Tetrahedron Vol. 41, No. 21, pp. 4965 to 4972, 1985
Printed in Great Britain.

0040–4020/85 \$3.00 + .00
Pergamon Press Ltd.

DIASTEREOSELECTIVE DIELS–ALDER REACTIONS OF OPTICALLY-ACTIVE VINYL SULPHOXIDES

MARGARET A. BRIMBLE and BRIAN R. DAVIS*
Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

(*Received in UK* 19 *March* 1984)

Abstract—The Diels–Alder reaction of an optically active vinyl sulphoxide containing a second electron withdrawing group with cyclopentadiene gave separable diastereomers. The effect of Lewis acid catalysis on the reaction was studied. Reaction of an acetylenic anion with menthyl *p*-toluene sulphinate gave an anomalous product.

Recent work by Maignan and Raphael[1] described the Diels–Alder reaction between cyclopentadiene and (+)-(*R*)-*p*-tolyl vinyl sulphoxide, but it was noted that production of all four diastereomers in the initial cycloaddition made the process inefficient. Introduction of a second electron withdrawing group to the double bond would facilitate the Diels–Alder reaction, and thus should improve its stereoselectivity. Studies to this end were initiated by one of us (B.R.D.) in collaboration with Professor Raphael in Cambridge, and are now reported.

We turned our attention initially to the synthesis of an acetylenic sulphoxide, making use of the nucleophilic properties of the acetylide ion in reaction with (−)-menthyl *p*-toluene sulphinate **1**.

As the Grignard reagent is incompatible with an ester or acid function, the latter would need to be present in masked form. We therefore studied the reaction of ethers of 3-propyn-1-ol. The protected primary alcohol can be converted to a carboxyl group at a later stage.

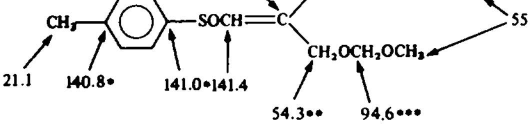
3-Propyn-1-ol methoxymethyl ether[2] was converted to its Grignard reagent which was reacted with the sulphinate ester **1**. A single product was obtained in 65% yield, based on unreacted starting material. If the reaction was interrupted at an early stage a cleaner product resulted; otherwise, the reaction solution became dark brown and more polar compounds appeared. The product obtained was a clear oil, assigned structure **2** on the basis of the following evidence. High resolution mass spectrometry established a formula of $C_{17}H_{22}O_5S$, the product was optically active, and the IR spectrum showed, in addition to a series of strong bands due to an acetylenic ether, bands characteristic of the sulphoxide group.

The ^{1}H- and ^{13}C-NMR spectra were of critical importance in establishing the structure (Table 1). Assignments are based on comparisons with related compounds of known structure and all signals in the ^{13}C-NMR spectra showed the expected s.f.o.r.d. multiplicities. Measurement of the ^{13}C-NMR spectrum with zero pulse delay showed the five non-protonated carbon atoms as very weak signals, which became of much increased relative intensity when the spectrum was measured utilising a five-second pulse delay. The stereochemistry about the double bond was not assigned, although other workers examining the conjugate addition of Grignard reagents to acetylenic sulphoxides have shown the products to be those of *cis* addition.[3] The reason for the ready conjugate addition of the acetylenic Grignard reagent in the absence of Cu(I) is not apparent.

Exploratory studies using the tetrahydropyranyl ether of 3-propyn-1-ol again resulted in addition of two moles of the organometallic, although the introduction of two new chiral centres in the two THP groups in addition to that in the sulphoxide group gave a diastereomeric mixture, showing complex ^{1}H- and ^{13}C-NMR spectra. Reaction of equimolar amounts of the two reagents gave the product **3** together with much recovered sulphinate. Using inverse addition of the acetylenic Grignard reagent, and monitoring the course of the reaction by TLC, only the anomalous product **3** was detected, even in the early stages of the reaction. Clearly, conjugate addition to the acetylenic sulphoxide is faster than nucleophilic attack on the sulphinate ester.

Table 1. Compound **2**: ^{1}H- and ^{13}C-NMR spectra

Chemical shift	Multiplicity
a 2.38	s
b 7.28	d, J = 8
c 7.54	d, J = 8
d 6.70	t, J = 8
e, e 4.12, 4.44	t, J = 7, s
f, f 4.56, 4.72	s, s
g, g 3.28, 3.38	s, s



* Asterisked pairs may be interchanged.

Attention was then focused on vinyl sulphoxides of the general type ROOC—CH=CH—SOAr. The Diels–Alder reaction of the racemic (*E*) and (*Z*) acids (R = H) had been studied.[4] Chirality transfer is likely to be more efficient using a vinyl sulphoxide, rather than an alkynyl sulphoxide, as the Diels–Alder product from the former has a new chiral centre vicinal to the sulphoxide group. Although a number of routes to vinyl sulphoxides have been employed, the available options were limited by our requirement to include an ester or carboxylic acid group.

Treatment of the anion of (+)-*S*-dimethylphosphoryl methyl *p*-toluene sulphoxide[5] **4** with freshly distilled butyl glyoxylate[6] **5** gave a mixture of three compounds. Column chromatography yielded (*E*)-(+)-(*R*)-butyl-3-*p*-tolylsulphinylpropenoate **6** (49%), and two unidentified compounds.

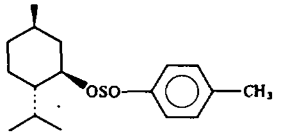
The structure of the major product **6** was identified as follows. The compound analysed for $C_{14}H_{18}O_3S$, and showed a molecular ion in the mass spectrum at *m/e* 266. Ions at *m/e* 250 ($M^+ - O$) and 218 ($M^+ - SO$) were indicative of an aromatic sulphoxide. Infrared absorption at 1720 cm^{-1} (carbonyl) and 1010 cm^{-1} (sulphoxide) supported the assigned structure, while the ^1H- and ^{13}C-NMR spectra (Experimental) proved decisive. In particular, the vicinal vinylic proton coupling constant, 14.5 Hz, was in the range expected for an (*E*) alkene. The optical rotation of the product varied from batch to batch. The highest rotation recorded was $[\alpha]_D^{25} + 414°$ but the use of a chiral lanthanide shift reagent or a chiral solvent did not permit the measurement of enantiomeric excess. Bulb-to-bulb distillation at 150°/0.7 mm Hg caused complete racemisation.

