Tetrahedron Letters,Vol.29,No.34,pp 4281-4284,1988   0040-4039/88 $3.00 + .00
Printed in Great Britain   Pergamon Press plc

RING-OPENING OF OXIRANES BY SILYL-SUBSTITUTED ALLYL ANIONS. A REGIOCHEMICAL CHAMELEON

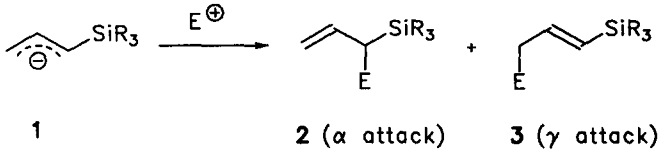
Ernst Schaumann* and Andreas Kirschning

Institut für Organische Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Fed. Rep. Germany

Summary - Lithiated allylsilanes **1** undergo smooth addition to epoxides **4** with variable α,γ regioselectivity yielding the C-silylated enols **5**,**7** and **6**,**8**, respecively. γ-Selectivity can be successfully enhanced by use of cuprates.

Although there has been an explosive growth of organosilicon chemistry over the past fifteen years[1], deficiencies are still encountered in the selective introduction of silicon into complex molecules. An important tool is the addition of electrophiles to deprotonated allylsilanes **1** which, depending on the regioselectivity of the attack, results in the formation of allyl- **2** (α attack) or vinylsilanes **3** (γ attack; cf. Scheme 1).

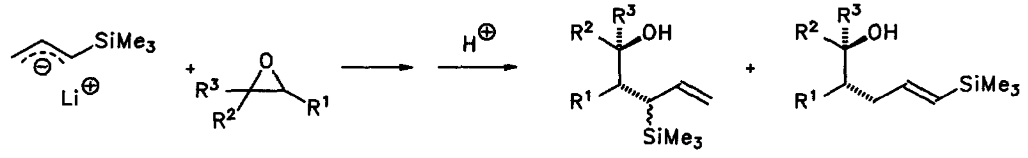
Scheme 1



Considerable work has been carried out in order to control the regiochemistry of this reaction and, in cases where carbonyl derivatives are the electrophiles, the problem has been satisfactorily solved[2]. Also alkyl halides[3,4] and carbon dioxide were intensively employed[4], whereas epoxides have seen only limited use[3c,d]. We here report on the steric effects, of the substituents on the oxirane or on the silicon, and of the counterion on the regioselectivity of the reaction of allylsilane anions **1** with epoxides **4**.

Under our standard conditions (THF, -40°C, 2.5 h), the reaction of lithiated allylsilane **1a**[5] with oxiranes **4** shows a preference for α adducts **5**[6] when ethylene oxide (**4a**) and monosubstituted derivatives **4b,c** are used (Table I, entries 1-3). However, 1,2 disubstituted epoxides **4d-g,i** and the 1,1,2 trisubstituted derivative **4h** predominantly give γ adducts **6**[6] (Table I,

Table I.



1 a 4 5 6

Entry	Oxirane	R^1	R^2	R^3	Ratio		Yield	Olef. ^{1}H-NMR Data				$^3J_{HH}$
					5	6	[%]	5		6		[Hz]
								1H m	2H m	1H dt	1H d	
1	**4a**	H	H	H	>10	<1	67	5.50	4.88[b]	-	-	-
2	**4b**	H	CH_3	H	4.5	1	83	5.55	4.90	6.07	5.79	18.5[c]
3	**4c**	H	C_2H_5	H	2	1	72	5.48	4.76	6.09	5.73	18.5[b]
4	**4d**	CH_3	CH_3 (cis)	H	1	2	97	5.72	4.90	6.06	5.68	18.4[b]
5	**4e**	CH_3	CH_3 (trans)	H	1	2.5	76	5.65	4.85	6.05	5.70	19.0[b]
6	**4f**	$-(CH_2)_3-$		H	1	3	80	5.79	4.92	6.00	5.68	18.6[c]
7	**4g**	$-(CH_2)_4-$		H	1	6	87	5.78	4.93	5.99	5.63	18.6[c]
8	**4h**	$-(CH_2)_4-$		CH_3	<1	>10	71	-	-	6.11	5.75	18.5[b]
9	**4i**[a]	$-(CH_2)_3-CH(CH_3)-$		H	1	10	81	5.66	5.06	6.05 6.00	5.67 5.66[a]	18.4[c]

