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UNSATURATED SULFINAMIDES II [1]. AN EFFICIENT PREPARATION OF 4-(2'-ALKENESULFINYL)-MORPHOLINES BY THE REACTION OF 4-MORPHOLINESULFENYL CHLORIDE WITH ALLYLIC ALCOHOLS

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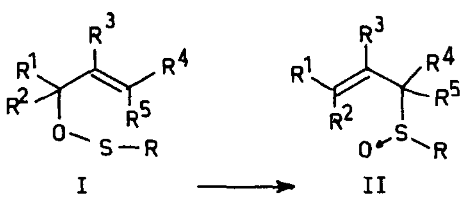
Summary: By the title reaction carried out in the presence of triethylamine, several allylic alcohols have been converted via the transient 4-morpholinesulfenate esters Id into 4-(2'-alkenesulfinyl)-morpholines 2.

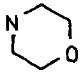
Twenty years ago, it was demonstrated that simple allylic alcohols on treatment with aryl-[2] or trichloromethane-[3] sulfenyl chlorides in the presence of a base were smoothly transformed via the sulfenate esters Ia,b into the rearranged allylic sulfoxides IIa,b; this type of isomerization can occur by a stereospecific presumably [2.3] sigmatropic shift mechanism [5]. Since then the allylic sulfoxides have been recognized as useful intermediates in organic synthesis [6].



a R = Aryl (ref.2)

b R = CCl_3 (ref. 3)

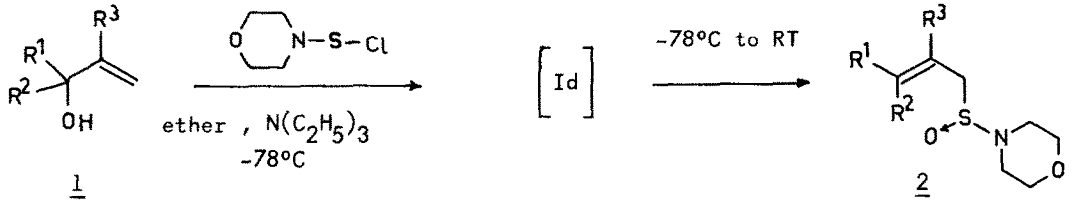
c R = $n.C_3H_7$ (ref. 4)

d R = 

In view of the behaviour of these allylic sulfenates Ia,b,c we have investigated the possible analogous rearrangement of allylic 4-morpholinesulfenate esters Id to sulfinamides IId. The project was initiated by some reports on the reaction of N,N-dialkyl-aminosulfenyl chlorides with saturated alcohols in the presence of a base; the alkyl N,N-dialkyl-aminosulfenates [7] thus obtained are characterized by the interesting presence of three contiguous heteroatoms.

For our preliminary study we chose the 4-morpholinesulfenyl chloride for its easy access [8] and for simplification of the ^1H NMR spectra of the derived compounds. Reaction of this chloride with various allylic alcohols 1 in the presence of triethylamine at low temperature then at room temperature [9] readily affords the corresponding unsaturated sulfinamides 2 whose structures are completely ascertained by their physical data [10] and their chemical transformations [11]. The results are summarised in the table and the following features are noteworthy:

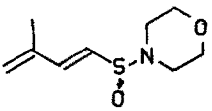
- The rearrangement of the intermediate 4-morpholinesulfenate esters was generally rapid (1-2 hrs) excepting the sulfenate of the alcohol 1a which required 42 h for complete conversion.



Table

substrate	R^1	R^2	R^3	time (h)	yields (%) of sulfinamides 2	ratios E : Z
1a	H	H	H	42	83	-
1b	CH_3	H	H	2	87	10:0
1c	CH_3	CH_3	H	<1	81	-
1d	$Br-CH_2$	CH_3	H	<1	*	
1e	$C_6H_5-CH_2-O-CH_2$	H	CH_3	2	86	9:1 [12]
1f	$(CH_3)_2C=CH-(CH_2)_2$	CH_3	H	<1	79	5,5:4,5[12]
1g	p.$CH_3-C_6H_4$	H	H	<1	80	10:0
1h	n.C_8H_{17}	H	H	2	82	10:0
1i	H	n.C_3H_7	$\underset{O}{C}-CH_3$	<1	86	1:9
1j	H	n.C_3H_7	$\underset{O}{C}-OCH_3$	<1	82	3,4:6,6
1k	H	C_6H_5	$\underset{O}{C}-CH_3$	<1	92	0:10
1l	H	C_6H_5	$\underset{O}{C}-OCH_3$	<1	91	0:10

