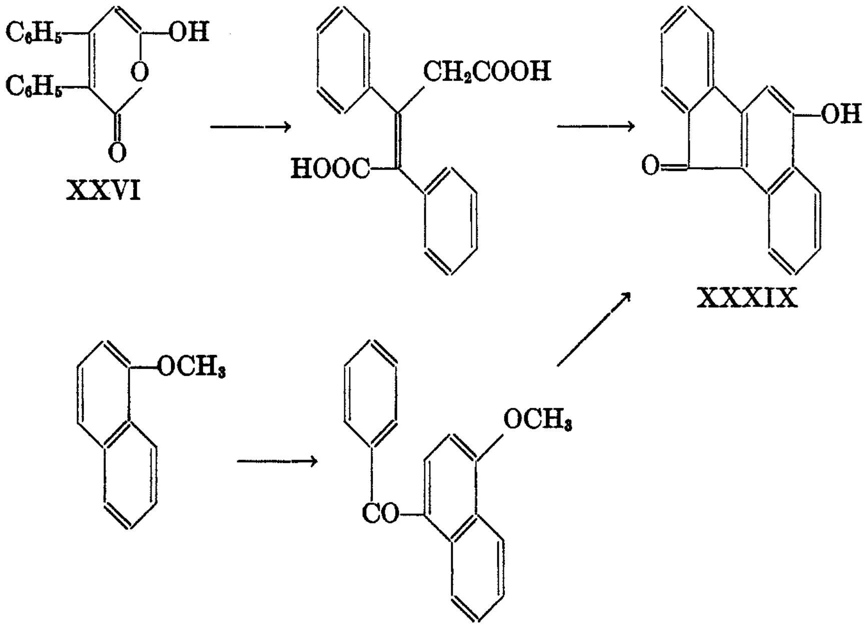
[20] ZIEGLER AND SCHNELL, *Ann.*, **445**, 266 (1925).

obtained by oxidizing it by means of lead tetraacetate to the known 1,2,3,5-tetraphenylpentene-2-dione-1,5 (XXXVI).[21]

The anhydride (XXVI) of α,β-diphenylglutaconic acid, which was obtained by hydrogen peroxide cleavage of the diketone, was found to titrate as a monobasic acid and to give two isomeric dibasic acids (XXXVII) under different conditions of hydrolysis. As Thorpe and Bland[22] have shown, such behavior is characteristic of α,β-disubstituted glutaconic anhydrides, which exist in their enolic forms. The structure of the anhydride was made certain by subjecting it to distillation with soda-lime, producing the known α-methyl stilbene (XXXVIII).

An interesting reaction took place when the anhydride (XXVI) was dissolved in sulfuric acid. Upon the addition of a trace of water the initially yellow-brown solution became green, and on further dilution a red compound was precipitated. This substance was identified as 1,2-benzo-3-oxyfluorenone (XXXIX) by comparison with an authentic sample prepared by the method of Fierz-David[23] and of Scholl and Seer.[24]

The formation of the fluorenone from the anhydride and the method used for its synthesis are shown in the following equations.



XXVI

XXXIX

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[21] Dilthey, *Ber.*, **52**, 2052 (1919).

[22] Thorpe and Bland, *J. Chem. Soc.*, **101**, 1563 (1912).

[23] Fierz-David and Jacard, Helv. Chem. Acta, **11**, 1042 (1928).

[24] Scholl and Seer, *Ann.*, **394**, 154 (1912).

EXPERIMENTAL

3,4-Diphenylcyclopentenone, (XXI).—The following procedure gives a much better yield of the ketone than the original one of Japp and Lander.[15] A mixture of 100 g. of anhydroacetone benzil,[14] 12.5 ml. of 45% hydriodic acid, 22.5 g. of red phosphorus, and 400 ml. of acetic acid was boiled for one hour, then filtered into a cold dilute solution of sodium bisulfite. The precipitate was taken up in ether and washed with water and sodium carbonate. Part of the product separated at once; the remainder was obtained by removal of the ether and distillation at 20 mm. These two parts, combined, and crystallized from benzene, gave a total of 70 g. of white crystals that melted at 108–110°.

2-Isonitroso-3,4-diphenylcyclopentenone, (XXII).—To a solution of 72 g. of diphenylcyclopentenone in 350 ml. of ethanol was added 46 g. of butyl nitrite and 15 ml. of concentrated hydrochloric acid. The mixture was kept at 50–55° for one hour, and then allowed to stand for several hours at room temperature. After collection by filtration and washing with alcohol, the product (67 g.) was yellow, and melted at about 210° with decomposition. The impurities were largely extracted by boiling for fifteen minutes with 200 ml. of benzene and filtering hot. The undissolved, nearly colorless product weighed 52 g., melted at 216–218° with decomposition, and was used for the preparation of the diketone without further purification. An analytical sample of m.p. 223–224° (dec.) was obtained by crystallization from ethyl acetate-acetic acid, and then from alcohol.

