Addition of 4-Chlorobenzenesulphenyl Chloride to 3-Methylbut-1-yne, Hex-1-yne, and Phenylacetylene: Isomerization and Hydrolysis of the Adducts

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The addition of (4-ClC_6H_4SCl, (2), to RCH≡CH, (1; R = Pr^i, Bu^n), gives (*E*)-4-ClC_6H_4(R)C = C(H)Cl, (*E*)-(3), and (*E*)-4-ClC_6H_4(H)C=C(R)Cl, (E)-(4) in a fixed ratio; the addition to (1; R = Ph) gives regiospecifically (*E*)-(3; R = Ph) in ethyl acetate, but different proportions of (*E*)-(3) and (*E*)-(4) (R = Ph) in chloroform, *sym*-tetrachloroethane, and acetic acid. With an excess of the sulphenyl chloride (2), (*E*)-(3) and (*E*)-(4) isomerize to (*Z*)-(4) (same R). The sulphuric-acid catalysed hydrolysis of (*E*)-(3; R = Pr^i,Bu^n, Ph) gives α-chloroketones $RCOCH_2Cl$ (5) (same R). The (*E*)-(4) isomers do not hydrolyse.

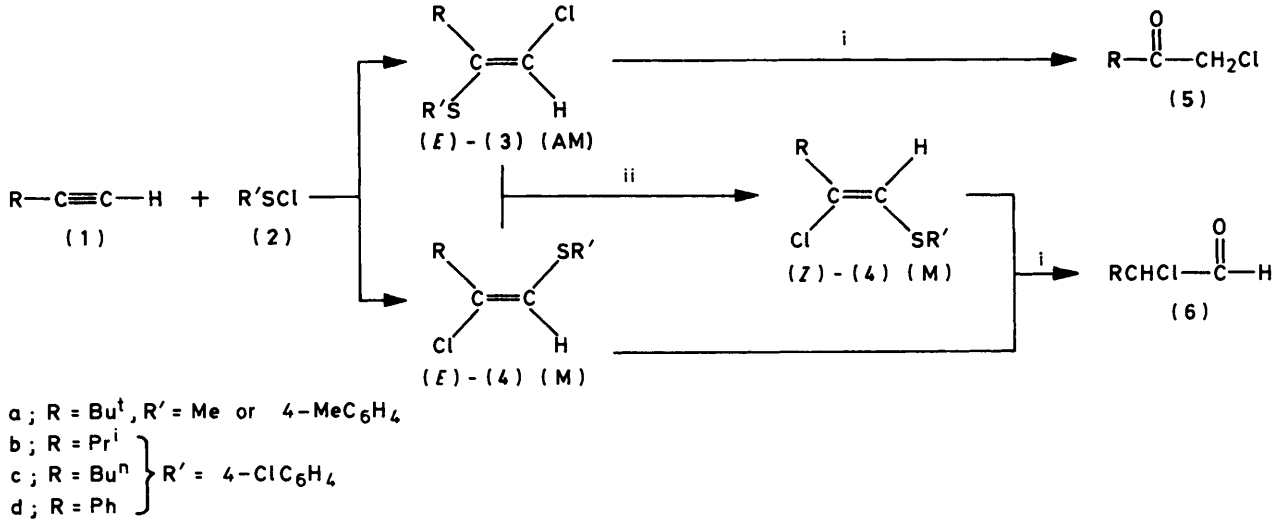
The addition of sulphenyl chlorides to acetylenes gives 1 : 1 adducts in the *trans*-configuration.[1] When asymmetrical acetylenes are used, as in the case of terminal acetylenes, mixtures of anti-Markownikov (AM) and Markownikov (M) adducts are sometimes obtained (Scheme 1). Structural effects of the sulphenyl chloride are not relevant for the regioselectivity, except in the particular case of 2-nitro-substituted arenesulphenyl chlorides.[2] The addition probably occurs *via* thiirenium ions; these have been detected at low temperature,[1d,3] and in some cases isolated as salts which are stable at room temperature.[1d,4,5] The regio-orientation is determined by the subsequent nucleophilic attack of chloride ion at either carbon atom of the three-membered ring.

