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A useful method for configurational assignment of vinyl sulfides; stereochemical reassessment of the radical addition of benzenethiol to alkynes

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A comparative analysis of the ¹H NMR spectra of (E)- and (Z)-phenyl and alkyl sulfides and their corresponding sulfones provides a useful method for establishing their configuration. Although by employing this method we generally confirm our previous configurational assignments for benzene-thiol/alkyne adducts, those for (E)- and (Z)-3-(phenylsulfanyl)hex-3-ene and 4-(phenylsulfanyl)oct-4-ene, are shown to have been assigned incorrectly. In the light of the present results it is concluded that radical addition of benzenethiol to alkynes at 100 °C generally proceeds with *trans*-stereoselectivity. This conclusion is the reverse of our earlier claim for the effect that benzenethiol adds to terminal alkynes and alkyl-phenylacetylenes in a *trans*-stereoselective mode, but in a *cis*-stereoselective mode to dialkylacetylenes bearing (rather) bulky alkyl groups.

Recently we have studied the free-radical reactions of benzenethiol¹ and alkanethiols² with various mono- and disubstituted phenyl- and alkyl-acetylenes. The reaction of benzenethiol, carried out at 100 °C both in the presence and in the absence of azoisobutyronitrile (AIBN), proceeded by regioselective addition of benzenesulfanyl radicals to carboncarbon triple bonds to afford 1-alkyl- and 1-phenyl-2-(phenylsulfanyl)vinyl radicals.¹ The intermediate sulfanylvinyl radicals smoothly underwent hydrogen transfer from the thiol to give varying mixtures of (E)- and (Z)-vinyl sulfides. The stereochemistry of these radical additions was investigated by determining the proportion of the (E)- and (Z)-adducts produced under kinetic reaction conditions.¹ The addition of benzenethiol to hex-1-yne 1a and tert-butylacetylene 1b led preferentially to the formation of (Z)-adducts (Z)-3a, b (Scheme 1) in line with related radical additions of PhSeH,³ Me₃SiH,⁴ and CHCl₃⁵ to terminal alkynes, which generally occurs with trans-stereoselectivity [to give (Z)-adducts]. Preferential formation of the (Z)-adduct (Z)-3c was similarly observed with but-2-yne 1c (Scheme 1). In contrast, other dialkylacetylenes such as hex-3-yne 1d, oct-4-yne 1e and dec-5-yne 1f were believed to lead predominantly (or exclusively) to the (E)-adducts (E)-3d-f as a result of preferred thiol cis-addition (Scheme 1). The above results were explained in terms of the rapidly inverting (E)- and (Z)-sulfanylvinyl radicals 2a-f, whose reactivity would be largely determined by steric hindrance between their cis-2substituent (*i.e.* PhS and R^1) and the thiol scavenger rather than by their equilibrium position. On the other hand, the phenylacetylenes 1g-k generally reacted with benzenethiol in a highly trans-stereoselective mode to give mainly the corresponding (Z)-adducts (Z)-3g-k. This observation led us to suggest that intermediate sp-hybridized 1-phenyl-2-(phenylsulfanyl)vinyl radicals 2g-k, irrespective of the size of the R¹ substituent, would prefer to be trapped by the thiol scavenger on the side opposite to the PhS owing to bonding interaction between the unpaired electron and the adjacent phenylsulfanyl sulfur (Scheme 1).

Configurational assignments to the geometrical isomers of the sulfides $3\mathbf{a}-\mathbf{j}$ were made on the basis of ¹H NMR spectroscopic analysis. The stereochemistry of the (Z)- and (E)-styrenes (Z)- and (E)- $3\mathbf{h}-\mathbf{j}$ was established by comparative nuclear Overhauser enhancement (NOE) measurements, whereas the stereochemistry of the (E)- and (Z)-alkenes $3\mathbf{c}-\mathbf{f}$ was exclusively assigned on the basis of the observed values of



Scheme 1 Reactions and conditions: AIBN, neat alkyne 1g-k, 100 °C; ii, AIBN, neat alkyne 1a-f, 100 °C; iii, PhSH, -PhS

the coupling constant for the vinylic proton and the vicinal vinylic methyl or methylene protons. The assumption was made that the magnitudes of the *trans* coupling constants should be larger than the *cis* ones, as is normally observed.

