Tetramethylguanidine-Catalyzed Addition of Nitromethane to α,β-Unsaturated Carboxylic Acid Esters

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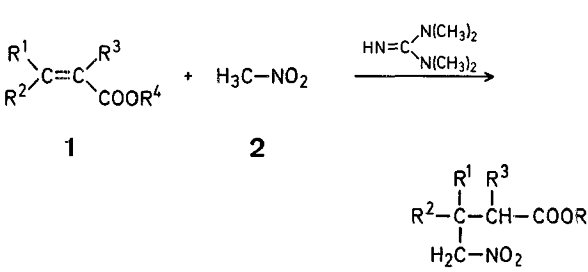
In connection with previously reported studies on γ-substituted butyrolactams[1], the ready availability of the unknown methyl ester of 3,3-dimethyl-4-nitrobutanoic acid **3e** became of great interest.

A direct approach to **3e** appears to be the Michael addition of nitromethane (**2**) to methyl 3-methylcrotonate (**1e**). However, whilst this reaction has been studied extensively and has been successfully applied to a great number of α,β-unsaturated esters using a variety of catalysts[2], no examples are reported with ester **1e**.

Attempts to prepare the γ-nitro ester **3e** by means of the usual Michael catalysts failed to give any results. This fact may be ascribed to steric hindrance due to the two methyl groups at the β-position of the acceptor. The failure of nitromethane to add to methyl cinnamate in the presence of potassium fluoride and the relatively low yield of adduct obtained from nitromethane and methyl crotonate have been explained in terms of a similar steric hindrance by Kambe and Yasuda[3].

We were able to prepare the γ-nitro ester (**3e**) under Michael conditions by use of tetramethylguanidine; to our knowledge, only one example af employment of this powerful catalyst in Michael reactions has been reported[4].



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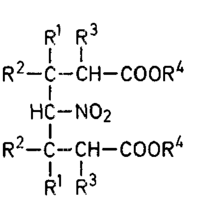
We have studied the compounds listed in Table 1. The results show that substituents at the β-position of the acceptor are necessary to obtain only 1:1 addition products, whereas methyl acrylate and methyl methacrylate yield mixtures of 1:1 adducts (**3**) and 1:2 adducts (**4**), which can be separated by distillation.



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Addition of Nitromethane to α,β-Unsaturated Esters; General Procedure:

A mixture of nitromethane (5 mol), α,β-unsaturated ester (1 mol), and tetramethylguanidine (0.2 mol) was stirred at room temperature for 2–4 days. (In the case of methyl acrylate, the ester has to be added at a temperature below 30°.) The progress of

Table 1. Preparation of Compounds **3a**–**f** and **4a** and **b**

	R^1	R^2	R^3	R^4	Yield %		b. p./2 mm	
					3	**4**	**3**	**4**
a	H	H	H	$COOCH_3$	39	45	79–80°	148–150°
b	H	H	CH_3	$COOCH_3$	24	43	86–88°	155–157°
c	H	CH_3	H	$COOCH_3$	65		82–83°	
d	H	C_6H_5	H	$COOCH_3$	75		140°	
e	CH_3	CH_3	H	$COOCH_3$	45		88–90°	
f	CH_3	CH_3	$COOC_2H_5$	$COOC_2H_5$	83		120–125°	

the reaction was followed by I.R. (disappearance of the C=C band) and G.L.C. analysis. The reaction mixture was washed with dilute hydrochloric acid and extracted with ether. The organic extract was dried, the solvent removed at reduced pressure, and the residue distilled at a pressure of 2 torr.

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