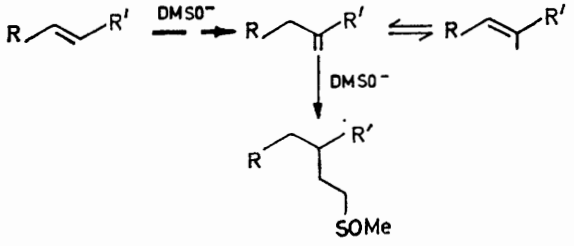
One-stage Double Methylene Transfer Reactions from Methylsulphinylmethanide to Activated Double Bonds. Mimetic of *in vivo C*-Ethylation

By **Brian G. James** and **Gerald Pattenden,*†** Department of Chemistry, University College, Cathays Park, Cardiff CF1 3NR

One-stage sequential double methylations of the C=C bonds in stilbene, 2-methylstilbene, and 4,4'-dimethoxystilbene from methylsulphinylmethanide ($DMSO^-$) leading to methyl diarylbutyl sulphoxides [*e.g.* (3) and (14)] are described. The same methyl diarylbutyl sulphoxides are produced when the corresponding α-methylstilbenes [*e.g.* (6)] or, in one case, the corresponding styrene (5) and lower homologous sulphoxide (4) are similarly treated with $DMSO^-$; the double methylene transfer process follows according to Scheme 2. Thermal elimination of methanesulphenic acid from the sulphoxides (3) and (14) produces 3,4-diarylbut-1-enes, which are smoothly isomerised by $DMSO^-$ to a mixture of *Z*- and *E*-isomers of α-ethylstilbenes and α-benzyl-β-methylstyrenes. Cyclopropane intermediates are shown not to be implicated in any of the reaction schemes by the observation that authentic *trans*-1,2-diphenylcyclopropane is recovered unchanged after treatment with $DMSO^-$; the corresponding *cis*-cyclopropane is quantitatively converted into the *trans*-isomer in $DMSO^-$–DMSO. (*E*)-Stilbene reacts with the anion produced from diethyl sulphoxide and sodium hydride to give a mixture of *Z*- and *E*-isomers of α-ethylstilbene and α-benzyl-β-methylstyrene. The relationship between this work and *in vivo C*-ethylation from L-methionine is discussed.

In the preceding paper [1] we described some studies on the suitability of methylsulphinylmethanide ($DMSO^-$) for the selective α-methylation of unsymmetrically substituted stilbenes. We observed that in one system sequential double methylation of a C=C bond took place in a single-stage reaction, according to Scheme 1. In view of the possible synthetic usefulness of this transformation, and also its relationship with what is known



Scheme 1

about the sequence of events occurring in biological *C*-ethylation, we have examined the transformation in greater detail.

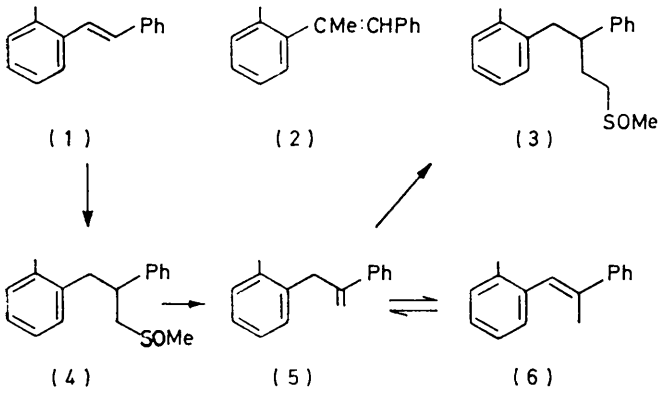
Treatment of the stilbene (1) with $DMSO^-$ for long periods was shown in our previous studies [1] to produce an isomeric mixture of methylation products (2) accompanied by the sulphoxide (3). The same sulphoxide (3) was the sole product (*ca.* 75%) when either of the hydrocarbons (5) and (6), or the lower homologous sulphoxide (4), was treated with $DMSO^-$, and its formation from (1) was thus rationalised according to Scheme 2.

