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A HIGHLY STEREOSELECTIVE SYNTHESIS OF (E)-1-SUBSTITUTED-1,3-DIENES.

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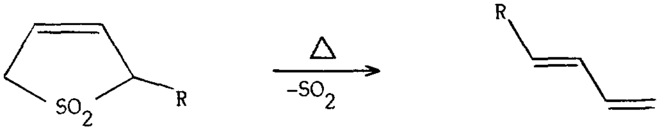
Summary : (E)-1-substituted-1,3-dienes are obtained with high stereoselectivity by the thermal extrusion of SO_2 from 2-substituted-2,5-dihydrothiophene-1,1-dioxides generated by a retro Diels-Alder reaction. An application to the synthesis of (E)-9,11-dodecadien-1-yl acetate, a sex pheromone of the red-bollworm moth is described.

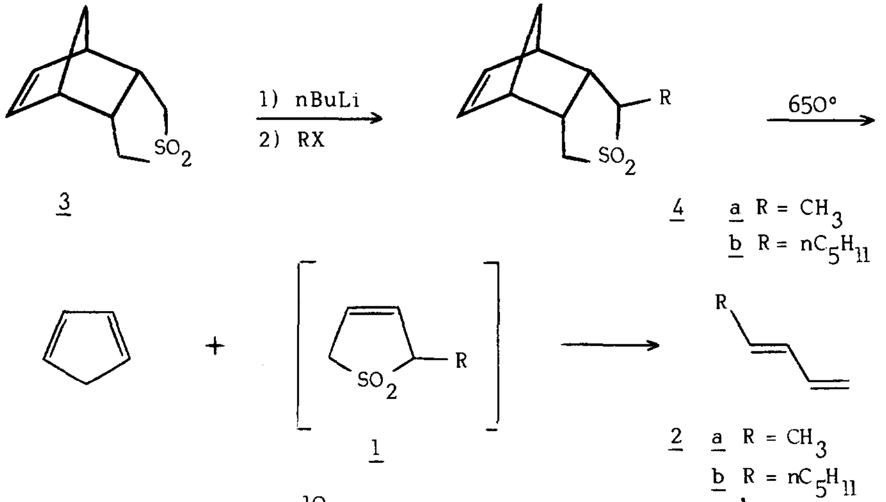
Stereoselective syntheses of conjugated dienes are of considerable interest in organic chemistry since such dienes are often encountered in the insect sex pheromones ([1]) and are also valuable intermediates in the total synthesis of complex natural products via inter- or intramolecular Diels-Alder reactions ([2]). Recently a number of new methods for the stereoselective preparations of conjugated dienes have appeared, utilizing either the cross coupling of alkenyl organometallic species with alkenyl halides ([3]), or some modified Wittig reactions ([4]), or the thermal ring opening of cyclobutenes ([5]). We wish to report a different approach to (E)-1-substituted-1,3-dienes based on two successive thermal reactions : a retro Diels-Alder reaction followed by a concerted SO_2 extrusion.

It is well known that the thermolysis of 2-substituted-2,5-dihydrothiophene-1,1-dioxides 1 is a concerted chelotropic reaction, leading to (E)-conjugated dienes 2 with excellent yield ([6]) :

