Dramatic Solvent Effects and Stereospecificity in Allylic Sulphinate–Sulphone Rearrangements

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Dramatic solvent effects were observed in the thermolysis of allyl sulphinates; heating of chiral *trans*- and *cis*-allyl sulphinates (*S*)-(−)-(**1a**—**g**) in *N,N*-dimethylformamide at 90—120 °C provided chiral sulphones (**2a**—**d**) in good yields with very high stereospecificity.

In recent years asymmetric synthesis with chiral organosulphur compounds has received much attention.[1] In order to develop methods for asymmetric synthesis based on chiral sulphur centres, we have studied the thermolysis of chiral allyl sulphinates to investigate the transfer of asymmetry from sulphur to carbon.

Dramatic solvent effects were observed in the thermolysis of allyl sulphinates. Heating of (**1a**) in *N,N*-dimethylformamide (DMF) at 90—100 °C gave the corresponding γ-rearranged sulphone (**2a**) in 86—100% yield, much higher than yields in other solvents (Table 1).[2,3]

The chiral *trans*-allyl sulphinates (*S*)-(−)-(**1a**),-(**1c**),-(**1e**),

Table 1. Solvent effect on the thermal rearrangement of the sulphinate (**1a**) to the sulphone (**2a**).

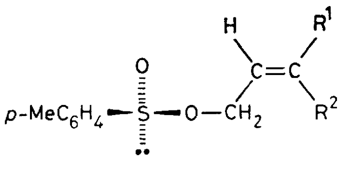
	Reaction conditions		Product	
Solvent[a]	Temp./°C	Time/h	% Yield of (**2a**)	% Recovered (**1a**)
EtOH	80	10	10	30 (30)[b]
EtOH–H_2O (3:2)	90	6	31	— (20)[b]
THF	66	24	—	90
DME	82	8	—	80
Dioxane	101	19	—	80
Dioxane–H_2O (3:1)	90	42	20	20
Toluene	110	6	21	31
Xylene	144	2	31	20
DMF	90—100	12	86—100	—

[a] THF = tetrahydrofuran; DME = 1,2-dimethoxyethane. [b] Yields of ethyl toluene-*p*-sulphinate are described in parentheses.

Table 2. Stereospecificity in thermal rearrangements of chiral *trans*- and *cis*-allyl sulphinates to sulphones.

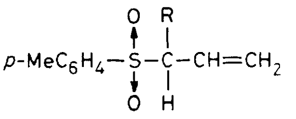
(1)		Reaction conditions		Product			
	% e.e.	Temp./°C	Time/h	(2)	% Yield	$[\alpha]_D$ (EtOH)	% Stereospecificity,[a] (1) → (2)
(**1a**)	57.4	90	12	(*S*)-(**2a**)	86	+4.4°	86.8
(**1b**)	45.9	120	20	(*R*)-(**2a**)	76	−4.1°	88.9
(**1c**)	57.5	110	18	(*S*)-(**2b**)	84	+18.0°	83.6
(**1d**)	47.8	120	20	(*R*)-(**2b**)	67	−14.7°	82.2
(**1e**)	56.8	110	20	(*S*)-(**2c**)	70	+16.6°	80.8
(**1f**)	91.2	120	20	(*R*)-(**2c**)	67	−28.4°	86.1
(**1g**)	62.1	90	18	(**2d**)	36[b]	−13.7°	—

[a] Calculated by n.m.r. analysis using the shift reagent Eu(hfc)$_3$, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium(III). [b] A double bond-isomerized product of (**2d**), *p*-$MeC_6H_4SO_2CH{=}CMePh$, was obtained in 14% yield and 40% of the starting material (**1g**) was recovered.



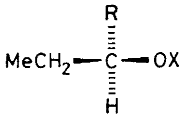
(*S*)-(−)-(**1**)

	R^1	R^2
a;	Me	H
b;	H	Me
c;	$[CH_2]_2Me$	H
d;	H	$[CH_2]_2Me$
e;	$[CH_2]_4Me$	H
f;	H	$[CH_2]_4Me$
g;	Ph	H



(**2**)

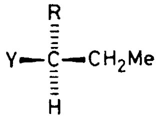
	R
a;	Me
b;	$[CH_2]_2Me$
c;	$[CH_2]_4Me$
d;	Ph



(**3**)

a; X = H

b; X = SO_2Me

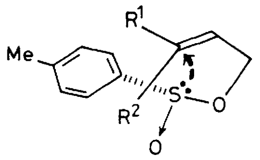


(**4**)

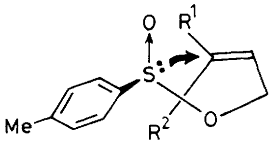
a; Y = *p*-MeC_6H_4-S

b; Y = *p*-MeC_6H_4-SO_2

R = Me, $Me[CH_2]_2$, or $Me[CH_2]_4$



(**5a**)



(**5b**)

and -(**1g**), obtained by boron trifluoride–diethyl ether-catalysed esterification of (*S*)-(+)-*N*,*N*-diethyltoluene-*p*-sulphinamide,[4] were heated in DMF under the conditions given in Table 2, and afforded the corresponding sulphones (*S*)-(+)-(**2a**—**c**) and (−)-(**2d**) with extremely high stereospecificity in good yields.† Thermolysis of the *cis*-allyl sulphinates (*S*)-(−)-(**1b**), (**1d**), and (**1f**) in DMF at 120 °C provided (*R*)-(−)-(**2a**—**c**) with high stereospecificity. No α-rearranged sulphone was detected in any case.

The absolute configurations of the products (**2a**—**c**) were determined by correlation of the corresponding saturated sulphones (**4b**) with authentic sulphones prepared by methanesulphonation of the corresponding chiral alcohols (**3a**) of known configuration,[5] followed by substitution with sodium toluene-*p*-thiolate[6] and subsequent oxidation of the sulphides (**4a**) with $NaIO_4$. On the basis of the high stereospecificity in this transformation, the complete retention of chirality in the starting sulphinates recovered at any stage of the reaction, and the exclusive formation of the γ-sulphones (**2a**—**d**), we conclude that these reactions occur by a concerted cyclic intramolecular mechanism, *e.g.* a [2,3] sigmatropic rearrangement. We suggest that this transfer of asymmetry from sulphur to carbon occurs because the steric interference between the tolyl group and the substituents R^1 and R^2 would be much more severe in the cyclic intramolecular transition state (**5a**) than in (**5b**), and so (*S*)-(−)-(**1a**),-(**1c**), and -(**1e**), or (*S*)-(−)-(**1b**), -(**1d**), and -(**1f**) rearrange preferentially *via* the transition state (**5b**) to provide (*S*)-(+)- or (*R*)-(−)-(**2a**—**c**), respectively, with high stereospecificity.

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† All new compounds gave satisfactory analytical data, which were in full agreement with the proposed structures.

Thus, a highly stereospecific transfer of chirality from sulphur to carbon may be accomplished in good yields by this thermolysis of chiral *trans*- and *cis*-allyl sulphinates.

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