Thermal elimination of methanesulphenic acid from (3) produced a homogenous hydrocarbon product whose spectral data were consistent with the expected butene structure (7a). Isomerisation of this in $DMSO^-$–DMSO gave a hydrocarbon product (80% recovery) which was found to be a mixture of compounds (8a), (9a), (10a), and (11a), in the proportions *ca.* 2 : 3 : 4 : 2. These four isomers could be separated by g.l.c. and their constitution and geometry followed from chromatographic and spectral comparison with authentic samples.

† *Present address:* Chemistry Department, Nottingham University, University Park, Nottingham NG7 2RD.

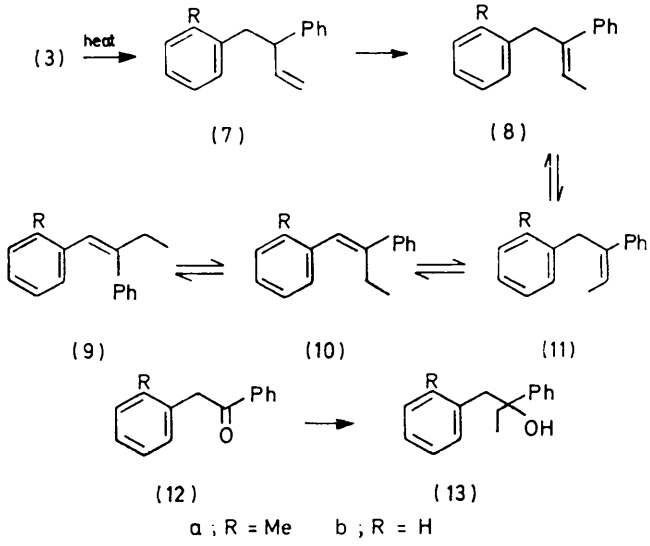
[1] B. G. James and G. Pattenden, preceding paper.

Authentic specimens were obtained by preparative g.l.c. of the mixture formed by dehydration of the carbinol



SCHEME 2

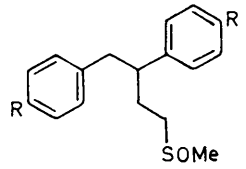
product (13a) from the Grignard reaction between ethylmagnesium iodide and the deoxybenzoin (12a).



SCHEME 3

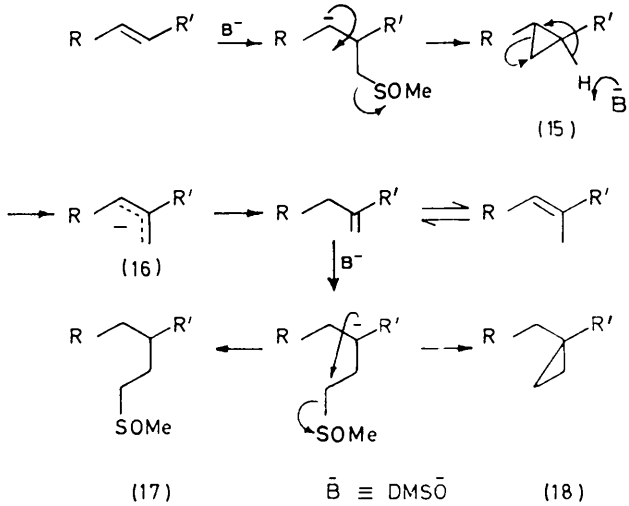
In two further illustrations of this single-stage double methylene transfer process, (*E*)-stilbene and (*E*)-4,4'-dimethoxystilbene were treated similarly. Methylation of (*E*)-stilbene by $DMSO^-$ has been reported previously;[2] it was claimed that the only product was (*E*)-α-methylstilbene. We found this claim to be substantially correct for a 0·25 h reaction, except that we also observed the formation of (*Z*)-α-methylstilbene (*ca.* 10%). However, when a solution of (*E*)-stilbene in DMSO–$DMSO^-$ was stirred at 25° for 24 h, the only product isolated was a diastereoisomeric mixture of sulphoxides (14a). In separate experiments, the reaction of (*E*)-α-methylstilbene with $DMSO^-$ at 25° for 3 h produced a comparable yield of (14a). Similarly, the sulphoxide (14b), as a mixture of diastereoisomers, could be obtained from the reactions of $DMSO^-$ with 4,4'-dimethoxystilbene and 4,4'-dimethoxy-α-methylstilbene. Elimination of the elements of methanesulphenic acid from the sulphoxide (14a) produced a butene (7b), which was easily isomerised in DMSO–$DMSO^-$ to a mixture of the isomeric hydrocarbons, (8b), (9b), (10b), and (11b), identified by chromatographic and spectral comparison with authentic samples synthesised from dehydration of the carbinol (13b), obtained from the deoxybenzoin (12b) and ethylmagnesium iodide.