Moreover, the configuration of the sulfide adduct 3k was assigned as Z on the basis that it was exclusively formed under both kinetic and thermodynamic conditions. In such a case spectral assignment by ¹H NMR spectroscopy was precluded by the non-availability of both geometrical isomers.

We now wish to report a further, easy method for establishing the stereochemistry of vinyl sulfides which is based on comparative ¹H NMR spectral analysis of these compounds and their corresponding sulfonyl derivatives. As we shall see later, a reinvestigation of the stereochemistry of our trisubstituted alkene adducts (E)/(Z)-3c-e and (Z)-3k, employing such a method, substantiated our previous structural assignments for compounds (E)-3c and (Z)-3c, k, but showed that those made for compounds 3d, e were incorrect.

Table 1	1H NMR o	chemical shift	$(\delta)^a$ of the	e vinylic protons	of $(E)/(Z)$ -3a-e	, g, h, k, l-o and (E)/(Z)-4

		$\stackrel{-S(O_2)}{\longleftarrow} \stackrel{H}{\underset{\mathbb{R}^2}} (E)$		$\xrightarrow{-S(O_2)} \overset{\mathbb{R}^2}{\bigvee} (Z)$		$\xrightarrow{-S(O_2)}_{H} \xrightarrow{(E)}_{R^2}$		$ \begin{array}{c} -S(O_2) \\ \searrow \\ H \end{array} $		2 (Z)			
Entry	Sulfide/ Sulfone	δ(3)	δ(4)	Δδ ^b	δ(3)	δ(4)	Δδ ^b	δ(3)	$\delta(4)$	Δδ	δ(3)	$\delta(4)$	$\Delta \delta^{b}$
1	3a/4a	6.0	6.95	0.95	5.84	6.22	0.38	6.15	6.25	0.10	6.20	6.24	0.06
2	3b/4b	6.12	6.96	0.84	5.81	6.10	0.29	6.15	6.18	0.03	6.18	6.10	-0.08
3	3c/4c	5.94	7.00	1.06	5.88	6.15	0.27						
4	3d/4d	5.90	6.90	1.00	5.97	6.00	0.03						
5	3e/4e	5.90	6.95	1.05	5.92	6.02	0.10						
6	3g/4g ^c	6.68	7.66	0.98	6.54	7.06	0.52	6.83	6.86	0.03	6.45	6.50	0.05
7	3h/4h	6.85	7.85	1.00	6.85	7.05	0.20						
8	3k/4k				7.15	7.22	0.07						
9	31/41	6.05	7.00	0.95	5.88	6.26	0.38	6.18	6.30	0.12	6.25	6.33	0.08
10	3m/4m	5.66	6.95	1.29	5.58	6.42	0.84	5.95	6.22	0.27	5.95	6.16	0.21
11	3n/4n	5.90	6.84	0.94	5.67	6.43	0.76	6.07	6.20	0.13	6.10	6.07	-0.03
12	30/40	5.62	6.88	1.26	5.53	6.36	0.83	5.91	6.25	0.34	5.89	6.13	0.24

^a δ Values determined at 200 MHz for solutions in CDCl₃ with Me₄Si as internal standard. ^b $\Delta \delta = \delta(4) - \delta(3)$. ^c Values assigned by means of α -deuteriation of (E)- and (Z)-(phenylsulfanyl) styrene 3a achieved by treating PhSD with phenylacetylene 1g.

Results and discussion

Very recently we reported a novel procedure for the bromosulfenylation of alkynes leading to 2-bromovinyl phenyl sulfides in a highly *trans*-stereoselective and regiospecific fashion.⁶ In the course of this study, ¹H NMR spectral evidence led us to observe that a bromovinyl sulfide vinylic proton *cis* to PhS exhibited a much greater downfield shift (*ca.* 1.4–1.7 ppm), on passing to the corresponding sulfone, than a *trans* (or geminal) vinylic one (*ca.* 0.2).⁶ This observation prompted us to examine a variety of simple (*E*)- and (*Z*)-vinyl sulfides and their sulfonyl derivatives in order to ascertain whether the above spectral trend would generally apply to these two classes of unsaturated sulfur compounds. The compounds selected for this study were (*E*) and (*Z*)-phenyl vinyl sulfides **3a**, **b**, **g**, **h** and l and the alkyl vinyl sulfides (*E*)- and (*Z*)-**3m–0**.

