each substance and the figures given in Table I are average values.

The author appreciates the interest and advice of Professor L. F. Fieser during the course of this research.

Summary

A study has been made of substituted pyrocatechol-*o*-benzoquinone systems in regard to their potentials in aqueous and benzene solutions. For the latter it was necessary to use a new optically active hydroquinone–quinone pair of high oxidation–reduction level. The three optically active systems which have been used serve adequately for the interval between 0.590 and 0.870 v.

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[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Mixed Melting Point Curves of Some Dialkylbarbituric Acids[1]

BY H. A. SHONLE AND E. C. KLEIDERER

Mixed melting point studies were made of the following three pairs of barbituric acids: (a) diethylcarbinylethyl and propylmethylcarbinylethyl barbituric acids; (b) diethylcarbinylallyl and propylmethylcarbinylallyl barbituric acids; and (c) isoamylethyl and active amylethyl[2] barbituric acids. The general procedure is given by Caldwell and MacLean.[3] Definite mixtures of the barbituric acids were weighed out, dissolved in acetone, evaporated to dryness and held in a desiccator until they were either hardened or crystallized. The total weights of samples of propylmethylcarbinylethylbarbituric acid and diethylcarbinylethylbarbituric acid, and propylmethylcarbinylallylbarbituric acid and diethylcarbinylallylbarbituric acid were 30 mg. in each determination. The total weights of samples of active amylethylbarbituric acid and isoamylethylbarbituric acid were 0.5 g. in each determination. Some of those mixtures which exhibited a minimum melting point required many weeks to harden and even then were only wax-like solids. It was found that a more intimate mixture could be obtained by dissolving the samples in acetone than by merely grinding them together in an agate mortar.

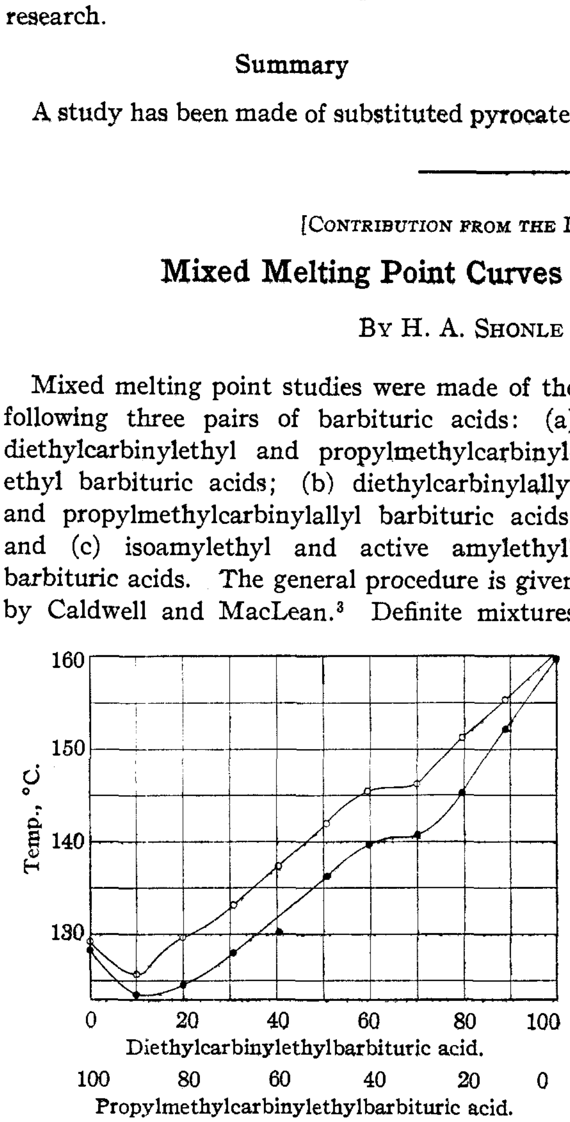

Fig. 1.

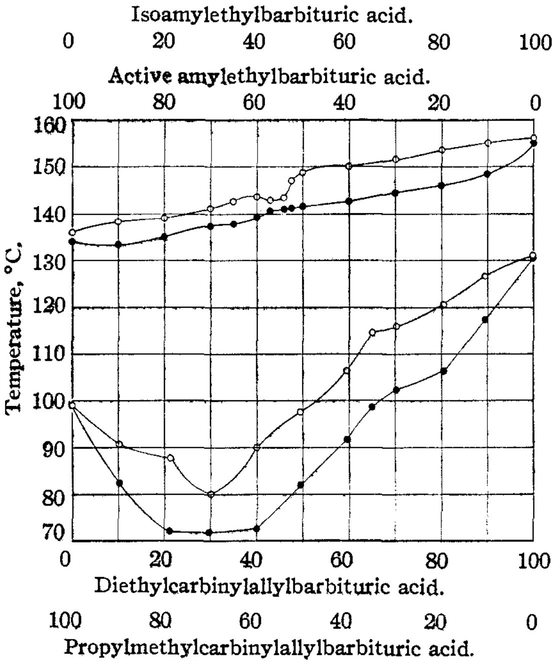

Fig. 2.

