

It has also been shown that tephrosin is a hydroxydeguelin and that the hydroxyl group in tephrosin occupies the position of one of the hydrogen atoms attached to either carbon atom 7 or 8 in the deguelin formula.

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NOTES

The Decomposition of *n*-Valerolactone

BY RALPH W. THOMAS AND H. A. SCHUETTE

Proof has already been presented¹ in support of the statement that *n*-valerolactone will not withstand distillation at atmospheric pressure—reports to the contrary notwithstanding—since it undergoes partial decomposition as it approaches its boiling point. The nature of this decomposition has now been traced to the formation, in the main, of a polymerization product, and an explanation has been found for the discrepancies in the vapor pressure curves of this compound when obtained by two different methods of procedure, a dynamic² and a static.³ How the former conclusion has been arrived at is summarized in this communication.

In order to fix a point of departure in the study of this problem, the assumption was made that the decomposition in question is accompanied by the evolution of carbon dioxide and the formation of a butene (2:3 or 1:2). The set-up in which the decomposition studies were carried out closely simulated the conditions which obtain in the determination of pressure-temperature relationships. To that end the lactone was heated under thermostatically controlled conditions in a 2.5-cc. bulbous glass decomposition chamber to which had been sealed an 8-mm. delivery tube provided with a short upright side arm which was later to serve the dual purpose of introducing or removing samples and as an aid in sweeping out the air from the apparatus with nitrogen. At a distance of about 25 mm. from this side arm, the tube was bent at an angle of 45°; beyond that, as a precautionary measure against loss of material during heating, it took the form of a spiral condenser. A delivery tube leading from the latter to an inverted, mercury-filled buret completed the system.

That the reaction herein involved is not wholly due to a decarboxylation with the formation of a butene was shown by the fact that a 3.16-g. sample yielded only about 1 cc. of gas on heating for 530 hours at 202 ± 0.5°, which is four degrees below the alleged boiling point of this compound at atmospheric pressure. Although this gas was found to contain some carbon dioxide, yet no evidence could be secured that ethylenic hydrocarbons had been formed in the decomposition. A repetition of the

¹ Schuette and Thomas, *THIS JOURNAL*, **52**, 2028 (1930).

² Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

³ Smith and Menzies, *THIS JOURNAL*, **32**, 1412 (1910).

experiment during the course of which, at three time intervals, samples were removed for ultimate analysis showed that the residue, except for change in color, had altered only slightly during a 773-hour heating, having changed from C = 59.58 and H = 8.17 to C = 59.32 and H = 7.74. For these reasons it appears quite probable that the main course of the reaction is such as to favor the formation of a polymerization product. Further support for this conclusion may be found in the fact that the observed vapor pressures¹ when measured by a dynamic method² were lower than the calculated at any given temperature above that at which this compound begins to decompose. This is to be expected were a polymerization takes place.

The static method³ of measuring pressure-temperature relationships which was employed is very susceptible to the influence of gaseous decomposition products even though their quantity may be small. An immediate effect of this characteristic is to be found in the higher values which were obtained by this method of measurement. The foregoing observations account, it seems, for the discrepancies which were previously noted in vapor pressure measurements by two different methods of approach.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 23, 1932
PUBLISHED JULY 6, 1932

Preparation and Properties of the Normal Barium Salt of *l*-Cystine.¹

By CLIFFORD J. B. THOR AND ROSS AIKEN GORTNER

Several normal metallic salts of cystine have already been described. In 1900, Embden² prepared the normal copper salt and employed it in the isolation of the amino acid. A little later, Neuberg and Mayer³ prepared the corresponding salts of silver, mercury, lead and cadmium as well as of copper. Recently, Toennies and Lavine⁴ have succeeded in obtaining the lithium, sodium and potassium salts of cystine in crystalline form.

In the course of a study of the alkaline decomposition of cystine, which will be presented in a separate paper, it was observed while adding crystalline barium hydrate to a hot aqueous suspension of *l*-cystine that most of the cystine went into solution at a certain stage and that immediately thereafter a pale yellow precipitate separated out. By filtering off this pre-

¹ Published as Paper No. 1079, Journal Series, Minnesota Agricultural Experiment Station. Abstracted from a thesis submitted by Clifford J. B. Thor to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1931.

² Embden, *Z. physiol. Chem.*, **32**, 94 (1901).

