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LEWIS ACID CATALYZED RING OPENING REACTION OF CYCLOBUTANE-1,2-DIOLS HAVING 1-ALKOXYALKYL SUBSTITUENTS. SELECTIVE SYNTHESIS OF α,α-DISUBSTITUTED β-HYDROXYCYCLOPENTANONES

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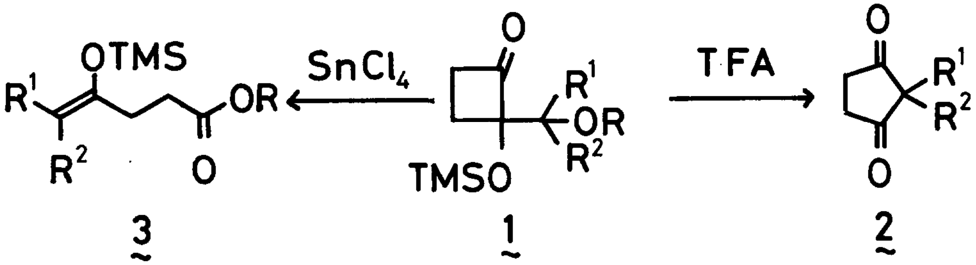
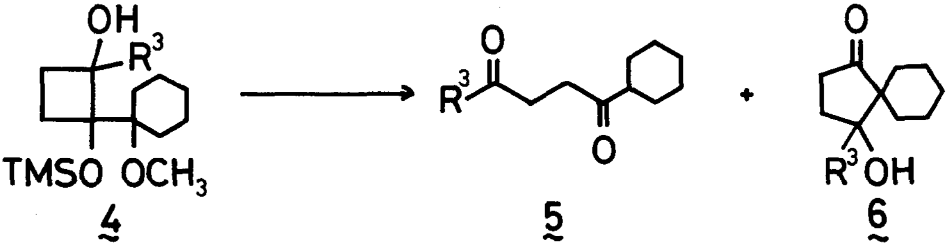
Summary: On treating with stannic chloride, silyl ethers of cyclobutane-1,2-diols having 1-alkoxyalkyl substituents at 1-position undergo a facile ring opening reaction to afford the corresponding β-hydroxycyclopentanones or 1,4-diketones in good yield.

Cyclobutanone derivatives have frequently been employed as versatile synthetic intermediates.[1] For example, such kind of compounds possessing appropriate substituents are shown to undergo a facile ring opening reaction under basic conditions to afford various synthetically useful materials.[2] Recently, we have described a synthetic utility of 1,2-bis(trimethylsiloxy)-1-cyclobutene for the preparation of cyclobutanone derivatives and have shown that 2-trimethylsiloxy-2-(1-alkoxyalkyl)cyclobutanones 1, prepared easily from the reaction of the cyclobutene with acetals, undergo ring cleavage to yield the corresponding rearrangement products 2,[3] 2-substituted cyclopentane-1,3-diones, or ring opening ones 3,[4] silyl enol ethers of γ-keto esters, selectively upon treating with trifluoroacetic acid or stannic chloride, respectively.



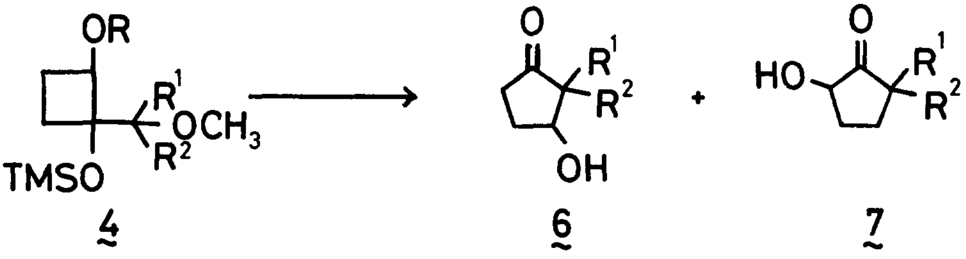
In the present paper, we wish to describe a ring opening reaction of silyl ethers of cyclobutane-1,2-diols 4 having 1-alkoxyalkyl substituents at 1-position and some mechanistic aspects of Lewis acid catalyzed reaction of 1 and 4. Initially, the reaction of 1,2-disubstituted cyclobutane-1,2-diol derivative 4 (R^1,R^2 = $-(CH_2)_5-$, R^3 = CH_3), prepared by Grignard reaction[5] of 1, was examined in the presence of Lewis acid. High selectivity was observed on the cleavage manner of cyclobutane ring, and two types of product, 5 and 6, could be isolated as shown in the following equation.

Similarly, treatment of 4 (R^1,R^2 = $-(CH_2)_5-$, R^3 = H) with stannic chloride[6] or trifluoroacetic acid[3] led to the formation of the corresponding β-hydroxycyclopentanone 6, resulting from selective cleavage of linkage between C-1 and C-2, in good yield. In this case, the product of type 6 was obtained predominantly or exclusively.



R^3 = CH_3			R^3 = H		
5	6		5	6	
41%	22%	(with $SnCl_4$)[7]	0%	81%	(with $SnCl_4$)[9]
30	48	(with $TiCl_4$)[8]	9	74	(with CF_3CO_2H)[10]

In contrast to the selective manner in the above ring opening, bond cleavage between C-1 and C-4 appears to accompany with that between C-1 and C-2 with other types of 4 (R^3 = H), and the corresponding products 7 were usually formed as minor ones along with 6. Interestingly, it was also found that the formation of α-hydroxycyclopentanones 7 could be depressed efficiently by employing the corresponding 1,2-bis(trimethylsiloxy)cyclobutane derivatives and treating them under the same conditions[9] to afford 6 in good yield.

