water of crystallization in this compound is held as tenaciously as the alcohol in 1-*d*-glucosidocytosine alcoholate.

Anal. Calcd. for $C_{10}H_{15}O_6N_3 \cdot HNO_3H_2O$: C, 33.88; H, 5.12; N, 15.82; HNO_3, 17.79. Found: C, 34.13; H, 5.15; N, 14.94, 15.18;[8] HNO_3 (by titration), 17.36.

1-Tetraacetyl-*d*-glucosido-7-acetylcytosine.—To a solution of 1.9 cc. of acetic anhydride and 2.5 cc. of pyridine was added 0.5 g. of 1-*d*-glucosidocytosine hydrate. The nucleoside gradually dissolved and after standing for three days at room temperature the solution was added to 10 g. of ice. The crystalline material that deposited was collected and dried; yield 0.7 g. It was crystallized twice from 2 cc. of alcohol and separated as clusters of elongated plates; m. p. 225°; $[\alpha]^{23}_D$ +38.1° (C = 1.7 in c. p. chloroform).

Anal. Calcd. for $C_{20}H_{25}O_{11}N_3$: C, 49.67; H, 5.21; N, 8.70; $COCH_3$, 44.52. Found: C, 49.94; H, 5.29; N, 8.73; $COCH_3$, 43.85.

Summary

1-*d*-Glucosidocytosine was prepared by the interaction of ammonia and 1,2-dihydro-2-keto-4-ethoxy-1-tetraacetyl-*d*-glucosidopyrimidine. A curious physical property of this synthetic nucleoside is the tenacity with which it attaches itself to alcohol. In general, its chemical properties are quite similar to those of cytidine.

WASHINGTON, D. C. RECEIVED NOVEMBER 25, 1935

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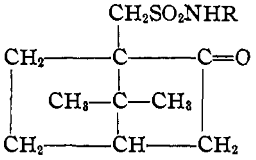
(8) The Dumas method has been found to give low results for a number of pyrimidines.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

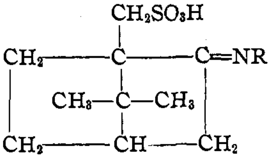
Anomalous Mutarotation of Salts of Reychler's Acid. IV. Comparison of 2-(N-phenylketimine)-*d*-camphane-10-sulfonic Acid with *d*-Camphor-10-sulfonanilide

BY HARRY SUTHERLAND[1] AND R. L. SHRINER

It has been pointed out that the dehydration product obtained from primary amine salts of Reychler's acid could possess the structure of a substituted sulfonamide (I), as well as that of a substituted ketimine (II). .



I



II

Since sulfonamides cannot ordinarily be obtained by direct dehydration of a salt of a sulfonic acid, the ketimine structure was preferred. However, it must be admitted that most of the evidence thus far cited[2] could be explained on the basis of either formula. Hence, it was desirable to prepare a substituted sulfonamide of Reychler's acid and compare it with the corresponding product to which the ketimine structure had been assigned.

d-Camphor-10-sulfonanilide has been prepared by Reychler,[3] who merely recorded its melting point, and by Armstrong and Lowry,[4] who recorded its optical rotation, but no information was available concerning its stability, ease of hydrolysis or possible mutarotation in solvents containing water. Hence, the preparation of this sulfonanilide was repeated, its properties determined and compared with those of the compound obtained by dehydration of the aniline salt of *d*-camphor-10-sulfonic acid. The information obtained has been collected in Table I.

TABLE I

COMPARISON OF ANILINE SALT AND ANILIDE OF REYCHLER'S ACID WITH N-PHENYLKETIMINE-*d*-CAMPHANE-10-SULFONIC ACID

Property	Aniline salt	Anilide	N-Phenylketimine
Melting point, °C.	184–186	120.5–121	294–295
Specific rotation[5] in chloroform	+37.5°	+76.0°	−170.5°
Mutarotation			
(a) 95% alcohol	Yes	No	Yes
(b) Chloroform	Yes	No	No
Neutral equivalent (by titration)	325	None	306.3
Hydrolysis	.....	Difficultly	Readily

Examination of the data in Table I shows that the *dextro*-rotatory anilide differs markedly from the *levo*-rotatory dehydration product. It behaved like a typical substituted sulfonanilide in that it gave no neutral equivalent and was hydrolyzed with difficulty. It did not mutarotate in a solvent containing water—a property characteristic of the ketimine. These results show definitely that the dehydration product of an amine

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(1) Chemical Foundation Fellow in Organic Chemistry.

(2) Schreiber and Shriner, THIS JOURNAL, **57**, 1306, 1445, 1896 (1935).

(3) Reychler, *Bull. soc. chim.*, [III] **19**, 124 (1898).

(4) Armstrong and Lowry, *J. Chem. Soc.*, **81**, 1447 (1902).

(5) All specific rotations were determined at 25° with sodium D light at a concentration of 1 g. per 100 cc. of solvent.

salt of Reychler's acid is not a substituted sulfonamide (I) and hence, by exclusion, constitute further evidence in favor of the ketimine structure (II).

