Regiospecificity of Methylation of Unsymmetrical Stilbenes by Methylsulphinylmethanide

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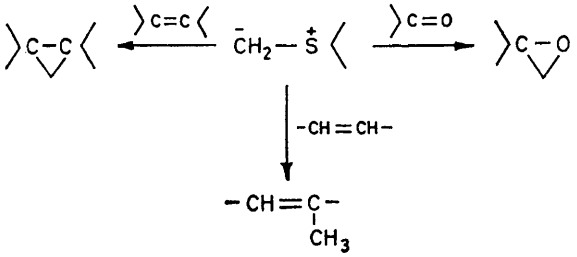
Treatment of (*E*)-2-methylstilbene with methylsulphinylmethanide (DMSO⁻) for short periods produces a mixture of α′,2-dimethylstilbene (6) (>95% *E*-) and methyl 3-phenyl-2-(*o*-tolyl)propyl sulphoxide (22), from which (6) can be separated in *ca.* 50% yield. Longer periods of reaction give a 4 : 5 mixture of α,2-dimethylstilbene [(10) + (11)] and methyl 3-phenyl-4-(*o*-tolyl)butyl sulphoxide (29). (*Z*)-2-Methylstilbene gives identical products with DMSO⁻ under similar conditions. Convenient syntheses of the *Z*- and *E*-isomers of α,2- and α′,2-dimethylstilbenes [(6), (7), (10), and (11)] and of the methyl 2-phenyl-3-(*o*-tolyl)propyl sulphoxides (21) and (22) are reported, and studies of their reactions with DMSO⁻ are described. The reaction of the sulphoxide (22) with DMSO⁻ produces a 2 : 1 mixture of (10) and (11) exclusively, whereas a similar reaction of the isomeric sulphoxide (21) gives a mixture of the stilbene (6) and the butyl sulphoxide (29), the proportion varying with the time of reaction; long periods of reaction between (21) and DMSO⁻ give only (29). The sulphoxide (29) also results from the reaction of (6) and 2-phenyl-3-(*o*-tolyl)propene (36) with DMSO⁻. By contrast α,2-dimethylstilbene does not react further with DMSO⁻. The α-(α′-)methylation process by DMSO⁻ is rationalised in terms of a nucleophilic addition–prototropic shift–β-elimination–isomerisation sequence, and an explanation for the 'apparent' regiospecificity of α- and α′-methylation of 2-methylstilbene under the different reaction conditions is presented.

Methylation of the 2,6-dimethylstilbene (41) with DMSO⁻ is almost totally (>95%) regiospecific and produces largely the α-methylstilbene products [(42) + (43)] and the α-sulphoxide (52); <1% α′-methylstilbene (47) was produced. The 2,2′,6,6′-tetramethylstilbene (59) does not react with DMSO⁻.

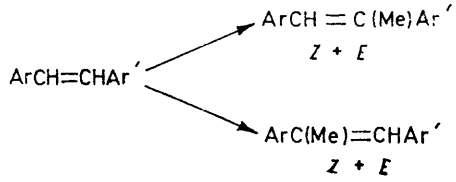
Sulphonium ($R_2\overset{+}{S}-\bar{C}H_2$) and sulphoxonium [$R_2\overset{+}{S}(O)\bar{C}H_2$] methylides and sulphinylmethanides [$R\overset{+}{S}(\bar{O})-\bar{C}H_2$] have enjoyed widespread use as reagents in organic synthesis,[1] particularly for methylene insertions across the double bond of a carbonyl group or an electrophilic olefin (see Scheme 1). These ylides can also function, to differing extents, as reagents for *C*-methyl transfer to certain olefinic bonds, *e.g.* some condensed aromatic and styryl systems, *etc.*[2] Neither the synthetic potential nor the reaction mechanism for this *C*-methylation method has yet been fully examined. In connection with development of synthetic routes to α-alkyl stilbenes of potential biological importance, this paper reports an examination



Scheme 1

of the regio- and stereo-specificity of α-methylation of unsymmetrically *ortho*-substituted stilbenes with methylsulphinylmethanide [$MeSO\bar{C}H_2 \leftrightarrow Me\overset{+}{S}(\bar{O})-\bar{C}H_2$] (DMSO⁻) (see Scheme 2).

2-Methylstilbene was chosen as a suitable model compound. Authentic samples of the *Z*- and *E*-isomers, and of α,2- and α′,2-dimethylstilbene, the expected mono-α-methylation products, were synthesised as outlined in Scheme 3. The 1 : 1 mixture of *Z*- and *E*-isomers [(2) and (3)] of 2-methylstilbene, prepared by Wittig condensation between benzaldehyde and the ylide derived from the phosphonium salt (1a), was separated by column chromatography, and the configurations of the isomers followed from their spectral data; the relevant n.m.r. data are summarised on formulae (12) and (13). In addition, iodine-catalysed isomerisation of the isomer assigned the *Z*-configuration quantitatively converted it into the thermodynamically more stable *E*-isomer. α,2- and α′2-Dimethylstilbene were separately prepared from the deoxybenzoin (4) formed by Friedel–Crafts acylation of benzene by *o*-tolylacetyl chloride (1b). Reaction between (4) and methylmagnesium iodide, followed by dehydration of the resulting alcohol (5) in acetic acid–polyphosphoric acid, produced a 9 : 1 mixture of *E*- and *Z*-isomers [(6) and (7)] of α′,2-dimethylstilbene. A similar mixture of isomers of α′,2-dimethylstilbene was formed by Wittig condensation between acetophenone and the ylide from (1a), but this procedure was less convenient. A 1 : 2 mixture of *E*- and *Z*-isomers [(10) and (11)] of α,2-dimethylstilbene was prepared from (4) by methylation (MeI–NaH) to give (8), reduction to (9) with



Scheme 2

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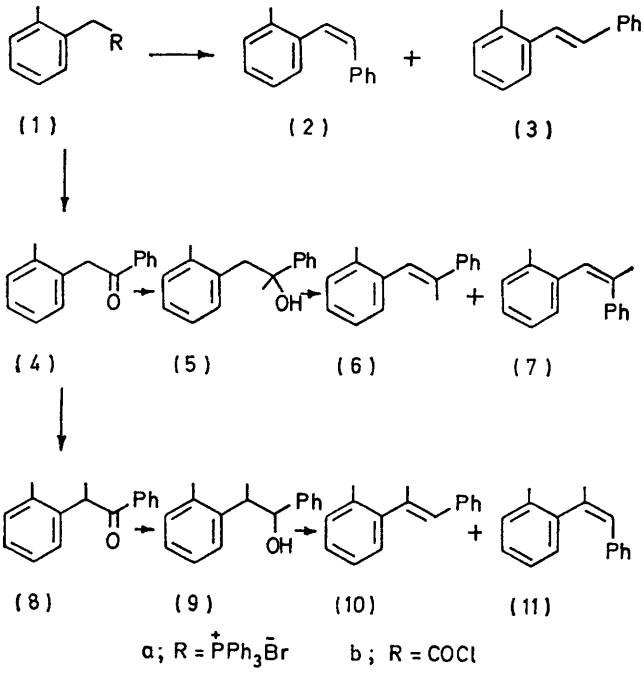
[1] For recent reviews see (*a*) T. Durst, *Adv. Org. Chem.*, 1969, **6**, 285; (*b*) P. A. Lowe, *Chem. and Ind.*, 1970, 1070; (*c*) L. Field, *Synthesis*, 1972, 101; (*d*) 'Organic Compounds of Sulphur, Selenium, and Tellurium,' Chem. Soc. Specialist Periodical Reports, vols. 1 and 2.

[2] *Cf.* (*a*) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345; (*b*) P. A. Argabright, J. E. Hoffman, and A. Schriesheim, *J. Org. Chem.*, 1965, **30**, 3233; (*c*) C. Walling and L. Bollyky, *ibid.*, 1964, **29**, 2699; (*d*) G. A. Russell and S. A. Weiner, *ibid.*, 1966, **31**, 248; (*e*) M. Feldman, S. Danishefsky and R. Levene, *ibid.*, 1966, **31**, 4322; (*f*) B. M. Trost, *Tetrahedron Letters*, 1966, 5761; (*g*) H. Nozaki, Y. Yamamoto, and R. Noyori, *ibid.*, 1966, 1123.

