

PREPARATION OF VINYL KETONES FROM CARBOXYLIC ACIDS AND VINYL LITHIUM

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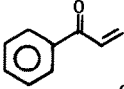
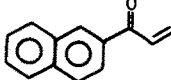
Vinyl ketones continue to be widely used intermediates in organic synthesis due to their ability to function as excellent Michael acceptors. Many approaches have been taken to the synthesis of vinyl ketones,¹ but all suffer either from poor yields or from the requirement of not-so-readily available starting material. Although the reaction of organolithium reagents with carboxylic acids constitutes a simple method for the synthesis of ketones,² reports of the reaction of carboxylic acids with vinyl lithium to prepare vinyl ketones are not found.

Initial studies carried out with vinyl lithium and stearic acid using tetrahydrofuran or diethyl ether as solvent resulted in little reaction in either solvent in 24 hours. The use of 1,2-dimethoxyethane (DME or glyme) as solvent, however, enabled us to obtain easily the desired reaction. For example, vinyl lithium³ (1 mole) was slowly added to a suspension of stearic acid (0.5 mole) in dry DME at 5-10°. The reaction mixture was warmed to 38° and allowed to stir for 18 hours. The reaction was then quenched by siphoning into a well-stirred ice-cold aqueous hydrochloric acid solution. Subsequent workup gave in 70% yield as a white, crystalline (waxy) solid 1-icosen-3-one, m.p. 37.5-40° (lit.^{1a} m.p. 41°).

This reaction appears to be quite general. Both aliphatic and aromatic acids react with vinyl lithium, usually in good yield, as is shown in the table. Where applicable, the reaction of vinyl lithium using DME as solvent is probably the simplest and most straightforward route available to vinyl ketones since it is a one-step reaction using vinyl lithium, which is commercially available, and carboxylic acids, which are generally readily available either commercially or synthetically.

Table

The Preparation of Vinyl Ketones from Vinylolithium and Carboxylic Acids in 1,2-Dimethoxyethane^a

Carboxylic Acid	Vinyl Ketone	Yield (%)
Stearic Acid	$\text{CH}_3(\text{CH}_2)_{16}\overset{\text{O}}{\parallel}\text{CCH}=\text{CH}_2$	70
Propionic Acid	$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}=\text{CH}_2$	92 ^{b,d}
Benzoic Acid		86 ^{b,e}
2-Naphthoic Acid		50 ^{c,e}

^aReaction conditions were all as described in the text for stearic acid.

^bIsolated yield of 2,4-dinitrophenylhydrozone derivative.

^cIsolated yield of 1-phenyl-3-(2-naphthyl)-2-pyrazoline.

^dIdentified by nmr, ir, and by comparison of the 2,4-DNP derivative with authentic material.

^eIdentified by nmr, ir, and by comparison of the 1-phenyl-2-pyrazoline with authentic material.

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- 2 M. J. Jorgenson, *Org. Reactions*, **18**, 1 (1970).
- 3 Vinylolithium, 2M in tetrahydrofuran, was obtained from Alfa Inorganics or Research Organic/Inorganic Chemical Corp.