

Synthesis with Sulfones (n°XXXI) * : The Stereospecific Reduction of 2-Benzenesulfonyl-1,3 dienes to conjugated Z,E-Dienes. Synthesis of (9Z,11E)-9,11-Tetradecadienyl acetate.

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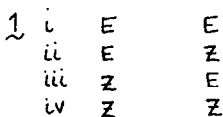
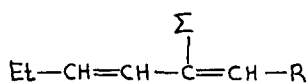
Summary : The stereospecific reduction of 2-phenylsulfonyl-1,3-dienes 1i to conjugated *EZ* dienes 2 catalysed by transition metal complexes in the presence of *n*-butyl magnesium chloride is described. This method is illustrated by the synthesis of the pheromone of *Spodoptera littoralis* : 9Z,11E-tetradecadien-1 yl acetate 2, R=Ac ^{1,2}.

A ready access to 2-benzenesulfonyl-1E-3E- dienes 1 of very high (99.5) stereochemical purity has been reported in the preceding letter ⁽³⁾. A satisfactorily stereospecific hydrogenolysis of the benzenesulfonyl group would open a new way to 1E, 3Z dienes, 2.

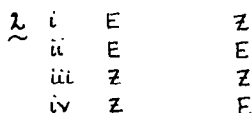
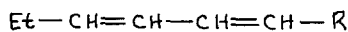
We first tried the technique which had proved very efficient for the stereospecific hydrogenolysis of vinylic sulfones to olefins ⁽⁴⁾, namely sodium dithionite with phase transfer catalysis. In the case of 1a, however the main product was the allylic sulfone 3, R=Et. Aluminium amalgam ⁽⁵⁾ or buffered sodium amalgam ⁽⁶⁾ also produced the allylic sulfone 3, R=Et.

We next turned to the recently ⁽⁷⁾ reported stereospecific hydrogenolysis of vinylic sulfones with Grignard reagents in the presence of transition metals, which proved efficient for monoolefin synthesis. The reaction of 1bi with *n*-BuMgBr, Pd(acac)₂, *n*-Bu₃P gave a 60% yield of the corresponding diene 2b with however a notable (15%) loss of stereochemical purity. We checked that dienes 2b were not isomerized under those reaction conditions. However, upon heating during evaporation of the solvent, isomerization did occur. The catalyst must therefore be carefully removed before isolation of the products. A few other palladium catalysts were tried (runs 2, 3, 4) ; all gave acceptable (40%) yields of diene 2b with high (93-97%) stereochemical purity.

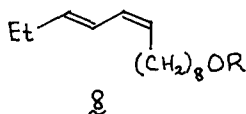
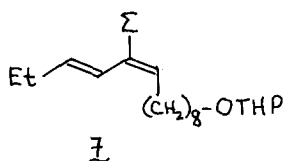
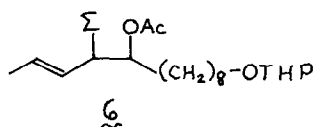
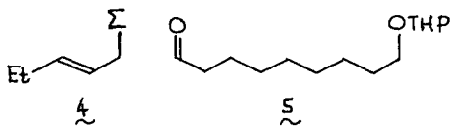
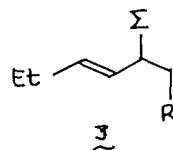
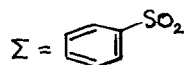
* Synthesis with Sulfones (n°XXX) see reference 3.



a R=Et



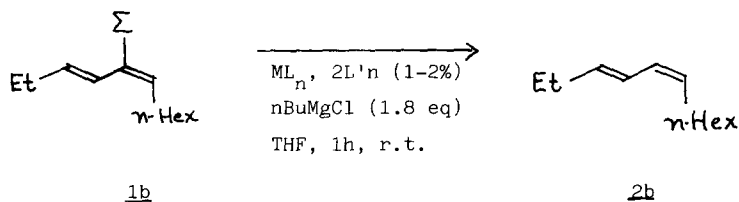
b R=n-Hex



Several nickel catalysts were tried (runs 5-8) with slightly better yields (45-50%) and stereochemical purity (96-97%). The EZ diene sulfone 1b ii was then prepared (3%i ; 97%ii) and hydrogenolysed to the EE diene 2bii (10%i, 90%ii) in low yield. Similarly a mixture of EE and ZE diene sulfones 1b (77%i ; 5%ii ; 18%iii) led to the corresponding EZ and ZZ dienes 2b (75%i, 4%ii, 21%iii) in 40% yield thus indicating that this reduction is stereospecific. This completes a 3-step route from readily available ⁽⁸⁾ E allylic sulfones 3 to conjugated EZ dienes.