Experimental

***d*-Camphor-10-sulfonyl Chloride.**—The conversion of Reychler's acid to the sulfonyl chloride may be accomplished by means of either phosphorus pentachloride or thionyl chloride. Both reagents were used in order to determine which was the better. Treatment of one mole of *d*-camphor-10-sulfonic acid with one mole of phosphorus pentachloride according to the directions of Reychler[3] gave a 38% yield of the sulfonyl chloride. The thionyl chloride method described by Smiles and Hilditch[6] gave a 98% yield, provided four moles of thionyl chloride is used for each mole of the acid. The recrystallized product melted sharply at 67°, and had a specific rotation[5] of +32.1°.

***d*-Camphor-10-sulfonanilide.**—Three-tenths mole of the above sulfonyl chloride and 0.9 mole of aniline were heated on the steam-bath for several hours. The reaction mixture was poured into 1 liter of water, and the product removed by filtration. For purification the anilide was dissolved in ether, extracted several times with 10% hydrochloric acid, and the ether evaporated. The residue was recrystallized repeatedly from alcohol until the melting point became constant at 120.5–121°. The anilide possessed specific rotations[5] of +76° in chloroform, and +29.5° in 95% alcohol. Its solutions did not exhibit mutarotation over a period of three days. It was insoluble in alkalies and could not be titrated to give a neutral equivalent. A sample of the anilide was also prepared by the usual Hinsberg procedure, using *d*-camphor-10-sulfonyl chloride, aniline and 10% sodium hydroxide solution. The anilide precipitated from the alkaline solution. After recrystallization it melted at 120–121°, and was identical with the sample prepared by the first method.

Anal. Calcd. for $C_{16}H_{21}O_3NS$: S, 10.43; N, 4.56. Found: S, 10.38; N, 4.48.

Hydrolysis of *d*-Camphor-10-sulfonanilide.—The sulfonanilide did not undergo hydrolysis on standing in aqueous alcoholic solution. Refluxing the anilide with 25% hydrochloric acid for thirty-six hours, according to the method previously described for benzenesulfonanilides,[7] hydrolyzed it to aniline (77% yield) and *d*-camphor-10-sulfonic acid.

Summary

The anilide of *d*-camphor-10-sulfonic acid has been prepared and found to differ markedly from the dehydration product of the aniline salt of Reychler's acid. This excludes the sulfonanilide from consideration as the dehydration product, and constitutes further proof that the ketimine structure is correct.

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(6) Smiles and Hilditch, *J. Chem. Soc.*, **90**, 522 (1907).

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

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Sulfuryl Chloride—Sulfuryl Chlorofluoride

BY HAROLD SIMMONS BOOTH AND CARL V. HERRMANN[1]

Of the two possible fluorination products of sulfuryl chloride only one, sulfuryl fluoride, is mentioned in the literature. Moissan and Lebeau[2] prepared sulfuryl fluoride by passing fluorine into sulfur dioxide. Ruff[3] found that sulfuryl fluoride could not be made by distillation of fluorosulfonic acid. Traube[4] was able to prepare the gas by the decomposition of sodium fluorosulfonate according to the reaction $2NaSO_3F \longrightarrow Na_2SO_4 + SO_2F_2$. None of these methods appeared to be of use in the preparation of a possible sulfuryl chlorofluoride.

This Laboratory has prepared a number of inorganic chlorofluorides[5] by a reaction first developed by F. Swarts[6] for the fluorination of organic compounds. The method involves the heating of a non-polar chloride with antimony trifluoride in the presence of an antimony pentahalide as a catalyst. In a preliminary study[7] it was found that the reaction

$$SbF_3 + 3SO_2Cl_2 + (SbCl_5) \longrightarrow SbCl_3 + 3SO_2ClF + (SbCl_5)$$

did not proceed appreciably under reduced pressure, but at atmospheric pressure a small amount of gas was produced which had approximately the anticipated boiling point.

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(1) Submitted by Carl V. Herrmann to the Graduate School, Western Reserve University, in partial fulfilment of the requirements for the degree of Master of Arts, June, 1934. Reported in the Fluorine Symposium, Cleveland Convention of the American Chemical Society, September 13, 1934.

(2) H. Moissan and P. Lebeau, *Compt. rend.*, **132**, 374 (1901).

(3) Otto Ruff, *Ber.*, **47**, 656 (1914).

(4) W. Traube, *ibid.*, **46**, 2523 (1913).

(5) Booth and Swinehart, THIS JOURNAL, **54**, 4750, 4751 (1932); **57**, 1333, 1337 (1935); Booth and Bozarth, *ibid.*, **55**, 3890 (1933); Booth and Stillwell, *ibid.*, **56**, 1531 (1934).

(6) F. Swarts, *Bull. soc. chim.*, [4] **35**, 1557 (1924).

(7) We are indebted to Miss Ida Lieb of this Laboratory for this preliminary study.