Free-Radical Reactions of Benzenethiol and Diphenyl Disulphide with Alkynes. Chemical Reactivity of Intermediate 2-(Phenylthio)vinyl Radicals

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Reaction of benzenethiol at 100 °C with neat alkyl- and dialkyl-acetylenes leads to virtually quantitative formation of isomeric mixtures of (*E*)- and (*Z*)-vinyl sulphide adducts in ratios which depend largely upon both the extent and the nature of alkyl substitution. Results are explained in terms of rapidly interconverting sp^2-hybridized (*E*)- and (*Z*)-1-alkyl-2-(phenylthio)vinyl radical intermediates which can undergo hydrogen transfer from benzenethiol to an extent which is essentially dependent upon the steric hindrance of their *cis*-2-substituent. Consistent results are provided by related radical reactions of diphenyl disulphide with alkyl-substituted alkynes to afford varying amounts of 1,2-bis(phenylthio)ethylene adducts ascribable to S_H2 reaction of the resulting 1-alkyl-2-(phenylthio)vinyl radicals with the disulphide present. Under analogous conditions benzenethiol and diphenyl disulphide react with phenylacetylenes to give vinyl sulphide or bis-sulphide adducts in a *trans*-stereoselective fashion. The findings are interpreted by suggesting, for the intermediate sp-hybridized 1-phenyl-2-(phenylthio)vinyl radicals, the occurrence of significant bonding interaction between the unpaired electron and the adjacent sulphur, which would essentially prevent attack of radical scavenger on the side *cis* to PhS. Evidence is also presented that 1-phenyl-2-(phenylthio)vinyl radicals can exhibit homolytic intramolecular cyclization reactions, leading to benzothiophene products to a comparatively much greater extent than the 1-alkyl-2-substituted analogues; however, 1-*tert*-butyl-2-(phenylthio)vinyl radical would represent a special case.

In spite of the many reports available in the literature concerning the reversible addition of thiyl radicals to carbon–carbon triple bonds,[1,2] the structure and the reactivity of the intermediate 2-mercapto-substituted vinyl radicals still remains rather unclear. In principle, the structure (and then the reactivity) of β-thiovinyl radicals should be expected to be strongly affected by the nature of the α-substituent. Previous chemical and spectral evidence seems, in fact, to suggest that the α-alkyl vinylic radicals should be the sp^2-hybridized σ-radicals, whereas the α-phenyl vinylic ones should be the linear sp-hybridized π-radicals.[1,3,4] However, the actual role of possible structural effects on the reactivity of β-thiovinyl radicals still remains largely unknown particularly since the available chemical data are essentially confined to reactions of those β-thiovinyl radicals which result from addition of thiyl radicals to the terminal carbon of monosubstituted acetylenes. In fact, aromatic and aliphatic thiols have been shown to add smoothly to monosubstituted aryl- and alkyl-acetylenes to give anti-Markovnikov olefinic adducts by a radical chain mechanism involving β-thiovinyl radicals intermediates.[5] Stereochemical studies showed that additions of benzenethiols to phenylacetylenes and of thioacetic *S*-acid to hex-1-yne lead preferentially to the formation of *cis*-adducts.[5c–e] The preferential *trans*-addition was explained in terms of equilibrated *cis–trans* mixtures of bent thiovinyl radicals as well as in terms of preferential hydrogen abstraction by the *cis*-radicals due to favourable approach of the thiol H-donor from the unhindered side. The intermediacy of β-(alkylthio)vinyl radicals has been shown to occur also in the light-induced radical chain addition of dialkyl disulphides to propyne and hept-1-yne to afford high yields of the corresponding 1,2-bis(alkylthio)ethenes.[6] Moreover, very recently, thermal reactions of benzenethiol or diphenyl disulphide with acetylene, phenylacetylene, and prop-2-yn-1-ol at 500–590 °C have been reported to lead to the formation of benzothiophenes.[7] Under these drastic thermal conditions, 2-(phenylthio)vinyl radicals preferentially underwent intramolecular homolytic substitution reaction on the aromatic ring of the adjacent phenylthio substituent. On these bases we undertook a study of the thermal free-radical reactions at 100 and 180 °C of benzenethiol and diphenyl disulphide with various alkynes, including a number of mono- and di-substituted alkyl- and phenyl-acetylenes. Our aim was to investigate the chemical reactivity of variously substituted 2-(phenylthio)vinyl radicals under varying experimental conditions, in order to shed further light on the chemistry of thiovinyl radicals. In this paper we report the results of our study.

Results

When a solution of benzenethiol (0.1 mol dm^{-3}) in the appropriate neat alkyne **1a–k** was kept at 100 °C, virtually complete reaction generally occurred within *ca.* 15 min as monitored by TLC. Column chromatography of the resulting reaction mixtures led to the isolation of varying mixtures of the vinyl sulphides (*Z*)- and (*E*)-**3a–k**. With the alkynes examined the geometrical adducts (*Z*)- and (*E*)-**3** were generally produced in nearly quantitative overall yields, but with *tert*-butyl(phenyl)-acetylene **1e** a *ca.* 90:10 mixture of the sulphide (*Z*)-**3e** and the benzothiophene **5e** was obtained. With the unsymmetrical alkynes **1a–g** exclusive formation of the anti-Markovnikov adducts **3a–g** was observed. This supports the general involvement of a free-radical mechanism in these thiol–alkyne additions. Both product yields and product compositions were found to remain essentially unchanged when the above reactions were carried out in the presence of azoisobutyronitrile (AIBN) (0.05 mol dm^{-3}), this indicating that, under the conditions employed, benzenethiol can smoothly add to the alkynes **1a–k** by a radical-chain mechanism both in the presence and in the absence of a radical initiator.