Anal. Calc'd for $C_{17}H_{13}NO_2$: C, 77.6; H, 4.9.
Found: C, 77.6; H, 4.8.

The substance is insoluble in aqueous 5% sodium hydroxide, but dissolves in aqueous-alcoholic 3% caustic, giving a deep yellow solution from which it is precipitated unchanged by acids.

On treatment with benzoyl chloride and aqueous sodium hydroxide, or better with benzoyl chloride in dry pyridine, the oxime is converted into its *benzoate*, fine yellow needles that melt at 142–143° with decomposition. The benzoate dissolves in alcoholic alkali giving a yellow solution.

Anal. Calc'd for $C_{24}H_{17}NO_3$: C, 78.4; H, 4.6.
Found: C, 78.0; H, 4.7.

3,4-Diphenylcyclopentendione-1,2 (XXIII).—A mixture of 52 g. of the isonitroso compound (XXII), 300 ml. of acetic acid, 300 ml. of 40% formalin, and 50 ml. of concentrated hydrochloric acid was boiled under a reflux condenser for thirty minutes. During this time the isonitroso compound dissolved, and the diketone started to separate. The mixture was then allowed to stand overnight; the product was filtered off and washed well with water. It was yellow-orange, and weighed 27 g.

The melting point of the diketone varied considerably in different samples. Crystallized from benzene or acetic acid, the substance formed yellow needles that melted with decomposition at 178–182°, while one sample crystallized from bromobenzene and petroleum ether was obtained in the form of deep yellow leaflets that melted at 186–188° with slow decomposition. Possibly dimorphic modifications were in hand; both the high- and low-melting samples gave the same phenazine.

Anal. Calc'd for $C_{17}H_{12}O_2$: C, 82.3; H, 4.8.
Found: C, 82.6; H, 4.6.

The diketone did not dissolve in cold dilute aqueous alkali, and on warming in alkali it was converted into an insoluble red oil. The addition of aqueous sodium hydroxide to an alcoholic solution of the compound caused the formation of a greenish-yellow color.

The *phenazine* (XXV) was obtained by boiling the diketone with a benzene solution of *o*-phenylenediamine. Crystallized from benzene, the substance formed soft white needles that melted at 236–237°. The phenazine dissolved in concentrated hydrochloric acid with a deep-red color and was precipitated unchanged by aqueous ammonia.

Anal. Calc'd for $C_{23}H_{16}N_2$: C, 86.3, H, 5.0.
Found: C, 86.7; H, 5.4.

The *oxime* (XXIV, 2-isonitroso-4,5-diphenylcyclopentenone) was obtained when an alcoholic suspension of the diketone was boiled for fifteen minutes with an excess of hydroxylamine hydrochloride neutralized with sodium hydroxide. It formed pale-yellow needles that darkened at 215° and melted at 237–239° with decomposition. A mixture with XXII (m.p. 223–224) melted at 217–218° with decomposition.

Anal. Calc'd for $C_{17}H_{13}NO_2$: C, 77.6; H, 4.9.
Found: C, 78.0, H, 4.9.

Cleavage with hydrogen peroxide.—To a suspension of 5 g. of the diketone in 50 ml. of alcohol was added 2.5 ml. of 30% hydrogen peroxide and then, dropwise and with shaking, 5 ml. of 20% aqueous sodium hydroxide. The solution was allowed to stand for five minutes, poured into water, and extracted several times with ether, the ether extracts being discarded. Acidification of the aqueous solution precipitated the product, which weighed 4.7 g. and melted at 121–126°. Recrystallized from ether-petroleum ether the α,β-diphenylglutaconic anhydride (XXVI) formed pale yellow needles that melted at 126–127°.

Anal. Calc'd for $C_{17}H_{12}O_3$: C, 77.3; H, 4.6; Neutr. equiv. (monobasic acid), 264.
Found: C, 77.3; H, 4.6; Neutr. equiv., 262.

Crystallized from benzene-petroleum ether, the anhydride separated in pale yellow plates of m.p. 111–112° that contained solvent of crystallization. This solvent was lost on heating at 105° for ten minutes, the residue then melting at 126–127°.

The anhydride can be distilled unchanged at 20 mm. When heated with phenol and sulfuric acid for five minutes at 140° it gave a melt which dissolved in alkali with a wine-red color. When treated with benzaldehyde in alcoholic hydrochloric acid, the anhydride was converted into a compound that melted at 152.5–153.5°. On heating with aniline, the anhydride yields a tan substance crystallizing in needles that melt at 224–225°; this is partly converted into a red substance melting at 246–248° when boiled with methanol.

