Regio- and Stereo-selective Desulphurizative γ-Substitution of α-Substituted β-Methylallyl Sulphoxides and Sulphones with Lithium Dialkylcuprates providing Trisubstituted Olefins

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α-Substituted β-methylallyl sulphoxides (**2**) and sulphones (**3**) undergo regio- and stereo-selective desulphurizative γ-substitution by the action of lithium dialkylcuprates in ether. The reaction provides a new method for the synthesis of trisubstituted *E*-olefins *E*-(**4**).

Activation of an allylic position by introduction of a sulphur-containing group provides both a useful and widely used method for carbon–carbon bond formation using allylic carbanions.[1] For completion of the carbon–carbon bond formation however removal of the sulphur-containing group by reduction is usually necessary. Although several methods have been developed, the process sometimes suffers from serious problems, particularly elimination to give a diene and migration of the double bond.[2] Since thermal, photochemical, and acid catalytic isomerization and rearrangement[3] of sulphur-containing allylic derivatives generally tends to occur between the α and γ positions, we considered that the α and γ positions would be reactive toward nucleophiles and radicals on removal of the sulphur-substituent. This prompted us to investigate the direct alkylative substitution of sulphur-containing allylic compounds.[4]

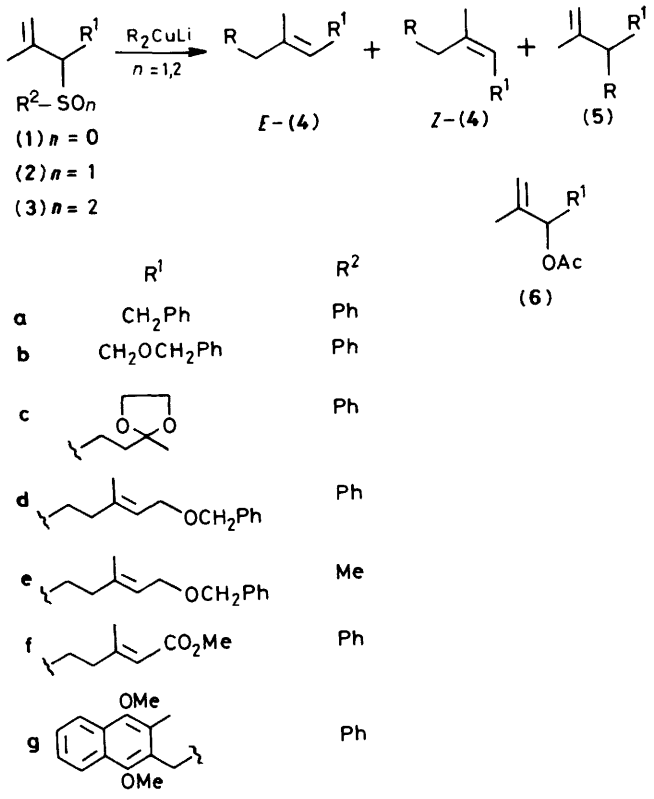
During the course of our study, several reports concerning the substitution of the sulphur-containing groups at the allylic position have been appeared. Thus, Gendreau,[5a] Calo,[5b] Takei,[5c] and Julia[5d] and the respective co-workers found independently that allylic sulphides, sulphones, and sulphonium salts undergo substitution with Grignard reagents in the presence of a copper(I) salt or a nickel-phosphine complex to give carbon–carbon bond formation. In most of these reactions, relatively simple, primary allylic substrates were employed and the stereoselectivity associated with migration of the double bond in the γ-substitution which sometimes is observed as the major course of the reactions, has not been discussed in detail. Replacement of the allylic sulphenyl or sulphonyl group with a tributylstannyl group was also found to proceed *via* the radical (S_H,) process with migration of the double bond.[6] Recently, Trost and co-workers reported that regio- and stereo-selective nucleophilic displacement of allylic sulphones with a stabilized carbanion such as malonate occurred under the influence of palladium(0) catalysis.[7] Here we disclose full details of our preliminary communication[4] concerning the regio- and stereo-selective γ-substitution of α-substituted β-methylallyl sulphoxides (**2**) and sulphones (**3**) with lithium dialkylcuprates (R_2CuLi) to provide the trisubstituted *E*-olefins *E*-(**4**).

Results and Discussion

A simple β-methylallyl sulphide, 2-methyl-4-phenyl-3-phenylthiobut-1-ene (**1a**), was prepared in 66% yield by base-promoted C–C coupling[1] between β-methylallyl phenyl sulphide and benzyl bromide. The other α-substituted β-methylallyl sulphides (**1b**—**g**) were prepared in high yields by the terminal functionalization of isoprenoids *via* benzenesulphenyl chloride addition and subsequent dehydrochlorination.[8] We chose organocopper reagents as nucleophiles since they are generally known to be less basic and softer nucleophiles than Grignard reagents[9a] and are recognized to be highly efficient for regio- and stereo-selective γ-alkylation of allylic acetates[9b] and chlorides.[9c] These properites seemed to be suited to the preparation of trisubstituted olefins by γ-substitution, particularly the *E*-olefin *E*-(**4**) which we expect when the α-substituted β-methylallyl sulphides (**1**), sulphoxides (**2**), or sulphones (**3**) are employed.

