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AN IMPROVED SYNTHESIS OF SUBSTITUTED CYCLOPROPANONE ACETALS AND HEMIACETALS

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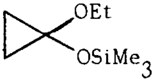
Abstract. Cyclopropanation of ketene alkylsilylacetals or ketene disilylacetals with diethylzinc-methylene iodide leads to cyclopropanone acetals in high yield, and after methanolysis to cyclopropanone hemiacetals or hydrates.

Cyclopropanone acetals and hemiacetals appeared in recent years as new and interesting synthons in organic synthesis. For example cyclopropanone ethyl-trimethylsilylacetal 1 reacts with aldehydes in the presence of titanium (IV) chloride to give γ-butyrolactones[1].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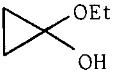
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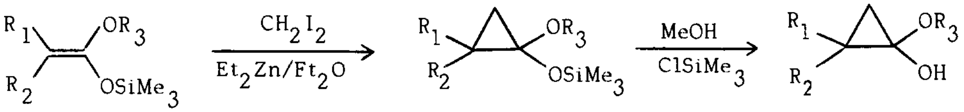
In another connection the transformation of hemiacetal 2 into the parent β-lactam had been reported [2], while its reaction with Grignard reagents led to 1-substituted cyclopropanols [3]. In the particular case of vinylmagnesium halides, 1-vinylcyclopropanols were obtained, which could be rearranged either into cyclobutanones [4] or, after O-silylation of the alcohols, into 1-trimethylsiloxycyclopentenes [5, 6].

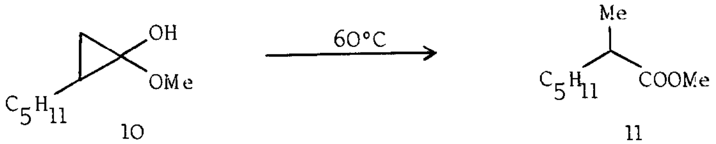
As far as we know, no synthetic applications of substituted cyclopropanone acetals or hemiacetals have been yet reported. This is probably due to the difficult access to these compounds. As a matter of fact, if the parent compounds 1 and 2 can be now easily prepared [7], the substituted acetals and hemiacetals are obtained only by tedious procedures, such as the low temperature reaction of ketene with diazoalkanes [8] or the photolysis of 1,3-cyclobutanediones[9].

Our interest in the chemistry of these compounds led us to investigate a more convenient preparation. We chose to attempt the cyclopropanation of alkylsilylketene acetals, readily available from esters[10]. Until now, few examples of cyclopropanation of ketene acetals have been reported [11] : the reaction of diazomethane with ketene diethylacetal giving cyclopropanone diethylacetal with a low yield [11a] ; the Simmons-Smith reaction applied to substituted ketene dialkylacetals giving moderate yields of cyclopropanation products (10-60%) [11b-11e].

In preliminary experiments we observed that, in the reaction of diazomethane with ketene alkylsilylacetals in the presence of cuprous salts, esters formed by ring opening of the intermediate cyclopropanone acetals were obtained. However we found that by cyclopropanation with 1.5 equivalent ot the reagent diethylzinc-methylene iodide [12] in ether the cyclopropanone acetals could be isolated. A smooth and fast reaction was observed. The yields were generally high, even from the less reactive and more sensitive ketene disilylacetals 8, 9 (see table I). The cyclopropanone acetals were isolated by distillation after a non-aqueous work-up (vide infra) [13]. We observed also that the methylmethylenation (with ethylidene iodide-diethylzinc [14] and the phenylmethylenation (with benzylidene iodide-diethylzinc [15]) can be carried out similarly (see table I). The cyclopropanone alkylsilylacetals were converted quantitatively into cyclopropanone hemiacetals [13] by methanolysis in the presence of a catalytic amount of $ClSi(CH_3)_3$ [17]. From cyclopropanone disilylacetals the cyclopropanone hydrates were also easily obtained ; to our knowledge, only the parent cyclopropanone hydrate has been reported yet [16].



In contrast to the parent compound 2, the substituted cyclopropanone hemiacetals and hydrates are thermally unstable, and they should be used as rapidly as possible for subsequent reactions. For example, attempted distillation of hemiacetal 10 at 60°C led quantitatively to the ring opening product methyl methyl-1 heptanoate 11. However the hemiacetals were stable enough to allow further reactions. So, the hemi-acetal 12 reacted with an excess of vinylmagnesium bromide in tetrahydrofuran to give the vinylcyclopropanol 13 (Y : 50%), which by subsequent O-silylation and flash-thermolysis at 600°C led regiospecifically to 4-phenyl 1-trimethylsiloxycyclopentene 14 [13] (Y : 80%).