In none of the studies discussed in either this paper or the preceding one were we able to obtain evidence to suggest the formation of cyclopropane products in addition to *C*-methyl products during reactions involving sulphoxide anions. It was possible that the *C*-methylation process involving $DMSO^-$ proceeded *via* a cyclopropane intermediate [*e.g.* (15)] formed by γ-elimination



(14) a ; R = H
b ; R = OMe

of methanesulphenate anion, and that the three-membered ring was then cleaved by $DMSO^-$ to afford (16) and thence the *C*-methyl derivative (see Scheme 4 and refs. 2 and 3); it was equally possible that the further addition of $DMSO^-$ to the styryl system leading to sulphoxide (17) was accompanied by the formation of a 1,1'-disubstituted cyclopropane [*e.g.* (18)] according to Scheme 4. We therefore examined the possibility of

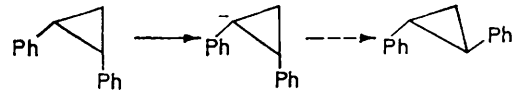


SCHEME 4

the formation of cyclopropane intermediates in these transformations, by studying the reaction between

[2] M. Feldman, S. Danishefsky, and R. Levine, *J. Org. Chem.*, 1966, **31**, 4322.
[3] R. Baker and M. J. Spillett, *J. Chem. Soc.* (*B*), 1969, 581.

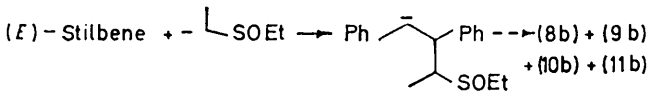
1,2-diphenylcyclopropane and $DMSO^-$. A mixture of *cis*- and *trans*-isomers of the cyclopropane is easily available,[4] and the individual isomers can be separated by g.l.c. Reaction between the *trans*-isomer (20) and $DMSO^-$ produced a deep red solution, consonant with carbanion formation, but the usual work-up produced starting material only (*ca.* 90%); rigorous g.l.c. analysis showed the complete absence of either (*Z*)- or (*E*)-α-methylstilbene. When the *cis*-cyclopropane (19) was treated similarly with $DMSO^-$, the corresponding *trans*-isomer only was produced, and there was no evidence to suggest formation of ring-cleavage products.



(19) (20)

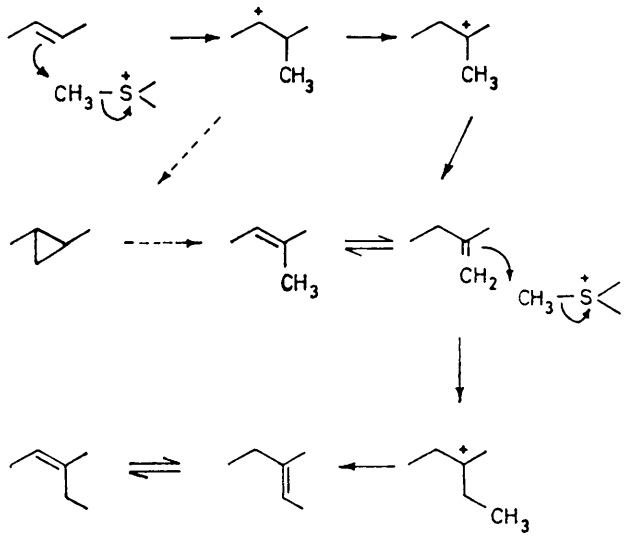
SCHEME 5

We also examined briefly *C*-alkyl transfer reactions with alkyl sulphoxide anions other than $DMSO^-$. Treatment of diethyl sulphoxide with sodium hydride produced a homogeneous solution containing the



