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THE STEREOSELECTIVE SYNTHESIS OF FUNCTIONALIZED CONJUGATED DIENES : PREPARATION OF (E,E)-α-HYDROXY DIENES AND OF VINYLALLENES.

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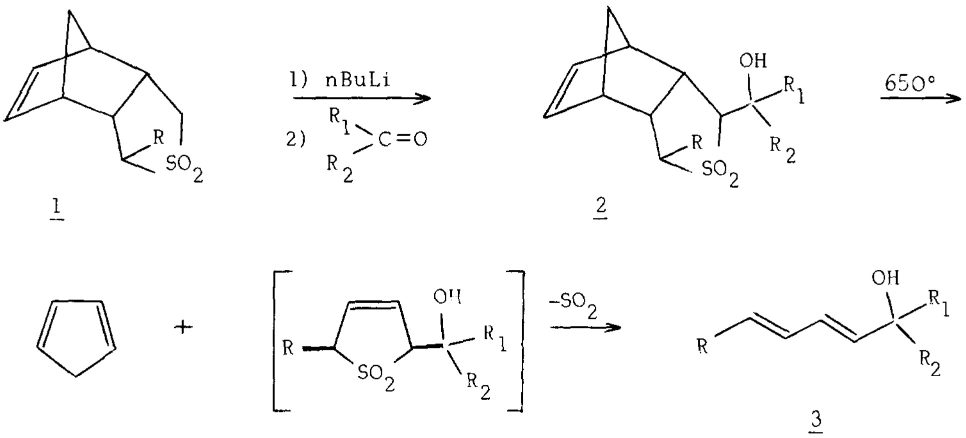
Summary : A simple procedure has been developped for the synthesis of (E,E)-α-hydroxy conjugated dienes of high stereoisomeric purity. A stereoselective preparation of vinylallenes by thermal extrusion of SO_2 from 2-alkylidene-2,5-dihydrothiophene-1,1-dioxides is described.

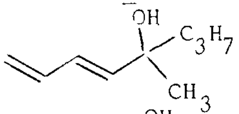
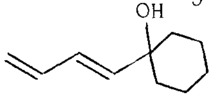
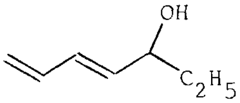
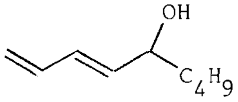
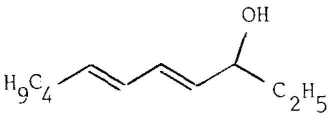
We recently reported a highly stereoselective synthesis of (E)-1-substituted 1,3-dienes and of (E,E)-1,4-disubstituted-1,3-dienes by disrotatory ring-opening of substituted-2,5-dihydrothiophene-1,1-dioxides generated by a retro Diels-Alder reaction (1). We have now investigated the extension of this method to the obtention of functionalized conjugated dienes and we report in this communication the selective preparation of (E,E)-α-hydroxy conjugated dienes and of vinylallenes which are both important synthetic intermediates (2,3).

The synthetic scheme used for the dienic alcohols is as follows :



The anions of the sulfones 1 (1), treated with an equimolar quantity of a carbonyl compound in THF solution at -78°C, afforded the alcohols 2 with good yields for ketones and fair yields for aldehydes (4). In this latter case, the presence of diols, coming from the reaction of two equivalents of aldehydes in α and α' position

Table I. Stereoselective synthesis of α -hydroxy conjugated dienes.

Formation of sulfones 2				Thermolysis (a)		
Starting Material	Carbonyl Compound	Product	Yield (%) (b)	Dienes 3	Yield (%)	Stereoisomeric Purity (E) or (E,E)(c)
1 R = H	Pentanone-2	2a	95		73	⩾ 98
1 R = H	Cyclohexanone	2b	77		78	⩾ 98
1 R = H	Propanal	2c	56		77	⩾ 98
1 R = H	Pentanal	2d	52		73	⩾ 98
1 R = C_2H_5	Pentanone-2	2e	88	mixture of trienes		
1 R = CH_3	Cyclohexanone	2f	68	mixture of trienes		
1 R = C_4H_9	Propanal	2g	56		74	93

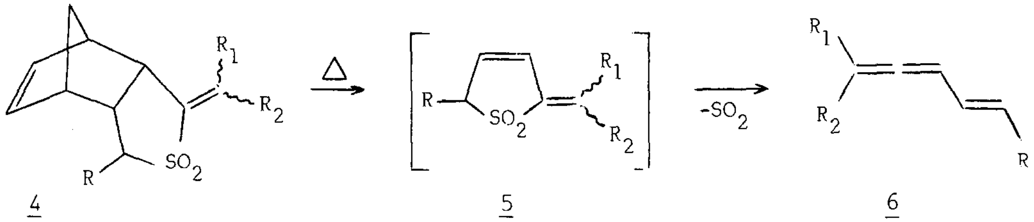
a) 650° in vapor phase.

b) The yields of products 2 are based on the sulfone 1 (R = H). All yields are given for isolated compounds purified by column chromatography on silica gel.

c) The stereoisomeric purity was estimated by ^{13}C N.M.R. for (E) terminal dienes and by gaz capillary chromatography for (E,E) conjugated dienes.

