# Reactions between Lithium Dimethylcuprate and Alkenyl Bromides, Chlorides, and Fluorides: Synthetic, Mechanistic, and Stereochemical Aspects

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The reactions of *cis*- and *trans*-1-halogeno-2-phenylsulphonylethylenes (I)—(VI) and 1-halogeno-2-phenyl-ethylenes (VII)—(X) with lithium dimethylcuprate in ether have been investigated. In most cases cross-coupling products are formed in good yield but reductive dehalogenation, which occurs with retention of configuration, may become an important process depending upon the nature of the substrate. At variance with the styrene system, in the sulphonyl compounds the stereochemical course of the substitution is influenced by the leaving group and by the temperature, a high degree of stereospecificity being observed only for bromides and chlorides at low temperature. Low and high leaving group effects have been observed respectively for the sulphonyl and styrene systems thus suggesting the operation of different mechanisms. These and related results are discussed in the light of the following pathways: (i) electron transfer; (ii) formation of a vinyl carbanion; (iii) concerted substitution of the halogen; (iv) addition—elimination. Mechanism (iv) appears a likely candidate for the reactions of the sulphonyl derivatives whereas mechanisms (ii) and/or (iii) may be followed by the halogenostyrene system.

ORGANOCOPPER reagents are enjoying deserved popularity as reagents for the formation of C–C bonds. Addition to activated unsaturated compounds as well as substitution in aliphatic, aromatic, and vinylic systems have been reported.[1] The reaction between the latter type of compounds and cuprates [2–5] or monocopper(I) reagents [6] has appeared particularly promising for organic synthesis due to the degree of stereospecificity observed in the few cases investigated.[1-4,6] However, systematic studies on this reaction are rare and as a result very little is known on the mechanism. With the aim of exploring the scope and limitations of the reaction as well as the fundamental features of the mechanism we have undertaken an investigation using *cis*- and *trans*-1-halogeno-2-phenylsulphonylethylenes
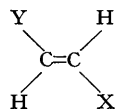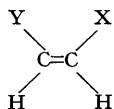
(I) Y = PhSO₂, X = Br   (II) Y = PhSO₂, X = Br
(III) Y = PhSO₂, X = Cl   (IV) Y = PhSO₂, X = Cl
(V) Y = PhSO₂, X = F   (VI) Y = PhSO₂, X = F
(VII) Y = Ph, X = Br   (VIII) Y = Ph, X = Br
(IX) Y = Ph, X = Cl
(X) Y = Ph, X = F

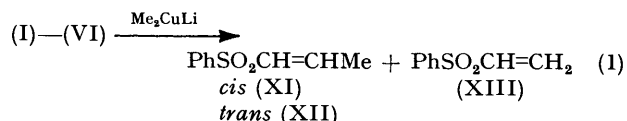(I)—(VI) and 1-halogeno-2-phenylethylenes (VII)—(X) as substrates and lithium dimethylcuprate as reagent.

These systems were chosen as substrates because their behaviour with a variety of common nucleophiles is known.[7,8] Furthermore, 1-bromo-2-phenylethylenes (VII) and (VIII) have been used for coupling with dialkylcuprates [1a,2] and their reactions have been now reconsidered in more detail for purposes of comparison.

RESULTS

Reactions of 1-Halogeno-2-phenylsulphonylethylenes (I)—(VI) *with Lithium Dimethylcuprate.*—The title reactions were performed in ether and found to lead to products of substitution, (XI) and (XII), and reduction, (XIII) [equation (1)].

The formation of the reduction product (XIII) was important only in the case of the *cis*-isomers (I) and (III).