The importance of the steric and electronic factors in the ring-opening reaction has been noted.[1,5] t-Butylacetylene (1a) gives rigorously the AM adducts (*E*)-(3), while with 3-methylbut-1-yne (1b) and hex-1-yne (1c) the M isomers (*E*)-(4) are also formed. The picture may be complicated by the possibility of subsequent isomerization processes: we have in fact recently found that the AM to M isomerization may be catalysed by the sulphenyl chloride itself.[6]

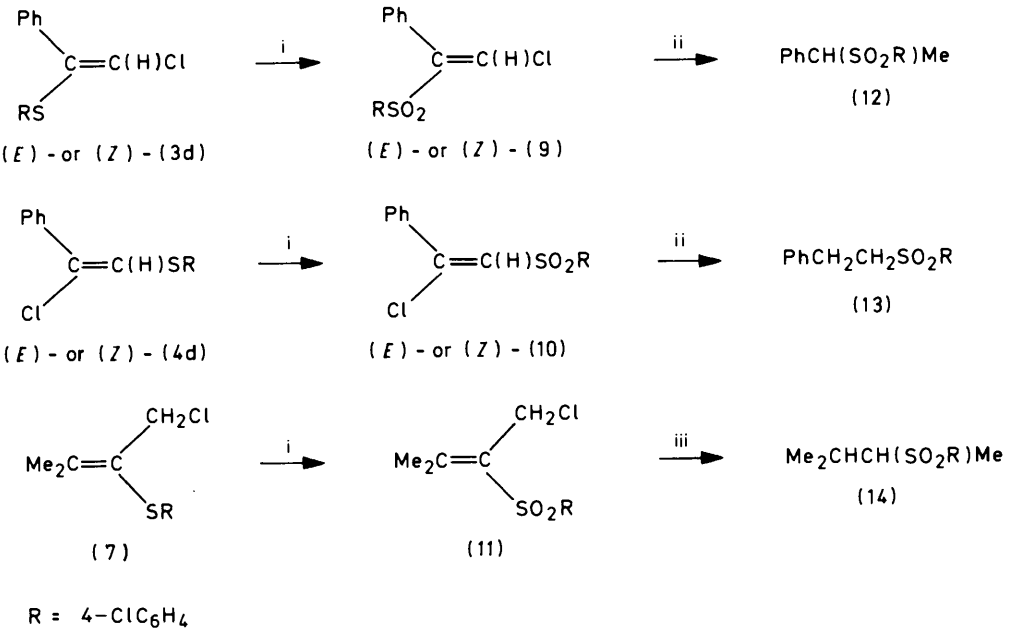
The control of regioselectivity is important as the acid-catalysed hydrolysis of AM and M adducts may lead to α-chloroketones (5) and α-chloroaldehydes (6), respectively.[6] The potentially available reaction routes are illustrated in Scheme 1.

In the addition of 4-methylbenzenesulphenyl chloride to phenylacetylene (1d), the orientation is also affected by the solvent: with solvents showing increasing polarity, a shift from AM to M orientation was observed (in ethyl acetate, 100% AM; in chloroform, AM : M = 65 : 35; in acetic acid, AM : M = 29 : 71).[2] This change in regioselectivity was attributed to a greater chloride ion–solvent interaction, which leads to a lower nucleophilicity of the chloride ion and to a more S_N1-like transition state.[1d,2]

However, a recent report[7] claims that the addition of 4-chlorobenzenesulphenyl chloride (2b) to phenylacetylene (1d) in *sym*-tetrachloroethane is totally regiospecific, giving quantitatively the M adduct. This result conflicts with previous findings, as this sulphenyl chloride does not exhibit particular structural features and the solvent should show a similar degree of solvation of chloride ion as chloroform. The discrepancy might again be explained by a late, unobserved AM to M isomerization.



