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

THE REACTIONS AND ENOLIZATION OF CYCLIC DIKETONES. IV.[1] 1,2-DIKETO-3,4,5-TRIPHENYLCYCLOPENTENE*

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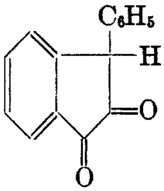
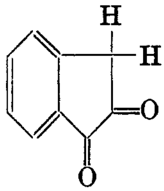
Evidence available from investigations carried out in this laboratory and from data in the literature indicates that among the many factors which affect the enolization of diketocyclopentane derivatives, two are of especial importance. These are (1) the nature of the second substituent on the carbon which bears the hydrogen atom involved in enolization, and (2) the state of saturation of the five-membered ring.

The first effect may be illustrated by a comparison of 1,2-diketo-3-phenylhydrindene (A) (enolic)[2] with 1,2-diketohydrindene (B) (ketonic).[3] From this comparison the conclusion may be drawn that a second hydrogen atom on the carbon bearing the one involved in the tautomerism hinders enolization.

The second effect may be illustrated by a comparison of 1,2-diketo-3,4-diphenylcyclopentene (C) (ketonic)[1] with 1,2-diketo-3,4-diphenylcylopentane (D) (enolic).[4] From this example it may be concluded that a double bond in the five-membered ring hinders enolization.


A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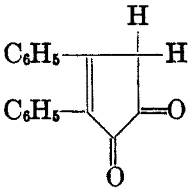
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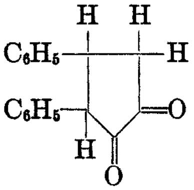
D

In the present paper the preparation and properties of 1,2-diketo-3,4,5-triphenylcyclopentene (V) are described. This diketone is related in

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[1] Previous paper in this field, GEISSMAN AND KOELSCH, J. ORG. CHEM., 3, 489 (1938).

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

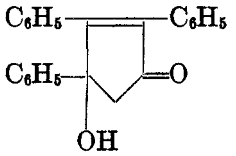
[2] KOELSCH, *J. Am. Chem. Soc.*, **58**, 1321 (1936).

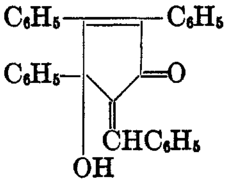
[3] KOELSCH AND HOCHMANN, J. ORG. CHEM., **3**, 503 (1938).

[4] VORLANDER AND SCHROEDTER, *Ber.*, **36**, 1490 (1903).

structure to 1,2-diketo-3-phenylhydrindene (A) but the properties of the two substances are markedly different. The hydrindene derivative is reddish-purple and behaves as an enol, while the cyclopentene is orange yellow and is ketonic. This difference may be explained as an instance of the second effect. In the cyclopentene diketone the double bond is definitely present in the five-membered ring, preventing enolization. In the hydrindene analog, however, the double bond, being part of an aromatic nucleus, is not necessarily within the five-membered ring, and indeed according to the Mills-Nixon hypothesis,[5] it is prevented from entering it.

The condensation of benzil with phenylacetone in the presence of alkali gave anhydrophenylacetonebenzil (I).[6] The location of the methylene group in this compound was established by the preparation of the benzal derivative (II) of the condensation product. Partial reduction led to the ketone (III), which was nitrosated, the nitroso compound (IV) being then hydrolyzed to the diketone (V).


I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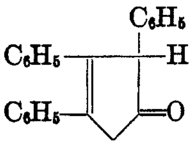
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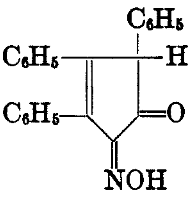
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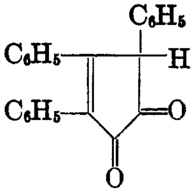
V

1,2-Diketo-3,4,5-triphenylcyclopentenone formed a phenazine (VI) with *o*-phenylenediamine, and was cleaved readily by hydrogen peroxide with the formation of α,β,γ-triphenylglutaconic anhydride (VII). It reacted with bromine in hot acetic acid, slowly at first, rapidly after some

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[5] Brockway and Taylor, "Ann. Reports of the Progress of Chemistry", The Chem. Soc., London, **1937**. Vol. 34, p. 219.