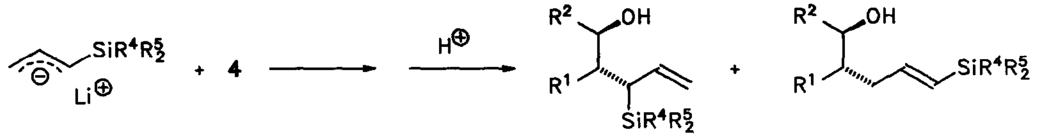
[a] A mixture of both diastereomers of **4i** was used (cis/trans 1:2). - [b] Solvent : C_6D_6 · [c] Solvent : $CDCl_3$

entries 4-9). As to the regiochemistry of epoxide ring-opening, unsymmetrically substituted oxiranes **4b,c,h** are invariably attacked on the less hindered ring carbon by the allylsilane anion (Table 1; entries 2,3, and 8); only **4i** gives a 4% yield of the γ product resulting from the alternative mode of epoxide ring-opening.

In a second series of experiments, the additional substituents R^4,R^5 on the silicon of the allylsilane component 1 were varied and the effects on the regiochemistry of the reaction with epoxides **4** (R^3 = H) studied[3b] (Table II). Obviously, sterically demanding alkyl groups (Table II, entries 4, 8) exhibit a pronounced effect favoring the γ isomer **8**[6], especially in the case of the 1,2 disubstituted epoxide **4g**. On the contrary, phenyl substituents on the silicon lead to a divergent behavior depending on the epoxide. In the case of cyclohexene oxide (**4g**; Table II, entries 6, 7), the exclusive formation of the γ isomers **8** seems to indicate a steric effect, whereas in the reaction with propene oxide (**4b**; Table II, entries 2, 3) the preponderance of the α isomers **7**[6] may be due to orbital control as has been invoked to explain the regiochemistry in the alkylation of 1 (R^4 = Ph, R^5 = Me)[4b].

Finally, we studied the influence of the counterion on the regiochemistry of attack of epoxides on anions 1 focusing on cases where for the lithiated species no pronounced γ selectivity was observed (Table III). Surprisingly,

Table II.

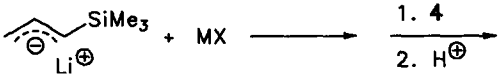


1 7 8

Entry	Oxirane (cf. Table I)	R^4	R^5	Ratio 7	Ratio 8	Yield [%]	Olef. ^{1}H-NMR Data 7 1H m	7 2H m	8 1H dt	8 1H d	$^3J_{HH}$ [Hz]
1	**4b**	CH_3	CH_3	4.5	1	83	5.55	4.90	6.07	5.79	18.5[c]
2	**4b**	Ph	Ph	9	1	91	5.75	4.97	6.21[c]		
3	**4b**	CH_3	Ph	>9	1	81	5.68	4.84[b]	-	-	
4	**4b**	$-C(CH_3)_2-CH(CH_3)_2$	CH_3	1.6	1	91[a]	5.59	4.91	6.05	5.80	18.3[b]
5	**4g**	CH_3	CH_3	1	6	87	5.78	4.93	5.99	5.63	18.6[c]
6	**4g**	Ph	Ph	<1	10	94	-	-	6.27[c]		
7	**4g**	CH_3	Ph	<1	10	76	-	-	6.19	6.03	18.4[c]
8	**4g**	$-C(CH_3)_2-CH(CH_3)_2$	CH_3	1	10	82[a]	5.75	5.05	6.04	5.72	18.4[b]

[a] Reaction conditions: -40°C/4 h, THF, one equiv. **4**. - [b] and [c] see Table I.