As can be seen in Table 1 (entries 1–11, A) the isomer ratios of

Table 1 Isomer ratios[a] of (*Z*)- and (*E*)-phenyl vinyl sulphides **3** obtained from free-radical addition of benzenethiol to alkynes **1** at 100 °C[b]

Entry	Alkyne	Vinyl sulphide	(*Z*):(*E*) Isomer ratio A[c]	B[d]
1	Phenylacetylene **1a**	**3a**	90:10	10:90
2	1-Phenylpropyne **1b**	**3b**	90:10	10:90
3	1-Phenylbut-1-yne **1c**	**3c**	90:10	50:50
4	1-Phenylpent-1-yne **1d**	**3d**	90:10	60:40
5	*tert*-Butyl(phenyl) acetylene **1e**	**3e**	100:0	100:0
6	Hex-1-yne **1f**	**3f**	75:25	50:50
7	*tert*-Butylacetylene **1g**	**3g**	60:40	0:100
8	But-2-yne **1h**	**3h**	56:44 (60:40)[f]	53:47[e]
9	Hex-3-yne **1i**	**3i**	30:70 (15:85)[f]	33:67[e]
10	Oct-4-yne **1j**	**3j**	25:75 (0:100)[f]	33:67[e]
11	Dec-5-yne **1k**	**3k**	25:75 (0:100)[f]	30:70[e]

[a] Isomer ratios determined by ^{1}H NMR spectral analysis, unless otherwise stated. [b] Reactions were run in the appropriate neat alkyne **1** by using a 0.1 mol dm^{-3} concentration of benzenethiol (procedure A) or in benzene solution in the presence of one mol equiv. of alkyne **1** (0.1 mol dm^{-3}) and AIBN (0.05 mol dm^{-3}) (procedure B). [c] Isomer ratio referring to reaction carried out according to procedure A. [d] Isomer ratio referring to reaction carried out according to procedure B. [e] Isomer ratio determined by GLC analysis. [f] Isomer ratio referring to reaction carried out with 0.05 mol dm^{-3} concentration of benzenethiol.

the resulting (*Z*)- and (*E*)-vinyl sulphide adducts **3a–k** were found to depend largely upon the nature of the alkyne **1a–k** employed. The observed values of (*Z*):(*E*) isomer ratios could be confidently taken as being indicative of the stereochemical trend of these radical benzenethiol–alkyne additions provided that they were not largely due to thermodynamic vinyl sulphide products which might have resulted from isomerization of the kinetic products under the reaction conditions. In order to ascertain this point we carried out a comparative study of the addition of benzenethiol (0.1 mol dm^{-3}) to equimolar amounts of the alkynes **1a–k** in benzene solution at 100 °C. The employment of such a strongly reduced alkyne concentration was expected to have greatly favoured addition of benzenethiyl radical to the kinetically formed vinyl sulphide product, thereby favouring its possible isomerization. Isomerization of alkenes (including vinyl sulphides) is known to be effectively promoted by reversible additon of thiyl radicals to C=C double bonds.[5d,e,6]

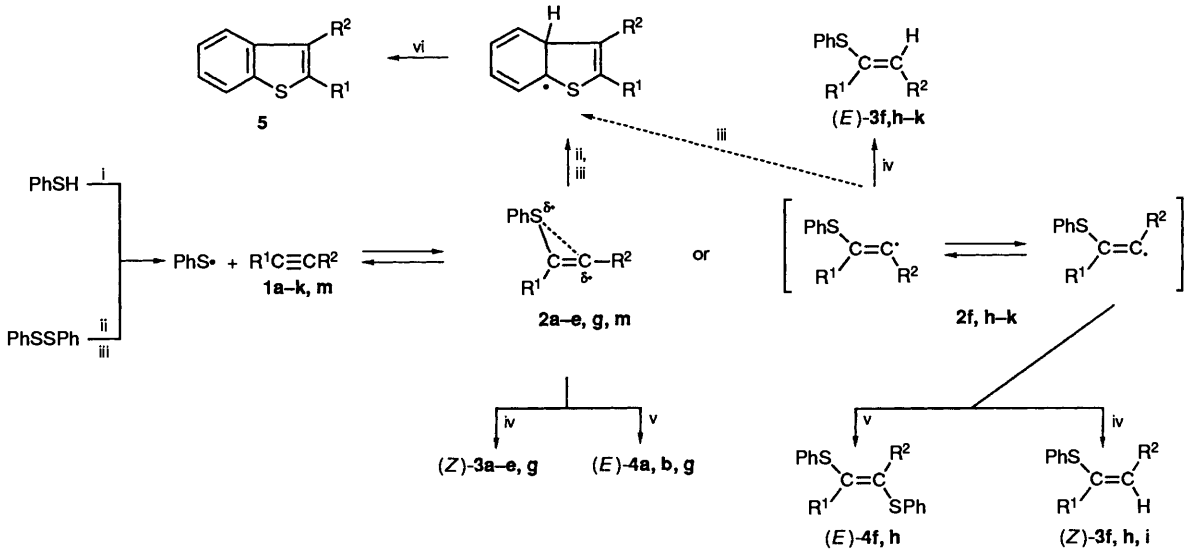
Reaction of benzenethiol with one molar equiv. of the alkynes **1a–d,f–k** in benzene at 100 °C (*ca.* 45 min) generally led to mixtures of the corresponding adducts (*Z*)- and/or (*E*)-**3a–d,f–k** in 70–80% yield. Small amounts of diphenyl disulphide were generally produced under these circumstances. With the alkynes **1a–d,f,g** the resulting (*Z*) and (*E*) adducts **3a–d,f,g** were produced in ratios quite different from those observed from the corresponding reactions carried out in the neat alkynes **1a–d,f,g** (Table 1, entries 1–4, 6 and 7, A and B). Independent experiments showed that, upon being heated in benzene at 100 °C in the presence of benzenethiol, the isomeric product mixtures obtained from reaction of benzenethiol with the neat alkynes **1a,b,f,g** led to isomeric compositions strictly comparable with those of the corresponding reactions carried out in benzene solution. Analogous results were provided by the pure (*Z*)-isomers (*Z*)-**3a,b,g** upon treatment with benzenethiol under the same conditions. In the light of these observations it may be reliably concluded that in the neat alkynes **1a–d,f,g** benzenethiol actually led to (*Z*)- and (*E*)-vinyl sulphide adducts **3a–d,f,g** in ratios largely due to kinetic control. Consequently, in the light of our data reported in Table 1 (entries 1–4, 6 and 7, A), it may be concluded that *trans*-addition is clearly preferred with the alkynes **1a–d,f,g**, although the exact stereochemical course of these addition reactions remains uncertain due to possibly significant (*Z*) ⟶ (*E*) isomerization of the preferred (*Z*)-adducts (*Z*)-**3a–d,f,g** under our 'kinetic reaction conditions.'