³ Neuberg and Mayer, *ibid.*, **44**, 498 (1905).

⁴ Toennies and Lavine, *J. Biol. Chem.*, **90**, 203 (1931).

cipitate at once, washing it with a small amount of water, then with alcohol and ether and finally drying at 105°, a product was obtained (Preparation I) which analyzed fairly well for the normal barium salt of cystine.

Since no mention of this substance could be found in the literature and since it is involved in studies dealing with the decomposition of cystine by alkalis, it was thought desirable to prepare the salt in pure form and to determine its more important properties.

Method of Preparation.—A very satisfactory method consists in mixing equivalent amounts of aqueous Ba(OH)₂ and cystine in the cold and precipitating the resulting salt with alcohol. More exactly, 16 g. of Ba(OH)₂·8H₂O was dissolved in 250 cc. of boiled distilled water and cooled to 0°. Then 12 g. of the *l*-cystine was added and the mixture shaken in a stoppered Erlenmeyer flask until only very little undissolved material remained. The cold mixture was filtered through a Buchner funnel and after washing with distilled water the slight residue was discarded. The combined filtrate and washings, amounting to about 300 cc., were treated with 1600 cc. of 95% ethyl alcohol, which caused abundant precipitation of a white granular material. After thorough shaking, this mixture was placed in a refrigerator at -15° overnight. In the morning, the precipitate was filtered off with suction, washed with 600 cc. of 95% ethyl alcohol, then with ether and finally dried in an air oven at 100°. The yield was 18.1 g., which is 96.5% of the theoretical calculated from the cystine taken.

Properties.—The above product (Preparation II) was a perfectly white, finely divided powder which under the microscope showed no clearly defined crystalline form.

Anal. Calcd. for C₂H₁₀O₄N₂S₂Ba: N, 7.46; S, 17.07; Ba, 36.57. Found: N (Prepn. I), 7.32, (Prepn. II), 7.31; S (I), 16.20, (II) 16.65; Ba (I), 35.78; (II) 36.42.

A saturated solution of the salt was prepared by shaking 4 g. with 50 cc. of distilled water, allowing it to stand overnight at 25°, and filtering to remove excess salt. The saturated solution was very faintly yellow in color but seemed to be perfectly stable under the conditions of observation. Forty cc. of this solution was diluted to 200 cc. with water and aliquots were taken for nitrogen, sulfur and barium analyses to determine solubility, as indicated. This new salt of cystine then is water soluble at 25° to the extent of 6.15 g. per 100 cc. of saturated solution.

SOLUBILITY OF THE NORMAL BARIUM SALT OF *l*-CYSTINE IN WATER AT 25°

Basis of calculation.....	Nitrogen content	Sulfur content	Barium content	
Barium salt in 100 cc. of				
satsd. soln.....	6.14	6.17	6.14	Av. 6.15

When placed in a 1-decimeter tube, the saturated solution gave a saccharimeter reading of -11.0° at 25° and on dilution to five times its volume with water a proportionate value of -2.2°. Calculated on the basis of concentration of the barium salt, this gives a specific rotation of -61.9°; or calculated for cystine contained in the salt, of -96.9°. The latter agrees quite well with similar figures reported by Toennies and Lavine⁴ for the lithium, sodium and potassium salts of cystine. Free cystine was isolated from some of the salt and 0.2 g. of this dissolved in 25 cc. of normal hydrochloric acid at 25°, when placed in a 1-decimeter tube, gave a reading of -4.6° saccharimeter units. The corresponding specific rotation of -199.1° as compared with -204.2° for the original cystine indicates that racemization had not occurred to any considerable extent during the formation of the barium salt. Hence, it is safe to conclude that Preparation II consisted almost entirely of the barium salt of *l*-cystine.

If the saturated aqueous solution of the substance is diluted sufficiently with water,

hydrolysis takes place and a portion of the cystine precipitates out in the form of hexagonal plates. That hydrolysis had not taken place in preparing the saturated solution is clearly shown by the very close agreement between solubilities calculated from contents of nitrogen and sulfur on the one hand and barium on the other.

When the dry salt was heated in a melting point tube it showed no signs of decomposition or fusion up to about 250°; then it began to brown very gradually but without sintering.