RS H
$$3m R = PhCH_2CH_2, R^1 = H, R^2 = Bu$$

 R^1 R^2 $3n R = Bu^t, R^1 = H, R^2 = Bu$
 $R^1 R^2$ $3o R = C_{12}H_{25}, R^1 = H, R^2 = Bu$

The sulfides **3m–o** were produced as isomeric E/Z mixtures by allowing 2-phenylethanethiol, 2-methylpropane-2-thiol and dodecanethiol to react with hex-1-yne **1a**. Configurational assignments for the new compounds (*E*)- and (*Z*)-**3**l, **n**, **o** were promptly performed by ¹H NMR spectroscopic analysis.

All the sulfides (E)- and (Z)-3a, b, g, h, l-o were quantitatively converted into their corresponding sulfones (E)- and (Z)-4a, b, g, h, l-o oxidation with *m*-chloroperbenzoic acid at room temperature (Scheme 2).

$$(E)'(Z)-3a-e, g, h, k, l-o \xrightarrow{i} PhSO_2 H RSO_2 H RSO_2 H R^1 R^2 R^1 R^2$$

$$(E)'(Z)-4a-e, g, h, k, l (E)'(Z)-4m-o$$

Scheme 2 Reagents: i, m-chloroperbenzoic acid, CHCl₃, 25 °C

As can be seen in Table 1 (entries 1,2,6,7,9-12), the chemical shift of a vinylic (*E*)-sulfone proton vicinal to the sulfur substituent generally occurred at much lower field (0.85–1.30 ppm) than that of the analogous proton in the corresponding (*E*)-sulfide. A similar shift, but comparatively much smaller, was commonly displayed by a vinylic (*Z*)-sulfide proton vicinal to the sulfonyl substituent on passing to the corresponding (*Z*)-

sulfonyl derivative [0.03-0.38 ppm in the case of the phenyl sulfides (Z)-**3a**, **b**, **g**, **h**, I (Table 1, entries 1,2,6,7,9); *ca*. 0.8 ppm in the case of the alkyl ones (Z)-**3m-o** (Table 1, entries 10-12)]. On the other hand, only a modest downfield shift was normally exhibited by a vinylic (E)- or (Z)-sulfide proton geminal to the sulfur substituent.

Thus, comparison of the ¹H NMR spectra of the two above series of sulfur compounds points to a general spectral trend consistent with the findings previously furnished by 2bromovinyl phenyl sulfides and sulfones. Therefore, such a spectral trend can be employed to establish the geometry of aryl and alkyl vinyl sulfides through their conversion into the corresponding sulfones. This tool seems useful whenever direct ¹H NMR spectral comparison between the two geometrical sulfides fails to give a definite answer or is precluded by the unavailability of either isomer.

We were consequently led to re-examine the stereochemistry of our vinylic adducts (E)/(Z)-3c-e and (Z)-3k through ¹H NMR spectral comparison with their sulfonyl derivatives (E)/(Z)-4c-e and (Z)-4k which were prepared (Scheme 2).

The vinylic signal of the presumed (Z)-sulfide (Z)-3k appeared at δ 7.15, whereas that of its sulfonyl derivative (Z)-4k was found at δ 7.22. The observed extent of the vinylic proton deshielding was, therefore, clearly consistent with our earlier assignment (Table 1, entry 8). The two geometrical isomers of 2-(phenylsulfanyl)but-2-ene 3c had signals for their vinylic proton at δ 5.94 (qq, J_{q1} 6.5, J_{q2} 1.4 Hz) and δ 5.88 (qq, J_{q1} 6, J_{q2} 1.1 Hz). The former proton, presenting a higher allylic coupling constant, was consequently assigned to (E)-3c and the latter proton to (Z)-3c. In agreement with such assignments the original sulfide proton at δ 5.94 was found to be much more deshielded (1.06 ppm) than the one at δ 5.87 (0.27 ppm) in their respective sulfonyl derivatives (E)- and (Z)-4c (Table 1, entry 3).