With the alkynes **1h–k** benzenethiol in benzene led to isomeric mixtures of (*Z*)- and (*E*)-adducts **3h–k** similar to those obtained from the corresponding reactions performed in the neat alkynes **1h–k**, hence allowing no definite conclusion about the possible stereochemistry of such addition reactions (Table 1, entries 8–11, A and B) to be drawn. However, when the same reactions in neat alkynes **1h–k** were repeated with a 0.05 mol dm^{-3} (instead of 0.1 mol dm^{-3}) concentration of the thiol, a definite enhancement of the amount of the adducts (*E*)-**3i–k** and (*Z*)-**3h** was found to occur respectively with the alkynes **1i–k** and **1h**. On this basis and in the light of the data reported in Table 1 (entries 8–11, A) it may be concluded that *trans*-addition should preferentially occur with the alkyne **1h**, whereas *cis*-addition should essentially (or exclusively) occur with the alkynes **1i–k**.

Reaction of benzenethiol with one mol equiv. of *tert*-butyl(phenyl)acetylene **1e** gave a 40:60 mixture of the sulphide (*Z*)-**3e** and the benzothiophene **5e** in low yield (15%) as well as major amounts of diphenyl disulphide. Since this reaction exclusively gave the same geometrical vinyl sulphide as that obtained from the corresponding reaction performed in the neat alkyne **1e**, we conclude that the sulphide (*Z*)-**3e** was probably both the kinetic and the thermodynamic product. Incidentally, we wish also to report that we attempted to obtain reaction between benzenethiol and di-*tert*-butylacetylene **1l** in benzene at 100 °C. However, our attempt was unsuccessful since benzenethiol in the presence of one mol equiv. of the alkyne **1l** and AIBN, afforded diphenyl disulphide as the exclusive detectable product.

The stereochemistry (and regiochemistry) of the geometrical isomers of the vinyl sulphides **3a–d,f–k** was determined by ^{1}H NMR spectroscopic analysis. In particular, the geometrical isomers of β-(phenylthio)styrene **3a** were identified by comparison of their ^{1}H NMR spectra with those reported in the literature.[5d] The stereochemistry of the (*E*)- and (*Z*)-isomers of 1-(phenylthio)hex-1-ene **3f** and of 3,3-dimethyl-1-(phenylthio)but-1-ene **3g** could be readily established on the basis of the observed values of the coupling constant for the two vinylic protons, whereas the *E* or *Z* configuration of the vinyl sulphides **1h–k** was assigned on the basis of the observed values of the coupling constant for the vinylic proton and the vicinal vinylic methylene protons, in addition to the observation that a downfield shift of the vinylic protons occurs on passing from the (*Z*)- to the (*E*)-isomers in the adducts **3f–k** (see Experimental section). The stereochemistry of the (*E*)- and (*Z*)-sulphides **3b–d** was established by comparative nuclear Overhauser enhancement (NOE) measurements. Irradiation of the vinylic methylene protons of (*Z*)-**3c,d** caused a *ca.* 4% increase in the intensity of the signal of the corresponding vinylic proton, while the intensity of the vinylic proton in the (*E*)-adducts (*E*)-**3c,d** showed a smaller enhancement (*ca.* 0.7%). Moreover, upon irradiation of the sole vinylic signal of an unresolved mixture of (*Z*)- and (*E*)-**3b**, the intensity of the vinylic methyl protons of the (*Z*)-isomer showed a *ca.* 2% increase, while the intensity of the corresponding methyl protons of the (*E*)-isomer showed a *ca.* 0.2% decrease.

As for the vinyl sulphide (*Z*)-**3e**, the regiochemistry was clearly established on the basis of the fact that this compound, upon hydrolysis in 96% H_2SO_4–dichloromethane, gave 1-phenyl-3,3-dimethylbutan-2-one, whereas the (*Z*)-configuration was assigned on the basis of the reasonable assumption that the thermodynamically favoured isomer should be the one bearing



a; R^1 = H, R^2 = Ph **b**; R^1 = Me, R^2 = Ph **c**; R^1 = Et, R^2 = Ph **d**; R^1 = Pr, R^2 = Ph **e**; R^1 = Bu^t, R^2 = Ph **f**; R^1 = H, R^2 = Bu **g**; R^1 = H, R^2 = Bu^t **h**; R^1 = R^2 = Me **i**; R^1 = R^2 = Et **j**; R^1 = R^2 = Pr **k**; R^1 = R^2 = Bu **l**; R^1 = R^2 = Bu^t **m**; R^1 = R^2 = Ph

Scheme 1 *Reagents and conditions*: i, (AIBN-), benzene or neat alkyne **1a–k**, 100 °C; ii, $PhNH_2$ and n-$C_5H_{11}ONO$, benzene, 100 °C; iii, bromobenzene, 180 °C; iv, PhSH, −PhS•; v, PhSSPh, −PhS•; vi, −H•

Table 2 Product yields[a] (%) for free-radical reactions of diphenyl disulphide with alkynes **1**[b]

		Bis-sulphide		Benzothiophene	
Entry	Alkyne	A[c]	B[d]	A[c]	B[d]
1	Phenylacetylene **1a**	55, **4a**[e]	10, **4a**[f]	20, **5a**	9, **5a**
2	1-Phenylpropyne **1b**	6, **4b**[g]		35, **5b**	14, **5b**
3	Hex-1-yne **1f**	57, **4f**[h]	8, **4f**[e]		6, **5f**
4	*tert*-Butylacetylene **1g**	6, **4g**[g]	4, **4g**[g]	42, **5g**	28, **5g**
5	But-2-yne **1h**	9, **4h**[g]	2, **4h**[g]		3, **5h**
6	Hex-3-yne **1i**				1, **5i**
7	Di-*tert*-butylacetylene **1l**				
8	Diphenylacetylene **1m**			40, **5m**	43, **5m**

[a] Yields were determined by GLC and calculated as described in the Experimental section. [b] Reactions were carried out in benzene at 100 °C in the presence of the appropriate alkyne **1** (2 mol equiv.) and in the presence of aniline (1.5 mol equiv.) and n-pentyl nitrite (1.6 mol equiv.) (procedure A) or in bromobenzene at 180 °C in the presence of the appropriate alkyne **1** (10 mol equiv.) (procedure B). [c] Procedure A. [d] Procedure B. [e] Mixture of (*E*)- and (*Z*)-isomer in 70:30 ratio. [f] Mixture of (*E*)- and (*Z*)-isomer in 80:20 ratio. [g] Mixture of (*E*)- and (*Z*)-isomer in ratio not determined. [h] Mixture of (*E*)- and (*Z*)-isomer in ratio 90:10.