Scheme 1. *Reagents*: i, H_3O^+; ii, R'SCl



Scheme 2. *Reagents*: i, *m*-chloroperbenzoic acid; ii, H_2.Pd or $LiAlH_4$; iii, $LiAlH_4$

The renewed interest in the synthesis of halogenomethylketones [8] and the possibility of achieving differential triple-bond functionalization encouraged us to study in more detail the limits and applications of the reactions outlined in Scheme 1. We also reinvestigated the reaction of the sulphenyl chloride (2) with phenylacetylene (1d) in several solvents. In order to be certain that the detected products are kinetic products, the reactions were followed by n.m.r. spectroscopy. The identification of the products was accomplished by chemical transformations.

Results

Addition of 4-*Chlorobenzenesulphenyl Chloride* (2) *to* 3-*Methylbut*-1-*yne* (1b) *and Hex*-1-*yne* (1c).—The synthesis of the olefins (3b—c) and (4b—c) has been reported.[9] Inseparable mixtures of (*E*)-(3b) and (*E*)-(4b) (80 : 20) and of (*E*)-(3c) and (*E*)-(4c) (85 : 15) have been obtained; the ratio is independent of the solvent (CCl_4, $CHCl_3$, CH_2Cl_2, $CHCl_2$-$CHCl_2$).* Attempts to isomerize these adducts to (*Z*)-(4b) and (*Z*)-(4c) with catalytic amounts of the sulphenyl chloride [6] gave rise, according to n.m.r. and t.l.c. data, to a mixture (not further investigated) of many products, probably derived from anionotropic rearrangements of the intermediates. Therefore the hydrolyses were carried out on the crude reaction mixtures.

Addition of 4-*Chlorobenzenesulphenyl Chloride* (2b) *to Phenylacetylene* (1d).—Compound (2) was added at room temperature or below to a solution containing an excess of (1d) in a n.m.r. tube and the spectra were recorded immediately thereafter. Four solvents, [^{2}H]chloroform, *sym*-[$^2H_2$]-tetrachloroethane, [$^2H_4$]acetic acid, and ethyl acetate were used. The n.m.r. spectrum of the reaction mixture in ethyl acetate shows only one signal in the vinyl region. In the case of the other solvents, two signals at different ratios were detected in the same region (Table 1).

* Total AM orientation in the addition of toluene-4-sulphenyl chloride to hex-1-yne, determined by non-spectroscopic methods, was reported in an earlier paper: A. Dondoni, G. Modena, and G. Scorrano, *Boll. Sci. Fac. Chim. Ind. Bologna*, 1964, **22**, 26.

Table 1. ^{1}H N.m.r. chemical shifts and integrated ratios for the vinylic resonances of the products obtained from the addition of 4-chlorobenzenesulphenyl chloride (2) to phenylacetylene (1d) [a]

Solvent	(*E*)-(3d) (AM)	(*E*)-(4d) (M)	AM : M ratio
Ethyl acetate	6.62		
$CDCl_3$	6.68	6.63	70 : 30
$CDCl_3$ [b]	6.74	6.64	70 : 30
$CDCl_2CDCl_2$	6.67	6.64	70 : 30
$CDCl_2CDCl_2$ [b]	6.74	6.66	40 : 60
CD_3CO_2D	6.77	6.68	25 : 75

[a] At room temperature, unless otherwise stated. [b] −45 °C.

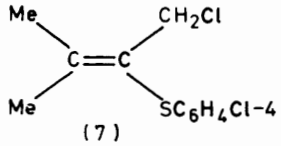
In acetic acid the addition rate is relatively slow at room temperature and it was possible to follow the progress of the reaction adequately. The ratio between the two vinylic signals remained constant throughout the reaction; this is a good indication that the observed products are kinetically formed and that no isomerization is occurring. In chloroform, the reaction course can be adequately followed at −45 °C and the same product ratio as that found at room temperature was observed. On the other hand, when the reaction was carried out in *sym*-tetrachloroethane, different product ratios were observed at room temperature and at −45 °C; the ratio observed at the completion of the reaction was not changed by varying the temperature.

Slightly different chemical shifts were observed for the two vinylic resonances in different solvents and at different temperatures. The pure isolated products or the mixture show the same variational behaviour. They were identified by the procedure described in Scheme 2.