The second product isolated from the Horner–Wittig reaction had molecular formula $C_{14}H_{14}O_2S_2$ with a mass spectral molecular ion of *m/e* 278 and fragment ions at *m/e* 262 ($M^+ - O$), 246 ($M^+ - 2O$), 182 ($M^+ - 2SO$), 139 ($CH_3C_6H_4SO$) and 123 ($CH_3C_6H_4S$). It had strong absorption in the infrared at 1050 and 1030 cm^{-1} while the ^1H- and ^{13}C-NMR spectra showed the presence of two non-equivalent *p*-tolyl groups. The compound was devoid of optical activity and had m.p. 106.5–107.5°. It is thus not the *p*-tolyl thiol *p*-toluene sulphonate **7**, which has m.p. 76°,[7] but we are unable to assign a structure.

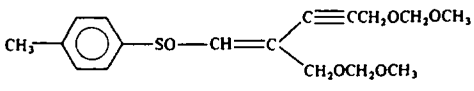
In their work with other aldehydes, Mikołajczyk *et al.*[5] had shown that both (*E*) and (*Z*) isomers were produced in the Horner–Wittig reaction, but the reaction here had produced only the (*E*) isomer of the desired product. We therefore planned to prepare the (*Z*) stereoisomer by oxidation of the known 3-(*Z*)-*p*-tolylthiopropenoic acid,[8] followed by resolution of the resulting sulphoxide. Addition of the toluene-*p*-thiolate anion to sodium propynoate yielded a mixture of (*Z*) and (*E*) acids, separable by fractional crystallisation. Oxidation of the major (*Z*) isomer with H_2O_2–SeO_2 in methanol at 65° for 3 hr[9] gave the corresponding sulphoxide in fair yield. Experimentation indicated that one diastereomeric cinchonidine salt could be crystallised from acetone. Four crystallisations, followed by regeneration, gave the (*Z*)-sulphinyl propenoic acid **8**, identified by combustion analysis, IR, mass, and ^1H- and ^{13}C-NMR spectra. Specifically, the vinyl proton coupling constant, 10 Hz, was consistent with the presence of a (*Z*) alkene. In order to provide comparison with the work with (*E*) alkene, the butyl ester was prepared from the acid by sulphuric acid catalysed reaction with 1-butanol at room temperature for 6 days. The mild conditions were used in order to minimise thermal racemisation of the sulphoxide.

With the two sulphinyl propenoate esters **6** and **9** in hand, we were in a position to examine the stereochemistry of their Diels–Alder reaction with cyclopentadiene in the presence and absence of Lewis-acid catalysts.

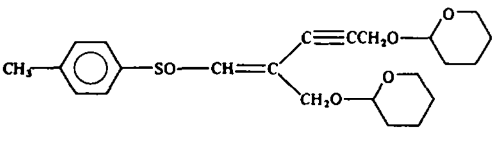
Reaction of the (*E*)-vinyl sulphoxide **6** with cyclopentadiene yielded four isomeric norbornenes



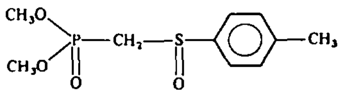
1



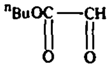
2



3

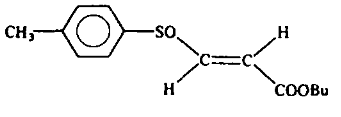


4

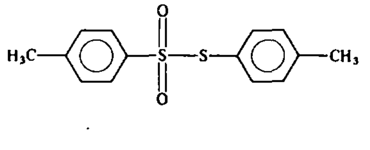


$$\overset{}{{}^{n}BuO\underset{\displaystyle O}{\underset{\|}{C}}—\underset{\displaystyle O}{\underset{\|}{C}}H}$$

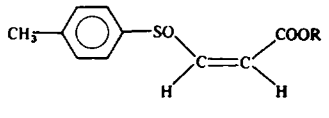
5



6

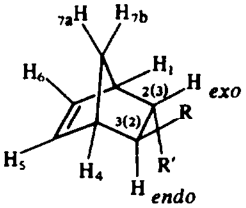


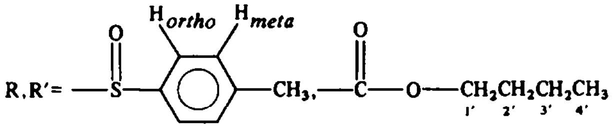
7



8 R = H
9 R = Bu

Table 2. ^{1}H-NMR chemical shifts[a] for the Diels–Alder adducts of (*E*)-(+)-(*R*)-(6) with cyclopentadiene





Isomer	Hydrogen atom[b]															Substituents
	1	4	H_{exo}	H_{endo}	5	6	7a	7b	1'	2'	3'	4'	H_{ortho}	H_{meta}	Ar—CH	
13	3.07	3.51	3.81[c]	1.96[d]	6.51	6.39	1.62	1.73	3.75	1.33	1.19	0.87	7.26	7.56	2.37	R = $CO_2{}^nBu$ R' = $\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}$-*p*-Tol
12	2.92	3.13	3.63[e]	2.82[e]	6.37	6.27	1.48	1.69	3.86	1.50	1.32	0.91	7.31	7.53	2.40	R = $CO_2{}^nBu$ R' = $\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}$-*p*-Tol
10	3.30, 3.32		2.92[e]	3.04[e]	6.08, 6.24		1.57	1.94	3.83	1.40	1.25	0.89	7.31	7.59	2.40	R = $\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}$-*p*-Tol R' = $CO_2{}^nBu$
11	3.23, 3.27		3.35[e]	2.92[e]	6.08, 6.33		1.48	2.05	3.73	1.36	1.24	0.88	7.27	7.46	2.38	R = $\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}$-*p*-Tol R' = $CO_2{}^nBu$

[a] Obtained from 400 MHz spectra.
[b] In parts per million relative to TMS.
[c] Assigned as position 3.
[d] Assigned as position 2.
[e] Assignment of the *exo* or *endo* protons to positions 2 or 3 cannot be decided unambiguously.

separated by column chromatography and assigned structures **10**, **11**, **12**, and **13** on the basis of the following evidence. All four analysed for $C_{19}H_{24}O_3S$ (*m/e* 332) and showed the expected IR spectra. Structural and stereochemical assignments were made on the basis of the ^{13}C and 400 MHz ^{1}H-NMR spectra (Tables 2, 3, 4). As they arise from (*E*) alkenes, each compound will have one *endo* and one *exo* substituent and thus one *exo* and one *endo* proton. Other factors being equal, protons α to a sulphinyl group resonate at lower field than protons α to a carbonyl group. The *exo* proton shows two vicinal couplings, to a bridgehead proton and the *endo* proton, while the *endo* proton shows coupling to the adjacent *exo* proton and a long range W-coupling to a proton on the methylene bridge. The methylene bridge protons couple to each other and one of them couples to an *endo* proton. The bridgehead protons each couple to one vinyl proton and an *exo* proton, but the bridgehead and *endo* protons are orthogonally disposed and hence coupling is not observed. Various assignments were confirmed by homonuclear decoupling experiments.

