to five hours the solution was poured into ice water and filtered. The filtrate upon evaporation left a brown crystalline residue which was recrystallized from dilute acetone; m. p. 213°.

Since the neutral equivalent determination indicated that the material was probably impure lactone acid, it was recovered and subjected to three more recrystallizations. This treatment yielded long blunt prisms, m. p. 242–244°, which proved to be the lactone acid by mixed melting point.

Summary

$\Delta^{4a,5a}$ - Dodecahydrophenanthrene - 9,10 - dicarboxylic acid and its anhydride are converted into a lactone ester and not into a diester upon esterification. Saponification of this lactone ester with alkali gives the alkali salt of an hydroxy dibasic acid which on acidification gives a monobasic acid monolactone. It is assumed by analogy to previous results on the study of γ,δ-olefinic acids that in these molecules a δ-lactone probably has formed.

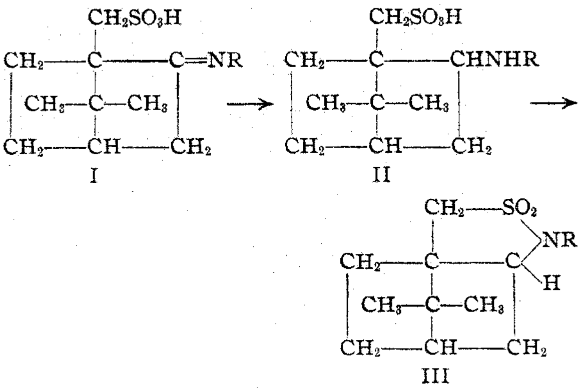
Urbana, Illinois Received September 30, 1938

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

Anomalous Mutarotation of Salts of Reychler's Acid. VI. Synthesis and Structure of the Sultam of 2-(N-Methylamino)-*d*-camphane-10-sulfonic Acid

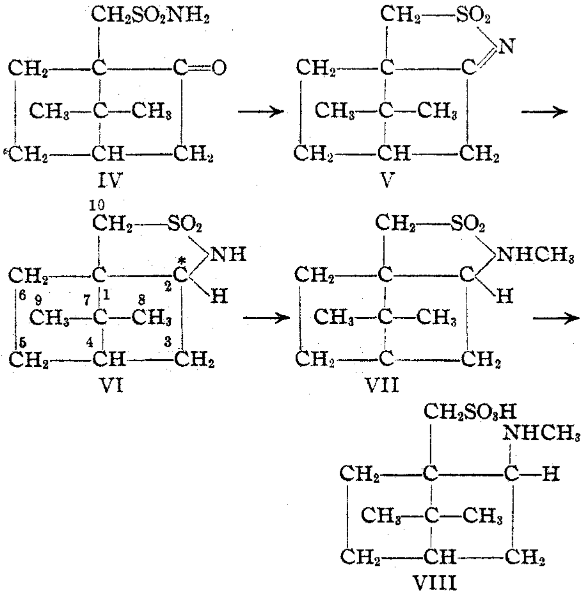
By R. L. Shriner, James A. Shotton and Harry Sutherland

One of the reactions used to establish the ketimine structure (I) of the dehydration products of primary amine salts of Reychler's acid[1] was reduction to the substituted amino sulfonic acid (II). The two forms of the latter underwent dehydration, producing compounds whose analyses and properties indicated the sultam structure,[1c] (III).



The purpose of the present investigation was to synthesize one of these sultams by an independent method in order to establish this structure.

Accordingly, use was made of an observation by Reychler[2] that *d*-camphor-10-sulfonamide (IV) underwent dehydration to an anhydro compound to which Armstrong and Lowry[3] had assigned the structure shown in formula V. In the present work this anhydramide was reduced catalytically with hydrogen and Raney nickel to the sultam, VI. Although the latter may exist in two diastereoisomeric forms, since carbon atom 2 is now asymmetric (*), only one form actually was produced. The sodium salt of this sultam was treated with methyl iodide and the N-methyl sultam, VII, obtained. Hydrolysis by means of concentrated hydrochloric acid opened the heterocyclic ring and produced the α-form of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid (VIII). Although Reychler's acid and its amide are dextrorotatory, all the derivatives V, VI, VII and VIII were levorotatory; the specific rotations being −32, −33, −59 and −98°, respectively.



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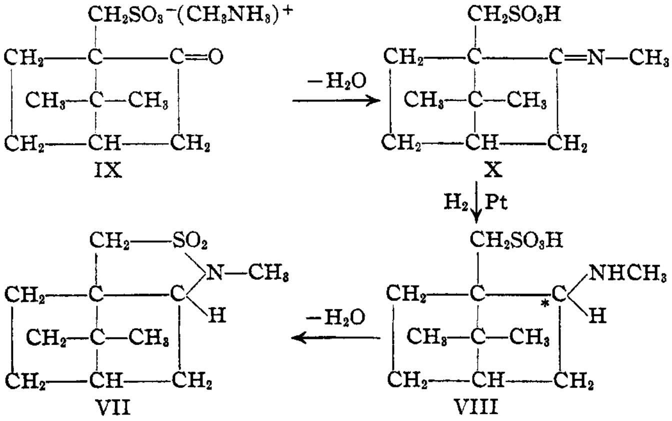
(1) (a) Schreiber and Shriner, This Journal, **57**, 1306 (1935); (b) *ibid.*, **57**, 1445 (1935); (c) *ibid.*, **57**, 1869 (1935); Sutherland and Shriner, *ibid.*, **58**, 62 (1936); *ibid.*, **60**, 1314 (1938).

