Tetrahedron Letters No. 3, pp 283 - 286, 1978. Pergamon Press. Printed in Great Britain.

COMPETITIVE PATHWAYS IN THE THERMAL REARRANGEMENT OF CIS-2-ETHYNYL-3-VINYL OXIRANES SUBSTITUTED BY ALKYL GROUPS

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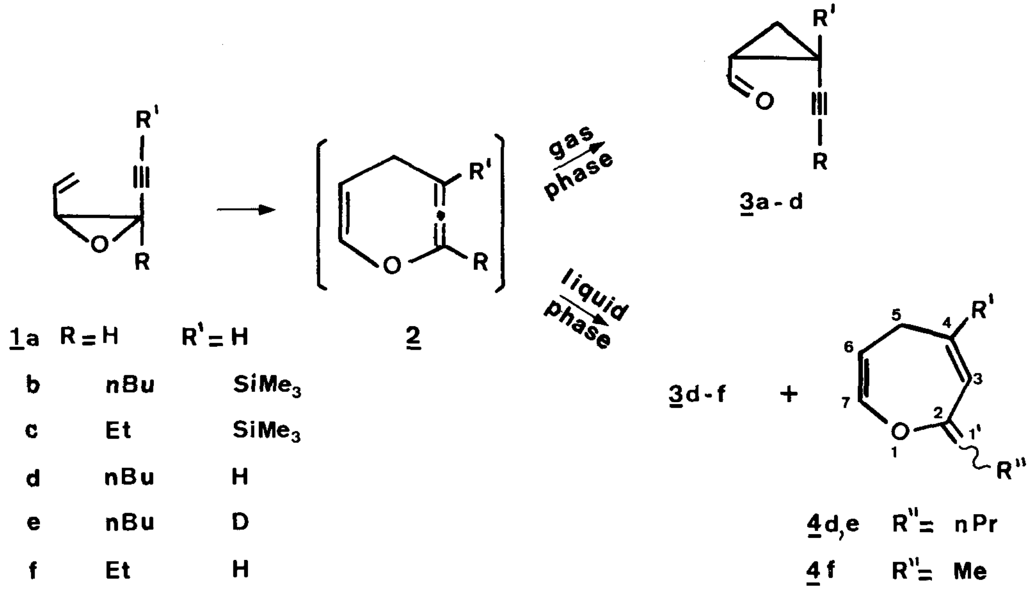
(Received in UK 22 November 1977; accepted for publication 24 November 1977)

The novel valence isomerization of cis-2-ethynyl-3-vinyl oxirane 1a has been recently communicated (1). The reaction conducted, either in liquid or gas phase, gave a single product 3a. A mechanism similar to that postulated for the thermal rearrangement of 1-vinyl-2-ethynyl cyclopropane (2) can be written ; it involves a highly strained seven membered intermediate 2 (scheme 1).



Scheme 1

We report here our investigations on the thermal isomerization of cis-2-ethynyl-3-vinyloxiranes 1b-f substituted at C-2 by an alkyl group. Our new results lend support to the proposed mechanism and bring a new insight into the reactivity of these molecules.

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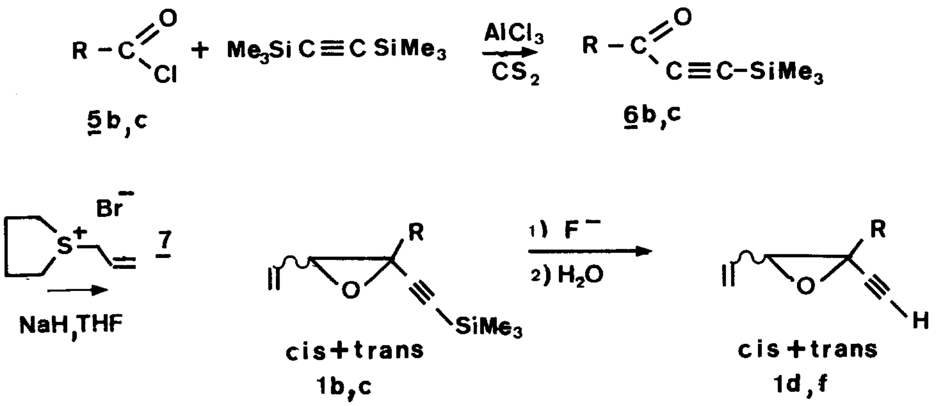
The oxiranes 1b-f were prepared as shown in scheme 2. Acetylenic ketones 6b,c that served as precursors to 1b-f were obtained from electrophilic condensation of acyl chlorides 5b,c with bis-trimethylsilyl acetylene (3). When the mixtures of allyl sulfonium salt 7 (4) and ketone 6b or 6c were treated with sodium hydride in dry tetrahydrofuran at -10°C, we obtained 1b or 1c (yield $\sim$ 40 %) (5) which were purified by distillation and chromatography. A competitive 2,3-sigmatropic rearrangement of 7 to 2-allyl tetrahydrothiophene was observed ; it was the only reaction which took place with allyl sulfonium salt derived from dimethylsulfide (6). To improve the yields of oxiranes, allyl tetramethylene sulfonium bromide was employed in large excess (ketone/salt : 1/3).