α-β-Diphenylglutaconic acid (XXXVII).—When the anhydride (XXVI) was boiled with 10% sodium hydroxide, dilute hydrochloric acid, or acetic acid containing phosphorus and iodine (the latter in an attempt to reduce the anhydride), there was obtained an acid which formed white leaflets that melted at 165–166° with decomposition (after crystallization from water). It was reconverted to the anhydride (XXVI) on distillation at 20 mm.

Anal. Calc'd for $C_{17}H_{14}O_4$: C, 72.4; H, 5.0; Neutr. equiv., 141.
Found: C, 72.6; H, 4.9; Neutr. equiv., 142.

An isomeric form of the acid was obtained when the anhydride was boiled for one hour with 10% sodium hydroxide in the presence of zinc dust. Crystallized from dilute alcohol this substance melted with decomposition at 204–205°. This acid was not identical with α,β-diphenylglutaric acid of m.p. 209–210°,[25] since, when it was

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[25] Borsche, *Ber.*, **42**, 4496 (1909); Avery and Maclay, *J. Am. Chem. Soc.*, **51**, 2833 (1929).

mixed with a sample of the latter, it softened at 185° and melted with decomposition at 195–199°.

Anal. Calc'd for $C_{17}H_{14}O_4$: C, 72.4; H, 5.0, Neutr. equiv., 141.
Found: C, 72.48; H, 495; Neutr. equiv., 140.

α-Methylstilbene (XXXVIII) from the anhydride (XXVI).—The dry sodium salt prepared from 1 g. of the anhydride was intimately mixed with an equal weight of soda-lime and distilled at 20 mm. The distillate, obtained in poor yield, solidified in the receiver and after crystallization from petroleum ether melted at 80–81.5°. This melting point was unchanged when the substance was mixed with an authentic sample of α-methylstilbene.[26]

1,2-Benzo-3-hydroxyfluorenone (XXXIX) from the anhydride.—The anhydride dissolved in concentrated sulfuric acid with a yellow-brown color, and when the solution was slowly diluted with water it became green and finally deposited a brick red substance. Recrystallized from nitrobenzene, this formed deep-red needles that melted at 307–308° on a copper block, (literature,[23] 305°).

Treated with benzoyl chloride in pyridine, the oxyfluorenone gave its benzoate, yellow needles that melted at 235–236°, (literature,[26] 236°).

The oxyfluorenone and its benzoate were identified by melting point determinations of mixtures with samples prepared by reactions described in the literature.

Reaction of the diketone with phenylmagnesium bromide.—A benzene solution of the diketone (2.9 g.) was added to a Grignard reagent prepared from 6.2 g. of bromobenzene and 0.96 g. of magnesium. The mixture was boiled for thirty minutes, decomposed with iced hydrochloric acid and worked up in the usual way. The 1,2,3,4-tetraphenylcyclopenten-3-diol-1,2 (XXXIV), obtained in a yield of 3 g., formed white needles that melted at 200–201° after crystallization from ethyl acetate-petroleum ether.

Anal. Calc'd for $C_{29}H_{24}O_2$: C, 86.1; H, 6.0.
Found: C, 86.1; H, 5.8.

When the glycol (0.5 g.) was boiled for five minutes with 25 ml. of methanol containing 4 drops of sulfuric acid, it was converted into *1,2,3,5-tetraphenyl-1-methoxycyclopentadiene* (XXXV)[19] in good yield. Crystallized from methanol, the ether formed white needles that melted at 150–151°.

Anal. Calc'd for $C_{30}H_{24}O$: C, 90.0; H, 6.0; OCH_3, 7.75.
Found: C, 89.6; H, 6.0; OCH_3, 7.9.

From the deep-red solution that resulted when the glycol (XXXIV) (0.2 g.) was boiled for fifteen minutes with 2 ml. of acetic acid containing a drop of sulfuric acid there was obtained about 20 mg. of 2,3,4,5-tetraphenylcyclopentadienone, m.p. 216–218°, identified by comparison with an authentic sample.[27] The addition of potassium bichromate to a similar reaction mixture had no effect on the yield of ketone.

Oxidation of the glycol with lead tetraacetate.—To a suspension of 0.5 g. of the glycol (XXXIV) in 20 ml. of acetic acid was added 0.7 g. of lead tetraacetate. The mixture was shaken for ten minutes and poured into water. Crystallization from methanol yielded 0.32 g. of a white product that melted at 110–112°, and gave a red-violet color with alcoholic alkali. It formed a ferric salt that melted at 187–188° when its solution in acetic acid was treated with ferric chloride. These properties are characteristic of the known 1,2,3,5-tetraphenylpenten-2-dione-1,5 (XXXVI).[21]

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[26] HELL, *Ber.*, **37**, 458 (1904).