Attempts to increase the yields of the formal substitution product by adding methyl iodide before quenching [2b] did not give any positive result.

$$(I)\text{—}(VI) \xrightarrow{\text{Me}_2\text{CuLi}}$$

$$\text{PhSO}_2\text{CH=CHMe} + \text{PhSO}_2\text{CH=CH}_2 \quad (1)$$
$$cis\ (XI) \qquad\qquad (XIII)$$
$$trans\ (XII)$$

The data in the Table refer to reactions performed using a slight excess (*ca.* 5%) of reagent over substrate and very

Reactions between 1-halogeno-2-phenylsulphonylethylenes (I)—(VI) (5—7 × 10⁻²M) and lithium dimethylcuprate (5—7 × 10⁻²M) in ether

Substrate	T/°C	Product (%)		
		(XI)	(XII)	(XIII)
(I)	−60	27	*ca.* 3	70
(I)	−20	35	5	60
(I)	0	45	8	47
(II)	−60		92	8
(II)	−20		92	8
(II)	0		95	5
(III)	−60	50	5	45
(III)	−20	45	10	45
(III)	0	41	18	41
(IV)	−60		97	*ca.* 3
(IV)	−20		97	*ca.* 3
(IV)	0		97	*ca.* 3
(V)	−60	70	30	
(V)	−20	60	40	
(V)	0	50	50	
(VI)	−60		100	
(VI)	−20		100	
(VI)	0		100	

short reaction times (30—45 s). The overall yields ranged between 75 and 95% (g.l.c. and n.m.r. analysis), the higher limit obtaining for the fluoro-derivatives, but in the case of the reactions of the bromo- and chloro-compounds at the lower temperatures some unconverted material (5—10%) could also be detected. With longer reaction times (a few minutes) and a large excess of reagent a more complex pattern was followed. Reaction mixtures were formed in which 2-methylpropyl phenyl sulphone (XIV) was found to predominate. The compound was shown to arise from further addition of reagent to the coupling products (XI) and (XII) [equation (2)]. This observation stimulated a parallel investigation on the addition of copper reagents to

vinylic sulphones. However, there is a precedent for this process reported by Posner and Brunelle.[9]

As shown in the Table, a fairly high degree of stereo-

$$(XI) \text{ or } (XII) \xrightarrow{Me_2CuLi} PhSO_2CH_2CH(Me)_2 \quad (2)$$
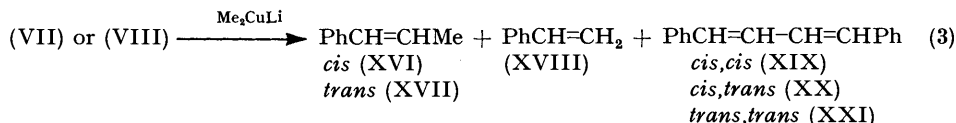$$(XIV)$$
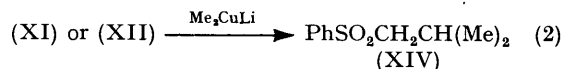
specificity was observed for the bromo- and chloro-compounds which reacted at $-60°$ following a retention pathway. The inversion component observed for the *cis*-isomers (I) and (III) became more significant with increasing temperature and in the case of the fluoro-compound (V) it was important even at $-60°$.

The stereochemical course of the reductive dehalogenation was also studied by quenching the reaction of compound (I) with deuteriomethanol (MeOD). N.m.r. analysis revealed that the extent of deuteriation was 85% and that *cis*-1-deuterio-2-phenylsulphonylethylene (XV) was formed, thus indicating that retention of configuration had occurred.

$$\begin{array}{cc} PhSO_2 & D \\ \diagdown & \diagup \\ \diagup & \diagdown \\ H & H \end{array}$$
$$(XV)$$
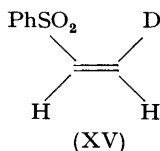
For evaluation of the reactivity order two substrates (in 1 : 1 ratio) were treated with half mol. equiv. of reagent and, assuming simple kinetic behaviour, the required reactivity ratios were evaluated from the composition of the recovered unchanged materials. The method, although it cannot be considered of high accuracy, allowed us to reach the following conclusions: (i) the leaving group effect is rather modest, the Br : Cl : F reactivity ratio being 3 : 1 : 2 in both *cis*- and *trans*-series; (ii) *cis*-isomers react at rates not markedly higher than those of the *trans*-counterparts, the *cis* : *trans* reactivity ratios being *ca.* 1.5 independent of the leaving group. For each substrate control experiments were performed in order to ascertain that no *cis–trans* isomerization of products or reactants occurred during the reaction.

