Asymmetric Induction and Racemisation in Allenic Sulphoxides [1]

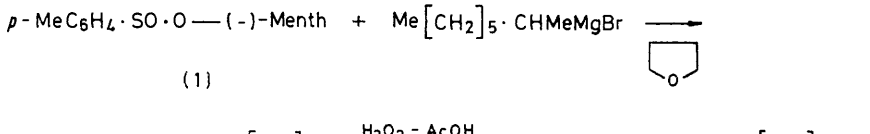
By **Mauro Cinquini, Stefano Colonna,** and **Franco Cozzi,** Università di Milano, Istituto di Chimica Industriale, via C. Golgi, 19, 20133, Milano, Italy
Charles J. M. Stirling,* School of Physical and Molecular Sciences, University College of North Wales, Bangor LL57 2UW

Menthyl sulphinates with Grignard reagents derived from α-acetylenic halides give mixtures of allenic and acetylenic sulphoxides. The extent of asymmetric induction in the allene groups is compared with that obtained in a simple alkyl sulphoxide by use of 1-methylheptylmagnesium bromide. Absolute configurations are assigned to the two chiral centres in the sulphoxides; that of the sulphinyl group follows from that of the sulphinate ester, and that of the allene system is derived from the sign of rotation of the allenic sulphone obtained by oxidation.

Allenic sulphoxides undergo racemisation of the sulphinyl group under conditions in which the chirality of the allene system is unaffected. The activation parameters for the process in which the sulphinyl group is racemised provide evidence for sulphoxide–sulphenate equilibration, and this conclusion is supported by interception, with an amine, of an intermediate sulphenate ester.

OUR objective in this investigation was to examine the extent of asymmetric induction in the synthesis of sulphoxides obtained in the reaction of organometallic compounds with sulphinate esters (the Andersen [2] synthesis), with particular reference to the formation of chiral allene systems.

A wide variety of saturated [3] and unsaturated [4] enantiomerically pure sulphoxides is available from the Andersen synthesis but, surprisingly, the extent of asymmetric induction in the alkyl group obtained when even simple organometallic derivatives are used has not been determined. In an experiment preliminary to our main study, treatment of optically pure (−)-menthyl (−)-(*S*)-toluene-*p*-sulphinate (1) with 1-methylheptylmagnesium bromide (Scheme 1) gave a mixture of the esters (1a and b) were treated with prop-2-ynyl Grignard reagents (4) (Scheme 2). The products were mixtures of allenic (6) and acetylenic (7) sulphoxides (Table 1) and this was consistent with the behaviour [6] of prop-2-ynyl metal derivatives which, in reactions with esters, give mixtures of acetylenic (major) and allenic (minor) ketones. In reactions with the bromide (4; $R^1 = R^2 = Me$, $R^3 = H$) and the esters (1a and b), the mixture (allene predominating) of sulphoxides (6 and 7; a and b; $R^1 = R^2 = Me$, $R^3 = H$) was separated chromatographically. Oxidation of the allenes gave the sulphones (8a and b; $R^1 = R^2 = Me$, $R^3 = H$), $[\alpha]_D$ −29 and +12°, respectively. The *initial* rotation of the sulphoxide (6a; $R^1 = R^2 = Me$, $R^3 = H$), $[\alpha]_D$ −120°, slowly decreased to a steady value of −20° in acetone



Menth = *p*-menthan-3-yl

SCHEME 1

diastereoisomeric sulphoxides (2) which had previously been separated [5] but not quantitatively. Oxidation of the mixture with hydrogen peroxide–acetic acid gave the mixture of enantiomeric sulphones (3) enriched with the (+)-enantiomer to the extent of 9% as judged by comparison of the rotation with that of a specimen claimed to be optically pure.[5] The absolute configuration assigned previously was (+)-(*R*) so that in this case the (−)-(*S*)-sulphinate ester yields a small excess of the ($S_{sulphur}$)(R_{carbon})-sulphoxide.

Against the background of this small degree of asymmetric induction in the sulphinate displacement reaction, solution. When, however, this sulphoxide was recovered and oxidised, the sulphone obtained had the *same rotation as that obtained from freshly prepared sulphoxide.*

Two conclusions follow directly from these results. First, asymmetry is induced in the allene systems under the influence of the chiral sulphinyl group of the sulphinate ester. Secondly, epimerisation at sulphur occurs by a pathway which allows retention of configuration in the allene system.

Asymmetric Induction and Absolute Configuration.— The degree of asymmetric induction involved in the formation of the allenic sulphoxide (6a; $R^1 = R^2 = H$,

[1] Preliminary communication, M. Cinquini, S. Colonna, and C. J. M. Stirling, *J.C.S. Chem. Comm.*, 1975, 256.
[2] K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Amer. Chem. Soc.*, 1964, **86**, 5637.
[3] P. Laur, 'Sulphur in Organic and Inorganic Chemistry,' ed. A. Senning, Dekker, New York, 1972.
[4] D. J. Abbott, S. Colonna, and C. J. M. Stirling, *J.C.S. Perkin I*, 1976, 492, and references cited therein.
[5] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simons, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1965, **87**, 1958.
[6] H. G. Viehe, 'Chemistry of Acetylenes,' Dekker, New York, 1960.