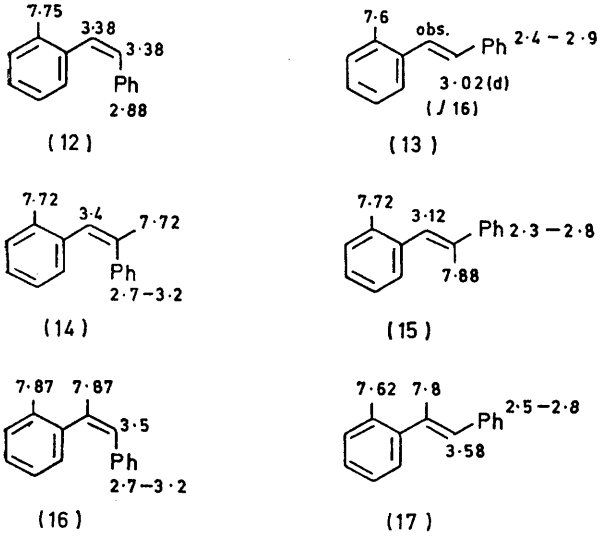
lithium aluminium hydride, and dehydration. The usual acidic dehydrating procedures were not successful



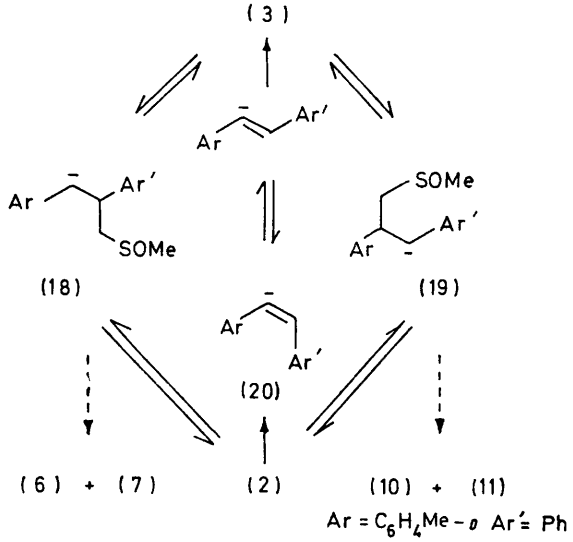
SCHEME 3

when applied to (9); we found it necessary to use fused potassium hydrogen sulphate. The individual isomers [(6), (7), (10), and (11)] were conveniently separated by g.l.c., and their configurations followed from spectral data. The relevant n.m.r. data are summarised on formulae (14)—(17).

In preliminary investigations of the selectivity of methylation of (3) by $DMSO^-$, the *E*-isomer was first treated with $DMSO^-$ at 70° for 2 h. Chromatographic



separation of the hydrocarbon products (*ca.* 40%), followed by g.l.c. and n.m.r. spectral comparison with authentic (6), (7), (10), and (11) showed that greater than 95% α-methylation had taken place [leading to a 7 : 3 mixture of (10) and (11)] and less than 5% α′-methylation [leading to only the *E*-isomer (6)]. No starting material [(3) or (2)] was found amongst the hydrocarbon products. Unfortunately, the *Z*-isomers (7) and (11) were not completely resolved on g.l.c. The relative percentages of (7) and (11) were obtained by integration of their olefinic proton (τ 3·4 and 3·5) and vinyl and aryl methyl (τ 7·72 and 7·87) resonances in the n.m.r. spectra of mixtures of *Z*- and *E*-isomers, and also of the mixture of *Z*-isomers obtained by preparative g.l.c. When the same reaction between (3) and $DMSO^-$ was terminated after just 2 min, analysis of the isolated α- and α′-methylation hydrocarbon products (*ca.* 55%) revealed that only *ca.* 5% α-methylation had occurred [leading to a 2 : 1 mixture of (10) and (11)], and that α′,2-dimethylstilbene (6) constituted *ca.* 92% of the methylated product [<2% (7) was produced].

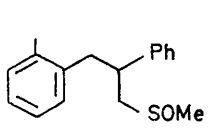


SCHEME 4

These preliminary studies indicated that methylation of (3) by $DMSO^-$ could be controlled to produce either α- or α′-methylated product. This conclusion was substantiated by analysing the hydrocarbon products at various intervals of time; this clearly showed the gradual disappearance of α′-methylated and accumulation of α-methylated product. Furthermore, these initial data suggested a mechanism for the formation of (6), (7), (10), and (11) involving a reversible first stage, no doubt leading to the anions (18) and (19), which under kinetic control leads to (18) [the precursor of (6) and (7)] and under thermodynamic control to (19) [the precursor of (10) and (11)]. An examination of the reaction between (2) and $DMSO^-$ showed that after 2 min the hydrocarbon product consisted of *ca.* 25% of the *E*-isomer (3) of (2), 11% (6), and *ca.* 60% starting *Z*-isomer (2). This observed $Z \longrightarrow E$ isomerisation might be interpreted as support for a fast reversible addition–elimination first stage [leading to (18) and (19)], but in

the case of *Z*-stilbene itself Cram and Hunter [3] have clearly shown by isotope techniques that the isomerisation to *E*-stilbene in DMSO–DMSO$^-$ does not take place by an addition–elimination mechanism (at 26°), but rather through the vinyl anion (20; Ar = Ar′ = Ph). Presumably the same situation applies to (2) and (3), though we have no evidence on this point.

The combined yield of hydrocarbon products [(6), (7), (10), and (11)] formed from methylation of (3) with DMSO$^-$, under all reaction conditions investigated, never exceeded 50%. Further examination of the reaction mixtures showed that other compounds were concurrently formed, and examination of their structures enabled us to present a rational explanation for the



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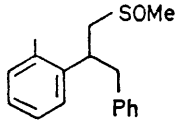
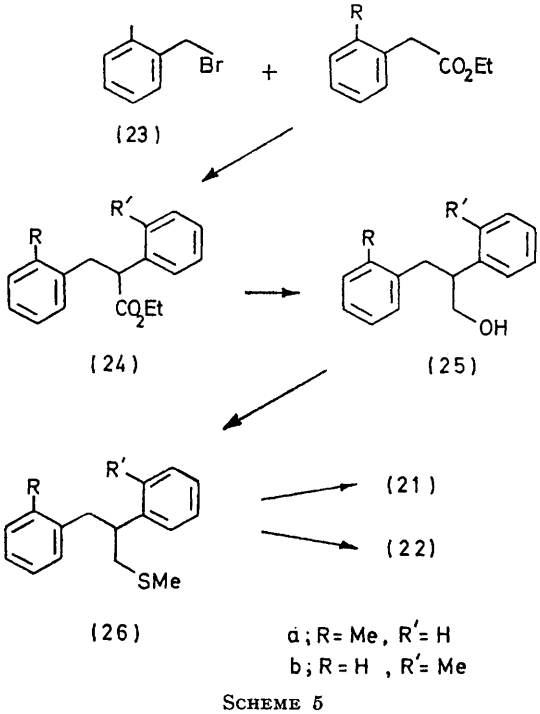


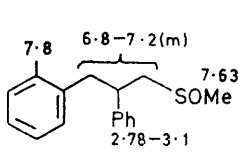
(22)

observed ' selectivity ' of α-methylation of (3) under the conditions employed. Thus, chromatography of the crude product from the 2 min methylation of (3) separated a crystalline polar compound, m.p. 73—74°, ($C_{17}H_{20}OS$) which exhibited spectral data interpretable in terms of structure (21) or (22). Authentic samples of the sulphoxides (21) and (22) were synthesised according to Scheme 5. Alkylation of ethyl phenylacetate by the bromide (23) followed by reduction of the resulting

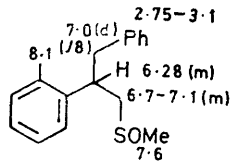


Scheme 5

ester (24a), gave the carbinol (25a). Reaction of the tosylate from (25a) with sodium methanethiolate then gave the sulphide (26a), which was converted into (21) by oxidation with periodate. The sulphoxide was obtained as a diastereoisomeric mixture, m.p. 119—120°, and displayed a strong S=O band in the i.r. at 1039 cm^{-1},

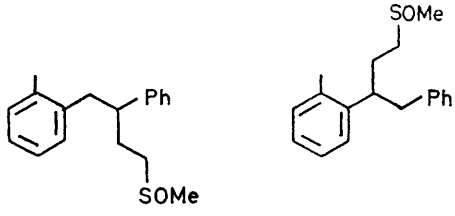


(27)

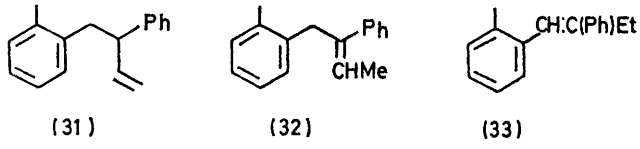


(28)

and an n.m.r. spectrum [see formula (27)] consistent with the formulation (21). The isomeric sulphoxide (22) was prepared by a similar route from ethyl *o*-tolylacetate; it was also obtained as a mixture of diastereoisomers, m.p. 73—74°, $\nu_{max.}$ 1050 cm^{-1}; for n.m.r. data see formula (28). The sulphoxide (22) was indistinguishable (spectra



(29) (30)



(31) (32) (33)

and mixed m.p.) from the sulphoxide obtained from reaction of (3) with DMSO$^-$ for 2 min.

