steam-bath. On dilution with water the sultam was precipitated. Recrystallized from methyl alcohol, it gave a melting point of 172–173°. No depression in melting point occurred when mixed with the product obtained above. Its specific rotation[3] in chloroform was −110°; in acetone −117.5°.

Sultam of β-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (V).—The β-form of IV could not be converted into a sultam by either of the two procedures used for the preparation of the α-form. In each case the original acid was recovered unchanged. It was prepared, however, by a slightly modified procedure. Two grams of the above β-form of IV was dissolved in 3 g. of pyridine to which was added 1.2 g. of benzenesulfonyl chloride. The mixture was warmed on a steam-bath for two hours, diluted with 10–15 cc. of water and filtered and recrystallized from ethyl alcohol. The yield was 1.2 g. or 64%. It melted at 137–138° and had a specific rotation in chloroform of +140.5°.

Anal. Calcd. for $C_{16}H_{21}O_2NS$: N, 4.81; S, 10.99. Found: N, 4.73; S, 10.99.

Hydrolysis of the α-Sultam of 2-(N-Phenylamino)-camphane-10-sulfonic Acid.—One gram of the sultam was refluxed with 35 cc. of concentrated hydrochloric acid for thirty-six hours, at the end of which time the insoluble material had disappeared. The solution was then evaporated to about 10 cc. and cooled. Filtration yielded 0.6 g. of crystals. The product melted at 300–302° and had the same specific rotation as the α-form of 2-(N-phenylamino)-camphane-10-sulfonic acid.

Hydrolysis of the β-Sultam of 2-(N-Phenylamino)-camphane-10-sulfonic Acid.—Four-tenths of a gram of the β-sultam was refluxed for eight hours with 20 cc. of concentrated hydrochloric acid. The solution was diluted with 25 cc. of water and evaporated nearly to dryness. On cooling, the β-form of 2-(N-phenylamino)-camphane-10-sulfonic acid crystallized. The yield was 0.25 g. or 60%. The melting point was 350–351° on the Maquenne block and the specific rotation checked that of the original β-isomer of IV.

Summary

The catalytic hydrogenation of the anil of *d*-camphor-10-sulfonic acid yielded two diastereoisomeric forms of 2-(N-phenylamino)-camphane-10-sulfonic acid. Loss of water converted each of these isomers into its corresponding sultam, and each of the latter could be hydrolyzed to their respective original isomers. These reactions constitute further evidence that the *levo*-rotatory products obtained by the dehydration of primary amine salts of Reychler's acid are ketimines.

Urbana, Illinois Received August 3, 1935

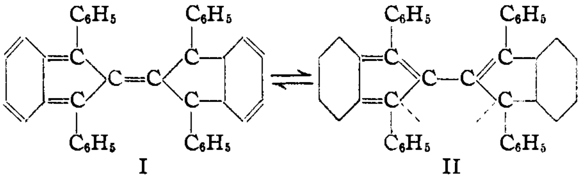
[Contribution from the Chemical Laboratory of the University of Illinois]

The Synthesis of Bis-2,2'-(1,3-diphenylindenol-3). A Contribution to the Rubrene Problem

By J. C. Eck and C. S. Marvel

The question of the structure of rubrene has become of considerable interest to us because of its relationship to the problems involved in the rearrangement of certain types of polyynes. Recently Dufraisse and Willemart[1] have reported that Moureu's hydrocarbon $C_{42}H_{30}$, which is formed by the spontaneous rearrangement of tetraphenyldiphenylethynylethane,[2] can be oxidized with lead dioxide to give a 34% yield of rubrene. This observation is somewhat surprising since previous work has shown that chromic acid converts rubrene to *o*-dibenzoylbenzene,[3] whereas the same reagent oxidizes Moureu's hydrocarbon to *o*-benzoylbenzoic acid.[4]

The discoverers of rubrene[5] have considered it to be a difulvene of structure I which may be in equilibrium with a diindenyl form containing two trivalent carbon atoms, II. This diradical structure has also been advocated by Schönberg.[6]



I II

The structural formulas which have been assigned to rubrene and its many known derivatives are based on the reactions of the compounds and no confirmatory synthesis has been given for any compound in the series. The present work was undertaken with the hope of accomplishing the synthesis of rubrene or its closely related derivative, dihydroxydihydrorubrene, which has been assigned structure III.

