The Influence of Chain-branching on the Steric Outcome of Some Olefin-forming Reactions

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When applied to the construction of internal disubstituted double bonds in compounds such as pentadec-7-ene and 2,6,11,15-tetramethylhexadeca-2,6,8,10,14-pentaene (5), the reductive elimination of vicinal benzoyloxy-sulphones gives products with a *trans* : *cis* ratio of *ca.* 4 : 1. When applied to the construction of disubstituted olefins in which branching occurs adjacent to the newly formed double bond, much higher *trans*-stereoselectivity is observed, *e.g.* for 5-ethyl-2-methylhept-3-ene (21) and 3,6-dimethylocta-2,4,6-triene (25) it is at least 98%. A similar effect of chain-branching is also observed in some Wittig and Horner reactions using primary allylic phosphorus derivatives. When a *Z*-allylic sulphone is used as the starting material in the benzoyloxy-sulphone method, the original *Z*-geometry is preserved in the product; (*Z*)-2-methylbut-2-enyl *p*-tolyl sulphone and tiglic aldehyde give almost exclusively (2*E*,4*E*,6*Z*)-3,6-dimethylocta-2,4,6-triene (27).

THE formation of olefins by the reduction of vicinal acyloxy-sulphones with sodium amalgam in alcoholic media was described in a preliminary paper by M. Julia in 1973.[1] We have recently [2,3] reported experiments using this method which related to two unanswered questions; first, can it be used for the synthesis of conjugated olefins—to which the answer is yes—and secondly, what are its stereochemical characteristics when used to construct a disubstituted olefin $R^1CH\vdots$ CHR^2? The present paper describes further experiments bearing on this second question.

We earlier found [2] that use of the reaction for constructing the disubstituted double bonds in the conjugated olefins (1) and (2) leads to virtually exclusive formation of the *trans*-isomers, irrespective of the stereochemical form (*erythro* or *threo*) of the acyloxy-sulphone used in the reductive-elimination step. We also found [3] that use of the reaction to construct the isolated double bond in the side-chain of the des-AB-ergostane derivative (3) † gave only the desired *trans*-isomer shown, which corresponds to the Windaus–Grundmann [4] C_{19} ketone. From these and other results we concluded [2] that 'when used for the synthesis of 1,2-disubstituted olefins in which the new double bond is either isolated or conjugated, the reaction is highly stereoselective and leads to the *trans*-isomers'. Our new experiments show that for really high stereoselectivity this conclusion is only valid for a restricted range of olefins, although a considerable degree of *trans*-stereoselectivity can be expected in the general case.

In other work we showed [5] that (*E*)-geraniol can be converted by way of (*E*)-geranyl phenyl sulphone and (*E*)-methyl geranate into (6*E*,10*E*)-2,6,11,15-tetramethylhexadeca-2,6,10-14-tetraen-8-yne, semihydrogenation of which provided a highly stereoselective route to the conjugated *E*,*Z*,*E*-triene (4). It was of interest to prepare the corresponding *E*,*E*,*E*-isomer (5), and with this aim the lithium derivative of (*E*)-geranyl phenyl sulphone (6) and (*E*)-citral (7) were brought into

† Structures (3) and (35)—(38) represent absolute configurations; the remainder, insofar as they are dissymmetric, represent racemates.

reaction to give, after treatment with benzoyl chloride, a mixture (*ca.* 2 : 1) of the diastereoisomeric benzoyloxy-sulphones (8). Treatment of the mixture with sodium amalgam in tetrahydrofuran–methanol (3 : 1) at −20 °C gave in high yield a mixture (*ca.* 80 : 20 by g.l.c.) of the conjugated *E*,*E*,*E*-isomer (5) and its *E*,*Z*,*E*-isomer (4). It was notable that in both products the original *E*-geometry of the starting compounds (6) and (7) was completely preserved. However, the formation of the central-*Z*-isomer (4) in substantial amounts was unexpected, and led us to re-examine the synthesis [2] of pentadec-7-ene (9) from n-octyl phenyl sulphone and n-heptaldehyde, which we earlier reported to give a product 'essentially free from the *cis*-isomer'. For comparison with our product we had available a sample of pentadec-7-ene, prepared by the 'salt-free' Wittig method,[6] which consisted mainly (92 : 8 by g.l.c.) of the *cis*-isomer (10). The olefin prepared by the reductive elimination of the mixed diastereoisomeric 7-benzoyloxy-8-phenylsulphonylpentadecanes (11) in tetrahydrofuran–methanol at −20 °C had the composition 80 *trans* : 20 *cis* (g.l.c.). This experiment has since been repeated with the same result, and it is clear that our previous result on this example of the Julia reaction (but not on the others) must be disregarded.

The 80 *trans* : 20 *cis*-mixtures obtained by the benzoyloxy-sulphone method in the examples of the conjugated olefin (5) and the mono-olefin (9) are probably typical of the degree of *trans*-stereoselectivity to be expected in the general case. This degree may be high enough to have appreciable value in synthetic work, but it falls much below that achieved with the olefins (1)—(3), and the question therefore presented itself, what special features in these last three compounds are responsible for the favourable stereochemical results achieved in their preparation? The most probable explanation seemed to lie in the branching which in these compounds is present at both positions adjacent to the newly formed double bond, a feature which is absent from the olefins (5) and (9). This explanation is supported by the experiments described below.