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

(3) Armstrong and Lowry, *J. Chem. Soc.*, **81**, 1448 (1902); Lowry and Desch, *ibid.*, **95**, 1340 (1909); Richards and Lowry, *ibid.*, **127**, 1503 (1925).

Samples of the N-methyl sultam (VII) and its hydrolytic product (VIII) were next prepared from the methylamine salt of Reychler's acid (IX) which was dehydrated to the ketimine (X).



Catalytic reduction produced the two diastereoisomeric forms of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid (VIII). These isomers were separated by fractional crystallization and the α-form possessed the same decomposition point and specific rotation as the sample of compound VIII obtained by the first series of reactions. By refluxing this α-form with acetic anhydride the N-methyl sultam (VII) was obtained which was identical in melting point with the N-methyl sultam described above.

These two series of reactions not only establish the structure of these sultams but also serve to confirm Lowry and Armstrong's formula for *d*-camphor-10-sulfonanhydramide.

Experimental

***d*-Camphor-10-sulfonanhydramide** (V).—A mixture of 25 g. of *d*-camphor-10-sulfonic acid and 5 cc. of thionyl chloride was warmed on the steam-bath until the reaction started and then another 30 cc. of thionyl chloride was added slowly. The mixture was heated on the steam-bath for four hours, cooled and poured slowly into a mixture of 100 cc. of concentrated ammonium hydroxide and 400 g. of cracked ice. The crude anhydramide was filtered and recrystallized from 95% ethanol. The aqueous mother liquor deposited additional crops of crystals of the anhydramide after standing overnight. Concentration of the ethanol mother liquor above yielded a product which melted at 126°, being an impure form of *d*-camphor-10-sulfonamide. When this material is warmed for ten minutes with concentrated hydrochloric acid, it is converted into the anhydramide. By working up all these fractions there resulted a total yield of 19.1 g. (90%) of colorless crystals of *d*-camphor-10-sulfonanhydramide which melted at 224° (corr.) and possessed a specific rotation[4] of −32° in chloroform (*c*, 5). These values check closely those given by Armstrong and Lowry.[3]

Sultam of 2-Amino-*d*-camphane-10-sulfonic Acid (VI).—A mixture of 10 g. of the anhydramide, 10 g. of Raney nickel catalyst and 150 cc. of warm 95% ethanol was shaken with hydrogen under 45 lb. (3 atm.) pressure. The anhydramide was only partially in solution at the start but dissolved as the reduction proceeded. The reduction was complete in one and one-half hours after which time the catalyst was removed by filtration and the filtrate concentrated. The sultam which separated melted at 181–182°. It was subjected to fractional crystallization but all the fractions melted at 181–182°, showing that only one form had been produced. The sultam was soluble in dilute aqueous sodium hydroxide and was precipitated upon acidification. It had a specific rotation in chloroform (*c*, 5) of −33.0°.

Anal. Calcd. for $C_{10}H_{17}O_2NS$: N, 6.51; S, 14.88. Found: N, 6.62; S, 14.83.

Sultam of 2-(N-Methylamino)-*d*-camphane-10-sulfonic Acid (VII).—A solution of 0.5 g. of sodium in 10 cc. of absolute ethanol was added to a solution of 5 g. of the above sultam (VI) in 25 cc. of absolute ethanol. To this solution was added 2.5 cc. of methyl iodide and the mixture refluxed for two hours. It was then poured into 50 cc. of water and acidified with hydrochloric acid. An oil separated which solidified on stirring and rubbing. The solid was removed by filtration and the filtrate concentrated to obtain an additional crop of crystals. The crude N-methyl sultam was recrystallized from hot water. A total yield of 4.5 g. (89%) of colorless crystals was obtained which melted at 80° and possessed a specific rotation in chloroform (*c*, 5) of −59.6°.

Anal. Calcd. for $C_{11}H_{19}O_2NS$: N, 6.11; S, 13.96. Found: N, 6.07; S, 14.10.

Hydrolysis of the N-Methyl Sultam (VII).—Three grams of the above N-methyl sultam was refluxed with 50 cc. of concentrated hydrochloric acid for twenty-four hours. The mixture was evaporated to dryness and the residue recrystallized from absolute ethanol. An 83% yield of the α-form of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid was obtained which decomposed at 325–326° on the Maquenne block. Its specific rotation in ethanol (*c*, 1) was −98.0°.

Anal. Calcd. for $C_{11}H_{21}O_3NS$: N, 5.66; S, 12.95. Found: N, 5.43; S, 13.10.

