the substance retained its yellow color and melted at 168–169° (reported[1] 168.5–171°).

o-Desylbenzoic Acid (III).—The lactone II dissolved rapidly when it was warmed with alcoholic sodium hydroxide. Dilution with water and acidification gave the acid in nearly quantitative yield. Recrystallized from alcohol, the product melted at 138–142° (reported[1] 139–142°).

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.7; H, 5.1. Found: C, 79.8; H, 5.3.

When the keto acid was boiled for two minutes in acetic acid containing 2% of sulfuric acid, it was reconverted into II. Although the product was identical in crystal form and melting point with the lactone obtained directly from the oxide, it was colorless. It gave the acid III on alkaline hydrolysis, and on analysis it gave figures which agree much better with the required values than do those reported by Weitz and Scheffer.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.5; H, 4.7. Found: C, 84.4; H, 4.7.

Boiling II with 30% sodium hydroxide in 1:1 methanol-water for three hours gave benzoic acid (removed by steam distillation) and diphenylmethane-o-carboxylic acid. The latter was identified by comparison with an authentic sample and by conversion into anthrone.

2,3-Dihydroxy-2,3-diphenylindanone (V).—A solution of I (1 g.) in 10 ml. of acetic acid was mixed at room temperature with 10 ml. of acetic acid which had been saturated with hydrogen chloride. After it had stood for five minutes, the mixture was poured on ice, and the product was washed with benzene. There was obtained 0.8 g. of V (insoluble in benzene) and 0.15 g. of II (soluble). Poorer yields of the glycol were obtained when oxalic or aqueous hydrochloric acid was used for the hydration. The pure glycol became yellow at 155°, sintered at 160°, and melted to a deep red liquid at 168°. The red color remained when the melt was cooled, but it was bleached on exposure to sunlight.

o-Benzoylbenzil.—A suspension of 0.5 g. of V in 100 ml. of benzene was treated with 0.85 g. of lead tetraacetate. A yellow color developed only slowly, and after it had been warmed for one hour the mixture was filtered and poured onto ice. Crystallized from ethanol, the product (0.28 g.) formed yellow needles that melted at 93–94°.

Anal. Calcd. for $C_{21}H_{14}O_3$: C, 80.2; H, 4.5. Found: C, 80.2; H, 4.5.

The same compound was obtained when 2 g. of diphenylindone in 20 ml. of acetic acid was treated with 1.5 g. of chromic anhydride and warmed at 80–85° for two minutes; yield, 0.85 g.

Summary

2,3-Diphenyl-2,3-epoxyindanone is rearranged to 3,4-diphenylisocoumarin by warm sulfuric acid in acetic acid, and hydrated to 2,3-dihydroxy-2,3-diphenylindanone by cold hydrogen chloride in acetic acid.

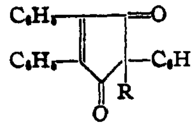
Minneapolis, Minnesota Received January 30, 1943

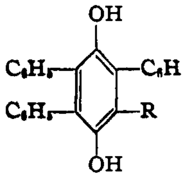
[Contribution from the School of Chemistry of the University of Minnesota]

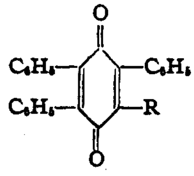
A Ring Enlargement of 2,4,4-Triphenylcyclopentenedione

By C. F. Koelsch and Stanley Wawzonek

After a convenient method for the synthesis of 2,4,4-triphenylcyclopentenedione-1,3 (I) had been developed,[1] it appeared of interest to see if this substance could be converted into the previously unknown triphenylquinone (VI) through a series of reactions analogous to that used for the synthesis of naphthoquinones from indandiones.[2] It was found that the conversion could be carried out smoothly, and in the present paper the details of the reaction and some of the transformations undergone by the product are described.


