Solanidine-*s* (*ex S. auriculatum*): Calcd. for $C_{26}H_{43}O_3N$: N, 3.35. Found: N, 3.33.

Solanidine-*s* sulfate: Calcd. for $C_{26}H_{43}O_3N \cdot H_2SO_4$: N, 2.72. Found: N, 2.81.

Solanidine-*s* hydriodide: Calcd. for $C_{26}H_{43}O_3N \cdot HI$: N, 2.57. Found: N, 2.53.

I am indebted for samples of "solancarpine" and derivatives to Professor Kanga and his colleagues who have confirmed the above identification and to the Australian and New Zealand Association for the Advancement of Science for a grant.

DEPARTMENT OF CHEMISTRY
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5-Triphenylmethylbarbituric Acid

BY HAROLD W. COLES[1]

The statement is made by Berggårdh[2] that 5-triphenylmethylbarbituric acid could not be prepared by the common procedure, namely, by condensation of the respective malonic ester with urea (in this instance, by heating a day or two on the water-bath). He reports, however, that he succeeded[3] in preparing this acid by melting together a mixture of triphenylchloromethane and barbituric acid in a vacuum at a bath temperature of 165°. The isolation of a yellowish-brown substance, m. p. 274–275°, difficultly soluble in alcohol, is described. He identified this barbituric acid by heating it with sodium hydroxide solution on a water-bath for three days and obtained triphenylpropionic acid (m. p. 175–176°). He made no mention of any crystalline material separating out of the alkaline solution during the prolonged saponification.

In view of this report, it seems desirable to record the experiences of the author, which are completely at variance with those of Berggårdh. It was found[4] that triphenylmethyl malonic ester reacted appreciably (16.8% yield) with urea after only four hours refluxing on the water-bath in the presence of sodium ethylate. The triphenylmethylbarbituric acid thus obtained, analyzing correctly for nitrogen, was a white crystalline substance, easily soluble in alcohol and alkali, melting at 197.6° (U. S. P. Corrected). The saponification of this acid also gave different results from those described by Berggårdh.

No explanation of these differences is submitted. It is possible that the prolonged heating carried out by Berggårdh is responsible for his failure to secure the barbituric acid in the usual way. It has been demonstrated[5] that better yields of the barbituric acids result if the refluxing is brief. Even with brief refluxing the yield is poor (16.8%), so that the two-day refluxing of Berggårdh would result in only negligible yields. The possibility of rearrangement of the triphenyl group must also not be overlooked. The reactions given in detail in the experimental part have been checked by another worker.[6]

The triphenylmethylmalonic ester was prepared by the use of the magnesio-malonic ester alcohol complex.[7]

Pharmacologically,[8] the 5-triphenylmethylbarbituric acid was inactive. In rabbits, doses up to 1250 mg. per kg. orally, and up to 800 mg. per kg. intravenously, produced no hypnotic effect. The animals with the high doses simply went into collapse and died. The toxicity is low. It was recognized that monosubstituted barbituric acids are regularly without useful activity and the 5-triphenylmethylbarbituric acid is, therefore, normal in this respect. Attempts to attach a second substituent to the 5-carbon atom failed.

Experimental Part

Preparation of the Triphenylmethylmalonic Ester.[9]—This malonic ester was prepared by employing the magnesio-malonic ester of Lund.[10] Magnesium shavings, 2.5 g. (one mole equivalent), were weighed out into a round-bottomed Pyrex flask and were covered with one-half of a mixture of 28 cc. of absolute alcohol and 16 g. (one mole equivalent) of malonic ester (Eastman). Carbon tetrachloride (0.5 cc.) was added to the flask as catalyst. The reaction started at once, and was controlled by immersion

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(1) Senior Industrial Fellow, E. R. Squibb and Sons Industrial Fellowship, Mellon Institute.

(2) Berggårdh, *Acta Acad. Aboensis Math. Phys.*, **9**, No. 3 (1935).

(3) An attempt by Aspelund [*J. prakt. Chem.*, **137**, 1 (1933)] to prepare this compound by starting with barbituric acid failed.

(4) This work was completed the latter part of 1934. Because of the physiological inactivity of the barbituric acid, the saponification products were not studied exhaustively.

(5) (a) Shonle, Keltch and Swanson, THIS JOURNAL, **52**, 2440 (1930); (b) Rosenberg, Kneeland and Skinner, *ibid.*, **56**, 1339 (1934).

(6) The author is indebted to Miss Mary Dodds for this assistance.

(7) (a) Lund, Hansen and Voigt, *Kgl. Dan. Vid. Selsk. Math.-fys. Medd.*, **12**, No. 9 (Dec. 1933); (b) Lund, *ibid.*, **13**, No. 13 (1935); (c) Lund, *Ber.*, **67**, 935 (1934).

(8) The author is indebted to the Biological Laboratories of E. R. Squibb and Sons, New Brunswick, N. J., for these tests.

(9) (a) Compare Fosse, *Compt. rend.*, **145**, 1290 (1907); (b) Henderson, *J. Chem. Soc.*, **51**, 225 (1887).

(10) While Lund's method permits the production of triphenylmethylmalonic ester, the author was unable to obtain *t*-butylmalonic ester by this procedure. *t*-Butyl bromide and the iodide were used, with and without solvents (acetone, benzene), and in a sealed tube. A combination of potassium iodide and *t*-butyl bromide was also tried on malonic ester and on ethylmalonic ester. The author is indebted to the Brooklyn Laboratory of E. R. Squibb & Sons for making available information regarding their earlier experiences in work on *t*-alkyl barbituric acids.

of the flask in cold water if it became too hot. After the reaction had subsided somewhat, the remainder of the ester–alcohol mixture was added, and the contents refluxed until all traces of magnesium had disappeared.