We consider first the mono-olefin series, in which 2-

methyldec-3-ene (20) and 5-ethyl-2-methylhept-3-ene (21) were prepared from appropriate benzoyloxy-sulphones. For example, n-heptyl phenyl sulphone (12) and ethylmagnesium bromide gave a derivative which was treated with isobutyraldehyde (14) to give, after hydrolysis, isomeric hydroxy-sulphones which were converted into the corresponding mixed benzoyloxy-sulphones (17) by successive treatment with n-butyl-

the starting compounds (13) and (16), reduction provided virtually exclusively the *trans*-isomer, *viz.* (21).
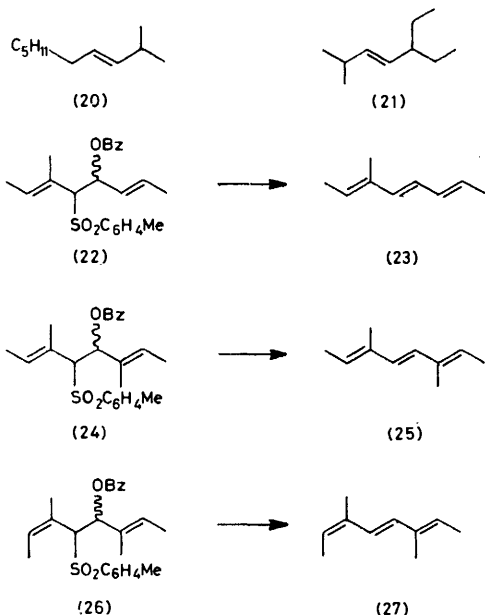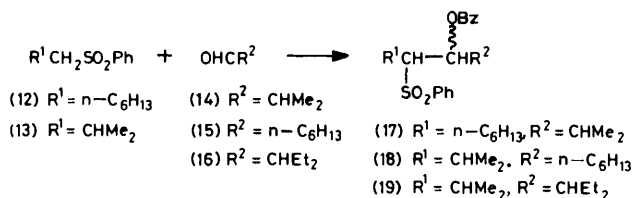
Similar results were obtained when the reaction was used to set up the central disubstituted double bond in some conjugated trienes. For this purpose, the lithium derivative of a primary allylic aryl sulphone was allowed to react with an αβ-unsaturated aldehyde (both components being used in geometrically homogeneous form)
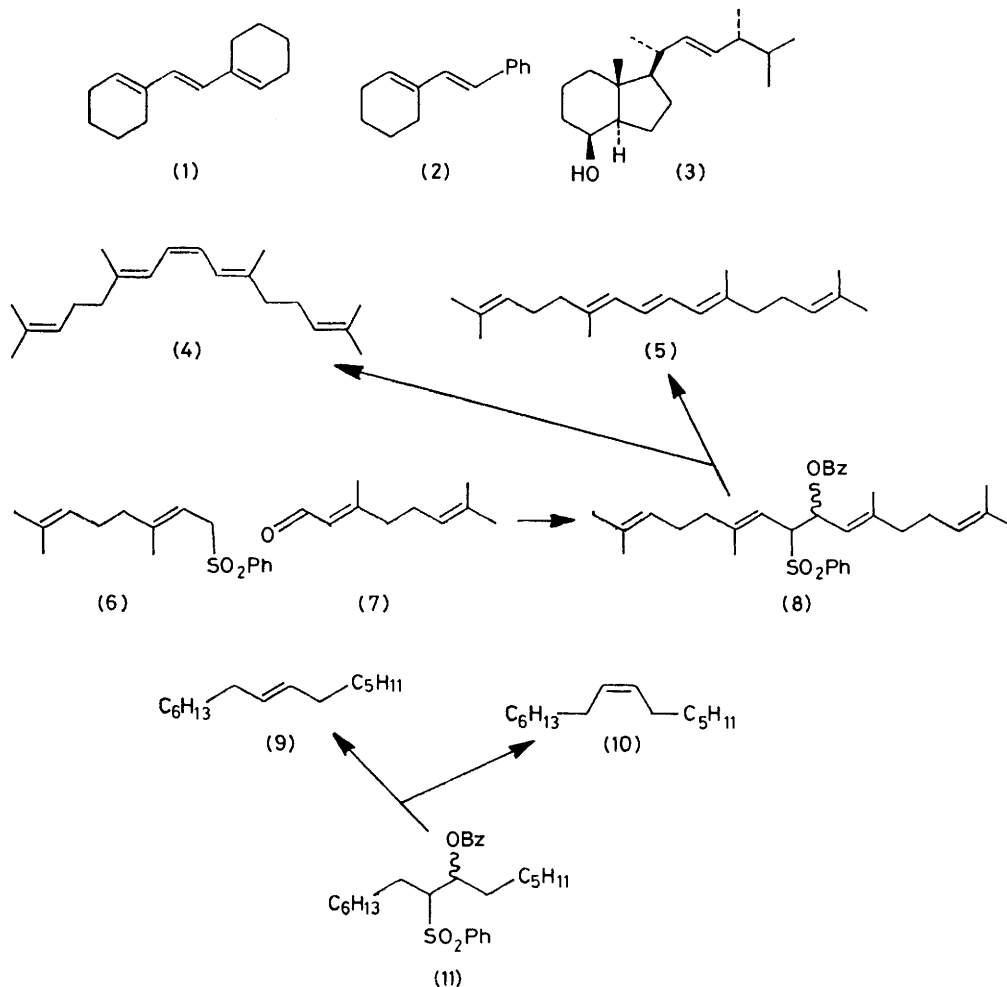
lithium and benzoyl chloride. The pure major diastereoisomer of (17) was isolated crystalline; it gave on reductive elimination (68% yield) a mixture of *trans*-2-methyldec-3-ene (20) and its *cis*-isomer in the ratio 9 : 1. Olefin of the same composition was obtained from the mixed diastereoisomers of (17) left after removal of much of the crystalline isomer. It was also of interest that olefin samples of the same composition were obtained from one pure diastereoisomer of the benzoyl-oxy-sulphone (18), which is a position-isomer of (17), and also from a mixture of both the diastereoisomers (18). The methyl branch in the olefin (20) clearly has the effect of increasing considerably the *trans*-stereospecificity of the elimination step of the synthesis. When two such branches were present, as in the diastereoisomeric benzoyloxy-sulphones (19), obtained from