I, R = H
II, R = $CH_2COOC_2H_5$


III, R = $COOC_2H_5$
IV, R = COOH
V, R = H


VI, R = H
VII, R = $COOC_2H_5$
VIII, R = COOH
IX, R = OH

Experimental

Ethyl 2,5-Diketo-1,3,4-triphenylcyclopentenylacetate (II).—A solution of 1.6 g. of sodium and 22.7 g. of triphenylcyclopentenedione (I) in 200 ml. of dry alcohol was treated with 15.4 ml. of ethyl bromoacetate, and the mixture was then boiled until its purple color had completely disappeared. Cooling gave 23 g. of crude product; the pure substance formed yellow needles (21.1 g., 74%) that melted at 126–127° after it had been recrystallized from alcohol.

Anal. Calcd. for $C_{27}H_{22}O_4$: C, 79.0; H, 5.4. Found: C, 79.3; H, 5.3.

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[1] Koelsch and Wawzonek, *J. Org. Chem.*, **6**, 684 (1941).

[2] Radulescu and Gheorgiu, *Ber.*, **60**, 186 (1927). For other references see Koelsch and Beyers, This Journal, **62**, 560 (1940)

Ethyl 3,4,6-Triphenylgentisate (III).—To a solution of 2 g. of sodium in 45 ml. of dry alcohol was added 10.3 g. of II. The mixture was boiled for four hours under hydrogen, then distilled to dryness and taken up in water. Acidification gave a precipitate which on drying and crystallization from benzene formed fine white needles (7.9 g., 76%) that melted at 155–157°.

Anal. Calcd. for $C_{27}H_{22}O_4$: C, 79.0; H, 5.4. Found: C, 78.9; H, 5.9.

The **diacetate,** prepared with acetic anhydride and potassium acetate and crystallized from acetic acid, formed fine needles that melted at 157–159°. A mixture with the unacetylated hydroquinone melted at a considerably lower temperature.

Anal. Calcd. for $C_{31}H_{26}O_6$: C, 75.3; H, 5.3. Found: C, 75.4; H, 5.4.

Triphenylgentisic Acid (IV).—A solution of 16.4 g. of III in 100 ml. of water, 10 ml. of alcohol, and 70 ml. of 10% potassium hydroxide was boiled under hydrogen for two hours. Acidification gave a precipitate which was crystallized from acetic acid yielding 10.8 g. (71%) of a white microcrystalline powder which melted at 216–221° with gas evolution.

Anal. Calcd. for $C_{25}H_{18}O_4$: C, 78.5; H, 4.7. Found: C, 78.5; H, 5.1.

Triphenylhydroquinone (V).—A solution of 3.8 g. of IV in 20 ml. of dry quinoline containing a trace of copper acetate was boiled under hydrogen for two hours (carbon dioxide was evolved even at 135°), then cooled and mixed with 6 *N* hydrochloric acid and ether. The solid (0.5 g., see below) was removed by filtration, and the ether was evaporated. The residue was crystallized from benzene yielding poorly formed white plates (1.8 g., 55%) that melted at 151–152°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.3. Found: C, 85.1; H, 5.5.

The solid noted above was found to be a 1:1 complex of triphenylhydroquinone and quinoline hydrochloride. It was synthesized by warming a solution of the quinone in quinoline and then adding hydrochloric acid. It gave a qualitative test for chlorine, it could be sublimed without decomposition under reduced pressure, and it was separated into its components when it was boiled with dilute acetic acid. Recrystallized from glacial acetic acid, it formed a deep yellow powder that melted at 188–192°.

Anal. Calcd. for $C_{33}H_{26}ClNO_2$: C, 78.7; H, 5.0. Found: C, 79.0; H, 5.2.

Triphenylquinone (VI).—A solution of 1.1 g. of V in 10 ml. of acetic acid was treated with 0.22 g. of chromic anhydride in 1 ml. of water. The mixture was boiled for two minutes and then poured into water and ether. Evaporation of the ether left 0.73 g. of orange plates that melted at 154.5–155°. The substance crystallized well from either alcohol or acetic acid, and its melting point was not changed by this treatment.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.7. H, 4.8. Found: C, 86.0; H, 4.9.

