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LITHIUM THIOALKYNOLATES AND ITS REACTION WITH CARBONYL COMPOUNDS

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The reaction of ketones with lithium thioalkynolates readily obtainable from corresponding acetylides and sulfur, followed by thermolysis gives trisubstituted olefins.

Procedures that involve the formation and subsequent reaction of enolate anions constitute a very important and synthetically useful class of organic reactions. However, the ynolates have hitherto remained unknown until the interesting reports by Schöllkopf[1,2] (Eq. 1). These reagents react with carbonyl

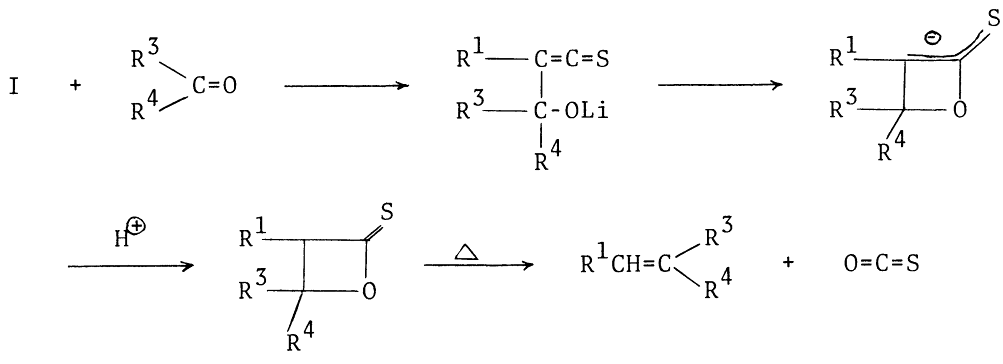
$$R'\text{-}C{\equiv}C\text{-}X^{\ominus} \longrightarrow R'\overset{\ominus}{C}{=}C{=}X \qquad X=O,\ NPh \tag{1}$$

compounds under mild conditions and provide a novel method for the synthesis of highly substituted β-lactones.

We wish to report here on the reaction of thioynolates (X=S) with carbonyl compounds. This procedure seems to be useful for the synthesis of alkenes from acetylenes and ketones. Lithium thioalkynolates (I) are readily prepared from sulfur and lithium acetylides (Eq. 2). They react at the sulfur atom on treatment with electrophiles such as alkyl halides[3] and aroyl halides[4] (Eq. 3). However,

$$R^1C{\equiv}CH \xrightarrow{n\text{-}BuLi} R^1C{\equiv}CLi \xrightarrow{S_8} \underset{\text{I}}{R^1C{\equiv}C\text{-}S\text{-}Li} \tag{2}$$

$$\text{I} + R^2X \longrightarrow R^1C{\equiv}C\text{-}S\text{-}R^2 \tag{3}$$



(4)

when we attempted to react I with ketones, it was found that the reaction proceeds smoothly and affords the trisubstituted alkenes after protonation and dethiocarbonylation (Eq. 4).

The following procedure for the preparation of benzylidenecyclohexane is representative. A dry 25-ml flask equipped with a rubber septum inlet, a magnetic stirring bar and a reflux condenser was flushed with nitrogen. In the flask was placed 0.22 ml (2.0 mmol) of phenylacetylene and 1.5 ml of anhydrous ether. Then 2.0 ml of 1.0 M solution in ether (2.0 mmol) of butyllithium was added at 0°C, and the reaction mixture was stirred for 30 min. To the solution was added 0.077 g (2.4 mmol) of sulfur. The reaction mixture was stirred at 0°C for 2 h to form lithium pheylethynolate. Then, 0.173 ml (1.67 mmol) of cyclohexanone was added at -30°C, followed by stirring 2 h at the same temperature. Finally, the reaction mixture was treated with 3 ml of 1 M HCl in methanol. The reaction products were extracted by benzene. The benzene extracts were washed by saturated sodium chloride solution, dried over anhydrous sodium sulfate and evaporated. The residure was heated at 120°C for 1 h. Analysis by glpc indicated that 1.42 mmol (85%) of the expected olefin had formed. Representative results are summarized in Table 1.

Table 1. The Reaction of Lithium Thioalkynolates with Ketones[a)]

Acetylene	Carbonyl compound		Yield (%) (E:Z)
R^1	R^3	R^4	
Ph	CH_3	CH_3	35
	—$(CH_2)_5$—		85
	CH_3	C_4H_9	53 (57:43)
	CH_3	iso-C_3H_7	22 (77:23)
	H	Ph	0
	H	C_5H_{11}	0
C_6H_{13}	—$(CH_2)_5$—		40
	CH_3	C_4H_9	79 (60:40)

a) $R^1C{\equiv}CH$/Ketone=1.2, at -30°C.
b) Based on ketone used.

This new reaction is applicable to representative acetylenes and ketones such as aliphatic and alicyclic ketones. However, aldehydes are inert to these reagents.

References and Notes

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