[6] This compound was also reported by Dilthey and Hurtig, *Ber.*, **67**, 2004 (1934), while the present research was in progress.

hydrogen bromide had formed. Bromination was somewhat easier than in the case of 1,2-diketo-3,4-diphenylcyclopentenone (C), indicating that although the triphenyl compound is not itself enolic, it is the more easily enolized of the two.

The diketone was not soluble in dilute aqueous alkali, but a drop of aqueous sodium hydroxide added to an alcoholic solution of the compound produced a blue-green coloration which faded almost immediately at room temperature but persisted about a minute at −10°. When a solution of sodium methoxide was added to the diketone in methanol, however, a deep blue-green color was produced which faded to yellow only after several hours at room temperature. A similar effect of the solvent on the stabilities of salts in other series has been observed. Thus, the red salts of 2-alkyl-1,3-diketohydrindene decompose to salts of *o*-alkylacetobenzoic acid much more rapidly in water than in alcohols,[7] and the rate at which the blue salts of isatin change into salts of isatinic acid is decreased as the proportion of alcohol in their solutions is increased.[8]

The diketone (V), unlike the diphenyl compound (C)[1] showed no tendency to form an acetal. It could be crystallized unchanged from acidic methanol, although such solutions did not possess the peculiar pink cast of those in non-polar solvents.

That the diketone can react in the enolic form was shown by its reaction with benzoyl chloride in pyridine. The benzoate (VIII) thus formed, in conformity with its cyclopentadienone structure, was deep-red, the color contrasting greatly with that of the diketone itself. Good evidence for the diketonic nature of the latter was found in its behavior towards phenylmagnesium bromide. Two moles of the Grignard reagent added to the diketone, forming the glycol (IX). This substance was not obtained crystalline, but its identity was established by treatment with hydriodic acid which dehydrated and reduced it to the known pentaphenylcyclopentadiene.[9]

The keto alcohol (X) which would have been formed if the diketone had reacted in its enolic form was obtained by treating the bromodiketone (XI) with phenylmagnesium bromide; this type of reaction is characteristic of α-bromoketones.[10] The product (X) was dehydrated to tetraphenylcyclopentadienone (XII), and reduced to tetraphenylcyclopentenone (XIII), both known compounds.

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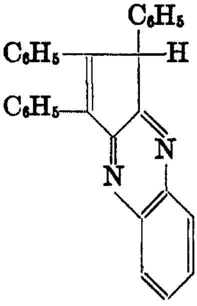
[7] Hantzsch and Czapp, *Z. phys. Chem.*, **146**, 135 (1930).

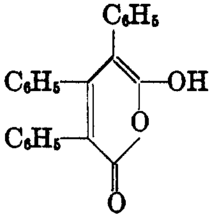
[8] Heller, "Sammlung Chem. und Chemisch-tech. Vorträge"; Ferdinand Enke, Stuttgart; **1931**, New Series, Vol. 5, p. 56.

[9] Ziegler and Schnell, *Ann.*, **445**, 266 (1925).

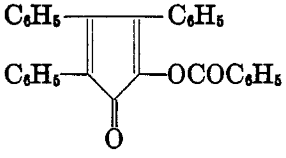
[10] Kohler and Tishler, *J. Am. Chem. Soc.*, **54**, 1494 (1932).



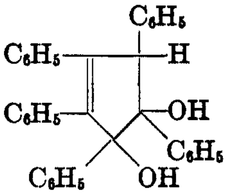
VI



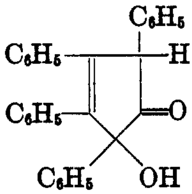
VII



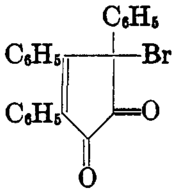
VIII



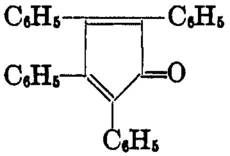
IX



X



XI



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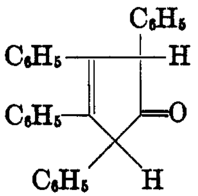

