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RING OPENING AND ENLARGEMENT OF CYCLOPROPYL TRIMETHYLSILYL KETONES BY ACIDS

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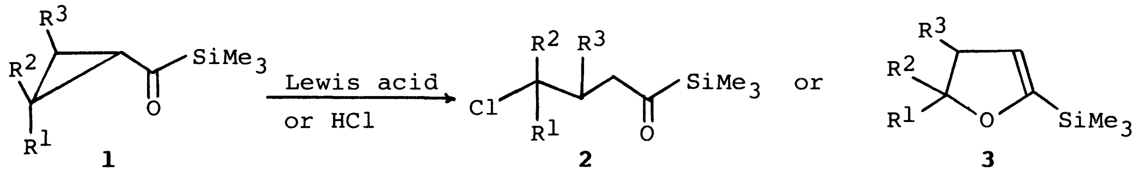
The reaction of a series of cyclopropyl trimethylsilyl ketones with acids proceeds under milder conditions compared to that of their carbon analogs to give either the ring opening products, 3-chloropropyl trimethylsilyl ketones, or the ring enlargement products, 2-trimethylsilyl-4,5-dihydrofuran derivatives.

The spectral data of cyclopropyl trimethylsilyl ketones (**1**) described in the preceding paper[1)] are strongly indicative of an unexpectedly low electron density on the carbonyl carbon, and hence the three-membered ring of **1** is anticipated to be more activated than that of the analogous cyclopropyl alkyl ketones.

We wish to report here that the ring opening reaction of **1** with Lewis acids or hydrogen chloride proceeded at lower temperature compared with that of their carbon analogs to give either 3-chloropropyl trimethylsilyl ketones (**2**) or 2-trimethylsilyl-4,5-dihydrofurans (**3**), depending upon the substituents on the three-membered ring and the acids used. Although the acid-catalyzed ring opening of simple cyclopropyl alkyl (or aryl) ketones has been studied extensively,[2)] little is known about the formation of the dihydrofurans under acidic conditions.[3,4)]



1 **2** **3**

To a solution of **1** (0.5 mmol) in CH_2Cl_2 (2 ml) was added a solution of Lewis acid (0.5 mmol) in CH_2Cl_2 dropwise at -70-0 °C (see conditions in Table 1). After being stirred for 2 – 4 h at the same temperature, the resulting mixture was poured onto crushed ice and extracted with ether. The extract was concentrated and distilled to give either **2** or **3**. Some results are summarized in Table 1.

In the reaction with $TiCl_4$, **1a-e** gave the corresponding ring opening products (**2a-e**), while **1f** provided the ring enlargement product (**3f**). However, it is noteworthy that the reaction of **1e** with $SnCl_4$ or BF_3OEt_2 gave only **3e** in good yield (entries 6 and 7). When HCl was used, the reaction of **1e-f** proceeded at 25 – 40 °C to give the same products as that in the case with $TiCl_4$. The concomitant formation of **2** and **3** could not be observed in any cases. Although it has recently been reported that treatment of cyclopropyl silyl ketone with $TiCl_4$ gave 2-silylcyclobutanone,[5)] such a compound could not be detected in our systems.

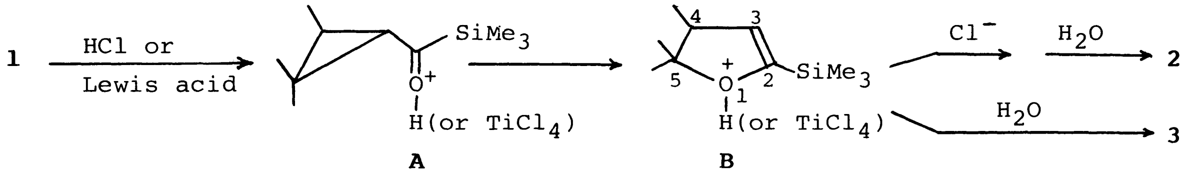
Table 1. Reaction of cyclopropyl silyl ketones (**1a-f**) with acids

Entry	Silyl ketone				Acid	Conditions		Products a)			
	1	(R^1	R^2	R^3)		Temp/°C	Time/h	2	Yield/% b)	3	Yield/% b)
1	**1a**	(H	Me	Me)	$TiCl_4$	-70	2	**2a**	70		
2	**1b**	(Me	H	Me)	$TiCl_4$	-70	2	**2b**	85		
3	**1c**	(H	$-(CH_2)_4-$)		$TiCl_4$	-70	2	**2c**	70		
4	**1d**	(H	H	H)	$TiCl_4$	-10	2	**2d**	41		
5	**1e**	(Me	Me	H)	$TiCl_4$	-70	2	**2e**	81		
6					$SnCl_4$	-10	2			**3e**	74
7					BF_3OEt_2	0	4				71
8					HCl c)	25	4		50		
9	**1f**	(H	Ph	H)	$TiCl_4$	-70	2			**3f**	56
10					HCl c)	25	4				70

a) **2** and **3** gave satisfactory spectral data. b) Based on **1** used, and determined by GLC. c) Reaction was run in THF, and HCl was used as 1 M solution of THF.

For comparison, cyclopropyl methyl ketone was treated with $TiCl_4$ at -10 °C or with HCl at 40 °C. However, the ring cleavage of this ketone did not occur at all under such conditions. Thus, it is evident that the three-membered ring of **1** is strongly activated by the silylcarbonyl group, as expected from the spectral data.

The conversion of **1e-f** into **3e-f** can be interpreted in terms of the intermediary formation of 1-oxacyclopent-2-enyl cation species 6) (**B**) derived from the protonated **1** (**A**) (or similar oxonium complex derived from the Lewis acid-coordinated **1**) as shown in Scheme 1. The attack of a chloride anion to C-5 in **B** induces the further ring cleavage of **B** to provide **2**, while the direct reaction of **B** with water affords **3**. The stability of **B** appears to determine the reaction route from **B** to the final product. The two substituents at C-4 and C-5 in **B** increase the ring strain and promote the ring cleavage. The different behavior of **1e** toward $TiCl_4$ and $SnCl_4$ (entries 5 and 6) has not been rationalized yet.



Scheme 1.

References

1) Preceding paper.
2) a) C. U. Pittman, Jr. and S. P. McManus, J. Am. Chem. Soc., 91, 5915 (1968); b) T. Nakai, E. Wada, and M. Okawara, Tetrahedron Lett., 1975, 1531; c) W. S. Murphy and S. Wattanasin, J. Chem. Soc., Perkin Trans. 1, 1981, 2920; d) W. S. Murphy and K. Hantawong, ibid., 1983, 817, and references cited therein.
3) E. Lee-Ruff and P. Khazanie, Can. J. Chem., 53, 1708 (1975).
4) Dihydrofuran derivatives have been known to be formed by the thermal and photochemical reaction of cyclopropyl alkyl ketones: D. E. McGreer and J. W. Mckinley, Can. J. Chem., 51, 1487 (1973); A. Accary, Y. Infarnet, and J. Huet, Bull. Soc. Chim. Fr., 1973, 2424.
5) R. L. Danheiser and D. M. Fink, Tetrahedron Lett., 26, 2513 (1985).
6) Lee-Ruff et al. 3) proposed a similar intermediate in the acid-catalyzed conversion of spiro[2.5]octane-2-one into 2,3,4,5,6,7-hexahydrobenzofuran, whereas Pittman et al. 2a) showed evidence only for the formation of the tautomeric 1-oxacyclopent-1-enyl cation in the reaction of simple cyclopropyl alkyl (or aryl) ketones with H_2SO_4.

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