to give, after addition of benzoyl chloride, a mixture of two diastereoisomeric benzoyloxy-sulphones. In this way (E)-2-methylbut-2-enyl *p*-tolyl sulphone and (E)-but-2-enal gave a mixture (*ca.* 65 : 35) of the two diastereoisomers (22). The major isomer was obtained pure and crystalline, and provided on reduction 3-methylocta-2,4,6-triene containing 97% of the all-*E*-isomer (23). Similar material was also obtained by reduction of a sample of the mixed diastereoisomers (22) in which the minor isomer was the predominant compound (*ca.* 85 : 15). Here again both isomers gave the same triene mixture, and the methyl branch adjacent to the new double bond greatly increased the *trans*-stereoselectivity. It is also noteworthy that the *E*-configurations of the starting materials were completely preserved in the product (23).

Reaction of (E)-2-methylbut-2-enyl p-tolyl sulphone and (E)-2-methylbut 2-enal led to a mixture (3 : 1) of diastereoisomeric benzoyloxy-sulphones (24). The major isomer provided on reduction a sample of 3,6-dimethyl-octa-2,4,6-triene in which the all-E-isomer (25) was present to the extent of at least 98%. Similarly, (Z)-2-methylbut-2-enyl p-tolyl sulphone and (E)-2-methylbut-

R^{1}CH$_2$SO$_2$Ph + OHCR^2 ⟶ R^{1}CH—CHR^2 (with OBz and SO$_2$Ph)

(12) R^1 = n—C$_6$H$_{13}$
(13) R^1 = CHMe$_2$

(14) R^2 = CHMe$_2$
(15) R^2 = n—C$_6$H$_{13}$
(16) R^2 = CHEt$_2$

(17) R^1 = n—C$_6$H$_{13}$, R^2 = CHMe$_2$
(18) R^1 = CHMe$_2$, R^2 = n—C$_6$H$_{13}$
(19) R^1 = CHMe$_2$, R^2 = CHEt$_2$

(20) (21)

(22) (23)
(with OBz and SO$_2$C$_6$H$_4$Me)

(24) (25)
(with OBz and SO$_2$C$_6$H$_4$Me)

(26) (27)
(with OBz and SO$_2$C$_6$H$_4$Me)

2-enal provided the mixed (85 : 15) benzoyloxy-sulphones (26). Reduction of the pure major isomer gave a sample of 3,6-dimethylocta-2,4,6-triene in which the 2E,4E,6Z-isomer (27) was present to the extent of at least 98%. These examples illustrate again the retention of the original sulphone geometry, and the favourable influence on the trans-stereoselectivity exerted by the presence of branches adjacent to the newly formed double bond.

In the reductive elimination of a benzoyloxy-sulphone, the first step may be the addition of one electron and the separation of phenylsulphinate anion to give a radical of the form (28) which, no matter what the configuration of the original, can undergo transformation to the less energetic form (28a). After uptake of a further electron [see (29)], benzoate anion can separate giving the olefin (30). The transition state presumably lies somewhere between (28a) and (30); whatever its exact structure, it clearly resembles the product (30), in the nature of the interactions between the two alkyl groups. Given two features of this situation, first, the possibility of change of relative configuration at the radical stage,

and secondly, the lower energy of a transition state in which R^1 and R^2 are remote, the preference of the reaction for formation of trans-olefin becomes clear, and so also does the effect of a branch adjacent to the benzoyloxy or the arylsulphonyl group. As shown above, this effect is particularly strong when the new double bond is

(28) (28a)

(29) (30)

(31) (32) (33) (34)

(35) (36) (37)

(39)

(38)