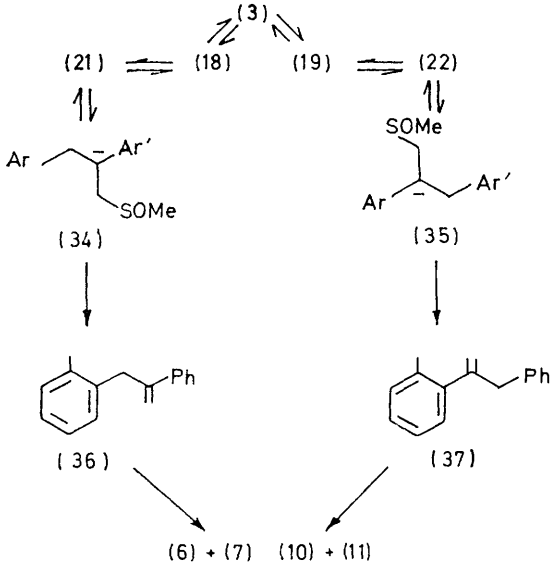
A homologous sulphoxide, which exhibited spectral data consistent with either structure (29) or (30), was separated in up to 50% yield from the 2 h reaction between (3) and DMSO$^-$. Structure (29) was confirmed by the results of thermal elimination of methanesulphenic acid [to give the butene (31)] and base-catalysed isomerisation of the latter to a *Z*–*E*-mixture of the known alkenes (32) and (33) (see following paper).

The isolation of the sulphoxides (22) and (29) from the reaction between (3) and DMSO$^-$ suggested that the ' selectivity ' observed in the α-methylation of (3) to either [(6) + (7)] or [(10) + (11)] was fortuitous, and that their formation could be accounted for as shown in Scheme 6. Initial nucleophilic addition of DMSO$^-$ to (3) leads to a mixture of sulphoxide carbanions (18) and (19). A slight preference (as suggested by the ratios of sulphoxide to methylated stilbene products formed in both the 2 min and 2 h reactions) for formation of the carbanion (18) is observed, and this arises presumably

[3] D. J. Cram and D. H. Hunter, *J. Amer. Chem. Soc.*, 1966, **88**, 5765.

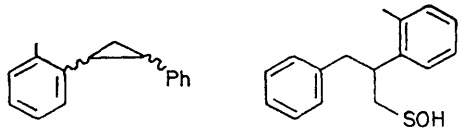
because of the greater (steric) accessibility of the α′-centre in (3). The addition may be a reversible process since the *Z*-isomer (2) is isomerised to the *E*-isomer (3) in the DMSO⁻–DMSO medium, but as outlined earlier this isomerisation might also proceed *via* the corresponding vinyl anions. Isomerisation of the carbanions (18) and (19) to the carbanions (34) and (35), respectively, probably involving DMSO solvent, followed by β-elimination of methanesulphenate anion, then produces the styrenes (36) and (37), which are isomerised to *Z*–*E*-mixtures of α- and α′-methyl homologues [(6) + (7) and (10) + (11), respectively].

The sulphoxide anion (18) is less stabilised than its isomer (19) (both steric and electronic effects), and this feature accounts for the isolation of only α-sulphoxide (22) from the 2 min reaction; during this period the more reactive sulphoxide anion (18) which had been

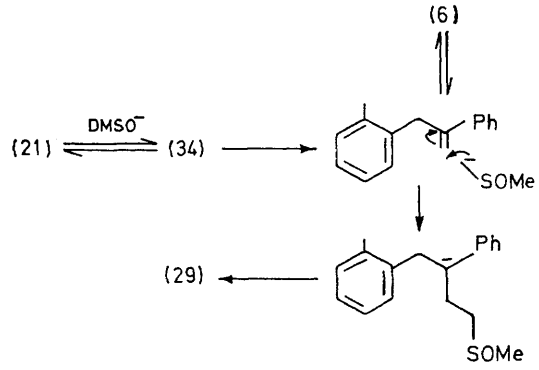


SCHEME 6

formed was almost quantitatively converted into a mixture of (6) and (7). When the authentic sulphoxide (21) was treated with DMSO⁻ for 5 min, a 70% yield of a 9 : 1 mixture of (6) and (7) was produced. The only other product isolated was the homologous sulphoxide (29), formed in up to 28% yield; no evidence was obtained for the accompanied formation of the ' crossed ' α-methylation products [(10) + (11)] (from a reversed elimination–addition–elimination sequence) or for cyclopropane ring formation [*viz.* (38), from γ-elimination of



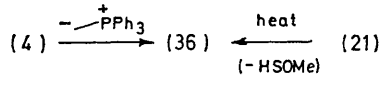
methanesulphenate anion; see following paper] or for products of type (39), expected from a Sommelet–Hauser-type rearrangement.[4] The homologous sulphoxide (29) was the sole product isolated when the



SCHEME 7

sulphoxide (21), (*E*)-2-methylstilbene (3), or the authentic styrene (36) was treated with DMSO⁻ for long periods; its formation from (21) is thus rationalised according to Scheme 7. In contrast, both the isomeric sulphoxide (22) and the styrene (37) gave only a 3 : 2 mixture of (10) and (11) even after prolonged treatment with DMSO⁻. Authentic samples of the styrenes (36) and (37) were conveniently obtained by thermal β-elimination of methanesulphenic acid from the corresponding sulphoxides; the styrene (36) was also prepared by a Wittig reaction of the deoxybenzoin (4).

The foregoing data thus indicate that methylation of (3) by DMSO⁻ is not ' selective ' in the sense that it produces quantitatively either α- or α′-methylated products. What they do show however, is that by appropriate choice of reaction times either pure α- or α′-methylated product can be exclusively isolated in upwards of 55% yield. The relative stabilities of the first-formed sulphoxide carbanions [*i.e.* (18) *versus* (19)] clearly play an important part in determining this feature of the reaction. Because it is less stabilised, the carbanion (18) is rapidly converted into its isomer (34), the immediate precursor of the styrene (36), and the α-methylstilbene [(6) + (7)] can be isolated in *ca.* 55% yield after 2 min reaction time. Over prolonged periods

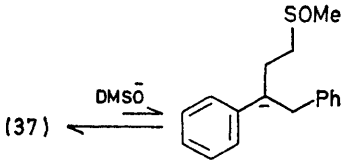


SCHEME 8

of reaction the sulphoxide anion (19) is slowly converted into a mixture of (10) and (11), whereas [(6) + (7)] reacts further with DMSO⁻, *via* the styrene (36), to give the sulphoxide (29). In separate experiments, the α-methylstilbene was recovered unchanged after prolonged treatment with DMSO⁻. This fortuitous lack of reactivity, necessary for the successful isolation of [(6) + (7)], is due either to a low proportion of styrene (37) in the equilibrium mixture of (37), (10), and (11) or