R^3 = Me) is calculable from the earlier observation [7] that thermal rearrangement of the sulphinate ester (9) prepared from but-3-yn-2-ol of 12.5% optical purity gave the sulphone (8a; $R^1 = R^2 = H$, R^3 = Me), $[\alpha]_D$ −7.8°. In initial experiments, the sulphone derived from the allenic sulphoxide had $[\alpha]_D$ +27.6° and therefore an optical purity of about 44%, in agreement with ^1H n.m.r. determinations on the sulphoxide. This value is based on the assumption that the pathway from 1-methylprop-2-ynyl toluene-*p*-sulphinate to the sulphone is completely stereospecific. In some experiments, the degree of asymmetric induction obtained *via* the prop-2-ynyl Grignard reagent was as high as 60%. Induction in the direct formation of the allene system is therefore much greater than that obtained from a simple secondary organomagnesium derivative.

Empirical rules have been formulated to allow the assignment of absolute configuration to allene systems based on the sign of rotation and *vice versa*.[8] As with the application of Brewster's rules,[9] the polarisability sequence of the substituents is required and, in the case of allenic sulphones, this is clearly $RSO_2 >$ alkyl > H. The absolute configurations of the allenic sulphones assigned in this way are in Table 2. Assignment of configurations to the allene systems of the sulphoxides follows from assignment to the allene system of the sulphones. The Andersen synthesis has been shown [5] unequivocally to occur with inversion of configuration at sulphur in the sulphinate ester, which, in turn, is of known absolute configuration from *X*-ray studies.[10] Complete assignment of configuration to the allenic sulphoxides can, therefore, be made.

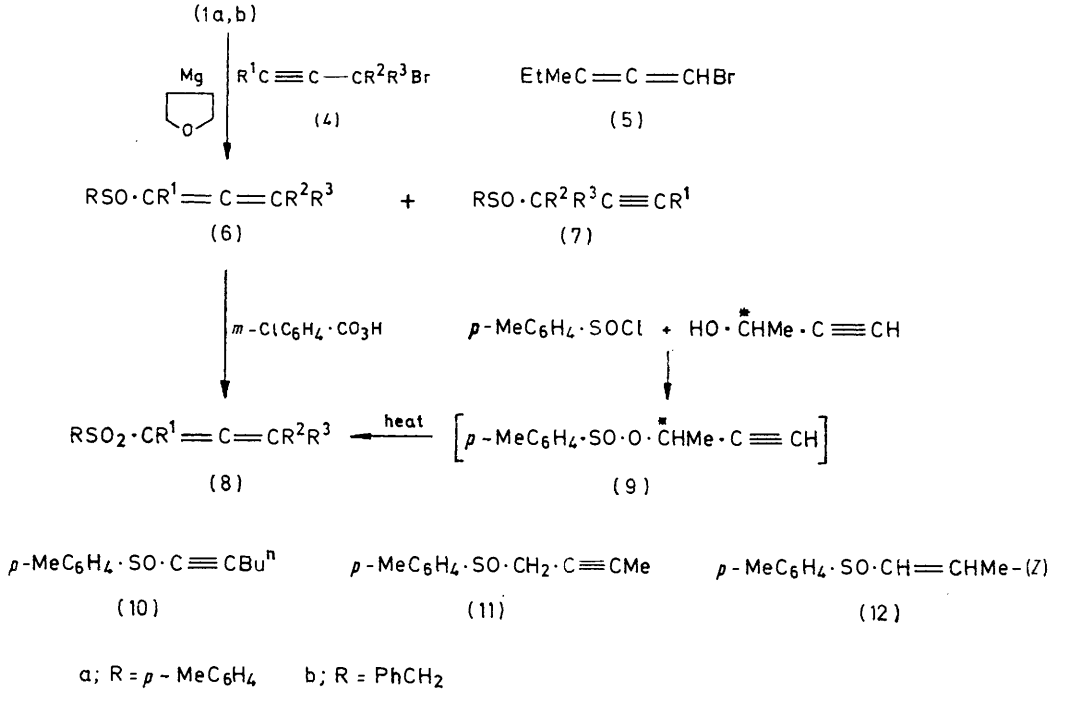
The tertiary prop-2-ynyl bromide (4; R^1 = H, R^2 =

TABLE 1

Allenic and acetylenic sulphoxides

Halide	Allenic sulphoxide [a]	$[\alpha]_D^{25}$ (°) [b]	Acetylenic sulphoxide [a]	$[\alpha]_D^{25}$ (°)	Overall yield (%)	Acetylene : allene ratio
MeC≡C·CH_2Br	ArSO·CMe=C=CH_2	−342	ArSO·CH_2·C≡CMe [c]	+68	62	25 : 75
EtC≡C·CH_2Br	ArSO·CEt=C=CH_2 [d]	−253	ArSO·CH_2·C≡CEt [e]	+41	50	30 : 70
MeC≡C·CHMeBr	ArSO·CMe=C=CHMe	−120	ArSO·CHMe·C≡CMe		48	13 : 87
	$PhCH_2$·SO·CMe=C=CHMe	+173			42	
Bu^nC≡C·CHMeBr	ArSO·CBu^n=C=CHMe [g]	−25 [h]	ArSO·CHMe·C≡CBu^n		36	17 : 83
HC≡C·CHMeBr	ArSO·CH=C=CHMe [j]	−106 [o,h]	ArSO·CHMe·C≡CH [k,l]	+11.7 [h]	50	60 : 40
HC≡C·CHPr^{n}Br	ArSO·CH=C=CHPr^n	−68.7 [o]	ArSO·CHPr^n·C≡CH [m,n]	+76.3	64	47 : 53
HC≡C·CMeEtBr	ArSO·CH=C=CMeEt [o]	−223 [o,h,p]			50	
EtMeC=C=CHBr					70	