The flask contents were chilled and the excess alcohol drained off by placing the flask on its side. Anhydrous ether (50 cc.) and 27.8 g. of triphenylchloromethane were then added to the solid magnesio-malonic ester and the flask gently warmed under reflux upon the water-bath. The reaction then proceeded spontaneously and a solid, partly magnesium chloride and partly the desired ester, separated out. After the spontaneous reaction ceased, the flask was warmed on the water-bath for another hour, and the contents were then removed to a separatory funnel where the magnesium chloride was removed by shaking several times with water. The ether solution was dried over anhydrous sodium sulfate, filtered, ether removed and the residue allowed to stay in contact with 200 cc. of absolute methyl alcohol for twenty-four hours. The solid, recrystallized from alcohol and dried in an 80° oven, amounted to 32 g. (80% yield), and melted at 131–132°. Lund[7a] and Henderson[9b] report a melting point of 133°.

Anal. (Schoeller). Calcd. for $C_{26}H_{26}O_4$: C, 77.57; H, 6.51. Found: C, 77.50; H, 6.40.

Preparation of 5-Triphenylmethylbarbituric Acid.—Four grams of urea (an excess) and 13 g. of triphenylmethylmalonic ester were added to sodium ethylate made from 2.7 g. of sodium and 60 cc. of absolute alcohol. The mixture was refluxed for four hours, chilled and 125 cc. of water added. After briefly stirring, the solid was washed on a Büchner funnel with 25 cc. of cold water. The filtrate was made strongly acid with concentrated hydrochloric acid while chilling. The white solid was washed on a Büchner funnel until free of acid and then dried.

The solid was treated with 25 cc. of hot benzene (to remove any triphenylpropionic acid or its ethyl ester) and washed on a Büchner funnel once with hot benzene. The residue, freed from benzene by suction, was washed repeatedly with hot water to free it of any unsubstituted barbituric acid and finally dried in the oven at 80°; yield 2 g.

The barbituric acid is insoluble in cold water, somewhat difficultly soluble in hot benzene, and readily soluble in alcohol and acetone. Insolubility in benzene is a characteristic of monosubstituted barbituric acids.[5a] The acid is readily soluble in cold dilute alkaline solutions. The m. p. is 197.6° (U. S. P. Corrected), the solid gradually turning purple before melting.

Anal. (micro-Dumas). Calcd. for $C_{23}H_{18}O_3N_2$: N, 7.56. Found: N, 7.67, 7.70.

The barbituric acid gave the characteristic triphenylmethyl group yellow color with concentrated sulfuric acid.

Alkaline Saponification.—One gram of the barbituric acid was refluxed for seventy-five hours with dilute sodium hydroxide. During this refluxing, an increasing amount of crystalline material separated out, having a total weight of 0.172 g. Triphenylcarbinol (m. p. 159°) was isolated by sublimation from this mixture and another crystalline product which, on the basis of the nitrogen assay and without further identification, was considered as triphenylmethylacetylurea. This compound, m. p. 141°, also gave a yellow color with concentrated sulfuric acid.

Anal. (micro-Dumas). Calcd. for $C_{22}H_{20}O_2N_2$: N, 8.14. Found: N, 8.31, 8.15.

The alkaline filtrate was not examined. Acidification resulted in the throwing out of a white solid amounting to 0.715 g. The alkaline solution gave no biuret reaction and produced no color with ferrous sulfate solution.

The author wishes to record his appreciation of the helpful advice of Drs. George D. Beal and Leonard H. Cretcher, Assistant Directors of Mellon Institute.

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The Reaction of *o*-Nitrophenylsulfur Chloride with Potassium Hydrosulfide

BY GREGG DOUGHERTY AND OTTO HAAS

The compound phenyl hydrogen disulfide, $C_6H_5—S—S—H$, has been postulated as the primary intermediate in the reaction of sulfur with benzene in the presence of aluminum chloride.[1] It has been suggested also by White[2] that compounds of this type are formed as intermediate products in a number of chemical processes such as, for example, the formation of sulfur dyes. White[2] described very briefly the preparation of a naphthyl hydrogen disulfide.

Lately we have attempted the synthesis of a substituted phenyl hydrogen disulfide with the object in view of determining whether it could be isolated or, if not, the nature of the decomposition products. When *o*-nitrophenylsulfur chloride and potassium hydrosulfide were brought together in equimolar amounts in absolute alcohol, a reaction took place at room temperature. The products were potassium chloride, hydrogen sulfide, sulfur and 2,2′-dinitrodiphenyl disulfide. The disulfide and sulfur were separated by fractional crystallization from alcohol. The dinitrodiphenyl disulfide had the correct melting point of 194° and the same melting point was obtained when it was mixed with some of the disulfide obtained from another source: found S, 20.5%; calcd. S, 20.78%. No compound corresponding to the nitrophenyl hydrogen disulfide was found.

Presumably, as evidenced by the formation of potassium chloride, the following reaction took place

$$NO_2—C_6H_4—S—Cl + KSH \longrightarrow NO_2—C_6H_4—S—S—H + KCl$$

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(1) Gregg Dougherty and Philip D. Hammond, THIS JOURNAL, **57**, 117 (1935).

(2) G. N. White, *J. Chem. Soc.*, **113**, 608 (1918).