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PREPARATION OF CYCLOPROPYLMETHYL KETONES FROM 3-BUTENYLSILANE AND ACID CHLORIDE[1]

Hideki Sakurai, Takafumi Imai, and Akira Hosomi
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

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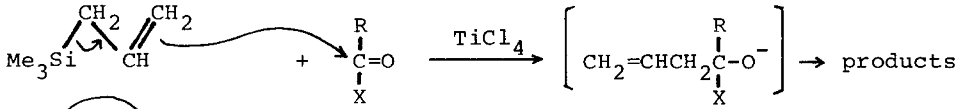
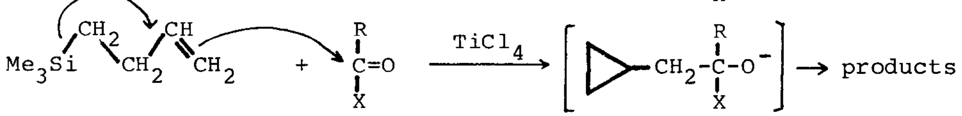
We have recently reported that reductive allylation with allylsilanes is a versatile method of introducing an allyl group into a carbonyl carbon (eq.1).[2] The high reactivity of the double bond of allylsilanes can be rationalized in terms of σ(Si-C)-π conjugation.[3] In an extention of the study, we have found that 3-butenyltrimethylsilane undergoes cyclodesilylation to form a cyclopropane ring in the reaction with acid chloride activated by a Lewis acid (eq.2). It would be interesting to note that the reaction corresponds formally with homo σ(Si-C)-π interaction in butenyltrimethylsilane, the double bond of which has been previously demonstrated to be activated slightly toward an electrophilic species compared to other alkenyltrimethylsilanes except for allytrimethylsilane.[4]



(1)

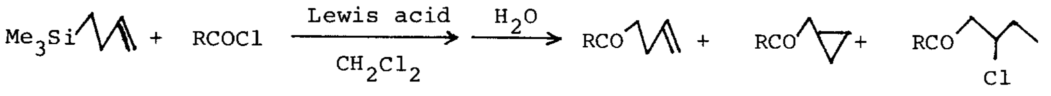


(2)

Cyclodemetalation reactions, formally represented as intramolecular α,ω-eliminations, are an interesting and important class of cyclization reactions for preparing cyclopropanes.[5-12] However, to our knowledge, the synthesis of cyclopropanes utilizing cyclodemetalations accompanied by the formation of a new carbon-carbon bond has not been reported up to date, although syntheses of ketones from organosilicon compounds by the reaction with acid chlorides and Lewis acids have been known generally.[13]

The following procedure is typical. To a mixture of an acid chloride (2 mmol) and titanium tetrachloride (2 mmol) was added slowly a solution of a 3-butenylsilane (2 mmol) in dry dichloromethane at -78°C. The resulting mixture was stirred for 3 hr at -78°C, then hydrolyzed, and extracted with ether. From the ether extracts, a cyclopropylmethyl ketone was isolated by GLC separation, along with a small amount of a 3-butenyl ketone and a β-chloroketone (eq.3).

Titanium tetrachloride was the most effective activator among Lewis acids such as aluminum chloride and stannic chloride. It was further found that boron trifluoride-etherate, zinc chloride and ferric chloride were inactive for the reaction. Similar reactions of 3-butenylsilanes with aldehydes, ketones, acetals and α,β-enones activated by Lewis acid were also attempted, but these compounds hardly effected toward this cyclodesilylation.

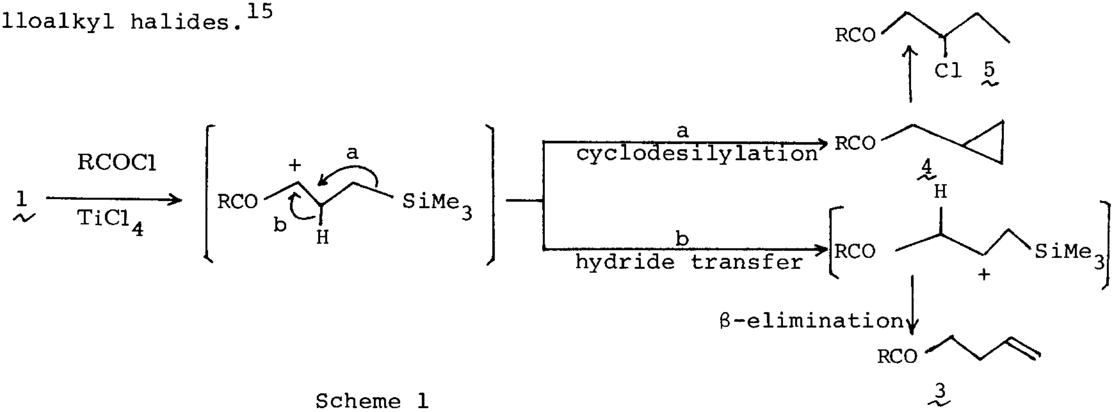


1 2 3 4 5 (3)

