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CHEMO- AND REGIOSELECTIVITIES IN ACID-CATALYZED RING EXPANSION OF 1-[1-METHYLSULFINYL-1-(METHYLTHIO)ALKYL]CYCLOBUTANOL DERIVATIVES

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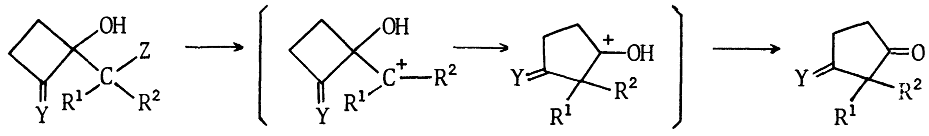
A new ring expansion of the title compounds catalyzed by an acid was studied. The reaction of 2-methyl-1-[1-methylsulfinyl-1-(methylthio)alkyl]cyclobutanol was regio- and chemoselective to afford 3-methyl-2-(methylthio)cyclopentanone derivative.

Cyclopentanone derivatives occur in a variety of natural products including jasmons, pyrethrins, or prostaglandins. Although ring expansion of a 1-hydroxycyclobutyl compound (1) *via* a carbinyl cation (2) is one of the methods for making cyclopentanone derivatives (4), only a few examples have been reported.[2-4)]



[Y = H_2 or O]

1 2 3 4

In this communication, we wish to describe chemo- and regioselectivities in ring expansion of 1-[1-methylsulfinyl-1-(methylthio)alkyl]cyclobutanol derivatives (5 and 11),[5)] which is easily achieved by treatment with a catalytic amount of 25% sulfuric acid. Starting from 5, two types of compounds (6 and 7) are expected as the products as shown in the following scheme.

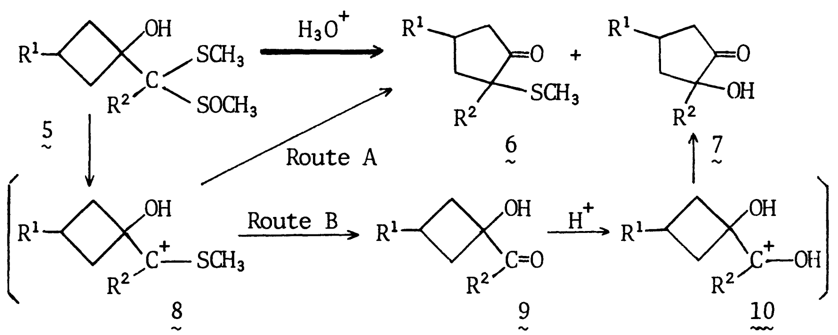


Table 1. Yields of 6 and 7

	R¹	R²	Yield (%)	
			6	7
a	$PhCH_2$	H	42	25
b	$PhCH_2$	*n*-Bu	21	53
c	$PhCH_2O$	*n*-Bu	7	53

If ring expansion in a hypothetical cation (8) is fast,[7)] Route A operates predominantly and a 2-(methylthio)cyclopentanone derivative (6) is produced as a major product. In contrast, a 2-hydroxycyclopentanone derivative (7) is preferably formed when the dithioacetal S-oxide group of 5 is first hydrolyzed (Route B) to afford a 1-acylcyclobutanol (9). A solution of 5 in diethyl ether containing a few drops of 25% sulfuric acid was stirred at room temperature for 13 – 45 h, and then the reaction mixture was neutralized and dried by addition of sodium hydrogencarbonate and anhydrous sodium sulfate. After filtration of the insoluble solid, the filtrate was evaporated and subjected to column chromatography on silica gel to give 6 and 7. The major product was 7 when R^2 was butyl, whereas 6 was predominantly formed when R^2 was hydrogen. These phenomena may be accounted for by stabilization of the intermediary 8 by the butyl group to make the life time of 8 longer, *i.e.*, increase the probability of the intermolecular reaction of 8 with water.

Next, we investigated the effect of introducing a 2-methyl group on the cyclobutane ring of 5. To our surprise, only one kind of product (12) was obtained when 11 was subjected to the reaction under acidic conditions similar to those used before. Formation of other possible products (13, 14, and 15) was not observed. This may suggest that the migrating ability of the carbon can be significantly enhanced by substitution of a methyl group, leading to the chemo- and regioselective formation of 12.

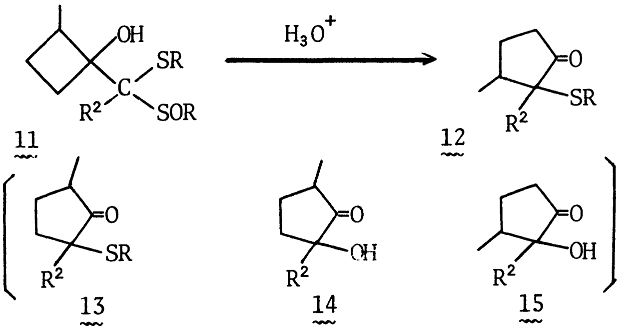


Table 2. Yield of 12

	R	R^2	Yield (%)
a	CH_3	H	76
b	CH_3	CH_3	82
c	CH_3	*n*-C_5H_{11}	77
d	*p*-Tol	H	76
e	*p*-Tol	*n*-C_5H_{11}	66

Finally, it should be noted that the thus-obtained 3-methyl-2-methyl(or *p*-tolyl)thio-2-pentylcyclopentanone (12c or 12e) can be converted into tetrahydrojasmone (16) and dihydrojasmone (17). Reductive desulfurization of 12c and 12e with Raney nickel (W-II) in ethanol gave 16 in 81 and 41% yields, respectively. After oxidation of 12c and 12e with sodium metaperiodate, the resulting sulfoxides were pyrolyzed in refluxing toluene to give 17 in 43 and 47% overall yields, respectively.

References

1) Present Address: Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223.
2) T.-L. Ho, Synthetic Commun., 4, 265 (1974).
3) E. Nakamura and I. Kuwajima, J. Am. Chem. Soc., 99, 961 (1977).
4) T. Cohen, D. Kuhn, and J. R. Falck, J. Am. Chem. Soc., 97, 4749 (1975).
5) The compounds 5 and 11 are easily synthesized by the reaction of cyclobutanone derivatives with the lithio compound derived by action of butyllithium (when R^2 = H) or lithium diethylamide (when R^2 = alkyl) on an aldehyde dithioacetal S-oxide.[6]
6) K. Ogura and G. Tsuchihashi, Tetrahedron Lett., 1972, 2681.
7) This also means that acid-promoted removal of the methylsulfinyl group and ring expansion take place simultaneously, *i.e.*, concertedly.

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