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REACTION OF A CHLOROVINYLCARBENE WITH KETENEALKYL SILYL ACETALS. SYNTHESIS OF NEW α- AND β-ALLENIC CARBOXYLATES.

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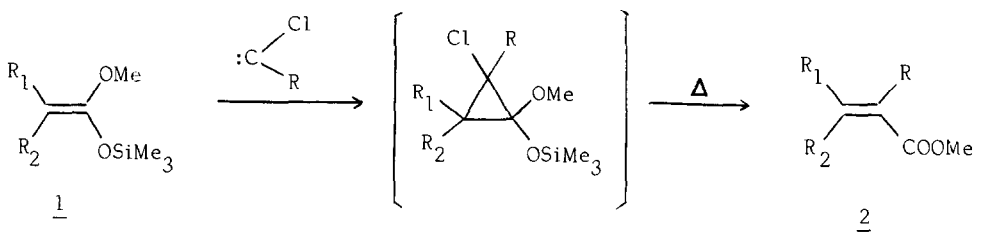
Abstract. The reaction of ketenealkylsilylacetals with 1,1-dimethyl-2,2,3-trichlorocyclopropane in the presence of methyllithium leads to cyclopropane compounds, which, when treated with tetrabutylammonium fluoride give α- or β-allenic carboxylates.

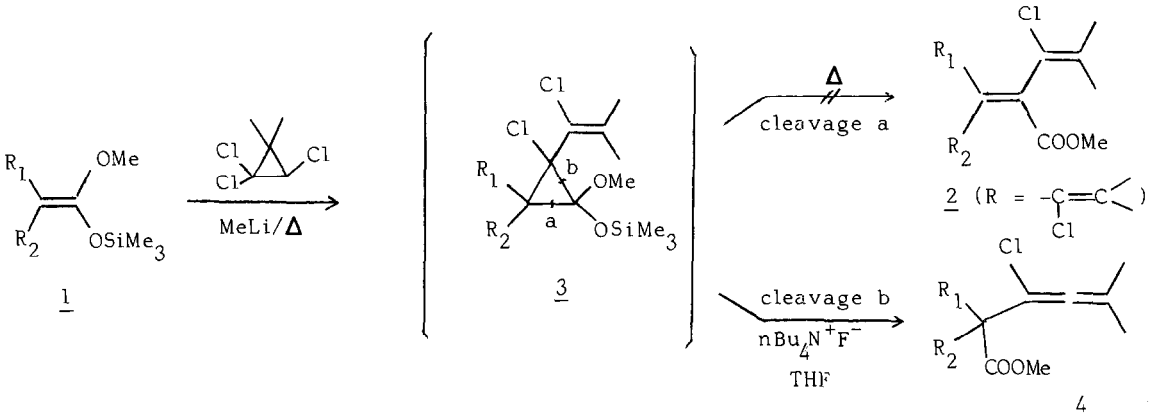
During our study on the reactivity of ketenealkylsilylacetals 1, we reported their [2+1] cycloaddition with chlorocarbenes [1], which after rearrangement of the cyclopropane intermediate provides a new synthesis of α,β-ethylenic α-substituted esters 2.



It was interesting to check the possibility to obtain by this pathway 1,4-butadiene-2-carboxylates (2, R = $CH=CH_2$). After some unsuccessful attempts to add chlorovinylcarbene to keteneacetals, we selected 1,2-dichloro-3-methyl but-2-ene-1-ylidene (chloro 1-chloro-2,2-dimethylvinyl carbene), which can be easily formed by thermal ring opening of 1,2-dichloro-3,3-dimethylcyclopropene, itself generated by reaction of 1,1-dimethyl-2,2,3-trichlorocyclopropane with methyllithium [2].

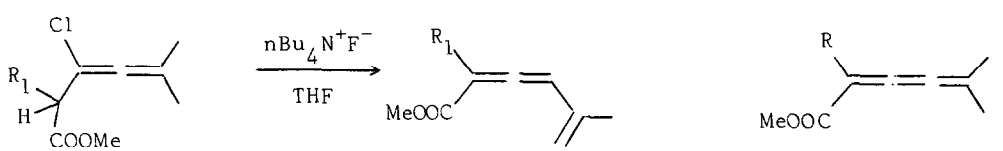
In the presence of ketenealkylsilylacetals 1, this chlorovinylcarbene led in good yield to unstable cyclopropane derivatives, whose NMR and IR spectra were consistent with the postulated structures 3. By heating in a methanol-triethylamine mixture, they did not lead to the expected 1,3-butadiene-2-carboxylates 2 (cleavage a), but to a complex mixture of products. However in the case of disubstituted keteneacetals 1, treatment of the cyclopropane intermediate 3 with tetrabutylammonium fluoride in THF promoted a clean rearrangement into unknown allenic esters 4 (cleavage b), the structure of which was derived from spectroscopic properties and elemental analysis (IR =

allene at 1960 cm^{-1}, ester at 1740-1750 cm^{-1} ; NMR : allenic methyl protons, singlet (6H) at δ 1.85 ppm, ester methoxy protons, singlet (3H) at δ 3.75 ppm ; MS, two molecular peaks in the 1.3 ratio indicative of the presence of a chlorine atom in the molecule). Several examples are reported in the table (entries 1-3). The formation of esters 4 was an unexpected reaction since the a cleavage of intermediate chlorocyclopropanone acetals was usually observed [1]. This b cleavage was probably favoured by the presence of the double bond, and the subsequent allene formation due to an elimination of the vinylic chloride [4].