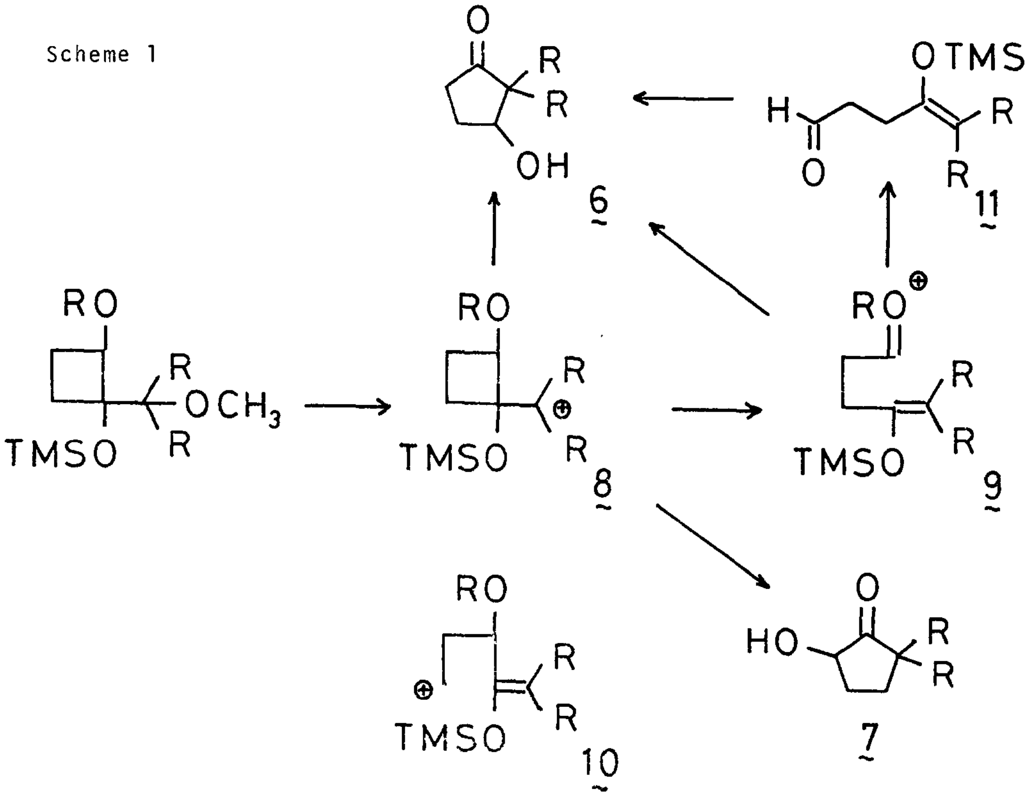


		R = H		R = $SiMe_3$	
R^1	R^2	6	7	6	7
CH_3	C_6H_{13}	56%	22%	79%	4%
$-(CH_2)_4CH(CH_3)-$		68	14	$55^{a)}$	3
$-(CH_2)_7-$		59	13	76	9
$-(CH_2)_{11}-$		63	15	79	6

a) The starting material was recovered as the diol in 20%.

The results can be explained as follows. Carbonium ion 8 is initially formed under the influence of Lewis acid. As the major reaction course, the ring opening reaction of cyclobutane ring may be followed succesively or in concerted manner to yield an another type of carbonium ion 9 or 10. On the stage of this ring cleavage, it should take place preferentially so as to result in the formation of a more stable one 9. The cationic site of the resulting 9 may be trapped by the internally formed silyl enol ether moiety to yield 6. As an another route to 6, cyclization of the intermediate 11 may

Scheme 1



also be conceivable. In this type of reaction, it is reported that ketones usually react much more slowly with silyl enol ethers than aldehydes under the influence of Lewis acid.[11] This is probably a reason why 5 is formed in an appreciable amount only from 4($R^3 = CH_3$). Higher predominance for the formation of 6 with bis-silyl ethers may be attributable to the increased stability of the intermediate 9 due to σ-π effect of silyl group. As an minor process, direct Pinacol rearrangement may be accompanied with the major reaction paths described above. Preference of migratory aptitude can not be expected in this rearrangement and both products of 6 and 7 may be formed. Since the reaction through intermediate 10 is considered to be highly unfavorable, the formation of 7 may be attributable to the process involving Pinacol rearrangement. High selectivity of acyl group rearrangement from 1 reported previously[3] is also explicable by the mechanism shown in Scheme 1.

References and Notes

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5) I. Kuwajima, I. Azegami, and E. Nakamura, Chemistry Lett., 1431 (1978).
6) Titanium tetrachloride gave rather complex results.
7) The reaction was carried out at -30°C for 3 hr in the presence of $SnCl_4$(leq)
8) The reaction was carried out at -78°∿0°C for 5 hr in the presence of $TiCl_4$ (1 eq).
9) The reaction was carried out at 0°C for 15 min in the presence of $SnCl_4$ (1 eq).
10) The reaction was carried out at room temperature for 15 min in CF_3CO_2H.
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