Reactions of 1-*Halogeno*-2-*phenylethylenes* (VII)—(X) *with Lithium Dimethylcuprate.*—As expected [2] *cis*- and *trans*-1-bromo-2-phenylethylenes, (VII) and (VIII), reacted with five mol. equiv. of reagent at -40 to $0°$ yielding 50—80% of the substitution products (XVI) and (XVII) with retention of configuration. An overall yield of 10—35% of a mixture of styrene and isomeric 1,4-diphenylbutadienes was also formed [equation (3)]. The presence of compounds (XVIII)—(XXI) was particularly important when lower

the temperature and working under normal conditions isomerization was observed and eventually only the *trans,trans*-diene was detected. Similar changes have been reported to occur also under different conditions.[10]

Addition of methyl iodide to the reacting solutions of (VII) before quenching was found to cause the disappearance of styrene and an increase in the yield of the substitution product (from 50 to 80% at $0°$).

The results obtained with the chloro and fluoro derivatives (IX) and (X) were in sharp contrast with those of the sulphonyl derivatives. The chloro compound (IX) was found to be much less reactive than the bromo derivative (VII). A $k_{Br} : k_{Cl}$ ratio of *ca.* 10^2 was measured by comparison of the half-lives of reactions involving the two substrates. The substitution product (XVI) was formed in 70% yield (g.l.c. analysis). The product of inversion was absent but 15% styrene and dienes were also detected. On the other hand fluoroethylene (X) did not show any significant reaction even after several hours at $0°$.

Finally, the *cis* : *trans* reactivity ratio was measured for the bromophenylethylenes (VII) and (VIII) as described for the sulphonyl derivatives (I)—(VI) and a value close to unity was found.

DISCUSSION

Synthetic Aspects.—The results emphasize the possibility of performing C–C cross-coupling of olefinic halogeno-sulphones in good yield, an interesting observation as unsaturated sulphones are useful intermediates in organic synthesis.[11] Furthermore, it appears from our work that, when activation of the vinylic halides is sufficiently high, fluorides can be conveniently used besides other halogeno derivatives.[1-6] This type of substrate does offer the considerable advantage of cleaner C–C cross-coupling with complete absence of the reduction product. However, when this is formed the stereoselective course of the reaction is of interest for the synthesis of labelled derivatives.
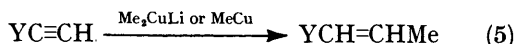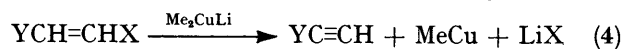
Finally, it is worth noting that, when *cis*-1-bromo-2-phenylethylene (VII) is used as substrate, the yield of the less easily accessible *cis,cis*-diene (XIX), although very low, is not far from those reported for more conventional routes leading to the same product.[10, 12] Obviously, further studies are needed in order to ascertain the possibility of influencing the role of the various competing processes.

Mechanistic and Stereochemical Aspects.—It is known

$$(VII) \text{ or } (VIII) \xrightarrow{Me_2CuLi} \begin{array}{l} PhCH=CHMe \\ cis \text{ (XVI)} \\ trans \text{ (XVII)} \end{array} + \begin{array}{l} PhCH=CH_2 \\ (XVIII) \end{array} + \begin{array}{l} PhCH=CH-CH=CHPh \quad (3) \\ cis,cis \text{ (XIX)} \\ cis,trans \text{ (XX)} \\ trans,trans \text{ (XXI)} \end{array}$$

yields of substitution products were obtained, *e.g.* in the reactions of the *cis*-bromo derivative (VII) at $0°$. The composition of the mixture appeared to change with time, a decrease of the ratio styrene : butadienes being observed until complete disappearance of styrene.