Scheme 2

Table I : Product distribution* from thermal rearrangements of cis-oxiranes 1b-f

	T° C and reaction times	R	R'	Unchanged Oxirane %		Formed Products % **			
Gas Phase	320	nBu	$SiMe_3$	1b	72	3b	28		
	330	Et	-	1c	50	3c	50		
	300	nBu	H	1d	24	3d	76		
Sealed tube 0.8 M CCl_4	1h 130°	nBu	$SiMe_3$	1b	unchanged				
	- -	Et	-	1c	-				
	- -	nBu	H	1d	5	3d		4d	95
	18h 87°	nBu	-	1d	47	3d	6	4d	47
	15h 100°	nBu	D	1e	18	3e	4	4e	78
	1h 130°	Et	H	1f	33	3f		4f	67

* Yields determined by nmr analysis.

** at these temperatures, the only detected products are shown in the table. At higher temperatures, trans-1-carboxaldehyde-2-alkynylcyclopropanes appeared (1b).

Oxiranes 1d,f (7) were isolated (90%) from the mild treatment of 1b,c with tetrabutylammonium fluoride in acetonitrile followed by hydrolysis (8,9). Deuterated 1e was prepared by stirring 1d with barium oxide in a large excess of D_2O (10). It was clear from the nmr spectra that the obtained oxiranes were a mixture of cis and trans isomers, but all attempts to separate them failed.

Thermal reactions of 1b,f (cis+trans) were conducted in two ways : (i) in gas phase through a hot pyrex tube (11) ($\sim$ 15 torr ; 300-330°C), (ii) in sealed tubes with inert solvent (CCl_4, 90-130°C). A 3,3-sigmatropic rearrangement being forbidden by the trans relationship between the vinyl and ethynyl groups, trans-isomers 1b-f were recovered unchanged under the above reaction conditions and separated from the rearrangement products by distillation or column chromatography.

Results are shown in table I. In the gas phase, we obtained only the expected cis-1 carboxaldehyde-2-alkynylcyclopropane 3b-d (12). In contrast, only trace amounts of these compounds were detected in solution, beside the main products, 2-alkylidene-2,5-dihydrooxepins 4d,e,f. The structural assignment of these compounds were based on their proton nmr spectra (13) : the chemical shifts and coupling constants (obtained from double irradiation experiments) find close correspondence with those reported for 2,5-dihydrooxepin (14).

Table II: Product distribution* from thermal rearrangement** of 1d as a function of concentration

Concentration	1d %	3d %	4d %
0.8 M	5		95
0.12 M	18	18	64
0.03 M	24	42	34

* Yields determined by nmr analysis ** 130°, 1h, sealed tube, CCl_4.

In order to understand the above results we studied the thermal rearrangement of 1d in the liquid phase at various concentrations. It is clear from the data listed in Table II that two competitive pathways take place and that the isomerization is directly dependent on the concentration of the substrate 1d : when the initial concentration was lowered (i) formation of 4d relative to 3d decreased, (ii) yields of isomerized product were reduced.

