Tetrahedron Letters,Vol.26,No.10,pp 1301-1304,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

# A NOVEL STEREOSELECTIVE SYNTHESIS OF 1,3,5-TRIENES VIA $SO_2$ EXTRUSION FROM SULFOLENES.

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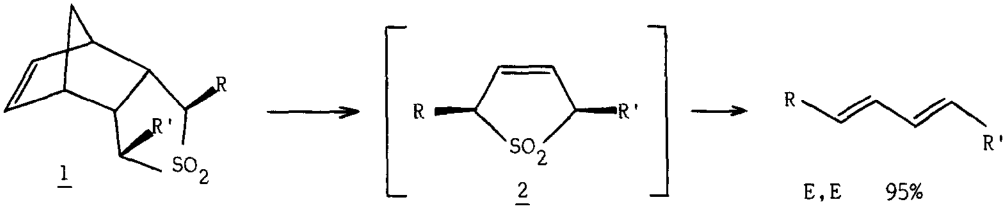
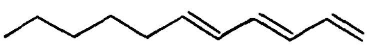
Summary : (E)-1,3,5-hexatriene as well as (E,E)-1,3,5-undecatriene and (E,Z)-1,3,5-undecatriene, two natural compounds isolated from the essential oils of Galbanum and Dictyoperis, were stereoselectively synthesized from sulfolenes generated by a retro-Diels-Alder reaction.

Recently, a simple method for the stereoselective preparation of (E)- and (E,E)-1,3-dienes by a thermal $SO_2$ extrusion from substituted sulfolenes 2, generated by a retro-Diels-Alder reaction, has been developed in this laboratory (1). This procedure is quite general and has been applied to the selective synthesis of α-functionnalized conjugated dienes such as alcohols (2), ketones, esters, amides and aldehydes (3) :



We wish to report now that a slight modification of this method allows the stereoselective preparation of terminal 1,3,5-trienes and in particular of (E,E)-1,3,5-undecatriene 3 and (E,Z)-1,3,5-undecatriene 4. These two natural compounds (4) have been isolated from the essential oils of both Galbanum (5) and the Hawaiian seaweed Dictyoperis (6) and are known to exhibit interesting olfactive properties.



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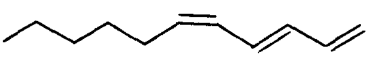

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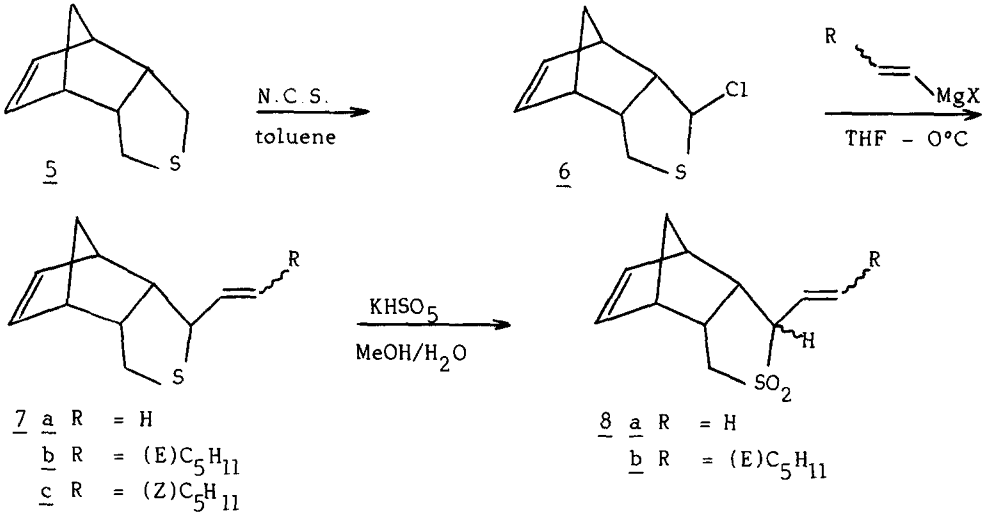
Since the precursors 1 (R = H, R' =  ) of such 1,3,5 -trienes could not be obtained through a simple alkylation of the parent sulfone 1 (R = R' = H), they were prepared from the corresponding sulfide 5 following the scheme:



5

6

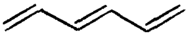
7 a R = H
b R = (E)$C_5H_{11}$
c R = (Z)$C_5H_{11}$

8 a R = H
b R = (E)$C_5H_{11}$

Sulfides which possess at least one α-hydrogen atom are known to react readily with N-chlorosuccinimide (N C S.) in an inert solvent to afford α-chlorosulfides (7) : thus, the sulfide 5, treated by one equivalent of N.C.S. in toluene at 20°C led to the unstable chlorosulfide 6 which was not isolated but reacted immediatly with a THF solution of an alkenyl Grignard reagent (8) at 0°C to give the alkenyl sulfides 7 (a-c) as a mixture of endo and exo stereoisomers with moderate yields (25 to 40% from 5). Oxidation of the sulfides 7 (a,b) with an aqueous methanolic solution of potassium hydrogen persulfate (11) afforded the sulfones 8 (a,b) in good yields (70-75%).

