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STEREOSELECTIVE FORMATION OF (E)-OLEFINS BY HYDROLYTIC DESULPHINYLATION OF SOME SUBSTITUTED 4-(2'-ALKENESULPHINYL)-MORPHOLINES [1]

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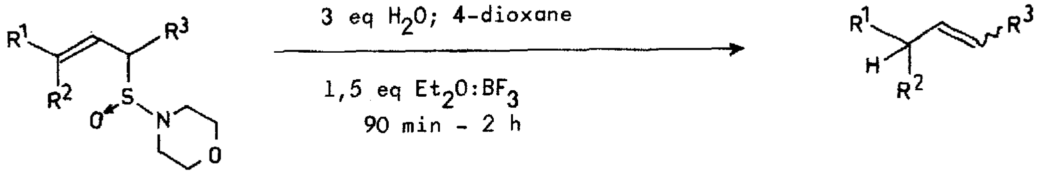
Summary: The boron trifluoride-etherate catalysed hydrolysis of the title sulphinamides 1 provide olefins with (E:Z)-ratios depending on the nature of the substituents on the allylic chain.

Five different methods for the *in situ* formation of the unstable homoconjugated sulphinic acids have been described [2-6], and their fragmentation with loss of sulphur dioxide has proceeded with apparently exclusive allylic rearrangement to provide olefins. There is however very little information concerning the geometry of the olefins arising from substituted allylic sulphinic acids [2b,c,d,5] and in order to investigate this question, the hydrolysis of a number of the title sulphinamides has been examined.

A variety of 1',3'-substituted 4-(2'-alkenesulphinyl)-morpholines 1 [1b] were converted by our previously described hydrolytic procedure [6] into the corresponding olefins (Table) and the more interesting observations were the following:

- Most of the hydrolytic desulphinylations were carried out at room temperature. A higher temperature (60°C) was found to be necessary for the transformation of some sulphinamides bearing a double bond which was reluctant to the protonation in the correct way to allow the loss of sulphur dioxide from the intermediate homoconjugated sulphinic acid (entries 1, 12, 13, 14).
- The yields of olefins [7] were generally acceptable, excepting those arising from styrenic (entry 1) or α-t.butyl substituted (entry 10) sulphinamides and the ratios of (E:Z)-olefins were in the range 67-82 : 33-18 (entries 1-7). More interestingly perhaps in the series of α-substituted (R^3) E-sulphinamides 1 (R^1 = n.C_7H_{15}, R^2=H) (entries 6-11), the ratio E:Z increases with increasing bulk of the substituent R^3 and the desulphinylation reaction becomes entirely stereoselective when the R^3 group is t.butyl or phenyl.

- The results of entries 8,9 show that the same ratio of E:Z olefins is formed starting from mixtures of different ratios of diastereoisomeric sulphinamides 1h and 1h'.
- Finally three sulphinamides bearing two substituents R^1 and R^2 on the Y-carbon of the allylic chain have furnished the corresponding pure (E)-olefins (entries 12-14).



1 2

Table

Entry	Substrate	R^1	R^2	R^3	temperature	Yields (%) of olefins	Ratios E:Z *
1	1a	p.Me-C_6H_4	H	Me	60°C	2a 18	72:28
2	1b	H	H	p.Me-C_6H_4-CH_2	60°C	2a 63	77:23
3	1c	H	H	n.C_8H_{17}	20°C	2b 81	71:29
4	1d	H	H	$\mathrm{Ph\text{-}\overset{H}{C}{=}\underset{H}{C}\text{-}CH_2}$	0°C	2c 60	77:23
5	1e	n.C_8H_{17}	H	Me	20°C	2d 70	69:31
6	1f	n.C_7H_{15}	H	Me	20°C	2b 78	82:18
7	1g	n.C_7H_{15}	H	Et	20°C	2e 77	67:33
8	1h (A:B=65:35)	n.C_7H_{15}	H	i.Pr	20°C	2f 77	91:9
9	1h'(A:B=20:80)	n.C_7H_{15}	H	i.Pr	20°C	2f 79	91:9
10	1i	n.C_7H_{15}	H	t.Bu	20°C	2g 25	100:0
11	1j	n.C_7H_{15}	H	Ph	20°C	2h 67	100:0
12	1k	Me	Me	n.C_8H_{17}	60°C	2f 50	100:0
13	1l	-$(CH_2)_5$-		p.Me-C_6H_4-CH_2	60°C	2i 54	100:0
14	1m	{Me_2C=CH-$(CH_2)_2$ Me}		Me_2C=CH-CH_2	60°C	2j 53	100:0

