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LETTERS TO THE EDITOR

NEW CONVENIENT METHOD OF ISOPROPYLIDENE METHYLMALONATE SYNTHESIS

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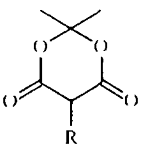
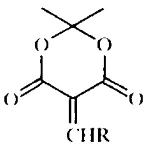
Isopropylidene alkylmalonates (**1**) are usually obtained by the reduction of ylidene derivatives **2** [1], since only dialkyl derivatives are formed on direct alkylation of malonate **1a**. However isopropylidene methylenemalonate (**2a**) is an extremely unstable compound [2] and is not suitable for the synthesis of isopropylidene methylmalonate (**1b**). A method for preparation of compound **1b** by the catalytic hydrogenation of isopropylidene methyl(α-methoxybenzyl)malonate (**3**) was reported [1]. This is a laborious, multistage synthesis requiring an absolutely dry reaction medium.

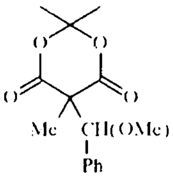
We propose a new convenient method for synthesis of compound **1b** from the readily obtained stable isopropylidene pyridiniummethylmalonate **4** [2]. Isopropylidene methylmalonate **1b** was obtained in 50% yield by reduction of malonate **4** with sodium borohydride in methanol. We note that the yield of compound **1b** was not stated in [1].



1a,b



2a,b



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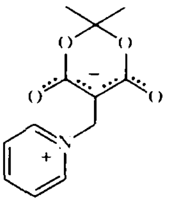

4

a R = H, b R = Me

EXPERIMENTAL

Isopropylidene Methylmalonate. A solution of compound **4** [2] (0.05 mole) in methanol (100 ml) was stirred for 1.5 h at 15-25°C with an equimolar quantity of sodium borohydride, and 1N hydrochloric acid (250 ml) was then added. Compound **1** (R = Me) was obtained (50%); mp 115-116°C (literature [1] 113-114°C). It was chromatographically pure (Silufol plates, solvent chloroform–methanol–glacial acetic acid, 9:1:1). ^{1}H NMR spectrum (CDCl$_3$): 1.55 (3H, d, CH$_3$); 1.82 (6H, s, 2CH$_3$); 3.64 (1H, d, CH).

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