Since the sulphide (**1a**) when treated with Me_2CuLi (5.0 equiv.) in Et_2O at −20 to 10 °C, gave recovery of unchanged starting material, we directed our attention to use of the corresponding allylic sulphoxides (**2**) and sulphones (**3**) as substrates. These could be easily obtained from the sulphides (**1**) by oxidation with 30% H_2O_2 (1 equiv.) and *m*-chloroperbenzoic acid (2 equiv.) respectively. Dropwise addition of an ethereal solution of the sulphoxide (**2a**) to a cold (−20 °C) stirred solution of $Bu^n{}_2CuLi$ (5 equiv.) in Et_2O followed by stirring of the mixture at −20 to 10 °C for 2 h gave an oily and sulphur-free substance in 75% yield after column chromatography of the crude product on silica gel. Although the purified product exhibited a single spot on t.l.c. it proved to be a mixture of three components, (*E*)-3-methyl-1-phenyloct-2-ene *E*-(**4a**; R = Bu), the corresponding *Z*-isomer *Z*-(**4a**; R = Bu), and 3-benzyl-2-methylhept-1-ene (**5a**; R = Bu) on the basis of ^1H n.m.r., g.l.c., and g.c.-mass spectral analyses. From its ^1H n.m.r. spectrum the product was assignable as the γ-substitution product (**4a**; R = Bu), diagnostic signals of which were appeared at δ 0.90 (3 H, t), 1.70 (3 H, s), 3.30 (2 H, d), and 5.29 (1 H t), together with a very minor broad singlet at δ 4.56 assignable to the terminal methylene of the α-product (**5a**; R = Bu); there was an absence of stereochemical information about the olefinic bond in (**4a**; R = Bu). The g.l.c. analysis revealed that the product contained three components, moving fast to slow in a ratio of 5.0:6.5:88.5, each of which showed an identical molecular ion peak at *m/z* 202 (g.c.–mass spec.). Although the components were not isolated, the structure and composition of the product was supported by ^1H n.m.r. and g.c.–mass spectral comparisons with the product obtained in a highly regio- and stereo-selective fashion [ratio *E*-(**4a**; R = Bu):*Z*-(**4a**; R = Bu):(**5a**; R = Bu), 95:2.5:2.5] by the known reaction[9b] of the terminal β-methylallyl acetate, 3-acetoxy-2-methyl-4-phenylbut-1-ene (**6a**) with $Bu^n{}_2CuLi$ in Et_2O. These analyses indicated that the ratio of the alkylated products *E*-(**4a**; R = Bu):*Z*-(**4a**: R = Bu):(**5a**; R = Bu) produced by the reaction of (**2a**) with $Bu^n{}_2CuLi$ was 88.5:6.5:5.0 and that a highly *E*-stereoselective (*E*:*Z* = 93:7) γ-substitution had taken place.

The allylic sulphone (**3a**) was, in turn, subjected to the same reaction conditions as those for the sulphoxide (**2a**). In this case as well, similar results were obtained, the γ-product (**4a**; R = Bu) being formed in a regioselectively fashion [(**4a**; R = Bu):(**5a**; R = Bu), 92:8]. The *E*:*Z*-ratio of the γ-product (**4a**; R = Bu) was shown to be 86:14 by g.l.c. analysis.



Scheme.

Table. Reaction* of allylic sulphoxides (**2**) and sulphones (**3**) with R_2CuLi

Substrate	$R^2S(O)_n$	R_2CuLi R	Yield (%)	Product ratio (4)/(5)	Product ratio E/Z of (4)
(**2a**)	PhSO	Me	65	94/6	†
		Bu^n	75	95/5	93/7
(**3a**)	$PhSO_2$	Me	63	95/5	†
		Bu^n	89	92/8	86/14
(**2b**)	PhSO	Me	53	86/14	57/43
		Bu^n	46	92/8	63/37
(**3b**)	$PhSO_2$	Me	26	83/17	66/34
(**2c**)	PhSO	Me	69	91/9	79/21
		Me	43 (Et_2O–THF, 1:1)	90/10	‡
		Bu^n	70	95/9	82/18
(**3c**)	$PhSO_2$	Me	74	95/5	93/7
		Bu^n	73	98/2	92/8
(**2d**)	PhSO	Me	71	90/10	78/22
		Me	52 (−40 °C)	87/13	
		Bu^n	75	97/3	87/13
(**2e**)	MeSO	Me	22	91/9	
(**3d**)	$PhSO_2$	Me	85	95/5	85/15
		Bu^n	73	97/3	86/14
(**3e**)	$MeSO_2$	Me	52	88/12	
(**2f**)	PhSO	Me	72	91/9	88/12
(**2g**)	PhSO	Me	65	86/14	77/23
(**3g**)	$PhSO_2$	Me	73	84/16	82/18

* The reaction was carried out at −20 to 15 °C for 2.0 h in Et_2O using *ca.* 5 equiv. of R_2CuLi unless otherwise noted. † The γ-product (**4a**; R = Me) showed a single peak on g.l.c.; the *E*/*Z*-ratio was not determined. ‡ The empty columns mean that the *E*/*Z*-ratio of the γ-products (**4**) has not been determined.