[a] Ar = *p*-MeC_6H_4. [b] In Me_2CO. [c] n_D^{26} 1.5751. [d] n_D^{26} 1.5738. [e] n_D^{18} 1.5082. Contaminated with allene. [g] n_D^{22} 1.5540. [h] In $CHCl_3$. [j] n_D^{23} 1.5830. [k] n_D^{23} 1.5758. [l] Sulphone, $[\alpha]_D^{25}$ +8° (*c* 3 in $CHCl_3$). [m] n_D^{18} 1.5650. [n] Sulphone, $[\alpha]_D^{25}$ −4.8° (*c* in $CHCl_3$). [o] n_D^{21} 1.5675. [p] Of diastereoisomer giving allene with larger $[\alpha]_D$.



SCHEME 2

[7] G. Smith and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1971, 1530.
[8] G. Lowe, *Chem. Comm.*, 1965, 411.
[9] G. Krow, *Topics Stereochem.*, 1970, **5**, 31.
[10] H. F. Herbrandson and C. M. Cusano, *J. Amer. Chem. Soc.*, 1961, **83**, 2124.

TABLE 2

Absolute configurations of allenic sulphoxides and sulphones

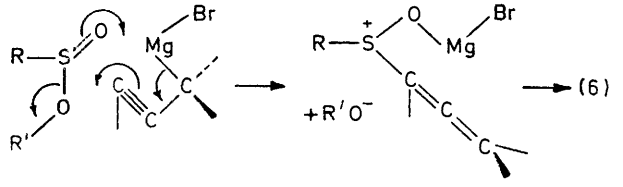
	X = SO [a]	X = SO_2	$[\alpha]_D^{25}$ (°)
ArX·CMe=C=CHMe	S_aR_{allene}	*R*	−29 [b]
$PhCH_2$·X·CMe=C=CHMe	R_aS_{allene}	*S*	+12 [c]
ArX·CBu^n=C=CHMe	S_aS_{allene}	*S*	+6 [c]
ArX·CH=C=CHMe	S_aS_{allene}	*S*	+28 [c]
ArX·CH=C=$CHPr^n$	S_aS_{allene}	*S*	+55 [c]
ArX·CH=C=CMeEt	S_aR_{allene}	*R*	−18 [c,d]

[a] Specific rotations in Table 1. [b] In Me_2CO. [c] In $CHCl_3$. [d] Of sulphone derived from more negatively rotatory sulphoxide diastereoisomer.

Me, R^3 = Et) and the allenic bromide (5) in Grignard reactions with the sulphinate ester (1a) each gave the sulphoxide (6a; R^1 = H, R^2 = Me, R^3 = Et). Oxidation of the diastereoisomeric mixture gave inactive sulphone (8a; R^1 = H, R^2 = Me, R^3 = Et), but when the diastereoisomeric sulphoxides were separated chromatographically, subsequent oxidation gave the optically active enantiomers of the sulphone.

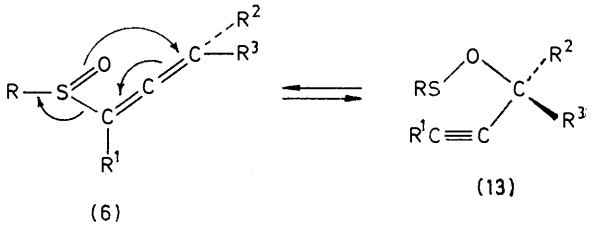
Reactions of sulphinic esters with Grignard reagents derived from α-acetylenic halides give both allenic and acetylenic sulphoxides. The latter are minor products when non-terminal acetylenic halides are used, but predominate in reactions with secondary prop-2-ynyl halides (Table 1). Oxidation of the acetylenic sulphoxides yields optically active acetylenic sulphones, demonstrating that asymmetric induction occurs in the formation of the S–C bond in this case also. For the sulphoxides (7a; R^1 = R^2 = H, R^3 = Pr^n), the diastereoisomer ratio shown by a ^1H n.m.r. spectroscopic study of the mixture is 33 : 66, indicating the degree of induction. In this case, it is not possible to assign the absolute configuration of the carbon centre in the major diastereoisomer because of the absence of reference compounds. The results for allenes and acetylenes thus demonstrate the transmission of chirality from sulphur to carbon centroaxially for the allenes and from centre to centre in the alkyl and acetylenic sulphoxides.

Alternatively, allenic sulphoxides may arise from prop-2-ynyl Grignard derivatives because of co-ordination of the metal centre to the sulphinyl group of the sulphinate ester (Scheme 3). This suggestion has precedent in earlier work with allyl sulphoxides [11] and in reactions of allylmagnesium derivatives with ketones [12,13] and orthoformates.[14] The degree of asymmetric induction in the present reactions is substantial and effective chirality transfer is to be expected from such a sterically constrained process if it is a significant contributor to the overall reaction.