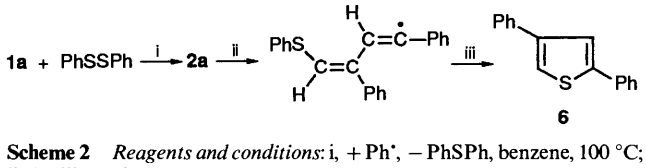
the highly bulky *tert*-butyl group *cis* to the hydrogen. Unambiguous establishment of the configuration of the presumed sulphide (*Z*)-**3e** was prevented by our failure to achieve any thermal isomerization to the geometrical isomer which was needed for ^{1}H NMR spectral comparison.

In the light of the overall above results we may conclude that benzenethiol *trans*-addition [giving (*Z*)-adducts] is mostly (or exclusively) preferred with phenyl-substituted acetylenes, but with alkyl-substituted acetylenes the stereochemistry of the thiol addition would strongly depend upon both the extent and the nature of alkyl substitution. In fact, the terminal alkynes **1f** and **1g**, as well as the disubstituted alkyne **1h**, underwent preferential *trans*-addition, while the other disubstituted alkynes **1i–k** showed a definite tendency to undergo *cis*-addition [giving (*E*)-adducts].

The radical reaction of diphenyl disulphide with a number of alkynes including the mono- and di-substituted acetylenes **1a,b,f–i,l,m** was investigated under two different experimental conditions, *i.e.* in benzene at 100 °C in the presence of a two-fold excess of alkyne (procedure A) and in bromobenzene at 180 °C in the presence of a ten-fold excess of alkyne (procedure B). Homolytic fission of diphenyl disulphide in benzene at 100 °C was promoted by S_H2 reaction with phenyl radicals which were produced in the reaction medium by aprotic diazotization of aniline with n-pentyl nitrite.

As can be seen in Table 2 (entries 1–5, A), in benzene at 100 °C the terminal alkynes **1a,f** and, to a minor extent, *tert*-butylacetylene **1g**, 1-phenylpropyne **1b**, and but-2-yne **1h**, were found to undergo radical addition by diphenyl disulphide to give isomeric mixtures of the corresponding (*E*)- and (*Z*)-bis-sulphide adducts **4a,b,f–h**. The ratios of the observed (*E*)-bis-sulphides (*E*)-**4a,f** to the corresponding (*Z*)-isomers were found to be *ca.* 70:30 and 90:10, respectively (Table 2, entries 1 and 3, A). These values point to a high *trans*-stereoselectivity of the addition of diphenyl disulphide to the alkyne **1a** and **1f**, although the exact stereochemical course remains unknown in view of the fact that some isomerization of the preferred (*E*)-isomers (*E*)-**4a,f** to the thermodynamically more stable (*Z*)-isomers[8] might have occurred under the reaction conditions. The isomer ratios of the (*E*)- and (*Z*)-bis-sulphides **4b,g,h** were instead not determined since the stereochemistry of these adducts was not established.

Besides the bis-sulphides adducts **4a,b,g**, phenylacetylene **1a**, phenylpropyne **1b**, and *tert*-butylacetylene **1g** led also to the benzothiophene products **5a** and **5b,g**, which were found to occur to a minor and major extent, respectively (Table 2, entries 1, 2 and 4, A). With phenylacetylene **1a** small amounts of 2,4-diphenylthiophene **6** were also formed. This compound was probably formed from an intermediate 1-phenyl-2-(phenylthio)-vinyl radical **2a** according to the mechanism outlined in Scheme 2.



Scheme 2 *Reagents and conditions*: i, +Ph•, −PhSPh, benzene, 100 °C; ii, **1a**; iii, −Ph•

Similarly to the alkynes **1a,b,g**, diphenylacetylene **1m** was found to afford the corresponding benzothiophene **5m**, but in this case this compound was shown to occur as the exclusive product (Table 2, entry 8, A). On the other hand, no bis-sulphide or benzothiophene product was found to result from the dialkyl-substituted acetylenes **1i,l** under analogous reaction conditions (Table 2, entries 6 and 7, A). As shown by the data reported in Table 2 (entries 1–8, B) the pyrolysis of diphenyl disulphide at 180 °C in bromobenzene in the presence of alkyne **1a,b,f–i,l,m** led to the formation of bis-sulphide **4** and/or benzothiophene **5** product in a fashion somewhat comparable to that revealed by the corresponding reactions in benzene at 100 °C. However, under these conditions the alkyl-substituted acetylenes **1f,h,i** could give rise to some benzothiophene product **5f,h,i**. On the other hand, no product could be observed with di-*tert*-butylacetylene **1l** even under such drastic conditions.