Furthermore, in the case of the reactions of the *cis*-bromo derivative (VII) at $-20°$ the *cis,cis*-diene was found to be the predominant isomer and was actually isolated by preparative t.l.c. provided that the reaction and the isolation procedure were performed in the dark. Upon increasing

that terminal and non-terminal acetylenes are able to add alkylcuprate and alkylcopper(I) reagents.[1b-d, 6b, 13, 14] On the other hand the first type of reagent has been found to promote elimination at least in olefin-forming reactions.[2b, 15] Consequently, the possibility has to be considered that the substitution products isolated in the reactions reported here might arise from an elimination–addition process according to equations (4) and (5).

Sequence (4) and (5) can be ruled out as only one isomer

with a configuration dependent upon the stereochemical course of addition would result from equations (4) and (5). Since the addition of the copper reagent is usually

$$YCH=CHX \xrightarrow{\text{Me}_2\text{CuLi}} YC\equiv CH + MeCu + LiX \quad (4)$$

$$YC\equiv CH \xrightarrow{\text{Me}_2\text{CuLi or MeCu}} YCH=CHMe \quad (5)$$

a *syn*-process [1b-d,6b,13,14] only the *trans*-isomer would be formed. Furthermore, if elimination–addition operated in the case of the halogenostyrene system a partial or complete attack on the carbon bearing the phenyl group would be expected to occur during the latter step on the basis of results obtained with similar reagents.[13b-d,14b,c]

Having settled that we are dealing with a substitution process we now discuss the mechanistic possibilities which are open to the reaction.

represented in a simplified manner rather than in a more accurate but more complex form.[19,20b,21]

(i) The electron transfer process comes first to attention since it is considered a likely candidate for the coupling of cuprates with electrophilic olefins.[19] However, isomerization of the starting material has not been observed for this reaction and, furthermore, a high degree of retention has been observed for halogenostyrenes and for bromo- and chloro-phenylsulphonylethylenes at lower temperatures. Therefore, accepting the evidence in favour of the stereochemical lability of the intermediate radicals,[4,19,22] mainly based upon data for simple vinylic radicals [22] or radical anions deriving from $\alpha\beta$-unsaturated carbonyl compounds,[19] we are compelled to rule out the electron transfer process in the reaction investigated.

