pyrethrin II. There was always more than 50% loss due to polymerization in the still, and the still residue consisted of a glassy mass almost insoluble in all solvents. The yield of pure pyrethrin II was in no case more than 20% of the quantity of material distilled, but an additional quantity was obtained on redistillation of the second fractions.

The analytical results and physical constants for several samples are given below.

**Preparation A.**—*Anal.* Calcd. for $C_{22}H_{30}O_5$: C, 70.54; H, 8.08; $1CH_3O$, 8.28. Found: C, 70.63, 70.84; H, 7.69, 7.69; $CH_3O$, 8.10. Calcd. to pyrethrin II (mol. wt. 374), 97.72; $n^{30}$D 1.5247; $n^{20}$D 1.5285. *Rotation:* 0.135 g. in 2.28 cc. ether at 20° rotated $-0.34°$; $l$ = 0.96 dm.; $[\alpha]^{20}$D $-6.0$. 0.235 g. in 2.28 cc. benzene at 20° rotated $-0.42°$; $l$ = 0.96 dm.; $[\alpha]^{20}$D $-4.2$.

**Preparation B.**—*Anal.* Found: $CH_3O$, 8.24, 8.33. calcd. to pyrethrin II (mol. wt. 374), 99.66, 100.38; $n^{29}$D 1.5258.

**Preparation C.**—*Anal.* Found: $CH_3O$, 8.07, 8.04; $n^{20}$D 1.5259.

**Preparation D.**—*Anal.* Found: $CH_3O$, 8.00; $n^{20}$D 1.5247.

It will be noted that none of the samples shows a pyrethrin II content of appreciably more than 100% as determined by the methoxyl method, indicating that none of them contained methyl pyrethrolone, alkyl esters of the chrysanthemum acids or other methoxyl containing impurities. These may have been present in the concentrates before distillation, but, being of much lower molecular weight, they would be removed in the more volatile fractions.

## Summary

A procedure for the preparation of pyrethrin II is described.

Petroleum ether extractives of pyrethrum flowers are separated from fats and waxes by the employment of acetic acid.

The acids are removed from the concentrate by extraction in aniline solution with potassium carbonate.

Partial separation of pyrethrin II from pyrethrin I is accomplished by taking advantage of their different solubilities in a system consisting of diluted acetic acid and petroleum ether. Pyrethrin II tends to concentrate in the acid solution, pyrethrin I in the petroleum ether.

Concentrates so obtained containing about 80% of pyrethrin II and about 6% of pyrethrin I are distilled in a molecular still and yield pure pyrethrin II.

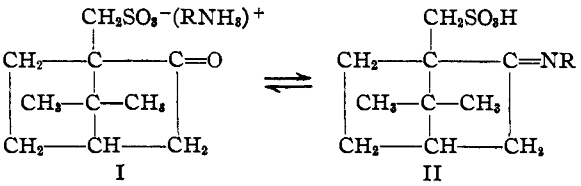
Washington, D. C. Received July 26, 1935

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

# Anomalous Mutarotation of Salts of Reychler's Acid. III. Reduction of Ketimines of *d*-Camphor-10-sulfonic Acid. Formation of Sultams

By R. S. Schreiber and R. L. Shriner

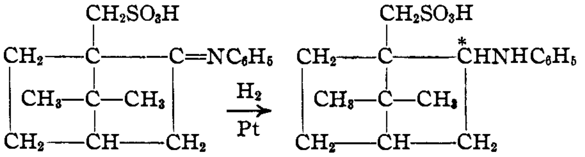
The mutarotation of salts of primary amines and Reychler's acid was ascribed[1] to the establishment of an equilibrium between the *d*-salt (I) and the *l*-ketimine (II).



I II

In order to establish the ketimine structure beyond question, the product of this reaction was subjected to catalytic reduction, since it is known that ketimines may be hydrogenated to secondary amines.[2]

The ketimine (III) obtained by the dehydration of the aniline salt of Reychler's acid readily absorbed one mole of hydrogen in the presence of platinum black and the hydrogenated product, 2-(N-phenylamino)-10-camphane-sulfonic acid (IV) was found to consist of the two diastereoisomers which would be expected because of the creation of a new asymmetric carbon atom at position 2. These isomers were separated by fractional crystallization. The $\alpha$-form melted at 300–302° and had a specific rotation[3] of $-88.5°$ whereas the $\beta$-form melted at 350–351° and was dextrorotatory, $+8.5°$.



III IV

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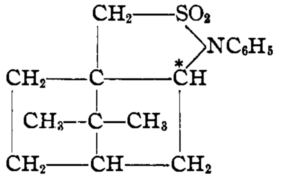
(1) Schreiber and Shriner. This Journal, 57, 1306, 1445 (1935).

(2) Mignonac, *Compt. rend.*, 171, 114 (1920); Rupe and Vogler, *Helv. Chim. Acta*, 8, 832 (1925); Rupe and Metzger, *ibid.*, 8, 838 (1925); 13, 457 (1930).

(3) All specific rotations reported in this paper were determined at 25° with sodium D light.

Further evidence supporting the above structures was obtained by causing each of the isomers of IV to undergo ring closure leading to the formation of two isomeric sultams of the structure shown in V.