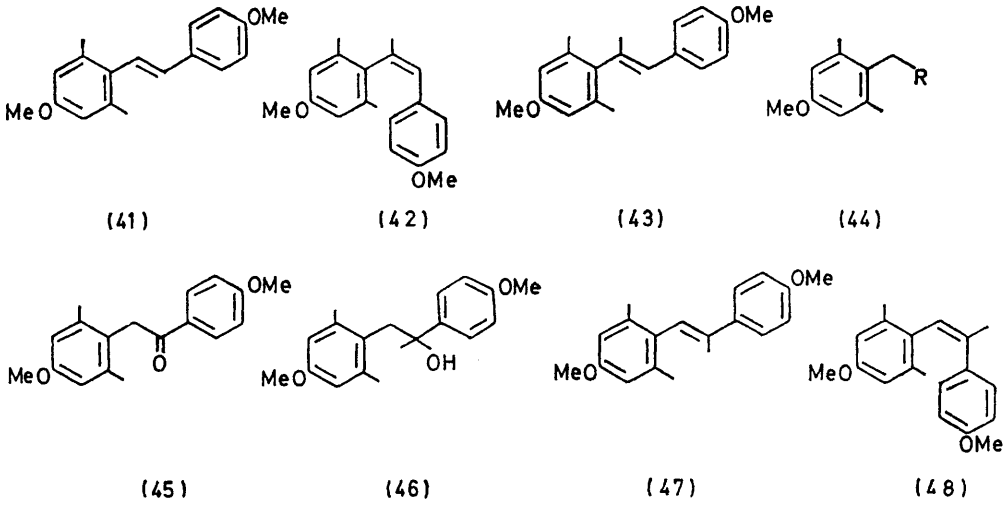
[4] *Cf.* B. S. Thyagarajan, *Mech. Mol. Rearrangements*, 1971, **3**, 297; D. A. Archer, *J. Chem. Soc.* (*C*), 1971, 1329.

to the instability of the sulphoxide carbanion (40) from (37) and $DMSO^-$, or perhaps to a combination of both features.



(40)

We also examined the methylation of the 2,6-dimethylstilbene (41) by $DMSO^-$. This molecule was prepared either from the deoxybenzoin (45), by reduction



(41) (42) (43) (44)

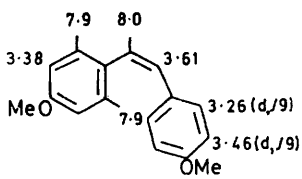
(45) (46) (47) (48)

SCHEME 9

with lithium aluminium hydride and dehydration, or by Wittig olefin-forming condensations between the appropriate monoarene intermediates.[5] Methylation of (41) by $DMSO^-$ was found to be almost totally selective. It produced a mixture of monomethylation products, corresponding to *ca.* 75% total yield, and a sulphoxide product corresponding to *ca.* 11% yield. Separation and analysis of the monomethylation products showed the presence of compounds (42), (43), and (47) in the approximate proportions 21 : 3 : 1. Compound (47) was identified by chromatographic and spectral comparison with an authentic sample. Authentic samples of both the *E*- (47) and *Z*- (48) isomers of the α′,2,6-trimethylstilbene were prepared either by Wittig condensation between the salt (44; R = $\overset{+}{P}Bu_3\bar{B}r$) and *p*-methoxyacetophenone or from deoxybenzoin (45) [Grignard reaction to (46) and dehydration [5]].

Structures (42) and (43) were assigned to the other monomethylation products on the basis of g.l.c. and spectral comparison, both with one another and with the isomeric α′-methylstilbenes (47) and (48). (*Z*)-α,2,6-Trimethylstilbene (42) showed the same g.l.c. retention time as (48), and the *E*-isomer (43) ran almost concurrently with (47). Similar comparative g.l.c. data were obtained for the related stilbene series (6), (7), (10), and (11). N.m.r. data for the two α-methyl isomers are summarised on formulae (49) and (50). Both the arylmethyl signals and all the aryl proton signals of the *Z*-isomer (42) occur at higher field than the corresponding resonances of the *E*-isomer. This suggests that the *Z*-isomer prefers a conformation in which these protons all lie above the adjacent phenyl rings and are shielded by them [*viz.* (51)].

Spectral analysis of the sulphoxide product obtained from treatment of (41) with $DMSO^-$ was consistent with either structure (52) or (53). Thermal elimination of methanesulphenic acid from the sulphoxide produced a liquid alkene whose spectral data could be interpreted in terms of either structure (54) or (55). A distinction was made by unambiguous synthesis of the latter alkene



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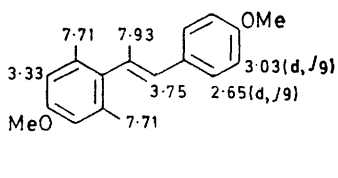

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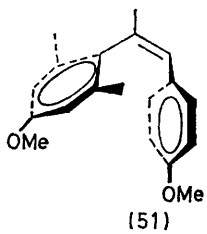
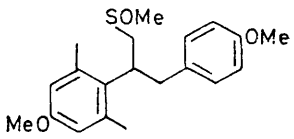


(51)

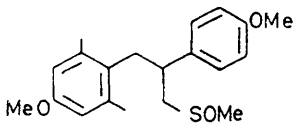
(55) by a Wittig reaction from the deoxybenzoin (45). This produced the styrene (55), m.p. 88—89°, exhibiting spectral data [see formula (55)] different from those

[5] B. G. James, Ph.D. Thesis, University of Wales, 1973.

for the liquid styrene produced from pyrolysis of the unknown sulphoxide [*cf.* τ values on formulae (54) and (55)]. The α-substituted structure (52) thus followed for the sulphoxide product obtained from (41) and $DMSO^-$.

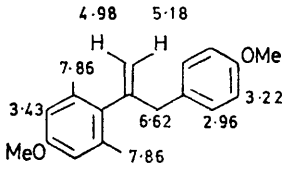


(52)

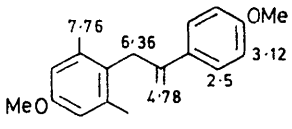


(53)

'heat'



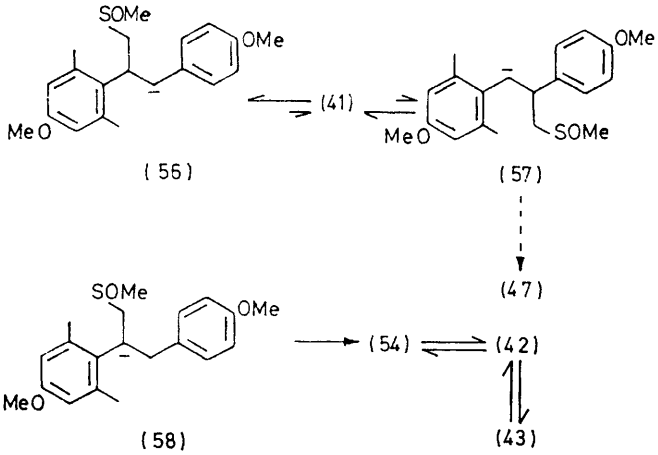
(54)



(55)

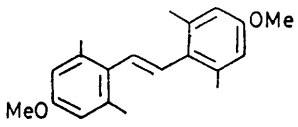
(45)

The main feature to emerge from the studies of the methylation of (41) by $DMSO^-$ is that the reaction is highly position specific, leading almost entirely (>95%) to α-substituted product(s). These data support the idea that the reaction is controlled largely by the relative

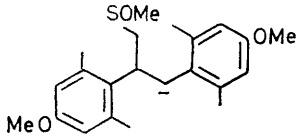


stabilities of the first-formed carbanions (56) and (57). Although the α'-centre in (41) is much more sterically accessible towards nucleophilic attack by $DMSO^-$, the resultant carbanion (57) is so destabilised that the equilibrium lies heavily on the side of starting stilbene (41).* Attack at the α-centre in (41), however, produces the relatively stable isomeric carbanion (56), which in time, is isomerised to (58) the precursor of (54) and the α-methylstilbenes (42) and (43).

The conclusion regarding the importance of intermediate carbanion stability in the foregoing system was substantiated when attempts were made to methylate the 2,2',6,6'-tetramethylstilbene (59) [6] with $DMSO^-$. In this case only starting material was recovered under several different conditions. Apparently even the first-formed carbanion (60) is so destabilised as to preclude reaction with $DMSO^-$.



(59)



(60)

EXPERIMENTAL

M.p.s are corrected. N.m.r. spectra were determined with a Perkin-Elmer R10 or R14 spectrometer as indicated, with tetramethylsilane as internal standard. Bands were singlets except where stated otherwise. Molecular weights were determined from mass spectra, measured with an A.E.I. MS9 double-focusing spectrometer.

Preparative g.l.c. separations were carried out on 25% Apiezon L (10 ft × ⅜ in column) and analytical g.l.c. was performed on 10% Apiezon L (5 ft × ⅛ in column) at the temperatures specified.