(ii) Attack at the halogen could be considered valid

SCHEME 1
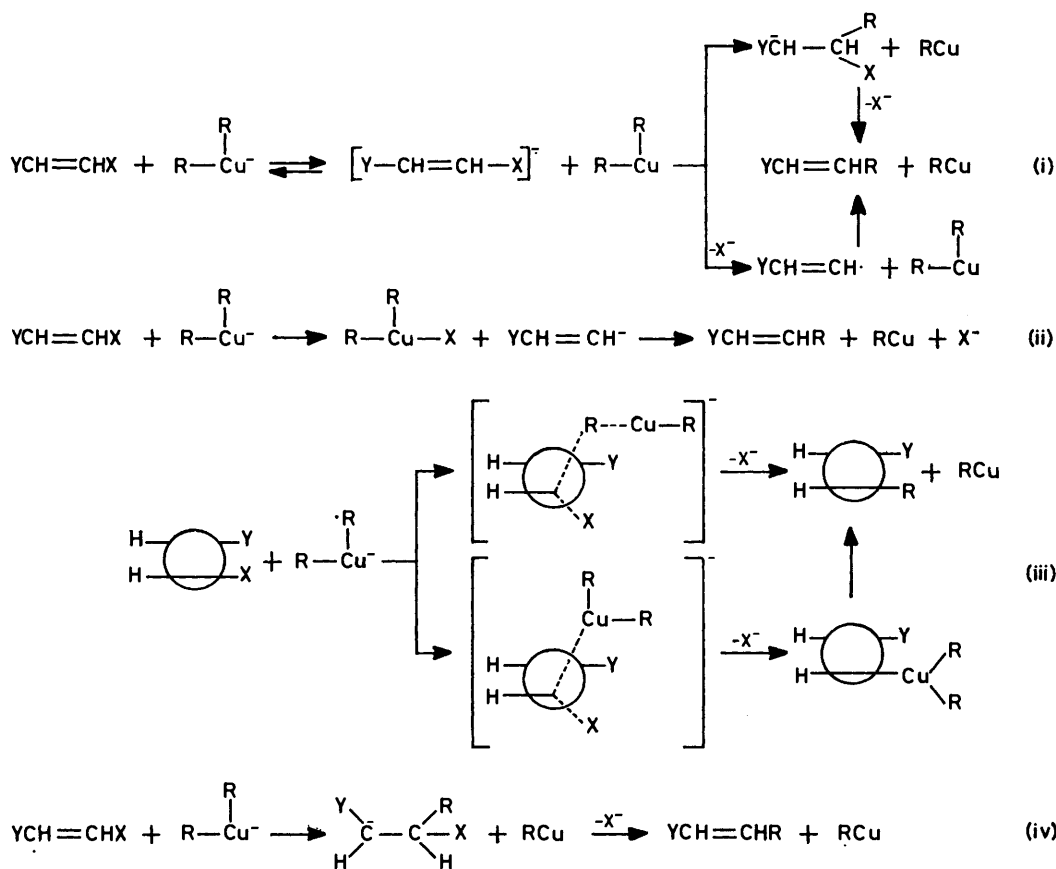
In agreement with current views concerning nucleophilic substitution on vinylic halides [7,16-18] and the behaviour of organocuprates for various kinds of C–C coupling [1,2c,4,14,15,19,20] the following routes appear to deserve consideration: (i) electron transfer; (ii) formation of a vinylic carbanion; (iii) concerted substitution of the halogen; (iv) addition–elimination. The main features of these mechanisms are summarized in Scheme 1, where for simplicity possible (minor) variations in the routes have not been shown. Also, the reagent has been

particularly for the reactions of the halogenostyrenes where a marked effect of the leaving group has been observed. The stereochemical course is in agreement with the intervention of a configurationally stable vinyl carbanion.[23] On the other hand, as the leaving group effect is insignificant when sulphonyl derivatives are used, it appears evident that attack on halogen, even if it operates with the styrene substrates, cannot be extended to the more activated sulphonyl compounds.

Furthermore, for the intermediacy of a vinyl carbanion

there is an important variation involving metal–halogen exchange leading to a mixed organocuprate according to equation (6).

$$YCH=CHX + Me_2Cu^- \rightleftharpoons$$
$$(YCH=CHCuMe)^- + MeX \quad (6)$$
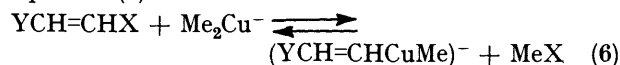
The observations on the reductive dehalogenation process are consistent with the intervention of a vinyl-metal species. In principle formation of the latter could be followed by nucleophilic attack on the methyl halide, leading eventually to the substitution product as shown in equation (7). Besides the organocuprate in equations

$$(YCH=CHCuMe)^- + MeX \rightarrow$$
$$YCH=CHMe + MeCu + X^- \quad (7)$$
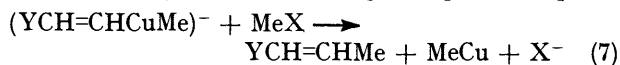
(6) and (7) other similar vinylmetal species, e.g. divinyl-cuprate, $(YCH=CH)_2Cu^-$, or vinylcopper(I), $YCH=CHCu$, could be present in the reacting mixture and play the same role.