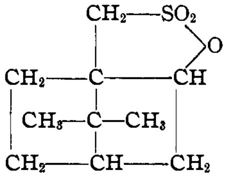


V

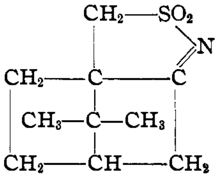
Treatment of the α-form of IV with either benzene-sulfonyl chloride or acetic anhydride produced the α-sultam (V) which melted at 172–173° and had a specific rotation of −110° in chloroform. The β-form of IV could be converted to the β-sultam (V) by slightly more drastic conditions. The β-sultam melted at 137–138° and had a rotation of +140.5° in chloroform.

These sultams were neutral compounds and their structure was proved not only by their analyses but by the fact that each isomer could be hydrolyzed by means of concentrated hydrochloric acid to the original α- and β-forms of 2-(N-phenylamino)-camphane-10-sulfonic acids (IV) in exactly the same fashion as other substituted sulfonanilides.[4]

The cyclization of the two forms of IV into the sultams shows that no rearrangements, which often occur in the camphor series, took place during the dehydration of the aniline salt. Examination of the literature revealed two similar cases of ring formation in the camphane series. Lipp and Holl[5] prepared a sultone VI by dehydrating 2-hydroxycamphane-10-sulfonic acid and Reychler prepared *d*-camphor-10-sulfonanhydramide[6] (VII).



VI



VII

Other sultams recorded are 1,8-naphthsultam prepared by Dannerth[7] and the sultam of 8-(2-aminophenyl)-naphthalene-1-sulfonic acid.[8]

Construction of the molecular models of the two isomeric forms of IV showed that in one model the sulfonic acid group and the amino group may approach closer to each other than in the isomeric model. Also, one model of the two isomeric sultams (V) possessed much more strain than the other. This difference is reflected in the properties of the two sultams. The β-sultam was formed with greater difficulty and hydrolyzed more easily than the α-sultam.

## Experimental

**Reduction of the Anil of *d*-Camphor-10-sulfonic Acid.**—Thirteen grams of the anil, prepared by dehydration[1] of the aniline salt of Reychler's acid, was dissolved in 50 cc. of methyl alcohol and hydrogenated catalytically with 0.1 g. of platinum oxide-platinum black.[9] One mole of hydrogen was absorbed in four hours after which time the absorption of hydrogen stopped. The mixture was heated and the catalyst removed by filtration. When cool, the filtrate deposited 4.6 g. of crystals which melted at 288–295° (Maquenne block) and had a specific rotation[2] of −78.0° in a mixture of equal volumes of chloroform and methyl alcohol. Several recrystallizations from methyl alcohol of this first crop gave 1.1 g. of the α-form in a pure state, with a constant melting point of 300–302° (Maquenne block) and a constant specific rotation of −88.5°. The mother liquor was evaporated to dryness, and then dissolved in 35 cc. of concentrated hydrochloric acid, which was heated to boiling and diluted with 150 cc. of water. This solution was allowed to stand overnight, during which time 4.6 g. of crystals separated. Recrystallization from dilute hydrochloric acid yielded 1.3 g. of the pure β-form. This form had a melting point of 350–351°, and a constant specific rotation of +8.5° in a mixture of chloroform and methyl alcohol.

**α-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (IV).**—*Anal.* Calcd. for $C_{16}H_{23}O_3NS$: N, 4.53; S, 10.35; neut. eq. by titration, 309. Found: N, 4.49; S, 10.30; neut. eq., 308.3.

**β-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (IV).**—*Anal.* Calcd. for $C_{16}H_{23}O_3NS$: N, 4.53; S, 10.35; neut. eq. by titration, 309. Found: N, 4.34; S, 10.21; neut. eq., 309.2.

**Sultam of α-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (V).**—Five grams of the α-form of IV was heated with 15 g. of benzenesulfonyl chloride on a steam-bath until solution was complete (one to two hours). The mixture was then poured into excess of 5% sodium hydroxide to destroy the unreacted sulfonyl chloride, and the solution then acidified with hydrochloric acid. The insoluble product was recrystallized from methyl alcohol. The yield was 3.1 g. or 65% of the theoretical, m. p. 172–173°.

*Anal.* Calcd. for $C_{16}H_{21}O_2NS$: N, 4.71; S, 10.99. Found: N, 4.81; S, 10.92.

This compound was neutral, and did not give a neutral equivalent. The same compound was prepared by heating the α-form of IV with acetic anhydride for an hour on a

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(4) Schreiber and Shriner, THIS JOURNAL, **56**, 1618 (1934).

(5) Lipp and Holl, *Ber.*, **62**, 499 (1929).

(6) Reychler, *Bull. soc. chim.*, **19**, 127 (1898).

(7) Dannerth, THIS JOURNAL, **29**, 1319 (1907).

(8) Steiger, *Bull. soc. chim.*, **53**, 1254 (1933).

(9) Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

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[2] 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

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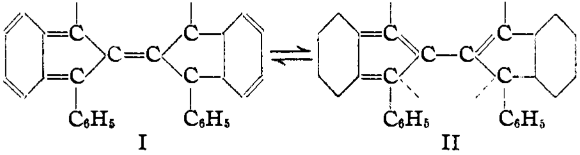
[Contribution from the Chemical Laboratory of the University of Illinois]

# 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).