1 3 4

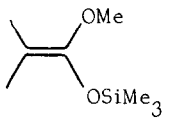
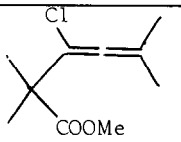
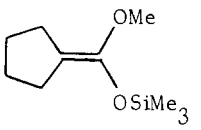
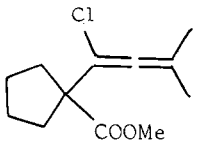
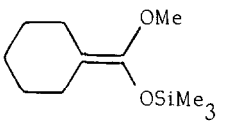
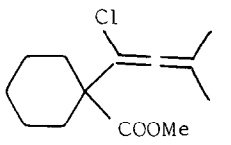
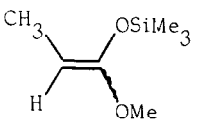
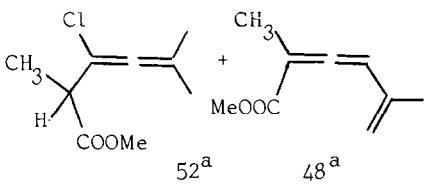
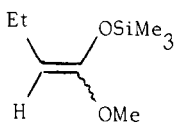
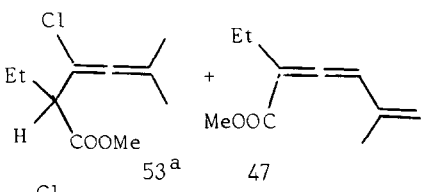
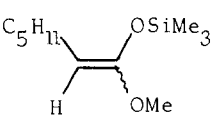
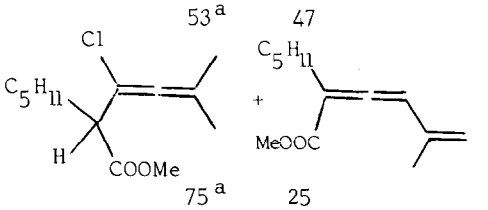
In the case of monosubstituted keteneacetals 1 we also observed the formation of other conjugated allenic carboxylates 5 (entries 4-6) whose structure was derived from their spectroscopic data (IR : allene at 1950 cm^{-1}, ester at 1725 cm^{-1}, olefin at 1630 cm^{-1} ; NMR methyl protons on a carbon-carbon double bond, multiplet (3H) at δ 1.8 ppm, methoxy protons (3H), 3.75 ppm, exomethylenic protons (2H) - 4.90 ppm and allenic proton (1H) - 6.15 ppm). We can explain the formation of these compounds by a subsequent reaction of tetrabutylammonium fluoride with the primarily formed chloro allenes 4. Indeed, in the presence of an excess of tetrabutylammonium fluoride we observed the total transformation of chloroallenic esters 4 into the also unknown allenic esters 5 (50-60% yield). The intermediate formation of trienic esters 6 formed also by a β elimination of a vinylic chloride can be postulated since it had been established that butatrienes are isomerized in basic conditions into enallenes [3].



4 5 6

α- and β-allenic carboxylates, prepared by various methods [5,6], are often used as intermediates in organic synthesis ; for instance they are precursors of 2E, 4Z or 2E, 4E dienoic esters which are pheromones or food aromas [7]. Our method opens a new route to substituted α- and β-allenic esters. Some synthetic applications of these compounds are being examined.

Table : Preparation of α- and β-allenic esters.

Entries	Ketene acetals 1	Allenic esters 4, 5,	Yields [b]
1			55%
2			50%
3			50%
4		 52[a] 48[a]	55%
5		 53[a] 47	57%
6		 75[a] 25	60%

a) Ratio determined by V.P.C. With 2 equivalents of nBu_4NF only esters 5 were isolated (50-60%).

b) Yields from 1, calculated after purification by liquid chromatography.

Preparation of chloroacetals of cyclopropanones

Under argon a solution of methyllithium in ether (7.5 mmol) was added dropwise to a stirred mixture of the ketenealkylsilylacetal (2.5 mmol) and 1,1-dimethyl-2,3,3-trichlorocyclopropane (2.5 mmol) at room temperature. After 4 h at r.t., the mixture was diluted with 5 ml of ether and 5 ml of water. The aqueous phase was extracted with ether (2 x 5 ml) and the organic layer washed with water (pH = 7). Then the organic phase was dried over sodium sulfate. The solvent was removed under vacuum and the crude reaction mixture used directly for the rearrangement.

Preparation of allenic esters

To the crude acetal of cyclopropanone dissolved in dried tetrahydrofuran (5 ml), a solution of tetrabutylammonium fluoride was added (2.5 mmol ; 2.5 ml sol. 1M/l). The mixture was stirred under nitrogen for 6 h at room temperature (entries 1, 4-6), or 22 h at reflux (entries 2, 3). The solvent was removed under vacuum, then ether and water were added (5 ml). The aqueous phase was extracted with ether (2 x 5 ml) and the organic layer washed with water (pH = 7). The organic phase was dried (Na_2SO_4), filtered and concentrated under vacuum. The products were isolated by column chromatography of the residue on SiO_2 (hexane-ether (98/2) (see the table).

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