The results obtained by adding methyl iodide before quenching in the case of the halogenostyrene system reveal that reaction between a vinylmetal species and the externally added electrophile is possible, but no conclusion can be reached on the importance of the analogous process occurring in the absence of methyl iodide.

carbon atom as a slow step. The attacking centre of the reagent could be either the carbon of the methyl group or the copper atom. This is shown for mechanism (iii) in which, when the metal is the attacking centre, the overall process becomes stepwise, a formal copper(III) species being involved as an intermediate leading to the final products. Consequently, in this case the situation is similar to the oxidative addition–reductive elimination mechanism proposed for the analogous substitution at an aliphatic centre.[1a,15,20]

In mechanism (iv) the attack on the carbon takes place before carbon–halogen fission and as a result a carbanionic intermediate is formed. In Scheme 1 the nucleophilic attack is shown as performed by the carbon atom of the reagent. This type of mechanism is commonly accepted for nucleophilic substitution at vinylic carbon whereas the concerted type has found few advocates.[4,7,16-18]

In principle, the boundary between the two processes should be blurred and, for instance, one could envisage a concerted process in which formation of the carbon–nucleophile bond is in the lead and carbon–halogen fission has occurred only to a small extent. It is worth noting that this is strikingly similar to the variable transition state theory of elimination reactions.[25]
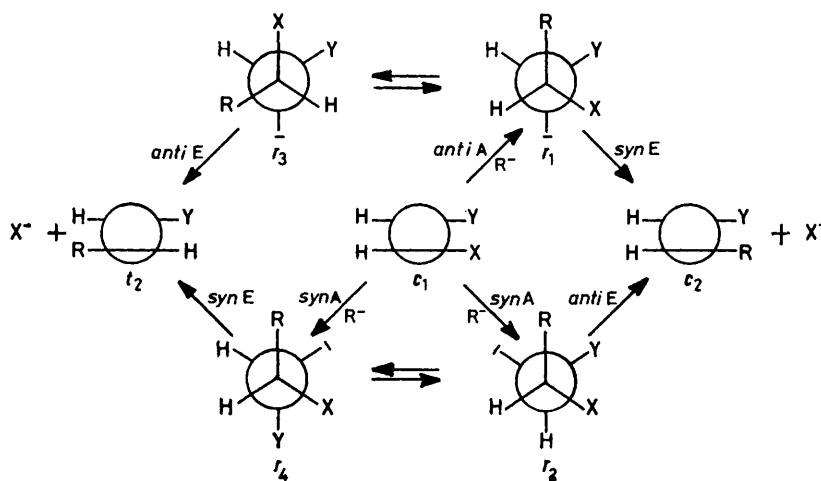

SCHEME ·2

Furthermore, we have observed that formation of dienes is accompanied by disappearance of styrene. This suggests that a different fate is possible for the vinyl-metal compound besides reaction with the alkyl halide. Diene formation from similar organometallic compounds has been reported and in agreement with our results retention of configuration has been found.[1a,22,24]

Once again sulphonyl derivatives behave differently. Indeed, addition of methyl iodide did not cause any increase in the yield of substitution product thus suggesting a low, if any, contribution by metal–halogen exchange to the observed coupling.

Our opinion is that the two remaining mechanisms (iii) and (iv) provide an explanation of the observations made. Both routes involve attack at the same vinylic

Within this framework we can now explain our results by assuming that in the reactions of the sulphonyl derivatives the high activation of the system permits the intervention of a carbanionic species, whereas in the case of the mildly activated styrenes the concerted process operates. Perhaps the intervention of this rare mechanism is stimulated by interaction between the leaving group and a metal atom of the reagent in the transition state, for instance as depicted in (a).

