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A FACILE ONE-STEP SYNTHESIS OF β,γ-UNSATURATED CARBOXYLIC ACID ESTERS VIA 1,2-CARBONYL TRANSPOSITIONS OF α,β-UNSATURATED KETONES

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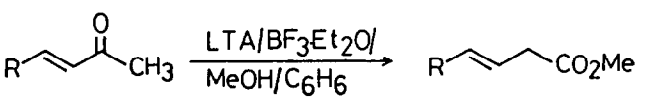
Abstract: Reaction of α,β-unsaturated ketone,1, with lead(IV)acetate and borontrifluoride etherate in the presence of methanol yielded the β,γ-unsaturated esters, 2, in a single step procedure, at room temperature.

The synthesis of α,β-unsaturated carboxylic acids are well documented and their methods of preparation are manifold and varied[1]. On the other hand, the corresponding β-γ-unsaturated compounds are less readily accessible[2]. The available methods involve: (1) addition of ethyl crotonate to a solution of lithium N-isopropylcyclohexylamide in tetrahydrofuran containing hexamethylphosphoramide[3]; (2) alkylation of ethylcrotonate by adding the ester to lithium diisopropylamide-hexamethylphosphoramide complex at low temperature[4]; (3) acylation of alcohols with crotonyl chloride using diisopropylethylamine as a base[5].

Recently we have described the use of lead(IV)acetate-borontrifluoride etherate combination in the conversion of acetophenones to methyl arylacetates[6] and in the ring contraction of the tetralones to the methyl indane-1-carboxylates[7]. We now wish to report a simple one-step synthesis of β,γ-unsaturated carboxylic acid esters via a 1,2-carbonyl transposition of α,β-unsaturated ketones using lead(IV)acetate borontrifluoride etherate-methanol combination. Thus when a mixture of benzalacetone (1a, 0.02 mole), methanol (0.06 mole) and borontrifluoride etherate (saturated, 15 ml) was added in one lot to a stirred suspension of lead(IV) acetate (0.023 mole) in



1 2

Scheme 1

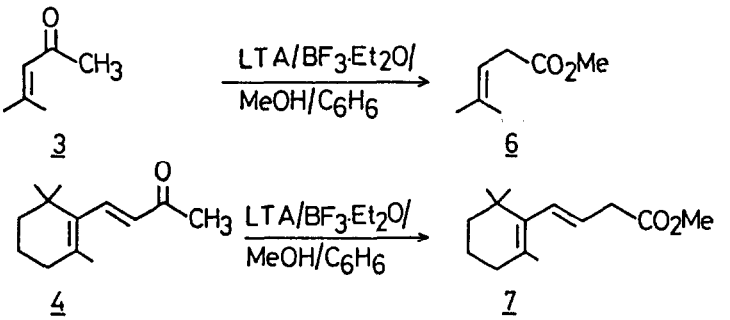
dry benzene (50 ml) at room temperature, work-up after 12 hr gave methyl 4-phenyl-but-3-ene carboxylate[8] (2a, 2.4g., 68%). These results are summarised in Table 1.

The generality of the method was further established when the aliphatic α,β-unsaturated ketones, viz. mesityl oxide (3), β-ionone (4) were similarly transformed under the same reaction conditions to the corresponding β,γ-unsaturated carboxylic acid esters, 6, and 7 (Scheme 2).

Table 1. One pot conversion of benzylidene acetones into methyl 4-phenyl-but-3-ene carboxylates (2).

Entry	Benzylideneacetone(1) R	Time (hr)	Yield of 2 (%)*	
1.	C_6H_5	12	a	68**
2.	4-$CH_3C_6H_4$	10	b	70**
3.	4-$OCH_3C_6H_4$	14	c	55**
4.	2-$OCH_3C_6H_4$	12	d	57
5.	3-$OCH_3C_6H_4$	12	e	60
6.	4-Cl C_6H_4	12	f	62
7.	2-Cl C_6H_4	13	g	50
8.	4-NO_2 C_6H_4	13	h	60
9.	2-Furyl	18	i	50

*
**Isolated by column chromatography on silica gel using hexane as eluent. The esters were hydrolysed to the corresponding acids, mps. of the acids compare well with the literature.



Scheme 2

Acknowledgement: One of us (F.M.) thanks NEHU for a Jr. Research fellowship.

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8. 2a: ^{1}H NMR ($CDCl_3$): δ3.12 (d,J=5.7Hz,2H,CH_2); 3.62 (s, 3H,OCH_3); 6.55-6.25 (m,2H,=CH); 7.32-10 (m,5H,ArH); IR(neat): 1740 cm^{-1}.
6: ^{1}H NMR δ 1.62 (s,3H,CH_3); 1.73 (s, 3H,CH_3); 2.91 (d, J=6Hz, 2H, CH_2); 3.58 (s,3H,OCH_3); 5.24 (brt J=6Hz, 1H olefenic). IR(neat): 1738 cm^{-1}.
7: ^{1}H NMR δ 0.80 (s,3H,CH_3); 0.90 (s,3H,CH_3); 1.1-1.51 [m, 4H, $(CH_2)_2$]; 1.58 (s,3H,CH_3); 1.83-2.20 (m, 2H, CH_2); 2.99 (d,J=6Hz, 2H, CH_2); 3.66 (s, 3H,OCH_3);5.40 (brdd,2H, olefenic) IR(neat): 1738 cm^{-1}.
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