Discussion

The bulk of the evidence provided by our present free-radical reactions of diphenyl disulphide and benzenethiol with the alkyl- and dialkyl-acetylenes **1f,h–k** indicates that formation of the intermediate 1-alkyl-2-(phenylthio)vinyl radicals **2f,h–k** can be conceivably explained in terms of the rapidly interconverting sp^2-hybridized σ-radicals, in line with results obtained to date which generally suggest a similar route for the vinylic radicals α-substituted by an alkyl group.[1,3,4] The reactivity of the interconverting (*E*)- and (*Z*)-thiovinyl radicals **2f,h–k** would be largely determined by steric hindrance between their *cis*-2-substituent (*i.e.*, PhS or R^1) and the radical scavenger rather than by their equilibrium position. In fact, with the thiovinyl radicals **2f,h** carrying an R^1 substituent (H and Me, respectively) smaller than PhS the (*Z*)-conformer was preferentially trapped by the benzenethiol H-donor, while preferential or exclusive trapping of the (*E*)-conformer was found to occur with the thiovinylic radicals **2i–k** bearing an R^1 substituent (*i.e.*, Et, Pr or Bu, respectively) rather bulkier than PhS (Scheme 1 and Table 1, entries 6, 8–11, A). With diphenyl disulphide both at 100 and at 180 °C the vinyl radicals **2f,h** could undergo S_H2 reaction leading to the bis-sulphides **4f,h** although to a very different extent, but no evidence for bis-sulphide formation could be provided from the radical **2i**. This evidence suggests that the bis-sulphides **4f,h** would arise from exclusive reaction of bulky diphenyl disulphide with the (*Z*)-radicals **2f,h**, which bear a *cis*-2-substituent as small as hydrogen or methyl. Such a reaction would be evidently prevented for the (*Z*)-radical **2i** substituted by the bulkier ethyl group (Scheme 1 and Table 2, entries 3, 5 and 6, A and B). The *trans*-stereochemistry revealed by the addition of diphenyl disulphide to hex-1-yne **1f** lends support to the above suggestion.

As for the evidence provided by the free-radical additions of benzenethiol to the phenylacetylenes **1a–e**, it strongly suggests that the resulting 1-phenyl-2-(phenylthio)vinyl radicals **2a–e** are not readily explicable in terms of only the linear sp-hybridized π-radicals, which a number of studies have suggested for the α-phenyl vinylic radicals.[1,4] If the radicals **2a–e** were simply linear π-radicals, a progressive increase in the size of the R^1 substituent should have progressively favoured the approach of the benzenethiol H-donor from the side *cis* to PhS. Instead, the thiovinyl radicals **2a–d**, irrespective of the size of the R^1 substituent, showed a definite preference for undergoing hydrogen transfer from benzenethiol on the side opposite to PhS (Scheme 1 and Table 1, entries 1–4, A). We explain this finding by assuming that significant bonding interaction occurs between the unpaired electron and the adjacent phenylthio sulphur. Such bonding interaction would make approach of the radical scavenger from the side *cis* to PhS essentially inpossible. It is possible that significant bonding between the sulphur substituent and the unpaired electron would occur in the α-phenyl but not in the α-alkyl vinylic radical as a result of a more favourable orientation of the p than the sp^2 orbital where the unpaired electron is respectively located in each radical.

The above suggestion is strongly supported by the fact that, in neat *tert*-butylphenylacetylene **1e**, benzenethiol led only to the (*Z*)-vinyl sulphide (*Z*)-**3e**. The vinyl radical intermediate **2e** was probably forced to undergo hydrogen transfer from benzenethiol on the side opposite to PhS despite the high steric hindrance of the *cis tert*-butyl substituent. This presumably caused some competing occurrence of the homolytic intramolecular cyclization reaction leading to the benzothiophene **5e** (Scheme 1 and Table 1, entry 5, A). Consistently, benzenethiol was shown to react in benzene with one mol equiv. of the alkyne **1e** to give a very poor yield of the adduct (*Z*)-**3e**. Under these circumstances, diphenyl disulphide was preferentially formed, presumably as the result of a marked tendency of the sterically hindered radical **2e** to eliminate phenylthio radical rather than to undergo hydrogen abstraction with benzenethiol.

Further support for this proposal was provided by our reactions of diphenyl disulphide with phenylacetylene **1a**, 1-phenylpropyne **1b**, and diphenylacetylene **1m** at 100 and 180 °C. In such cases the 1-phenylvinyl radical intermediates **2a**, **2b** and **2m** underwent intramolecular cyclization to give the benzothiophenes **5a**, **5b** and **5m**, and an S_H2 reaction with diphenyl disulphide to an extent strongly increasing with increasing size of the R^1 substituent (H, Me and Ph, respectively) (Scheme 1 and Table 2, entries 1, 2 and 8, A and B).

Diphenyl disulphide would be capable of approaching the radicals **2a,b,m** only from the side opposite to PhS, which would be supported by the observed stereochemical course of the addition of diphenyl disulphide to phenylacetylene **1a**. Consequently, radical trapping by bulky diphenyl disulphide would be strongly discouraged by increasing steric hindrance of the R^1 substituent in favour of homolytic intramolecular cyclization.

The observed tendency of the 1-phenylvinyl radicals **2a,b,m** to furnish a benzothiophene product **5** is noteworthy. In the presence of diphenyl disulphide the 1-alkyl-substituted radical analogues **2f,h,i** could afford the corresponding benzothiophenes **5f,h,i**, to some extent, only at 180 °C (Table 2, entries 3, 5 and 6, B). Conceivably, the much greater tendency of the radicals **2a,b,m** to undergo cyclization than the analogues **2f,h,i** may be ascribed to their different structural features.

Interestingly, a rather peculiar behaviour was exhibited by the 1-*tert*-butyl-substituted vinyl radical **2g**. This radical, while being found to react with benzenethiol in a manner apparently consistent with that of 1-alkyl-substituted 2-(phenylthio)vinyl radicals (Table 1, entry 7, A), was shown to react in the presence of diphenyl disulphide, both at 100 and 180 °C, to give preferential formation of the benzothiophene **5g** at the expense of bis-sulphide **4g** (Table 2, entry 4, A and B). In this respect the chemical behaviour of the radical **2g** was found to resemble that of the 1-phenylvinylic radicals **1a,b,m** which, under the same conditions, could similarly afford the benzothiophenes **5a,b,m** to a remarkable extent. This fact might suggest that the 1-*tert*-butylvinyl radical **2g** should show a significant amount of sp-hybridized radical character, similar to that of the 1-phenyl-substituted analogues, but the actual reasons for this are unclear. However, radical **2g** was found to exhibit a markedly lower tendency to react with diphenyl disulphide than both the 1-phenyl-substituted **2a** and the 1-butyl-substituted vinyl radical **2f**, although it bears the same C-2 substituent (H) (Table 2, entries 1, 3 and 4, A and B). It is possible that this was the consequence of high steric hindrance caused by the bulky 1-*tert*-butyl substituent.