(40)
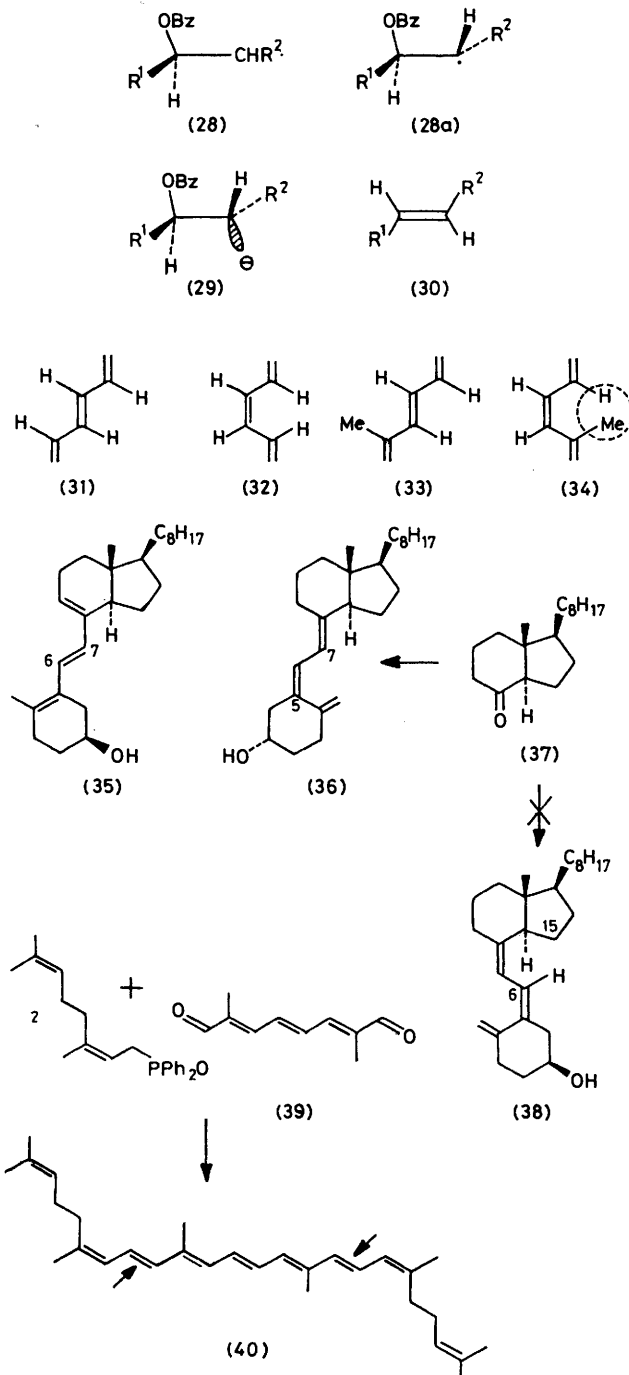
part of a conjugated triene system. If we use the interactions in the olefinic product as a guide to those in the transition state, and compare the four olefins (31)—(34), it is apparent that the major interaction

occurs in the *cis*-olefin (34), and that the energy difference between it and its *trans*-isomer (33) will be much greater than that between the pair (31) and (32). This effect, exercised in the transition state, is the origin of the chain-branching effect demonstrated in this paper.

The effect is not peculiar to the reductive benzoyloxy-sulphone elimination; it is also found in Wittig olefin syntheses with allylic phosphoranes where, because of the incidence of dissociation of the initially formed betaine, followed by recombination, *threo*-intermediate can be formed from *erythro*-intermediate. Since steric interactions of the kind discussed above should promote the dissociation of the *erythro*-forms in relation to their elimination, it would be expected that chain branching adjacent to the new double bond would strongly favour *trans*-stereoselectivity. An example of this is seen in the exclusive formation of tachysterol₃ (35) recorded in ref. 7 with construction of the 6,7-double bond; the outer double bonds of the triene system form part of cyclohexene rings, which introduce branching, and so prevent formation of the 6-*cis*-isomer, precalciferol₃.

In a similar manner, interaction between the 15-methylene group and the 6-methine hydrogen in the transition state leading to the 7Z-isomer (38) from the Brockmann–Busse ketone (37) is no doubt responsible for the exclusive formation of the natural 5Z,7E-isomer (36) during the synthesis [8] of vitamin D₃ using the Horner phosphine oxide method. Finally, we may recall the hitherto unexplained observation [9] that, in contrast to some similar reactions, treatment of (all-*E*)-2,7-dimethylocta-2,4,6-triene-1,8-dial (39) and neryl-diphenylphosphine oxide gives in high yield the conjugated heptaene (40), in which the two newly formed disubstituted double bonds (indicated by the arrows) have exclusively the *E*-configuration. This can now be recognised as the consequence of the methyl branch adjacent to both the new double bonds.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 60—80°, unless otherwise specified. T.l.c. was carried out using Kieselgel GF₂₅₄. N.m.r. data refer to solutions in CDCl₃ at 90 MHz (¹H) or 22.6 MHz (¹³C).

Pentadec-7-ene.—(a) *By Wittig reaction.* Following Bestmann's method,[6] sodium hexamethyldisilazide (1.01 g) was added to a solution of n-octyltriphenylphosphonium bromide [10] (2.275 g) in tetrahydrofuran (18 cm³) at 20 °C under dry nitrogen; the mixture was stirred for 45 min and then heated under reflux for 2 h. It was then cooled to 20 °C and heptaldehyde (684 mg) in tetrahydrofuran (5 cm³) was added. The mixture was stirred at 20 °C for 16 h and then poured into 2N-hydrochloric acid, the mixture then being extracted with light petroleum. The extract was washed with aqueous sodium carbonate and with water, and was evaporated to give a solid which was extracted with hot light petroleum. Evaporation of the extracts, and chromatography of the residue on silica gel (30 g) (light petroleum), followed by bulb-to-bulb distillation at 150 °C and 20 mmHg gave pentadec-7-ene as an oil (672 mg, 64%), ν_max. (film) 722m, 965w (due to *E*-isomer), 1 378m, 1 470s, and 3 002m cm⁻¹, τ 4.64 (2 H, apparent t, 2 × −CH=), g.l.c. on

43 m SF 96 WCOT at 110—148 °C, retention time 98.4 (*Z*-isomer, 92%) and 98.8 min (*E*-isomer, 8%).

(b) n-Octyl phenyl sulphone (10.0 mmol) and 1.5M ethereal ethylmagnesium bromide in tetrahydrofuran (30 cm³) were heated under reflux for 3.5 h. The mixture was then cooled (0 °C) and stirred during the dropwise addition of n-heptanal (10 mmol) in ether (10 cm³). After 30 min, ether (30 cm³) and 1N-hydrochloric acid (20 cm³) were added, the phases were separated, and the organic phase was washed (water), dried, and evaporated. To a stirred solution of the residue in tetrahydrofuran (30 cm³) containing 1,10-phenanthroline (5 mg) at −78 °C 1.5M-n-butyl-lithium in hexane was added until the dark colour persisted. Benzoyl chloride (12.5 mmol) was then added in one portion, the mixture was allowed to warm to room temperature (3 h) and the excess of benzoyl chloride was removed by the addition of 3-dimethylaminopropylamine (1 cm³). Ether (30 cm³) was added, and the mixture was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and was dried and evaporated.

