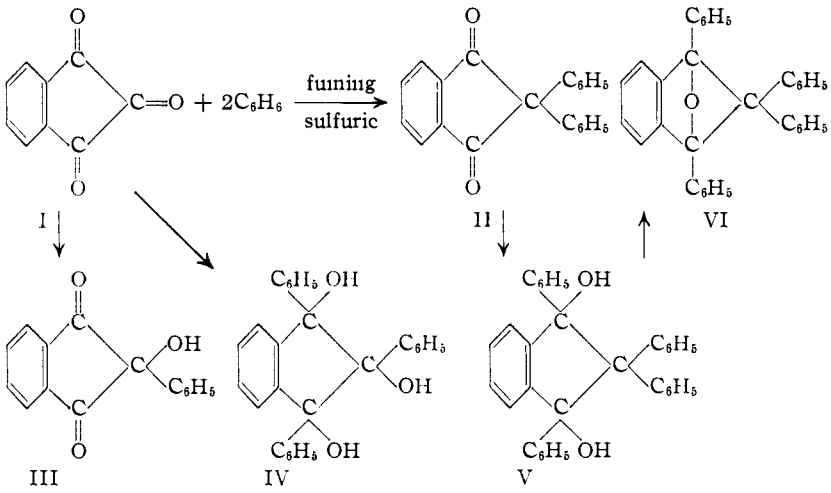
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

1,3-Diketo-2,2-diphenylhydrindene

BY RADWAN MOUBASHER

1,3-Diketo-2,2-diphenylhydrindene has been prepared and its behavior toward Grignard reagent studied. No evidence for cleavage was obtained. The reaction of triketoindane with phenylmagnesium bromide has been studied. Attempts to prepare the product of diaddition were unsuccessful.

The unknown 1,3-diketo-2,2-diphenylhydrindene (II) has been prepared by the condensation of triketoindane (I) with benzene using fuming sulfuric acid as a condensing agent.



This reaction is similar to that used by Dox and Thomas[1], Cope and McElvain[2]; and Guyot and Esteva[3] in the preparation of diphenylmalonic ester and 5,5-diphenylbarbituric acid.

When II is treated with excess of phenylmagnesium bromide, the corresponding diaddition product, 1,3-dihydroxy-1,2,2,3-tetraphenylindane (V) is formed in good yield. It reacts with diazomethane to produce the dimethyl ether of V. When V is dissolved in absolute methyl alcohol and refluxed for some hours allowing dry hydrochloric acid to pass through the solution, 2,2-diphenyl-1,3-diphenylepoxyindane VI is obtained. Attempts to obtain the mono-addition product of the diketone II using Grignard reagent in equimolecular proportions were unsuccessful. II reacts with 2,4-dinitrophenylhydrazine, giving 2,2-diphenyl-1,3-bis-(2,4-dinitrophenylhydrazone)-indane.

Triketoindane I reacts vigorously with excess of phenylmagnesium bromide with the formation of 1,2,3-trihydroxy-1,2,3-triphenylindane (IV). Considering the results published by Neuville and Pechmann[4] on triketones, it appears possible that the central carbonyl group is much the most active of the three. In fact when phenylmagnesium bromide and triketoindane are allowed to react in equimolar proportions, the mono-addition product, 1,3-diketo-2-phenyl-2-hydroxyindane (III) is obtained. (III) reacts with diazomethane giving 1,3-diketo-2-methoxy-2-phenylindane.

(1) Dox and Thomas, THIS JOURNAL, **45**, 1811 (1923).

(2) Cope and McElvain, *ibid.*, **54**, 4319 (1932).

(3) Guyot and Esteva, *Compt. rend.*, **148**, 564 (1909). Compare also THIS JOURNAL, **57**, 1303 (1935); **59**, 2348 (1937); *Helv. Chim. Acta*, **18**, 1254 (1935).

(4) Neuville and Pechmann, *Ber.*, **23**, 3379 (1890).

If two moles of Grignard reagent and one mole of triketoindane are allowed to react the triaddition product IV is obtained as the main product of the reaction and the diaddition product cannot be isolated.

Experimental

Preparation of 1,3-Diketo-2,2-diphenylindane (II).—Triketoindane (I) (4 g.) (prepared according to Schönberg and Moubasher, *J. Chem. Soc.*, 71 (1943), was suspended in 25 cc. dry thiophene-free benzene, cooled in ice and 10 cc. of fuming sulfuric acid (20% SO_3) was added dropwise with continuous shaking. The color of the reaction mixture changed from violet, through olive-green to tarry brown. The mixture was then shaken for 30 minutes at room temperature, poured into cold ice water and then the mixture was boiled to eliminate the small amount of excess benzene. The cooled mixture deposited 4.2 g. of colorless crystals which were collected and recrystallized from petroleum ether (60–80°), colorless needles, m.p. 118°, soluble in the majority of organic solvents, insoluble in alkali cold and hot. *Anal.* Calcd. for $C_{21}H_{14}O_2$: C, 84.5; H, 4.6. Found: C, 84.3; H, 4.4. It reacts with excess of 2,4-dinitrophenylhydrazine hydrochloride in refluxing ethyl alcohol to yield orange needles; m.p. after recrystallization from alcohol 130°. *Anal.* Calcd. for $C_{33}H_{22}O_8N_8$: N, 17.0. Found: N, 16.6.