The new method has been used to synthesize 9Z,11E-tetradecadienylacetate which is a pheromone of *Spodoptera littoralis* (Egyptian cottonleaf worm). The α -lithiated sulfone 4 was condensed with the readily available tetrahydropyranyloxyaldehyde ⁽⁹⁾ 5 and the product was acetylated in situ to give 6. Elimination of acetic acid was carried out by stirring in ether at room temperature with powdered sodium hydroxide which gave diene-sulfone 7. This was isolated by flash chromatography ⁽¹⁰⁾ in 49% yield and >99.5% stereochemical purity E.E.

Hydrogenolysis of diene sulfones by organomagnesium reagents with palladium or nickel catalysts.



Entry	<u>1b</u> ^a				Catalyst		<u>2b</u> ^{bcef}				Yield %
	Isomeric %		iii	iv	MLn	2L'n	Isomeric %		iii	iv	
i	ii	i			ii			i			ii
1	98.5-99	1	0.5		Pd(acac) ₂	nBu ₃ P	97	1	2	41	
2	"	"	"		"	Dabco	97	1	2	39	
3	"	"	"		"	nBu ₃ P	95	2	3	41	
4	"	"	"		Pd(allylCl)PPh ₃		93	3	1	4	35
5	"	"	"		Ni(acac) ₂	-	96	4			51
6	"	"	"		"	Dabco	97	3			46
7	"	"	"		"	nBu ₃ P	97	3			45
8	"	"	"		NiCl ₂ (PPh ₃) ₂	-	96	4			16 ^d

^a %(li+liii) is determined by HPLC ($\pm 0.5\%$) and capillary VPC ($\pm 0.5\%$)

% lii is determined by HPLC ($\pm 0.5\%$) and capillary VPC ($\pm 0.5\%$)

% liii is determined by 250 MHz NMR¹H ($\pm 2\%$); 1-phenyl-sulfonyl 2E-pentene used for the synthesis of 1b contained less than 0.5% of the Z isomer according to HPLC.

^b capillary VPC analysis (tridecane is the internal standard).

^c a significant amount of unidentified sulfones (M=472, i.e. M=1b + 2b) is also recovered 5-15%.

^d 51% of 1b is recovered unchanged ^e for typical procedure see ref. 11.

^f small amounts(1-3%) of dodecenes are also present.

Hydrogenolysis of the sulfonyl group was carried out with $n\text{-BuMgCl}$, $\text{Ni}(\text{acac})_2$ in THF (45%). In this case however the catalyst proved much more difficult to remove due probably to the THP ether group. After conversion (77%) into the corresponding acetate the stereochemical composition could be determined accurately and was found to be 9Z, 11E, 93%. Improvements in the removal of the catalyst will probably lead to an increase in stereochemical purity.

Thanks are due to the CNRS (LA. 32 and A.T.P., "Messagers chimiques").

Notes and references.

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- (3) T. Cuvigny, C. Hervé du Penhoat, M. Julia, preceding letter
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Elimination of acetic acid (NaOH ether) from 6 led to diene sulfone 7 98% EE which was easily purified by this method to afford 7 >99.5% EE.
- (11) Typical Procedure : 1,8 equivalents of $n\text{-BuMgCl}$ (1N, THF) are slowly added to a solution of the phenylsulfonyl diene 1 (or 7) and $\text{Ni}(\text{acac})_2$ (2 mole %) in THF at room temperature under a nitrogen atmosphere. After one hour the solution is poured onto saturated NH_4Cl /ice (10 volumes), extracted with pentane, washed with water (5 times) and eluted over silica gel to remove the catalyst (8 is eluted over a short alumina column). The dienes 2 (or 8) are analyzed without further purification. A second workup (extraction of the water layer and reelution of the silica gel column) with ether is carried out to recover sulfonyl products. Satisfactory 250 MHz ^1H NMR spectra and mass spectra were obtained for 2 and 8

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