Reactions of other allylic sulphoxides (**2**) and sulphones (**3**) provided analogous results (see Table), regio- and stereoselective substitution occurring to give a predominance of the γ- and (*E*)-product (*E*-**4**). In every case, structural determinations and alkylated product distributions were carried out on the basis of spectral and chromatographic comparisons with reference products prepared from the corresponding allylic acetates (**6**) by reaction with R_2CuLi.[9b] For the substrates (**2b**) and (**3b**) which possess an alkoxy functionality at the β′ position to the sulphur-containing group, a substantial amount (*ca.* 20—30%) of benzyl alcohol was produced on treatment with Me_2CuLi in addition to the methylated products among which the γ-product (**4b**; R = Me), however, was obtained with poor stereoselectivity. The benzyloxy group as leaving group at the β′ position might enhance the acidity of the α-proton to the sulphur-containing group and the elimination of benzyl alcohol might occur. Reactions in Et_2O–THF (1:1) or at low temperature (−40 °C) proceeded sluggishly and gave low yields of alkylated products. Reactions of (**2e**) and (**3e**) indicated that the methylsulphinyl and methylsulphonyl groups appeared to be not so effective for this reaction as phenylsulphinyl and phenylsulphonyl groups.

In conclusion, regio- and stereo-selective γ-substitution of allylic sulphoxides and sulphones has been shown to be attractive as a new method for the preparation of trisubstituted olefins, particularly since α-substituted β-methylallyl sulphoxides and sulphones are easily accessible. In addition, it has been shown the arylsulphinyl and arylsulphonyl groups may be used as suitable leaving groups in substitution reactions with organocopper reagents.[9a]

Experimental

General.—I.r. spectra were taken on a JASCO IRA-1 spectrometer in $CHCl_3$ solution and the absorption bands ($\nu_{max.}$) are reported in cm^{-1}. Mass spectra (m.s.) were obtained on a JMS-D300 instrument at an ionizing potential of 70 eV and peaks are reported as *m*/*z* values with relative intensities (%) in parenthesis. ^1H N.m.r. spectra were recorded on a Hitachi R-20B spectrometer (60 MHz) for CCl_4 solutions with tetramethylsilane (TMS) as an internal standard; chemical shifts are reported as δ values relative to TMS, and coupling constants (*J*) are reported in Hz. All the solvents used in reactions were freshly distilled to remove moisture; Et_2O over $LiAlH_4$ and THF over sodium diphenylketyl. Reactions were usually carried out under nitrogen unless otherwise noted. Reaction mixtures were usually worked up as follows: a mixture was extracted with Et_2O, the extract washed with water or saturated brine and saturated aqueous $NaHCO_3$, if necessary, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure below room temperature to give a crude product which was purified by column chromatography. Silica gel, Wakogel B5-F and Wakogel C-200 were employed respectively for analytical thin-layer (t.l.c.) and column chromatography using a hexane–Et_2O solvent system. Gas liquid chromatography (g.l.c.) was performed analytically on a JGC-1100 gas chromatograph (FID) using a stainless-steel column (3 mm × 2 m) packed with 2% silicone OV-105 on Chromosorb W-AW-DMCS (80-100 mesh) and gas-chromatographic mass spectroscopy (g.c.-m.s.) was performed on a JMS-D300 instrument equipped with a gas chromatograph using a glass column (2 mm × 2 m) with the same packing as described above.

Materials.—2-Methyl-4-phenyl-3-phenylthiobut-1-ene (**1a**) was prepared as follows. A 1.6M-solution of Bu^{n}Li–hexane (7.0 ml, 11 mmol) was added dropwise during 10 min to a cold (−70 °C) solution of methylallyl phenyl sulphide (1.64 g, 10 mmol) and hexamethylphosphoric triamide (HMPA) (1.0 ml) in THF (10 ml). After the mixture had been stirred for 30 min at

the temperature, benzyl bromide (1.4 ml, 11.5 mmol) was added dropwise at −70 °C. The mixture was stirred for 1 h at −70 °C and then the reaction was quenched by addition of MeOH. Work-up and product isolation gave the oily sulphide (**1a**) (1.68 g, 66%); δ 1.79 (3 H, s, =CMe), 2.82—2.98 [2 H, 2 d, *J* 9.0 and 6.0, (PhS)CHCH_2Ph], 3.79 [1 H, dd, *J* 9.0 and 6.0, (PhS)CHCH$_2$Ph], 4.50, 4.61 (each 1 H, br s, =CH$_2$), and 7.00—7.40 (10 H, br s, Ar-H) (Found: C, 80.1; H, 7.25. $C_{17}H_{18}S$ requires C, 80.3; H, 7.15%).

