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OXYGEN AND CARBON-ACYLATION OF ENOLATES BY KETENES

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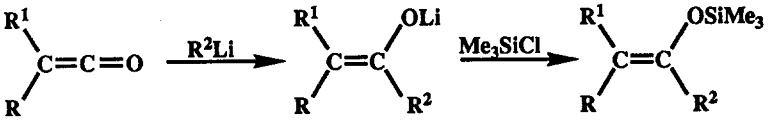
Abstract. Ketenes react with lithium enolates mainly by O-acylation, thus providing a convenient route to vinyl esters and their enolates.

The C-acylation of alkyl, alkenyl, alkynyl, and aryllithium reagents by ketenes has recently been exploited for the regio- and stereospecific generation of enolates (Eq. 1).[1] These enolates, many of which are not available by ketone enolization, have been further utilized in silylations, alkylations, aldol reactions, and ketone formation.[1]



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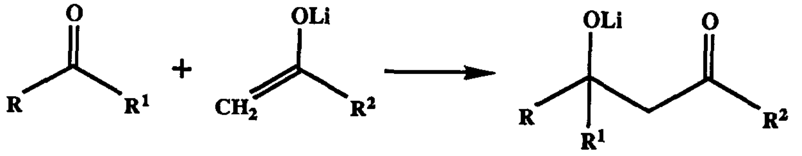
(1)

The O-acylation of alcohols and lithium alkoxides by ketenes has recently been reported to provide access to novel ketene acetals, ester enolates, and ester enols.[2]

Enolates can potentially be acylated by ketenes on either carbon or oxygen to give a new enolate, and polymerization of the ketene can result.[3a] There are only a few reported examples[3b,c,d] of the reaction of enolates with ketenes, and interestingly these give O-acylation of the enolate, contrary to the usual pattern of C-acylation of enolates by carbonyl compounds observed in the aldol reaction (Eq. 2).[4] We now report that acylation of enolates by ketenes is affected by the metal cation and the ketene structure, and provides a convenient route to many ester enolates (**2**, Eq. 3).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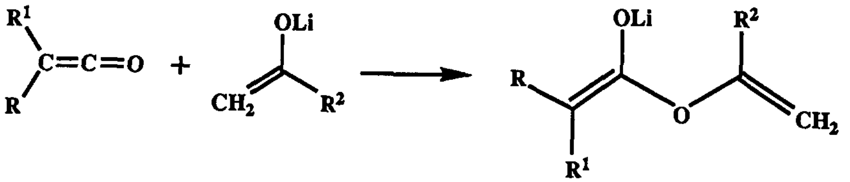
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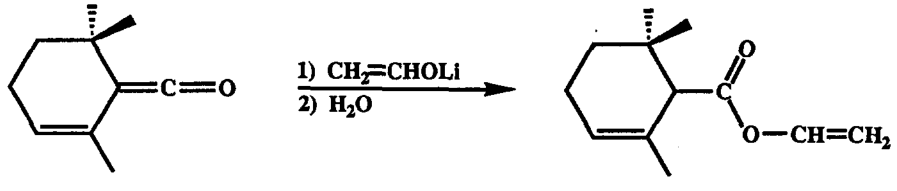
Thus reaction of the vinyl ketene 3[1e] with the lithium enolate of acetaldehyde (generated from THF and *n*-BuLi at 25°C), followed by hydrolysis, gave the vinyl ester 4. The reaction of other ketenes with lithium enolates followed by hydration gave the vinyl esters 5, as reported in Table I. Some C-acylation product was observed in the reaction of PhCMe=C=O with the enolate of acetophenone and for PhC(*i*-Pr)=C=O only C-acylation product 6 was observed.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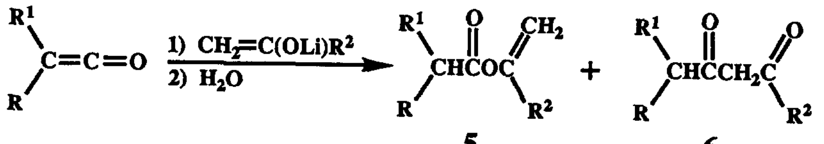
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$R = Ph$; $R^1 = Me, Et$; $R^3 = H, Me, Ph, t\text{-}Bu$

Table I. Acylation of Enolates by Ketenes

Ketene	RLi[a]	Product	Yield[b]
PhCMe=C=O	CH_2=CHOLi	$PhCHMeCO_2CH{=}CH_2$	40
"	CH_2=C(OLi)Me	$PhCHMeCO_2CMe{=}CH_2$	50
"	CH_2=C(OLi)-*t*-Bu	$PhCHMeCO_2C$(*t*-Bu)=CH_2	87
"	CH_2=C(OLi)Ph	$PhCHMeCO_2CPh{=}CH_2$	60[c]
PhCEt=C=O	CH_2=CHOLi	$PhCHEtCO_2CH{=}CH_2$	47
"	CH_2=C(OLi)Me	$PhCHEtCO_2CMe{=}CH_2$	40
"	CH_2=C(OLi)-*t*-Bu	$PhCHEtCO_2C$(*t*-Bu)=CH_2	59
"	CH_2=C(OLi)Ph	$PhCHEtCO_2CPh{=}CH_2$	60
PhC(*i*-Pr)=C=O	CH_2=C(OLi)Me	PhCH(*i*-Pr)$COCH_2COCH_3$[d]	54
	CH_2=C(OLi)Ph	PhCH(*i*-Pr)$COCH_2COPh$[d]	48

[a] Acetaldehyde enolate was generated from the reaction of THF with *n*-BuLi at 25°C; the other enolates were prepared by reaction of the ketones with *i*-Pr_2NLi in THF at -78°C, or with KH in THF at 25°C. The ketenes in THF at -78°C were then added dropwise to the enolate solutions at -78°C.

[b] Determined by VPC or product isolation; products were identified by ^1H and ^{13}C-NMR, IR, and accurate mass spectra.

[c] $PhCHMeCOCH_2COPh$(10%) also isolated

[d] The 1,3-diketones exist predominantly as enols.

Reaction of the potassium enolates $CH_2{=}C(OK)R^2$ (R^2 = Me, Ph, *t*-Bu), generated from the ketones by KH in THF, with $PhCR^1{=}C{=}O$ (R^1 = Me, Et) gave only the C-acylation products **6**, in 63-78% yields. Thus for these ketenes the choice of lithium or potassium cations permits formation of either the O-acylation product **5**, or the C-acylation product **6**, respectively.

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