The first and second crops of crystals were combined and dried (m. p. 199°). Eighteen and seven-tenths grams of crystalline material was obtained. Sixteen and seven-tenths grams of this was dissolved in 450 cc. of hot acetone, charcoal added and the solution filtered while hot. Forty cc. of hot carbon tetrachloride was added to the filtrate and the solution cooled in the refrigerator for several days. The crystalline material, separated and dried, amounted to 5.5 g. A second crop of less pure material obtained from the filtrate amounted to 4.8 g. A portion of the first crop of crystals was dissolved in hot acetone and the solution cooled. The separated crystalline material was pure white, and after thorough vacuum drying had a melting point of 201.5°.

Anal. Calcd. for $C_{26}H_{26}O_6$: C, 71.86; H, 6.03; OCH_3, 7.14; mol. wt., 434. Found: (micro)[3] C, 71.63, 71.56; H, 6.17, 6.03; (semimicro) OCH_3, 7.19, 7.19; mol. wt. 452 (titn. phenolphthalein); phenol, negative; nitrogen, none.

The material crystallizes from amyl acetate in the form of short, columnar crystals with the following refractive indices:[4] $\alpha = 1.510$; $\beta = 1.718$; γ considerably greater than 1.77.

The plant material for this work was kindly furnished by Mr. Oswaldo Stelling of Caracas, Venezuela.

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[3] The writer is indebted to Mr. J. R. Spies of the Insecticide Division for the determination of carbon and hydrogen by microcombustion.

[4] Refractive indices were determined by Mr. E. L. Gooden of the Insecticide Division.

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NOTES

Crystalline Guaiazulene

BY KENNETH STEWART BIRRELL

In the course of an investigation at present being carried out on the hydrocarbon designated by Ruzicka[1] as S-guaiazulene, it was observed that the liquid (b. p. 176° (17 mm.)) is in reality supercooled and when once frozen in liquid air remains solid indefinitely.

The solid melted initially at 27–28° and after recrystallization from alcohol had a constant m. p. of 31.5°. The picrate of the purified substance melted at 122° as before.

The crystalline azulene has the appearance of small shining blue-violet plates. Crystallographic examination shows that the substance is biaxial with a small optic axial angle and the crystals are probably orthorhombic.

Axial ratios: $a:b:c = 0.56:1:1.34$

Interfacial angles:

100 ∧ 110	29°7′
110 ∧ $\bar{1}$10	121°46′
011 ∧ 0$\bar{1}$1	106°30′ ± 1°

Habit: tabular, parallel to macropinacoid (100)

The hydrocarbon described by Ruzicka as Se-guaiazulene has been prepared and found to exhibit the same phenomenon. This substance shows the same melting point as the S-guaiazulene and gives no melting point depression on admixture with the latter. A comparison of the melting points of the picrates and of the styphnates of the two substances lends support to the view that they may be identical and not isomeric as stated by Ruzicka.[1] In some cases the Se-guaiazulene even after regeneration from the picrate may fail to crystallize. Here the melting point of the picrate remains low but gives no melting point depression with S-guaiazulene picrate. It seems probable that this behavior is connected with the efficiency of the Se dehydrogenation and that an obstinate impurity inhibits crystallization. With S-guaiazulene purification through the solid may advantageously replace purification through the picrate. It is hoped to extend this work to the other isomeric azulenes described by Ruzicka.

Acknowledgment is made to Prof. J. K. H. Inglis for helpful suggestions and to Dr. F. J. Turner of the Geology Department, who kindly worked out the crystallography.

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[1] Ruzicka and Haagan-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).

A Convenient Modification of the Kiliani Synthesis of Higher Carbon Acids (or their Lactones) from Reducing Sugars[1]

BY C. S. HUDSON, OLIVE HARTLEY AND CLIFFORD B. PURVES

The condensation of slightly alkaline, aqueous hydrogen cyanide[2] or of potassium or barium cyanide[3] with the carbonyl group of a reducing

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[1] Published by permission of the Director of the National Bureau of Standards and the Surgeon General of the U. S. Public Health Service.

[2] Kiliani, *Ber.*, **19**, 767 (1886).

