OXIRANE C-C BOND HOMOLYSIS

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Ring opening reactions of oxiranes by ionic or free radical mechanisms occur characteristically via severance of a carbon-oxygen bond ($\underline{2}$). Rarely does one find reference to opening of the ring at the carbon-carbon bond ($\underline{3}$). We wish to report the observance of a new type of oxirane C-C bond cleavage arising from the addition of thiols to vinyl oxiranes under radical conditions.

The generation of a radical on carbon α to an oxirane ring, either by a hydrogen abstraction process or radical addition to vinyl oxiranes has been observed to lead to the formation of allylic alcohols (4). These type of products occur as a consequence of homolytic scission of the C₂-O bond according to Path A in the following scheme:



On the basis of the known stabilities of oxygen and carbon radicals degeneration of I via Path B should be thermodynamically less important than Path A, particularly when the oxirane ring is in a terminal position so that the resulting intermediate III would be a primary radical. Indeed none of the studies to date have noted the product of C_2-C_1 cleavage, i.e., a vinyl ether. However, it seemed reasonable to expect that a redirection of bond homolysis from C_2-0 to the C_2-C_1 bond could be realized by changing substituents on C1.

Methanethiol was reacted with 2,2-dimethyl-3-vinyloxirane (5), 2,3-divinyloxirane (3), and 2-phenyl-3-vinyloxirane (6) in the temperature range of 0-65°. The methylthiyl radical was generated with either a sunlamp or AIBN. Results of this study are summarized below.

$$CH_3SH + \mathcal{A}_0^{R_1}$$

R1	<u>R2</u>	Product ^(a)	NMR, τ			
			CH2S	<u>СН2-СН=</u>	=C <u>H</u> Y	
сн ₃	сн _з	СН ₃ MeSCH ₂ CH=CHC-OH СН ₃	6.96(m)		4.40(m)	
Ph	н	MeSCH CH=CHOCH Pb	7 03(m)	4 49(a)	2 60(d) 2 00(d) (b)	

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		2			5105(2), 5150(2)
^{сн} 2 ^{=сн}	н	MeSCH2CH=CHOCH=CHCH3	7.03(m)	4.40(m)	3.80(m) ^(c)

(a) elemental analysis were in accord with structural assignments.

(b) Y=0, low field signal J trans=17 cps; J cis *7 cps

(c) Y=CH₃, J_{vic}=7 cps, J_{homoallylic}=1.6 cps Y=O, not discernible under Y=CH₃ multiplet

Examination of the reaction products by nmr and ir spectra clearly established that methyl groups on C_1 resulted in ring cleavage exclusively via Path A, i.e., C_2 -O rupture. Infrared absorbances at 2.9 and 8.8µ supported the tertiary alcohol structure. The absence of the vinyl ether product (Path B) was indicated by the appearance of methyl resonances only at 8.05 τ (CH₂S) and 8.72 τ [-C(CH₂)₂-] as singlets, area 1:2, respectively. In marked contrast to this was the influence of phenyl and vinyl functionality on the direction of ring opening. These two subscituents caused exclusive $C_2 - C_1$ scission. This degree of selectivity of bond scission in these two cases was based on absence of hydroxyl functionality (nmr and ir) in the products of the radical reaction. Structural assignments of the two vinyl ether products could be made on the basis of known 1 H nmr chemical shift values. The very intense infrared absorbance of the two products at 6.05μ is characteristic of a vinyl ether group (7).

Homolysis of the C_2 -0 bond appears to occur stereoselectively. The trans nature of the olefin in the allylic alcohol product was indicated by the splitting (J=5.5 cps) of the CH₂S signal at 6.96T and trans olefin absorbance at 10.35µ in the infrared. This level of stereoselectivity was not noted in the two products of C_2 - C_1 cleavage. The vinyl ether arising from phenyl vinyloxirane was approximately a 50/50 cis/trans mixture based on the low field pair of doublets and pair of doublets at 7.03T ($J_{vic H}$ =8 cps). The divinyl ether showed a similar pair of doublets at 7.03T. A pair of quartets at 8.44T (CH₃C=) is indicative of the cis/trans composition of the propenyl segment of the divinyl ether.

Our data is suggestive of a relationship between the type of substituent on C_1 and C-C vs C-O oxirane bond rupture. Tentatively, we attribute this crossover in mechanism to the degree of delocalization afforded to the incipient radical in III by the C_1 functionality.

It is interesting to note that the addition of thiyl radical to 2,3-divinyloxirane yielded exclusively V.



Apparently, abstraction of hydrogen from thiol by IV occurs preferentially on the terminal carbon to give V rather than VI.

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