

found on the paper chromatogram (Fig. 2). On the other hand  $\alpha$ -aminobutyric acid (29), pipercolic acid (60), 5-hydroxypipercolic acid (75), and 1-cyclopropane-1-aminocarboxylic acid (88) which occur as free amino acids in the berries are not found on the paper chromatogram. Also in berries of cranberry (*Oxycoccus quadripetalus*) homoserine was found in bound form.

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## Disubstitution of Ethyl Acetoacetate in one Step by Means of Sodium Hydride

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Hitherto it has not been considered possible to prepare the disubstituted derivatives of acetoacetic ester in one step. For instance, Finar<sup>1</sup> points out that "the introduction of two alkyl groups must be carried out in two steps; it *cannot* be done in one step". However, Wallingford and Homeyer<sup>2,3</sup> have reported that dimetallation and disubstitution of  $\beta$ -ketoesters is possible with alcohol-free sodium alkoxide in alkyl carbonate solution, and Weizmann<sup>4</sup> was able to dialkylate acetoacetic ester by means of a complex formed between potassium hydroxide and an acetal or dialkyleter of ethylene glycol.

The present writer has found that ethyl  $\beta$ -acetotricarballylate can be prepared in good yields from ethyl acetoacetate and ethyl bromoacetate, using sodium hydride as metallating agent in benzene solution.

It is the author's intention to further investigate the extent to which this method is applicable.

*Experimental:* The apparatus used was a three-necked flask, fitted with a dropping funnel, a sealed Hersberg stirrer and a condenser, the top of which had connections to a source of nitrogen and a vacuum line. The apparatus was evacuated, flame-dried and filled with nitrogen. With nitrogen flowing, the dropping funnel was closed and removed, and sodium hydride (28.8 g, 1.2 mole) rapidly placed in the flask and covered with benzene (700 ml). The funnel was then replaced, the flow of nitrogen stopped and the funnel filled with a solution of freshly distilled ethyl acetoacetate (65 g, 0.5 mole) in dry benzene (150 ml) and then stoppered with a calcium chloride tube. With stirring, this solution was added during 30 min and the reaction mixture then stirred until the evolution of hydrogen had stopped. The apparatus was now swept with nitrogen, before a solution of freshly distilled ethyl bromoacetate (200 g, 1.2 mole) in dry benzene (75 ml) was placed in the dropping funnel. This solution was added with vigorous stirring during two hours, the flask being gently heated to maintain a slight reflux (the reaction is exothermic). When the addition was finished, the reaction mixture was stirred and refluxed for another 45 min.

After cooling, the reaction mixture was washed three times with water, the water washings extracted once with ether and the combined benzene and ether solutions dried over anhydrous magnesium sulphate. The solvents were removed and the residual oil fractionated, yielding 116.5 g (77 %) of  $\beta$ -acetotricarballylate, b. p. 142°—47°/1.0—1.2 mm. Phenylhydrazone m. p. 99°—100.5°. Emery<sup>5</sup> reports 190°/16 mm and 100°—101°, respectively.

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