The other α-substituted β-methylallyl phenyl sulphides (**1b**—**g**) were prepared from the *gem*-dimethyl olefins *via* the benzenesulphenyl chloride addition[8] and the following is the general procedure. A solution of benzenesulphenyl chloride[10] (1.45 g, 10 mmol) in CH_2Cl_2 (5.0 ml) was added dropwise at −20 °C to a solution of a *gem*-dimethyl olefin (10 mmol) in CH_2Cl_2 (20 ml). After being stirred for 10 min at −20 °C, the mixture was concentrated under reduced pressure to give a crude adduct which, without purification, was warmed in *N,N*-dimethylformamide (DMF) (30 ml); for (**1c**) the reaction was carried out with Et_3N (1.5 equiv.) at 60 °C for 20 h. Work-up and product isolation afforded the allylic sulphides (**1b**—**g**) in 74—89% yield. Physicochemical properties for compounds (**1b**—**g**) are as follows. Compound (**1b**), an oil; ν$_{max.}$ 1 640 and 1 590; δ 1.81 (3 H, s, =CMe), 3.40—3.90 [3 H, m, CH(SPh)CH$_2$O], 4.40 (2 H, s, OCH$_2$Ph), 4.72 and, 4.77 (each 1 H, br s, =CH$_2$), and 6.95—7.45 (10 H, m, ArH) (Found: C, 76.15; H, 7.3. $C_{18}H_{20}OS$ requires C, 76.03; H, 7.09%).

Compound (**1c**), an oil; ν$_{max.}$ 1 640 and 1 590; δ 1.25 (3 H, s, MeCO$_2$), 1.78 (3 H, s, =CMe), 3.40—3.63 [1 H, m, CH(SPh)], 3.84 (4 H, s, OCH$_2$CH$_2$O), 4.56 and 4.67 (each 1 H, br s, =CH$_2$), and 7.07—7.40 (5 H, m, ArH) (Found: C, 69.3; H, 7.9. $C_{16}H_{22}O_2S$ requires C, 69.04; H, 7.97%).

Compound (**1d**), an oil; ν$_{max.}$ 1 635 and 1 595; δ 1.77 and 1.59 (each 3 H, s, 2 =CMe), 3.47 [1 H, t, *J* 7.0, CH(SPh)], 3.88 (2 H, d, *J* 7.0, =CHCH_2O), 4.35 (2 H, s, OCH$_2$Ph), 4.50, 4.60 (each 1 H, br s, =CH$_2$), 5.30 (1 H, br t, *J* 7.0, =CHCH$_2$O), and 6.97—7.28 (10 H, m, ArH) (Found: C, 78.25; H, 8.2. $C_{23}H_{28}OS$ requires C, 78.37; H, 8.01%).

Compound (**1f**), an oil; ν$_{max.}$ 1 705, 1 630, and 1 595; δ 1.89 (3 H, s, =CMe), 2.13 (3 H, d, *J* 1.5 (MeC=CCO$_2$), 1.57—2.68 (4 H, m, CH$_2$CH$_2$), 3.49 [1 H, t, *J* 7.0, CH(SPh)], 3.62 (3 H, s, MeCO$_2$), 4.60 and 4.72 (each 1 H, br s, =CH$_2$), 5.62 (1 H, br s, =CHCO$_2$), and 7.11—7.40 (5 H, m, ArH) (Found: C, 70.15; H, 7.7. $C_{17}H_{22}O_2S$ requires C, 70.32; H, 7.64%).

Compound (**1g**), m.p. 145—146 °C (Et$_2$O–hexane); ν$_{max.}$ 1 640, 1 580, 1 480, and 1 450; 378 (*M*$^+$, 21%), 269 (30), and 215 (100); δ 1.85 (3 H, s, =CMe), 2.47 (3 H, s, ArMe$_3$), 3.12 (2 H, d, *J* 8.0, ArCH$_2$), 3.76 (6 H, s, 2 OMe), 4.07 [1 H, t, *J* 8.0, CH(SPh)], 4.57, 4.60 (each 1 H, br s, =CH$_2$), 7.00—7.50 (7 H, m, ArH), 7.80—8.05 (2 H, m), and 7.80—8.05 (2 H, m, ArH) (Found: C, 76.3; H, 7.0. $C_{24}H_{26}O_2S$ requires C, 76.15; H, 6.92%).