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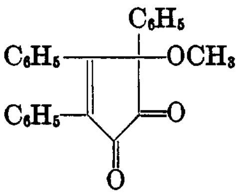
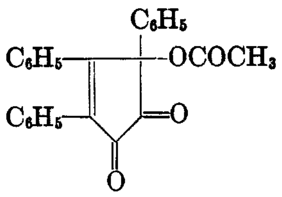


XIV

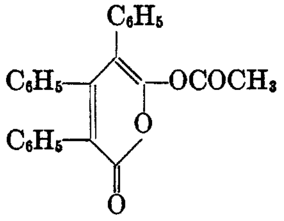
The bromine atom in the bromodiketone (XI) had a very marked reactivity. It was replaced by methoxyl when the bromodiketone was dissolved in methanol, the methoxydiketone (XIV) being formed. This substance possessed a striking cerise color similar to that of 3-phenyl-3-methoxy-1,2-diketohydrindene. Unlike the latter compound however, it showed no tendency to form an acetal, nor was an acetal of the methoxy compound formed during replacement of the bromine atom by methoxyl. The methoxydiketone (XIV) formed a phenazine, and was cleaved by alkaline hydrogen peroxide.

In contrast to the behavior of the bromodiketone towards methanol, with water the substance was converted into α,β,γ-triphenylglutaconic anhydride. This transformation probably occurred through the hydrolysis of the bromo compound to the diketone (V) and hypobromous acid, followed by oxidation of the diketone by the hypobromous acid to the anhydride. This mechanism was supported by the observation that hydrolysis of the bromodiketone in the presence of phenol yielded the diketone (V), and not the anhydride.

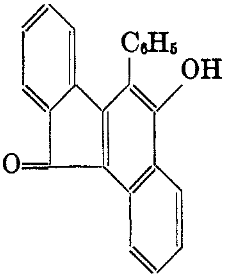
The bromodiketone showed two reactions which are probably closely related to this abnormal hydrolysis. It reacted with silver acetate in acetic acid with the production of an orange compound (XV or XVI) which by the action of cold concentrated sulfuric acid was converted into (XVII). This substance (XVII) was also obtained by the action of sulfuric acid on α,β,γ-triphenylglutaconic anhydride (VII). There can be little doubt that the compound is 1,2-benzo-3-hydroxy-4-phenylfluorenone, since it gave a red-violet solution in alkali, formed a yellow benzoate, and resembled the fluorenone (XVIII) obtained from α,β-diphenylglutaconic anhydride.[1] When the bromodiketone (XI) was treated directly with sulfuric acid there was obtained a bromine-containing compound (XIX) which acted in every way like the compound XVII. Since XIX was also obtained by bromination of XVII, its structure as x-bromo-1,2-benzo-3-hydroxy-4-phenylfluorenone was confirmed.



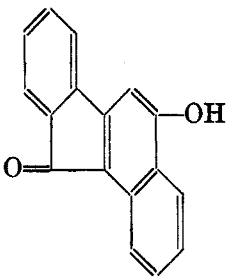
XV



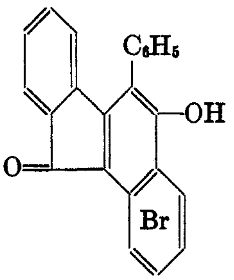
XVI



XVII



XVIII



XIX

EXPERIMENTAL

Anhydrophenylacetonebenzil (*I*).—To 59 g. of phenylacetone, 91 g. of benzil, and 500 ml. of methanol was added 25 ml. of a 20% alcoholic potassium hydroxide solution. The mixture was boiled for thirty minutes, and was poured into water. The gummy precipitate, which crystallized on standing, was ground in a mortar, washed thoroughly with water, dried and crystallized from benzene-ligroïn. There was obtained 95.5 gm. of a slightly yellow product which melted at 162–164°. For analysis, a portion crystallized from methanol formed silky white needles that melted at 164–165°.

Anal. Calc'd for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5.
Found: C, 84.7; H, 5.3.

The compound formed a phenylhydrazone which melted at 173–174° with decomposition and a *p*-nitrophenylhydrazone which melted at 214–215° with decomposition.