SCHEME 6

corresponding sulphoxide anion which indeed reacted with (*E*)-stilbene to give a mixture of isomers of the *C*-ethylated products (8b)—(11b) in similar proportions to the mixture from isomerisation of (7b).



SCHEME 7

Stepwise methylene transfer to double bonds leading to *C*-ethyl and *C*-ethylidene derivatives provides an interesting laboratory mimic of biological *C*-ethylation *via* methionine. The mechanism of biological *C*-alkylation of unsaturated carbon centres has been examined in detail in a number of systems. It is generally accepted [5] that these processes occur by nucleophilic attack on *S*-adenosylmethionine leading to carbonium ion intermediates which then rearrange as outlined in Scheme 7. Neither cyclopropane intermediates nor ethionine are thought to be involved in *in vivo C*-ethylation. Methionine *S*-oxide has been found in higher plants where transfer of the methyl group of methionine has also been demonstrated, but there is no evidence to suggest that the anion from methionine *S*-oxide or ylides formed from methionine sulphonium salts take part in biological *C*-alkylation processes.

EXPERIMENTAL

For general experimental details see preceding paper.

3-Phenyl-4-(o-tolyl)but-1-ene (7a).—Methyl 3-phenyl-4-(*o*-tolyl)butyl sulphoxide (0·12 g) [1] was heated at 200° (Woods metal bath) for 0·75 h, and the cooled residue was then chromatographed in benzene on silica gel to give the *alkene* (55 mg, 60%) as an oil, $\lambda_{max.}$ 250 nm; $\nu_{max.}$ (film) 1600, 1575, 1500, 990, 910, 740, and 695 cm^{-1}; τ 2·7—3·1 (m, 9 ArH), 3·98 (ddd, *J* 9, 10, and 17 Hz, $CH{\cdot}CH{:}CH_2$), 5·02 (dd, *J* 10 and 1·5 Hz, $:CHH$), 5·1 (dd, *J* 17 and 1·5 Hz, $:CHH$), 6·48 (dd, *J* 9 Hz, CHAr), 7·2 (d, *J* 8 Hz, CH_2Ar), and 7·8 (Me) (Found: *m/e* 222·141. $C_{17}H_{18}$ requires *M*, 222·1408).

Collection of the liquid eluted after pyrolysis of the sulphoxide at a high injection block temperature on a preparative g.l.c. column (180°) also produced the same alkene (identical i.r. and n.m.r. spectra).

Isomerisation of 3-Phenyl-4-(o-tolyl)but-1-ene.—The butene (0·15 g) was added to a solution of $DMSO^-$ [from sodium hydride (0·033 g)] in DMSO at 25°; the solution was stirred at 25° for 2 h, then diluted with water and extracted with ether (3 × 10 ml). Evaporation of the dried extracts left an oil which was chromatographed in chloroform on silica gel to give a hydrocarbon fraction (0·12 g, 80% recovery). Analysis of this fraction by both g.l.c. (180°) and n.m.r., and comparison with authentic samples, showed that it was composed of a mixture of (*Z*)-α′-ethyl-2-methylstilbene (9a), (*Z*)-2-phenyl-1-(*o*-tolyl)but-2-ene (8a), (*E*)-α′-ethyl-2-methylstilbene (10a), and (*E*)-2-phenyl-1-(*o*-tolyl)but-2-ene (11a) in the proportion *ca.* 3 : 2 : 4 : 2.

Attempts to effect a similar isomerisation with potassium t-butoxide in t-butyl alcohol or in DMSO were not successful; only starting butene was recovered.