When a portion of the salt equivalent to 2.5 g. of cystine was refluxed with 50 cc. of distilled water for twelve hours, nitrogen and sulfur analyses made after the removal of free hydrogen sulfide and ammonia indicated that decomposition to the extent of approximately 50% had taken place.

In its property of being water soluble, the barium salt of *l*-cystine resembles the alkali salts and differs from the heavy metal salts so far described. This characteristic as well as its ease of preparation and the ease of determination of its metallic constituent should make the barium salt useful in further studies on the mechanism of the alkaline decomposition of cystine. It might also find use in the preparation of derivatives of cystine, particularly in cases where the reaction requires anhydrous conditions.

CONTRIBUTION FROM THE
DIVISION OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
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RECEIVED MARCH 17, 1932
PUBLISHED JULY 6, 1932

The Structure of the Bromination Product of Ortho-Nitrotoluene

BY DAVID L. YABROFF

Wachendorff¹ obtained a dibromo product upon the bromination of *o*-nitrotoluene which he called a dibromonitrotoluene. He made the observation, however, that this product was soluble in alkali. Greiff² showed that the compound was a dibromo-anthranilic acid and suggested that it might be the *p-m*-dibromo-anthranilic acid obtained by Hübner³ upon the nitration and reduction of *p-m*-dibromobenzoic acid since both of the products melted at 225°.

If an intramolecular oxidation and reduction of the nitrotoluene occurs before the bromination, we should expect 3,5-dibromo-2-aminobenzoic acid as the final product. If bromination occurs before the oxidation-reduction process, we should expect 4,6-dibromo-2-aminobenzoic acid to be formed. These two compounds may be readily distinguished by allowing them to react for twenty-four hours in a dilute alcoholic solution with bromine water in the presence of a mineral acid. Under these conditions^{4,5} all positions ortho or para to the amino group which are not already substituted are brominated, and at the same time bromine is substituted for the carboxyl group. This may be represented as

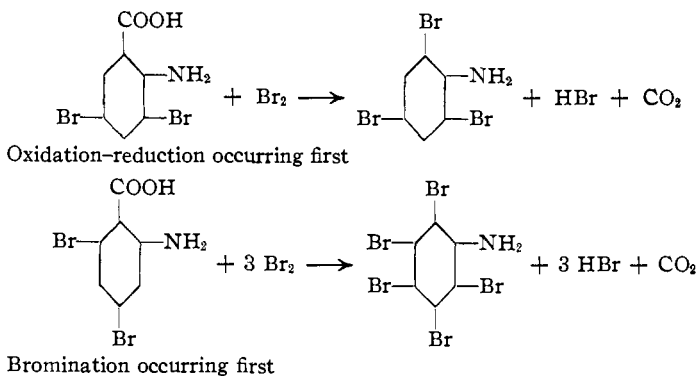
¹ Wachendorff, *Ann.*, **185**, 259 (1877).

² Greiff, *Ber.*, **13**, 288 (1880).

³ Hübner, *ibid.*, **10**, 1706 (1877).

⁴ Francis and Hill, *THIS JOURNAL*, **46**, 2498 (1924).

⁵ Flürscheim and Holmes, *J. Chem. Soc.*, 448 (1928).



In one case we would obtain tribromoaniline, in the other case pentabromoaniline. The product actually obtained by this treatment was tribromoaniline—m. p. 119°, mixed m. p. 120°; bromine analysis (Carius),⁶ found 72.3, 72.2%; calcd. for C₆H₂NH₂Br₃: 72.7.

These results indicate that the oxidation-reduction process of the nitro-toluene occurs first and the anthranilic acid formed is then brominated, giving rise to the 3,5-dibromo-2-aminobenzoic acid. Wheeler and Oates⁷ obtained this compound (m. p. 232°) by the direct bromination of anthranilic acid.

⁶ These analyses were carried out by Mr. Leslie H. Bayley.

⁷ Wheeler and Oates, *THIS JOURNAL*, **32**, 770 (1910).

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RECEIVED MARCH 25, 1932
PUBLISHED JULY 6, 1932

The Isomeric Desoxybenzansoins

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In a recent paper¹ S. S. Jenkins criticizes some of our work,² being apparently unable to reproduce certain of our results. The Friedel and Crafts reaction which is in question goes unusually well, and we have repeated the other two questioned preparations, with results identical to those which we reported previously.

