

Short Communications

The Base Catalysed Acidolysis of Diethyl Acylmalonates. A New Synthesis of β -Ketoesters of the Type $\text{RCOCH}_2\text{CO}_2\text{C}_2\text{H}_5$

ARNE BRANDSTRÖM

Chemical Institute, University of Uppsala, Uppsala, Sweden

In 1944 Breslow, Baumgarten and Hauser¹ described a method for the preparation of β -ketoesters of the type $\text{RCOCH}_2\text{CO}_2\text{C}_2\text{H}_5$. Their starting products were ethyl *t*-butyl acylmalonates, which were decomposed by heating with toluenesulphonic acid. This method seems to be the most promising one for the preparation of β -ketoesters of this type². It has however that weakness that ethyl *t*-butyl malonate is not commercially available. Some attempts to use diethyl acylmalonates in this preparation of β -ketoesters have been made^{1,3}, but none has been entirely satisfactory. This is due to the fact that the acid catalysed acidolysis of ethyl esters is a very slow reaction⁴.

The present author has recently shown⁵ that a base catalysed acidolysis of diethyl acylmalonates is readily effected in the preparation of β -diketones from diethyl malonate (1 mole) and an acid anhydride (2 moles). Preliminary experiments to stop this reaction at the β -ketoester stage by using one mole of diethyl malonate per mole of the anhydride resulted in mixtures of the β -diketone and the β -ketoester which could not be easily separated. This can, however, be avoided if the pure diethyl

acylmalonate is at first prepared from the acid chloride and diethyl malonate according to Lund⁶. The resulting diethyl acylmalonate can then be acidolysed with the theoretical quantity of the organic acid with the same acyl group as the diethyl acylmalonate used. A mixture of magnesium oxide and copper acetate is a good catalyst. *In all cases studied the yields obtained by this method were practically quantitative.* The method is probably applicable to the preparation of every β -ketoester if the corresponding diethyl acylmalonate can be obtained.

If an organic acid and a diethyl acylmalonate containing different acyl groups are used a redistribution of the acyl groups is possible. This reaction will be studied further.

Experimental: Pure diethyl propionylmalonate (1 mole) was mixed with the corresponding acid (propionic acid 1 mole), 0.1 g of magnesium oxide, and 0.05 g of copper acetate in a round-bottomed flask fitted with a reflux condenser. The mixture was refluxed for 5-8 hours, after which time the vigorous evolution of carbon dioxide had subsided. The mixture was then fractionated under reduced pressure. Ethyl propionate goes over in an almost quantitative yield at first, followed by a little middle fraction consisting of mainly propionic acid, and finally the *ethyl propionylacetate* is collected at 65-80°/10 mm in a yield of 92 %, leaving a little unchanged diethyl propionylmalonate in the distillation flask. If for any reason much middle fraction and residue are obtained they can be mixed and heated again

together with some fresh catalyst. Redistillation of the crude fraction shows that the product is quite pure, b.p. 72°/10 mm.

In the same way the following β -ketoesters were prepared: *Ethyl isobutyrylacetate* b.p. 70°/10 mm in 88 % yield, and *ethyl n-butyrylacetate* b.p. 86°/10 mm in 97 % yield.

1. Breslow, D., Baumgarten, E., and Hauser, C. R. *J. Am. Chem. Soc.* **66** (1944) 1286.
2. *Organic Reactions*. I (1942) 298.
3. Ross, J., Gebhart, A., and Gerech, F. *J. Am. Chem. Soc.* **67** (1945) 1275.
4. Cohen, S. *J. Am. Chem. Soc.* **66** (1944) 1395.
5. Brändström, A. *Arkiv Kemi*. **4** (1951) no. 9.
6. Lund, H. *Ber.* **67 B** (1934) 937.

Received June 6, 1951.