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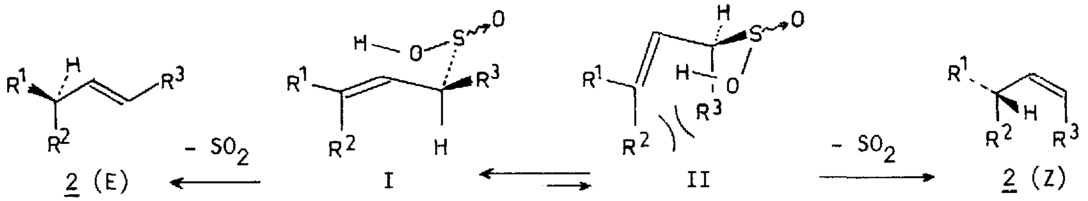
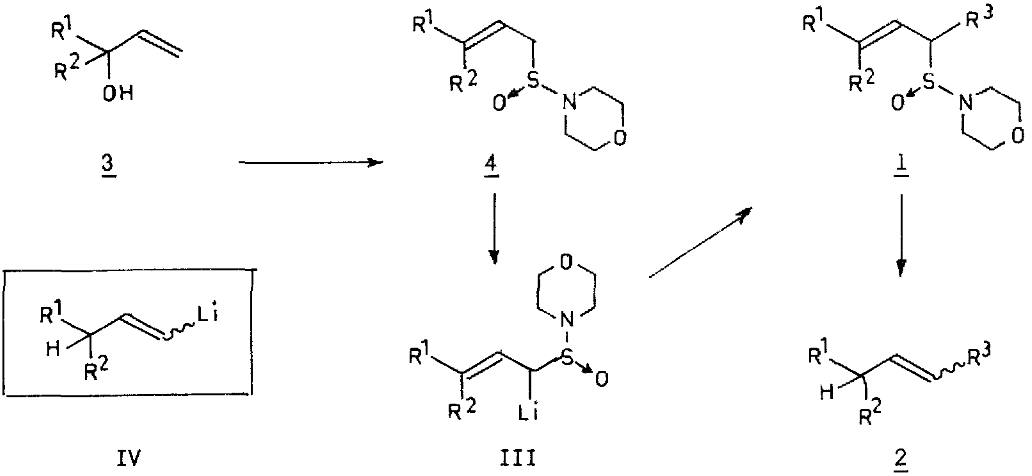
* The ratios E:Z of the olefins were determined with a capillary gas chromatograph (UCON 75 H column 25 m in lenght) and most of their structures were ascertained by comparison with authentic samples of pure E and Z compounds prepared by unambiguous procedures.

The aforementioned results concerning the geometry of the formed olefins may be rationalized by the transition states shown in I and II [8]. When R^2 = H, R^1 and R^3 = alkyles, the transition state I with a pseudoequatorial group R^3 is favoured and becomes increasingly predominant with increasing bulk of the equatorial "anchor" R^3.



When R^1, R^2 and R^3 are alkyl groups, the $A^{(1,3)}$-strain shown in transition state II is obviously the main reason which controls the formation of pure (E)-olefins through transition state I. This interpretation is consistent with previous results *concerning the hydrolyses* of substituted 3,6-dihydro-thiazine-1-oxides which have occurred through the transition state I (R^1=H or alkyle, R^2 and R^3=alkyles) to afford also pure (E)-olefins [2b,c,d].

In conclusion, the results obtained after the hydrolytic desulphinylations of the above substituted allylic sulphinamides 1 have led to a better understanding of the factors influencing the stereochemistry of the olefin formation. It is worth emphasizing that the reactions reported here, and earlier by us [1b], could together become a general method for regiospecific C-C coupling, owing to the fact that the α-lithioallylic sulphinamides III may be viewed as synthetic equivalents of the vinylic lithioderivatives IV.



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   b) Part IV: Baudin J.-B., Julia S.A., Tetrahedron Lett., 1989, preceding communication.
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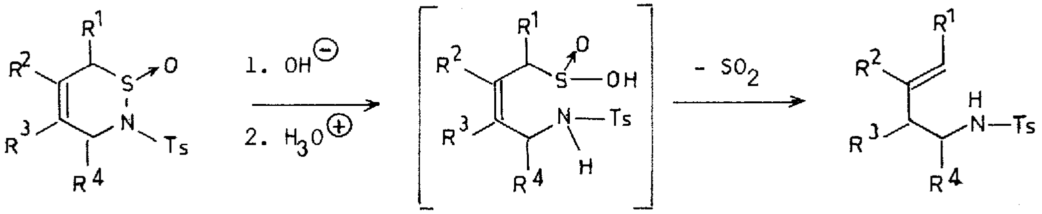
7. The identity of all new compounds reported in this communication was established by IR, ^{1}H NMR, ^{13}C NMR and M.S. For most of them, the elemental compositions were determined by combustion analysis.
8. The transition states are similar to those proposed for the hydrolysis of the Diels-Alder adducts of dienes and N-sulphinyl-toluenesulphonamides (ref. 2c,d):



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