As shown in Table 1, a variety of aliphatic, aromatic and olefinic acid chlorides can enter the reaction to afford the corresponding cyclopropylmethyl ketones (4) in fairly good yields. It has been verified by the controlled experiment that β-chloroketones (5), isolated as a by-product in low yield, were derived from 4 by a secondary reaction especially at high temperature. Therefore it is advisable to carry out the reaction at low temperature for the sake of minimizing the secondary reaction.

Several alkyl-substituted 3-butenylsilanes also react with privaloyl chloride in the presence of titanium tetrachloride to afford the corresponding cyclopropyl derivatives, as illustrated in Table 2.

From a mechanistic point of view, the electrophilically induced formation of a cyclopropyl ring has strongly suggested the interaction between a silicon-carbon σ bond and an electron deficient orbital[14] at the γ-carbon which arises from the regiospecific acylation to the olefinic double bond (Scheme 1). Indeed, such a participation, analogous to that proposed above, has been previously supposed as a general phenomenon for the formation of cyclopropanes from γ-metalloalkyl halides.[15]



Scheme 1

The presence of 3-butenyl ketones as a product from the reaction is of interest since it is known that trialkylsilyl group gives significant hydride character to its β-hydrogens.[16] Judging from the fact that 2-methylbut-3-enyl

Table 1. Reaction of 3-butenyltrimethylsilane with acid halides in the presence of titanium tetrachloride in CH_2Cl_2 at -78°C.

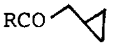
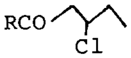
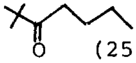
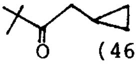
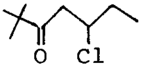
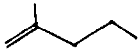
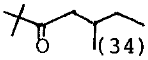
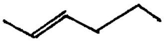
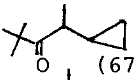
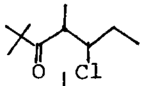
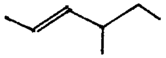
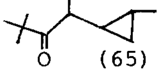
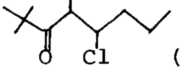
run	RCOCl	Products, % yield$^{a,b)}$		
				
1	$CH_3COCl^{c)}$	8	38	$-^{d)}$
2	i-C_3H_7COCl	28	55	4
3	n-C_4H_9COCl	12	65	6
4	i-C_4H_9COCl	24	54	6
5	t-C_4H_9COCl	25	46	22
6	n-$C_6H_{13}COCl$	18	63	7
7	 $COCl^{e)}$	6	51	6
8	C_6H_5COCl	10	50	14
9	C_2H_5OCOCl	0	0	0

Table 2. Reaction of alkyl substituted 3-butenylsilanes with pivaloyl chloride in the presence of titanium tetrachloride in CH_2Cl_2 at -78°C.

run	3-Butenylsilanes	Products (% Yield)$^{a,b)}$		
1	 $SiMe_3$	 (25)	 (46)	 (22)
2	 $SiMe_3$	 (34)		
3	 $SiMe_3$		 (67)	 (9)
4	 $SiMe_3$		 (65)	 (7)

Captions to Tables (common)
a) Determined by GLC using internal standard. b) Satisfactory spectral and elemental analyses were obtained for all new compounds. c) A similar result was obtained for CH_3COBr. d) Not determined. e) Cyclopropylcarbinyl-β-chloropropyl-ketone was obtained in 10 % yield.

t-butyl ketone was obtained as a sole product from the reaction of 3-methylbut-3-enyltrimethylsilane with pivaloyl chloride (run 2 in Table 2), the mechanism involving hydride transfer from β- to γ-carbon (path b in the Scheme)[17] followed by β-elimination of the type shown in the Scheme is reasonable, while the direct Friedel-Crafts type acylation on the butenyl-silicon σ-bond can not be excluded generally.

Because of easily accessible starting materials and simple manipulation for the conversion, this technique provides a facile means for the straightforward preparation of cyclopropyl derivatives. Related works are now in progress.

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