Its benzal derivative (II) was obtained when 1 g. of the cyclopentenolone, 0.5 ml. of benzaldehyde, and 10 ml. of 1% alcoholic potassium hydroxide were allowed to stand for several hours at room temperature. Crystallized from alcohol it formed pale-yellow needles that melted at 217.5–218°.

2,3,4-Triphenylcyclopentenone (III).—Eighty-nine grams of the cyclopentenolone (I) was placed in 500 ml. of acetic acid; 155 g. of 45% hydriodic acid was added in the cold, and the mixture was then boiled under a reflux for five minutes. The solution was poured into aqueous sodium bisulfite, and was extracted once with ether. When the ether solution was washed with water and sodium carbonate, the reduction product separated almost completely. It was filtered, washed with ether, and dried. Crystallized once from alcohol the product formed faintly-yellow flat needles (75 g.) which melted at 142–143°. The pure substance, from alcohol, was white, m. p. 142–143°.

Anal. Calc'd for $C_{23}H_{18}O$: C, 89.0; H, 5.9.
Found: C, 88.5; H, 6.1.

2-Isonitroso-3,4,5-triphenylcyclopentenone (IV).—Attempts to nitrosate the ketone (III) in alcohol gave only poor yields of the desired product, but the use of ether as a solvent led to excellent results. Fifty-four grams of the ketone (III) was boiled for ninety minutes in 1 liter of ether containing 65 ml. of butyl nitrite and 25 ml. of concentrated hydrochloric acid. The nitroso compound (45 g.) was then filtered off and washed. It was obtained as a white, poorly crystalline solid which melted with decomposition at 221–223°. For purification it was best dissolved in hot 2% caustic soda, filtered, precipitated with acid, and crystallized from acetic acid. It then formed small white nodules that melted with decomposition at 228–229°.

Anal. Calc'd for $C_{23}H_{17}NO_2$: C, 81.4; H, 5.05.
Found: C, 83.45, 82.79, 83.05, 83.18; H, 5.23, 5.25, 5.12, 5.04.

The *benzoate* obtained from the nitroso compound and benzoyl chloride in pyridine, and crystallized from dilute acetic acid, formed yellow plates that melted with decomposition at 154–155°.

Anal. Calc'd. for $C_{30}H_{21}NO_3$: C, 81.3; H, 4.7.
Found: C, 81.2; H, 5.2.

1,2-Diketo-3,4,5-triphenylcyclopentene (V).—A mixture of 45 g. of the crude isonitroso compound, 200 ml. of acetic acid, 200 ml. of 40% formalin, and 50 ml. of concentrated hydrochloric acid was boiled under a reflux for one hour. The isonitroso compound did not dissolve, but slowly changed in color and form until at the end of the boiling the liquid was filled with orange needles and small lumps of poorly crystalline orange solid. Water was added, the product was collected, washed with water and dried (41 g., m. p. 157–160°). This impure product was extracted with warm benzene, which left about 10 g. of a white by-product melting at about 235° (dec.) undissolved. The benzene solution was concentrated, and ligroïn was added. On cooling there was obtained 25 g. of orange needles that melted at 157–161°. Recrystallized from benzene, the diketone formed orange needles which melted at 162–163.5°.

Anal. Calc'd for $C_{23}H_{16}O_2$: C, 85.2; H, 5.0.
Found: C, 85.2; H, 4.7.

The diketone dissolved in concentrated sulfuric acid with a clear deep-red color. Its behavior towards aqueous and alcoholic alkali has been described in the first part of this paper, as has its behavior towards alcohol.

The *phenazine* (*VI*) obtained from the diketone and *o*-phenylenediamine in alcohol, crystallized from acetic acid in the form of white prisms that melted at 226–227° with decomposition. It dissolved in concentrated hydrochloric acid with a crimson color, and in sulfuric acid with a deep purple color.

Anal. Calc'd for $C_{29}H_{20}N_2$: C, 87.9; H, 5.1.
Found: C, 88.0; H, 5.1.

