2. When submitted to a partial hydrolysis with aqueous acid, hepta-acetyl-β-thiophenol maltoside yielded glucose and β-thiophenol glucoside of the normal ring structure. β-Thiophenol maltoside may accordingly be regarded as ordinary β-thiophenol glucoside substituted by a second glucose residue.

3. β-Thiophenol maltoside was obtained as a very hygroscopic glass with an approximate specific rotation of $[\alpha]_D^{27}$ 38° in water.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PREPARATION OF BENZOYLACETIC ESTER

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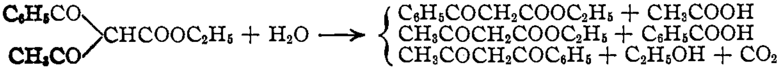
RECEIVED JULY 25, 1929 PUBLISHED DECEMBER 11, 1929

The usual method given for the preparation of benzoylacetic ester is the Claisen condensation[1] of ethyl acetate with ethyl benzoate. A yield of 33% is reported but all attempts to duplicate this yield have failed. A study of this condensation was made by Marvel and Shiao[2] who found that the best yield obtainable by this method was 18%. In many runs the reaction mixture turned brown, puffed up and decomposed entirely giving very little or no product at all. A similar condensation with methyl piperonylate[3] gave yields ranging from 20 to 35%.

Since benzoylacetic ester would be an extremely useful reagent if it were readily obtainable, a search was made for other methods of preparation. The present communication is a report on the preparation of benzoylacetoacetic ester and its partial hydrolysis to benzoylacetic ester.

Benzoylacetoacetic ester was prepared in the usual way by the reaction between benzoyl chloride and the sodium derivative of acetoacetic ester. It was found possible to raise the yield of product from 50 to 75% and to shorten the time materially by using a slight excess of benzoyl chloride in benzene as the medium for the reaction.

The primary hydrolysis of benzoylacetoacetic ester may take place in three different ways



$$\left.\begin{matrix}C_6H_5CO\\ CH_3CO\end{matrix}\right\rangle CHCOOC_2H_5 + H_2O \longrightarrow \left\{\begin{matrix}C_6H_5COCH_2COOC_2H_5 + CH_3COOH\\ CH_3COCH_2COOC_2H_5 + C_6H_5COOH\\ CH_3COCH_2COC_6H_5 + C_2H_5OH + CO_2\end{matrix}\right.$$

Complete hydrolysis, of course, will lead to the formation of benzoic acid, acetophenone, acetone or acetic acid and the final products obtained will depend on the conditions of hydrolysis, which evidently must be carefully adjusted in order to favor the first reaction.

The different methods reported in the literature for accomplishing this

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[1] Claisen, *Ber.*, 20, 646 (1887).

[2] Shiao, B. S. "Thesis," University of Illinois, **1923**.

[3] Shriner and Kleiderer, THIS JOURNAL, **51**, 1269 (1929).

hydrolysis were tried. The most promising one was a short time hydrolysis with ammonia and ammonium chloride.[4] Claisen carried out this hydrolysis on the crude sodium salt obtained by the action of benzoyl chloride on acetoacetic ester and sodium ethylate. In the present study the pure benzoylacetoacetic ester was isolated first and then subjected to hydrolysis under the influence of varying concentrations of ammonia and ammonium chloride. The results of these experiments are summarized in Table I.

TABLE I

EFFECT OF VARYING CONCENTRATIONS OF AMMONIA AND AMMONIUM CHLORIDE ON THE HYDROLYSIS OF BENZOYLACETOACETIC ESTER

Run	Benzoylacetoacetic ester, g.	Water, cc.	NH_4Cl, g.	NH_4OH, cc. (sp. gr. 0.9)	Temp., °C.	Time, min.	Yield of benzoylacetic ester g.	%
1	40.0	100	9	10	40	10	11	34.3
2	58.5 (0.25 mole)	150	16	20	40	10	23	47.9
3	58.5	150	16	40	40	10	21	43.8
4	58.5	150	32	20	40	10	29	60.3
5	58.5	150	32	10	40	10	37.5	78.1
6	58.5	150	32	none	40	10	..	..