The α-substituted β-methylallyl methyl sulphide (**1e′**) was prepared by the following procedure. A solution of methanesulphenyl chloride (MeSCl)[10] in CH_2Cl_2 was prepared by dropwise addition of SO_2Cl_2 (675 mg, 5.0 mmol) to a solution of dimethyl disulphide (470 mg, 5.0 mmol) in CH_2Cl_2 (2.0 ml) at −20 °C. The resulting mixture was then stirred for 1 h whilst it gradually warmed to 10 °C. The solution of MeSCl in CH_2Cl_2 thus obtained was then added dropwise to a solution of geraniol benzyl ether (1.10 g, 4.5 mmol) in CH_2Cl_2 (10 ml) at −20 °C. After being stirred for 10 min the mixture was concentrated under reduced pressure to give the crude adduct (1.40 g), which was warmed in DMF (15 ml) with Et_3N (2.0 ml) at 80 °C for 16 h. The mixture was worked up to give the crude product (1.02 g) which was purified by column chromatography to afford the pure oily sulphide (**1e′**) (875 mg, 67%); δ 1.60, 1.70 (each 3 H, s, 2 =CMe), 1.80 (3 H, s, MeS), 3.00 [1 H, t, *J* 7.0, CH(SMe)], 3.89 (2 H, d, *J* 6.0, =CHCH_2O), 4.37 (2 H, s, OCH$_2$Ph), 4.69 and 4.79 (each 1 H, br s, =CH$_2$), 5.32 (1 H, br t, *J* 6.0, =CHCH$_2$O), and 7.18 (5 H, s, ArH) (Found: C, 74.2; H, 9.0 $C_{18}H_{26}OS$ requires C, 74.44; H, 9.03%).

The terminal β-methylallyl sulphoxides (**2**) were prepared by oxidation of the corresponding sulphides (**1**) with 30% H_2O_2 (1.2 equiv.) in AcOH at room temperature for 15 h and used as a diastereoisomeric mixture.

The terminal β-methylallyl sulphones (**3**) were obtained by oxidation of the corresponding sulphides (**1**) with *m*-chloroperbenzoic acid (2.2 equiv.) in CH_2Cl_2 at 0 °C for 1 h. Physicochemical data for the sulphones (**3**) are as follows:

Compound (**3a**), m.p. 83—85 °C (Et$_2$O–hexane); ν$_{max.}$ 1 635, 1 600, 1 580, 1 490, and 1 440; 286 (*M*$^+$, 5%), 145 (100), 144 (90), 130 (57), 129 (59), 128 (58), 117 (60), 115 (55), 105 (53), and 103 (54); δ 1.81 (3 H, s, =CMe), 2.72—3.78 [3 H, m, CH(SO$_2$Ph)CH$_2$Ph], 4.60, 4.82 (each 1 H, br s, =CH$_2$), 6.90 (5 H, s, ArH), and 7.24—7.87 (5 H, m, ArH) (Found: C, 71.55; H, 6.35. $C_{17}H_{18}O_2S$ requires C, 71.30; H, 6.34%).

Compound (**3b**), an oil, ν$_{max.}$ 1 640, 1 580, and 1 440; 316 (*M*$^+$, 2%), 248 (4), 175 (26), 145 (38), 131 (26), and 107 (100); δ 1.81 (3 H, s, =CMe), 3.70—4.13 [3 H, m, CH(SO$_2$Ph)CH$_2$O], 4.43 (2 H, s, OCH$_2$Ph), 4.77 and 5.05 (each 1 H, brs, =CH$_2$), 7.20 (5 H, s, ArH), 7.30—7.90 (5 H, m), and 7.30—7.90 (5 H, m, ArH) (Found: C, 68.25; H, 6.35. $C_{18}H_{20}O_3S$ requires C, 68.33; H, 6.37%).

Compound (**3c**), an oil, ν$_{max.}$ 1 630, 1 580, and 1 440; 310 (*M*$^+$, 1%), 295 (8), 169 (100), 125 (36), and 107 (48); δ 1.22 (3 H, s, MeCO$_2$), 1.78 (3 H, s, =CMe), 3.40—3.66 [1 H, dd, *J* 10.0 and 4.5, CH(SO$_2$Ph)], 3.83 (4 H, s, OCH$_2$CH$_2$O), 4.60, 4.94 (each 1 H, br s, =CH$_2$), and 7.43—7.90 (5 H, m, ArH) (Found: C, 61.65; H, 7.0. $C_{16}H_{22}O_4S$ requires C, 61.91; H, 7.14%).

Compound (**3d**), m.p. 40—42 °C (Et$_2$O–hexane); ν$_{max.}$ 1 630, 1 580, and 1 440; 384 (*M*$^+$, 1%), 277 (22), 151 (27), 143 (33), 135 (100), 134 (72), and 107 (66); δ 1.57, 1.76 (each 3 H, s, 2 =CMe), 3.30—3.61 [1 H, m, CH(SO$_2$Ph)], 3.94 (2 H, d, *J* 7.0, =CHCH_2O), 4.43 (2 H, s, OCH$_2$Ph), 4.63, 4.97 (each 1 H, br s, =CH$_2$), 5.33 (1 H, br t, *J* 7.0, =CHCH$_2$O), 7.24 (5 H, s, ArH), and 7.35—7.90 (5 H, m, ArH) (Found: C, 71.4; H, 7.35. $C_{23}H_{28}O_3S$ requires C, 71.84; H, 7.34%).

Compound (**3e**), an oil; δ 1.64 and 1.88 (each 3 H, s, 2 =CMe), 2.70 (3 H, s, MeSO$_2$), 3.25—3.50 [1 H, m, CH(SO$_2$Me)], 3.94 (2 H, d, *J* 7.0, =CHCH_2O), 4.41 (2 H, s, OCH$_2$Ph), 5.07 and 5.17 (each 1 H, br s, =CH$_2$), 5.35 (1 H, br t, *J* 7.0, =CHCH$_2$O), and 7.24 (5 H, s, ArH) (Found: C, 66.9; H, 8.15. $C_{18}H_{26}O_3S$ requires C, 67.06; H, 8.13%).