Melting point tubes of the usual size were filled with the solid pulverized mixture and the temperatures recorded were those of the first appear-

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[1] Presented in part before the Division of Medicinal Chemistry at the Chicago Meeting of the American Chemical Society, September, 1933.

[2] *dl*-2-Methylbutylethylbarbituric acid.

[3] Caldwell and MacLean, THIS JOURNAL, **55**, 3458 (1933).

ance of melting and of the clearance of the last particle of solid. A hand lens was used in observing both of these points as the sample was slowly heated in an oil-bath under constant agitation. Close agreement was obtained in checked temperature determinations, usually 0.1 and never more than 0.5°. The results of the three experiments are recorded in Charts I and II (Anschütz thermometers were used).

Several significant points were found in the behavior of the various acids studied. Mixtures of diethylcarbinylethylbarbituric acid and propylmethylcarbinylethylbarbituric acids containing 60–70% of diethylcarbinylethylbarbituric acid showed almost constant melting ranges irrespective of the composition of the sample. A second example of this phenomenon occurs in mixtures of diethylcarbinylallylbarbituric acid and propylmethylcarbinylallylbarbituric acid containing 65–80% of diethylcarbinylallylbarbituric acid. Evidence of a eutectic point was found in mixtures of isoamylethylbarbituric acid and active amylethylbarbituric acid containing about 45% of isoamylethylbarbituric acid.

It was found possible to estimate, from melting point data, the composition of various "unknown" mixtures with an accuracy of 2 to 3%, the samples having been prepared by another investigator. It is thus possible to establish whether or not the alcohols used in the preparation of the barbituric acids were pure or whether in the case of secondary alcohols isomerization had occurred.

The authors wish to express their appreciation to Mr. W. J. Doran, who weighed samples of the barbituric acids for this investigation.

Summary

Temperature–composition phase curves have been established for (a) diethylcarbinylethyl and propylmethylcarbinylethyl barbituric acids; (b) diethylcarbinylallyl and propylmethylcarbinylallyl barbituric acids; and (c) isoamylethyl and active amylethyl barbituric acids.

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[CONTRIBUTION FROM LILLY RESEARCH LABORATORIES]

Barbituric Acids Containing a Secondary Amyl Group[1]

BY H. A. SHONLE

The preparation of certain barbituric acids containing the diethylcarbinyl and the propylmethylcarbinyl groups was described in a previous article from this Laboratory, wherein the following melting points were reported: (a) diethylcarbinylethylbarbituric acid, 127–129°; (b) propylmethylcarbinylallylbarbituric acid, 86–88°; (c) diethylcarbinylallylbarbituric acid as wax-like; and (d), diethylcarbinylbarbituric acid, 165–168°.[2]

Tabern and Volwiler[3] discuss the ease with which the diethylcarbinyl group isomerizes to the propylmethylcarbinyl group and give two procedures which overcome, at least in part, this tendency to isomerize, and describe the first three of the above barbituric acids as melting at 158.5–159.5°, 98–100° and 129–130°, respectively.

When the earlier work of this Laboratory was repeated, it was reported[1] that a certain and rather definite proportion of the propylmethylcarbinyl isomer was present in the barbituric acids obtained when urea was condensed with the ester resulting from the reaction of pure 3-bromopentane and the sodio-malonic ester. Through the use of mixed melting point curves, it is possible to estimate the degree of isomerization present in the barbituric acid.[4]

Although it was not possible to demonstrate the proportion of the isomers present in the ester, it is believed that they were present in approximately the same proportion as observed in the barbituric acid, and that the diethylcarbinylmalonic esters do not undergo further isomerization when condensed with urea.

The experimental data reported below give the method of preparation and the melting points of the isomer-free barbituric acid.

Experimental

Diethylcarbinylbarbituric Acid.—Diethylcarbinylmalonic ester, b. p. 85–86° (12 mm.), n^{20} 1.4293–4, was prepared

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[1] Presented in part before the Division of Medicinal Chemistry at the Chicago Meeting of the American Chemical Society, September, 1933.

[2] Shonle, Keltch and Swanson, THIS JOURNAL, **52**, 244 (1930).

[3] Tabern and Volwiler, *ibid.*, **56**, 1139 (1934).

[4] Shonle and Kleiderer, *ibid.*, **56**, 2489 (1934).