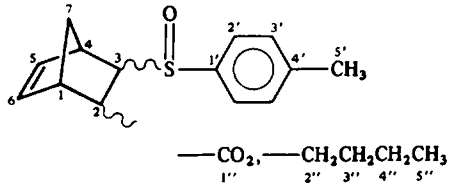
^{13}C-NMR spectral assignments were made on the basis of chemical shifts and multiplicities in the s.f.o.r.d. spectrum. The *p*-tolyl, butoxy, vinylic and C-7 bridge carbons were readily assigned. There remained four signals—all doublets in the s.f.o.r.d. spectrum—due to the two bridgehead and the carboxyl- and sulphinyl-bearing carbon atoms. Of these four signals, that at lower field was assigned to the carbon atom bearing the

Table 3. ^{1}H-NMR coupling constants[a] for the Diels–Alder adducts of (*E*)-(+)-(*R*)-(6) with cyclopentadiene

Isomer	Coupling constants, J Hz							
	$J_{2,3}$[b]	$J_{endo,7a}$	$J_{exo,1(4)}$	$J_{5,6}$	$J_{1,6}$	$J_{4,5}$	$J_{7a,7b}$	$J_{ortho,meta}$
13	4.8	1.5	3.3	5.6	3.0	3.0	9.0	7.0
12	4.6	1.5	3.2	5.8	2.8	3.2	8.8	7.0
10	4.5	1.5	3.5	5.6	2.7, 3.3		9.0	7.0
11	4.5	1.8	3.9	5.6	2.8, 3.0		8.8	7.0

[a] Obtained from 400 MHz spectra.
[b] Equivalent to $J_{exo,endo}$.

Table 4. ^{13}C-NMR data for the Diels–Alder adducts of (*E*)-(+)-(*R*)-(6) with cyclopentadiene



Isomer	1	4	2	3	5	6	7	1′	2′	3′	4′	5′	1″	2″	3″	4″	5″	Substituents
	Carbon atom[a]																	
13	44.5	48.1	45.3	70.9	137.7	135.6	46.5	141.9	125.3	129.8	139.7	21.4	172.3	64.7	30.4	18.9	13.6	*exo* $CO_2{}^n$Bu O ‖ *endo* S-*p*-Tol
12	45.4, 48.2		44.3	70.1	137.2	134.3	47.5	141.4	124.2	129.8	140.8	21.3	173.3	64.8	30.5	19.0	13.7	*exo* $CO_2{}^n$Bu O ‖ *endo* S-*p*-Tol
10	43.9, 46.5		46.1	67.7	137.1, 136.3		47.0	141.7	125.0	129.8	139.5	21.4	171.4	64.5	30.5	18.9	13.6	O ‖ *exo* S-*p*-Tol *endo* $CO_2{}^n$Bu
11	45.7, 47.2		41.8	66.1	137.6, 136.7		46.8	140.8	123.9	129.6	140.0	21.3	172.1	64.2	30.5	18.9	13.6	O ‖ *exo* S-*p*-Tol *endo* $CO_2{}^n$Bu

[a] In parts per million relative to TMS.

sulphinyl group. This, and the other assignments, were confirmed by the use of high power single frequency decoupling; irradiation at the resonance frequencies of the *exo* and *endo* protons in the four compounds revealed the attached carbon as a singlet in the ^{13}C spectrum.

There remained the assignment of stereochemistry about sulphur. It is assumed that rotation about the norbornene–sulphur bond places the large *p*-tolyl group away from the bicyclic ring system; the remaining two tetrahedral positions about sulphur are occupied by an oxygen atom and a pair of electrons. The presumed favoured conformation of the four isomers is shown in the formulae. A major factor in determining the chemical shift of the bridgehead protons is their placement with respect to the aromatic ring, protons above the plane of the ring being shielded. The proton at δ 3.51 is thus likely to be the one furthest removed from the aromatic ring and is thus assigned to epimer **13** in the conformation shown. The favoured conformer of the other epimer **12** places the bridgehead hydrogen more nearly above the plane of the aromatic ring and it resonates upfield at δ 3.13 or 2.92. In the isomers containing an *exo* sulphinyl and *endo* butoxycarbonyl, the favoured conformations are shown, **10** and **11**. A distinction between them can be made here on the basis of the chemical shift of the *exo* proton and its relationship to the benzene ring. In **10** it lies above the plane of the ring and is thus shielded (δ 2.92) with respect to the favoured conformer of the other epimer **11** in which the proton resonates at δ 3.35.

There has been much interest in recent years in the effect of Lewis-acid catalysts on diastereomeric ratios in the Diels–Alder reaction. Oppolzer *et al.*[10] studied the effects of various Lewis acids on the stereochemical outcome of the reaction between cyclopentadiene and some esters of acrylic acid. Having established the structure and stereochemistry of the four diastereomeric products from the uncatalysed Diels–Alder reaction, it was possible to study the reaction using Lewis-acid catalysis.

The product distributions resulting from carrying out the reaction in the presence of boron trifluoride etherate, tin(IV) chloride, or titanium(IV) chloride are listed in Table 5. Although the ratios vary, there is no indication that catalysis with these Lewis acids provides a synthetically useful yield of one diastereomer. In all cases, the *syn* isomer was favoured over the *anti* isomer.

Racemisation of the sulphoxide was shown to be minimal under each of the reaction conditions employed. Control experiments in which the sulphoxide was subjected to the various reaction conditions in the absence of the diene indicated that the optical rotation of the sulphoxide changed only slightly in each case. Measurement of the enantiomeric excess of the norbornene adduct using a chiral shift reagent and comparing this with the enantiomeric purity of the starting sulphoxide confirmed the above conclusions.

For convenience in discussing the NMR spectra, all the products obtained have been drawn as possessing the same absolute configuration about the bridgehead

Table 5. Yields of Diels–Alder adducts of (*E*)-(+)-(*R*)-(**6**) with cyclopentadiene

Reaction conditions	Diastereomeric product distribution[a]				Overall[b] yield
	(**13**)	(**10**)	(**12**)	(**11**)	
Reflux benzene 2 hr, ~ 80°	37%	42%	6%	15%	92%
1.5 eq. BF_3Et_2O 3.5 hr, 0°, toluene	56%	19%	22%	3%	98%
1.5 eq. $SnCl_4$ 3.5 hr, 0°	23%	55%	3%	19%	82%
1.5 eq. $TiCl_4$ 3.5 hr, 0°	25%	29%	21%	25%	63%

[a] e.g. $\dfrac{n(\mathbf{10})}{n(\mathbf{10})+n(\mathbf{11})+n(\mathbf{12})+n(\mathbf{13})} \times 100\%$.