The vinylic protons of (E)/(Z)-3-(phenylsulfanyl)hex-3-ene 3d and 4-(phenylsulfonyl)oct-4-ene 3e appeared in their ¹H NMR spectra at δ ca. 5.95 (tt, $J_{t1} \approx 7.1-7.5$, J_{t2} 1.1 Hz) and δ 5.90 (t, J 7.3 Hz). The first cited vinylic protons, again presenting a higher allylic coupling constant, were assumed to arise from (E)-3d, e and the last cited were assigned to (Z)-3d, e. However, comparison with the ¹H NMR spectra of the respective sulfones (E)/(Z)-4d, e clearly showed that the last cited protons only were those exhibiting marked deshielding (Table 1, entries 4,5). This fact, therefore, suggests that the compounds previously assumed to be (Z)-3d, e actually were (E)-3d, e, and vice versa. On this basis our previous claim that benzenethiol additions to hex-3-yne 3d, oct-4-yne 3e (and dec-5-yne 3f) would proceed with cis-stereoselectivity must be withdrawn.

In the light of present results it is concluded that, at least under our thermal conditions, the radical addition of benzenethiol to alkynes occurs with trans-stereoselectivity with both alkyl- and phenyl-acetylenes. This seems to be especially true with phenylalkyl- and dialkyl-acetylenes bearing rather bulky alkyl groups. The present conclusion is not consistent with the view that the stereochemistry of H-abstraction by bent and linear vinyl radicals is generally governed by the ease of approach of the H-donor to the radical centre,^{3-5,7} or, in the case of the bent radicals, by the equilibrium position of the (E)and (Z)-conformers (in turn determined by steric hindrance between their vinylic substituents).^{7c,d} A new interpretation of the factors governing the reactivity of intermediate β -(phenylsulfanyl)vinyl radicals towards benzenethiol must await further chemical evidence. For this purpose, studies are in progress to explore the reactivity of these radicals under very mild thermal conditions.

Experimental

All the employed sulfides and the alkynes 1a-e, g-h, l were commercially available. *tert*-Butylphenylacetylene 1k was prepared according to the literature.⁸ ¹H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) instrument and are for solutions in CDCl₃ with Me₄Si as internal standard. GC-MS analyses were performed on a Carlo Erba QMD 1000 instrument. MS spectra were recorded by the electron impact method on a VG 7070 instrument.

Phenyl vinyl sulfides (E)- and (Z)-**3a**-e, g-h, (E)- and (Z)-**3**l and (Z)-3k¹ were prepared by treating benzenethiol with the appropriate alkyne according to Procedure A and/or B previously described.¹ Alkyl vinyl sulfides 3m,² 3n and 3o were similarly prepared as (E)/(Z) mixtures by treating 2-phenylethanethiol, 1,1-dimethylethanethiol or dodecanethiol with hex-1-yne 1a. All the reaction mixtures were directly analysed by GC-MS and then chromatographed on silica gel column. Full ¹H NMR spectral data for all the sulfides (E)- and (Z)-3ac, g, h, m and (Z)-3k have been previously reported. The following new sulfides were prepared according to Procedure A in nearly quantitative yield as unresolved (E)/(Z) mixtures: pent-1-enyl phenyl sulfide 3l [(Z)/(E) ratio 60:40]; $\delta_{E-\text{isomer}}$ 0.98 $(3 \text{ H}, t, J7), 1.4-1.6 (2 \text{ H}, \text{m}), 2.20 (2 \text{ H}, \text{dt}, J_{\text{d}} = J_{\text{t}} = 7), 6.05 (1 \text{ H}, J_{\text{c}})$ H, A part of an ABX₂ system, J_{AB} 14.5, J_{AX} 6.5), 6.19 (1 H, B part of an AB system, J 14.5), 7.2–7.5 (5 H, m); $\delta_{Z-isomer}$ 1.0 (3 H, t, J 7), 1.4–1.6 (2 H, m), 2.25 (2 H, dt, $J_d = J_t = 7$), 5.88 (1 H, A part of an ABX₂ system, J_{AB} 9.5, J_{AX} 7.0), 6.25 (1 H, B part of an AB system, J9.5 and 7.2-7.5 (5 H, m); m/z 178.081 75 (M⁺, 100; C11H14S requires 178.081 62), 148 (100), 147 (50), 116 (80); tertbutyl hex-l-enyl sulfide 3n [(Z)/(E) ratio 10:1 (2:1 when Procedure B was instead used)] $\delta_{E-\text{isomer}}$ 0.9 (3 H, t), 1.2–1.4 [4 H, m, superimposed on 1.35 (9 H, s)], 2.15 (2 H, m), 5.9 (1 H, A part of an ABX₂ system, J_{AB} 15.0, J_{AX} 7), 6.07 (1 H, B part of an AB system, J 15); $\delta_{Z-\text{isomer}}$ 0.90 (3 H, t), 1.2–1.4 [4 H, m, superimposed on 1.40 (9 H, s)], 2.15 (2 H, m), 5.67 (1 H, dt, J_d 9.6, J_t 7 Hz), 6.11 (1 H, dt, J_d 9.6, J_t 1.0); *m*/*z* 172.120 75 (M⁺ 20; C₁₀N₂₀S requires 172.120 57), 116 (50), 57 (100); dodecyl hex-1-envl sulfide **30** [(Z)/(E) ratio 1:1] δ 0.8-1 (6 H, m), 1.2-1.4 (22 H, m), 1.5–1.7 (2 H, m), 2.0–2.2 (2 H, m), 2.55–2.7 (2 H, m), 5.53 (0.5 H, dt, J_d 9, J_t 6.7 Hz), 5.62 (0.5 H, dt, J_d 15, J_t 6.7 Hz), 5.89 (0.5 H, dt, J_d 9.0, J_t 1.0) and 5.91 (0.5 H, dt, J_d 15, J_t.1); m/z 284.253 90 (M⁺, 20; C₁₈H₃₆S requires 284.253 77), 241 (20) and 115 (100).