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(1) Dufraisse and Willemart, *Bull. soc. chim.*, [5] **1**, 576 (1934).

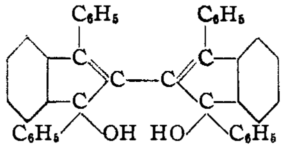
(2) Munro and Marvel, This Journal, **54**, 4445 (1932).

(3) Moureu, Dufraisse and Enderlin, *Compt. rend.*, **187**, 406 (1928); Dufraisse and Enderlin, *Bull. soc. chim.*, [4] **51**, 132 (1932).

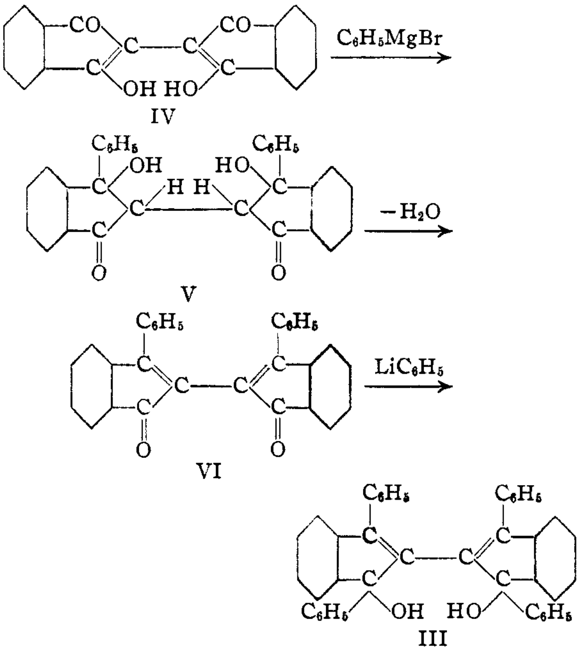
(4) Halley and Marvel, This Journal, **54**, 4450 (1932).

(5) The literature on rubrene has been summarized by Dufraisse, *Bull. soc. chim.*, [4] **53**, 789 (1933).

(6) Schönberg, *Ber.*, **67**, 633 (1934).

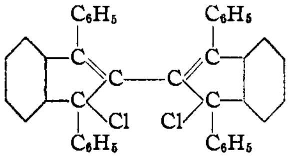

III

The starting point in our synthesis was bis-2,-2'-(1,3-indandione) (IV) which was prepared by the method of Gabriel and Leupold.[7] This was converted to bis-2,2'-(1-phenylindanone-3-ol-1) (V) by the action of excess phenylmagnesium bromide. Since only two phenyl groups can be introduced into the molecule by this treatment, the bis-indandione (IV) must exist largely in the di-enolic form. Dehydration of compound V gave a good yield of bis-2,2'-(1-phenylindenone-3) (VI) which, with lithium phenyl, gave bis-2,2'-(1,3-diphenylindenol-3) (III). Lithium phenyl was used in this step to lessen the chance of 1,4 addition to the conjugated systems involved.[8] That the final product of these reactions had the formula (III) expected from the synthesis was established by its oxidation to *o*-dibenzoylbenzene in yields of 88% of the theoretical amount, and by the fact that the two hydroxyl groups could be replaced by chlorine atoms.



