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A NEW METHOD FOR THE SYNTHESIS OF VINYL KETONES

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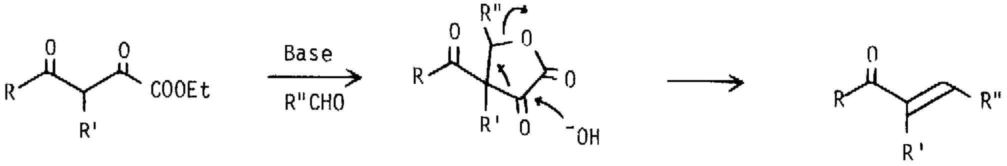
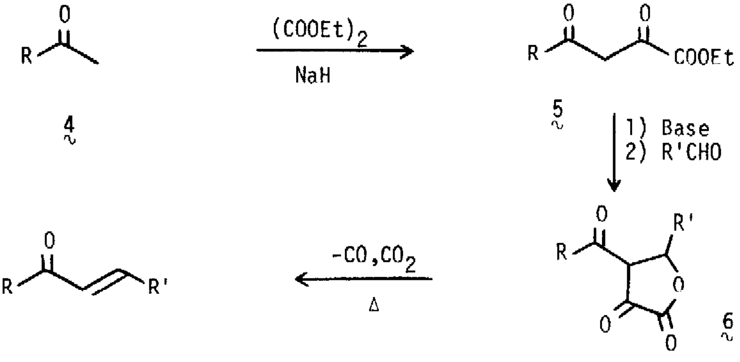
We have recently reported[1] a method for the synthesis of α-substituted α,β-unsaturated carbonyl compounds in which an oxalyl ketone or ester (**1**) is condensed with an aldehyde, generating a diketo lactone (**2**). Mild base cleavage then completes the synthesis.



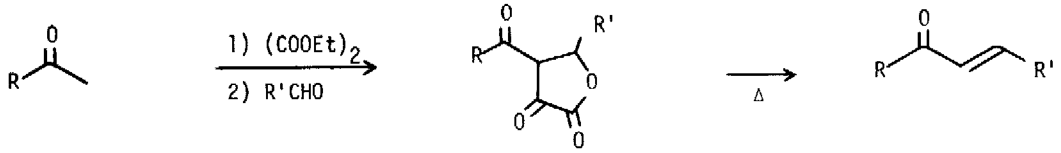
1 **2** **3**

This method, although efficient in many cases (ethyl oxalylcyclohexanone→α-methylenecyclohexanone, 87%) is unfortunately ineffective when R'=H, probably because of stable salt formation. Thus simple vinyl ketones can not be made in this way.

Vinyl ketones, however, are important intermediates in synthesis; although a number of methods are available for their synthesis, including such recent ones as the thermal elimination of α-keto sulfoxides[2], addition of vinyllithium to carboxylic acids[3], and the pyrolysis of propargyl esters[4], no good method is available starting from a methyl ketone. We have now found that vinyl ketones can be prepared from methyl ketones in good yield by pyrolysis of α-unsubstituted diketo lactones (**2**, R'=H). The overall scheme is formulated below.

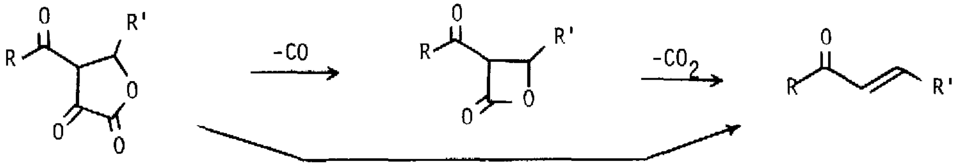


It is well-known[5] that methyl alkyl ketones react with diethyl oxalate at the less hindered, methyl side to give unsubstituted oxalyl ketones (5) in good yield. As shown many years ago[6-8], these oxalyl ketones react readily with aldehydes to give diketo lactones (6). Thus a wide variety of such lactones are available. When a wet ethyl acetate[9] solution of the diketo lactone is dropped into a 620° quartz pyrolysis tube swept by inert gas, thermal decarbonylation-decarboxylation occur to generate the vinyl ketone. Some specific examples are given in the Table.



R	R'	Diketolactone yield	Product (yield)
Ph	H	60% (ref 8b)	$PhCOCH=CH_2$ (82%)
CH_3	Ph	93% (ref 8b)	$CH_3COCH=CHPh$ (90%)
$(CH_3)_2CHCH_2$	H	72%	$(CH_3)_2CHCH_2COCH=CH_2$ (62%)
$CH_3(CH_2)_5$	H	81%	$CH_3(CH_2)_5COCH=CH_2$ (69%)
$CH_3(CH_2)_5$	CH_3	77%	$CH_3(CH_2)_5COCH=CHCH_3$ (84%)
Cyclopropyl	H	70%	 $COCH=CH_2$ (65%)

The mechanism of the pyrolysis reaction is unclear, but may well be analogous to the well-known decarbonylation of oxalyl ketones to β keto esters[10-13]. If the first step is indeed such a decarbonylation, the product β-lactone would be expected to undergo ready loss of CO_2 to the observed product[14]. Alternatively, of course, the reaction may be a concerted loss of CO and CO_2.



In a representative procedure, 2-oxo-3-benzoylbutyrolactone (564 mg, 3.0 mmole), prepared from acetophenone by published procedure[8b], was dissolved in 10 ml wet ethyl acetate and added dropwise to the top of a nitrogen swept quartz pyrolysis column heated to 620°. The organic products were trapped in a dry-ice cooled flask, diluted with dichloromethane, and washed with saturated bicarbonate solution. Solvent removal under reduced pressure and short path distillation gave the pure phenyl vinyl ketone (325 mg, 82%); ir (neat) 1660, 1650, 1603, 1600 cm^{-1}; nmr (CCl) δ 7.86 (m, 2H), 7.38 (m, 3H), 7.10 (d of d, J=10 Hz, J'=17 Hz, 1H), 6.31 (d of d, J=17 Hz, J'=2 Hz, 1H), 5.78 (d of d, J=10 Hz, J'=2 Hz, 1H).

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