[b] e.g. $\dfrac{n(\mathbf{10})+n(\mathbf{11})+n(\mathbf{12})+n(\mathbf{13})}{n(\mathbf{6})} \times 100\%$.

carbons of the norbornene ring but differing in the configuration about sulphur. Obviously, by starting with optically pure sulphoxide, the reaction would produce **10** and *enantio*-**11**, **12** and *enantio*-**13**. Thus, if the products were converted by standard means to a norbornanone,[1] with the carbonyl group marking the attachment of the sulphinyl moiety, **10** and **12** would produce one ketone and **11** and **13** its enantiomer.

The ratios of these products are as follows:

	11 + **13**/**10** + **12**
Reflux benzene, 2 hr	0.91
1.5 eq. BF_3Et_2O, 3.5 hr, 0°, toluene	1.39
1.5 eq. $SnCl_4$, 3.5 hr, 0°	0.72
1.5 eq. $TiCl_4$, 3.5 hr, 0°	1.00

It is apparent that these ratios, while allowing one to prepare both enantiomers in good yield, are not sufficiently attractive to meet criteria for the synthesis of one enantiomer.

We then turned our attention to the Diels–Alder reaction of the (*Z*) isomer **9**. Treatment with cyclopentadiene in the absence of Lewis acids gave a mixture of three compounds, separated by column chromatography. The major isomer (77% yield) gave the expected analytical and mass spectral data and its structure, stereochemistry and conformation were assigned as in **14**, from the ^{1}H- and ^{13}C-NMR spectra. In particular, the resonances at δ 3.15 and 3.67 appeared as quartets, $J_{2,3}$ 9.1 Hz, in the range expected for vicinal coupling between two *exo* protons, and $J_{1,2}$, $J_{3,4}$ 3.2 Hz.[11] Consistent with the *exo* orientation of the protons was the absence of the W-coupling previously observed between one of the bridgehead protons and an *endo* proton. Irradiation at a frequency corresponding to the bridgehead proton at δ 3.51 collapsed the quartets at δ 3.67 and δ 6.62 to doublets, thereby establishing the relationship between these protons. Assignment of the ^{13}C-NMR spectrum followed from work on the adduct from the (*E*) isomer. High power single frequency irradiation established that the proton at δ_H 3.67 was attached to the carbon at δ_C 70.7, bearing the sulphinyl group, with the proton at δ_H 3.15 being attached to the carbon at δ_C 47.7 bearing the carbonyl group.

Consideration of the favoured conformations of the possible *syn* and *anti* isomers about sulphur showed that the *syn* isomer would place the aromatic ring close to the —OCH_2— protons in the butoxy group. This is entirely consistent with the fact that these protons are observably diastereotopic (δ 3.96, δ 3.82) and indicates conformation **14**.

Consistent with the assignment of the *syn* conformation at the sulphur for this isomer was the observation that the resonance at δ 3.51, corresponding to the bridgehead proton adjacent to the sulphinyl group, occurred at the same chemical shift as the corresponding bridgehead resonance in **13** which also has a *syn* sulphinyl group in the *endo* position.

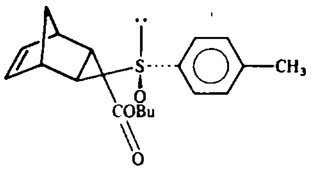
The minor products **15** (11%) and **16** (3%) were not fully characterised but **16** showed the resonance due to the carbon bearing the sulphinyl group at δ_C 74.5 while in isomer **15** it was observed at δ_C 67.6. Comparison with the adducts of the (*E*) isomer suggest that **16** contains the sulphinyl group in the *endo* position and isomer **15** contains the sulphinyl group in the *exo* position. As in **14** the sulphinyl group was assigned as *endo* and *syn*, in **16** the sulphinyl group must be *endo* but *anti* at sulphur. In the remaining isomer **15** both groups must be *exo* but it is not possible to determine the relative stereochemistry at sulphur. As the sulphoxide had been obtained by resolution, its absolute stereochemistry is not known. The good yield of one product indicates a use in synthesis but its application awaits an asymmetric synthesis of **8**.

Koizumi *et al.*[12] and Proust and Ridley[13] have very recently reported similar results on related systems.

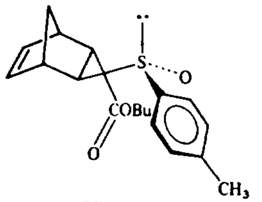
EXPERIMENTAL

IR spectra were run on Perkin–Elmer 297, 337 or 735B spectrometers. NMR spectra were recorded on a Varian T 60 or EM 360 in $CDCl_3$ with TMS as internal standard (60 MHz ^{1}H) or a JEOL PFT-FX60 or Varian CFT-20 (^{13}C). High field NMR ^{1}H spectra were recorded by Dr D. Ridley, University of Sydney, on a Bruker 400 MHz spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Mass spectra were obtained on a Varian MAT-CH7 (low resolution) or MAT-311 (high resolution).

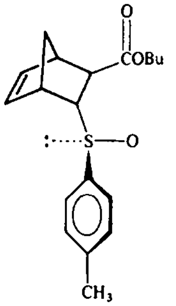
(−)-(S)-Methyl-p-tolylsulphinate **1**. This sulphinate was prepared by standard methods and recrystallised from



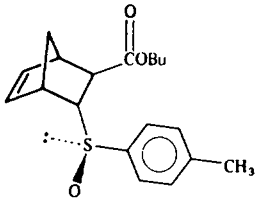
10



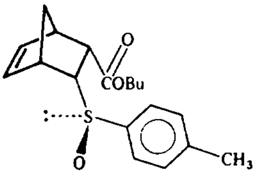
11



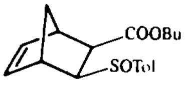
12



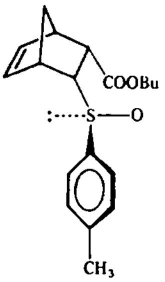
13



14



15



16

acetone: H_2O (17:3) as needles, m.p. 105–106° (lit.[14] m.p. 105–106°), $[\alpha]_D^{20} - 200°$ (c, 2.08, acetone), (lit.[14] $[\alpha]_D^{26} - 198°$).