Dimethyl sulphoxide was dried prior to use by vacuum distillation from pulverised calcium hydride. The anion $DMSO^-$ was prepared as outlined earlier.[1a] Unless stated otherwise all organic solutions were dried over anhydrous magnesium sulphate.

(E)- *and* (Z)-2-*Methylstilbene* [(2) *and* (3)].—*o*-Methylbenzyltriphenylphosphonium bromide [7] (11·2 g) was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·6 g)] in DMSO (40 ml) at 25°, and the solution was stirred at 25° for 0·25 h. Benzaldehyde (2·8 g) was added, and the mixture was stirred for 0·5 h and then poured into water (400 ml) and extracted with ether. Evaporation of the dried extracts left a solid residue which was triturated with light petroleum (60—80°). Evaporation of the light petroleum and distillation of the residue gave a 1 : 1 mixture (g.l.c.; 180°) of *Z*- and *E*-isomers of the stilbene (2·8 g, 60%), b.p. 108—110° at 0·75 mmHg. Chromatography of the distillate on silica gel (u.v. control) with 1% ether in light petroleum (b.p. 40—60°) as eluant gave: (i) (Z)-2-*methylstilbene* (eluted first), n_D^{22} 1·6009, $\lambda_{max.}$ 263 nm (ε 7350); $\nu_{max.}$ (film) 1603, 1576, 945, 920, 830, 780, 770, 735, and 695 cm^{-1}; τ see formula (12) (Found: C, 92·9; H, 7·6. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%), and (ii) (E)-2-*methylstilbene*, m.p. 31—32°, $\lambda_{max.}$ 297 nm (ε 20,100); $\nu_{max.}$ (film) 1603, 1576, 965, 760, 745, 715, and 690 cm^{-1}; τ see formula (13) (Found: C, 92·9; H, 7·3%).

Unresolved stilbene fractions were combined and isomerised to the *E*-isomer as follows. The stilbene mixture (1 : 1; 0·9 g) in glacial acetic acid (10 ml) containing iodine (30 mg) was boiled under reflux for 5 h, and then cooled to

* It seems necessary to propose an equilibrium addition–elimination scheme in this instance.

[6] W. H. Laarhoven, R. J. F. Nivard, and E. Havinga, *Rec. Trav. chim.*, 1961, **80**, 775.

[7] C. E. Griffin and M. Gordon, *J. Organometallic Chem.*, 1965, **3**, 414.

25°. The iodine was removed by washing with sodium thiosulphate solution and the mixture was then poured into water (100 ml) and extracted with ether (3 × 20 ml). Evaporation of the dried extracts and chromatography of the residue, as before, gave the (*E*)-stilbene (70% recovery) identical with that obtained previously.

2′-Methyldeoxybenzoin (4).—A solution of *o*-tolylacetic acid (15 g) in dry benzene (100 ml) was treated in portions during 0·5 h with phosphorus pentachloride (21 g). The mixture was stirred for 0·25 h and then evaporated to dryness to leave the acid chloride as an oil. The acid chloride in benzene (50 ml) was then added dropwise over 0·25 h to a cooled (0—5°), stirred suspension of freshly pulverised aluminium chloride (15 g) in dry benzene (100 ml). The mixture was boiled under reflux for 2 h, then cooled and poured onto iced 50% hydrochloric acid (500 ml). The mixture was thoroughly extracted with ether, and the combined ether–benzene extracts were washed successively with water, sodium hydrogen carbonate solution, and water, then dried and evaporated. Distillation of the residue (b.p. 128—130° at 0·1 mmHg) produced a solid (14 g, 72%) which crystallised from methanol to give the *ketone*, as needles, m.p. 62—62·5°, $\nu_{max.}$ (mull) 1690 cm^{-1}, τ 2·0 (2H, dd, *J* 9 and 2 Hz), 2·4—2·7 (3H, m), 2·8—2·95 (4H, m), 5·78 (CH_2·CO), and 7·78 (Me) (Found: C, 85·7; H, 6·3. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%).

(E)- *and* (Z)-2,α′-*Dimethylstilbene* [(6) *and* (7)].—(a) *From 2′-methyldeoxybenzoin* (4). The deoxybenzoin (3 g) in dry ether (25 ml) was added to a solution of methylmagnesium iodide [from magnesium (1 g)] in ether (50 ml), and the mixture was heated under reflux for 0·5 h. The ether was then replaced by dry benzene (75 ml), and the resulting solution was boiled under reflux for 3 h, then cooled, and poured onto ice-saturated ammonium chloride. The benzene solution was separated, washed (H_2O), dried, and evaporated to leave 2-phenyl-3-*o*-tolylpropan-2-ol (3·4 g) as an oil, $\nu_{max.}$ (film) 3420 cm^{-1}, which was dehydrated without further purification.

A solution of the alcohol in glacial acetic acid (50 ml) containing polyphosphoric acid (6 drops) was boiled under reflux for 14 h, and then poured onto ice–water and extracted with ether. The extracts were washed with sodium hydrogen carbonate solution and water, then dried and evaporated. Distillation of the residue produced a 1 : 9 mixture (g.l.c.) of *Z*- and *E*-stilbenes (2·3 g, 77%) as an oil, b.p. 112—114° at 0·05 mmHg. The isomers were separated by preparative g.l.c. (180°) to give: (i) (Z)-2,α′-*dimethylstilbene* (eluted first), $\lambda_{max.}$ 260 nm (ε 7400); $\nu_{max.}$ (film) 1603, 1580, 1500, 840, 770, 760, 740, and 705 cm^{-1}; τ see formula (14) (Found: *m/e* 208·1252. $C_{10}H_{16}$ requires *M*, 208·1252), and (ii) (E)-2,α′-*dimethylstilbene*, n_D^{20} 1·6118, $\lambda_{max.}$ 263 nm (ε 13,300), $\nu_{max.}$ (film) 1603, 1580, 1500, 800, 770, 750, and 700 cm^{-1}; τ see formula (15) (Found: C, 92·5; H, 7·9. $C_{16}H_{16}$ requires: C, 92·3; H, 7·7%).

(b) *From* o-*methylbenzyltriphenylphosphonium bromide* (1a). The salt [7] (4·5 g) was added to a solution of DMSO$^-$ [from sodium hydride (0·22 g)] in DMSO (30 ml), and the solution was stirred at 25° for 0·25 h. Acetophenone (1·2 g) was added, and the mixture was stirred for 3 h, and then poured into water (100 ml) and extracted with ether. Evaporation of the washed (H_2O) and dried extracts, followed by chromatography of the residue (silica gel; 3% ethyl acetate–benzene) produced a mixture of *Z*- and *E*-isomers of the stilbene (0·2 g, 10%) in the ratio 1 : 9 (by g.l.c.). The two isomers were separated by g.l.c. (as before) and were spectrally identical with those obtained in (a).

2′,α-Dimethyldeoxybenzoin (8).—A solution of 2′-methyldeoxybenzoin (6 g) in dry toluene (25 ml) was added to a suspension of sodium hydride (0·7 g) in dry toluene (75 ml), and the mixture was stirred and boiled under reflux for 1 h. The solution was cooled, and freshly distilled methyl iodide (12 g) was introduced at 25°. The mixture was heated under reflux for 12 h, then cooled and filtered. The filtrate was diluted with ether (100 ml) and was then washed (H_2O), dried, and evaporated. Distillation of the residue gave the *ketone* (5 g, 80%), b.p. 126—130° at 0·05 mmHg, which solidified and was recrystallised from aqueous methanol; m.p. 54—54·5°, $\nu_{max.}$ (mull) 1688 cm^{-1}; τ 2·16 (2H, dd, *J* 9 and 2 Hz), 2·5—3·0 (m, 7 ArH), 5·25 (q, *J* 7 Hz, C*H*Me), 7·53 (Me), and 8·55 (d, *J* 7 Hz, CH*Me*) (Found: C, 85·65; H, 6·9. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

(E)- *and* (Z)-2,α-*Dimethylstilbene* (10) *and* (11).—A solution of 2′,α-dimethyldeoxybenzoin (5 g) in dry ether (25 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0·4 g) in ether (75 ml) at such a rate that the ether refluxed gently. The mixture was boiled under reflux for 2·5 h, then cooled (ice–water) and cautiously treated with water to decompose the excess of hydride. Dilute hydrochloric acid was then added until two clear phases resulted. The ether phase was separated, dried, and evaporated to leave 1-phenyl-2-*o*-tolylpropan-1-ol (3·6 g, 75%) as an oil, $\nu_{max.}$ (film) 3550 and 3420 cm^{-1}, which was dehydrated without further purification.