The mixed diastereoisomeric benzoyloxy-sulphones were stirred in tetrahydrofuran (36 cm³) and methanol (12 cm³) at −20 °C with 5.65% sodium amalgam (11 g) for 3 h. It was then decanted into water and the product was isolated with light petroleum (b.p. 30—40°). Evaporation and bulb-to-bulb distillation gave pentadec-7-ene (yield from n-octyl phenyl sulphone, 53%), ν_max. (film) 722 m, 965vs, 1 378s, and 1 470vs cm⁻¹, τ 4.63 (2 H, m, 2 × −CH=), g.l.c. on 59m SF 96 WCOT at 98—141 °C, retention time 54.8 (*Z*-isomer, 20%) and 55.6 min (*E*-isomer, 80%).

2-Methyldec-3-ene.—(a) *From n-heptyl phenyl sulphone.* n-Heptyl phenyl sulphone and isobutyraldehyde were converted, by the method described for pentadec-7-ene, into a mixture of two diastereoisomeric benzoyloxy-sulphones. Crystallisation from methanol afforded (yield 47%) 3-benzoyloxy-4-phenylsulphonyl-2-methyldecane, m.p. 94—96°, ν_max. (CCl₄) 1 155, 1 270, 1 310, 1 320, and 1 720 (all s) cm⁻¹, τ 4.55 (1 H, m, >CH·OBz) and 6.63 (1 H, t, *J* 3 Hz, >CH·SO₂Ph) (Found: C, 69.2; H, 7.8; S, 7.7. C₂₄H₃₂O₄S requires C, 69.2; H, 7.7; S, 7.7%).

Reduction of this isomer in the usual way afforded (yield, 68%) 2-methyldec-3-ene as an oil, τ (*E*-isomer) 4.6—4.74 (2 H, m, 2 × −CH=) and 9.03 (6 H, d, *J* 7 Hz, Me₂CH), *Z*-isomer 4.75—4.91 (−CH=) and 9.05 (Me₂CH), g.l.c. on 40 m SF 96 WCOT at 108 °C, retention time 23.5 (*Z*-isomer, 10%) and 24.2 min (*E*-isomer, 90%) (Found: *M*⁺, 154.172 12. Calc. for C₁₁H₂₂: *M*, 154.172 14).

(b) *From isobutyl phenyl sulphone.* This sulphone and n-heptaldehyde were converted, by the method described for pentadec-7-ene, into a mixture of two diastereoisomeric benzoyloxy-sulphones. Crystallisation from methanol afforded 4-benzoyloxy-3-phenylsulphonyl-2-methyldecane (yield 53%), m.p. 68—70°, ν_max. (CCl₄) 1 150, 1 265, 1 310, 1 320, and 1 720 (all s) cm⁻¹, τ 4.61 (1 H, dd, *J* 4 and 8 Hz, >CH·OBz), 6.49 (1 H, m, >CH·SO₂), 7.30 (1 H, m, C*H*Me₂), 8.93 and 9.03 (each 3 H, d, *J* 7 Hz, Me₂CH) (Found: C, 69.4; H, 7.7; S, 7.8%).

Reduction of this isomer in the usual way gave (yield 63%) 2-methyldec-3-ene with the composition and properties described under (a).

(E)-5-*Ethyl-2-methylhept-3-ene* (21).—Isobutyl phenyl sulphone and 2-ethylbutanal were converted in the usual way into a mixture of two diastereoisomeric benzoyloxy-sulphones. Crystallisation from methanol afforded (yield 43%) 4-benzoyloxy-3-phenylsulphonyl-5-ethyl-2-methylheptane,

m.p. 115—116°, $\nu_{max.}$ (CCl$_4$) 1 155, 1 270, 1 310, 1 320, and 1 720 (all s) cm^{-1}, τ 4.31 (1 H, dd, J 3 and 8 Hz, $>$CH·OBz), 6.54 (1 H, dd, J 2.5 and 3 Hz, $>$CH·SO$_2$), and 8.85 and 8.97 (each 3 H, d, J 8 Hz, Me$_2$C) (Found: C, 68.75; H, 7.5; S, 7.95. C$_{23}$H$_{30}$O$_4$S requires C, 68.6; H, 7.5; S, 7.95%).

Reduction of this isomer in the usual way afforded (yield 71%) (E)-5-*ethyl-2-methylhept-3-ene* (21), $\nu_{max.}$ (film) 967m cm^{-1}, τ 4.58 (1 H, dd, J 7 and 16 Hz) 4.92 (1 H, dd, J 7 and 16 Hz), 9.00 (6 H, d, J 8 Hz), and 9.17 (6 H, t, J 8 Hz) (Found: M^+, 140.156 34. C$_{10}$H$_{20}$ requires M, 140.156 493), g.l.c. on 40 m SF-96 WCOT at 70 °C, retention time 32.3 min (100%).