Action of Phenylmagnesium Bromide on the Diketone (II).—A solution of phenylmagnesium bromide containing 0.2 g. of magnesium in 20 cc. of ether and 20 cc. of benzene was treated with I g. of 1,3-diketo-2,2-diphenylindane. The mixture was stirred rapidly for 2 hours on a boiling water-bath, decomposed with ammoniacal ammonium chloride solution and the ethereal solution was separated and dried with anhydrous sodium sulfate. The ether was evaporated in vacuum and the colorless residue was recrystallized from petroleum ether (60–80°) to give colorless needles of 1,3-dihydroxy-1,2,2,3-tetraphenylindane (V), m.p. 160°. *Anal.* Calcd. for $C_{33}H_{26}O_2$: C, 87.2; H, 5.7. Found: C, 87.0; H, 5.4.

Action of Diazomethane on the Diaddition Product (V).—To the diaddition product (V) (0.1 g.), an excess of ethereal solution of freshly prepared diazomethane (Arndt and Amende, *Z. angew. Chem.*, **45**, 444 (1930)) was added. A vigorous reaction took place with evolution of nitrogen. The mixture was left overnight and the ether was evaporated in vacuum. The colorless residue of the dimethyl ether of (V) (0.08 g.) was recrystallized from methyl alcohol, colorless needles, m.p. 130°. *Anal.* Calcd. for $C_{33}H_{24}(OCH_3)_2$: C, 87.1; H, 6.2; OCH_3, 12.8. Found: C, 86.6; H, 5.8; OCH_3, 11.8.

2,2-Diphenyl-1,3-diphenylepoxyindane (VI).—One-tenth gram of V was dissolved in absolute methyl alcohol (50 cc.) and a current of dry hydrogen chloride was allowed to pass through the solution while refluxing for 1 hour on a boiling water-bath. The mixture was then evaporated in vacuum and the solid residue was boiled with methyl alcohol for one-half hour. On evaporation of the alcohol and crystallizing the residue (0.06 g.) from petroleum ether (60–80°) several times, colorless prisms were obtained, m.p. 87°. *Anal.* Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5; mol. wt., 436. Found: C, 90.5; H. 5.4; mol. wt., 420.

Action of One Mole of Phenylmagnesium Bromide on Triketoindane (Inverse Grignard Reaction).—An ethereal solution of phenylmagnesium bromide containing 0.4 g. of magnesium was added gradually with continual stirring to a suspension of triketoindane (5.3 g.) in 50 cc. of dry benzene. The mixture was then refluxed for 2 hours on the boiling water-bath and decomposed with an ammoniacal ammonium chloride solution. The ethereal solution, separated, washed and dried, yielded yellow crystalline 2-phenyl-2-hydroxy-1,3-diketoindane (2.2 g.) which after recrystallization from ligroin (60–80°) melts at 192°, undepressed with authentic sample.

Action of Diazomethane on 2-Phenyl-2-hydroxy-1,3-diketoindane.—2-Phenyl-2-hydroxy-1,3-diketoindane (0.1 g.) was treated with an excess of freshly prepared ethereal solution of diazomethane. A vigorous reaction immediately took place with evolution of nitrogen. The mixture was left overnight and then evaporated in vacuum. The colorless residue (0.07 g.) was recrystallized from methyl alcohol to yield colorless needles of 2-methoxy-2-phenyl-1,3-diketoindane, m.p. 114°, undepressed with authentic sample.

Action of Excess Grignard Reagent on Triketoindane.—Triketoindane (I) (1 g.) was added to an ethereal solution of phenylmagnesium bromide (prepared from 1 g. of magnesium and 10 g. of bromobenzene in 50 cc. of ether), a vigorous reaction took place. Benzene (50 cc.) was then added and the mixture was refluxed for half an hour, left overnight, then treated with dilute hydrochloric acid and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate, evaporated up to dryness, and the residue (2 g.) was crystallized from benzene–petroleum ether (1:3 by volume) to give 1,2,3-triphenyl-1,2,3-trihydroxyindane, colorless needles, m.p. 124–130°. *Anal.* Calcd. for: $C_{27}H_{22}O_3 \cdot C_6H_6$: C, 83.8; H, 5.9. Found: C, 83.6; H, 6.0.