Compound (**3g**); ν$_{max.}$ 1 640, 1 590, 1 450, 1 370, 1 350, and 1 300; δ 1.70 (3 H, s, =CMe), 2.37 (3 H, s, ArMe), 3.27—3.49 [2 H, 2 d, *J* 9.0 and 6.0, Ar-CH_2CH(SO$_2$Ph)], 3.65 and 3.80 (each 3 H, s, 2 OMe), 4.07 [1 H, dd, J 9.0 and 6.0, ArCH$_2$CH(SO$_2$Ph)], 4.64 and 4.76 (each 1 H, br s, =CH$_2$), and 7.20—8.03 (9 H, m, ArH) (Found: C, 70.25; H, 6.3. $C_{24}H_{26}O_4S$ requires C, 70.23; H, 6.39%).

The α-substituted β-methylallyl acetates (**6**) except for (**6a**) were prepared by acetylation (Ac$_2$O–pyridine/15 °C/15 h) of the corresponding alcohols which were synthesized according to a known method[11] from *gem*-dimethyl olefins. The acetate (**6a**) was obtained by acetylation of the corresponding alcohol which was prepared by the Grignard reaction of 1-methylacrolein, magnesium, and benzyl bromide in Et$_2$O. ^{1}H N.m.r. data for the acetates (**6**) are as follows: (**6a**) 1.75 (3 H, s, =CMe), 1.90 (3 H, s, MeCO$_2$), 2.87 [2 H, d, *J* 6.5, CH(OAc)CH_2Ph], 4.84 (2 H, br s, =CH$_2$), 5.32 [1 H, t, *J* 6.5, CH(OAc)CH$_2$Ph], and 7.14 (5 H, s, ArH); (**6b**) 1.73 (3 H, s, =CMe), 1.99 (3 H, s, MeCO$_2$), 3.48 [2 H, d, *J* 6.0, CH(OAc)CH_2O], 4.48 (2 H, s, OCH$_2$Ph), 4.88, 4.98 (each 1 H, br s, =CH$_2$), 5.30 [1 H, t, *J* 6.0, CH(OAc)CH$_2$O], and 7.22 (5 H, s, ArH); (**6c**) 1.23 (3 H, s, MeCO$_2$), 1.72 (3 H, s, =CMe), 2.00 (3 H, s, MeCO$_2$), 3.86 (4 H, s, OCH$_2$CH$_2$O), 4.82 and 4.88 (each 1 H, br s, =CH$_2$), and 5.08 (1 H, br t, *J* 6.0, CHOAc); (**6d**) 1.62, 1.72 (each 3 H, s, 2 = CMe), 2.00 (3 H, s, MeCO$_2$), 3.92 (2 H, d, *J* 6.5, =CHCH_2O), 4.40 (2 H, s, OCH$_2$Ph), 4.33 and 4.39 (each 1 H, br s,

=CH_2), 5.07 (1 H, t, *J* 6.0 CHOAc), and 5.32 (1 H, br t, *J* 6.5, =C*H*CH_2O); (**6f**) 1.80 (3 H, s, =CMe), 1.95 (3 H, s, $MeCO_2$), 2.10 (3 H, d, *J* 1.5, $MeC{=}CHCO_2$), 3.65 (3 H, s, MeO_2C), 4.92 (2 H, br s, =CH_2), 5.11 (1 H, t, *J* 7.0 CHAcO), and 5.63 (1 H, s, =$CHCO_2$); (**6g**) 1.83 (6 H, s, =CMe and $MeCO_2$), 2.44 (3 H, s, Ar-Me), 3.08 [2 H, d, *J* 7.0, CH(OAc)CH_2Ar], 3.80, 3.88 (each 3 H, s, 2 OMe), 4.75, 4.89 (each 1 H, br s, =CH_2), 5.43 [1 H, t, *J* 7.0, C*H*(OAc)CH_2Ar], and 7.10—8.03 (4 H, m, ArH).