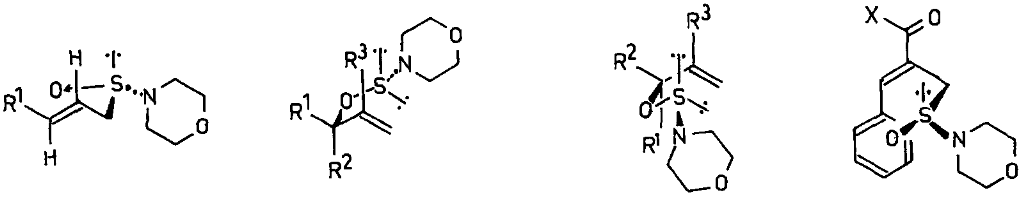
* This compound could not be purified by chromatography on silicagel (decomposition); it was readily converted by potassium hydroxide (2 equiv) in ethanol at RT into the pure (E) isoprenic sulfinamide



(55% overall yield from 1d).

- The rearrangement of the examined aliphatic aminosulfenates was found to be regioselective and those corresponding to the secondary alcohols (1b,g,h) afforded only the trans 4-(2'-alkenesulfinyl)-morpholines (2b,g,h). However rearrangement of the 4-morpholinesulfenate of linalool 1f gave a mixture of the two sulfinamides 2f (E:Z = 5,5:4,5) [12]. The four functionalised alcohols (1j,1)[13] and (1i,k)[14] were converted into the corresponding sulfinamides (2i-l) and only the phenyl-substituted compounds (1k,l) afforded the pure (Z)-compounds (2k,l).
- The aforementioned results concerning the geometry of the double bonds of the unsaturated sulfinamides 2 may be rationalized by the supposition that the transition states in the rearrangement of the allylic 4-morpholinesulfenates are similar to those of the classic arylsulfenates [2,5,15]. For the sake of clarity, we propose the two "boat-like" transition states [16] IIIA and B with a quasi equatorial morpholino-group. The formation of the pure (E) compounds (2b,g,h) is readily explained by considering the struc-

ture IIIA (R^2=R^3=H; R^1=alkyl) which should be the preferred conformation owing to the quasi equatorial orientation of the alkyl group R^1. However the (Z)-compounds (2k,l) may have arisen from the conformation IIIb (R^1=C_6H_5, R^2=H, R^3=C(O)X) with a quasi axial aryl group which would allow a better delocalization in the transition state leading to the final substituted cinnamic compounds.



2b,g,h ← III A ⇄ III B → 2k,l

In conclusion we have described a new and facile preparation of 4-(2'-alkenesulfinyl)-morpholines. This procedure should be applicable to other N,N-disubstituted aminosulfenyl chlorides and may be considered as a complementary one to the known ene reaction of olefins with N-sulfinylarenesulfonamides [17] and N-sulfinyl-carbamates[18] which afforded the corresponding 2-alkenesulfinamides bearing a hydrogen and an electron-withdrawing group on the nitrogen atom. The accessibility of the unsaturated sulfinamides 2 should extend considerably the range of compounds available for the study of sulfinamide reactivity.

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8. Baudin J.-B., Julia S.A., Ruel O., Tetrahedron, 1987, 43, 881-889 and references cited therein. This chloride can be stored at -18°C (crystalline) during several weeks.

9. General procedure: A solution of alcohol 1 (10 mmol) and triethylamine (20 mmol) in anhydrous ether (25ml) was stirred at -78°C under nitrogen. A solution of 4-morpholinesulfenyl chloride (10 mmol) in ether (15 ml) was added dropwise and then the cooling bath was removed. The mixture was allowed to warm to room temperature (1 h) and was filtered on celite. After evaporation of the solvent under reduced pressure, the crude product was left at room temperature under nitrogen for the time indicated in the table and purified by flash-chromatography (kieselgel Merck 60 230-240 mesh, gradient elution ether : 0 to 10% ethanol).

10. The identity of all new compounds reported in this communication was established by IR, ^{1}H NMR, ^{13}C NMR and MS. The elemental compositions were determined by combustion analysis.

11. Baudin J.-B., Julia S.A., following communication.

12. The ratios E:Z of these sulfinamides cannot be determined by HPLC (decomposition) nor spectroscopic data. They were determined by a sequence of transformations: sulfinamides → methyl sulfinates → phenyl sulfoxides → phenyl sulfones and measuring the ratios E:Z of the latter.

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