

The Acyl Exchange in Acidolysis of Diethyl Acylmalonates with Organic Acids

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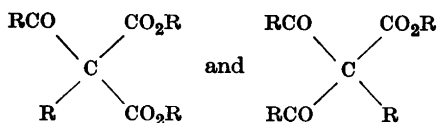
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The present author has recently shown that diethyl acylmalonates are very valuable substances in the synthesis of β -ketoesters¹. The diethyl acylmalonates were acidolysed with the organic acid containing the *same* acyl group thus giving excellent yields of the corresponding ethyl acylacetate according to the reaction:



However, if the acid and the diethyl acylmalonate have *different* acyl groups a mixture of the two possible β -ketoesters, corresponding to the two different acyl groups is obtained. This indicates that the acyl group in the diethyl acylmalonate is not held so firmly by the rest of the molecule.

A similar mobility of the acyl group has been observed by Dickmann and Wittmann² who studied the catalytic cleavage of compounds of the types:



with an alcoholic solution of sodium ethoxide. This reaction was found to proceed easily even when cold.

As the mobility of the acyl group is of great interest from both theoretical and preparative points of view a preliminary result of the investigation will be given here.

Equimolecular amounts of diethyl acetylmalonate and an organic acid were heated, using a little magnesium oxide and copper acetate as catalyst¹, for 5–8 hours, and the resulting product was fractionated in vacuo through a 30 cm Widmer column. In this way *ethyl n-butyrylacetate* b. p. 84–88°/10 mm (yield 38 %) and *ethyl isobutyrylacetate* b. p. 78–82°/10 mm (yield 35 %) were obtained. The actual amounts of these β -ketoesters in the mixtures are probably still higher, since there were losses in the isolation of the products. It seems to me very probable that this exchange is the result of a "redistribution

reaction"³ and that the yields hence would be 50 %.

From preparative point of view this method of preparing β -ketoesters has the advantage that the corresponding diethyl acylmalonate is not required as a starting material.

The reaction will be studied further to see if the acyl group exchange will be effected by other reagents, and if the reaction might be forced in a desired direction to give high yields of β -ketoesters.

1. Brändström, A. *Acta Chem. Scand.* **5** (1951), 22.
2. Dickmann, W., and Wittmann, A. *Ber.* **55** (1922) 3331.
3. Gilman, H. *Organic Chemistry II* (1943) 1807.

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