termediates. How far it is really applicable can only be determined by further experiment. Nevertheless, it is interesting to consider a few of the possible consequences if we do assume that the phenomenon is general. First, the scope of the semiquinone theory is considerably broadened. Thus it may now be possible to treat, in a more satisfactory manner than has hitherto been possible, systems where no intermediate form has been shown to exist. In the light of the present theory it is entirely possible that an intermediate form does exist, but that the maximum concentration of the radical is not great enough to raise the index potential beyond the limits of error. In the case presented here, the high value of the dimerization constant enables us to recognize the intermediate form in acid solution, which scarcely would be possible if there were no dimerization. Second, we have dealt only with homogeneous systems. It is suggestive that under physiological conditions and with biologically occurring oxidation–reduction systems, adsorption at interfaces, or combination with specific proteins or enzymes, may have a similar influence as variation in concentration or *p*H has in a simple and homogeneous system. Finally, this theory removes the question which of the intermediate forms exists in any given case; for the radical and its polymer can exist at all times in equilibrium, the constants of which are determined by the substances in question and by the conditions of the surrounding medium. The resonance of the radical is one of the essential factors determining the equilibrium constants.

Summary

The intermediate form of oxidation–reduction of phenanthrenequinone-3-sulfonate may be present in two forms, as a semiquinone radical, or as a valence-saturated dimeric compound of the radical. There is an equilibrium between the four forms of the dye: the oxidized, the reduced, and the two intermediate forms. According to this equilibrium the existence of the dimer is favored by increasing the total concentration of the dye. In alkaline solution the intermediate form is represented mainly by the radical even in moderately concentrated solution, and practically entirely so at the concentration of 0.001 *M* and below. In acid solution the radical exists in any case only in extremely small amounts. The dimeric form is just as scarce when the total concentration of the dye is low; but it may increase very considerably if the total concentration of the dye is high. The values of the equilibrium constants are

		at *p*H 4.6	at *p*H 12
Semiquinone formation constant	k =	$\lesssim 10^{-3}$	28.6
Dimer formation constant	q =	230	2000
Dimerization constant	γ =	$\lesssim 2 \times 10^{6}$	70

Increase of alkalinity not only increases the total intermediate form, but also the fraction of this which is in the form of a radical.

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NOTES

The Identity of Solancarpine with Solanine-*s*

BY LINDSAY H. BRIGGS

A comparison, by the method of mixed melting points, of "solancarpine" from *Solanum xanthocarpum*[1] and solanine-*s* both from *S. sodomaeum*[2] and *S. auriculatum*[3] as well as of the related aglyco alkaloids and their derivatives has shown that the alkaloids from all three botanical sources are identical.[4] The names solancarpine and solancarpidine should therefore be removed from the literature.

This observation tends to confirm the formulas $C_{44}H_{75}O_{18}N$ or $C_{44}H_{77}O_{19}N$ for solanine-*s* and $C_{26}H_{43}O_3N$ for solanidine-*s*[5] with which the following additional analyses[6] are also in agreement.

Solanine-*s* (*ex S. sodomaeum*): Calcd. for $C_{44}H_{75}O_{18}N \cdot 2H_2O$: C, 56.11; H, 8.39; N, 1.47. Found: C, 56.10, 55.98; H, 8.64, 8.68; N, 1.83, 1.75.

Solanidine-*s* (*ex S. sodomaeum*): Calcd. for $C_{26}H_{43}O_3N$: C, 74.82; H, 10.31; N, 3.35. Found: C, 75.18, 75.10; H, 10.51, 10.57; N, 3.32, 3.38.

(1) Saiyed and Kanga, *Proc. Indian Acad. Sci.*, **4A**, 255 (1936).
(2) Oddo and Caronna, *Ber.*, **69B**, 283 (1936), and earlier papers.
(3) Anderson and Briggs, *J. Chem. Soc.*, 1036 (1937).
(4) *Cf.* Briggs, THIS JOURNAL, **59**, 1404 (1937).
(5) *Cf.*, however, Rochelmeyer, *Arch. Pharm.*, **275**, 336 (1937).
(6) Analyses by Dr.-Ing. A. Schoeller.

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 "solanicarpine" 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.

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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

(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.