SCHEME 3

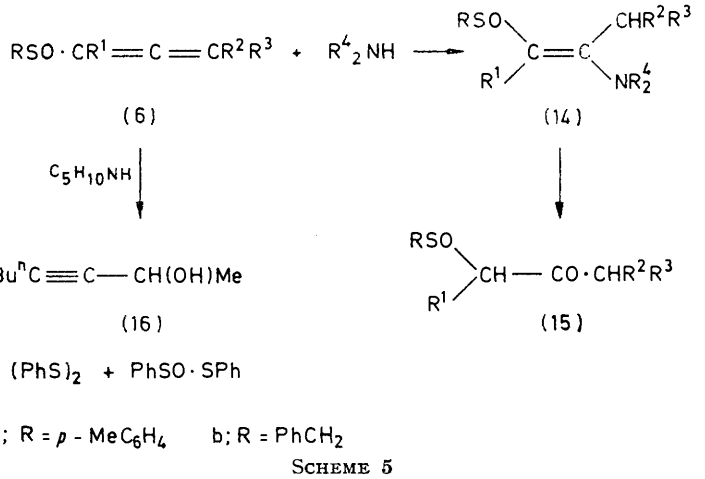
Racemisation in Allenic Sulphoxides.—The observation that, in an allenic sulphoxide, epimerisation of the sulphinyl group occurs under mild conditions without a corresponding change in the enantiomeric purity of the allene system, is striking. Mislow [15–18] and his collaborators have defined the structural parameters which affect the ease of sulphinyl group epimerisation. In simple dialkyl, alkyl aryl, and diaryl sulphoxides,[16] epimerisation occurs, but at high temperatures, and pyramidal inversion is suggested. In compounds in which the C–S bond is weak, *e.g.* benzylic sulphoxides, epimerisation is shown [17] to occur by dissociation–recombination involving radicals which may be diverted from recombination. The third type of situation arises in allylic sulphoxides for which a low-activation 2,3-sigmatropic rearrangement involving formation of an achiral sulphenate ester (13) (Scheme 4) can occur.[18] In the present case, the dissociation–recombination pathway can be ruled out. Vinylic, and, by implication allenic, radicals do not maintain configurational integrity,[19] and epimerisation at sulphur would be accompanied by allene epimerisation. To allow a distinction between pyramidal inversion and sigmatropic rearrangement, both of which preserve stereochemical integrity in the allene, activation parameters for sulphinyl epimerization in the sulphoxide (6a; R^1 = Et, R^2 = R^3 = H) have been determined: $\Delta G^{\ddagger}_{298}$ 24 kcal mol^{-1}, $\Delta H^{\ddagger}$ 22 kcal mol^{-1}, and $\Delta S^{\ddagger}$ −5.4 cal mol^{-1} K^{-1}. These values are similar to those obtained [18] for the racemisation of allylic sulphoxides, in which it is clear that the process occurs by sulphoxide–sulphenate equilibration. The activation parameters are very different from the pyramidal inversion [16] pathway in which $\Delta G^{\ddagger}_{298}$ values are *ca.* 36 kcal mol^{-1}. Pyramidal inversion can thus be excluded unless the allene system is playing a role in reducing $\Delta G^{\ddagger}_{epimerisation}$. This seems improbable because the alk-1-ynyl, alk-2-ynyl, and alk-1-enyl sulphoxides (10)—



SCHEME 4

[11] P. Bickhart, R. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.
[12] R. H. De Wolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.
[13] J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 494.
[14] Y. Pasternak and J. C. Trayhard, *Bull. Soc. chim. France*, 1966, 356 and references cited therein.
[15] K. Mislow, *Rec. Chem. Progr.*, 1967, **28**, 217.
[16] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.
[17] E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4861.
[18] P. B. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.
[19] J. W. Wilt in ' Free Radicals,' vol. 1, ed. J. K. Kochi, Wiley, New York, 1973, p. 458.

(12), respectively, are all optically stable under the conditions which cause epimerisation of sulphoxides (6). We thus prefer sulphoxide–sulphenate equilibration to pyramidal inversion, and this also nicely explains the retention of configuration in the allene system while the sulphinyl group undergoes epimerisation (Scheme 4). In this equilibration, chirality is transferred specifically between the alkene system of the sulphoxide and the asymmetric carbon atom of the prop-2-ynyl group. Transfer of chirality in the opposite sense, (9) to (8), has been observed previously,[7] and provides further evidence for sulphenate–sulphoxide equilibration. Further, treatment of prop-2-ynyl alcohols with chlorophosphines leads directly to allenic phosphine oxides,[20] and prop-2-ynyl phosphites [21] give allenyl phosphates spontaneously.



SCHEME 5

The products of both reactions clearly result from 2,3-sigmatropic rearrangements, but there is no information on the stereospecificity of these processes.

The kinetics of epimerisation of several allenic sulphoxides have been determined. Results are in Table 3.

TABLE 3

Rates of racemisation of allenic sulphoxides [a]

Sulphoxide	10^5k/s^{-1}
p-MeC$_6$H$_4$·SO·CEt=C=CH$_2$	12.0 [b]
PhCH$_2$·SO·CMe=C=CHMe	4.5
p-MeC$_6$H$_4$·SO·CH=C=CHMe	2.6
p-MeC$_6$H$_4$·SO·CH=C=CHPr^n	0.7
p-MeC$_6$H$_4$·SO·CH=C=CMeEt *	3.8
p-MeC$_6$H$_4$·SO·CH=C=CMeEt *	3.4

* Diastereoisomers.