Finally, our unsuccessful attempted reactions of benzenethiol

and diphenyl disulphide with di-*tert*-butylacetylene **1l** deserve brief comment. Since no evidence for any product ascribable to a thiovinyl radical **2l** intermediate could be obtained, a possible explanation might be that the high steric hindrance of the two *tert*-butyl substituents would totally prevent thiyl attack on the triple bond of the alkyne **1l**. However, particularly in the light of our present findings obtained with 1-*tert*-butyl-2-(phenylthio)vinyl radical **2g**, an alternative explanation might be that elimination of benzenethiyl radical was the exclusive reaction allowed to the possibly formed vinyl radical **2l**. If we assume a somewhat linear radical for **2l** (as suggested above for the radical **2g**) the approach of benzenethiol or diphenyl disulphide scavenger to either side of the radical centre should be expected to be seriously discouraged by steric hindrance of both the α-*tert*-butyl and the β-phenylthio and β-*tert*-butyl substituents. Moreover, possible homolytic intramolecular cyclization might be expected to be not readily feasible for the radical **2l** owing to serious steric constraints caused by the two adjacent *tert*-butyl groups in the transition state, which would lead to a cyclohexadienyl radical intermediate.

In conclusion we have shown that the two rapidly interconverting sp^2-hybridized vinyl radical conformers, which would result from reversible addition of benzenethiyl radical to alkyl- and dialkyl-acetylenes, can undergo hydrogen transfer from benzenethiol and S_H2 reaction with diphenyl disulphide to an extent strongly dependent upon both the size of either of the radical scavengers and that of the substituent *cis* to either of the radical centres. Therefore steric hindrance between thiol or disulphide scavenger and radical *cis*-2-substituent would be primarily responsible for the stereochemistry and yield of the resulting ethylene adducts. On the other hand, the sp-hybridized 1-phenylvinylic radicals which would result from addition of phenylthio radical to phenyl- and phenylalkylacetylenes appear to be generally scavenged by benzenethiol or diphenyl disulphide on the side opposite to the phenylthio substituent, as a possible result of some bonding occurring between the unpaired electron and the adjacent sulphur substituent. Moreover, we have shown that sp-hybridized 2-(phenylthio)vinyl radicals can undergo homolytic intramolecular cyclization leading to benzothiophene products to a degree comparatively higher than that found with the sp^2-hybridized radical analogues.

Experimental

Alkynes **1a–d,f–k,m** were commercially available. *tert*-Butyl(phenyl)acetylene **1e**[9] and di-*tert*-butylacetylene **1l**[10] were prepared according to literature methods. Reaction products such as the (*E*)- and (*Z*)-1,2-bis(phenylthio)ethylenes **4a**[11] and **4f**,[5b] the benzothiophenes **5a**,[12] **5b**,[12], **5f**,[13] **5g**[14] and **5m**,[15] and 2,4-diphenylthiophene **6**[16] were identified by spectral comparison with authentic specimens. The 1,2-bis(phenylthio) adducts **4b,g,h**[11] and the benzothiophenes **5h**[17] and **5i**[18] were identified by GLC–MS analysis of the reaction mixtures. The previously unknown 2-*tert*-butyl-3-phenylbenzo[*b*]thiophene **5e** was obtained as a solid, m.p. 68–69 °C; δ_H(60 MHz) 1.33 (9 H, s) and 7.2–8.0 (9 H, m); *m/z* 266 (M^+), 251, 236, 221, 142 and 117. The β-styryl phenyl sulphides (*E*)- and (*Z*)-**3a**[5d] were previously known and fully characterized. The sulphides **3b**,[12] **3c**,[19] **3h**[12,20] and **3k**[21] had been previously obtained as isomeric (*E*)/(*Z*)-mixtures, but no configurational assignment had been performed. The sulphides (*E*)-**3f**,[22] (*Z*)-**3f**,[23] (*E*)-**3g**[24] and (*Z*)-**3g**[25] had been previously reported, but satisfactory spectral data had not been provided. The homogeneity of the compounds (*E*)- and (*Z*)-**3b–g,i–k** was confirmed by TLC and GLC–MS analysis. The geometrical isomers of the sulphide **3h** were obtained as an unresolved mixture.

^{1}H NMR spectra were measured on a Varian Gemini 200 (200 MHz) or a Varian T 60 (60 MHz) instrument, and are for solutions in $CDCl_3$ with Me_4Si as internal standard. *J*-Values are given in Hz. Mass spectra were determined by the electron-impact method on a VG 7070 instrument. GLC analyses were performed on a Varian 3700 instrument equipped with an FID detector. GLC-MS analyses were performed on a GC-MS workstation HP 59970. Column chromatography was carried out on Merck silical gel (0.040–0.063 mm particle size) by elution with light petroleum (b.p. range 40–70 °C).

Reaction of Benezenethiol with Alkynes.—Procedure A. A solution of benzenethiol (1 mmol) in the appropriate alkyne **1a–k** (10 cm^3) was heated in a sealed tube at 100 °C for *ca.* 15 min. After this time the excess of alkyne was removed under reduced pressure, and the residue was analysed by GLC and GLC–MS and chromatographed on a silica gel column. With all alkynes examined the corresponding (*E*)- and (*Z*)-adducts **3** were isolated in virtually quantitative overall yield, but with *tert*-butyl(phenyl)acetylene **1e** a *ca.* 90:10 mixture of the adduct **3e** and the benzothiophene **5e** was obtained in quantitative overall yield. The observed values of (*E*):(*Z*) isomer ratios are reported in Table 1, column A.

Procedure B. A solution of benzenethiol (1 mmol), AIBN (0.5 mmol), and the appropriate alkyne **1a–l** (1 mmol) in benzene (10 cm^3) was heated in a sealed tube at 100 °C for *ca.* 20 min [2 h in the case of *tert*-butyl(phenyl)acetylene **1e** and di-*tert*-butylacetylene **1l**], after which time the solvent was removed under reduced pressure and the residue was analysed by GLC and GLC–MS and chromatographed on a silica gel column. In the case of the alkynes **1a–d,f–k** chromatography gave the corresponding (*E*)- and (*Z*)-adducts **3a–d,f–k** in ~70–80% overall yield, besides diphenyl disulphide (~10–15%). In the case of *tert*-butyl(phenyl)acetylene **1e** chromatography gave: i, the adduct (*Z*)-**3e** (10%); ii, the benzothiophene **5e** (15%); and iii, major amounts of diphenyl disulphide. With di-*tert*-butylacetylene **1l** chromatography gave diphenyl disulphide as the only product in undetermined yield. The observed values of (*E*):(*Z*) isomer ratios are reported in Table 1, column B.