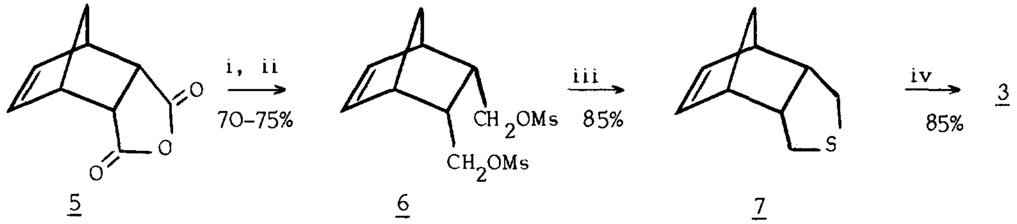


1 2

However this simple process suffers from the lack of availability of the sulfolenes 1 ([7]) and has not been developped ([8]). In particular direct substitution of the parent 2,5-dihydrothiophene-1,1-dioxide is precluded by the opening of the five membered ring in basic medium ([9]). But after protection of the double bond, it should be possible to generate a stable anion which, by reaction with various electrophiles followed by deprotection, could lead to 2-substituted sulfolenes 1 and then to dienes 2. The sulfone 3 is an interesting synthon for such a process since the protective group being thermally labile, its removal and the SO_2 extrusion can be effected in one single step ; furthermore, due to the geometry of the molecule, attack of the electrophiles should occur from the exo face and this selectivity should be important for further studies. Accordingly two simple conjugated dienes have been prepared following the scheme :



The known sulfone 3 ([10]) was prepared in 50-55% overall yield from the adduct 5 of cyclopentadiene and maleic anhydride. Reduction of the anhydride 5 with $LiAlH_4$ followed by treatment with methanesulfonylchloride in pyridine afforded the dimesylate 6 which was converted to the sulfide 7 by action of an aqueous solution of sodium sulfide in the presence of small amounts of a phase transfer catalyst. The sulfide 7 was then easily oxidized to the sulfone 3 by an aqueous methanolic solution of potassium hydrogen persulfate (oxone) at 0° ([11]) :

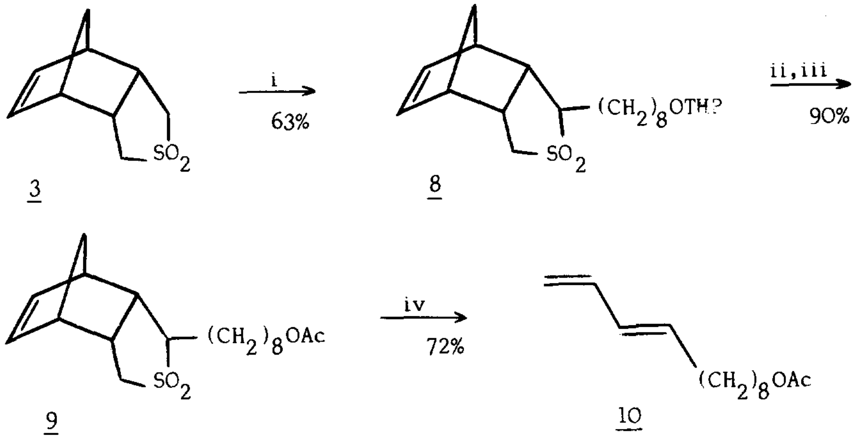


i : $LiAlH_4$-THF ; ii : CH_3SO_2Cl-Pyridine ; iii : Na_2S, H_2O-Toluène, Aliquat 336, 90°C, 4 h ; iv : $KHSO_5$, 0°C, 8 h.

The alkylation step 3 $\longrightarrow$ 4 was tested with two alkyl halides of different reactivities : CH_3I and $nC_5H_{11}I$. The best results were observed with nBuLi in THF solution at -78°C : the sulfone 4a was obtained in high yield (85%) and the sulfone 4b was isolated in 60-65% yield ([12]). Interestingly, in the two cases, the alkylation seemed to be highly stereoselective since only one isomer could be detected by g.l.c. (quartz capillary column, CPSIL 5, 25 m).

The thermolyses were best performed in vapor phase (13) at 650°C and the following dienes were obtained : E-1,3-pentadiene 2a as a 1:1 mixture with cyclopentadiene - Yield 85% - stereoisomeric purity higher than 95%, estimated by ^{1}H NMR ; (E)-1,3-nonadiene 2b - Yield 90% - The chemical purity was shown to be 99% by g.l.c.; the stereoisomeric purity estimated by ^{13}C NMR was at least 98%.

This method of preparation of (E)-conjugated dienes was then applied to a short and efficient stereoselective synthesis of (E)-9,11-dodecadien-1-yl acetate 10, a component of the sex pheromone of the red-bollworm moth (14) :



i : n-BuLi-THF, $I(CH_2)_8OTHP$, -78°C ; ii : CH_3OH-pTsOH, 45°C ; iii : CH_3COCl-NEt_3 ; iv : Heating at 600° in vapor phase.