Benzoylation of the diketone.—Treatment of the diketone (1 g.) in pyridine (10 ml.) with benzoyl chloride (3 ml.) gave the benzoate (VIII) in good yield. The product was purified by solution in ether, washing with dilute hydrochloric acid and with sodium carbonate, and crystallization from acetic acid. 2,3,4-Triphenyl-5-benzoyloxycyclopentadienone formed copper-red needles which melted with decomposition at 242–243°.

Anal. Calc'd for $C_{30}H_{20}O_3$: C, 84.1; H, 4.7.
Found: C, 83.9; H, 4.7.

Cleavage of the diketone with hydrogen peroxide.—To a suspension of 1 g. of the diketone in 30 ml. of alcohol was added 0.5 ml. of 30% hydrogen peroxide, and then, dropwise, 1 ml. of 20% sodium hydroxide. After the solid had dissolved, the solution was poured into water and washed with ether. Acidification of the aqueous layer gave a α, β, γ-triphenylglutaconic anhydride (0.45 g.) which formed white needles that melted at 166–167° from benzene-petroleum ether. The anhydride gave a green color with alcoholic ferric chloride, and behaved as a monobasic acid, although the end-point of the titration drifted.

Anal. Calc'd for $C_{23}H_{16}O_3$: C, 81.2; H, 4.8; Neut. equiv., 340.
Found: C, 81.2, H, 5.0; Neut. equiv., 334.

Reaction of the diketone with phenylmagnesium bromide.—To the Grignard reagent prepared from 6.2 g. of bromobenzene and 1 g. of magnesium was added a benzene solution of 3.25 g. of the diketone. The mixture was boiled for thirty minutes and then decomposed with iced ammonium chloride. The solvents and biphenyl were removed by steam distillation in the presence of aqueous sodium carbonate, but the product could not be obtained crystalline. The glassy product was boiled for thirty minutes with an excess of hydriodic acid in acetic acid, which gave a good yield of 1,2,3,4,5-pentaphenylcyclopentadiene, yellow needles that melted at 252–254°.

Anal. Calc'd for $C_{35}H_{26}$: C, 94.2, H, 5.9.
Found: C, 94.1; H, 6.3.

This hydrocarbon is described by Ziegler[9] as melting at 244–246°, but a sample prepared by his method was found to melt at 252–254° either alone or mixed with the substance obtained from the diketone.

Bromination of the diketone.—Five grams of the diketone was placed in 30 ml. of acetic acid containing 3 g. of bromine; the mixture was warmed to 65°, a higher temperature causing the formation of a tarry product. The diketone went into solution, and, on scratching, the bromo compound (XI) (4.45 g.) separated. From acetic acid the product formed yellow-orange needles that melted at 145–146°.

Anal. Calc'd for $C_{23}H_{15}BrO_2$: C, 68.5; H, 3.7.
Found: C, 68.5; H, 4.0.

When the bromo compound was boiled in dilute acetic acid it was converted in rather poor yield into α,β,γ-triphenylglutaconic anhydride (m. p. 166–167°), identified by comparison with a sample obtained by hydrogen peroxide cleavage of the diketone (V).

1,2-Diketo-3,4,5-triphenyl-3-methoxycyclopentene (XIV).—A deep red solution was formed when the bromodiketone (XI) (2 g.) was boiled for five minutes with methanol (20 ml.). Boiling was continued for ten minutes, the solution was then poured into water and extracted with ether. The ether solution was washed with sodium carbonate, dried, and concentrated, giving 1.1 g. of a pink solid. The product, crystallized from benzene-petroleum ether and then from methanol, formed small cerise prisms which melted at 148–150°.

Anal. Calc'd for $C_{24}H_{18}O_3$: C, 81.4; H, 5.1; OCH_3, 8.8.
Found: C, 81.2; H, 4.9; OCH_3, 8.9.

The phenazine of the methoxydiketone formed colorless prisms that melted at 200–201° after crystallization from methanol.

Treated with alkaline hydrogen peroxide in methanol-water, the methoxydiketone (0.2 g.) gave a colorless product (0.06 g.) (*α-methoxy-α,β,γ-triphenylglutaconic anhydride*) which formed white needles from acetic acid that melted at 161–162° with gas evolution.