The following vinyl sulphides **3** were obtained (as oily products, unless otherwise stated):

(*E*)-β-(Phenylthio)styrene (*E*)-**3a**; δ_H(200 MHz) 6.76 (2 H, AB system, δ_{AB} 0.14 ppm, J_{AB} 15.5) and 7.1–7.5 (10 H, m); *m/z* 212 (M^+), 179, 178, 167, 135, 134, 121, 91 and 77; (*Z*)-β-(phenylthio)styrene (*Z*)-**3a**; δ_H(200 MHz) 6.49 (2 H, AB system, δ_{AB} 0.09 ppm, J_{AB} 11.0) and 7.1–7.5 (10 H, m); (*E*)-1-phenyl-2-(phenylthio)propene (*E*)-**3b**; δ_H(200 MHz) 2.3 (3 H, d, *J* 1.2), 6.85 (1 H, br s) and 7.3–7.8 (10 H, m); irradiation of the signal at δ 6.85 caused ~ 0.6% decrease in the intensity of the signal at δ 2.3; *m/z* 226 (M^+), 211, 193, 167, 115 and 91; (*Z*)-1-phenyl-2-(phenylthio)propene (*Z*)-**3b**; δ_H(200 MHz) 2.2 (3 H, d, *J* 1.2), 6.85 (1 H, br s) and 7.3–7.8 (10 H, m); irradiation of the signal at δ 6.85 caused ~2% enhancement of the intensity of the signal at δ 2.2; (*E*)-1-phenyl-2-(phenylthio)but-1-ene (*E*)-**3c**; δ_H(200 MHz) 1.2 (3 H, t, *J* 7.5), 2.45 (2 H, q, *J* 7.5), 6.68 (1 H, s) and 7.1–7.6 (10 H, m); irradiation of the signal at δ 2.45 caused ~0.5% enhancement of the intensity of the singlet at δ 6.68; *m/z* 240 (M^+), 211, 179, 167, 129, 115 and 91; (*Z*)-1-phenyl-2-(phenylthio)but-1-ene (*Z*)-**3c**; δ_H(200 MHz) 1.1 (3 H, t, *J* 7.5), 2.3 (2 H, q, *J* 7.5), 6.81 (1 H, s) and 7.1–7.6 (10 H, m); irradiation of the signal at δ 2.3 caused a 3.5% enhancement of the intensity of the singlet at δ 6.81; (*E*)-1-phenyl-2-(phenylthio)pent-1-ene (*E*)-**3d**; δ_H(200 MHz) 0.88 (3 H, t, *J* 7), 1.5–1.8 (2 H, m), 2.40 (2 H, t, *J* 7.5), 6.65 (1 H, s) and 7.1–7.6 (10 H, m); irradiation of the signal at δ 2.40 caused a 0.7% enhancement of the intensity of the singlet at δ 6.65; *m/z* 254 (M^+), 211, 179, 167, 129, 115, 91 and 65; (*Z*)-1-phenyl-2-(phenylthio)pent-1-ene (*Z*)-**3d**; δ_H(200 MHz) 0.85 (3 H, t, *J* 7.5), 1.5–1.8 (2 H, m), 2.25 (2 H, t, *J* 7.5), 6.80 (1 H, s) and 7.1–7.6 (10 H, m); irradiation of the signal at δ 2.25