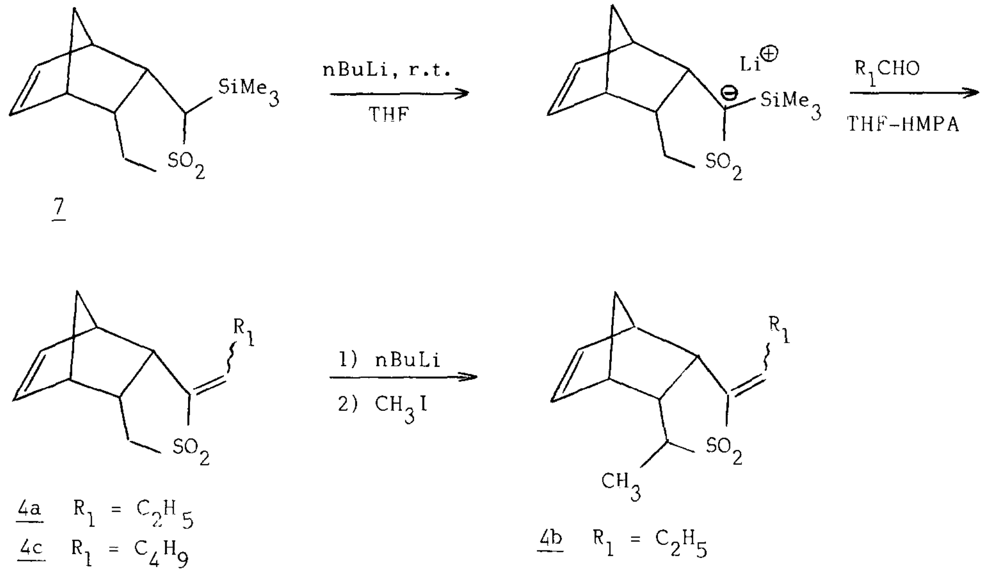
of the SO_2 group, could not be avoided. The thermolyses were carried out in vapor phase at 650°C with a short contact time in the hot tube (5). In these conditions, α-hydroxy conjugated dienes could be prepared with good yields and high selectivity as summarized in Table I. However tertiary alcohols of the type R-CH=CH-CH=CH-C(OH)-R_1R_2 (R,R_1, R_2 = alkyl) were not stable at the temperature used and only a mixture of trienes arising from a non selective dehydration of these alcohols could be observed in the pyrolysate.

We next turned our attention to the eventual obtention of vinylallenes by thermal SO_2 extrusion from 2-alkylidene-2,5-dihydrothiophene-1,1-dioxides 5 :



4 5 6

The preparation of precursors 4 by basic elimination of the acetates derived from alcohols 2 was not successfull but 4 (R_2 = H) could be easily obtained by a Peterson olefination (6) starting from the readily available silylated sulfone 7 :



7

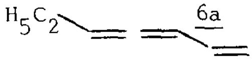
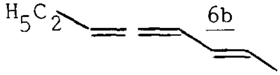
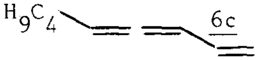
4a $R_1 = C_2H_5$
4c $R_1 = C_4H_9$

4b $R_1 = C_2H_5$

The thermodynamic anion (7), α to silicon, generated by adding one equivalent of n-BuLi to the sulfone 7 at room temperature was allowed to react with various carbonyl compounds. In the case of ketones, the products formed (1 + 2) are coming from the desilylation of the starting material 7. However aldehydes reacted smoothly to give directly the olefins 4 as a mixture of two stereoisomers in nearly the same proportions. Thermolysis at 650° of the alkylidene sulfones 4a-c affords the vinylallenes 6a-c with good purity (∼ 90% estimated either by ^{1}H NMR or gaz chromatography) as shown in Table 2. The major isomer of 6b (∼ 90%), purified by preparative G.C. presented in I.R. an intense absorption at 960 cm^{-1} , characteristic of an (E) double bond. The stereoselectivity observed in this case is in good agreement with a concerted SO_2 extrusion process, not affected by the presence of the exo double bond in the sulfolenes 5.

The syntheses of conjugated dienes bearing other functional groups are currently under investigation.

Table 2. Synthesis of vinylallenes.

Preparation of 4			Thermolysis	
Aldehyde	Product	Yield based on 7	Vinylallene	Yield
C_2H_5CHO	4a R = R_2 = H R_1 = C_2H_5	79	 6a	78
C_2H_5CHO	4b R = CH_3 R_2 = H R_1 = C_2H_5	63	 6b	83
C_4H_9CHO	4c R = R_2 = H R_1 = C_4H_9	61	 6c	86

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2) Some preparations and utilizations of α-hydroxy conjugated dienes have been recently reported : a) A.P. Kozikowski and Y. Kitigawa, Tetrahedron Lett., 23, 2087 (1982) ; b) P.A. Wender, S. Mc N. Sieburth, J.J. Petraitis and S.K. Singh, Tetrahedron, 37, 3967 (1981) ; c) E. Piers and M.E. Morton, J. Org. Chem., 45 4264 (1980).

3) For a review on the chemistry of vinylallenes see I.Z. Egenburg, Russian Chem. Rev., 47, 470 (1978) ; see also R. Baudouy and J. Goré, J. Chem. Research (S), 278 (1981) and references therein.

4) The stereoisomers obtained are assumed to be formed by an exo attack of the carbonyl compound, as was already observed for the reaction of 1 with alkyl halides (Ref. (1)).

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7) The kinetic anion, in α' position, can be generated by treatment of the sulfone 7 with one equivalent of nBuLi at -90°C (R. Bloch and J. Abecassis, unpublished results).

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