We desire to correct Jenkins' statement that, with regard to the reduction of benzansoin to *p*-methoxybenzyl phenyl ketone, we reported none of the isomeric ketone. On the contrary we specifically stated³ that isomeric ketones might be present but that no serious attempt to isolate these was made. Jenkins neglects to mention that we proved the structure of our compounds by the Beckmann reaction. His work

¹ Jenkins, *THIS JOURNAL*, **54**, 1155 (1932).

² Buck and Ide, *ibid.*, **53**, 1536 (1931).

³ Ref. 2, p. 1538.

has not contradicted any of our conclusions as to the structures of the compounds obtained by us.

In view of the difficulties which have arisen, we submit descriptions of the methods of preparation in question at greater length. The preparations have been checked, and we reaffirm our earlier statements.

Benzyl *p*-Methoxyphenyl Ketone.—15.5 g. of phenylacetyl chloride⁴ and 13.0 g. of anisole (calcd. 10.8) were dissolved in 100 cc. of carbon bisulfide (Baker c. p.), in a flask fitted with a reflux condenser and a wide tube for adding the aluminum chloride; 15.0 g. of powdered aluminum chloride (Baker, anhydrous, c. p.) was then added in portions over thirty minutes. The bisulfide refluxes gently during the addition, and hydrogen chloride is evolved. The mixture becomes deep crimson in color and a dark crimson oil sinks to the bottom. After standing at room temperature for a further ninety minutes, 150 g. of crushed ice was added and then 20 cc. of concd. hydrochloric acid. The bisulfide layer was separated and washed twice with dilute hydrochloric acid (further bisulfide being added if the product starts to separate). The bisulfide was then evaporated on the steam-bath, 100 cc. of water added and steam bubbled through for ten minutes. On cooling the product solidified, and was then filtered off, washed with water, drained and dissolved in hot alcohol. On standing the ketone crystallized out. The melting point was 72°, raised to 74–75° on recrystallization. On three consecutive runs the yields were 19.4, 18.3 and 19.0 g., average, 84%. A further quantity (about 1.5 g.) may be obtained on diluting the liquors. Washing with alkali is unnecessary.

***p*-Methoxybenzyl Phenyl Ketone.**—50.0 g. of benzanisoin was dissolved in 200 cc. of 96% alcohol, in a flask fitted with a reflux condenser; 50.0 g. of mossy tin and 50.0 cc. of concd. hydrochloric acid were added, together with 0.5 g. of copper sulfate. The mixture was refluxed on the steam-bath for twelve to fifteen hours, a little (0.5 g.) copper sulfate being added occasionally as the reaction slowed down. After the first six hours, an additional 50 cc. of concd. hydrochloric acid was added to the mixture. When the reaction was complete, the mixture was filtered hot, the product rapidly crystallizing out on cooling. After standing, it was filtered off and washed with water, and then with cold alcohol; yield (unrecrystallized) 87%. Recrystallized from alcohol, the product melted at 91–92° and weighed 37.7 g. (82%). The melting point is raised to 94° after two further recrystallizations. The writers were unable to obtain a pure specimen of benzyl *p*-methoxyphenyl ketone from the liquors of this preparation.

Oximes of *p*-Methoxybenzyl Phenyl Ketone.—14.4 g. of *p*-methoxybenzyl phenyl ketone was dissolved in 100 cc. alcohol (96%) and hydroxylamine acetate solution (from 8.0 g. hydroxylamine hydrochloride and 13.0 g. potassium acetate) added. The reaction mixture was kept at 40–50° for two hours, when crystals commenced to separate. The mixture was then put in a cold place (0°) overnight and the crystals which formed were filtered off next day. After one recrystallization from alcohol the melting point was 132°. The liquors, after evaporation under reduced pressure, deposited a product, which, recrystallized several times from alcohol, melted at 95–96° (previously reported as 94°). The yield of the *anti* oxime (m. p. 132°) is about 10 g. and that of the *syn* oxime about 2 g., the relative amounts varying somewhat in different preparations.

Erratum.—In the paper in question,² p. 1540, line 19, for "Ketone E" read "Benzoin 5."

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RECEIVED APRIL 25, 1932
PUBLISHED JULY 6, 1932

⁴ Vanino and Thiele, *Ber.*, 29, 1727 (1896).