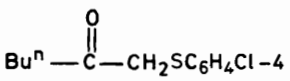
The *trans* AM adduct (*E*)-(3d), as well as the mixture of *trans* AM and M adducts (*E*)-(3d) and (*E*)-(4d), undergo complete (24 h at room temperature) conversion into the *cis* M adduct (*Z*)-(4d) upon treatment with 4-chlorobenzenesulphenyl chloride (2). The conversion was followed in chloroform and in tetrachloroethane. The same product was obtained from the reaction of phenylacetylene (1d) with a two-

Table 2. Hydrolysis of β-chlorovinyl sulphides (3b—d) to give α-chloromethyl ketones (5b—d)

Sulphide	Reagent	Temperature	Time	Ketone	Yield (%)	M.p. (°C)	B.p. (mmHg)	Ref.
(3b)	H_2SO_4–CH_2Cl_2	Reflux	1 h	(5b)	25		70 (20)	15
(3c)	H_2SO_4–CH_2Cl_2	Reflux	3 h	(5c)	50		73 (20)	16
(3d)	H_2SO_4–CH_2Cl_2	Reflux	30 min	(5d)	82	57—58	140 (15)	17
(3d)	TFA	Room temp.	4 days	(5d)	43			



(7)



(8)

fold excess of sulphenyl chloride (2). The compound was isolated in 85% yield and gave correct elemental analyses. Its regiochemistry was determined by the procedure of Scheme 2.

Hydrolysis of Adducts (3b—d) *and* (4b—d) *with Sulphuric Acid or Trifluoroacetic Acid* (TFA).—Some typical catalytic systems were checked for the hydrolysis of AM adducts (3b—d); the best results were obtained with the two-phase system dichloromethane–95% sulphuric acid. In all cases, the chloromethylketones (5b—d) were obtained, the yield depending on the individual compound. The relevant data are reported in Table 2.

The hydrolysis with TFA in chloroform is less efficient and may also be non-specific: compound (5d) was obtained from (3d) in much lower yield (43%), while (3b) and (3c) gave different products. Compound (*E*)-(3b) rearranges to the vinyl sulphide (7) which was identified by its n.m.r. and mass spectra, and elemental analysis and through the chemical transformations of Scheme 2; compound (7) was also detected by n.m.r. during the hydrolysis of (3b) with sulphuric acid. From (*E*)-(3c) an almost equimolar mixture of (5c) and (8) was obtained, from which only compound (8) could be isolated in pure form, albeit in low yield. When 4-chlorobenzenethiol was added to compound (3c) in TFA, (8) could be isolated in 62% yield.

The hydrolysis of the olefins (3b—d) was also attempted with mercuric salts: no evidence for the formation of the chloromethylketones (5) was obtained with this catalyst.

The hydrolysis of the M adducts (4b—d), either as pure compounds or mixed with the AM isomers, by means of the sulphuric-acid system was unsuccessful. The chloroaldehydes (6b—d) could not be isolated nor detected by n.m.r. *E–Z* Isomerization was observed in some cases; prolonged reaction times gave rise to black tars.

Identification of the Adducts.—The AM or M regiochemistry of the primary adducts (3d) and (4d) and the configuration of the rearranged product (7) were determined with the oxidation–reduction method outlined in Scheme 2.[10]

The products, either pure or as an isomeric mixture, were oxidized to the sulphones (9), (10), or (11), which could be separated eventually by column chromatography. The reduction of the vinyl sulphones afforded the alkyl sulphones (12), (13), and (14), which were unambiguously distinguished on the basis of the alkyl n.m.r. patterns, so that the primary products can be attributed the correct configuration.

On the other hand, the *E*-configuration must be assigned to the primary addition products (3d) and (4d). As a matter of fact, when these adducts, either pure or as a mixture and characterized by their specific vinyl hydrogen resonances, were treated in chloroform with TFA, different vinyl resonances were observed. As β-thiovinyl chlorides are more stable in the *Z*-configuration,[6] it is safe to assume that conversion from the (*E*)-(3d) or (*E*)-(4d) adducts into the (*Z*)-(3d) or (*Z*)-(4d) isomers had occurred.