According to Dufraisse and Badoche[9] dihydroxydihydrorubrene, to which they assign structure III, melts at 307–308°; moderate heat converts it to rubrene monoxide by loss of water; dehydrating agents convert it to a white compound whose solutions have an intense violet fluorescence; and reduction converts it to rubrene. Our synthetic bis-2,2'-(1,3-diphenylindenol-3) (III) melts at 293°; sublimes unchanged at 280° at 3 mm. pressure; heating it with potassium acid sulfate at 250° or with phosphorus pentoxide at 100° affects it only very slightly, giving a trace of a substance which, in solution, shows a greenish fluorescence; reduction with iron in hydrochloric or acetic acid does not affect it.

The chloride VII which was prepared from the dihydro compound was treated with silver in the hope that the diradical II could be prepared. This reaction has not been studied extensively but sufficient work has been done to show that rubrene is not produced.


VII

Inspection of the formula of bis-2,2'-(1,3-diphenylindenol-3) (III) shows that it may exist in meso and racemic forms. It is possible that we have obtained one of these forms by our synthesis, whereas the other results from the oxidation of rubrene. However, the difference in chemical properties between our synthetic product and that obtained from rubrene seems to us to be too marked for these products to be meso and racemic forms.[10]

Experimental

Bis-2,2'-(1-phenylindanone-3-ol-1).—To a solution of phenylmagnesium bromide prepared from 15.7 g. of bromobenzene and 2.4 g. of magnesium in 200 cc. of anhydrous ether was added 10 g. of bis-2,2'-(1,3-indandione) suspended in 200 cc. of dry benzene. The reaction mixture was stirred for about twelve hours, and then the solvent was decanted from the black unreacted material into an aqueous solution of ammonium chloride. The reaction product precipitated in the ether–benzene mixture as soon as hydrolysis of the magnesium complex occurred. The straw-colored precipitate was collected on a filter, washed with water and dried in the air. The yield was 10 g. (65%).

This product was recrystallized by suspending it in about 300 cc. of dioxane, heating the solvent to boiling

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(7) Gabriel and Leupold, *Ber.*, **31**, 1159 (1898).

(8) Lüttringhaus, *ibid.*, **67**, 1602 (1934).

(9) Dufraisse and Badoche, *Compt. rend.*, **193**, 63 (1931).

(10) Koelsch and Richter have synthesized bis-2,2'-(1,3-diphenylindenol-3) and the corresponding dichloride by another series of reactions. Their products are identical in physical properties with the compounds which we have obtained. See Koelsch and Richter, THIS JOURNAL, **57**, 2010 (1935).

and filtering hot. On cooling the first extract, a yellow crystalline compound, melting at 345° (bloc Maquenne), was obtained.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.71; H, 4.93. Found: C, 80.78; H, 4.92.

The filtrate from this first fraction was used to re-extract the material which did not dissolve in the first treatment with hot dioxane. On cooling the second extract, a mixed product was obtained. However, when the filtrate from this portion was again used to extract the undissolved portion of the original material, a second isomer of the hydroxy ketone, melting at 358° (bloc Maquenne), was obtained.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.71; H, 4.93. Found: C, 80.91; H, 5.00.

Either of these products or the mixture of the two gave satisfactory results in the following experiment.

Bis-2,2'-(1-phenylindenone-3).—An intimate mixture of 10 g. of bis-2,2'-(1-phenylindanone-3-ol-1) and 10 g. of powdered, freshly-fused, potassium acid sulfate was placed in a large Pyrex test-tube and slowly immersed in a Wood's metal bath previously heated to 250°. This temperature was then maintained for twenty-five minutes. The reaction mass was occasionally stirred with a glass rod. The reaction mixture was cooled and extracted with water. The water-insoluble material was dissolved in 200 cc. of benzene and boiled with 2 g. of decolorizing carbon for about a half hour. This solution was filtered and concentrated to 25 cc. Slow addition of an excess of low-boiling petroleum ether precipitated the product as beautiful, red crystals. The yield was 7.8 g. (80%) of a product melting at 213–214°.

Anal. Calcd. for $C_{30}H_{18}O_2$: C, 87.8; H, 4.39. Found: C, 87.52; H, 4.44.