(a)
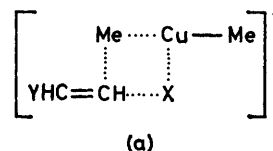
Similar interactions have been postulated in other substitution reactions of cuprates.[26] It is worth emphasizing that even the classical nitro activated $S_N Ar$ reactions may become one-step processes when interaction between the reagent and the leaving group occurs in the transition state.[27]

The stereochemical course observed for all the substrates finds a convincing rationale in the hypothesis formulated above. Indeed, the halogenostyrene reacting through the concerted mechanism should lead to complete retention [4,17] whereas the variable stereochemical course observed for the sulphonyl compounds is strictly connected with the lifetime of the intermediate involved in the stepwise process. A description of the stereochemical course of nucleophilic substitution in vinylic systems and related processes has been given by various workers.[7,16a,17,18] A graphic analysis has recently been performed by Miller [18] and a detailed picture presented. In order to provide a rationale of our results we summarize the current views in a simple manner in Schemes 2 and 3. In Scheme 2 it is assumed
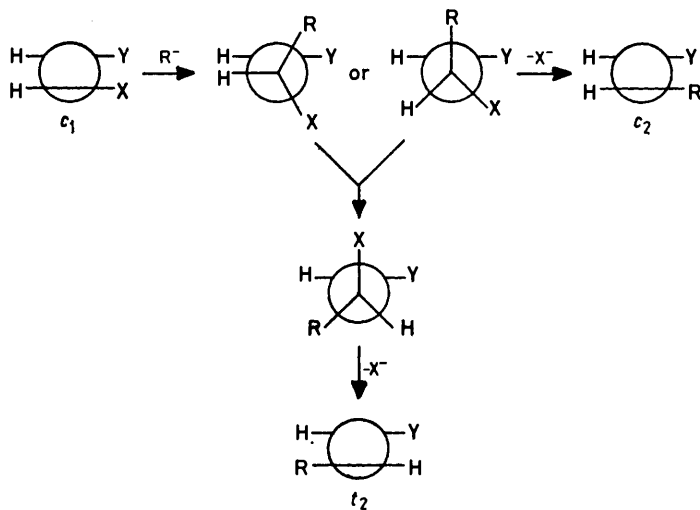
SCHEME 3

that the carbanion is pyramidal and the possible stereochemical outcome for attack on a cis-isomer is shown. The retention course may proceed through an anti-addition–syn-elimination $(c_1 \rightarrow r_1 \rightarrow c_2)$ or syn-addition–anti-elimination route $(c_1 \rightarrow r_2 \rightarrow c_2)$. Inversion can derive from anti-addition–anti-elimination $(c_1 \rightarrow r_1 \rightarrow r_3 \rightarrow t_2)$ or syn-addition–syn-elimination $(c_1 \rightarrow r_4 \rightarrow t_2)$ pathways. Alternatively, the r_4 rotamer can be considered as arising from rotation of r_2. In Scheme 3 the intermediate carbanion is considered as a rapidly inverting sp^3 or sp^2 species and routes leading to inversion or retention are shown.[7,16a,18] Independently of the model chosen it can be easily seen that when the leaving group is changed from bromine to fluorine the greater strength of the carbon–halogen bond allows a longer life and consequently increased possibility of rotation for achieving conformations leading to inversion.[7] We can also explain the dependence of the stereochemical course on

the temperature by assuming that activation barriers leading to inverted conformations are higher than those related to retention pathways.[28]

EXPERIMENTAL

U.v. spectra were taken in n-hexane with a Zeiss DMR 21 spectrophotomer. N.m.r. spectra were recorded with a Varian HA 100 spectrometer.