The thermolysis of 8a at 600°C, with a short contact time in the hot zone, gave rise to (E)-1,3,5-hexatriene 9 with an excellent stereoisomeric purity ( $\geqslant$ 98%) as shown by $^{13}$C N.M.R. : only three peaks could be detected at $\delta$ = 137.0 ; 133.9 and 118.0 ppm. The I.R. spectrum indicated characteristic bands of the (E) isomer at 1430, 1010 and 940 cm$^{-1}$ ; no bands corresponding to the (Z) isomer were present (12). However when the sulfone 8b was heated in the same conditions, the formation of five isomeric compounds (M = 150) was observed by G.C./M.S. spectroscopy.

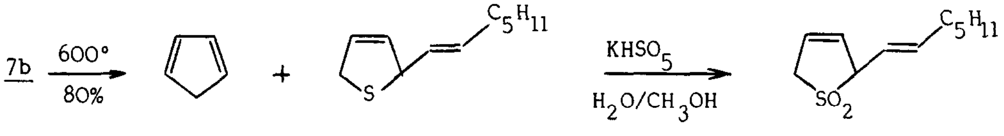
8a $\xrightarrow[75\%]{600°}$



9 E $\geqslant$ 98%

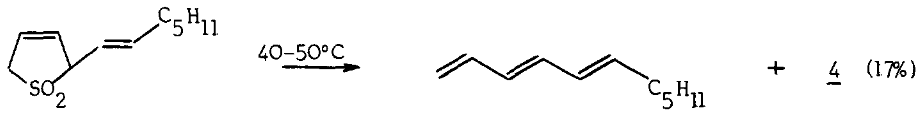
8b $\xrightarrow{600°}$ Five isomers

This results is probably due to the unstability of 1,3,5-undecatriene 3 at this temperature. In order to obviate this difficulty, the sulfolene 11 was prepared following a slightly different procedure (13). The tricyclic sulfide 7b, heated at 600°C, gave rise via a retro-Diels-Alder reaction to the dihydrothiofene 10 which was oxidized into the sulfolene 11 by KHSO$_5$ at room temperature :



10 11

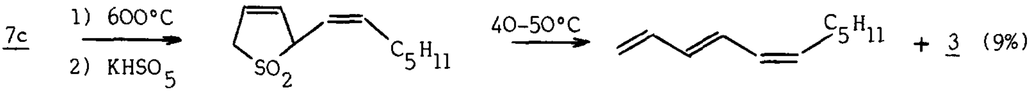
The presence of the exocyclic double bond lowers the transition state energy of the $SO_2$ extrusion so that we could observe the formation of the triene 3, even at room temperature (14), during an attempted purification of 11 by column chromatography on silicagel. The undecatriene 3 (15) was best obtained by simple heating of the crude sulfolene 11 at 40-50°C/0.05 torr and trapping at -78°C (yield = 45% from sulfide 10).



11 3 (83%)

The stereoisomeric purity, estimated by gaz capillary chromatography was only 83% : this relatively low selectivity was partly due to the fact that the (E)-1-bromo-1-heptene used for the preparation of the Grignard reagent was not stereochemically pure (9).

Analogously, the sulfolene 12, prepared from the sulfide 7c afforded the (E,Z)-1,3,5-undecatriene 4 (15) with 91% stereoselectivity as shown by capillary G.C. (yield = 42% from 7c) :



12 4 (91%)

It has been reported (16) that the formation of alkenyl Grignard reagents from alkenyl halides is not stereospecific and this observation might account for the loss of selectivity obtained in this case. This method constitutes however the most stereoselective synthesis of (E,Z)-1,3,5-undecatriene.

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13) The direct preparation of sulfide 10 from 2,5-dihydrothiofene was not successful.

14) Usually $SO_2$ extrusion from 2-alkyl sulfolenes proceeds at 100-150°C.

15) In each case, the major product stereochemistry was easily established by comparison of the spectra (I.R., N.M.R., Mass) with those of pure 3 and 4 already reported in ref. 4a.

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**(Received in France 21 November 1984)**