[a] At 40 °C in acetone. [b] $\Delta G^{\ddagger}$ 24 ± 0.3 kcal mol^{-1}, $\Delta H^{\ddagger}$ 22 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ −5.4 ± 1 cal mol^{-1} K^{-1}.

The diastereoisomeric compositions of the sulphoxides (6a; R^1 = R^2 = H, R^2 = Me) and (6a; R^1 = R^2 = H, R^3 = Pr^n) are unknown and hence the racemisation rate constants are mean values for the two diastereoisomers; there is little difference between diastereoisomers as the last two entries in the Table show. In the allenes, there is little steric interference with the attainment of the cyclic transition state for the sigmatropic rearrangement, and there is consequently little response of rate to structural variation. This is in contrast to the measurements made by Jones and his collaborators [22] on allylic steroidal sulphoxides in which substantial variation of rate constant with structure, especially configuration at sulphur, is found.

Another simple line of evidence for sulphenate–sulphoxide equilibration as the cause of epimerisation of allylic sulphoxides is the interception of the sulphenate ester (13) by nucleophilic attack at sulphur. This has been achieved with amines [23] and thiophiles such as phosphites [24] and thiols.[25] Thiols, however, readily add to electrophilic allenes [26,27] and addition of dibenzylamine to the sulphoxide (6b; R^1 = R^2 = R^3 = H) gives a mixture of enamines (14a; R^1 = R^2 = R^3 = H, R^4 = PhCH$_2$) [28] (Scheme 5). The enamines (14; SO$_2$ for SO) derived from the corresponding sulphones (6; SO$_2$ for SO) are hydrolysed [29] readily to the ketones (15; SO$_2$ for SO), and in the present work addition of piperidine to to the optically active sulphoxide (6a; R^1 = Me, R^2 = R^3 =H) gave the enamine (14a; R^1 = Me, R^2 = R^3 = H, R$^4_2$ = C$_5$H$_{10}$) which on chromatography on alumina gave the optically inactive mixture of diastereoisomeric sulphoxides (15a; R^1 = Me, R^2 = R^3 = H), identical with that obtained by oxidation of the corresponding sulphide. In this case, addition to the allene system is preferred to interception of the prop-2-ynyl sulphenate, whose formation is responsible for sulphinyl epimerisation. Asymmetric induction in addition of amines to αβ-unsaturated sulphoxides has been observed previously;

[20] A. P. Boiselle and N. A. Meinhardt, *J. Org. Chem.*, 1962, **27**, 1828.
[21] V. Mark, *Tetrahedron Letters*, 1962, 281.
[22] D. N. Jones, J. Blenkinsopp, A. C. F. Edmonds, El Helmy, and R. J. K. Taylor, *J.C.S. Perkin I*, 1973, 2602.
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[24] R. D. G. Cooper and F. L. Jose, *J. Amer. Chem. Soc.*, 1970, **92**, 2575.
[25] D. A. Evans, G. C. Andrews, and C. L. Sims, *J. Amer. Chem. Soc.*, 1971, **93**, 4956.
[26] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.
[27] J. W. Batty, P. D. Howes, and C. J. M. Stirling, *J.C.S. Perkin I*, 1973, 59.
[28] C. H. McMullen and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1966, 1217.
[29] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.

failure to detect induction in this case can be attributed to the rapid racemisation, under basic conditions, of ketones bearing a chiral centre adjacent to the carbonyl group.[30]

By contrast, the sulphoxide (6; R = Ph, R^1 = Bu^n, R^2 = Me, R^3 = H) on treatment with piperidine gives only the interception product (16) and the accompanying diaryl sulphide and thiolsulphinate. Capmau [31] has found similar results in that chromatography on alumina of the sulphoxide (6a; R^1 = Ph, R^2 = R^3 = H) gives 3-phenylprop-2-yn-1-ol. The balance between interception of the sulphenate ester and addition of amine to the electrophilic allene system is a delicate one which depends on structure in a manner not at present clear. Addition to electrophilic alkenes is strongly inhibited by alkyl substituents [32] and, on this basis, the success of interception with substituted allenic sulphoxides is understandable. In a wide-ranging study of the synthesis and reactivity of allenic sulphoxides, Horner and Binder [33] have found that 2,3-sigmatropic rearrangement occurs in the *adducts* of allenic sulphoxides with nucleophiles such as alkoxides, thiolates, and amines.

EXPERIMENTAL

General

Light petroleum had b.p. 40—60 °C. Ether was dried over sodium and tetrahydrofuran was distilled from lithium aluminium hydride. Extractions were performed with dichloromethane and extracts were dried over Na_2SO_4. ^1H N.m.r. spectra were recorded with a Varian A-60 and/or a Varian HA 100 instrument; i.r. spectra were recorded on a Perkin-Elmer 377 spectrometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. (−)-Menthyl (−)-(*S*)-toluene-*p*-sulphinate, $[\alpha]_D^{25}$ −200 ° (*c* 2.0 in Me_2CO) {lit.,[34] $[\alpha]_D^{25}$ −202° (*c* 2.0 in Me_2CO)} and (−)-menthyl (+)-(*R*)-toluene-α-sulphinate, $[\alpha]_D^{25}$ +105° (*c* 2.0 in $CHCl_3$) {lit.,[35] $[\alpha]_D^{25}$ +105° (*c* 2 in $CHCl_3$)} were prepared as previously described. 1-Bromobut-2-yne,[36] 1-bromopent-2-yne,[36] 4-bromopent-2-yne,[37] 2-bromo-oct-3-yne,[38] 3-bromobut-1-yne,[39] 3-bromohex-1-yne,[40] 3-bromo-3-methylpent-1-yne,[41] and 1-bromo-3-methylpenta-1,2-diene [42] were prepared according to literature methods.