caused a 3.7% enhancement of the intensity of the singlet at δ 6.80; (*Z*)-3,3-dimethyl-1-phenyl-2-(phenylthio)but-1-ene (*Z*)-**3e**, m.p. 68–70 °C; δ_H(200 MHz) 1.30 (9 H, s) and 6.9–7.6 (11 H, m); *m/z* 268 (M^+), 211, 176, 159, 117, 101 and 57; (*E*)-1-(phenylthio)hex-1-ene (*E*)-**3f**; δ_H(200 MHz) 0.93 (3 H, t, *J* 7), 1.2–1.5 (4 H, m), 2.19 (2 H, dt, $J_d = J_t = 7$), 6.0 (1 H, dt, A part of an AB system, J_{AB} 13, J_t 7), 6.15 (1 H, br d, B part of an AB system, J_{AB} 13) and 7.1–7.4 (5 H, m); *m/z* 192 (M^+), 149, 134, 116, 115, 110 and 55; (*Z*)-1-(phenylthio)hex-1-ene (*Z*)-**3f**; δ_H(200 MHz) 0.94 (3 H, t, *J* 7), 1.2–1.5 (4 H, m), 2.27 (2 H, ddt, $J_{d1} = J_t = 7$, $J_{d2} = 1$), 5.84 (1 H, dt, A part of an AB system, J_{AB} 9.5, J_t 7), 6.20 (1 H, dt, B part of an AB system, J_{AB} 9.5, J_t 1) and 7.1–7.4 (5 H, m); (*E*)-3,3-dimethyl-1-(phenylthio)but-1-ene (*E*)-**3g**; δ_H(200 MHz) 1.2 (9 H, s), 6.20 (2 H, AB system, δ_{AB} 0.04 ppm, J_{AB} 15) and 7.2–7.5 (5 H, m); *m/z* 192 (M^+), 177, 135, 83, 65 and 56; (*Z*)-3,3-dimethyl-1-(phenylthio)but-1-ene (*Z*)-**3g**; δ_H(200 MHz) 1.40 (9 H, s), 6.0 (2 H, AB system, δ_{AB} 0.38 ppm, J_{AB} 12.5) and 7.2–7.5 (5 H, m); an unresolved mixture of (*E*)- and (*Z*)-2-(phenylthio)but-2-ene **3h**; δ_H(200 MHz) [(*E*)-isomer] 1.71 (3 H, dq, J_d 6, J_q 1.1, collapsing to a quartet upon irradiation of the vinylic proton at δ 5.94), 1.82–1.92 (3 H, m), 5.94 (1 H, qq, J_{q1} 6, J_{q2} 1.4) and 7.1–7.4 (5 H, m); [(*Z*)-isomer] 1.82–1.92 (6 H, m, collapsing to a multiplet at δ 1.84–1.86 and a quartet at δ 1.89, *J* 1.4, upon irradiation of the vinylic proton at δ 5.87), 5.87 (1 H, qq, J_{q1} 6.5, J_{q2} 1.1) and 7.1–7.4 (5 H, m,); *m/z* 164 (M^+), 149, 110, 59 and 55; (*E*)-3-(phenylthio)hex-3-ene (*E*)-**3i**; δ_H(200 MHz) 1.08 (3 H, t, *J* 7.5), 1.12 (3 H, t, *J* 7.5), 2.26 (2 H, dq, J_d 1.1, J_q 7.5, collapsing to a quartet upon irradiation of the vinylic proton at δ 5.97), 2.42 (2 H, dq, $J_d = J_q = 7.5$, collapsing to a quartet upon irradiation of the vinylic proton at δ 5.97), 5.97 (1 H, tt, J_{t1} 7.5, J_{t2} 1.1) and 7.1–7.4 (5 H, m); *m/z* 192 (M^+), 177, 163, 135, 110, 83, 67 and 55; (*Z*)-3-(phenylthio)hex-3-ene (*Z*)-**3i**; δ_H(200 MHz) 1.1 (6 H, t, *J* 7.3), 2.23 (4 H, sextet, *J* 7.3), 5.90 (1 H, t, *J* 7.3) and 7.1–7.6 (5 H, m); (*E*)-4-(phenylthio)oct-4-ene (*E*)-**3j**; δ_H(200 MHz) 0.85 (3 H, t, *J* 7.3), 0.98 (3 H, t, *J* 7.3), 1.35–1.60 (4 H, m), 2.13 (2 H, br t, *J* 7.3, collapsing to a triplet upon irradiation of the vinylic proton at δ 5.92), 2.31 (2 H, dt, $J_d = J_t = 7.1$), 5.92 (1 H, tt, J_{t1} 7.1, J_{t2} 1.1) and 7.1–7.4 (5 H, m); *m/z* 220 (M^+), 191, 150, 135, 110, 87, 69 and 55; (*Z*)-4-(phenylthio)oct-4-ene (*Z*)-**3j**; δ_H(200 MHz) 0.9 (3 H, t, *J* 7.5), 1.0 (3 H, t, *J* 7.5), 1.3–1.6 (4 H, m), 2.08–2.24 (4 H, m), 5.90 (1 H, t, *J* 7.3) and 7.1–7.4 (5 H, m); (*E*)-5-(phenylthio)dec-5-ene (*E*)-**3k**; δ_H(200 MHz) 0.82 (3 H, t, *J* 7.5), 0.90 (3 H, t, *J* 7.5), 1.1–1.6 (8 H, m), 2.15 (2 H, t, *J* 7.4), 2.25–2.40 (2 H, m), 5.90 (1 H, t, *J* 7.0) and 7.0–7.4 (5 H, m); *m/z* 248 (M^+), 150, 135, 110, 83 and 55; and (*Z*)-5-(phenylthio)dec-5-ene (*Z*)-**3k**; δ_H(200 MHz) 0.88 (3 H, t, *J* 7.5), 0.90 (3 H, t, *J* 7.5), 1.15–1.60 (8 H, m), 2.06–2.23 (4 H, m), 5.85 (1 H, t, *J* 7.0) and 7.1–7.4 (5 H, m).

Reaction of Diphenyl Disulphide with Alkynes.—Procedure A. A solution of the appropriate alkyne **1a**,**b**,**f**–**i**,**l**,**m** (2 mmol), diphenyl disulphide (1 mmol), aniline (1.5 mmol), and n-pentyl nitrite (1.6 mmol) in benzene (10 cm^3) was heated in a sealed tube at 100 °C for 1 h. After this time the solvent and the excess of alkyne were removed under reduced pressure, and the residue was analysed by GLC and GLC–MS and chromatographed on a silica gel column. Column chromatography generally afforded, in addition to the appropriate bis-sulphides **4** and benzothiophenes **5**, biphenyl (*ca.* 0.2 mmol), diphenyl sulphide (*ca.* 0.3 mmol), unchanged diphenyl disulphide, and a mixture of unidentifiable coloured products. Yields of the bis-sulphides **4** and the benzothiophenes **5** are given in Table 2, column A, and are based on the produced diphenyl sulphide by assuming that benzenethiyl radical and diphenyl sulphide were produced to an equimolar extent from reaction of diphenyl disulphide with aniline and n-pentyl nitrite. In the case of phenylacetylene **1a**, 2,4-diphenylthiophene **6** (15%) was also isolated.

Procedure B. A solution of the appropriate alkyne **1a**,**b**,**f**–**i**,**l**,**m** (10 mmol) and diphenyl disulphide (1 mmol) in bromobenzene (10 cm^3) was heated in a sealed tube at 180 °C for 48 h. After this time the solvent and the excess of alkyne were removed under reduced pressure, and the residue was chromatographed and analysed by GLC and GLC–MS. Yields of the bis-sulphides **4** and benzothiophenes **5** are reported in Table 2, column B, and are based on the amount of starting diphenyl disulphide.

In the case of phenylacetylene **1a**, 2,4-diphenylthiophene **6** (2%) was also obtained in addition to two products deriving from dimerization of starting alkyne, as evidenced by GLC–MS. These products were not further characterized.

Hydrolysis of 3,3-*Dimethyl*-1-*phenyl*-2-(*phenylthio*)*but*-1-*ene* **3e**.—A mixture of the vinyl sulphide **3e** (100 mg) and 96% sulphuric acid (0.16 cm^3, 3 mmol) in dichloromethane (5 cm^3) was stirred at room temperature for *ca.* 2 h (after which time TLC showed the absence of starting material **3e**). The reaction mixture was washed with water, the organic layer was separated, and the solvent was removed. The resulting residue was shown by GLC, GLC–MS and ^1H NMR analysis to be mainly diphenyl disulphide and 3,3-dimethyl-1-phenylbutan-2-one,[26] in a ~1:2 ratio, as the only detectable products.

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