Reaction of the α-Substituted β-Methylallyl Sulphoxide (**2a**) *with Lithium Dibutylcuprate: General Procedure for Regio- and Stereo-selective Alkylative Substitution of α-Substituted β-Methylallyl Sulphoxides* (**2**) *and Sulphones* (**3**) *to give Trisubstituted* E-*Olefins* E-(**4**).—To a solution of Bu^n_2CuLi (5.0 mmol) in Et_2O (10 ml) was added dropwise a solution of the sulphoxide (**2a**) (270 mg, 1.0 mmol) in Et_2O (1.5 ml) at —20 °C under argon. The mixture was stirred for 1 h at this temperature and then gradually warmed to room temperature during 1 h. The reaction was quenched by addition of saturated NH_4Cl. The product was extracted with Et_2O, washed successively with saturated NH_4Cl and water, dried, and concentrated. The crude product was purified by column chromatography to give a t.l.c.-pure oil (152 mg, 75%) which proved to be mainly composed of the γ-substituted (*E*)-olefin, *E*-(**4a**; R = Bu), the γ-substituted (*Z*)-olefin *Z*-(**4a**; R = Bu), and the α-product (**5a**; R = Bu) in the proportions 88.5:6.5:5.0; the latter were determined by ^1H n.m.r., g.l.c., and g.c.–mass spectral analyses and spectral and chromatographic comparisons with the reference products obtained from the corresponding allylic acetate (**6a**), *vide infra*. Physicochemical data for the product obtained from (**2a**) are as follows: b.p. 120—122 °C (9 Torr); ^1H n.m.r. (signals assignable to *E*-(**4a**; R = Bu) 0.90 (3 H, t, *J* 6.0, CH_2Me), 1.10—1.58 [6 H, m, $(CH_2)_3$], 1.71 (3 H, s, =CMe), 1.82—2.29 (2 H, m, Bu^nCH_2C=), 3.29 (2 H, d, *J* 7.0, =CHCH_2Ph), 5.30 (1 H, br t, *J* 7.0, =C*H*CH_2Ph), and 7.09 (5 H, s, ArH); $\nu_{max.}$ 1 660, 1 600, 1 490, 1 450, and 1 370; g.c.–mass spec. (the fast-moving fraction assignable to (**5a**; R = Bu) 202 (M^+, 41%), 146 (69), 131 (29), 117 (14), 111 (42), 110 (52), and 104 (100); g.c.–m.s. (the secondly-moving fraction assignable to *Z*-(**4a**; R = Bu) 202 (M^+, 60%), 146 (13), 131 (100), 117 (13), and 104 (64); g.c.–m.s. (the slowest-moving fraction assignable to *E*-(**4a**; R = Bu) almost identical with the data for *Z*-(**4a**; R = Bu) (Found: C, 88.8; H, 11.1. $C_{15}H_{22}$ requires C, 89.04; H, 10.96%). Results from the reaction of the other sulphoxides (**2**) and sulphones (**3**) with R_2CuLi under the same conditions as described above are summarized in the Table.

Reaction of the Allylic Acetates (**6**) *with* R_2CuLi *to give Highly Regio- and Stereo-selectively the* (E)-*Olefins* E-(**4**): *General Procedure*.—The reaction was carried out by the same procedure as described for (**2a**) using the allylic acetates (**6**) as the substrate in place of the sulphur-containing allylic compounds; the products were analysed by ^1H n.m.r., g.l.c., and g.c.–m.s.

Physicochemical properties of the *E*-olefins *E*-(**4**) are as follows. Compound *E*-(**4a**; R = Me), b.p. 98—100 °C (22 Torr); $\nu_{max.}$ 1 600, 1 490, and 1 450; *m/z* 160 (M^+, 26%), 145 (5), 131 (100), 117 (5), and 104 (13); δ 1.01 (3 H, t, *J* 7.0, *Me*CH_2C=), 1.70 (3 H, s, =CMe), 2.04 (2 H, q, *J* 7.0, $MeCH_2C$=), 3.27 (2 H, d, *J* 7.0, =CHCH_2Ph), 5.26 (1 H, br t, *J* 7.0 =C*H*CH_2Ph), and 7.10 (5 H, s, ArH) (Found: 81.3; H, 9.2. $C_{12}H_{16}$ requires C, 89.94; H, 10.06%).

Compound *E*-(**4b**; R = Me), b.p. 89—91 °C (1.0 Torr); $\nu_{max.}$ 1 660, 1 600, 1 490, 1 440, 1 370, and 1 350; *m/z* 190 (M^+, 1%), 161 (2), 107 (5), 99 (6), and 91 (100); δ 1.00 (3 H, t, *J* 7.5, *Me*CH_2C=), 1.60 (3 H, s, =CCH_3), 2.02 (2 H, q, *J* 7.5, CH_3CH_2C=), 3.91 (2 H, d, *J* 6.5, =CHCH_2O), 4.40 (2 H, s, OCH_2Ph), 5.30 (1 H, br t, *J* 6.5, =C*H*CH_2O), and 7.24 (5 H, s, ArH) (Found: C, 81.65; H, 9.65. $C_{13}H_{18}O$ requires C, 82.06; H, 9.54%).

Compound *E*-(**4b**; R = Bu), b.p. 120—122 °C (0.9 Torr); $\nu_{max.}$ 1 660, 1 490, 1 450, 1 370, and 1 350; *m/z* 232 (M^+, 1%), 188 (4), 161 (23), 141 (40), 123 (58), 107 (28), 97 (81), and 91 (100); δ 0.88 (3 H, t, *J* 6.0, *Me*CH_2), 1.57 (3 H, s, =CMe), 1.78—2.15 (2 H, m, Bu^nCH_2C=), 3.86 (2 H, d, *J* 7.0, =CHCH_2O), 4.33 (2 H, s, OCH_2Ph), 5.26 (1 H, bt, *J* 7.0, =C*H*CH_2O), and 7.12 (5 H, s, ArH) (Found: C, 88.8; H, 11.1. $C_{16}H_{24}O$ requires C, 89.04; H, 10.96%).