Reaction of 1-*Methylheptylmagnesium Bromide with Menthyl Toluene*-p-*sulphinate* (with G. Griffiths).—2-Bromo-octane (5.799 g, 0.03 mol) in tetrahydrofuran (40 ml) was treated with magnesium (0.72 g, 0.03 g atom) and the solution was added dropwise with stirring to menthyl toluene-*p*-sulphinate (6 g, 0.02 mol) in toluene (50 ml). The mixture was added to saturated aqueous ammonium chloride and extraction gave the diastereoisomeric mixture of 1-methylheptyl *p*-tolyl sulphoxides (9.6 g) $[\alpha]_D^{25}$ +99.75° (*c* 1 in $CHCl_3$).

The mixture of sulphoxides (3 g) was kept with aqueous hydrogen peroxide (30% w/v; 30 ml) in acetic acid (60 ml) at 100 °C for 1 h. The mixture was poured into water and extraction gave crude sulphone (3 g), which was kept at 40 °C and 0.1 mmHg for 3 h. The resultant waxy solid had m.p. 46°, n_D^{19} 1.5138 (supercooled), $[\alpha]_D^{25}$ +0.90° (*c* 1 in $CHCl_3$) (Found: C, 66.8; H, 9.3, Calc. for $C_{15}H_{24}O_2S$: C, 66.9; H, 9.3%). The material was chromatographed (thick-layer plates) on silica in light petroleum (b.p. 60—80 °C)–ether (5 : 1). The first pass gave material with $[\alpha]_D^{25}$ 0.85° and a second $[\alpha]_D^{25}$ 0.90°.

Authentic 1-methylheptyl *p*-tolyl sulphone was prepared by treatment of sodium toluene-*p*-thiolate with 1-methylheptyl bromide in ethanol and oxidation of the sulphide [b.p. 146° at 0.3 mmHg, n_D^{25} 1.5228 (lit.,[5] b.p. 118° at 0.25 mmHg)] with hydrogen peroxide in acetic acid as before. It had n_D^{25} 1.5105 (Found: C, 66.7; H, 9.45%).

Synthesis of Optically Active Allenic and Acetylenic Sulphoxides.—The Grignard reagent was prepared by dropwise addition of acetylenic or allenic bromide (0.02 mol) to a stirred suspension of magnesium turnings (0.02 g atom) in anhydrous ether (30 ml) in the presence of catalytic amounts of mercury(II) chloride. When most of the magnesium had dissolved, the mixture was cooled to −40 °C. A solution of (−)-menthyl (−)-(*S*)-toluene-*p*-sulphinate or (−)-menthyl (+)-(*R*)-toluene-α-sulphinate in anhydrous ether (50 ml) was rapidly added, and the mixture was allowed to reach room temperature and stirred overnight. The reaction was quenched by addition of saturated ammonium chloride solution and the aqueous layer was extracted. The combined organic phases were concentrated on a rotatory evaporator, below 10 °C. The residue was chromatographed on silica with ether–light petroleum (2 : 8 and then 1 : 1) as eluant. In the case of terminal acetylenes or allenes, the formation of the Grignard reagent was favoured by irradiating the reaction vessel with a 300 W lamp.[41] With 2-bromo-oct-3-yne, activated magnesium, prepared from magnesium(II) chloride and potassium [42] in tetrahydrofuran, was used.

I.r. spectra of neat allenic sulphoxides showed the characteristic sulphoxide band at 1 060—1 030 cm^{-1} and the allenic absorption at 1 965—1 950 cm^{-1}. Non-terminal acetylenic sulphoxides had an absorption at 2 240—2 220 cm^{-1}, whereas in the case of terminal derivatives a strong band at 3 300—3 200 cm^{-1} occurred together with a weak band at 2 100 cm^{-1}. ^1H N.m.r. spectra were in agreement with assigned structures. Allenic and acetylenic sulphoxides were characterised by oxidation to the corresponding sulphones (Table 4) and in some cases through independent synthesis.

3-*Methylpenta*-1,2-*dienyl* p-*Tolyl Sulphoxide.*—This was obtained by the reaction of the Grignard reagent derived from 3-bromo-3-methylpent-1-yne or from 1-bromo-3-methylpenta-1,2-diene, as a mixture of diastereoisomers. Oxidation of part of the mixture afforded almost inactive sulphone. The second portion was chromatographed (SiO_2; gradient elution) to give two diastereoisomerically enriched fractions, $[\alpha]_D^{25}$ −223° and −173° (*c* 1.0 in $CHCl_3$), which

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were separately oxidized to the enantiomeric sulphones, $[\alpha]_D^{25}$ −18° and +9.5° (*c* 3.0 in $CHCl_3$), respectively.