The vinyl sulfones (E)- and (Z)-4a-e, g, h, l-o and (Z)-4k were prepared in virtually quantitative yield by treating the cor-

responding sulfide mixtures of (E)- and (Z)-**3a**-e, g, h, l-o and the sulfide (Z)-**3k** with *m*-chloroperbenzoic acid (2 mol equiv.) in chloroform at room temperature for 48 h, according to a reported procedure.^{6,9} The homogeneity of these compounds was confirmed by TLC and GLC-MS analysis.

¹H NMR spectral data for the already known sulfones **4a**-c, **g**, **h**, 1 are as follows: **4a**: ${}^{9} \delta_{E\text{-isomer}} 0.85 (3 \text{ H}, t), 1.2-1.5 (4 \text{ H}, m), 2.20 (2 \text{ H}, dt, <math>J_d = J_t = 7$), 6.25 (1 H, A part of an AB system, J 15), 6.95 (1 H, B part of an ABX₂ system J_{AB} 15, J_{AX} 7), 7.4-7.6 (3 H, m) and 7.8–7.95 (2 H, m); $\delta_{Z-isomer}$ 0.85 (3 H, t), 1.2–1.5 (4 H, m), 2.50 (2 H, m), 6.22 (1 H, A part of an ABX₂ system, J_{AB} 10, J_{AX} 6), 6.24 (1 H, B part of an AB system, J_{AB} 10), 7.4–7.6 (3 H, m) and 7.8–7.95 (2 H, m); **4b**:¹⁰ $\delta_{E-\text{isomer}}$ 1.30 (9 H, s), 6.18 (1 H, d, J 15.5), 6.96 (1 H, d, J 15.5), 7.4–7.6 (3 H, m), 7.8–7.9 (2 H, m); $\delta_{Z-isomer}$ 1.05 (9 H, s), 6.10 (2 H, AB system, J 12, inner line separation 1.5), 7.4–7.6 (3 H, m), 7.8–7.9 (2 H, m); 4c:¹¹ $\delta_{E-isomer}$ 1.85 (6 H, m), 7.0 (1 H, br q, J 7), 7.4–7.7 (3 H, m), 7.8–7.95 (2 H, m); δ_{Z-isomer} 2.0 (3 H, br s), 2.15 (3 H, br d, J7), 6.15 (1 H, qq, J_1 7, J_2 1), 7.4–7.7 (3 H, m), 7.8–7.95 (2 H, m); 4g: ¹¹ $\delta_{E-\text{isomer}}$ 6.85 $(1 \text{ H}, d, J 15.5; \text{ as singlet in the } \alpha$ -deuterio derivative), 7.66 (1 H, d, J 15.5, absent in the α -deuterio derivative), 7.3–7.6 (8 H, m) and 7.94 (2 H, br d); $\delta_{Z-isomer}$ 6.50 (1 H, d, J 12; as singlet in the α deuterio derivative), 7.06 (1 H, d, J 12; absent in the a-deuterio derivative), 7.3–7.6 (8 H, m) and 7.78 (2 H, br d); **4h**: ${}^{12} \delta_{E-\text{isomer}}$ 2.10 (3 H, br s), 7.85 (1 H, br s), 7.2-7.7 (8 H, m) and 7.9-8.1 (2 H, m); $\delta_{z-\text{isomer}}$ 2.20 (3 H, br s), 7.05 (1 H, br s), 7.2–7.7 (8 H, m) and 7.9–8.1 (2 H, m); $4l:^{13} \delta_{E-isomer} 0.9 (3 H, t, J 7), 1.3–1.6 (2 H, t, J 7)$ m), 2.20 (2 H, dd, $J_1 = J_2 = 7$), 6.32 (1 H, A part of an AB system J 14.5), 7.0 (1 H, B part of an ABX₂ system, J_{AB} 14.5, J_{AX} 7), 7.5–7.7 (3 H, m), 7.8–8.0 (2 H, m); $\delta_{Z\text{-isomer}}$ 0.90 (3 H, t, J 7), 1.3–1.6 (2 H, m), 2.55 (2 H, dd, $J_1 = J_2 = 7$), 6.23 (1 H, A part of an ABX₂ system, J_{AB} 10, J_{AX} 7), 6.32 (1 H, B part of an AB system, J 10), 7.5–7.7 (3 H, m) and 7.8–8.0 (2 H, m).