(Z)- and (E)-α′-Ethyl-2-methylstilbene [(9a) *and* (10a)] *and (Z)- and (E)-2-Phenyl-1-(o-tolyl)but-2-ene* [(11a) *and* (8a)] *from 2′-Methyldeoxybenzoin.*—A solution of the deoxybenzoin (4 g) in ether (20 ml) was added dropwise to a stirred solution of ethylmagnesium iodide [from magnesium (0·5 g)] in ether (50 ml); the mixture was then heated under reflux for 2·5 h, cooled, poured onto iced dilute sulphuric acid, and extracted with ether. Evaporation of the extracts left 2-phenyl-1-(*o*-tolyl)butan-2-ol as an oil, which was dehydrated without further purification. A solution of the alcohol in glacial acetic acid (20 ml) containing 3 drops of polyphosphoric acid was boiled under reflux for

[4] S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 1952, 4686.

[5] E. Lederer, *Quart. Rev.*, 1969, **23**, 453; T. W. Goodwin, *Biochem. J.*, 1971, **123**, 293.

2 h, and then diluted with water and extracted with ether (3 × 70 ml). Evaporation of the dried extracts, followed by chromatography of the residue in benzene on silica gel, gave a hydrocarbon fraction (eluted first) (3·4 g, 83% overall). Separation by g.l.c. (180°) gave: (i) (*Z*)-α'-ethyl-2-methylstilbene (eluted first), an oil, $\lambda_{max.}$ 259 nm, $\nu_{max.}$ (film) 1605, 1580, 1500, 755, 735, and 700 cm^{-1}; τ 2·85—3·25 (m, 9 ArH), 3·52 (:CH), 7·43 (q, *J* 8 Hz, CH_2·CH_3), 7·75 (Me), and 8·9 (t, *J* 8 Hz, CH_2·CH_3) (Found: *m/e* 222·1410. Calc. for $C_{17}H_{18}$: *M*, 222·1408); (ii) (*Z*)-2-phenyl-1-(*o*-tolyl)but-2-ene, an oil, $\nu_{max.}$ (film) 3040, 1610, 1580, 1500, 820, 755, 745, and 700 cm^{-1}; τ 2·75—2·9 (m, 9 ArH), 4·77 (q, *J* 8 Hz, :C*H*·CH_3), 6·4 (CH_2Ar), 7·75 (Me), and 8·45 (d, *J* 8 Hz, :CH*Me*); *m/e* 222·1412; (iii) (*E*)-α'-ethyl-2-methylstilbene (eluted last), m.p. 33°, $\lambda_{max.}$ 257 nm (ε 11,800); $\nu_{max.}$ (film) 1600, 1575, 1495, 755, 750, 745, and 700 cm^{-1}; τ 2·5—3·05 (m, 9 ArH), 3·37 (:CH), 7·43 (q, *J* 8 Hz, CH_2·CH_3), 7·75 (Me), and 9·05 (t, *J* 8 Hz, CH_2·CH_3); *m/e* 222·1412; and (iv) (*E*)-2-phenyl-1-(*o*-tolyl)but-2-ene, τ 2·65—2·95 (m, 9 ArH), 3·88 (q, *J* 8 Hz, :C*H*·CH_3), 6·25 (CH_2Ar), 7·67 (Me), and 8·22 (d, *J* 8 Hz, :CHMe). This isomer could not be resolved completely from (*E*)-α-ethyl-2-methylstilbene by g.l.c.

Reaction of Stilbene with DMSO$^-$.—(a) 15 *min Reaction.* (*E*)-Stilbene (2 g) was added to a stirred solution of DMSO$^-$ [from sodium hydride (0·5 g, 1 molar excess)] in DMSO (30 ml), and the solution was stirred at 25—30° for 0·25 h, and then diluted with water (100 ml). The solid which was precipitated was filtered off and recrystallised from ethanol to give (*E*)-α-methylstilbene (1·6 g, 80%), m.p. 81° (lit.,[6] 82°), spectrally identical with an authentic sample. The aqueous filtrate was extracted with ether, and the combined extracts were then dried and evaporated to leave an oil. Preparative g.l.c. (180°) separated (*Z*)-α-methylstilbene, an oil, τ 2·6—3·0 (ArH), 3·5 (:CH), and 7·80 (Me).[6] In another experiment, the reaction mixture was diluted with water and extracted with ether. G.l.c. analysis of this mixture indicated that the (*Z*)- and (*E*)-α-methylstilbenes were present in *ca.* 1 : 9 ratio.