Discussion

Vinyl sulphides have long been recognized as masked ketones.[11] Chlorovinyl sulphides (3), prepared regiospecificially or with a high degree of regioselectivity from terminal alkynes and sulphenyl chlorides, could be obvious synthons for the synthesis of ketones of type (5).

Our results indicate that α-chloroketones (5) are in fact accessible from the vinyl chloride (3), irrespective of the nature of the R residue (aryl or primary, secondary, or tertiary alkyl). On the other hand, the reaction conditions are critical for acceptable yields in ketonic products.

The generally accepted mechanism for the hydrolysis of vinyl sulphides can also be applied to compound (3). However, other mechanisms may be operative, as indicated by the detection of the ketone (8) during the hydrolysis of (1b) with TFA. The resistance to hydrolysis of compounds (4b—d) with respect to (3b—d) is simply explained: protonation at the α-carbon in the AM adducts (3) leads to sulphur-assisted tertiary carbonium ions, while the analogous protonation of the M adducts (4) generates less stable secondary carbonium ions. Also, the possible protonation at sulphur may be more competitive toward the formation of a secondary carbonium ion than that of a tertiary one.

The formation of compound (8) in the TFA-catalysed hydrolysis of (1c) in the presence of 4-chlorobenzenethiol represents a valuable approach to these compounds, which is the key intermediate step for the synthesis of the anti-inflammatory 5-chloro-3-n-butylbenzo[*b*]thiophen. This compound has been prepared in 10% yield from hexan-2-one.[12] The low yield is due to the chlorination reaction which, as it is well known, gives mixtures of chloroketones.

As for the solvent dependency of the regio-orientation in the addition to phenylacetylene (1d), particular care has to be taken in handling this and similar systems: not only does the presence of acids have to be avoided, but also the proportions of reagents used are important as far as the regio- and stereoselectivity is concerned.

Experimental

Phenylacetylene (1d) and hex-1-yne (1b) are commercial products. 3-Methylbut-1-yne (1c),[13] 4-chlorobenzenesulphenyl chloride,[14] and the adducts (*E*)-(3b,c) and (*E*)-(4b,c)[9] were prepared by literature methods. ^{1}H N.m.r. spectra were recorded on a Bruker WP-60 instrument equipped with a variable-temperature unit.

Reaction of 4-*Chlorobenzenesulphenyl Chloride* (2) *with Phenylacetylene* (1d).—(*i*) *With an excess of phenylacetylene.* Reactions were carried out in ethyl acetate, [^{2}H]chloroform,

sym-[$^2H_2$]tetrachloroethane, and [$^2H_4$]acetic acid, following the published procedure.[10] In ethyl acetate only the *trans* AM adduct, (E)-2-*chloro*-1-(4-*chlorophenylthio*)-1-*phenylethene*, (*E*)-(3d) (90%) was isolated. When the addition was run in the other solvents, a mixture of (*E*)-(3d) and of (E)-1-*chloro*-2-(4-*chlorophenylthio*)-1-*phenylethene*, (*E*)-(4d) was obtained (total yield 90%) in different ratios depending on the solvent; for (*E*)-(3d): δ($CDCl_3$) 6.68 (s, CH), 7.07—7.65 (m, ArH); for (*E*)-(4d): δ($CDCl_3$) 6.63 (s, CH), 7.07—7.65 (m, ArH). The separation was achieved *via* the sulphonyl derivatives (*E*)-(9) and (*E*)-(10).

(*ii*) *With an excess of sulphenyl chloride.* From the reaction, in chloroform or in *sym*-tetrachloroethane, of phenylacetylene (1d) with two equivalents of the sulphenyl chloride (2) (1 day at room temperature) the Z-*isomer* (*Z*)-(4d) (85%) was obtained; column chromatography (silica gel; eluant, light petroleum), m.p. 66—67 °C (from n-pentane); δ($CDCl_3$) 6.83 (s CH), 7.35 (s, ArH) (Found: C, 59.45; H, 3.6; Cl, 25.15; S, 11.4. $C_{14}H_{10}Cl_2S$ requires C, 59.8; H, 3.6; Cl, 25.3; S. 11.3%).

