

calculated from the formula, can be determined by analysis and used as a positive means of identification of the product to distinguish it from, or detect the presence of similar products which might result in case homologs of furfural were present. For example, if a mixture of furfural and sufficient methylfurfural were precipitated, the determinations of nitrogen and sulfur on the product should enable us to compute the relative amounts of these two aldehydes, and, therefore, the relative amounts of pentosans and methylpentosans in the original sample. At present the only means of estimating separately the furfural and methylfurfural present in a mixture such as is frequently met with in analysis, is the supposed differential solubility of their phloroglucides in alcohol, and this is admittedly unreliable.

It is suggested that thiobarbituric acid, which is not difficult to prepare in a pure state, may be found useful in the analysis of agricultural products, in place of phloroglucinol or barbituric acid, for the determination of pentoses and pentosans.

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[CONTRIBUTION FROM THE CHEMICAL SECTION, IOWA STATE COLLEGE.]

## CONDENSATION OF THIOBARBITURIC ACID WITH AROMATIC ALDEHYDES.

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The condensation occurring between aldehydes and the methylene group of malonic acid or its ester is well known. Less known, however, is the fact that the same reaction can be made to occur between aldehydes and the ureides of malonic acid. Conrad and Reinbach<sup>1</sup> condensed malonylurea (barbituric acid) with benzaldehyde, salicylaldehyde, *o*-nitrobenzaldehyde, *o*-aminobenzaldehyde, cinnamic aldehyde, and furfural. The reaction was carried out in aqueous solution at the temperature of the water bath. Salicylic aldehyde condensed with two molecules of barbituric acid, but in every other instance the condensation was in equimolecular proportions. Weinschenk<sup>2</sup> condensed barbituric acid with *p*-hydroxybenzaldehyde and with *p*-dimethylaminobenzaldehyde, heating the mixtures with alcohol on the water bath. Later, Whiteley<sup>3</sup> condensed 1,3-diphenylbarbituric acid with benzaldehyde and with cinnamic aldehyde, by heating with alcohol under a reflux. The same reaction was subsequently carried out by Whiteley and Mountain,<sup>4</sup> using 1,3-diphenylthiobarbituric acid. Jäger and Unger<sup>5</sup> found that in the pres-

<sup>1</sup> *Ber.*, **34**, 1339 (1900).

<sup>2</sup> *Ibid.*, **34**, 1685 (1900).

<sup>3</sup> *J. Chem. Soc.*, **91**, 1330 (1907).

<sup>4</sup> *Proc. Chem. Soc.*, **25**, 121 (1909).

<sup>5</sup> *Ber.*, **35**, 4440 (1902).

ence of 12% hydrochloric acid, barbituric acid and furfural condense quantitatively in the cold. This reaction has been applied by the writers<sup>1</sup> to the condensation of thiobarbituric acid with furfural and methylfurfural as a quantitative method for furfural in preference to the barbituric acid method. The two resulting products, furfuralmalonylthiourea and methylfurfuralmalonylthiourea, have been described in a previous paper.

In the present paper this reaction has been extended to other aromatic aldehydes and a number of new derivatives are here described.

**Benzalmalonylthiourea.**—Molecular proportions of benzaldehyde and thiobarbituric acid were dissolved in 12% hydrochloric acid and the solutions mixed. A lemon yellow precipitate at once formed. After standing a few moments, it was filtered, washed thoroughly with hot water, and finally with alcohol and ether. The product was only slightly soluble in alcohol and glacial acetic acid, but readily soluble in pyridine and in caustic alkalies. In ether, petroleum ether, benzene and carbon disulfide it was practically insoluble.

Calc. for  $C_6H_5CH : C_4H_2O_2N_2S$ : N, 12.07%; S, 13.79%. Found: N, 12.19; S, 13.71.

***o*-Hydroxybenzalmalonylthiourea.**—Salicylaldehyde and thiobarbituric acid in 12% hydrochloric acid reacted in like manner, giving an immediate precipitation of a bright vermilion colored product. It showed the same solubilities as the corresponding product previously described. With dilute ammonia or caustic alkalies it gave a deep wine red color which rapidly disappeared.

Calc. for  $HO.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 11.30%; S, 12.94%. Found: N, 11.41; S, 12.61.

