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DECARBOXYLATIVE ELIMINATION:

A NEW METHOD FOR THE SYNTHESIS OF α,β-UNSATURATED KETONES

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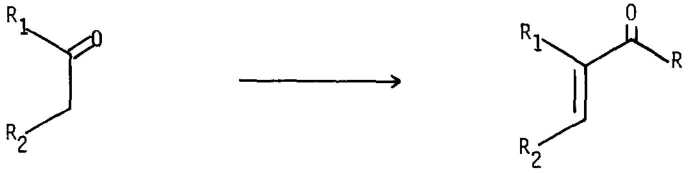
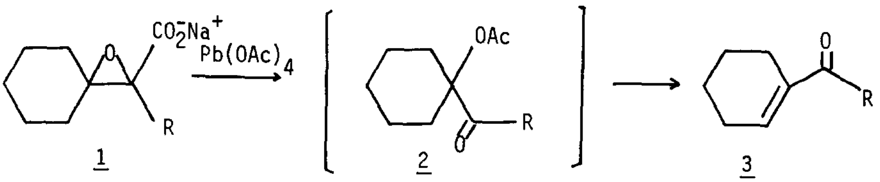
An efficient one-pot synthesis of α,β-unsaturated ketones via the decarboxylative elimination of sodium glycidates with lead tetraacetate is described.

The transformation of a carboxylic acid (or derivative) to ketone with a loss of one carbon atom has been a subject of considerable interest[1]. We wish to report a novel decarboxylation reaction which is highly convenient for the synthesis of α,β-unsaturated ketones[2] from the corresponding carbonyl compounds (equation 1).



(1)

The process involves the decarboxylation of sodium glycidate[3] 1 with lead tetraacetate, followed by the pyrolytic elimination[4] of the α-acetoxyketone intermediate 2 as indicated in equation (2).

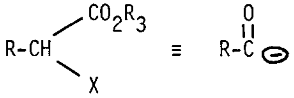


(2)

a, R = $-CH_3$(90% yield); b, R = $-CH_2CH_3$(94% yield);
c, R = n-Pr-(90% yield); d, R = n-pentyl-(80% yield);
e, R = n-hexyl-(82% yield).

The following procedure is representative: a mixture of sodium glycidate **1e** (0.01 mole), pyridine (0.02 mole), lead tetraacetate (0.02 mole) and dry benzene (100 ml) was stirred under nitrogen for 0.5 hr at room temperature, before being refluxed for 5 hr. Excess lead tetraacetate was decomposed with ethylene glycol. The product was purified by preparative thick layer chromatography (Merck PF_{254} silica gel; 7:3 chloroform-light petroleum; $R_f = 0.6$) to give **3e** in 82% yield.

The overall process represented by equation (1) involves the introduction of both an acyl and a double bond at the original carbon. The C-2 atom of the α-haloester functions as a masked nucleophilic acyl carbon[4].



$$R\text{-}CH\begin{matrix}\diagup CO_2R_3\\ \diagdown X\end{matrix} \equiv R\text{-}\overset{\overset{O}{\|}}{C}{\ominus}$$

We are presently exploring the scope and limitation of this reaction.

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