

SHORT
COMMUNICATIONS

Dimerization of Sodium Enolates of Malonic Ester
and Acetylacetone Effected by the Action
of 4-Methyl-3,4-dibromotetrahydropyran

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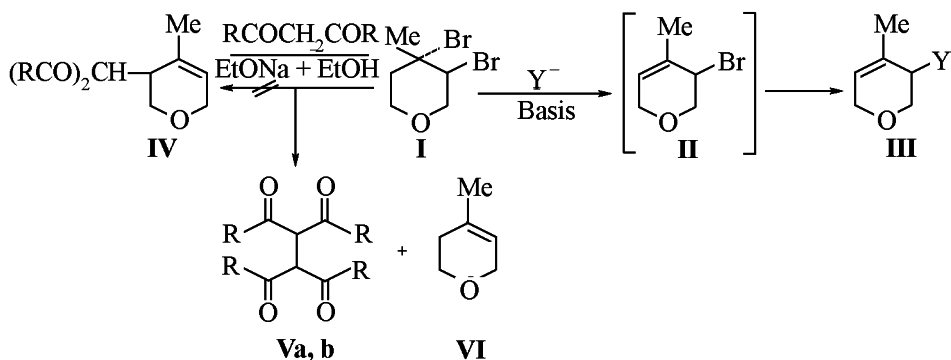
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It was shown formerly that 4-methyl-3,4-dibromotetrahydropyran (**I**) in reactions with a number of nucleophiles formed in succession products of dehydrobromination and substitution, dihydropyrans **II** [1–3]. In performing similar reactions with enolates of β -dicarbonyl compounds we revealed an unusual process: formation of “dehydrodimers” **V** of the initial dicarbonyl compounds. For instance, from malonic ester malonylmalonic ester (**Va**) was obtained [4], and acetylacetone gave rise to 3,4-diacetylhexane-2,5-dione (**Vb**) [5].

Dimeric compounds **V** are known to be prepared by oxidizing the corresponding sodium enolates with various oxidants: iodine, silver oxide, copper(II) triflate etc. [6]. In our case the reaction occurred under the effect of only dibromide **I** which evidently plays the role of an oxidant being converted into 4-methyl-2H-dihydropyran (**VI**).

By this procedure under standard conditions of dicarbonyl compounds alkylation [7] [at reagents ratio (**I**)- RCOCH_2COR 1:2] we obtained diethyl 2,3-diethoxycarbonylsuccinate (**Va**, $\text{R} = \text{OEt}$), yield 63%



$\text{R} = \text{OEt}$ (**a**), Me (**b**); $\text{Y} = \text{N}(\text{Alkyl})_2$; NHAr , NHAlkyl , OCOMe ; OAr .

(with respect to the initial dibromide), mp 74–75°C [4], ^1H NMR spectrum, δ , ppm: 1.27 t (12H, J 7.1), 3.93 s (2H), 4.17 q (4H); ^{13}C NMR spectrum, δ , ppm: 13.42 (Me), 50.56 (CH), 60.95 (CH_2), 165.78 (C=O), and 3,4-diacetylhexane-2,5-dione (**Vb**, $\text{R} = \text{Me}$): yield 18%, mp 192–193°C [5], ^1H NMR spectrum, δ , ppm: 1.99 s (12H), 12.74 s (2H);

^{13}C NMR spectrum, δ , ppm: 2.81 (Me), 191.66 (C=O).

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