Reaction of 4,6-dioxahept-1-ynyl magnesium bromide with menthyl-p-tolylsulphinate

A soln of 4,6-dioxahept-1-ynyl magnesium bromide [from Mg (0.24 g, 10 mmol), bromoethane (1.64 g, 15 mmol) and 4,6-dioxahept-1-yne (1.06 g, 10 mmol)] was added portionwise over 1.5 hr to a stirred cooled soln of **1** (1.0 g, 3.3 mmol) in dry THF under N_2. The progress of the reaction was monitored by TLC (ether), showing the disappearance of sulphinate and the appearance of product, R_f 0.24. After 5 hr the brown soln was poured into satd NH_4Cl aq and worked up to give an orange oil. Chromatography on silica gave some unchanged sulphinate and **2**. 60 MHz PMR, 15 MHz CMR see table in discussion. Found: M^+ 338.1212. $C_{17}H_{22}O_5S$. Requires: 338.1188.

Reaction of 3-(tetrahydropyranyloxy)prop-1-ynyl magnesium bromide with **1**

(a) 3-Tetrahydropyranyloxyprop-1-yne (2.3 g, 0.016 mol) was heated under reflux with EtMgBr [from Mg (0.40 g, 0.016 mol)] for 1 hr. **1** (4.14 g, 0.014 mol) in dry THF (40 ml) was added to give an opaque brown soln after 20 min. The mixture showed the presence of **1** and was stood at room temp for 60 hr and heated under reflux for 9½ hr. Work-up and chromatography gave **1** and the bis-adduct **3**.

(b) *With excess of the alkyne.* Repetition of the above reaction using alkyne (3.1 g, 0.022 mol) and **1** (2.35 g, 0.008 mol) in dry THF showed the presence of the bis-adduct after 1 min. Work-up after 40 min gave a mixture containing very little **1**. Chromatography on silica (ether) gave **3** (1.5 g).

(c) *Inverse addition with excess of acetylene.* A soln of the ethynyl magnesium bromide [from alkyne (2.3 g, 0.016 mol) and Mg (0.40 g, 0.016 mol)] in THF was added under N_2 to a stirred cooled soln of **1** in THF and the course of the reaction monitored by TLC. After the addition of 2 mol equivs of Grignard reagent over 2 hr and stirring for a further 2 hr, work-up and chromatography gave the same bis-adduct, **3**. 60 MHz PMR 1.2–1.74 (12H, m), 2.42 (3H, s), 2.9–4.15 (10H, m), 6.70 (1H, m), 7.29 and 7.58 (4H, 2d, J = 8 Hz). Found: M^+ 418. $C_{23}H_{30}O_5S$ Requires: 418 (low resolution).

(+)-(S)-*Dimethylphosphorylmethyl-p-tolyl sulphoxide* **4**

A soln of BuLi (14 ml, 22 mmol) was added to a soln of dimethyl methylphosphonate (2.16 ml, 20 mmol) in dry THF

(30 ml) under N_2 at $-78°$. After 30 min a soln of **1** (2.94 g, 10 mmol) in dry THF (20 ml) was added. After 15 min the mixture was warmed to $-20°$ and quenched with satd NH_4Cl aq. Work-up and careful removal of dimethyl methylphosphonate gave **4** (1.37 g, 52%), 60 MHz PMR identical to lit. $[\alpha]_D^{20} + 103°$ (*c*, 6.21, acetone), lit.[5b] $[\alpha]_D^{25} + 144°$ (*c*, 1.0, acetone).

(E)-(+)-(S)-*Butyl*-3(p-*tolylsulphinyl*)*propenoate* 6

A soln of BuLi (5.2 ml, 8.3 mmol) in hexane was added to a stirred soln of **4** (2.2 g, 8.4 mmol) in dry THF (20 ml) under N_2 at $-78°$. After 1.5 hr, **5** (1.5 g, 11.4 mmol, freshly distilled from P_2O_5) in dry THF (20 ml) was added. The soln was stirred at $-78°$ for 1 hr, allowed to warm to room temp and stirred for 2 hr. Work-up gave a crude product (2.62 g) which was separated by column chromatography, eluting with hexane:Et_2O to give:

(a) Compound **6** (1.11 g, 49%). 60 MHz PMR ($CDCl_3$) δ 0.7–0.9 (7H, m), 2.39 (3H, s), 4.10 (2H, t, J = 6), 6.67 (1H, d, J = 14.5), 7.10–7.71 (5H, m). ^{13}C-NMR ($CDCl_3$) δ 13.6, 19.0, 21.5, 30.5, 65.1, 123.9, 124.9, 130.4, 138.3, 142.4, 151.5, 163.8. IR ($CHCl_3$): $\bar{\nu}$ 1720, 1620 and 1060 cm^{-1}. MS: (*m/e*) 266, 250 and 218. $[\alpha]_D^{25} + 211°$ (*c*, 2.95, $CHCl_3$). Found: C, 62.1; H, 6.8. $C_{14}H_{18}O_3S$ Requires: C, 63.1; H, 6.8%.

(b) Unidentified compound (354 mg, 30%) pale yellow needles from hexane, m.p. 106.5–107.5°. 60 MHz PMR δ 2.39 (3H, s), 2.41 (3H, s), 7.05–7.59 (8H, two AB q). ^{13}C-NMR ($CDCl_3$) 36.9, 37.0, 139.8, 141.7, 145.1, 145.6, 150.2, 156.2, 156.5, 157.6. MZ (*m/e*) 278, 262, 246, 182, 139 and 123. IR $\bar{\nu}$ 1050 and 1030 cm^{-1}.

(c) An unidentified pale yellow oil (159 mg).

(Z)-(+)-*Butyl*-3(p-*tolylsulphinyl*)*propenoate*

3(*p*-Tolylthio)propenoic acid was prepared by published methods and was crystallised from aq EtOH as plates, m.p. 139–143° (lit.[15] m.p. 144–145°). 60 MHz PMR δ 2.40 (3H, s), 5.81 (1H, d, J = 10), 6.88–7.38 (6H, m) along with smaller quantities of the more soluble (*E*) isomer as needles, m.p. 163–165° (lit.[15] m.p. 164–165°). 60 MHz PMR δ 2.40 (3H, s), 5.51 (1H, d, J = 14.5), 6.20 (1H, bs, exchangeable with D_2O), 7.00–7.42 (4H, 2d, J = 8), 7.81 (1H, d, J = 14.5).