2-(N-Methylimino)-*d*-camphane-10-sulfonic Acid (X).—One sample of this ketimine was prepared according to the method previously described.[1b] Fifty grams of Reychler's acid was added to an ethanol solution of 9.2 g. of methylamine and the salt obtained by evaporation to dryness. Dehydration was effected by heating the salt for six hours at 184° *in vacuo*. Four recrystallizations from absolute ethanol with the use of Norite were necessary in order to obtain a pure product.

A modified procedure proved simpler and yielded a product more easily purified. To a solution of 6.8 g. of methylamine in 100 cc. of ethanol were added 30 g. of Reychler's acid and 150 g. of ethylene glycol. The mixture was dis-

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[4] All rotations were taken at 25° with sodium D light. The concentration in grams per 100 cc. of solution is denoted by *c*.

tilled until the volume of the residue was about 50 cc. This residual solution was cooled and the ketimine filtered and washed with cold ethanol. Recrystallization from absolute ethanol gave 12.8 g. of colorless crystals which melted at 312–313° (Maquenne block) and possessed a specific rotation of −137.6° in ethanol (*c*, 1). These constants checked with those previously obtained.[1b]

2-(N-Methylamino)-*d*-camphane-10-sulfonic Acid (XI).—2-(N-Methylimino)-*d*-camphane-10-sulfonic acid (18.8 g.) was dissolved in 150 cc. of absolute ethanol and catalytically reduced with hydrogen and platinum-oxide platinum black. It was necessary to use two successive portions of 0.5 g. of catalyst in order to secure complete reduction, which required about twenty-four hours. The catalyst was removed by filtration and the filtrate concentrated. The crude product was fractionated by a series of systematic crystallizations from 95% ethanol. The two diastereoisomers were isolated as colorless crystals.

α-Form.—This form had a decomposition point of 320° and a specific rotation in ethanol (*c*, 1) of −98.6°. *Anal.* Calcd. for $C_{11}H_{21}O_3NS$: C, 53.41; H, 8.56; N, 5.66. Found: C, 53.51; H, 8.54; N, 5.54.

β-Form.—This isomer decomposed at 338–343° and had a specific rotation in ethanol (*c*, 1) of +38.8°. *Anal.* Calcd. for $C_{11}H_{21}O_3NS$: C, 53.41; H, 8.56; N, 5.66. Found: C, 53.52; H, 8.49; N, 5.65.

The α-form was identical with the compound obtained by hydrolysis of the N-methyl sultam (VII).

Conversion of the α-Form of 2-(N-methylamino)-*d*-camphane-10-sulfonic Acid to the Sultam (VII).—One-tenth of a gram of the α-form of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid was heated with 3 cc. of acetic anhydride for eighteen hours. The mixture was then poured into 5 cc. of water and evaporated to dryness. Three cubic centimeters of acetic anhydride was added and the mixture again heated to the boiling point. The mixture was cooled and then 3 cc. of water was added. This mixture was then evaporated to dryness. Two cubic centimeters of water was added and the white crystals collected on a filter. The substance melted at 79°. The mixed melting point with the methyl sultam (VII) was 79–80°.

Summary

The sultam of 2-(N-methylamino)-*d*-camphane-10-sulfonic acid was synthesized by alkylation of the sultam of 2-amino-*d*-camphane-10-sulfonic acid which was obtained by catalytic reduction of *d*-camphor-10-sulfonanhydramide. The sultam was hydrolyzed to 2-(N-methylamino)-*d*-camphane-10-sulfonic acid. The latter was shown to be identical with the α-form obtained by catalytic reduction of 2-(N-methylimino)-*d*-camphane-10-sulfonic acid. This α-form was converted to the N-methyl sultam by acetic anhydride.

URBANA, ILLINOIS RECEIVED SEPTEMBER 6, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Determination of Dissolved Oxygen by Means of the Dropping Mercury Electrode, with Applications in Biology

BY HAROLD G. PETERING AND FARRINGTON DANIELS

The measurement of respiration constitutes but one of the many demands for an accurate and rapid method for the quantitative determination of oxygen. The differential pressure manometer such as the Warburg–Barcroft manometer is widely used for this purpose. The Winkler process is another standard method. The results of this investigation show that for many purposes the concentration of dissolved oxygen can be determined with great simplicity, accuracy, and rapidity by means of the dropping mercury electrode.

The method described here is a modification of the polarographic method, shown by Vitek[1] to be applicable to the determination of oxygen. The recording features of the polarograph are dispensed with and the apparatus is constructed from ordinary laboratory materials in such a way that readings of oxygen concentration in water or other conducting solvents can be made in a few seconds. It is especially useful for studying systems which involve a changing oxygen concentration.

This method may be regarded merely as an empirical analytical procedure which has been checked against chemical standards. On the other hand, theoretical interpretations of the polarographic method have been proposed.

Theory

The use of the dropping mercury electrode for analytical purposes depends on the fact that solutes (electrolytes or non-electrolytes) are reduced (or oxidized) when a current is passed through the solution at voltages above the decomposition potential. The current flowing de-

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(1) Vitek, *Chimie et Industrie*, **29**, 215 (1933); *Coll. Czech. Chem. Comm.*, **7**, 537 (1935).