4-Methyl-2-octanone.—2,4-Dimethyl-1-octene (26.7 g., 0.19 mole) was treated in the manner employed to prepare 2-hexanone. On distillation, fractions b. p. 90–94° (40 mm.), were collected, amounting to 18.6 g. (0.131 mole) or 68.9% of the theoretical yield. Refractionation gave a center cut, b. p. 92–94° (40 mm.); 2,4-dinitrophenylhydrazone, oil; semicarbazone, m. p. 69–70°.

Summary

Practical directions are given to obtain 60 to 70% of aldehydes, ketones or acids by oxidation of olefins with ozone.

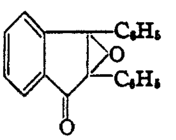
Columbus, Ohio Received November 27, 1941

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

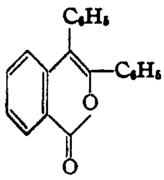
The Action of Acids on 2,3-Diphenyl-2,3-epoxyindanone

By C. F. Koelsch and C. D. Le Claire

By the action of sulfuric acid on 2,3-diphenyl-2,3-epoxyindanone (I) in acetic acid solution, Weitz and Scheffer[1] obtained a straw yellow compound which they formulated as a lactone (II). When hydrochloric acid was used in place of sulfuric acid, there was obtained a colorless substance formulated as a hydroxy lactone (IV). Acidification of a solution of II in sodium hydroxide yielded an acid (III), but when a similar solution of IV was acidified, IV was precipitated unchanged. When an alkaline solution of IV was warmed, a neutral yellow compound (m. p. 127–129°) isomeric with II precipitated. It was suggested that this yellow compound might be 3,3-diphenylindandione (VI), although not much weight was attached to this suggestion because the compound gave no quinoxaline.



I



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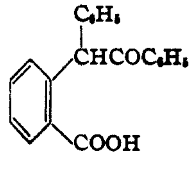
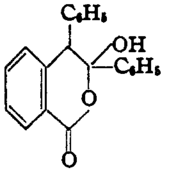
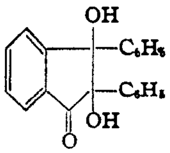


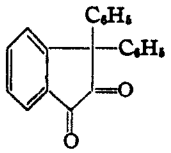
III



IV



V



VI

A synthesis of VI was of considerable interest,[2] and a detailed investigation of the compounds of Weitz and Scheffer was, therefore, undertaken in the hope that one of their yellow compounds might actually be a diketone. The results of this investigation are reported in the present paper.

The sulfuric acid product is II, as previously formulated, for on hydrolysis with alcoholic alkali it yields the acid III, and this acid must be *o*-desylbenzoic acid since on treatment with stronger alkali it yields benzoic acid and *o*-benzylbenzoic acid. When III is dehydrated, it yields a white substance which despite its lack of color, is identical with II. The yellow color of II, a former basis for criticism of the structure assigned, is thus caused by adsorbed impurities.

In view of the behavior of II toward alkali, the compound obtained from the oxide and hydrochloric acid cannot have structure IV, for a substance having this structure should likewise be hydrolyzed to the acid III. The compound reacts with lead tetraacetate yielding *o*-benzoylbenzil, and, therefore, it must be the glycol V.

The reported conversion of the glycol (V) into a yellow compound of m. p. 127–129° could not be repeated. Boiled for a short time with alkali, the glycol was unchanged, and when the boiling was prolonged, the compound yielded benzoic acid, *o*-benzoylbenzoic acid, and *o*-benzoylbenzil.

Consideration of the structure now established for II renders it likely that the substance obtained by the action of acids on 3-(*p*-dimethylaminophenyl)-2,3-epoxy-2-(*o*-formylphenyl)-indanone[3] is 4 - (*p* - dimethylaminophenyl) - 3 - (*o* - formylphenyl)-isocoumarin rather than 3-(*p*-dimethylaminophenyl) - *spiro* - [indan - 2,1′(3′) - isobenzofuran]-dione-1,3′; the new formulation accounts for the aldehydic properties reported for the substance.

Experimental

3,4-Diphenylisocoumarin (II).—A suspension of 5 g. of the oxide (I) in 25 ml. of acetic acid containing one drop of sulfuric acid was warmed gently for a few minutes. The solid dissolved, and the yellow lactone (5 g.) rapidly separated. Recrystallized from acetic acid several times,

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(1) Weitz and Scheffer, *Ber.*, **54**, 2344 (1921).

(2) The desired synthesis has been carried out using 3,3-diphenylindanone-1 as the starting material: Koelsch and Le Claire, *J. Org. Chem.*, **6**, 516 (1941).

(3) Weitz, *Ann.*, **418**, 1 (1918).

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.

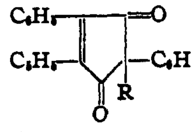
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 30, 1943

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

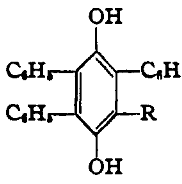
A Ring Enlargement of 2,4,4-Triphenylcyclopentenedione

BY C. F. KOELSCH AND STANLEY WAWZONEK

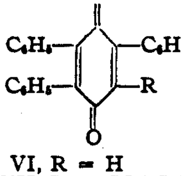
After a convenient method for the synthesis of 2,4,4-triphenylcyclopentenedione-1,3 (I) had been developed,[1] it appeared of interest to see if this substance could be converted into the previously unknown triphenylquinone (VI) through a series of reactions analogous to that used for the synthesis of 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)