The alcohol (1·1 g) and fused potassium hydrogen sulphate (3·5 g) were heated together at 250° for 1 h, and the mixture was then cooled and extracted with ether. Evaporation of the dried extracts and chromatography of the residue on silica gel [light petroleum (b.p. 40—60°) as eluant] produced the stilbene (0·62 g, 75%) as a 2 : 1 mixture (by g.l.c.) of *Z*- and *E*-isomers. Preparative g.l.c. (180°) gave: (i) (Z)-2,α-*dimethylstilbene* (eluted first), n_D^{22} 1·5932, $\lambda_{max.}$ 256 nm (ε 14,000); $\nu_{max.}$ (film) 1603, 1500, 770, 760, 735, and 700 cm^{-1}; τ see formula (16) (Found: C, 92·5; H, 7·7. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%), and (ii) (E)-2,α-*dimethylstilbene*, n_D^{22} 1·5982, $\lambda_{max.}$ 254 nm (ε 13,400); $\nu_{max.}$ (film) 1603, 1500, 920, 770, 730, and 705 cm^{-1}; τ see formula (17) (Found: *m/e* 208·1252. $C_{16}H_{16}$ requires *M*, 208·1252).

Reaction of 2-Methylstilbene with DMSO$^-$.—(a) *2 h Reaction*. (*E*)-2-Methylstilbene (0·3 g) was added to a stirred solution of DMSO$^-$ [from sodium hydride (0·19 g); 4 molar excess] in DMSO (10 ml) and the solution was stirred at 70° for 2 h. The mixture was cooled to 25°, then diluted with water (50 ml) and extracted with ether (3 × 50 ml). Evaporation of the dried extracts left an oil, which was chromatographed on silica gel (chloroform as eluant) to give (i) a fast moving methylated stilbene fraction (0·13 g, 40%). G.l.c. analysis (165°) and comparison with authentic material showed that this was a mixture of compounds (11), (10), and (6) in the ratio *ca.* 29 : 68 : 3. The *Z*- and *E*-isomers of 2,α-dimethylstilbene were separated by g.l.c. and each was spectrally indistinguishable from an authentic sample. Fraction (ii) was methyl 3-phenyl-4-(*o*-tolyl)butyl sulphoxide (0·23 g, 52%), spectrally (i.r., n.m.r.) identical with an authentic sample. Pyrolysis of this sulphoxide at 200° produced 3-phenyl-4-(*o*-tolyl)but-1-ene, spectrally identical with an authentic sample.[8]

(b) Repetition of the reaction conditions in (a) but employing 0·5 g of 2-methylstilbene and 1 molar excess of

[8] B. G. James and G. Pattenden, following paper.

hydride gave identical methylated stilbene and sulphoxide products in approximately the same proportions.

(c) Repetition of the reaction conditions in (a) but employing 0·1 g of (*Z*)-2-methylstilbene in place of the *E*-isomer, and 5 mol. equiv. of $DMSO^-$ produced a similar yield of α- and α′-methylstilbene products in similar proportions to those found in (a). Removal of a 1 ml sample from the reaction mixture after 1 min reaction, followed by g.l.c. analysis, showed that the mixture consisted mainly of (*E*)-2-methylstilbene, (*Z*)-2-methylstilbene, and (*E*)-2,α′-dimethylstilbene in the proportions *ca.* 25 : 60 : 11.

(d) 2 *min Reaction.* (*E*)-2-Methylstilbene (0·5 g) was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·31 g)] in DMSO (20 ml) at 70°, and the solution was stirred for 2 min, then diluted with water (50 ml), and extracted with ether (3 × 50 ml). Evaporation of the dried extracts left an oil which was chromatographed on silica gel (chloroform as eluant) to give: (i) a fast moving methylated stilbene fraction (0·3 g, 55%). G.l.c. analysis, and n.m.r. comparison with authentic samples, showed that this was a mixture of compounds (7), (11), (10), and (6) in the ratio *ca.* 2 : 2 : 4 : 92. The (*E*)-2,α′-dimethylstilbene was separated by g.l.c. and found to be spectrally indistinguishable from an authentic sample. Fraction (ii), methyl 3-phenyl-2-(*o*-tolyl)propyl sulphoxide (0·25 g, 40%), was spectrally (i.r., n.m.r.) identical with an authentic sample. Pyrolysis of this sulphoxide, as described later, followed by chromatography, gave a mixture of (11), (10), and 3-phenyl-2-(*o*-tolyl)prop-1-ene in the proportions *ca.* 3 : 2 : 5.

Ethyl 2-*Phenyl*-3-(o-*tolyl*)*propionate* (24a).—Ethyl phenylacetate (40 g) in dry ether (50 ml) was added during 0·25 h to a stirred suspension of sodamide [from sodium (5·75 g)] in liquid ammonia (500 ml) and the mixture was stirred for 0·75 h. *o*-Methylbenzyl bromide (46·5 g) in dry ether (50 ml) was then added during 0·25 h, and the mixture was stirred for a further 4 h, then ammonium chloride (15 g) was added in portions. The ammonia was evaporated off, and ether (300 ml) was added to the residue, followed by iced 2N-hydrochloric acid (300 ml). The ether layer was separated, and the aqueous phase was thoroughly washed with ether. Evaporation of the washed ($NaHCO_3$ then NaCl) and dried extracts followed by distillation of the residue gave the *ester* (48 g, 74%), b.p. 134—136° at 0·05 mmHg, n_D^{18} 1·5418; $\nu_{max.}$ (film) 1733, 1610, 1500, 1155, 865, 760, and 750 cm^{-1}; τ 2·76 (5 ArH), 2·98 (4 ArH), 5·98 (q, *J* 7·5 Hz, $CH_2{\cdot}CH_3$), 6·22 (dd, *J* 7·5 and 9 Hz, $CH{\cdot}CO_2Et$), 6·6 (dd, *J* 9 and 14 Hz, CHH), 7·05 (dd, *J* 7·5 and 14 Hz, CHH), 7·78 (Me), and 8·98 (t, *J* 7·5 Hz, $CH_2{\cdot}CH_3$) (Found: C, 80·7; H, 7·3%; M^+, 268. $C_{18}H_{20}O_2$ requires C, 80·7; H, 7·3%; *M*, 268).

Ethyl 3-*Phenyl*-2-(o-*tolyl*)*propionate* (24b).—The *ester* (24b) was prepared from ethyl *o*-tolylacetate (50 g) and benzyl bromide (50 g) under conditions identical with those described for the preparation of the isomeric ester (24a), and was obtained as a liquid (63 g, 84%), b.p. 140° at 0·05 mmHg, n_D^{18} 1·5448; $\nu_{max.}$ (film) 1730, 1610, 1500, 1150, 860, and 750 cm^{-1}; τ 2·4—3·0 (m, 9 ArH), 6·0 (q, *J* 7·5 Hz, $CH_2{\cdot}CH_3$), 5·95 (dd, *J* 6 and 8 Hz, $CH{\cdot}CO_2Et$), 6·56 (dd, *J* 8 and 14 Hz, CHH), 7·08 (dd, *J* 6 and 14 Hz, CHH), 7·8 (Me), and 8·98 (t, *J* 7·5 Hz, $CH_2{\cdot}CH_3$) (Found: C, 80·9; H, 7·2%; *M*, 268. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%; *M*, 268).

2-*Phenyl*-3-(o-*tolyl*)*propyl Toluene*-p-*sulphonate*.—A solution of ethyl 2-phenyl-3-(*o*-tolyl)propionate (40 g) in dry ether (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (3·75 g) in dry ether (200 ml), at such a rate that the ether refluxed gently. The mixture was boiled under reflux for a further 2·5 h, and was then cooled in ice and treated dropwise with water to destroy the excess of hydride. 2N-Hydrochloric was added to the stirred mixture until two clear liquid phases separated. The ether layer was then washed successively with water and saturated sodium hydrogen carbonate solution and dried. Evaporation left 2-phenyl-3-(*o*-tolyl)propan-1-ol (25a) (32·2 g, 95%), n_D^{18} 1·5714; $\nu_{max.}$ (film) 3400 and 1070 cm^{-1}, τ 2·75—3·05 (m, 9 ArH), 6·25br ($CH_2{\cdot}OH$), 7·04 (3H, m), 7·75 (Me), and 8·5 (OH, exchanged in D_2O) (Found: M^+, 226), which was used in the next stage without further purification.