(Z)-(±)-3(p-*Tolylsulphinyl*)*propenoic acid* 8

A soln of selenium dioxide (0.56 g, 5 mmol) and 100 vol H_2O_2 (0.43 ml, 5 mmol) in water (2.5 ml) was added dropwise to a soln of the thiol (0.97 g, 5 mmol) in MeOH (10 ml) at 65° over 2 min and the mixture stirred at this temp for 3 hr. Satd NaCl aq was added and the mixture extracted with CH_2Cl_2 to give (Z)-**8** (0.71 g, 67%) as prisms from CH_2Cl_2, m.p. 138–139°. 60 MHz PMR ($CDCl_3$) δ 2.20 (3H, s), 6.18 (1H, d, J = 10), 6.79 (1H, d, J = 10), 7.10–7.75 (4H, 2d, J = 8), 8.00 (1H, bs, exchangeable with D_2O). ^{13}C-NMR ($CDCl_3$) 21.4, 125.5, 125.5, 130.2, 139.9, 142.3, 153.8, 165.8. MS (*m/e*) 210, 194, 162. IR ($CHCl_3$) $\bar{\nu}$ 3500–2500, 1710, 1620 and 1040 cm^{-1}. Found: C, 57.0; H, 4.8. $C_{10}H_{10}O_3S$ Requires: C, 57.1; H, 4.8%.

Resolution of **8**. Cinchonidine (3.79 g, 12.9 mmol) was added to a soln of **8** (2.71 g, 12.9 mmol) in acetone (50 ml). Upon standing for 2 hr the soln yielded a solid which was recrystallised four times from acetone. Regeneration (dil HCl aq) of the free acid and recrystallisation from CH_2Cl_2 gave (+)-**8** (425 mg, 15%) as prisms, m.p. 138–139°, $[\alpha]_D^{24} + 575°$ (*c*, 1.15, $CHCl_3$), identified by its PMR spectrum.

(Z)-(+)-*Butyl*-3(p-*tolylsulphinyl*)*propenoate*

Conc H_2SO_4 (0.1 ml) was added to a soln of (+)-**6** (244 mg, 116 mmol) in 1-BuOH (8 ml). The soln was stood at room temp for 6 days to yield **9** (241 mg, 77%). 60 MHz PMR 0.7–0.9 (7H), 2.38 (3H, s), 4.20 (2H, t, J = 6), 6.15 (1H, d, J = 10), 6.71 (1H, d, J = 10), 7.17–7.78 (4H, 2d, J = 8). $[\alpha]_D^{25} + 421°$ (*c*, 1.05, $CHCl_3$).

Investigation of racemisation of 6 *under the conditions used in cycloaddition reactions*

A soln of **6** (100 mg), $[\alpha]_D^{25} + 211°$ (*c*, 3.51, $CHCl_3$) in benzene (2 ml) was heated gently under reflux for 2 hr. Removal of benzene *in vacuo* gave **6** with $[\alpha]_D^{24} + 197°$ (*c*, 3.51, $CHCl_3$).

Diels–Alder cycloaddition

A soln of **6** (523 mg, 1.97 mmol) $[\alpha]_D^{24} + 414°$ (*c*, 2.18, $CHCl_3$) and freshly distilled cyclopentadiene (0.74 ml, 9.1 mmol) in benzene (10 ml) was heated under reflux for 2 hr. Removal of benzene at reduced pressure gave a pale yellow oil (799 mg) separated on a silica column (hexane:EtOAc) to yield 4 fractions:

(a) (+) - *Butyl* 3 - endo - syn - p - *tolylsulphinyl bicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - exo - *carboxylate* **13** (204 mg, 34%) as needles m.p. 51–53°. 400 MHz PMR ($CDCl_3$) 0.87 (3H, t), 1.19 (2H, m), 1.33 (2H, m), 1.62 (1H, dd, J = 9.0, J = 1.5), 1.73 (1H, d, J = 9.0), 1.96 (1H, dd, J = 4.8, J = 1.5), 2.37 (3H, s), 3.07 (1H, bs), 3.51 (1H, bs), 3.75 (2H, m), 3.81 (1H, dd, J = 4.8, J = 3.3), 6.39 (1H, dd, J = 5.6, J = 3.0), 6.51 (1H, dd, J = 5.6, J = 3.0), 7.26 (2H, d, J = 7), 7.56 (2H, d, J = 7). ^{13}C-NMR δ 13.6, 18.9, 21.4, 30.4, 44.5, 45.3, 46.5, 48.1, 64.7, 70.9, 125.3, 129.8, 135.6, 137.7, 139.7, 141.9, 172.3. *m/e* 332 (M), 316 (M–O). $[\alpha]_D^{25} + 150°$ (*c*, 2.32, $CHCl_3$). Found: C, 68.8; H, 7.6. $C_{19}H_{24}O_3S$ Requires: C, 68.6; H, 7.3%.

(b) (+) - *Butyl* 3 - exo - syn - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - endo - *carboxylate* **10** (231 mg, 39%) as needles, m.p. 54–56°. 400 MHz PMR ($CDCl_3$) 0.89 (3H, t), 1.25 (2H, m), 1.40 (2H, m), 1.57 (1H, dd, J = 9.0, J = 1.5), 1.94 (1H, d, J = 9.0), 2.40 (3H, s), 2.92 (1H, dd, J = 4.5, J = 3.5) 3.04 (1H, dd, J = 4.5, J = 1.5), 3.30 (1H, bs), 3.32 (1H, bs), 3.83 (2H, m), 6.08 (1H, dd, J = 5.6, J = 2.7), 6.24 (1H, dd, J = 5.6, J = 3.3), 7.31 (2H, d, J = 7.0), 7.59 (2H, d, J = 7.0). ^{13}C-NMR δ 13.6, 18.9, 21.4, 30.5, 43.9, 46.1, 46.5, 47.0, 64.5, 67.7, 125.0, 129.8, 136.3, 137.1, 139.5, 141.7, 171.4. *m/e* 332 (M), 316 (M–O). $[\alpha]_D^{25} + 134°$ (*c*, 1.58, $CHCl_3$). Found: C, 69.0; H, 7.5. $C_{19}H_{24}O_3S$ Requires: C, 68.6; H, 7.3%.