Bis-2,2'-(1,3-diphenylindenol-3).—A solution of lithium phenyl was prepared from 0.5 g. of lithium and 5.7 g. of bromobenzene in 150 cc. of anhydrous ether.[11] Unreacted lithium was removed and then 5 g. of bis-2,2'-(1-phenylindenone-3) dissolved in 200 cc. of dry benzene was added dropwise. The reaction mixture was stirred during this addition, and for about an hour afterward. This solution was hydrolyzed with aqueous ammonium chloride solution, the ether–benzene solution was washed thoroughly with water and dried over anhydrous sodium sulfate. The solution was then concentrated and, on cooling, the product separated. The yield was 4.9 g. (70%) of a product which melted at 293° (bloc Maquenne).

Anal. Calcd. for $C_{42}H_{30}O_2$: C, 89.04; H, 5.30. Found: C, 88.76; H, 5.28.

This reaction product was separated into two isomers by careful recrystallization from benzene. The less soluble form was yellow, and melted at 273° (bloc Maquenne). The more soluble form melted at 293° (bloc Maquenne). Heating the lower-melting product or allowing it to stand converted it to the higher-melting product.

Anal. Calcd. for $C_{42}H_{30}O_2$: C, 89.04; H, 5.30. Found: (low-melting isomer) C, 89.28; H, 5.57; (high-melting isomer) C, 89.20; H, 5.48.

Oxidation of Bis-2,2'-(1,3-diphenylindenol-3).—A mixture of 0.5 g. of the dihydroxy compound and 2.5 g. of potassium dichromate in 50 cc. of glacial acetic acid was heated under a reflux condenser for ten hours. The reaction mixture was poured into water and filtered. The precipitate was taken up in ether and the ether solution was extracted with aqueous sodium carbonate. The ether was removed in a current of air, and the residue taken up in alcohol, decolorized by boiling with norite, filtered and concentrated to a small volume. On cooling, 0.44 g. (88%) of *o*-dibenzoylbenzene, m. p. 145–146°, separated. The product showed no depression in melting point when mixed with a known specimen of *o*-dibenzoylbenzene.

Bis-2,2'-(1,3-diphenyl-3-chloroindenyl).—A solution of 0.1 g. of bis-2,2'-(1,3-diphenylindenol-3) in 25 cc. of anhydrous ether was saturated with hydrogen chloride and allowed to stand overnight. The solvent was evaporated and the residue recrystallized three times from acetone. The yield was 0.07 g. of a light yellow product which melted at 245–247° (bloc Maquenne).

Anal. Calcd. for $C_{42}H_{28}Cl_2$: Cl, 11.77. Found: Cl, 11.86.

A solution of this chloride in benzene was shaken with molecular silver for several days. The solution became greenish-yellow, and there was no indication of the red color of rubrene in solution.

Attempted Dehydration of Bis-2,2'-(1,3-diphenylindenol-3).—A small sample of the dihydroxy compound was heated for ten minutes at 250° with potassium acid sulfate. When the dehydrating reagent was removed, the organic material was dissolved in benzene. This solution showed a slight green fluorescence which was not shown by the original dihydroxy compound in benzene solution. However, no product except the starting material could be isolated from the reaction mixture. Treatment of the dihydroxy compound with phosphorus pentoxide at 100° for ten minutes gave the same results. The dihydroxy compound itself was heated to 280° at 3 mm. Under these conditions it sublimed undecomposed.

Attempted Reduction of Bis-2,2'-(1,3-diphenylindenol-3).—A suspension of the dihydroxy compound in hydrochloric acid was treated with iron filings but, after the iron had dissolved, the unchanged starting material was recovered. Likewise, treating the dihydroxy compound with iron and glacial acetic acid did not affect it.

Summary

Bis-2,2'-(1,3-diphenylindenol-3) has been synthesized and shown not to be identical with the product known as dihydroxydihydrorubrene.

URBANA, ILLINOIS

RECEIVED AUGUST 2, 1935

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[11] Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).