The alcohol (10 g) in pyridine (100 ml) was treated with tosyl chloride (9·3 g) at 0° and the mixture was kept at −5° for 2 h, diluted with water (100 ml), and then extracted with chloroform (3 × 100 ml). The extracts were combined and washed successively with ice-cold 2N-sulphuric acid (5 × 150 ml), water (200 ml), and saturated sodium hydrogen carbonate solution (5 × 150 ml). Evaporation of the dried extracts, and crystallisation of the residue from ether–light petroleum (b.p. 40—60°) gave the *tosylate* (14 g, 83%), m.p. 61—62°, $\nu_{max.}$ (mull) 1600, 1500, 1365, 1180, and 750 cm^{-1}; τ 2·45—3·2 (m, 13 ArH), 5·85 (d, *J* 6 Hz, $CH_2{\cdot}O$), 6·9—7·3 (3H, m), 7·65 (Me), and 7·88 (Me) (Found: C, 72·4; H, 6·5. $C_{23}H_{24}O_3S$ requires C, 72·6; H, 6·4%).

3-*Phenyl*-2-(o-*tolyl*)*propyl Toluene*-p-*sulphonate*.—The tosylate was prepared from ethyl 3-phenyl-2-(*o*-tolyl)propionate, under identical conditions to those described for the tosylate of (25a). Reduction of the ester (24b) (40 g) with lithium aluminium hydride produced 3-phenyl-2-(*o*-tolyl)-propan-1-ol (25b) (90%), n_D^{18} 1·5738, $\nu_{max.}$ (film) 3400 cm^{-1}; τ 2·7—3·1 (m, 9 ArH), 6·28 (d, *J* 6 Hz, $CH_2{\cdot}O$), 6·63 (tt, *J* *ca.* 7 Hz, $CH{\cdot}CH_2$), 6·9—7·3 (2H), 7·9 (Me), and 8·4 (OH, exchanged in D_2O), M^+ 226. Treatment of this alcohol, as before, with tosyl chloride in pyridine, produced the *tosylate* (89%), m.p. 65—66° [from ether–light petroleum (b.p. 60—80°)], $\nu_{max.}$ (mull) 1360 and 1180 cm^{-1}; τ 2·3—3·2 (m, 13 ArH), 5·85 (d, *J* 6 Hz, $CH_2{\cdot}O$), 6·62 (tt, *J* *ca.* 7 Hz, $CH{\cdot}CH_2$), 6·85—7·25 (2H, m), 7·61 (Me), and 8·0 (Me) (Found: C, 72·7; H, 6·4. $C_{23}H_{24}O_3S$ requires C, 72·6; H, 6·4%).

Methyl 2-*Phenyl*-3-(o-*tolyl*)*propyl Sulphoxide* (21).—Methanethiol (15 g) was added to a stirred suspension of sodium hydride (5·2 g) in dry tetrahydrofuran (100 ml) at 0°; the mixture was stirred at 0° for 0·5 h, and then treated during 0·3 h with a solution of 2-phenyl-3-(*o*-tolyl)propyl tosylate (40 g) in dry tetrahydrofuran (150 ml). The mixture was stirred at 25° for 0·25 h, and then at 50° for 18 h, cooled (ice–water) and treated dropwise with water during 1 h. It was then evaporated to dryness *in vacuo*. The residue was shaken with a mixture of ether (200 ml), pentane (100 ml), and water (200 ml), and the organic phase was separated and washed successively with water (2 × 200 ml), N-hydrochloric acid (200 ml), saturated aqueous sodium hydrogen carbonate (200 ml), and water (2 × 200 ml). Evaporation of the dried organic phase left an oil which was chromatographed on silica gel [ether–pentane (1 : 3)] to give methyl 2-phenyl-3-(*o*-tolyl)propyl sulphide (11·3 g, 43%) as a liquid, b.p. 170° at 4 mmHg; $\nu_{max.}$ (film) 1605, 1500, 750, and 700 cm^{-1}; τ 2·8—3·2 (m, 9 ArH), 6·75—7·2 (m, 5H), 7·8 (Me), and 8·1 (SMe), M^+, 256.

A solution of the sulphide (5 g) in methanol (40 ml) and water (10 ml) was treated at 0° with aqueous 0·5M-sodium

periodate (40 ml). The resulting mixture was stirred vigorously at 0° for 14 h and was then poured onto water (120 ml) and extracted with chloroform (120 ml). Evaporation of the washed (H_2O) and dried extract left a solid residue which was chromatographed on silica gel [chloroform–methanol (4 : 1)] to give the *sulphoxide* (2·4 g, 50%) as a diastereoisomeric mixture which crystallised from benzene–light petroleum (b.p. 60—80°) as needles, m.p. 119—120°, $\nu_{max.}$ (mull) 1039 cm^{-1}, τ 2·78—3·1 (m, 9 ArH), 6·8—7·2 (5H, m), 7·63 (SOMe), and 7·8 (Me) (Found: C, 75·05; H, 7·4. $C_{17}H_{20}OS$ requires C, 75·0; H, 7·4%).

Methyl 3-Phenyl-2-(o-tolyl)propyl Sulphoxide (22).—The sulphoxide was prepared from 3-phenyl-2-(*o*-tolyl)propyl tosylate, under conditions identical with those described for the isomeric sulphoxide (21). Methyl 3-phenyl-2-(*o*-tolyl)propyl sulphide, obtained in 53% yield from the tosylate, had b.p. 140° at 0·5 mmHg, τ 2·75—3·1 (m, 9 ArH), 6·58 (tt, *J ca.* 7 Hz, C*H*·CH_2), 6·6—7·2 (m, CH_2·CH), 7·23 (d, *J* 7 Hz, CH_2S), 7·9 (SMe), and 8·05 (Me), M^+ 256. Oxidation of this sulphide with aqueous sodium periodate gave the *sulphoxide* as a diastereoisomeric mixture, m.p. 73—74° [benzene–light petroleum (60—80°)], $\nu_{max.}$ (mull) 1600, 1495, 1050, and 760 cm^{-1}; τ 2·75—3·1 (m, 9 ArH), 6·28 (m, C*H*·CH_2), 6·7—7·1 (m, CH_2·CH), 7·0 (d, *J* 7 Hz, CH_2·SO), 7·6 (SOMe), and 8·1 (Me) (Found: C, 75·3; H 7·8. $C_{17}H_{20}OS$ requires C, 75·0; H, 7·4%).

Reaction of Methyl 2-Phenyl-3-(o-tolyl)propyl Sulphoxide (21) *with DMSO⁻*.—The sulphoxide (0·1 g) was added to a solution of $DMSO^-$ [from sodium hydride (0·054 g)] in DMSO (6 ml) and the mixture was stirred and heated at 70° for 5 min, then diluted with water (25 ml) and extracted with ether. Evaporation of the dried extracts left an oil, which was chromatographed in benzene on silica gel to give (i) a 1 : 9 mixture (by n.m.r. and g.l.c.) of (*Z*)- and (*E*)-2,α′-dimethylstilbene (55 mg, 70%) (eluted first), and (ii) methyl 3-phenyl-4-(*o*-tolyl)butyl sulphoxide (30 mg, 28%), spectrally identical with an authentic sample. Longer reaction periods resulted in exclusive formation of the sulphoxide.

Methyl 3-Phenyl-4-(o-tolyl)butyl Sulphoxide (29).—(a) *From 2,α′-dimethylstilbene* (6). The stilbene (0·125 g) was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·054 g)] in DMSO (10 ml) and the mixture was kept at 70° for 2 h, then cooled, diluted with water (30 ml), and extracted with ether (3 × 4 ml). Evaporation of the dried extracts and chromatography of the residue in chloroform on silica gel gave the sulphoxide (diastereoisomeric mixture) (0·13 g, 75%) as a viscous oil, $\lambda_{max.}$ 262 nm, $\nu_{max.}$ (film) 1600, 1575, 1500, 1040, 750, and 700 cm^{-1}; τ 2·8—3·1 (m, 9 ArH), 7·1br (3H), 7·5—8·0 (2 × CH_2), 7·7 (SOMe), and 7·82 (Me). Attempts to purify the oil (for analysis) by distillation resulted in elimination of sulphenic acid and formation of 3-phenyl-4-(*o*-tolyl)but-1-ene.