Triphenylquinone was recovered unchanged after it had been boiled for ten minutes with acetic anhydride containing sulfuric acid. It formed no quinhydrone when it was mixed with triphenylhydroquinone in acetic acid, and when this solution was cooled, the components crystallized separately. Triphenylquinone was reduced to the hydroquinone when it was warmed with zinc dust in acetic acid.

A solution of triphenylquinone (0.3 g.) in 40 ml. of acetic acid was treated at 10° with an aqueous benzene, diazonium sulfate solution prepared from 0.5 g. of aniline. Sodium acetate (3 g.) was added, and the mixture was allowed to stand for ten hours at 10°. From the solid products, there was recovered some unchanged triphenylquinone. There was also obtained 0.02 g. of tetraphenylquinone which melted at 309–314° alone or mixed with an authentic sample.[3]

Ethyl Triphenylquinonecarboxylate (VII).—A solution of 1 g. of III and 0.25 g. of chromic anhydride in 10 ml. of acetic acid was boiled for ten minutes and then allowed to stand at room temperature for twelve hours. The product was removed by filtration and recrystallized from alcohol, giving small orange needles (0.5 g.) that melted at 207–208°.

Anal. Calcd. for $C_{27}H_{20}O_4$: C, 79.4; H, 4.9. Found: C, 79.4; H, 5.2.

Warmed with zinc dust in acetic acid, the quinone ester was reduced to the corresponding hydroquinone.

When VII (1.9 g.) was boiled for four hours with 3% aqueous-alcoholic potassium hydroxide, it gave a red oil and 0.6 g. of triphenylgentisic acid (IV), reduction as well as hydrolysis taking place.

Triphenylquinonecarboxylic Acid (VIII).—A hot solution of 8.1 g. of ferric chloride in 10 ml. of water was added to a boiling solution of 3.8 g. of IV in 45 ml. of acetic acid. The resulting dark red solution was boiled for ninety minutes and then poured into dilute hydrochloric acid and ether. The ether layer was washed several times with dilute hydrochloric acid and then evaporated. The crystalline orange residue (2.1 g., 55%) melted at 213–215° with decomposition but, after recrystallization from acetic acid and then from ethyl acetate, the product melted at 202–207° with decomposition.

Anal. Calcd. for $C_{25}H_{16}O_4$: C, 78.9; H, 4.2. Found: C, 78.9; H, 4.6.

Attempts to carry out the oxidation of IV with chromic anhydride or with lead dioxide gave complex products which were not investigated.

Warmed with zinc dust in acetic acid, the quinone acid was reconverted into the corresponding hydroquinone (VII).

2-Hydroxy-3,5,6-triphenylquinone. (IX).—A mixture of 1 g. of III with 20 ml. of ethanol and 20 ml. of 5% potassium hydroxide was heated on a steam-bath for twenty-four hours while a stream of air was bubbled in. During this time the originally red solution became deep purple. The mixture was then acidified and extracted with ether. The oil so obtained could not be crystallized directly, but extraction with 10% potassium hydroxide gave a difficultly soluble purple salt which was filtered off. Acidification of a solution of the purified salt gave 0.12 g. of the hydroxyquinone, which formed orange-red needles

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[3] Kvalnes, THIS JOURNAL, 56, 2479 (1934)

that melted at 160–161.5° after crystallization from benzene–ligroin.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.8; H, 4.6. Found: C, 81.7; H, 4.6.

2-Acetoxy-3,5,6-triphenylquinone, prepared from the hydroxyquinone with acetic anhydride and sulfuric acid, formed orange needles that melted at 185.5–187.5° after crystallization from acetic acid.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6. Found: C, 79.5; H, 4.5.