***o*-Nitrobenzalmalonylthiourea.**—Under the above conditions, nitrobenzaldehyde gave a greenish yellow product, with the same solubilities.

Calc. for  $NO_2.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 15.00%; S, 11.55%. Found: N, 15.07; S, 11.29.

***p*-Methoxybenzalmalonylthiourea.**—With anisic aldehyde and thiobarbituric acid, the product was a deep yellow precipitate, insoluble in the usual solvents except alkalies.

Calc. for  $CH_3O.C_6H_4.CH : C_4H_2O_2N_2S$ : N, 10.70%; S, 12.21%. Found: N, 10.58; S, 12.05.

**3-Methoxy-4-hydroxybenzalmalonylthiourea**—Vanillin condensed readily with thiobarbituric acid, giving a brilliant orange colored precipitate. In caustic alkalies the product gave a mahogany red solution, but the color rapidly faded.

Calc. for  $(CH_3O)(HO)C_6H_3.CH : C_4H_2O_2N_2S$ : N, 10.07%; S, 11.87%. Found: N, 10.05; S, 11.79.

**3,4-Methylenedioxybenzalmalonylthiourea.**—In the same manner piperonal condensed with thiobarbituric acid, with the formation of a bright orange colored precipitate, soluble only in alkalies.

<sup>1</sup> THIS JOURNAL, 38, 2156 (1916).

Calc. for  $\text{CH}_2\text{O}_2 = \text{C}_6\text{H}_3\text{CH} : \text{C}_4\text{H}_2\text{O}_2\text{N}_2\text{S}$ : N, 12.07%; S, 13.79%. Found: N, 12.19; S, 13.71.

**3,5-Dihydroxyphthalaldimalonylthiourea.**—Resorcinoldialdehyde condensed with two molecules of thiobarbituric acid. The product was a reddish brown precipitate, soluble in alkalis, to a mahogany red solution.

Calc. for  $(\text{HO})_2\text{C}_6\text{H}_2(\text{CH})_2 (= \text{C}_4\text{H}_2\text{O}_2\text{N}_2\text{S})_2$ : N, 13.40%; S, 15.40%. Found: N, 13.90; S, 15.50.

**Cinnamylidenemalonylthiourea.**—Cinnamic aldehyde yielded with thiobarbituric acid a bright orange red precipitate, soluble only in alkalis.

Calc. for  $\text{C}_6\text{H}_5\text{CH} : \text{CHCH} : \text{C}_4\text{H}_2\text{O}_2\text{N}_2\text{S}$ : N, 10.85%; S, 12.40%. Found: N, 10.69; S, 12.15.

None of the substances described above could be melted without decomposition. The temperatures at which decomposition and charring began varied from  $220^\circ$  to  $300^\circ$ , but in no case was the decomposition temperature sufficiently sharp to serve as a means of identification. It is of interest to note that the condensation products of thiobarbituric acid with the three aldehydes which contain a hydroxyl group on the benzene nucleus gave a deep red coloration with caustic alkalis, while the others remained colorless under this treatment. In all cases the yield was practically quantitative.

The precipitation of aromatic aldehydes by thiobarbituric acid in the presence of 12% hydrochloric acid appears to be a general reaction. The products all have an intense yellow or yellowish red color. Three aliphatic aldehydes tried—formaldehyde, acetaldehyde and citral—failed to react under these conditions.

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[CONTRIBUTION FROM THE SYNTHETIC PRODUCTS LABORATORY OF THE BUREAU OF CHEMISTRY.]

## RESEARCHES ON ORGANIC PERIODIDES.

### II. PERIODIDES OF ANTIPYRINE, IODOANTIPYRINE AND PYRAMIDONE.

By W. O. EMERY AND S. PALKIN.

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#### Introduction.

The earliest available record of the action of iodine on antipyrine is that of Manseau,<sup>1</sup> who found that in aqueous solution and in the absence of free acid a relatively small but constant quantity of iodine was absorbed, which behavior he proposed to utilize as a basis for the proximate assay of antipyrine. Beyond noting the fact that apparent substitution took place until a point was reached when further addition of iodine produced a tarry precipitate, no attempt was made to ascertain the nature of the reaction or of the compounds formed. From a quantita-

<sup>1</sup> *Bull. soc. pharm. Bordeaux*, 1889, 148.