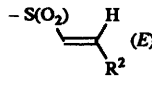
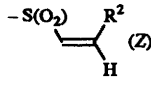
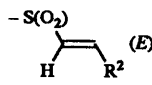
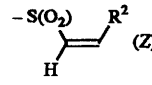


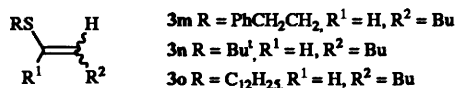
Table 1 ^1H NMR chemical shift (δ)^a of the vinylic protons of (*E*)/(*Z*)-**3a-e**, **g**, **h**, **k**, **l-o** and (*E*)/(*Z*)-**4**

Entry	Sulfide/ Sulfone	 (<i>E</i>)			 (<i>Z</i>)			 (<i>E</i>)			 (<i>Z</i>)		
		$\delta(3)$	$\delta(4)$	$\Delta\delta^b$	$\delta(3)$	$\delta(4)$	$\Delta\delta^b$	$\delta(3)$	$\delta(4)$	$\Delta\delta^b$	$\delta(3)$	$\delta(4)$	$\Delta\delta^b$
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	3l/4l	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	3o/4o	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 CDCl_3 with Me_4Si as internal standard. ^b $\Delta\delta = \delta(4) - \delta(3)$. ^c Values assigned by means of α -deuteration of (*E*)- and (*Z*)-(phenylsulfanyl)styrene **3a** achieved by treating PhSD with phenylacetylene **1g**.

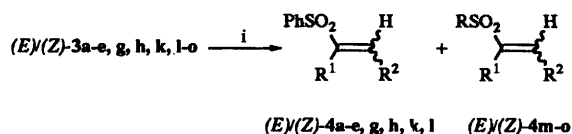
Results and discussion

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-o**.



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



Scheme 2 Reagents: *i*, *m*-chloroperbenzoic acid, CHCl_3 , 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**, **l** (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 2-bromovinyl 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-(phenylsulfanyl)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**, **1** 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**,¹ (*E*)- and (*Z*)-**3l** and (*Z*)-**3k**¹ 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*)-**3a-c**, **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 H, t, *J* 7), 1.4–1.6 (2 H, m), 2.20 (2 H, dt, $J_d = J_t = 7$), 6.05 (1 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); $\delta_{Z\text{-isomer}}$ 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, *J* 9.5 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); *tert-butyl hex-1-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-enyl sulfide* **3o** [(*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, l** are as follows: **4a**:⁹ $\delta_{E\text{-isomer}}$ 0.85 (3 H, t), 1.2–1.5 (4 H, m), 2.20 (2 H, dt, $J_d = J_t = 7$), 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); $\delta_{Z\text{-isomer}}$ 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); $\delta_{Z\text{-isomer}}$ 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 $\delta_{E\text{-isomer}}$ 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); $\delta_{Z\text{-isomer}}$ 2.0 (3 H, br s), 2.15 (3 H, br d, *J* 7), 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 H, d, *J* 15.5; as singlet in the α -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); $\delta_{Z\text{-isomer}}$ 6.50 (1 H, d, *J* 12; as singlet in the α -deuterio derivative), 7.06 (1 H, d, *J* 12; absent in the α -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 $\delta_{E\text{-isomer}}$ 0.9 (3 H, t, *J* 7), 1.3–1.6 (2 H, 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-3-ene **4d** [(*E*)/(*Z*) mixture]; $\delta_{E\text{-isomer}}$ 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); $\delta_{Z\text{-isomer}}$ 0.95 (3 H, t, *J* 7), 1.05 (3 H, t, *J* 7), 2.2 (2 H, br q, *J* 7), 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/z* 224.087 25 (M⁺, 10; C₁₂H₁₆O₂S requires 224.087 10), 143 (40) and 67 (100); 4-(phenylsulfonyl)oct-4-ene **4e** [(*E*)/(*Z*) mixture]; $\delta_{E\text{-isomer}}$ 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); $\delta_{Z\text{-isomer}}$ 0.88 (3 H, s), 0.92 (3 H, s), 1.3–1.6 (4 H, m), 2.30 (2 H, br t, *J* 7), 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-1-ene **4m** [(*E*)/(*Z*) mixture]; $\delta_{E\text{-isomer}}$ 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-1-ene **4n** [(*E*)/(*Z*) mixture]; $\delta_{E\text{-isomer}}$ 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-1-ene **4o** [(*E*)/(*Z*) mixture]; $\delta_{E\text{-isomer}}$ 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).

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References

- 1 L. Benati, P. C. Montecchi and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2103.
- 2 L. Benati, L. Capella, P. C. Montecchi and P. Spagnolo, *J. Org. Chem.*, 1994, **59**, 2818; see also, for related work, L. Benati, P. C. Montecchi 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. Chatgililoglu, 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. Montecchi 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).

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