(b) Repetition of the reaction conditions in (a) but employing (*Z*)-stilbene in place of the (*E*)-isomer produced a similar yield of (*Z*)- and (*E*)-α-methylstilbenes in a similar ratio. Removal of a 1 ml sample from the reaction mixture after 1·5 min, followed by g.l.c. analysis (180°) showed that the mixture consisted mainly of (*Z*)-stilbene (eluted first), (*E*)-α-methylsilbene (eluted second), and (*E*)-stilbene (eluted last), in the proportions *ca.* 85 : 5 : 10.

(c) 24 *h Reaction.* Repetition of the reaction in (a), but stirring the mixture 24 h, then diluting it with water and extracting the product with ether, gave, after chromatography in chloroform on silica gel, methyl 1,2-diphenylbutyl sulphoxide (2 g, 60%), spectrally identical with an authentic specimen. This was pyrolysed to produce **3**,4-diphenylbut-1-ene (see later).

Methyl 1,2-*Diphenylbutyl Sulphoxide* (14a).—(*E*)-α-Methylstilbene (0·5 g) was added to a solution of DMSO$^-$ [from sodium hydride (0·45 g)] in DMSO (30 ml); the mixture was stirred at 25—30° for 3 h, then diluted with water (60 ml), and extracted with ether (3 × 50 ml). Evaporation of the dried extracts and chromatography of the residue in chloroform on silica gel gave the *sulphoxide* (0·53 g, 60%) as a mixture of diastereoisomers which crystallised from benzene–petroleum (b.p. 40—60°) as needles, m.p. 80—81°, $\lambda_{max.}$ (EtOH) 258 nm; $\nu_{max.}$ (film) 1600, 1575, 1500, 1050, 900, 750, 725, and 695 cm^{-1}; τ 2·6—2·9 (m, 10 ArH), 7·0 (3 ArC*H*), 7·5—7·9 (m, 2 CH_2), and 7·63 (SOMe) (Found: C, 74·8; H, 7·5. $C_{17}H_{20}O_2S$ requires C, 75·0; H, 7·4%). It seems probable that this is the same sulphoxide as prepared by Baker and Spillett,[3] who identified their product as methyl 1,2-diphenylpropyl sulphoxide (m.p. 81·5—82·5°).

3,4-*Diphenylbut*-1-*ene* (7b).—Methyl 1,2-diphenylbutyl sulphoxide (0·16 g) was heated at 220—230° (Woods metal bath) for 0·6 h, and the cooled residue was then chromatographed in benzene on silica gel to give the *alkene* (66 mg, 56%), as an oil, $\nu_{max.}$ (film) 1640, 1600, 1575, 1500, 920, 750, and 695 cm^{-1}; τ 2·8—3·1 (m, 10 ArH), 4·01 (ddd, *J* 8, 10, and 17 Hz, CH·C*H*:CH_2), 5·04 (dd, *J* 10 and 1·5 Hz, CH:C*H*H), 5·11 (dd, *J* 17 and 1·5 Hz, CH:CH*H*), 6·45 (dt, *J ca.* 8 Hz, ArC*H*), and 7·01 (d, *J* 8 Hz, ArCH_2) (Found: *m/e* 208·1252. $C_{16}H_{16}$ requires *M*, 208·1252).

Collection of the liquid eluted after pyrolysis of the sulphoxide at a high injection block temperature on a preparative g.l.c. column (180°) produced the same alkene (identical i.r. and n.m.r. spectra).