Hex-1-ynyl p-*Tolyl Sulphoxide*.—Hex-1-ynylmagnesium bromide, prepared from ethylmagnesium bromide and hex-1-yne in anhydrous ether, was treated with (−)-menthyl (−)-(*S*)-toluene-*p*-sulphinate, $[\alpha]_D^{25}$ −200° (*c* 1.0 in Me_2CO) (1 mol. equiv.). The usual work-up afforded the acetylenic *sulphoxide* (70%), $[\alpha]_D^{20}$ +91° (*c* 1.0 in Me_2CO), n_D^{21} 1.5548 (Found: C, 70.9; H, 7.3. $C_{13}H_{16}OS$ requires C, 70.9; H, 7.3%).

Racemic Allenic Sulphoxides.—Racemic allenic sulphoxides were prepared according to literature methods [33] by reactions of benzene- or toluene-*p*- sulphenyl chloride with the appropriate acetylenic alcohol in the presence of triethylamine (method A) or phenyl-lithium (method B).

Buta-1,2-dienyl phenyl sulphoxide (35% by method A) was a 75 : 25 mixture of diastereoisomers (by ^1H n.m.r. spectroscopy).

4-*Phenylsulphinylocta*-2,3-*diene* (31% by method A) was a 55 : 45 mixture of diastereoisomers (by ^1H n.m.r.), n_D^{21} 1.5610 (Found: C, 66.9; H, 7.2. $C_{12}H_{18}OS$ requires C, 67.2; H, 7.2%). The diastereoisomeric ratio remained unaltered on heating a solution of the mixture of sulphoxides in chloroform at 40 °C for 18 h.

4-p-*Tolylsulphinylocta*-2,3-*diene* (33% by method A) was a 57 : 43 mixture of diastereoisomers (by ^1H n.m.r.), n_D^{22} 1.5410 (Found: C, 72.3; H, 8.0. $C_{15}H_{20}OS$ requires C, 72.5; H, 8.1%).

3-Phenylbuta-1,2-dienyl phenyl sulphoxide [33] (35% by method B) was a 60 : 40 mixture (by ^1H n.m.r.) and was chromatographed on silica gel with gradient elution. Two fractions having diastereoisomeric ratios of 24 : 76 and 79 : 21 were separately dissolved in chloroform and kept at 40 °C for 18 h to afford the equilibrium mixture of diastereoisomers in the ratio 45 : 55.

Synthesis of Racemic Acetylenic Sulphoxides.—Sulphoxides were prepared by oxidation of the corresponding sulphides with *m*-chloroperbenzoic acid (1 mol. equiv.) in chloroform at 20 °C for 24 h.

But-2-ynyl *p*-tolyl sulphoxide (60% from the sulphide, b.p. 100 °C at 0.4 mmHg, n_D^{20} 1.5810) had n_D^{26} 1.5751 (Found: C, 68.6; H, 6.35. $C_{11}H_{12}OS$ requires C, 68.7; H, 6.3%).

3-p-*Tolylsulphinylbut*-1-*yne* (80% from the sulphide, b.p. 120 °C at 6 mmHg, n_D^{23} 1.5635) was obtained as a diastereoisomeric mixture in the ratio 65 : 35 (by ^1H n.m.r.), opposite to that (33 : 67) for the mixture prepared *via* the Grignard reaction. The compounds were characterized by oxidation to the corresponding sulphones (below).

Allenic and Acetylenic Sulphones.—Allenic and acetylenic sulphoxides obtained *via* the Grignard reaction (above) were oxidized with a stoicheiometric quantity of *m*-chloroperbenzoic acid at 20 °C for 24 h and purified by column chromatography (silica; light petroleum–ether, 8 : 2). Details are in Table 4. Some representative compounds were prepared independently by oxidation of the corresponding racemic sulphoxides or sulphides.

4-p-*Tolylsulphonylocta*-2,3-*diene* (70% from the sulphoxide) had n_D^{22} 1.5410 (Found: C, 68.3; H, 7.7. $C_{15}H_{20}O_2S$ requires C, 68.1; H, 7.6%).

Buta-1,2-dienyl *p*-tolyl sulphone (70% from the sulphoxide) had m.p. 47–48° (lit.,[7] 47—48°).

But-2-ynyl *p*-tolyl sulphone (65% from the sulphide) had m.p. 71° (lit.,[7] 71°).

4-p-*Tolylsulphonylpent*-2-*yne* (72% from the sulphide) had n_D^{20} 1.6568, m.p. 60—61° (Found: C, 64.6; H, 6.2. $C_{12}H_{14}O_2S$ requires C, 64.8; H, 6.35%).

3-p-*Tolylsulphonylbut*-1-*yne* (75% from the sulphide; 70% from the mixture of diastereoisomeric sulphoxides) had m.p. 81° (Found: C, 63.2; H, 5.8. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8%).