Hydrolysis of Compounds (E)-(3*b*—*d*) *with Sulphuric Acid in Dichloromethane.*—Compound (3) (10 mmol), either as the pure compound or mixed with (4), was dissolved in dichloromethane (50 ml) and 95% H_2SO_4 (30 mmol) added. The mixture was refluxed for a suitable time, washed with water and $NaHSO_4$ in water until neutral, and dried (Na_2SO_4). The solvent was removed under reduced pressure at room temperature and the residue distilled under vacuum. The chloromethylketones (5b—d) obtained were identified by comparison with authentic samples (Table 2).[15-11] The ketone (5d) can be recrystallized from light petroleum.

Hydrolysis of Compounds (E)-(3*b*—*d*) *with Trifluoroacetic Acid* (*TFA*).—To compound (3) (5 mmol), either pure or mixed with the isomer (4), in CH_2Cl_2 (30 ml), a ten-fold excess of TFA was added at room temperature. After convenient reaction times [(3b), 2.5 h; (3c), 1 day; (3d), 4 days] the solution was neutralized as above.

(i) From (3b) an oil was obtained; chromatography (silica gel; eluant, light petroleum) gave 4-*chloro*-3-(4-*chlorophenylthio*)-2-*methylbut*-2-*ene* (7) (46%) as a low melting product; vacuum distillation of (7) caused extensive decomposition; *m/e* 246 (M^+), 248 (M + 2, 68% of M^+); δ($CDCl_3$) 2.02 (s, Me), 2.04 (s, Me), 4.21 (s, CH_2), and 7.18 (m, ArH) (Found: C, 53.6; H, 4.9. $C_{11}H_{12}Cl_2S$ requires C, 53.44; H, 4.86%).

(ii) From (3c) an oily residue was obtained. The n.m.r. spectrum showed the presence of compounds (5c) and (8) in the ratio 40 : 60 4-chlorophenylthiomethyl n-butyl ketone (8) was partially purified by column chromatography (silica gel; eluant, light petroleum) and crystallized from n-pentane; yield 22%, m.p. 50—51 °C (lit.,[12] 49.5—51.5 °C). When the hydrolysis was carried out in the presence of an equimolar amount of 4-chlorobenzenethiol, compound (8) (63%) was obtained under the same conditions.

(iii) From (3d) the same work-up as described for the hydrolysis in H_2SO_4 gave chloromethyl phenyl ketone (5d) (43%). Shorter reaction times (2 h) gave the partial conversion into the (*Z*)-(3d) isomer. After work-up a *E* : *Z* mixture (95%) was isolated; δ($CDCl_3$) for (*Z*)-(3d); 6.58 (s, CH), 7.08 (s, ArH).