The sulfone 3 was alkylated in the usual way with 2-(8-iodooctyl-1-oxy) tetrahydropyran (15) and the resulting tetrahydropyranyl ether 8 was converted by conventional methods to the acetate 9. The thermolysis of 9 was carried out at 600°C since at 650° small amounts of acetic acid coming from partial decomposition of the acetate 10 were observed (16). All the yields are given for pure products isolated by liquid chromatography on silicagel and thus (E)-9,11-dodecadien-1-yl acetate 10 was prepared in 41% overall yield from the sulfone 3. G.l.c. analysis on a high resolution glass capillary column showed that 10 had 97,3% chemical purity and at least 97,5% stereoisomeric purity (17).

Further utilizations of the sulfone 3 for the stereoselective preparations of 1,4-disubstituted-1,3-dienes and of functionnalized conjugated dienes are currently under investigation and will be reported in due course.

References and Notes

1) For a recent review see K. Mori, "The total synthesis of natural products", Vol. 4 (Edited by J. ApSimon), John Wiley and Sons, New-York, 1981.

2) For recent reviews see a) W. Oppolzer, Angew. Chem. Int. Ed., 16, 10 (1977) ; b) G. Brieger and J.N. Bennett, Chem. Rev., 80, 63 (1980).

3) N. Jabri, A. Alexakis and J.F. Normant, Tetrahedron Lett., 959 (1981) and references cited there in.

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5) B.M. Trost, S.A. Godleski and J. Ippen, J. Org. Chem., 43, 4559 (1978).

6) a) W. Mock, J. Amer. Chem. Soc., 88, 2857 (1966) ; b) S.D. Mc Gregor and D.M. Lemal, J. Amer. Chem. Soc., 88, 2858 (1966).

7) In general, sulfolenes 1 are prepared by reaction of the corresponding dienes with SO_2.

8) While this work was in progress, a non selective preparation of some 1,3-dienyl ketones was published by this method : K. Kosugi, A.V. Anisimov, H. Yamamoto, R. Yamashiro, K. Shirai and T. Kumamoto, Chem. Lett., 1341 (1981).

9) Y. Gaoni, Tetrahedron Lett., 4521 (1977) and references cited therein.

10) J.M. Photis and L.A. Paquette, J. Amer. Chem. Soc., 96, 4715 (1974).

11) B.M. Trost and D.P. Curran, Tetrahedron Lett., 1287 (1981). In contrast to this published procedure, we observed in our case the formation of an epoxide (∼ 20%) at room temperature.

12) Unchanged 3 and a dialkylation product were also present in the reaction mixture. The yield of 4b, based on recovered 3 was 75%.

13) Thermolyses were carried out in a flow apparatus analogous to the one described by J.F. King, P. De Mayo, C.L. Mc Intosh, K. Piers and D.J.H. Smith, Can. J. Chem., 48, 3704 (1970). Samples of 200 mg to 1 g of sulfones were used.

14) For previous syntheses of 10 see : a) R. Rossi, A. Carpita and M.G. Quirici, Tetrahedron, 37, 2617 (1981) and references cited therein ; b) G.R. Knox and I.G. Thom, J.C.S. Chem. Comm., 373 (1981).

15) D. Savoia, C. Trombini and A. Umani-Ronchi, J. Org. Chem., 47, 564 (1982).

16) At 600°C the conversion of 9 was not total and the yield of acetate 10 was 80-85% based on recovered 9.

17) The E and Z stereoisomers of 10 have been reported to be difficult to resolve by conventional g.l.c. methods. However this resolution can be effective on a 50 m x 0,2 mm i.d. WCOT capillary column (SE 52) at 180°C. This analysis was carried out by M. Gallois from the "Laboratoire des médiateurs chimiques" of Dr C. Descoins (Magny les Hameaux - France).

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