(b) *From methyl 2-phenyl-3-(o-tolyl)propyl sulphoxide* (21). The propyl sulphoxide (1 g) was treated with $DMSO^-$ [from sodium hydride (0·6 g)] under conditions identical with those described in (a). Chromatography gave the butyl sulphoxide (0·7 g, 66%), spectrally indistinguishable from that obtained in (a).

(c) *From 2-phenyl-3-(o-tolyl)propene* (36). The styrene (0·1 g) was treated with $DMSO^-$ [from sodium hydride (0·05 g)] under conditions identical with those described in (a), and produced a comparable yield of the butyl sulphoxide spectrally identical with that obtained before.

Reaction of Methyl 3-Phenyl-2-(o-tolyl)propyl Sulphoxide (22) *with DMSO⁻*.—The sulphoxide (0·5 g) was added to a solution of $DMSO^-$ [from sodium hydride (0·27 g)] in DMSO (20 ml) and the mixture was stirred and heated at 70° for 1·5 h, then diluted with water (50 ml). Evaporation of the dried ethereal extracts left an oil, which was chromatographed in chloroform on silica gel to give 2,α-dimethylstilbene (0·36 g, 93%) as a 2 : 1 mixture of *Z*- and *E*-isomers (comparative g.l.c. and n.m.r. data).

2-Phenyl-3-(o-tolyl)propene (36).—Methyltriphenylphosphonium iodide (1 g) was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·087 g)] in DMSO (10 ml); the mixture was stirred for 0·5 h, then treated with 2′-methyldeoxybenzoin (0·4 g). The resulting mixture was heated at 45° for 3 h, then cooled, diluted with water, and extracted with ether (3 × 40 ml). Evaporation of the dried extracts and chromatography of the residue in benzene on silica gel gave the *alkene* (0·11 g, 26%), as an oil, $\lambda_{max.}$ 242 nm; $\nu_{max.}$ (film) 890, 765, 735, and 695 cm^{-1}; τ 2·6—2·9 (m, 9 ArH), 4·6 (:C*H*H), 5·3 (:CH*H*), 6·36 (CH_2), and 7·73 (Me) (Found: *m/e* 208·1252. $C_{16}H_{16}$ requires *M*, 208·1252).

Pyrolysis of Methyl 3-Phenyl-2-(o-tolyl)propyl Sulphoxide (22).—The sulphoxide (0·9 g) was heated at 240° (Woods metal bath) for 0·75 h, and the cooled residue was distilled to give a mixture of hydrocarbon products (0·5 g, 73%), b.p. 110—120° at 0·5 mmHg. Analysis of this mixture by both g.l.c. and n.m.r., and comparison with authentic samples, showed that it consisted of compounds (10) and (11) and 3-phenyl-2-(*o*-tolyl)propene (37) [τ 2·7—2·9 (m, 9 ArH), 4·9 (d, *J* 1·5 Hz; :C*H*H), 5·03 (d, *J* 1·5 Hz, :CH*H*), 6·38 (CH_2), and 7·73 (Me)], in the proportions *ca.* 38 : 26 : 36.

Preparative g.l.c. (180°) separated an unresolved 2 : 3 mixture of (11) and the styrene (eluted first, as one peak), addition of which to $DMSO^-$, followed by the usual work-up, gave a 3 : 2 mixture of (11) and (10).

Pyrolysis of Methyl 2-Phenyl-3-(o-tolyl)propyl Sulphoxide (21).—The sulphoxide (0·9 g) was pyrolysed under conditions identical with those for the isomeric sulphoxide. G.l.c. and n.m.r. analysis of the hydrocarbon product (95%) showed that it was composed of compounds (6) and (7) and 2-phenyl-3-(*o*-tolyl)propene (36) in the proportions *ca.* 80 : 15 : 5.

Reaction of 4,4′-Dimethoxy-2,6-dimethylstilbene (41) *with DMSO⁻*.—The stilbene (0·5 g) [5] was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·24 g)] in DMSO (20 ml); the mixture was stirred at 70° for 3·5 h, cooled, diluted with water (50 ml), and extracted with ether (3 × 75 ml). Evaporation of the dried extracts, and chromatography of the residue in chloroform on silica gel gave (i) a methylated stilbene fraction (0·38 g, 73%) (eluted first); g.l.c. (220°) gave (*a*) (Z)-4,4′-*dimethoxy*-2,6,α-*trimethylstilbene* (42), eluted first, major (*ca.* 85%) product, b.p. 180° at 0·1 mmHg, $\lambda_{max.}$ 264 nm (ε 18,500); $\nu_{max.}$ film) 2840, 1610, 1575, 1515, 1250, 870, and 850 cm^{-1}, τ 3·26 (2H, d, *J* 9 Hz), 3·38 (2H), 3·46 (2H, d, *J* 9 Hz), 3·61 (:CH), 6·26 (OMe), 6·38 (OMe), 7·9 (2 × Me), and 8·0 (Me) (Found: C, 81·0; H, 8·0%; M^+, 282. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·85%; *M*, 282); and (*b*) an unresolved 3 : 1 mixture of (*E*)-4,4-dimethoxy-2,6,α-trimethylstilbene (42), τ 2·65 (2H, d, *J* 9 Hz), 3·03 (2H, d, *J* 9 Hz), 3·33 (2H), 3·75 (:CH), 6·31 (OMe), 7·71 (2 × Me), and 7·93 (Me), and (*E*)-4,4′-dimethoxy-2,6,α′-trimethylstilbene (47) [identical (n.m.r. and g.l.c.) with an authentic sample].[9] Fraction (ii), *methyl 2-(4-methoxy-2,6-dimethylphenyl)-3-(4-methoxyphenyl)propyl sulphoxide* (52) (0·075 g, 11%), was obtained as an oily

[9] B. G. James and G. Pattenden, unpublished work.

diastereoisomeric mixture τ 3·1 (2H, d, *J* 9 Hz), 3·35 (2H, d, *J* 8 Hz), 3·5 (1H), 3·6 (1H), 6·3 (2 × OMe), 6·2 (m, ArC*H*), 6·95 (m, ArCH_2 and CH_2·SO), 7·58 (Me), 7·62 (Me), and 7·92 (SOMe).

3-(4-*Methoxy*-2,6-*dimethylphenyl*)-2-(4-*methoxyphenyl*)-*propene* (55).—Methyltriphenylphosphonium bromide (1·3 g) was added to a stirred solution of $DMSO^-$ [from sodium hydride (0·17 g)] in DMSO (5 ml); the mixture was stirred for 0·5 h and then treated with 4,4′-dimethoxy-2′,6′-dimethyldeoxybenzoin (0·6 g).[5] The resulting mixture was heated at 40—60° for 1 h, then cooled, diluted with water, and extracted with ether. Evaporation of the dried extracts and chromatography of the residue in benzene on silica gel gave the *propene* (0·2 g, 32%), m.p. 88—89° (from methanol), τ 2·52 (2H, d, *J* 9 Hz), 3·11 (2H, d, *J* 9 Hz), 3·48 (2H), 4·80 (:C*H*H), 5·65 (:CH*H*), 6·18 (OMe), 6·22 (OMe), 6·36 (CH_3), and 7·78 (2 × Me) (Found: C, 80·7; H, 7·8%; M^+, 282. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8%; *M*, 282).

2-(4-*Methoxy*-2,6-*dimethylphenyl*)-3-(4-*methoxyphenyl*)-*propene* (54).—Methyl 2-(4-methoxy-2,6-dimethylphenyl)-3-(4-methoxyphenyl)propyl sulphoxide (0·075 g) was heated at 210° (Woods metal bath) for 0·6 h, and the residue was then chromatographed in benzene on silica gel to give the propene (45 mg) as an oil, τ 2·95 (2H, d, *J* 9 Hz), 3·2 (2H, d, *J* 9 Hz), 3·43 (2H), 4·98 (d, *J* 1·5 Hz, :C*H*H), 5·18 (d, *J* 1·5 Hz, :CH*H*), 6·23 (2 × OMe), 6·6 (CH_2), and 7·86 (2 × Me).

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