TABLE 4

Allenic and acetylenic sulphones

Sulphone [a]	Yield (%)	M.p. (°C)	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
$ArSO_2{\cdot}CMe{=}C{=}CH_2$	80	64—65	63.3	5.8	$C_{11}H_{12}O_2S$	63.4	5.8
$ArSO_2{\cdot}CEt{=}C{=}CH_2$	70	56—57	64.6	6.4	$C_{12}H_{14}O_2S$	64.8	6.35
$ArSO_2{\cdot}CMe{=}C{=}CHMe$	62	36—38	64.7	6.4	$C_{12}H_{14}O_2S$	64.8	6.35
$PhCH_2{\cdot}SO_2{\cdot}CMe{=}C{=}CHMe$	93	43—45	65.0	6.35	$C_{12}H_{14}O_2S$	64.8	6.35
$ArSO_2{\cdot}CBu^n{=}C{=}CHMe$	68	*b*	68.1	7.6	$C_{15}H_{20}O_2S$	68.1	7.6
$ArSO_2{\cdot}CH{=}C{=}CHMe$	92	43—44	63.5	5.85	$C_{11}H_{12}O_2S$	63.4	5.8
$ArSO_2{\cdot}CH{=}C{=}CHPr^n$	80	*c*	66.1	6.8	$C_{13}H_{16}O_2S$	66.1	6.8
$ArSO_2{\cdot}CH{=}C{=}CMeEt$	75	72—73 [d]	65.9	6.8	$C_{13}H_{16}O_2S$	66.1	6.8
$ArSO_2{\cdot}CH_2{\cdot}C{\equiv}CMe$	72	70—71 [e]					
$ArSO_2{\cdot}CHMe{\cdot}C{\equiv}CH$	81	88—89	6.33	5.9	$C_{11}H_{12}O_2S$	63.4	5.8
$ArSO_2{\cdot}CHPr^n{\cdot}C{\equiv}CH$	65	65—67	66.2	6.7	$C_{13}H_{16}O_2S$	66.1	6.8

[a] Ar = *p*-MeC_6H_4. [b] n_D^{22} 1.5110. [c] n_D^{21} 1.5510. [d] Of sulphone derived from more negatively rotatory sulphoxide diastereoisomer. [e] Lit.,[26] m.p. 71°.

Reactions of Allenic Sulphoxides with Piperidine.—The sulphoxide (1 mmol) and piperidine (2.5 mmol) in anhydrous diethyl ether (15 ml) or anhydrous chloroform (5 ml) was kept at room temperature for 24 h. The solvent was distilled off and the residue was chromatographed (SiO_2; gradient elution).

(*a*) 3-*p*-Tolylsulphinylbuta-1,2-diene afforded 3-p-*tolylsulphinylbutan*-2-*one* (40%) as a mixture of diastereoisomers (60 : 40 by ^1H n.m.r.), n_D^{18} 1.5560 (Found: C, 62.8; H, 6.6. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7%), together with minor amounts of di-*p*-tolyl sulphide and *S*-*p*-tolyl toluene-*p*-thiosulphinate, identified by comparison with authentic samples. ^1H N.m.r. analysis of the crude mixture before column chromatography showed the presence of the intermediate enamine. The structure of the ketone was confirmed by independent synthesis (below). When the reaction was repeated, starting from the optically active allenic sulphoxide, racemic oxo-sulphoxide was obtained.

(*b*) 3-Phenyl-buta-1,2-dienyl phenyl sulphoxide gave 1-*phenylsulphinyl*-3-*phenylbutan*-2-*one* (47%) as a diastereoisomeric mixture (57 : 43) (Found: C, 70.7; H, 5.9. $C_{16}H_{16}O_2S$ requires C, 70.6; H, 5.9%) together with starting material (40%). Column chromatography (silica; gradient elution) afforded fractions enriched in each one of the two diastereoisomers which were separately oxidized to afford 1-*phenylsulphonyl*-3-*phenylbutan*-2-*one*, m.p. 110° (from cyclohexane) (Found: C, 66.8; H, 5.7. $C_{16}H_{16}O_3S$ requires C, 66.7; H, 5.6%).

(*c*) 4-Phenylsulphinylocta-2,3-diene afforded oct-3-yn-2-ol (40%) together with diphenyl disulphide, *S*-phenyl benzenethiosulphinate and unidentified products. The alcohol was identified by comparison with an authentic sample (i.r., ^{1}H n.m.r., and refractive index).

(*d*) 4-*p*-Tolylsulphinylocta-2,3-diene gave oct-3-yn-2-ol (38%), n_D^{22} 1.4563 (lit.,[43] n_D^{25} 1.4503), together with *p*-tolyl disulphide, *S*-*p*-tolyl toluene-*p*-thiosulphinate, and unidentified products.

3-p-*Tolylthiobutan*-2-*one*. Treatment of 3-chlorobutan-2-one (0.1 mol) with potassium toluene-*p*-thiolate (0.1 mol) in ethanol (100 ml) gave the sulphide (55%), b.p. 115—120° at 0.8 mmHg, n_D^{20} 1.5532 (Found: C, 67.9; H, 7.4. Calc. for $C_{11}H_{15}OS$: C, 68.0; H, 7.25%) (lit.,[44] b.p. 150—152° at 13 mmHg, n_D^{20} 1.5515).

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3-p-*Tolylsulphinylbutan*-2-*one*. The sulphoxide was obtained as a mixture of diastereoisomers (60 : 40 by ^{1}H n.m.r.) by oxidation of the corresponding sulphide with an equimolecular amount of *m*-chloroperbenzoic acid. It had n_D^{18} 1.5564.

Racemisation Kinetics.—The solution was contained in a temperature-controlled polarimeter cell, and rotations were continuously recorded as a function of time over a period of two to four half-lives. Values were determined after at least ten half-lives. First-order rate constants and activation parameters were calculated as described in ref. 45.

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[6/569 *Received*, 25*th March*, 1976]

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