[27] DILTHEY AND QUINT, *J. prakt. Chem.*, **128**, 139 (1930).

Bromination of the diketone: the monobromo compound (XXVII).—A solution of 2.0 g. of the diketone and 1.3 g. of bromine in 40 ml. of acetic acid was boiled a few minutes, or until the bromine color had disappeared. The solution was cooled, whereupon the product (2.2 g.) separated in the form of soft yellow needles that melted at 181–182.5° with decomposition.

Anal. Calc'd for $C_{17}H_{11}BrO_2$: C, 62.4; H, 3.4.
Found: C, 62.4; H, 3.4.

Treatment of the bromo compound with methanol, sodium methoxide in methanol, sodium acetate in acetic acid, or with phenylmagnesium bromide led to uncrystallizable products in each case.

The dibromo compound (XXVII).—Two grams of the diketone treated as above, but with 2.6 g. of bromine, gave the dibromo compound (2.9 g.), crisp orange needles that melted at 162–165° and decomposed at about 185°.

Anal. Calc'd for $C_{17}H_{10}Br_2O_2$: C, 50.2; H, 2.5.
Found: C, 50.2; H, 2.5.

Treatment of the dibromodiketone with methanol gave no crystallizable product. Aniline reacted with the dibromo compound to give the calculated amount of aniline hydrobromide, but the other product was an uncrystallizable red oil.

Reaction of the diketone with aniline.—A deep-green solution was formed when the diketone (0.5 g.) was boiled with aniline (1 ml.) in benzene (20 ml.). Replacement of half of the solvent with petroleum ether precipitated 0.7 g. of a yellow crystalline powder that melted at 81–83°, but this could not be recrystallized without decomposition, and a satisfactory analysis was not obtained. The analogous compound formed with *p*-toluidine melted at 87.5–89°.

When aniline (1 ml.) was added to an ether solution of 0.3 g. of the diketone in the cold, a product (XXXIII, $R = C_6H_5$) that crystallized in small yellow needles that melted with decomposition at 108–110° was obtained. This substance decomposed to an oil when its recrystallization was attempted. It regenerated the diketone when treated with dilute hydrochloric acid.

Anal. Calc'd for $C_{23}H_{19}NO_2$: C, 80.9; H, 5.6.
Found: C, 81.2; H, 5.8.

The *p*-toluidine addition product (XXXIII, $R = p - C_7H_7$) had similar properties and melted at 120–122° with decomposition.

Anal. Calc'd for $C_{24}H_{21}NO_2$: C, 81.1; H, 5.9.
Found: C, 81.6; H. 6.2.

Reaction of the diketone with methanol.—One gram of the diketone was boiled for an hour in 15 ml. of methanol containing 5 drops of concentrated hydrochloric acid. The solution was concentrated and cooled, and the product which separated was recrystallized from methanol. There was obtained 0.65 g. of 1,1-dimethoxy-3,4-diphenylcyclopentenone-2 (XXIX): flat white needles that melted at 120–121°.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.6; H, 6.1; OCH_3, 21.1.
Found: C, 77.8; H, 6.7; OCH_3, 21.3.

The diketone was regenerated when the acetal was boiled with acetic acid containing a drop of hydrochloric acid.

1,1-Dimethoxy-2,3,4-triphenylcyclopentenol-2, (*XXX*).—An ether suspension of the acetal (XXIX) (2.94 g.) was added to a solution of phenylmagnesium bromide containing 0.52 g. of magnesium. The mixture was boiled for fifteen minutes, and was decomposed with iced ammonium chloride. The product, obtained in the usual way and crystallized from methanol, formed white needles which melted at 124–125°; yield 3.2 g.

Anal. Calc'd for $C_{25}H_{24}O_3$: C, 80.6; H, 6.5.
Found: C, 80.5; H, 6.5.

Dimer of 2,3,4-triphenylcyclopentadienone (XXXI).—A solution of 1,1-dimethoxy-2,3,4-triphenylcyclopentenol-2 in acetic acid containing 2% of sulfuric acid was boiled for a few minutes and then poured into water. The product was crystallized from ether, when it formed pale yellow needles that melted at 257–258° with darkening.

Anal. Calc'd for $C_{46}H_{32}O_2$: C, 89.6; H, 5.2.
Found: C, 89.5; H, 5.6.

The same compound was prepared by the action of acetic-sulfuric acid on anhydrophenylacetonebenzil.[16]

SUMMARY

A discussion of some of the properties of previously known cyclic α-diketones is presented.

The preparation and reactions of 1,2-diketo-3,4-diphenylcyclopentendione are described. It is noted that this diketone has little or no tendency to enolize, and that it has one particularly reactive carbonyl group.