(c) (+) - *Butyl* 3 - endo - anti - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - exo - *carboxylate* **12** (32 mg, 6%) as a yellow oil. 400 MHz PMR 0.91 (3H, t), 1.32 (2H, m), 1.48 (1H, dd, J = 8.8, J = 1.5), 1.50 (2H, m), 1.69 (1H, d, J = 8.8), 2.40 (3H, s), 2.82 (1H, dd, J = 4.6, J = 1.5), 2.92 (1H, bs), 3.13 (1H, bs), 3.63 (1H, dd, J = 4.6, J = 3.2), 3.86 (2H, m), 6.27 (1H, dd, J = 5.8, J = 2.8), 6.37 (1H, dd, J = 5.8, J = 3.2), 7.31 (2H, d, J = 7.0), 7.53 (2H, d, J = 7.0). ^{13}C-NMR δ 13.7, 19.0, 21.3, 30.5, 44.3, 45.4, 47.5, 48.2, 64.8, 70.1, 124.2, 129.8, 134.3, 137.2, 140.8, 141.4, 173.3. *m/e* 332 (M), 316 (M–O). $[\alpha]_D^{25} + 110°$ (*c*, 3.21, $CHCl_3$). Found: C, 68.1; H, 7.5. $C_{19}H_{24}O_3S$ Requires: C, 68.6; H, 7.3%.

(d) (+) - *Butyl* 3 - exo - anti - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - endo - *carboxylate* **11** (81 mg, 14%) as a yellow oil. 400 MHz PMR 0.88 (3H, t), 1.24 (2H, m), 1.36 (2H, m), 1.48 (1H, dd, J = 8.8, J = 1.8), 2.05 (1H, d, J = 8.8), 2.38 (3H, s), 2.92 (1H, dd, J = 4.5, J = 1.8), 3.23 (1H, bs), 3.27 (1H, bs), 3.35 (1H, dd, J = 4.5, J = 3.9), 3.73 (2H, m), 6.08 (1H, dd, J = 5.6, J = 2.8), 6.33 (1H, dd, J = 5.6, J = 3.0), 7.27 (2H, d, J = 7.0), 7.46 (2H, d, J = 7.0). ^{13}C-NMR 13.6, 18.9, 21.3, 30.5, 41.8, 45.7, 46.8, 47.2, 64.2, 66.1, 123.9, 129.6, 136.7, 137.6, 140.0, 140.8, 172.1. *m/e* 332 (M), 316 (M–O). $[\alpha]_D^{25} + 87°$ (*c*, 8.13, $CHCl_3$). Found: C, 68.3; H, 7.5. $C_{19}H_{24}O_3S$ Requires: C, 68.6; H, 7.3%.

Titanium(IV) *chloride catalysis of cycloaddition*

Investigation of racemisation of **6**. Titanium(IV) chloride (2 drops) was added to a soln of **6**, $[\alpha]_D^{24} + 203°$ (*c*, 2.20, toluene) in dry toluene (1 ml) at 0°. The mixture was stood at 0° for 2 hr, quenched with water (1 ml) and extracted with CH_2Cl_2. Removal of solvent gave **6**, $[\alpha]_D^{24} + 194°$ (*c*, 2.20, toluene).

Diels–Alder cycloaddition

Titanium(IV) chloride (0.3 ml) was added to a soln of cyclopentadiene (0.75 ml, 9.1 mmol) and **6** (505 mg, 1.89 mmol), $[\alpha]_D^{24} + 200°$ (*c*, 1.89, $CHCl_3$) in dry toluene (10 ml) at 0°. The mixture was stirred at 0° for 3 hr, quenched with water and extracted with CH_2Cl_2 to give a dark brown oil, separated on silica (hexane:EtOAc) into four fractions:

(a) **13** (99 mg, 16%) as needles, m.p. 50–53°, $[\alpha]_D^{25} + 79°$ (*c*, 9.94, $CHCl_3$).

(b) **10** (116 mg, 18%) as needles, m.p. 53–56°, $[\alpha]_D^{25} + 79°$ (*c*, 2.94, $CHCl_3$).

(c) **12** (84 mg, 13%) as a yellow oil, $[\alpha]_D^{25}+67°$ (*c*, 8.38, $CHCl_3$).

(d) **11** (100 mg, 16%) as a yellow oil, $[\alpha]_D^{25}+55°$ (*c*, 10.04, $CHCl_3$).

Boron trifluoride–etherate catalysis of cycloaddition

Investigation of racemisation of **6**. BF_3–etherate (2 drops) was added to a soln of **6**, $[\alpha]_D^{24}+203°$ (*c*, 2.20, toluene) in dry toluene at 0°. After 2 hr, work-up gave **6**, $[\alpha]_D^{24}+192°$ (*c*, 3.64, toluene).

Diels–Alder cycloaddition

BF_3–etherate (0.5 ml) was added to a soln of cyclopentadiene (0.75 ml, 9.1 mmol) and **6** (770 mg, 2.92 mmol), $[\alpha]_D^{25}+414°$ (*c*, 2.18, $CHCl_3$) in dry toluene (15 ml) at 0°. The mixture was stood at 0° for 3.5 hr and worked-up to give a yellow oil, separated on silica (hexane–EtOAc) into four fractions:

(a) **13** (528 mg, 54%) as needles, m.p. 51–53°, $[\alpha]_D^{25}+154°$ (*c*, 1.07, $CHCl_3$).

(b) **10** (178 mg, 19%) as needles, m.p. 54–56°, $[\alpha]_D^{25}+118°$ (*c*, 1.52, $CHCl_3$).

(c) **12** (205 mg, 21%) as a yellow oil, $[\alpha]_D^{25}+106°$ (*c*, 1.07, $CHCl_3$).

(d) **11** (34 mg, 3%) as a yellow oil, $[\alpha]_D^{25}+88°$ (*c*, 3.41, $CHCl_3$).

Tin(IV) *chloride catalysis of cycloaddition*

Investigation of racemisation of **6**. Tin(IV) chloride (2 drops) was added to a soln of **6**, $[\alpha]_D^{24}+203°$ (*c*, 2.20, toluene) in dry toluene (1 ml) at 0°. Work-up after 2 hr gave **6**, $[\alpha]_D^{25}+188°$ (*c*, 4.39, toluene).

Diels–Alder cycloaddition

Tin(IV) chloride (0.3 ml) was added to a soln of cyclopentadiene (0.75 ml, 9.1 mmol) and **6** (486 mg, 1.83 mmol), $[\alpha]_D^{24}+211°$ (*c*, 3.51, $CHCl_3$) in dry toluene (10 ml) at 0°. After 3.5 hr, the mixture was worked-up to give a yellow oil separated on silica to give:

(a) **13** (115 mg, 19%) as needles, m.p. 51–53°, $[\alpha]_D^{25}+100°$ (*c*, 1.72, $CHCl_3$).

(b) **10** (272 mg, 45%) as needles, m.p. 54–56°, $[\alpha]_D^{25}+71°$ (*c*, 2.18, $CHCl_3$).

(c) **12** (17 mg, 3%) as a yellow oil, $[\alpha]_D^{25}+54°$ (*c*, 1.65, $CHCl_3$).