The acetate was readily saponified by alcoholic potassium hydroxide.

Summary

2,4,4-Triphenylcyclopentenedione-1,3 is readily alkylated by ethyl bromoacetate, and when the resulting diketoester is treated with sodium ethoxide it undergoes rearrangement to ethyl 3,4,6-triphenylgentisate. A number of transformations of this rearrangement product are described, including its conversion into triphenylhydroquinone and hydroxytriphenylquinone.

MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 30, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Polymerization of Styrene in the Presence of Nitrobenzene, 2,4-Dinitrochlorobenzene and Nitromethane

BY CHARLES C. PRICE AND DOROTHY ANN DURHAM

The few brief observations[1] that certain vinyl-type polymerizations are inhibited or retarded by various aromatic nitro compounds have attracted very little attention. There has been no direct experimental evidence as to the specific nature of the effect and no explanation has been suggested to account for this very interesting phenomenon.

Since the polymerizations which are subject to this effect of aromatic nitro compounds are those which proceed through an intermediate active free radical,[1c,2] there exists the possibility that the active radical may become inactivated by coupling with the aromatic nitro compound. The preparation of polystyrene in the presence of nitrobenzene and 2,4-dinitrochlorobenzene has confirmed this surmise since the samples contained the elements of the nitro compound in a ratio as high as the theoretical ratio of one nitroaryl residue per polymer molecule.

Several samples of polystyrene prepared in the presence of a small amount of 2,4-dinitrochlorobenzene contained chlorine (2.3 to 3.2%) and nitrogen (2.3 to 2.7%) corresponding to one dinitrochlorophenyl group per polymer molecule. A sample of polystyrene prepared in the presence of nitrobenzene contained nitrogen (0.53%) corresponding to one nitrophenyl group for every other polymer molecule.

Several other samples of polystyrene prepared in the presence of smaller amounts of these two nitro compounds also contained the elements of the nitro compound but in an appreciably smaller proportion than the maximum of one per polymer molecule. These results may be accounted for on the basis of competition between the reaction of the growing chain with retarder and the normal cessation process. The chance for normal cessation to occur would, of course, be favored by decreased concentration of the retarder.

The most logical and satisfactory manner to account for the destruction of the activity of the growing free radical polymer chain by reaction with a *molecule* is by a process which will transform the "active" radical into an "inactive" one[3]: the odd electron characteristic of the free radical may only be "neutralized" by pairing with the odd electron of another free radical.

On this basis, the observed coupling of the growing chain with aromatic nitro compounds must involve an intermediate addition compound in which the odd electron has become sufficiently stabilized so that it will no longer add to monomer molecules. Since coupling of free radicals with nitrobenzene takes place principally in the *para*-position, the over-all scheme for the benzoyl peroxide-catalyzed polymerization of styrene in the presence of nitrobenzene may be indicated as follows

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[1] (a) Ostromislensky and Shepard, U. S. Patent 1,550,323, August 18, 1925; (b) Foord, *J. Chem. Soc.*, 48 (1940); (c) Price, Kell and Krebs, THIS JOURNAL, **64**, 1103 (1942).

[2] Staudinger, *Trans. Faraday Soc.*, **32**, 323 (1936); Flory, THIS JOURNAL, **59**, 241, (1937); Schulz and Wittig, *Naturwissenschaften*, **27**, 387, 456 (1939); Schulz, *ibid.*, 659 (1939); Norrisn and Brookman, *Proc. Roy. Soc.* (London), **A171**, 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1087 (1939); Kamenskaya and Medvedev, *Acta Physicochem.*, *U. S. S. R.*, **13**, 565 (1940); Melville, *Proc. Roy. Soc.* (London), **A163**, 511 (1937).

[3] The terms "active" and "inactive" here refer solely to whether or not the radicals are reactive enough to add to a monomer molecule and propagate the polymerization.