SYNTHESIS OF 1-CHLORO-2-ALKANONES USING MELDRUM'S ACID S. I. Zav'yalov, G. I. Ezhova, and T. K. Budkova

We have found that the reaction of C-acyl derivatives of Meldrum's acid (I) with SO_2Cl_2 for 12 h at 20°C yields 2,2-dimethyl-4,6-diketo-5-chloro-5-acyl-1,3-dioxanes (II) which are converted by the action of aqueous acetic acid at 80-90°C for 1 h to 1-chloro-2-alkanones (III) in 20% overall yield; the conversion involves hydrolytic decomposition and decarboxylation

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R = Et (a), n-Pr (b), and n-Bu (c).

The chloroketones (III) obtained were identified by conversion to the 2,4-dinitrophenylhydrazones and 1-phthalimido-2-alkanones (IV) according to Haworth [1] and Bunnett [2].

A sample of 4 ml SO_2Cl_2 was gradually added to 8.8 g ketone (Ia), maintained for 12 h at 20°C, and then heated with a mixture of 10 ml water and 6 ml acetic anhydride for 1.5 h at 90°C to yield 1 g (IIIa) with bp 132-135°C, n_D^{20} 1.4340; the phthalimido derivative (IVa) had mp 106-107°C. Similarly, we obtained (IIIb) with bp 152-154°C, n_D^{20} 1.4350, and 2,4-dinitrophenylhydrazone derivative with mp 137-139°C, and (IIIc) with bp 70-74°C (15 mm Hg), n_D^{20} 1.4355.

This new method permits the regional ective introduction of a chlorine atom into the methyl group of methyl alkyl ketones and thereby the production of important compounds for organic synthesis.

LITERATURE CITED

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