Anal. Calc'd. for $C_{24}H_{18}O_4$; C, 77.8; H, 4.9.
Found: C, 77.2; H, 5.4.

Reaction of the bromodiketone with phenylmagnesium bromide.—The bromodiketone (XI) (4.5 g.) was added to the Grignard reagent prepared from 2 g. of magnesium and 12.5 g. of bromobenzene. The solution was refluxed for thirty minutes, decomposed with iced ammonium chloride, and worked up in the usual way. The product (4.35 g.) after crystallization from benzene-ligroïn and then from acetic acid, formed colorless prisms which melted at 208.5–210°.

Anal. Calc'd for $C_{29}H_{22}O_2$: C, 86.6; H, 5.5.
Found: C, 86.6; H, 5.4.

On warming with acetic acid containing a little sulfuric acid, or on distillation at reduced pressure the tetraphenylcyclopentenolone obtained above gave tetraphenylcyclopentadienone[11] (m. p. and mixture m. p. 217–218°). On boiling with acetic acid containing hydriodic acid the cyclopentenolone yielded tetraphenylcyclopentenone[11] (m.p. and mixture m.p. 162–163°) and with acetic acid, hydrogen chloride and zinc, it yielded tetraphenylcyclopentenol[12] (m.p. and mixture m.p. 174–176°).

Reaction of the bromodiketone with silver acetate.—Silver bromide was rapidly precipitated when the bromodiketone was warmed with an excess of silver acetate in acetic acid. Dilution of the filtered solution resulting gave a good yield of an acetoxy compound (XV or XVI) which formed bright orange prisms that melted at 174–177°.

Anal. Calc'd for $C_{25}H_{18}O_4$: C, 78.5; H, 4.7.
Found: C, 78.2; H, 4.9.

The above compound gave a bright green solution in sulfuric acid, and dilution of this with water precipitated an orange substance. Recrystallized from benzene-ligroïn, this substance formed deep orange needles which melted at 237–238° and gave a deep red-violet solution in aqueous sodium hydroxide.

The same orange compound [1,2-benzo-3-hydroxy-4-phenylfluorenone, (XVII)] was obtained when α,β,γ-triphenylglutaconic anhydride was allowed to stand in

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[11] Dilthey and Quint., *J. prakt. Chem.*, **128**, 139 (1930).

[12] Dilthey, Braun, and Trösken, *ibid.*, **139**, 12 (1933).

cold concentrated sulfuric acid for a short time. Because of the formation of water-soluble products, the orange fluorenone was not obtained in good yield from either the anhydride or the acetoxy compound.

Anal. Calc'd for $C_{23}H_{14}O_2$: C, 85.7; H, 4.3.
Found: C, 85.6; H, 4.4.

Reaction of the bromodiketone with sulfuric acid.—When 3.0 g. of the bromodiketone (XI) was dissolved in about 25 ml. of concentrated sulfuric acid, the initially red-brown solution rapidly became green, and hydrogen bromide was evolved. The solution was poured into water after five minutes, and the orange precipitate was crystallized from xylene. It formed deep red-orange needles which melted at 287–289°, gave a deep red-violet solution in dilute alkali, and formed a benzoate (m.p. 240–241°) on treatment with benzoyl chloride in pyridine.

x-Bromo-1,2-benzo-3-hydroxy-4-phenylfluorenone was also obtained when a slight excess of bromine in acetic acid was added to the green solution obtained by dissolving α,β,γ-triphenylglutaconic anhydride in sulfuric acid.

Anal. Calc'd for $C_{23}H_{13}BrO_2$: C, 68.8; H, 3.2.
Found: C, 71.3; H, 3.9.

SUMMARY

The preparation and reactions of 1,2-diketo-3,4,5-triphenylcyclopentene are described. It is noted that the ketonic nature of this diketone is in agreement with the postulated hindrance of enolization of such diketones by the presence of a double bond in the five-membered ring. It is also noted that this diketone is apparently more easily enolized than 1,2-diketo-3,4-diphenylcyclopentene. This conforms with the postulated hindrance of enolization in such diketones by a second hydrogen on the carbon atom bearing the hydrogen involved in the enolization.