These observations give support to the proposed formation(1) of an allenic intermediate 2. From our results on oxiranes substituted at C-2, it seems clear that 3 and 4 respectively are produced by way of competing unimolecular and bimolecular processes. It is very likely that the first step of the reaction (1 $\rightleftarrows$ 2) is reversible.

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5. 1b : ^1H nmr (CCl_4, δ_{Me_4Si}) 0.18 (s, 9H), 0.93 (m, 3H, CH_3), 1.1 - 1.76 (m, 6H, $3CH_2$),

3.07 and 3.43 (2d, 1H, H_3 cis and H_3 trans, J_{cis} = 6.5 Hz J_{trans} = 5 Hz), 5.1-5.8 (m, 3H, -CH = CH_2).

1c : ^{1}H nmr (CCl_4, δ_{Me_4Si}) nearly identical to the spectrum of 1b except for : 0.97 (bt, 3H, CH_3, J = 7Hz), 1.47 (b quad, 2H, CH_2) ; IR (CCl_4, cm^{-1}) 2161, 1630.

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7. 1d : ^{1}H nmr (CCl_4, δ_{Me_4Si}) 0.93 (m, 3H, CH_3), 1.13-1.75 (m, 6H, $3CH_2$), 2.20 and 2.26 (2s, 1H, H-≡trans and H-≡cis), 3.09 and 3.45 (2d, 1H, H_3 cis and H_3 trans, J_{cis} = 6.5 Hz J_{trans} = 5 Hz), 5.15-5.95 (m, 3H, -CH=CH_2) ; IR (CCl_4, cm^{-1}) 3307, 2217, 1636.

1e : ^{1}H nmr (CCl_4, δ_{Me_4Si}) identical to the spectrum of 1d except for the signals at 2.20 and 2.26 which are lacking.

1f : ^{1}H nmr (CCl_4, δ_{Me_4Si}) nearly identical to the spectrum of 1d except for : 1.0 (bt, 3H, CH_3), 1.51 (b quad, 2H, CH_2).

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12. 3b : ^{1}H nmr (CCl_4, δ_{Me_4Si}) 0.09 (s, 9H), 0.93 (m, 3H, CH_3), 1.11-1.7 (m, 7H, $2CH_2$ and 3H cyclop.), 1.93-2.3 (m, 2H, CH_2-C≡), 9.01 (d,1H, $\overset{O}{\text{H-C}}$, J = 6Hz) ; IR (CCl_4, cm^{-1})1698.

3c : ^{1}H nmr (CCl_4,δ_{Me_4Si}) nearly identical to the spectrum of 3b except for : 2.0 (b quad, 2H, CH_2-≡, J = 7Hz).

3d : ^{1}H nmr (CCl_4, δ_{Me_4Si}) 0.9 (m, 3H, CH_3) ; 1.11-1.55 (m, 6H, $2CH_2$ and 2H cyclop.), 1.62-2.23 (m, 4H, CH_2-≡ and ), 9.15 (d, 1H, $\overset{O}{\text{H-C-}}$, J = 6 Hz) ; IR ($CHCl_3$, cm^{-1}) 2760, 1703.

13. 4d : ^{1}H nmr ($CDCl_3$, δ_{Me_4Si}) 0.8-1.03 (m, CH_3), 1.13-1.6 (m, CH_2), 2.17 (quad, CH_2-=exocyc), 4.8 (t, H_1, J = 7.2 Hz), 4.82 (d, t, H_6, $J_{6,7}$ = 7 Hz and $J_{6,5}$ = 5Hz), 5.33-5.73 (m, H_4), 5.9 (d, t, H_3, $J_{1,3}$ = 1.6 Hz and $J_{3,4}$ = 11.5 Hz), 6.29 (d, t, H_7, $J_{6,7}$ = 7Hz and $J_{7,5}$ = 1.7Hz).

4e : ^{1}H nmr ($CDCl_3$, δ_{Me_4Si}) identical to the spectrum of 4d except for m at 5.33-5.73 which is lacking and for d, t 5.9 which appears as a broad t.

4f : ^{1}H nmr ($CDCl_3$, δ_{Me_4Si}) nearly identical to the spectrum of 4d except for : 1.70 (bd, CH_3, J = 7 Hz).

The stereochemistry of the exocyclic double bond has not been established.

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