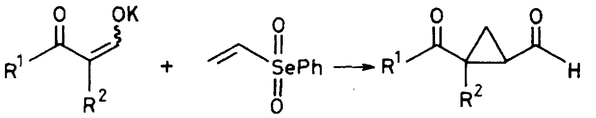
Reactions of Active Methyne Compounds with Vinyl Selenones. One-step Synthesis of 2-Acylcyclopropanecarbaldehydes

Ryoichi Ando, Tomoo Sugawara, and Isao Kuwajima*

Department of Chemistry, Tokyo Institute of Technology, Meguroku, Tokyo 152, Japan

The reactions of anionic species of 2-substituted 1,3-dicarbonyl compounds with vinyl selenones afford the corresponding 1,2-diacylcyclopropanes in good yields through conjugate and 1,2-addition reactions followed by rearrangement and substitution processes.

Although a variety of procedures have been developed for the preparation of 1,2-diacylcyclopropanes,[1] the preparation of 2-acylcyclopropanecarbaldehydes is difficult because of the high reactivity of the aldehyde function, and so they have only been prepared as their acetals.[1b] We recently reported that vinyl selenoxides[2] and vinyl selenones (**1**)[3] behave as unique reagents in their reactions with nucleophiles. The seleninyl or selenonyl groups of these substrates usually activate the C=C bonds for conjugate addition of anionic species and further act as excellent leaving groups in substitution reactions, which have allowed the production of the corresponding cyclopropyl ketones from the reaction with enolate anions. We now report reactions of vinyl selenones with active methyne compounds, which involve a rearrangement reaction of an acyl group to afford the corresponding 1,2-diacylcyclopropanes. Treatment of the potassium salt† of the ketone or ester (**2**) with a vinyl selenone in tetrahydrofuran (3 h to overnight at room temperature) followed by purification with column chromatography afforded the cyclopropyl ketone or ester (**3**) as a mixture of *trans*- and *cis*-isomers (*ca.* 4 : 1) in good yield as shown in equation (1).



(**2**) (**1**) (**3**) (1)

R^1	R^2	Yield of (3) (%)
Et	Me	64
$-[CH_2]_4-$		66
$-[CH_2]_6-$		73
$-[CH_2]_{10}-$		53
EtO	Me	59
$-OCH_2CH_2-$		55

The reaction may possibly proceed through an initial conjugate addition of an enolate to the vinyl selenone. In contrast to facile cyclopropanation of the adduct produced from active methylene compounds through proton transfer,[3b] the resulting anionic species (**4**) appears to add to the formyl group to yield the corresponding four-membered aldol type adduct (**5**), which then undergoes a retro-aldol type bond cleavage to give another anionic species (**6**). At this stage, the selenonyl group seems to act as a leaving group in the substitution reaction to yield the 2-acylcyclopropanecarbaldehydes (**3**) as shown in Scheme 1.

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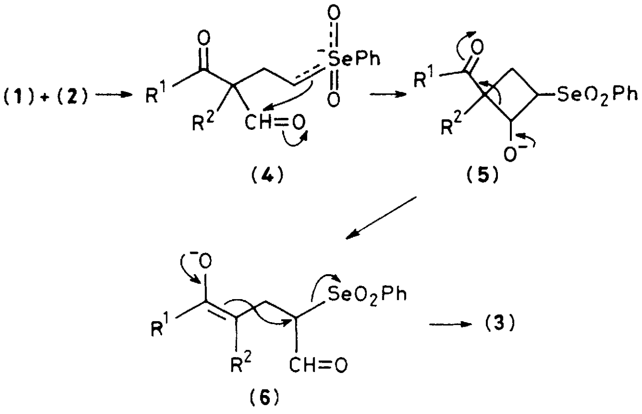
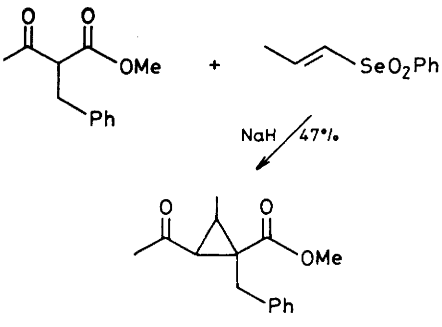
† Sodium salts usually gave less satisfactory results.



Scheme 1

The difference in reactivities between two types of carbonyl functions has allowed the preparation of (**3**) regioselectively. For example, the formyl group rearranges selectively to yield (**3**) owing to preferable attack of the anionic part of (**4**) on an aldehyde rather than a ketone function. Similarly, on treating an anionic species of a β-keto ester derivative with a vinyl selenone, rearrangement of the ketone function was preferable to that of the ester group giving the corresponding 2-acylcyclopropanecarboxylic ester (**7**) selectively, equation (2).

Thus, the easy accessibility of starting materials as well as simplicity of the procedure makes this method attractive for the preparation of such synthetically useful materials as (**3**).



(**7**)

(2)

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