[3] Rupp and Hoelzle, *Arch. Pharm.*, **253**, 404–415 (1915). See also the Höchster Farbwerke German Patents, 24,526 and 253,754.

sugar produces the nitriles of the two stereoisomeric monocarboxylic acids containing an additional carbon atom in the molecule. These nitriles can be hydrolyzed subsequently to the corresponding acids by an excess of hot alkali and the well-known Kiliani synthesis is then complete. We believe that the more convenient modifications used by us since 1926 to carry out these important reactions may be of general interest and therefore we describe as an example the preparation of the α- and β-glucoheptonic lactones from glucose.

Five liters of a filtered aqueous solution containing 200 g. of anhydrous calcium chloride (3.6 equivalents) and 163 g. of sodium cyanide (3.3 moles) was used to dissolve 540 g. of anhydrous glucose (3.0 moles).[4] The temperature of the solution rose from 20 to 33° within an hour and after two hours 94% of the theoretical amount of ammonia could be expelled from a sample by distillation. Thus the formation of the glucoheptonic nitriles and their hydrolysis to α- and β-calcium glucoheptonate and ammonia is quite rapid. The reaction was complete within twenty-two hours at ordinary temperature. Calcium hydroxide (222 g., 3 moles) was then dissolved in the solution and in a short while the basic calcium salts of the two glucoheptonic acids precipitated and were filtered off, washed with cold lime water until the filtrate showed only a faint chloride test, and decomposed with oxalic or sulfuric acid in the usual way. By concentrating the solution a yield of 42% of α-glucoheptonic lactone was crystallized, and a yield of 11% of the crystalline lactone of the beta acid was obtained from the residue through the brucine salt.[5] By working up mother liquors these yields were increased to 58 and 21%, respectively.

This preparative method has been applied by various workers associated with us to the conversion of xylose to gulonic lactone, lactose to a corresponding 13 carbon acid, and to the preparation of the gluco-octonic lactones. It seems to be generally the case that the basic calcium and barium salts of the monobasic sugar acids are only sparingly soluble. In the case of mannose, barium chloride was used in place of calcium chloride and the neutral barium salt of α-mannoheptonic acid, which is of low solubility and crystallizes well, could be obtained directly from the reaction mixture. It will be observed that sodium cyanide is used in the preparations in place of hydrocyanic acid, an alteration which is markedly convenient in large scale work. The preparation of α-glucoheptonic lactone from glucose is now so readily performed that it might well be used in college instruction.

The work was carried out during 1926–8 in the National Bureau of Standards and subsequently in the National Institute of Health.

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[4] One may prefer to use calcium cyanide in place of the two salts, if it is available.

[5] E. Fischer, *Ann. Chem.*, **270**, 64 (1892).

WASHINGTON, D. C.

RECEIVED MARCH 12, 1934

COMMUNICATIONS TO THE EDITOR

THE AMPHOTERIC CHARACTER OF SILVER HYDROXIDE

Sir:

A recent paper by H. L. Johnston, F. Cuta and A. B. Garrett on this subject [THIS JOURNAL, **55**, 2311 (1933)] agrees satisfactorily with the conclusions reached by E. Laue in a paper "Ueber den amphoteren Charakter des Silberhydroxyds" [*Z. anorg. allgem. Chem.*, **165**, 325 (1927)] which escaped the attention of these authors. In this paper it was pointed out that silver hydroxide is amphoteric and that the solubility product of argentic acid is about 2×10^{-18}.

Johnston, Cuta and Garrett's value 2.22×10^{-4} mole per liter for the solubility of silver hydroxide in neutral solution at 25° is not in agreement, however, with my figure of 1.36×10^{-4}, which I believe to be correct within 5%. This discrepancy would be easily understood if the water employed by Johnston and his co-workers had contained the usual equilibrium amount of carbon dioxide and had had in consequence a conductivity of 2×10^{-6} mho or more [methods for the calculation of such carbon dioxide corrections, E. Laue, *Z. anorg. allgem. Chem.*, **165**, 305 (1927)]. However, Dr. Johnston informs me that the water