Isomerisation of 3,4-*Diphenylbut*-1-*ene.*—The butene (0·16 g) was added to a solution of DMSO$^-$ [from sodium hydride (0·035 g)] in DMSO (30 ml); the solution was stirred at 25° for 2 h, then diluted with water (5 ml), and extracted with ether (3 × 5 ml). Evaporation of the dried extracts left an oil which was chromatographed in chloroform on silica gel to give a hydrocarbon fraction (0·1 g, 66%). Analysis of this fraction by both g.l.c. (180°) and n.m.r., and comparison with authentic samples, showed that it was a mixture of (*Z*)-α-ethylstilbene, (*Z*)-1,2-diphenylbut-2-ene, (*E*)-1,2-diphenylbut-2-ene, and (*E*)-α-ethylstilbene in the proportions *ca.* 1 : 1 : 3 : 5.

(Z)- *and* (E)-α-*Ethylstilbene* [(9b) *and* (10b)] *and* (Z)- *and* (E)-1,2-*Diphenylbut*-2-*ene* [(11b) *and* (8b)] *from Deoxybenzoin.*—Reaction of deoxybenzoin with ethylmagnesium iodide, followed by dehydration of the intermediate alcohol and chromatographic purification of the hydrocarbon products (*ca.* 65%), as described for the related 2-methylstilbene, series gave: (i) (*Z*)-α-ethylstilbene [eluted first; *ca.* 12%, but not completely resolved from (*Z*)-1,2-diphenylbut-2-ene], τ 2·8—3·0 (m, 10 ArH), 3·6 (:CH), 7·48 (q, *J* 8 Hz, CH_2·CH_3), and 8·92 (t, *J* 8 Hz, CH_2·CH_3); [7] (ii) (*Z*)-1,2-diphenylbut-2-ene [eluted second; *ca.* 12%, but not completely resolved from (*Z*)-α-ethylstilbene], τ 2·8—3·0 (m, 10 ArH), 4·45 (q, *J* 8 Hz, :C*H*·CH_3), 6·38 (ArCH_2), and 8·41 (d, *J* 8 Hz, :CH·CH_3); [7] (iii) (*E*)-1,2-diphenylbut-2-ene (eluted third; *ca.* 50%), an oil, $\lambda_{max.}$ 245 nm; $\nu_{max.}$ (film) 1610, 1575, 1500, 830, 750, 720, and 695 cm^{-1}, τ 2·7—2·9 (10 ArH), 3·98 (q, *J* 8 Hz, :C*H*·CH_3), 6·18 (ArCH_2), and 8·18 (d, *J* 8 Hz, :CH·CH_3) [7] (Found: *m/e*, 208·1252. Calc. for $C_{16}H_{16}$: *M*, 208·1252); and (iv) (*E*)-α-ethylstilbene (eluted fourth; *ca.* 36%), m.p. 56° (lit.,[8] 57°), $\nu_{max.}$ (mull) 1600, 1575, 1500, 1060, 1020, 855, 750, and 725 cm^{-1}; τ 2·6—2·8 (m, 10 ArH), 3·35 (:CH), 7·28 (q, *J* 8 Hz, CH_2·CH_3), and 8·98 (t, *J* 8 Hz, CH_2·CH_3); [7] *m/e* 208·1252.

A 3 : 1 mixture of *Z*- and *E*-isomers of 1,2-diphenylbut-2-ene was also formed (*ca.* 10%) by a Wittig condensation from deoxybenzoin.

[6] *Cf.* M. Michman and H. H. Zeiss, *J. Organometallic Chem.*, 1968, **15**, 139.

[7] *Cf.* A. F. Casy, A. Parulkar, and P. Pocha, *Tetrahedron*, 1968, **24**, 3031.