Run No. 1 was made according to Claisen's directions and resulted in a yield of 34%, although Claisen[5] claims 64–67% yields. A comparison of Runs 2 and 3 indicates that an increase in the ammonia concentration decreases the yield. An increase in ammonium chloride is beneficial up to a certain point. Run No. 6 resulted in the production of large quantities of benzoic acid. The optimum conditions are those given in No. 5. It was also found that the use of a higher temperature or longer time of hydrolysis resulted in lower yields.

It is evident that this same method can be applied to the preparation of substituted benzoylacetic esters.

Experimental

Preparation of Benzoylacetoacetic Ester.—Claisen[4] prepared this compound by adding benzoyl chloride slowly to a solution of acetoacetic ester in a sodium ethylate solution. Other investigators[6] have prepared the benzoylacetoacetic ester by adding metallic sodium to an ether solution of acetoacetic ester and then adding benzoyl chloride. The first method is objectionable because considerable amounts of ethyl benzoate are formed and the second requires a long time because of the slowness with which the sodium reacts with the acetoacetic ester. By using benzene and warming the mixture the time of preparation is considerably shortened. The optimum conditions are as follows.

In a 5-liter flask fitted with a mechanical stirrer and reflux condenser were placed

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[4] Claisen, *Ann.*, **291**, 71 (1896).

[5] From a consideration of Claisen's experimental data it is evident that two runs were combined in order to obtain the above yield. Attempts to duplicate Claisen's work by several different workers have given yields ranging from 29 to 34%.

[6] Bonné, *Ann.*, **187**, 1 (1877); Fischer and Bülow, *Ber.*, **18**, 2131 (1885); Nef. *Ann.*, **266**, 99 (1891); Pechmann, *Ber.*, **25**, 1046 (1892).

4.5 liters of dry benzene, 260 g. (2 moles) of acetoacetic ester and 46 g. (2 moles) of sodium. The mixture was stirred and allowed to reflux gently for twenty-four hours. The solution was then cooled slightly and 350 g. (2.5 moles) of benzoyl chloride added slowly over a period of three hours. The mixture was refluxed with stirring for eight hours. It was then cooled to room temperature and 500 g. of cracked ice added. After shaking thoroughly the benzene layer, which contains the benzoylacetoacetic ester, was separated and the benzene distilled. The residue was then distilled from a Claisen flask with modified side-arm and the fraction boiling at 177–181° at 20 mm. collected; yield, 350 g. or 74.8% of the theoretical.

Hydrolysis of Benzoylacetoacetic Ester.—The first hydrolysis recorded in Table I was made according to Claisen's directions.[4] The remaining hydrolyses were made in accordance with the procedure outlined below, the only variables being the amounts of ammonia and ammonium chloride. The amounts stated in the following procedure are those of Run 5 which represents the optimum conditions.

Thirty-two grams (0.6 mole) of ammonium chloride was dissolved in 150 cc. (8.3 moles) of water and 10 cc. (0.10 mole) of ammonia (sp. gr. 0.9) added. The solution was warmed to 40° and 58.5 g. (0.25 mole) of benzoylacetoacetic ester added. The solution was kept at 40° for ten minutes and then cooled rapidly by placing the flask in an ice-bath. It was extracted twice with 100 cc. of ether and the ether solution dried with anhydrous magnesium sulfate. The ether was distilled and the residue distilled *in vacuo;* yield, 37.5 g. (78.1% of the theoretical) of benzoylacetic ester boiling at 165–169° at 20 mm.; sp. gr. at 20°, 1.1098; n_D^{20} 1.5498.

Summary

The preparation and partial hydrolysis of benzoylacetoacetic ester to give benzoylacetic ester have been studied and optimum conditions worked out.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF AMINES.
V. DERIVATIVES OF TERTIARY AMINES

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RECEIVED JULY 26, 1929 PUBLISHED DECEMBER 11, 1929

Solid derivatives of tertiary amines suitable for identification purposes are not always available. The methiodides, picrates, chloroplatinates, chloro-aurates and simpler salts such as the hydrochlorides, hydrobromides, etc., are at times useful but no one derivative is generally applicable to a wide number of amines. These derivatives have the common fault of melting with some decomposition and the temperature of decomposition is usually dependent on the rate of heating.

The most characteristic reaction of tertiary amines is the formation of quaternary ammonium compounds by addition to the nitrogen atom. It is generally true that the greater the proportion of the hydrocarbon part of the molecule in a quaternary ammonium salt, the more likely the compound is to have a sharp melting point. With this idea in mind, the addition of