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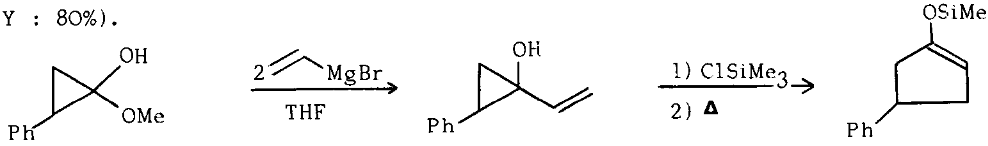

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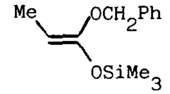
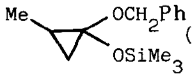
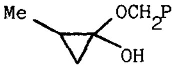
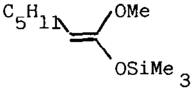
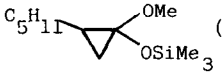
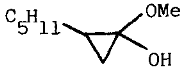
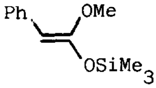
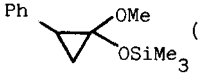
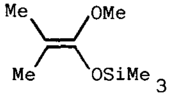
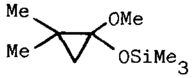
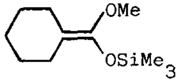
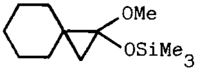
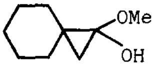
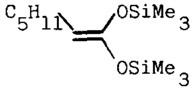
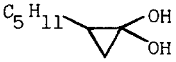
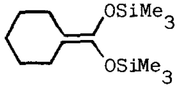
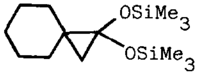
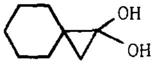
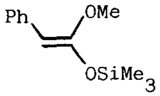
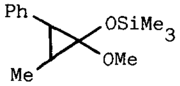
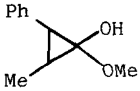
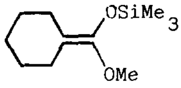
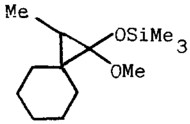
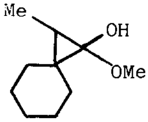
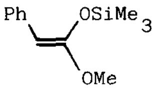
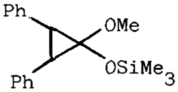
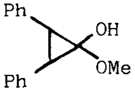
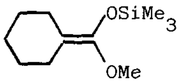
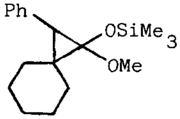
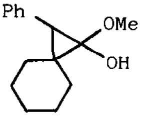
General procedure for the preparation of substituted cyclopropanone acetals

To a stirred mixture of 10^{-2} mole of keteneacetal [10], 7.5 ml of a 2M ethereal solution of diethylzinc (1.5 10^{-2} mole) and 15 ml of ether was added, under nitrogen within 1 hour at room temperature 1.5 10^{-2} mole of alkylidene iodide. The solution was stirred two hours and then diluted with 25 ml of pentane. After cooling to 0°C, an excess of ammonia was bubbled through the solution for 10 minutes to preci-

Table I : Cyclopropanation of ketene acetals

Ketene acetals		Cyclopropanone acetals (a)	Yield (b)	b.p. (°C/torr)	Cyclopropanone hemiacetals (or hydrates) (c)
a) Reaction with CH_2I_2					
	3	 (d)	90%	80-82°/10^{-1}	 (d)
	4	 (d)	76%	43°/0.3	 (d)
	5	 (d)	85%	60-70°/0.2	 (d)
	6		70%	52°/12	
	7		80%	50°/0.5	
	8		80%	90°/0.06	
	9		80%	65°/0.05	
b) reaction with CH_3CHI_2					
	5	 (d)	86%	86°/0.05	 (d)
	7	 (d)	91%	65-66°/0.1	 (d)
c) reaction with $C_6H_5CHI_2$					
	5	 (d)	68%	135°/0.05	 (d)
	7	 (d)	64%	140°/0.2	 (d)

a) 1.5 equiv. of the reagent $Et_2Zn/RCHI_2$ was used for all the reactions, except with 8 and 9 for which two equiv. were necessary ; b) yield of distilled products ; c) the yield of the crude product was quantitative ; d) diastereoisomeric mixture.

pitate completely the zinc salts. The mixture was filtered over Celite and the precipitate washed with pentane. The filtrate was concentrated and distilled under reduced pressure.

General procedure for the preparation of substituted cyclopropanone hemiacetals and hydrates

10^{-2} mole of cyclopropanone acetal was dissolved in 20 ml of methanol, and 5 µl of chlorotrimethylsilane [17] were added. After 3 hours at room temperature, the solvent was removed under vacuum. The residue is the crude hemiacetal (or hydrate) so isolated with quantitative yield.

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