2,6,11,15-*Tetramethylhexadeca*-2,6,8,10,14-*pentaene*.—
1.5м-n-Butyl-lithium in hexane (3.7 cm^3) was added dropwise to a stirred solution of (E)-geranyl phenyl sulphone (1.39 g) in tetrahydrofuran (10 cm^3) at —78 °C under nitrogen. After 15 min (E)-citral (836 mg; 98% pure by g.l.c.) in tetrahydrofuran (5 cm^3) was added dropwise. After a further 45 min at —78 °C benzoyl chloride (1.545 g) was added, and the mixture was allowed to warm to 20 °C during 30 min. Stirring was continued for 20 h, after which 3-dimethylaminopropylamine (1 g) was added. After 10 min the mixture was diluted with ether, washed with dilute hydrochloric acid, aqueous sodium carbonate, and water, and was dried and evaporated. Chromatography of the residue on silica gel (90 g) with ethyl acetate–light petroleum (1 : 9) gave the mixed (35 : 65) diastereoisomeric benzoyloxy-sulphones (2.441 g, 91%), $\nu_{max.}$ (film) 711s, 1 150s, 1 270vs, 1 308s, 1 318s, and 1 724vs cm^{-1}, τ 2.0—2.75 (10 H, m, ArH), 3.55 (dd, J 3 and 9 Hz, $>$CH·O of minor isomer), 3.70 (dd, J 7 and 9 Hz, $>$CH·O of major isomer), 4.4—5.1 (4 H, m, 4 × =CH—), 5.58 (dd, J 7 and 11 Hz, $>$CH·SO$_2$Ph of major isomer), and 5.98 (dd, J 3 and 10 Hz, $>$CH·SO$_2$Ph of minor isomer) (Found: M^+, 534.279 19. Calc. for C$_{33}$H$_{42}$O$_4$S: M, 534.280 36).

The mixed benzoyloxy-sulphones (534 mg) and 5.65% sodium amalgam (1.7 g) were stirred together in tetrahydrofuran (6 cm^3) and methanol (2 cm^3) at —20 °C under nitrogen for 4 h. The mixture was diluted with light petroleum, washed with water, dried, and evaporated. Chromatography on silica gel (light petroleum) under nitrogen gave the pentaene as an oil (245 mg, 90%), $\nu_{max.}$ (film) 956s, 1 102m, 1 376s, 1 450s, and 1 642m cm^{-1}, τ 3.63 (2 H, dd, J 4 and 8 Hz, H-8 and -9 of 6E,8E,10E-isomer), 4.08br (2 H, d, J 8 Hz, H-7 and -10) 4.87 (2 H, m, CH=CMe$_2$), 8.22 (6 H, s, 2 × Me), 8.30 (6 H, s, 2 × Me), and 8.37 (6 H, s, 2 × Me), $\lambda_{max.}$ (hexane) 287 (ε 42 800) and 298 nm (36 100) (Found: M^+, 272.250 01. Calc. for C$_{20}$H$_{32}$: M, 272.250 39), g.l.c. on 5 ft 5% Carbowax at 172°, retention times 17.7 (E,E,E-isomer, 78%), 18.8 (unknown impurity, 4%), and 24.7 min (E,Z,E-isomer, 18%) (this last assignment was confirmed by the addition of authentic [5] material), δ_C 16.77, 17.75, 25.74, 26.78, 40.24, 124.18, 125.61, 127.35, 131.59, and 138.03 p.p.m.; signals due to the E,Z,E-isomer at δ_C 40.57, 120.47, 123.53, and 139.33 p.p.m.

(E)-2-*Methylbut*-2-*enyl* p-*Tolyl Sulphone*.—(E)-2-Methyl-but-2-enol (1.72 g; prepared by reduction [11] of tiglic acid with lithium aluminium hydride) in dimethylformamide (15 cm^3) was added to a stirred and cooled (0 °C) suspension of chloromethylenedimethylammonium chloride (3.07 g) in dimethylformamide. After 45 min the mixture was diluted with ether (50 cm^3) and light petroleum (b.p. 30—40°; 50 cm^3) and the solution was washed with water, dried, and the solvent removed carefully at atmospheric pressure to give the crude allylic chloride (2.0 g). A portion (1.26 g)

was stirred with sodium toluene-p-sulphinate (5 g) in dimethylformamide at 20 °C for 40 h, and then at 60 °C for 2 h. Ether–light petroleum (1 : 1; 150 cm^3) was added and the mixture was washed with water, dried, and evaporated. Recrystallisation from ether–light petroleum gave the *sulphone* as prisms (1.58 g), m.p. 68.5—69.5°, $\nu_{max.}$ (Nujol) 675s, 737s, 830s, 1 094s, 1 155vs, 1 298vs, 1 310vs, 1 320vs, and 1 600m cm^{-1}, τ 2.26 (2 H, d, J 8 Hz, ArH), 2.66 (2 H, d, J 8 Hz, ArH), 4.78 (1 H, q, J 7 Hz, —CH=), 6.30 (2 H, s, CH$_2$·SO$_2$), 7.55 (3 H, s, CH$_3$Ar), 8.26 (3 H, s with fine splitting, CH$_3$C=), and 8.44 (3 H, d, with fine splitting, J 7 Hz, CH_3CH=) (Found: C, 64.35; H, 7.3; S, 14.0. C$_{12}$H$_{16}$O$_2$S requires C, 64.3; H, 7.2; S, 14.3%).