Table III.



1a

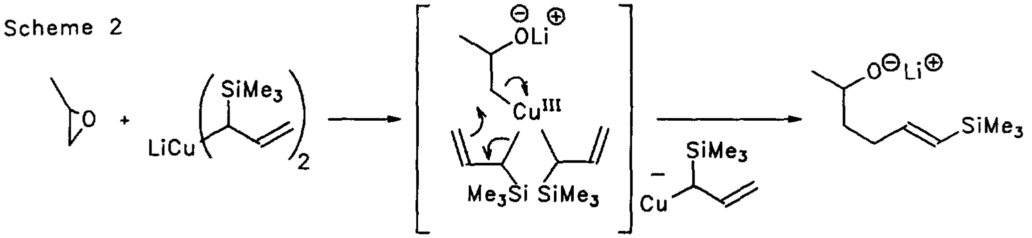
Entry	Oxirane (cf. Table I)	MX	Ratio 5	Ratio 6	Yield [%]
1	**4b**	-	4.5	1	83
2	**4b**	$CeCl_3$	2.3	1	60[a,b]
3	**4b**	$TiCl(O\text{-}iPr)_3$	1.5	2	25[a,b]
4	**4b**	CuI	1	2	82[a,c,f]
5	**4b**	$CuBr\cdot SMe_2$ [d]	1	3.4	79[a,c,f]
6	**4c**	$CuBr\cdot SMe_2$	1	3.7	55[a,e,f]
7	**4d**	$CuBr.SMe_2$	<1	10	77[a,e,f]
8	**4e**	$CuBr.SMe_2$	<1	10	68[a,e,f]

[a] The lithium/metal exchange was achieved by adding the salt MX at -78°C to the lithio species and warming up to -45°C for 30 min. - [b] Reaction conditions: one equiv. **4b**, 4 h, -78°C -> 0°C. - [c] Reaction conditions: 2 h, -78°C -> -10°C. - [d] Ref.[7]. - [e] Reaction conditions: 12 h, -78°C -> room temperature. - [f] Ratio of reactants **1a** : **4** : CuHal = 1 : 0.5 : 0.5.

cerium or titanium complexation did not improve the γ selectivity dramatically (Table III, entries 2,3); only a more sluggish reaction was observed for the allyl titanium species (entry 3)[8]. However, use of the corresponding allyl cuprates results in a reversed regiochemistry (Table III, entries 4-8). Thus, the acyclic mono- or 1,2-disubstituted epoxides **4b,d,e** give excellent γ regioselectivity. A limitation is found in the failure of the only moderately reactive allylsilyl cuprates to achieve ring-opening of the cyclic epoxides **4f,g**.

Earlier studies with other electrophiles[2c,9] had shown that use of copper as counterion encourages bond formation with the γ carbon of the allylsilyl anion. For our examples, the shift in regioselectivity may be explained by a two-step process[10]: after initial ring-opening by copper, an allylic rearrangement may follow (Scheme 2).

Scheme 2



The ability to control the regiochemistry in the attack of epoxides on allylsilane anions opens new possibilities in the synthetic applications of oxiranes and some of these are currently under investigation.

Acknowledgement - Support of this work by *Fonds der Chemischen Industrie*, Frankfurt, as well as preparative assistance by cand. chem. *F. Narjes* and *C. Hente* are gratefully acknowledged.

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5. The lithiated species was generated by deprotonation of trialkylsilylpropene with sec-BuLi in THF in the presence of one equivalent of TMEDA at -50°C for 2 h. - Anions of phenyl substituted allylsilanes were obtained under the same conditions, but in the absence of TMEDA.
6. The constitutions of **5**-**8** were confirmed by IR, ^{1}H-NMR, and ^{13}C NMR spectroscopy. All new compounds gave satisfactory microanalytical results. α/γ ratios were determined by ^{1}H NMR spectroscopy; the isomers were separated by preparative column chromatography.
7. $CuBr-SMe_2$ was prepared according to:
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(Received in Germany 3 May 1988)