Compound *E*-(**4c**; R = Me), b.p. 62—64 °C (0.9 Torr); $\nu_{max.}$ 1 630, 1 440, and 1 370; *m/z* 184 (M^+, 14%), 169 (12), 155 (20), 122 (47), 111 (26), 107 (15), and 87 (100); δ 0.97 (3 H, t, *J* 7.0, *Me*CH_2C=), 1.22 (3 H, s, $MeCO_2$), 1.60 (3 H, s, =CMe), 3.83 (4 H, s, OCH_2CH_2O), and 5.06 (1 H, br t, *J* 7.0, =CH) (Found: C, 70.75; H, 11.05. $C_{11}H_{20}O_2$ requires C, 71.70; H, 10.94%).

Compound *E*-(**4c**; R = Bu), b.p. 98—100 °C (0.9 Torr); $\nu_{max.}$ 1 630, 1 440, and 1 360; *m/z* 226 (M^+, 19%), 211 (18), 164 (17), 155 (51), 124 (36), and 87 (100); δ 0.88 (3 H, t, *J* 6.0, *Me*CH_2), 1.22 (3 H, s, $MeCO)_2$, 1.58 (3 H, s, =CMe), 3.83 (4 H, s, OCH_2CH_2O), and 5.03 (1 H, br t, *J* 7.0, =C) (Found: C, 74.0; H, 11.75. $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%).

Compound *E*-(**4d**; R = Me), b.p. 138—142 °C (0.9 Torr); $\nu_{max.}$ 1 660, 1 490, 1 450, 1 370, and 1 350; *m/z* 258 (M^+, 8%), 167 (29), 150 (65), 137 (91), 121 (100), and 107 (55); δ 0.98 (3 H, t, *J* 7.5, $MeCH_2C$=), 1.60 (6 H, s, 2 =CMe), 1.70—2.20 (6 H, br, 3 CH_2C=), 3.93 (2 H, d, *J* 6.0, =CHCH_2O), 4.40 (2 H, s, OCH_2Ph), 5.05 (1 H, br, =CH), 5.32 (1 H, br t, *J* 6.0, =C*H*CH_2O), and 7.22 (5 H, s, ArH) (Found: C, 83.6; H, 10.35. $C_{17}H_{26}O$ requires C, 83.67; H, 10.14%).

Compound *E*-(**4d**; R = Bu), b.p. 124—130 °C (0.8 Torr); $\nu_{max.}$ 1 660, 1 490, 1 450, 1 370, and 1 350; *m/z* 300 (M^+, 4%), 209 (10), 192 (19), 179 (23), 121 (45), 108 (31), and 93 (100); δ 0.90 (3 H, t, *J* 6.0, *Me*CH_2), 1.60 (6 H, s, 2 =CCH_3), 1.75—2.23 (6 H, br, 3 CH_2C=), 3.95 (2 H, d, *J* 6.5, =CHCH_2O), 4.40 (2 H, s, OCH_2Ph), 5.05 (1 H, br, =CH), 5.33 (1 H, br t, *J* 6.5, =C*H*CH_2O), and 7.23 (5 H, s, ArH) (Found: C, 83.65; H, 10.85. $C_{21}H_{32}O$ requires C, 83.94; H, 10.73%).

Compound *E*-(**4f**; R = Me) an oil; $\nu_{max.}$ 1 700, 1 630, 1 430, and 1 370; *m/z* 196 (M^+, 4%), 165 (7), 137 (15), 122 (11), 134 (50), 107 (8), and 83 (100); δ 0.97 (3 H, t, *J* 7.0, *Me*CH_2C=), 1.16 (3 H, s, =CMe), 2.12 (3 H, d, *J* 1.5, $MeC{=}CHCO_2$), 3.60 (3 H, s, $MeCO_2$), 5.00 (1 H, br, =CH), and 5.55 (1 H, s, =$CHCO_2Me$) (Found: C, 73.35; H, 10.25. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%).

Compound *E*-(**4g**; R = Me), an oil; $\nu_{max.}$ 1 590, 1 450, 1 370, and 1 350; *m/z* 284 (M^+, 100%), 269 (24), 213 (32), and 199 (31); δ 0.99 (3 H, t, *J* 7.5, *Me*CH_2C=), 1.81 (3 H, s, =CMe), 2.02 (2 H, q, *J* 7.5, $MeCH_2C$=), 2.32 (3 H, s, Ar-Me), 3.51 (2 H, d, *J* 6.0, ArCH_2CH=), 3.79, 3.81 (each 3 H, s, 2 OMe), 5.10 (1 H, br t, *J* 6.0, $ArCH_2CH$=), and 7.02—7.46 and 7.80—8.05 (each 2 H, m, ArH) (Found: C, 80.35; H, 8.5. $C_{19}H_{24}O_2$ requires C, 80.24; H, 8.51%).

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