(Z)-2-*Methylbut*-2-*enyl* p-*Tolyl Sulphone*.—A crude sample (purity ca. 80%) of Z-2-methylbut-2-enol was prepared [12] by the reduction of 3,4-epoxy-3-methylbut-1-ene with di-isobutylaluminium hydride in hexane. The crude alcohol (2.127 g) was treated as described for the pure E-isomer, and gave a crystalline mixture of sulphones containing ca. 8% of the E-isomer. Crystallisation from chloroform–light petroleum afforded the pure Z-*sulphone* as prisms (2.56 g) m.p. 94—95°, $\nu_{max.}$ (Nujol) 750s, 1 132vs, 1 163s, 1 290s, 1 310vs, and 1 595m cm^{-1}, τ 2.23 (2 H, d, J 8 Hz, ArH), 2.68 (2 H, d, J 8 Hz, ArH), 4.45br (1 H, q, J 7 Hz, —CH=), 6.18 (2 H, s, CH$_2$·SO$_2$), 7.55 (3 H, s, CH$_3$), 8.16 (3 H, s with fine splitting, CH$_3$C=), and 8.76 (3 H, d with fine splitting, J 7 Hz, CH_3CH=) (Found: C, 64.35; H, 7.1; S, 14.4. C$_{12}$H$_{16}$O$_2$S requires C, 64.3; H, 7.2; S, 14.3%).

(all-E)-3-*Methylocta*-2,4,6-*triene* (23).—Reaction of (E)-2-methybut-2-enyl p-tolyl sulphone (1.12 g), 1.5м-n-butyl-lithium in hexane (3.7 cm^3), (E)-crotonaldehyde (420 mg), and benzoyl chloride (1.55 g) in the usual way gave a crystalline solid which ^{1}H n.m.r. showed to be a mixture (35 : 65) of two diastereoisomers. The pure major isomer of 5-*benzoyloxy*-4-p-*tolylsulphonyl*-2-*methylocta*-2,6-*diene* (22) was obtained by recrystallisation from chloroform–light petroleum as crystals, m.p. 148—149°, $\nu_{max.}$ (Nujol) 669s, 708s, 721s, 812m, 955m, 1 145s, 1 270s, 1 300s, and 1 710s cm^{-1}, τ 2.1—3.0 (9 H, m, ArH), 5.92 (1 H, d, J 10 Hz, $>$CH·SO$_2$), 7.77 (3 H, s, ArCH$_3$), and 8.15—8.45 (9 H, m, 3 × CH$_3$) (Found: C, 69.2; H, 6.6; S, 8.0. C$_{23}$H$_{26}$O$_4$S requires C, 69.3; H, 6.6; S, 8.0%). The minor isomer (not isolated pure) showed τ 6.14 (1 H, d, J 6 Hz, $>$CH·SO$_2$) and 7.60 (3 H, s, ArCH$_3$).

The above pure benzoyloxy-sulphone (885 mg) was reduced in the usual way, and the product was isolated by chromatography on silica gel and bulb-to-bulb distillation at 135—140 °C and 200 mmHg. The *triene* (23) (184 mg, 68%) was obtained as an oil, $\nu_{max.}$ (film) 815s, 928m, 982vs, 1 632w, and 1 645w cm^{-1}, $\lambda_{max.}$ (hexane) 236 (infl.), 246 (infl.), 256 (ε 32 700), 266 (42 200), and 276 nm (33 900), τ 3.77—4.70 (5 H, m, 5 × —CH=) and 8.13—8.35 (9 H, m, 3 × CH$_3$), δ_C 11.96, 13.91, 18.20, 126.20, 126.39, 128.08, 132.31, 134.78, and 135.30 p.p.m. (Found: M^+, 122.109 48. C$_9$H$_{14}$ requires M, 122.109 54), g.l.c. on 40 m SF WCOT at 107 °C, retention time 11.7 (3%, probably the 4Z-isomer) and 12.6 min (97%; all-E-isomer).

(all-E)-3,6-*Dimethylocta*-2,4,6-*triene* (25).—(E)-2-Methyl-but-2-enyl p-tolyl sulphone (896 mg), 1.5м-n-butyl-lithium in hexane (2.93 cm^3), tiglic aldehyde (412 mg), and benzoyl chloride (1.26 g) were brought into reaction in the usual way to give a crystalline mixture (1.728 g) of two diastereoiso-meric benzoyloxy-sulphones (ca. 75 : 25 by n.m.r.). Crystal-lisation from chloroform–light petroleum afforded the major *isomer* as needles, m.p. 175—176°, $\nu_{max.}$ (Nujol) 730s,

1 150s, 1 260s, 1 275s, 1 305s, and 1 715s cm^{-1}, τ 2.2—3.0 (9 H, m, ArH), 3.88 (1 H, d, J 11 Hz, >CH·O), 4.22br (1 H, q, J 7 Hz, −CH=), 4.41br (1 H, q, J 7 Hz, −CH=), 5.82 (1 H, d, J 11 Hz, >CH·SO$_2$), 7.80 (3 H, s, ArCH$_3$), 8.24 (3 H, s with fine splitting, CH$_3$C=C), and 8.30—8.50 (9 H, m, 3 × CH$_3$C=) (Found: C, 69.7; H, 6.85; S, 7.8. C$_{24}$H$_{28}$O$_4$S requires C, 69.9; H, 6.8; S, 7.8%). Purification of the mother-liquor material by p.l.c. (ethyl acetate–light petroleum, 1 : 4), and crystallisation from chloroform–light petroleum afforded the minor *isomer*, m.p. 136—138°, τ 1.9—2.8 (9 H, m, ArH), 3.84 (1 H, d, J 7 Hz, >CH·O), 4.24br (1 H, q, J 7 Hz, −CH=), 4.46br (1 H, q, J 7 Hz, −CH=), 5.98 (1 H, d, J 7 Hz, >CH·SO$_2$), 7.59 (3 H, s, ArCH$_3$), 8.20 (3 H, s with fine splitting, CH$_3$C=C), and 8.35—8.55 (9 H, m, 3 × CH$_3$C=) (Found: C, 69.8; H, 6.8; S, 7.6%).