Materials.— cis-1-Bromo-2-phenylsulphonylethylene [29a] (I), m.p. 41—42°, trans-1-bromo-2-phenylsulphonylethylene [29a] (II), m.p. 59—60°, cis-1-chloro-2-phenylsulphonylethylene [29b] (III), b.p. 157° at 3.5 mmHg, trans-1-chloro-2-phenylsulphonylethylene [29b] (IV), m.p. 49—50°, cis-1-fluoro-2-phenylsulphonylethylene [29c] (V), b.p. 89—90° at 0.02 mmHg, trans-1-fluoro-2-phenylsulphonylethylene [29c] (VI), m.p. 43—44°, cis-1-bromo-2-phenylethylene [30a] (VII), m.p. − 6 to − 7°, trans-1-bromo-2-phenylethylene [30a] (VIII), m.p. 6—7°, cis-1-chloro-2-phenylethylene [8b] (IX), b.p. 54—55° at 2 mmHg, cis-1-fluoro-2-phenylethylene [30b] (X), b.p. 43—44° at 13 mmHg, were prepared according to known procedures. The solid sulphones were purified by crystallization from light petroleum (b.p. 80—120°). Bromostyrenes (VII) and (VIII) were crystallized from methanol.

Reactions.—Lithium dimethylcuprate was obtained by adding freshly prepared methyl-lithium (2 mol. equiv.) free from LiBr, to a stirred suspension of copper(I) iodide (1 mol. equiv.) in ether at − 20° under argon. By inverting the flask the solution of cuprate was transferred into a jacketted, cooled dropping funnel connected on one side with the flask containing the reagent and on the other with a second empty flask. A solution of substrate was then added and cooled to the required temperature. The cuprate was then dropped into this solution over ca. 15 s. Aqueous ammonium chloride was used to quench the reaction and the mixture was extracted with ether. After evaporation of the solvent the products were subjected to instrumental analysis (g.l.c. or n.m.r.). The products cis- and trans-phenyl propenyl sulphones [31a−c] (XI) and (XII), phenyl vinyl sulphone [31a] (XIII), and isobutyl phenyl sulphone [31d] (XIV) were known compounds characterized by comparison with authentic samples.

Two analytical procedures were used for determining the reactivity of sulphonyl derivatives. Usually g.l.c. analysis [Hewlett–Packard instrument; 5% silicone oil (SE 30) on 80—100 mesh Chromosorb W] was performed on the recovered organic material. Experiments were also performed by comparing bromides and chlorides with fluorides using volumetric analysis of unchanged substrates. These were treated with methoxide ion in methanol to give halide ions which were titrated by the Volhard method or with $Th(NO_3)_4$.

The n.m.r. spectra of phenyl vinyl sulphone (XIII) and the deuteriated counterpart (XV) were analysed with the aid of the LAOCOON 3 program. The following chemical shifts and coupling constants were obtained in $CDCl_3$: $PhSO_2\text{–}CH_a\text{=}CH_bH_c$ (XIII) (H_a and H_b cis-related), τ 3.3 (H_a), 4.0 (H_b), and 3.6 (H_c), J_{ab} 9.7, J_{bc} 0.3, and J_{ac} 16.4 Hz; cis-$PhSO_2CH_a\text{=}CH_bD$ (XV), τ 3.4 (H_a) and 4.1 (H_b), J_{ab} 9.9 and J_{aD} 2.5 Hz.

As pointed out in the Results section the reactions of 1-bromo-2-phenylethylenes (VII) and (VIII) (0.025M) with cuprate (0.125M) showed a ratio styrene : dienes which was dependent on the time. For example, in the case of compound (VII) at − 20° after 1 h 25% styrene and 5%

diene were found and after 5 h 25% dienes and no styrene. The reactions were followed by g.l.c. and t.l.c. [silica gel; light petroleum (b.p. 60—80°)–carbon tetrachloride (8 : 2)]. The latter technique was also used on a preparative scale to isolate *cis,cis*-1,4-diphenylbutadiene (XIX), m.p. 70—70.5° (from methanol).

The effect of addition of methyl iodide was studied at 0°. Compound (VII) was allowed to react with lithium dimethylcuprate (5 mol. equiv.) for 5 min. Subsequently, methyl iodide (5 mol. equiv.) was added and the mixture stirred for an additional 10 min before quenching.

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