Oxidation of the Vinyl Sulphides (E) *and* (Z)-(3*a*), (E)- *and* (Z)-(4*a*), *and* (7) *to the corresponding Vinyl Sulphones* (E)- *and* (Z)-(9), (E)- *and* (Z)-(10), *and* (11).—Following the reported procedure,[10] the title compounds, either conformationally pure or as an isomeric mixture, were oxidized with 3-chloroperbenzoic acid to the corresponding sulphones and purified by column chromatography [silica gel; eluant: (*E*)-(9), chloroform; (*E*)-(9)–(*E*)-(10)–(*Z*)-(10) mixture, light petroleum–ether 2 : 1; (*E*)-(9)–(*Z*)-(9) mixture, light petroleum–ether 3 : 1; (11), light petroleum]; (E)-2-*chloro*-1-(4-*chlorophenylsulphonyl*)-1-*phenylethene*, (*E*)-(9), m.p. 129—130 °C (from methanol), δ($CDCl_3$) 7.76 (s, CH), 7.00—7.63 (m, ArH) (Found: C, 53.45; H, 2.85; Cl, 22.75; S, 10.3%); Z-*isomer*, (*Z*)-(9), m.p. 131—132 °C (from methanol), δ($CDCl_3$) 6.75 (s, CH), 7.18—7.85 (m, ArH) (Found: C, 53.8; H, 2.9; Cl, 22.7; S, 10.15%); (E)-1-*chloro*-2-(4-*chlorophenylsulphonyl*)-1-*phenylethene*, (*E*)-(10), m.p. 118 °C (from methanol), δ($CDCl_3$) 6.95 (s, CH), 7.26—7.62 (m, ArH) (Found: C, 53.5; H, 3.05; Cl, 22.7; S, 10.1%); Z-*isomer*, (*Z*)-(10), m.p. 79 °C (from chloroform–light petroleum), δ($CDCl_3$) 7.12 (s, CH), 7.28—8.10 (m, ArH) (Found: C, 53.85; H, 3.05; Cl, 22.55; S, 10.3. $C_{14}H_{10}Cl_2O_2S$ requires C, 53.65; H, 3.2; Cl, 22.3; S, 10.2%); 1-*chloro*-2-(4-*chlorophenylsulphonyl*)-3-*methylbut*-2-*ene* (11), m.p. 92.5—93.5 °C (from chloroform–n-pentane), δ($CDCl_3$) 2.07 (s, Me), 2.12 (s, Me), 4.61 (s, CH_2), 7.43—8.01 (m, ArH) (Found: C, 47.35; H, 4.45; Cl, 25.2; S, 11.3. $C_{11}H_{12}Cl_2O_2S$ requires C, 47.3; H, 4.3; Cl, 25.45; S, 11.45%).

Reduction of Vinyl Sulphones (E)- *and* (Z)-(9), (E)- *and* (Z)-(10), *and* (11).—Compound (*E*)-(9) (3.3 mol) was reduced with $LiAlH_4$ (3.9 mmol) in refluxing anhydrous diethyl ether. After 1 h water was carefully added to the reaction mixture which was cooled to 0 °C. The organic layer was washed with water until neutral and dried (Na_2SO_4); column chromatography (silica gel; eluant, light petroleum–ether 2 : 1) gave 4-*chlorophenyl* 1-*phenylethyl sulphone* (12) (70%), m.p. 100—101 °C (from methanol); δ($CDCl_3$) 1.77 (d) and 4.32 (quart.) (CHMe, ^3J 7.3 Hz), 7.04—7.60 (m, ArH) (Found: C, 59.75; H, 4.55; Cl, 12.3; S, 11.1. $C_{14}H_{13}ClO_2S$ requires C, 59.9; H, 4.65; Cl, 12.65; S, 11.4%). Hydrogenation of (*Z*)-(5) with 5% palladium–charcoal in ethanol (3.5 atm for 4 days at room temperature) gave (12) in 85% yield.

Reduction of the sulphones (*E*)-(10) or (*Z*)-(10) with $LiAlH_4$ (5 h reflux in anhydrous diethyl ether) yielded after column chromatography (silica gel; eluant, light petroleum–ether 25 : 1) the same 4-*chlorophenyl* 2-*phenylethyl sulphone* (13) [60% from (*E*)] [50% from (*Z*)], m.p. 76 °C (from methanol); δ($CDCl_3$) 2.85 and 3.56 (complex m, AA'BB', CH_2CH_2), 6.86—7.95 (m, ArH) (Found: C, 59.8; H, 4.85; Cl, 12.65; S, 11.55%).

Reduction for 4 h of (11) (0.9 mmol) with $LiAlH_4$ (3 mmol) in refluxing ether gave, after neutralization and chromatography (silica gel; eluant, chloroform), 4-*chlorophenyl* 3-*methylbutyl sulphone* (14) (85%), m.p. 47—47.5 °C (from n-pentane); δ($CDCl_3$) 0.83 (d, Me_2, ^3J 5.1 Hz), 1.5 (m, Me), 3.08 (m, CHCH), 7.45—7.93 (m, ArH) (Found: C, 53.6; H, 5.95; Cl, 14.3; S, 12.85. $C_{11}H_{15}ClO_2S$ requires C, 53.55; H, 6.1; Cl, 14.4; S, 13.0%).

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