Reductive elimination of the above major benzoyloxy-sulphone in the usual way, and bulb-to-bulb distillation at 135 °C and 100 mmHg gave the *triene* as an oil (84 mg, 61%), λ$_{max.}$ (hexane) 237 (infl.), 246 (infl.), 257 (ε 34 100), 267 (42 300), and 277.5 nm (33 300), ν$_{max.}$ (film) 791m, 820s, 955vs, 1 021m, 1 282m, and 1 638m cm^{-1}, τ 3.81 (2 H, s, −CH=CH−), 4.43 (2 H, q with fine splitting, J 7 Hz, 2 × CH$_3$CH=), 8.22 (6 H, s, 2 × CH$_3$C=), and 8.25 (6 H, d, J 7 Hz, 2 × CH_3CH=), δ$_C$ 12.02, 13.91, 126.00, 130.68, and 134.91 p.p.m. (Found: M^+, 136.125 32. C$_{10}$H$_{16}$ requires M, 136.125 19), g.l.c. on 58 m SF 96 WCOT at 107 °C, retention time 10.2 (<2%), 10.9 min (>98%).

(2E,4E,6Z)-*Dimethylocta-2,4,6-triene* (27).—(Z)-2-Methylbut-2-enyl *p*-tolyl sulphone (1.568 g), 1.53M-n-butyl-lithium in hexane (5.05 cm³), tiglic aldehyde (681 mg), and benzoyl chloride (2.1 g) were brought into reaction in the usual way to give a crystalline mixture (3.099 g; 85 : 15 by n.m.r.) of two diastereoisomeric benzoyloxy-sulphones. Crystallisation from chloroform–light petroleum afforded the major *isomer*, m.p. 168—170°, ν$_{max.}$ (Nujol) 659m, 720m, 1 096m, 1 141s, 1 277s, and 1 725s cm^{-1}, τ 2.2—3.05 (9 H, m, ArH), 3.76 (1 H, d, J 11 Hz, >CH·O), 4.11 (1 H, q with fine splitting, J 7 Hz, −CH=), 4.36 (1 H, q, with fine splitting, J 7 Hz, −CH=), 5.26 (1 H, d, J 11 Hz, >CH·SO$_2$), 7.80 (3 H, s, ArCH$_3$), 8.12 (3 H, s, with fine splitting, CH$_3$C=), and 8.25—8.55 (9 H, m, 3 × CH$_3$C=) (Found: C, 69.7; H, 6.75;

S, 7.85. C$_{24}$H$_{28}$O$_4$S requires C, 69.9; H, 6.8; S, 7.8%). The minor benzoyloxy-sulphone, not isolated pure, showed *inter alia* τ 3.82 (1 H, d, J 7 Hz, >CH·O), 5.41 (1 H, d, J 7 Hz, >CH·SO$_2$), 7.58 (3 H, s, ArCH$_3$), and 8.0 (3 H, s with fine splitting, CH$_3$C=).

Reductive elimination in the usual way of the pure major benzoyloxy-sulphone gave material which was distilled from bulb to bulb at 135—140 °C and 80 mmHg to give the *triene* (27) as an oil (222 mg, 75%), ν$_{max.}$ (film) 781s, 861m, 955vs, 1 028m, 1 278w, and 1 625 w cm^{-1}, λ$_{max.}$ (hexane) 262 (ε 29 500), 270.5 (37 700), and 281 nm (30 300), τ 3.39 (1 H, d, J 16 Hz, −CH= of central double bond), 3.71 (1 H, d, J 16 Hz, −CH= of central double bond), 4.34br (1 H, q, J 7 Hz, CH$_3$CH=), 4.56br (1 H, q, J 7 Hz, CH$_3$CH=), and 8.2—8.4 (12 H, m, 4 × CH$_3$), δ$_C$ 12.09, 13.13, 14.04, 20.54, 122.62, 123.99, 127.04, 133.15, 133.41, and 135.23 p.p.m., g.l.c. on 59 m SF 96 WCOT at 96°, retention time 26.5 min (98%).

REFERENCES

[1] M. Julia and J. M. Paris, *Tetrahedron Letters*, 1973, 4833.
[2] P. J. Kocienski, B. Lythgoe, and S. Ruston, *J.C.S. Perkin I*, 1978, 829.
[3] P. J. Kocienski, B. Lythgoe, and D. A. Roberts, *J.C.S. Perkin I*, 1978, 834.
[4] A. Windaus and W. Grundmann, *Annalen*, 1936, **524**, 295.
[5] B. Lythgoe and I. Waterhouse, *J.C.S. Perkin I*, 1979, 2429.
[6] H. J. Bestmann, W. Stransky, and O. Vostrowsky, *Chem. Ber.*, 1976, **109**, 1694.
[7] R. S. Davidson, S. M. Waddington-Feather, D. H. Williams, and B. Lythgoe, *J. Chem. Soc.*, 1967, 2534.
[8] B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, J. Tideswell, and P. W. Wright, *J.C.S. Perkin I*, 1978, 590.
[9] J. M. Clough and G. Pattenden, *Tetrahedron Letters*, 1978, 4159.
[10] C. T. Eyles and S. Trippett, *J. Chem. Soc. (C)*, 1966, 67.
[11] L. F. Hatch and P. R. Noyes, *J. Amer. Chem. Soc.*, 1957, **79**, 345.
[12] J. A. Katzenellenbogen and R. S. Lenox, *J. Amer. Chem. Soc.*, 1973, **95**, 957.