[8] 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

Reaction of (E)-4,4′-*Dimethoxystilbene with DMSO*⁻.—The stilbene [9] (0·2 g) was added to a stirred solution of DMSO⁻ [from sodium hydride (0·25 g)] in DMSO (20 ml), and the mixture was stirred at 25° for 24 h, then diluted with water. The solid which precipitated was filtered off, and recrystallised from glacial acetic acid to give (*E*)-4,4′-dimethoxy-α-methylstilbene (115 mg, 55%), m.p. 122—123° (lit.,[10] 124°), spectrally identical with an authentic sample. The aqueous filtrate was extracted with ether (3 × 50 ml) and the extracts were then dried and evaporated. Chromatography of the residue in chloroform on alumina gave: (i) (*E*)-4,4′-dimethoxy-α-methylstilbene (32 mg) (eluted first) and (ii) methyl 2,3-bis-(4-methoxyphenyl)propyl sulphoxide (60 mg, 20%) (eluted last) as an oily diastereoisomeric mixture, $\nu_{max.}$ (film) 1610, 1585, 1515, 1250, 1035, 835, and 735 cm⁻¹; τ 3·0—3·4 (m, 8 ArH), 6·28 (OMe), 6·3 (OMe), 7·18 (3 ArC*H*), 7·6 (4H), and 7·82 (SOMe).

Reaction of (*E*)-4,4′-dimethoxy-α-methylstilbene with DMSO⁻ produced a comparable yield of the propyl sulphoxide.

cis- *and* trans-1,2-*Diphenylcyclopropane*.—A mixture of isomers of the cyclopropane was prepared from chalcone as described previously.[4] Separation by g.l.c. (170°) gave: (i) *cis*-1,2-diphenylcyclopropane, n_D^{22} 1·5872; $\nu_{max.}$ (film) 1600, 1575, 1500, 910, 775, and 695 cm⁻¹; τ 2·8—3·1 (m, 10 ArH), 7·5 (dd, *J* 9 and 10 Hz, 2 ArC*H*), and 8·55 (m, CH_2); and (iii) *trans*-1,2-diphenylcyclopropane (eluted second), n_D^{22} 1·6000; $\nu_{max.}$ (film) 1600, 1575, 1500, 910, 775, and 695 cm⁻¹; τ 2·65—2·9 (m, 10 ArH), 7·85 (dd, *J* 9 and 10 Hz, 2 ArC*H*), and 8·66 (m, CH_2).

Reaction of cis- *and* trans-1,2-*Diphenylcyclopropane with DMSO*⁻.—(a) cis-*Isomer*. The *cis*-isomer (0·194 g) was added to a solution of DMSO⁻ [from sodium hydride (0·05 g)] in DMSO (10 ml); the mixture was stirred for 2 h, then diluted with water (50 ml), and extracted with ether (3 × 50 ml). Evaporation of the dried extracts gave *trans*-1,2-diphenylcyclopropane (0·175 g, 90%) spectrally (i.r. and n.m.r.) and chromatographically indistinguishable from an authentic sample.

(b) trans-*Isomer*. The *trans*-isomer was similarly treated with DMSO⁻. Work-up gave the starting *trans*-isomer (*ca.* 90% recovery).

Diethyl sulphoxide. The sulphoxide, prepared by oxidation of diethyl sulphide with sodium periodate, had b.p. 66° at 1·5 mmHg (lit.,[8] 88—90° at 15 mmHg), $\nu_{max.}$ (film) 1030 cm⁻¹; τ 7·36 (q, *J* 8 Hz, CH_2) and 8·75 (t, *J* 8 Hz, CH_3).

Reaction of (E)-*Stilbene with Diethyl Sulphoxide Anion*.—(*E*)-Stilbene (0·1 g) was added to a solution of diethyl sulphoxide anion [from sodium hydride (0·065 g)] in diethyl sulphoxide (10 ml); the mixture was stirred at 70° for 1 h, then cooled and diluted with water, and extracted with ether. Evaporation of the dried extracts left an oil, which was chromatographed in benzene on silica gel to give a hydrocarbon fraction (0·05 g, 45%). Analysis of this fraction by both g.l.c. (180°) and n.m.r., and comparison with authentic samples, showed that it was a mixture of (*Z*)-α-ethylstilbene, (*Z*)-1,2-diphenylbut-2-ene, (*E*)-1,2-diphenylbut-2-ene, and (*E*)-α-ethylstilbene in the proportions *ca.* 2 : 1 : 2 : 4.

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