(d) **11** (95 mg, 16%) as a yellow oil, $[\alpha]_D^{25}+54°$ (*c*, 1.25, $CHCl_3$).

Diels–Alder cycloaddition of **9**

A soln of **9** (538 mg, 2.02 mmol), $[\alpha]_D^{25}+421°$ (*c*, 1.05, $CHCl_3$) and cyclopentadiene (0.75 ml, 9.1 mmol) in benzene (10 ml) was heated under reflux for 2 hr. Removal of benzene under reduced pressure gave a pale yellow oil (880 mg) showing 3 spots on TLC (hexane–EtOAc, 1:1). Separation of the product by column chromatography on silica gave 3 fractions:

(a) (+) - *Butyl* 3 - endo - syn - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - endo - *carboxylate* **14** (212 mg, 77%) as needles, m.p. 70–72°. 400 MHz PMR 0.88 (3H, t), 1.27 (2H, m), 1.45 (2H, m), 1.45 (1H, d, J = 9), 1.64 (1H, d, J = 9), 2.37 (3H, s), 3.15 (1H, dd, J = 9.1, J = 3.2), 3.27 (1H, bs), 3.51 (1H, bs), 3.67 (1H, dd, J = 9.1, J = 3.2), 3.82 (1H, m), 3.96 (1H, m), 6.26 (1H, dd, J = 5.3, J = 2.8), 6.62 (1H, dd, J = 5.3, J = 2.8), 7.25 (2H, d, J = 7.0), 7.51 (2H, d, J = 7.0). ^{13}C-NMR δ 13.6, 19.0, 21.4, 30.4, 46.2, 47.7, 48.2, 48.6, 64.6, 70.7, 126.2, 129.5, 135.1, 135.9, 141.4, 141.4, 171.4. *m/e* 332 (M), 316 M (M–O). $[\alpha]_D^{25}+27°$ (*c*, 1.24, $CHCl_3$). Found: C, 68.4; H, 7.4. $C_{19}H_{24}O_3S$ Requires: C, 68.6; H, 7.3%.

(b) (−) - *Butyl* 3 - endo - anti - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - endo - *carboxylate* **16** (20.6 mg, 3%). ^{13}C-NMR δ 13.7, 19.1, 21.5, 30.6, 46.0, 46.6, 48.0, 49.6, 65.0, 74.5, 125.3, 129.9, 133.2, 136.1, 141.2, 142.0, 171.9. *m/e* 332 (M), 316 (M–O). $[\alpha]_D^{25}-177°$ (*c*, 2.06, $CHCl_3$).

(c) (+) - *Butyl* 3 - exo - p - *tolylsulphinylbicyclo*[2.2.1]*hept* - 5 - *ene* - 2 - exo - *carboxylate* **15** (76 mg, 11%). ^{13}C-NMR 13.7, 19.1, 21.4, 30.4, 43.3, 46.8, 47.3, 45.2, 65.0, 67.6, 125.7, 129.8, 137.7, 138.7, 141.0, 141.6, 172.6. *m/z* 332 (M), 316 (M–O). $[\alpha]_D^{25}+33°$ (*c*, 0.72, $CHCl_3$).

Enantiomeric excess determinations using (+) - *2,2,2 - trifluoro - 1 - (9 - anthranyl) - ethanol* **17**

To a soln of (+)-**13** (38.3 mg, 0.115 mmol), $[\alpha]_D^{25}+100°$ (*c*, 2.52, $CHCl_3$) in $CDCl_3$ (0.3 ml) was added **17** in small portions (*ca* 20 mg). The PMR spectrum was recorded after each addition. After the addition of 86 mg (0.311 mmol) the PMR spectrum showed two aromatic Me resonances at δ 2.10 (relative integral 1) and δ 2.21 (relative integral 4.9) indicating an enantiomeric excess of 66%.

A similar procedure with (+)-**16**, $[\alpha]_D^{25}+27°$ (*c*, 1.24, $CHCl_3$) indicated an enantiomeric excess of 82%.

Acknowledgements—We express our warmest thanks to Professor Raphael for suggesting this topic and for his interest and encouragement, to Dr D. Ridley, University of Sydney, Australia, for the measurement of 400 MHz ^1H-NMR spectra and for valuable discussions. The award of New Zealand Universities Research Grants is gratefully acknowledged.

REFERENCES

[1] C. Maignan and R. A. Raphael, *Tetrahedron* **39**, 3245 (1983).

[2] A. S. Atavin, B. A. Trofimov and V. I. Lavrov, *J. Org. Chem. USSR* **8**, 1603 (1972).

[3] W. E. Truce and M. J. Lusch, *J. Org. Chem.* **43**, 2252 (1978); P. Vermeer, J. Meijer and C. Eylander, *Rec. Trav. Chim.* **93**, 240 (1974).

[4] S. Ghersetti, H. Hogeveen, G. Maccagnani, F. Montanari and F. Taddei, *J. Chem. Soc.* 3718 (1963); H. Hogeveen, G. Maccagnani and F. Montanari, *Ibid.* (C) 1585 (1966).

[5a] M. Mikołajczyk, S. Grzejszczak and A. Zatorski, *J. Org. Chem.* **40**, 1979 (1975); [b] M. Mikołajczyk, W. Midura, S. Grzejszczak, A. Zortorski and A. Chefczyńska, *Ibid.* **43**, 473 (1978).

[6] H. C. J. Ottenheijm, S. P. J. M. van Nispen and M. J. Sinnige, *Tetrahedron Letters* 1899 (1976).

[7] U. Marangelli, G. Modena and P. E. Todesco, *Gazz. Chim. Ital.* **90**, 681 (1960).

[8] W. E. Truce and R. F. Heine, *J. Am. Chem. Soc.* **79**, 5311 (1957).

[9] J. Drabowicz and M. Mikołajczyk, *Synthetic Commun.* **11**, 1025 (1981).

[10] W. Oppolzer, M. Kurth, D. Reichlin and F. Moffatt, *Tetrahedron Letters* 2545 (1981).

[11] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry.* Pergamon Press, London (1969).

[12] T. Koizumi, I. Hakamada and E. Yoshi, *Tetrahedron Letters* 87 (1984).

[13] S. M. Proust and D. D. Ridley, *Aust. J. Chem.* **37**, 1677 (1984).

[14] K. Mislow, M. M. Green, P. Laur, J. P. Melillo, T. Simmons and A. L. Ternay, Jr., *J. Am. Chem. Soc.* **87**, 1958 (1965).

[15] L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.* 3109 (1949).