The following new sulfones 4d, e, k, m, n-o were prepared: 3-(phenylsulfonyl)hex-3ene **4d** [(E)/(Z) mixture]; $\delta_{E-isomer}$ 0.90 (3 H, t, J 7), 1.10 (3 H, t, J 7), 2.25–2.4 (4 H, m), 6.90 (1 H, t, J 7), 7.4–7.6 (3 H, m) and 7.8–7.9 (2 H, m); $\delta_{Z-isomer}$ 0.95 (3 H, t, J 7), 1.05 (3 H, t, J7), 2.2 (2 H, br q, J7), 2.65 (2 H, dq, $J_d = J_q = 7$), 6.00 (1 H, t, J 7), 7.4–7.6 (3 H, m) and 7.8–7.9 (2 H, m); m/z224.087 25 (M⁺, 10; C₁₂H₁₆O₂S requires 224.087 10), 143 (40) and 67 (100); 4-(phenylsulfonyl)oct-4-ene 4e [(E)/(Z) mixture]; δ_{E-isomer} 0.85 (3 H, t), 0.95 (3 H, t), 1.3–1.6 (4 H, m), 2.10–2.25 (4 H, m), 6.95 (1 H, t, J 7), 7.5-7.7 (3 H, m) and 7.8-8.0 (2 H, m); δ_{Z-isomer} 0.88 (3 H, s), 0.92 (3 H, s), 1.3–1.6 (4 H, m), 2.30 (2 H, br t, J7), 2.60 (2 H, dt, $J_d = J_t$ 7), 7.5–7.7 (3 H, m) and 7.8–8.0 (2 H, m); m/z 252.118 20 (M⁺, 15; C₁₄H₂₀O₂S requires 252.118 40); (Z)-2-3,3-dimethyl-1-phenyl-2-(phenylsulfonyl)but-1-ene 4k; mp 113-115 °C; δ 6.8-6.84 (2 H, m), 7.0-7.28 (8 H, m) and 7.22 (1 H, s); m/z 300.118 70 (M⁺, 10; C₁₈H₂₀O₂S requires 300.118 40), 159 (100), 143 (65) and 117 (50); 1-(2-phenethylsulfonyl)hex-1ene 4m [(E)/(Z) mixture]; $\delta_{E-isomer}$ 0.95 (3 H, t), 1.2–1.6 (4 H, m), 2.25 (2 H, dd, $J_1 = J_2 = 7$), 6.22 (1 H, dt, J_d 15, J_t 1), 6.95 (1 H, dt, J_d 15, J_t 7), 7.2–7.4 (5 H, m); $\delta_{Z\text{-isomer}}$ 0.95 (3 H, t), 1.2– 1.6 (4 H, m), 2.74 (2 H, dd, $J_1 = J_2 = 7$), 6.16 (1 H, dt, J_d 11, J_t 1) and 6.42 (1 H, dt, J_d 11, J_t 7); m/z 105 (85, PhCH₂CH₂⁺), 104 (100), 91 (25) and 77 (45); 1-(1,1-dimethylethylsulfonyl)hex-1ene 4n [(E)/(Z) mixture]; $\delta_{E-isomer}$ 0.90 (3 H, t), 1.35 [9 H, s, superimposed to 1.2–1.6 (4 H, m)], 2.30 (dd, $J_1 = J_2$ 7), 6.20 (1 H, dt, J_d 15, J_t 1) and 6.84 (1 H, dt, J_d 15, J_t 7); $\delta_{Z-\text{isomer}}$ 0.90 (3 H, t), 1.40 [9 H, s, superimposed to 1.2-1.6 (4 H, m)], 2.65 (dd, $J_1 = J_2$ 7), 6.07 (1 H, dt, J_d 11, J_t 1), and 6.43 (1 H, dt, J_d 11, J_t 7); m/z 149 (10), 57 (100) and 41 (80); 1-(dodecylsulfonyl)hex-1ene 40 [(E)/(Z) mixture]; $\delta_{E-isomer}$ 0.8–0.95 (6 H, m), 1.1–1.5 (22 H, m), 1.65–1.85 (2 H, m), 2.25 (dd, $J_1 = J_2$ 7), 2.85–3.0 (2 H, m), 6.25 (1 H, dt, J_d 15, J_t 1) and 6.88 (1 H, dt, J_d 15, J_t 7); $\delta_{Z\text{-isomer}}$ 0.8–0.95 (6 H, m), 1.1–1.5 (22 H, m), 1.65–1.85 (2 H, m), 2.65 (dd, $J_1 = J_2$ 7), 2.85–3.0 (2 H, m), 6.13 (1 H, dt, J_d 11, J_t 1) and 6.36 (1 H, dt, J_d 11, J_t 7); m/z 316.243 85 (M⁺, 20; C18H36O2S requires 316.243 60), 149 (55), 83 (60), 55 (90) and 41 (100).