When this substance is left for a few days at room temperature or dried in vacuum, benzene of crystallization is lost giving colorless crystals, m.p. 178°. *Anal.* Calcd. for: $C_{27}H_{22}O_3$: C, 82.2; H, 5.6. Found: C, 82.3; H, 5.8. It is soluble in benzene and ethyl alcohol, insoluble in sodium hydroxide, and gives a yellow orange color with concentrated sulfuric acid.

CAIRO, EGYPT RECEIVED MAY 23, 1950

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

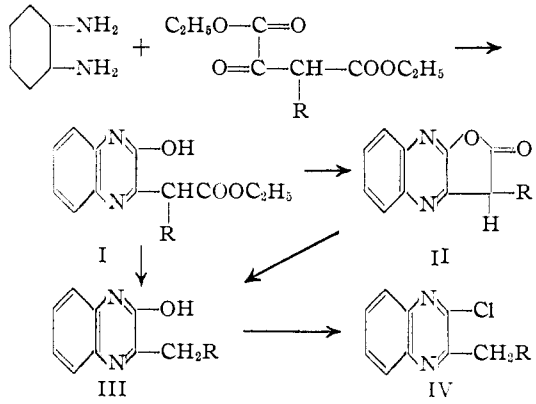
2-Hydroxy-3-alkylquinoxalines

BY YVON J. L'ITALIEN AND C. K. BANKS[1]

It was desired to prepare several 1,10-phenanthrolines and so the reactions of *o*-phenylenediamine with ethyl ethoxymethylenemalonate, ethyl oxalacetate and ethyl oxalpropionate were studied. It was found, however, that the products of the reaction were quinoxalines rather than phenanthrolines. Hydrolysis and decarboxylation of the quinoxalines led to 2-hydroxy-3-alkylquinoxalines which could be converted to the corresponding 2-chloro compounds. In contrast with *o*-phenylenediamine, *p*-phenylenediamine gave 4,7-phenanthrolines when reacting with the same ring closure compounds.

The development of methods for the syntheses of quinolines utilizing primary arylamines and ethyl ethoxymethylenemalonate,[2] ethyl oxalacetate and ethyl oxalpropionate[3] suggests that these same reactions may be utilized for the production of phenanthrolines. Snyder and Freier[4] have condensed *o*-phenylenediamine with ethyl ethoxymethylenemalonate to yield a 1,10-phenanthroline. When the phenylenediamines were treated with ethyl oxalacetate and ethyl oxalpropionate, the *o*-phenylenediamine gave a quinoxaline (I) rather than a phenanthroline. Such behavior is not unexpected since Gowenlock, *et al.*,[5] found that ethyl glyoxylate reacted with *o*-phenylenediamine to yield 2-hydroxyquinoxaline.

The reaction between the oxal esters and the diamine was very rapid, being essentially completed in ten minutes at steam-bath temperatures. A further condensation occurred when the reactants were cyclized in boiling diphenyl ether or when the quinoxaline (I, R = CH_3) was heated in diphenyl ether. This product proved to be 3-methyl-2-furo[2,3-b]quinoxalone (II, R = CH_3). The corresponding oxalacetate (I, R = H) failed to yield an isolatable furoquinoxalone (II, R = H), only starting material and gums being obtained. Both I and II, when hydrolyzed with alkali and then acidified, lost carbon dioxide rapidly to yield the 2-hydroxy-3-alkylquinoxalines (III). I and III (R = H) have been prepared by Ruhemann and Stapleton[6] from *o*-phenylenediamine and ethyl acetylenedicarboxylate. The hydroxyquinoxalines were converted to the corresponding chloroquinoxalines (IV) by phosphorus oxychloride. The chlorine atom of the 2-chloroquinoxalines was sufficiently active to react with arylamines.



In contrast to the behavior of *o*-phenylenediamine, even in excess of oxal esters, *p*-phenylenediamine reacted with two equivalents of ethyl oxalpropionate to give a bis-anil which cyclized to a 4,7-phenanthroline.

Experimental[7]

Ethyl 2-Hydroxy-3-quinoxalylacetate.—*o*-Phenylenediamine (0.1 mole) was dissolved in hot 95% ethanol, the solution treated with Darco G-60 and filtered. A concd.

(1) Metal and Thermit Corporation, Rahway, N. J.
(2) Price and Roberts, THIS JOURNAL, **68**, 1204 (1946).
(3) Surrey and Hammer, *ibid.*, **68**, 113 (1946).
(4) Snyder and Freier, *ibid.*, **68**, 1320 (1946).
(5) Gowenlock, Newbold and Spring, *J. Chem. Soc.*, 622 (1945).
(6) Ruhemann and Stapleton, *ibid.*, **77**, 248 (1900).
(7) The microanalytical data were obtained by our Microanalytical Department under the direction of C. E. Childs.