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and CNR (Rome) for financial support.

References

- 1 L. Benati, P. C. Montevecchi and P. Spagnolo, J. Chem. Soc., Perkin Trans. 1, 1991, 2103.
- 2 L. Benati, L. Capella, P. C. Montevecchi and P. Spagnolo, J. Org. Chem., 1994, 59, 2818; see also, for related work, L. Benati, P. C. Montevecchi and P. Spagnolo, J. Chem. Soc., Perkin Trans. 1, 1992, 1659.
- 3 T. Kataoka, M. Yoshimatsu, T. Sato, H. Shimizu and M. Hou, J. Chem. Soc., Perkin Trans. 1, 1993, 121.
- 4 B. Kopping, C. Chatgilialoglu, M. Zehnder and B. Giese, J. Org. Chem., 1992, 57, 3994.

- 5 R. M. Kopchik and J. A. Kampmeier, J. Am. Chem. Soc., 1968, 90, 6733.
- 6 L. Benati, P. C. Montevecchi and P. Spagnolo, Tetrahedron. 1993, 49, 5365.
- 7 (a) J. K. Stille, Angew. Chem., Int. Ed. Engl., 1986, 25, 508; (b) W. P. Neumann, Synthesis, 1987, 665; (c) M. Journet, E. Magnol, W. Smadja and M. Malacria, Synlett, 1991, 58; (d) M. Journet and M. Malacria, Tetrahedron Lett., 1992, 33,1893.
- 8 A. Mortreux and M. Blanchard, Bull. Chem. Soc. Fr., 1970, 4035.
- 9 D. J. Ager, J. Chem. Soc., Perkin Trans. 1, 1986, 183.
- 10 V. Fiandanese, G. Marchese and F. Naso, Organomet. Chem., 1978, 160.
- 11 A. Bongini and D. Savoia, Org. Magn. Reson., 1977, 175. 12 K. Ankner, B. Lamm and J. Simonet, Acta Chem. Scand., Sect. B, 1977, 31, 742.
- 13 L. I. Zakharkin, Zhur. Obshchei Khim., 1960, 30, 3960 (Chem. Abstr., 1961, 55, 22204i).

Paper 4/06772J Received 7th November 1994 Accepted 19th December 1994