petition with chlorobenzene), 2.1×10^{-3} mol of hydroxylamine-*O*-sulfonic acid and 0.017 g of $FeSO_4 \cdot 7H_2O$ in 24 mL of acetic acid and 12 mL of water. The solution was stirred at 40 °C for 2 h and then made basic with 30% NaOH and extracted with ether. GC analyses of the ethereal solutions were performed by using the following columns: OV 101 10% on Chromosorb W-HP-DMCS 80–100 mesh, capillary Carbowax (benzene, toluene, anisole, fluoro-, chloro-, and bromobenzene, *tert*-butylbenzene, benzonitrile); 3% Dexsil 300 on 100/120 Supelcopat (ethyl benzoate). Pure samples were used to check the response of the quantitative GC. The results are reported in Table I.

Synthetic Procedure. The procedure is substantially identical with that utilized in the competitive kinetics with the difference that only one aromatic substrate is used, and hydroxylamine-*O*-sulfonic acid is used in equimolecular amount with the aromatic substrate.

The reaction products were analyzed by quantitative GC, using the following internal standards: aniline (anisole, chlorobenzene, *tert*-butylbenzene, ethyl benzoate), *p*-xylene (benzene and toluene), *p*-chloroaniline (benzonitrile), chlorobenzene (fluorobenzene), *p*-methylaniline (bromobenzene). The results are reported in Table II.

Amination of 1,2-Dimethoxybenzene and (Methylenedioxy)benzene. A flask, equipped with a magnetic stirrer, was charged with 9.6 g of 1,2-dimethoxybenzene (or an equivalent amount of (methylendioxy)benzene), 8 g of hydroxylamine-*O*-sulfonic acid and 7 g of sulfuric acid in 50 mL of dimethylformamide and 50 mL of water; 1.9 g of $FeSO_4 \cdot 7H_2O$ was added and the resulting solution was stirred for 1 h at 30–35 °C. The solution was then made basic with 30% NaOH and extracted with ether. GC analysis of the ethereal extract (internal standard, aniline) revealed the presence of 3.6 g of 1.2-dimethoxybenzene, 6.3 g of 3,4-dimethoxyaniline, and 0.2 g of 2,3-dimethoxyaniline; conversion 62%. Yields of 3,4-dimethoxyaniline, based on converted 1,2-dimethoxybenzene, 96%.

With (methylendioxy)benzene the conversion is 45%; the yields of 4-amino(methylendioxy)benzene (93%) and 3-amino(methylenedioxy)benzene (4%) are based on the converted aromatic substrate.

Amination of Anisole by $^+NH_3OH$ and $^+NH_3OSO_3^-$ and $Ti_2(SO_4)_3$. A flask, equipped with a magnetic stirrer, was charged with 2×10^{-2} mol of anisole and 2×10^{-2} mol of hydroxylamine sulfate (or hydroxylamino-*O*-sulfonic acid) in 24 mL of acetic acid and 10 mL of water. A 20% $Ti_2(SO_4)_3$ solution was added under stirring at room temperature until the persistency of the violet color. The resulting solution was made basic, extracted with ether, and analyzed by GC. The results are reported in Table III.

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Registry No. $Ti_2(SO_4)_3$, 10343-61-0; $FeSO_4$, 7720-78-7; $\cdot^+NH_3$, 19496-55-0; $(CH_3)_2{}^+NH\cdot$, 34536-36-2; PhOMe, 100-66-3; PhMe, 108-88-3; Ph-*t*-Bu, 98-06-6; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhCOOEt, 93-89-0; PhCN, 100-47-0; $^+NH_3OSO_3^-$, 2950-43-8; $^+NH_3OH$, 20712-83-8; 1,2-dimethoxybenzene, 91-16-7; (methylenedioxy)benzene, 274-09-9; 3,4-dimethoxyaniline, 6315-89-5; 4-amino(methylenedioxy)benzene, 14268-66-7.

Reaction of 1,2,3-Benzothiadiazoles with Radicophilic Alkenes and Alkynes in Di-*tert*-butyl Peroxide†

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The reaction of 6-X-1,2,3-benzothiadiazoles (**1**) with the radicophilic alkenes 1,1-diphenylethylene (**2**) and 1-cyano-1-(*tert*-butylthio)ethylene (**3**) and the alkynes PhC≡CR (**4**, R = H or Ph) in di-*tert*-butyl peroxide (TBP) leads to the cycloadducts **5**, **7**, and **8**. The proposed mechanism involves an initial attack by *tert*-butoxy radical at the sulfur atom of **1** affording the radical intermediate **9** which is responsible for the formation of all the reaction products.

Introduction

1,3-Dipolar cycloadditions of aromatic 1,2-ketocarbenes to unsaturated compounds are known to give fair to excellent yields of cycloadducts.[1] The analogous 1,2-thioketocarbenes, on the other hand, show a quite different behavior. The latter species, even though they afford high yields of cycloadducts in reaction with compounds containing carbon–sulfur double bonds, do not react at all or, at most, to a very small extent with alkenes, alkynes, nitriles, and aromatic compounds.[2] This behavior has been ascribed to the high reactivity toward radical species of the precursor of benzene 1,2-thioketocarbene, i.e., 1,2,3-benzothiadiazole. In fact, 1,2,3-benzothiadiazole is easily attacked by carbon, oxygen, and sulfur centered radicals, as well as by carbenes and nitrenes, giving a series of reactions of theoretical and, in a few cases, of synthetic interest.[3]

Results and Discussion

We report here that the addition of ring-substituted benzene 1,2-thioketocarbene equivalents to carbon–carbon multiple bonds can be achieved by an indirect method which allowed us to synthesize sulfurated cycloadducts not always easily accessible.

The reaction of 6-X-1,2,3-benzothiadiazole (**1**) with 1,1-diphenylethylene (**2**), 1-cyano-1-(*tert*-butylthio)-

† Dedicated to Prof. Giuseppe Leandri on his 70th birthday.

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(1) (a) Huisgen, R.; Binsch, G.; König, H. *Chem. Ber.* **1964**, *97*, 2884–2892. (b) Huisgen, R. *Proc. J. Chem. Soc.* **1961**, 357–369. (c) Huisgen, R.; König, H.; Binsch, G.; Sturn, H. J. *Angew. Chem.* **1961**, *73*, 368–371. (d) Cadogan, J. I. G.; Sharp, J. I.; Trattles, M. J. *J. Chem. Soc., Chem. Commun.* **1974**, 900–901.

(2) (a) Huisgen, R.; Weberndörfer V. *Experientia* **1961**, *17*, 566. (b) Benati, L.; Montevecchi, P. C.; Zanardi, G. *J. Org. Chem.* **1977**, *42*, 575–577.

(3) (a) Benati, L.; Montevecchi, P. C.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1276–1279. (b) Benati, L.; Montevecchi, P. C.; Tundo, A.; Zanardi, G. *J. Org. Chem.* **1976**, *41*, 1331–1333. (c) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Chem. Commun.* **1980**, 715–717. (d) Benati, L.; Montevecchi, P. C.; Spagnolo, P.; Tundo, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1544–1548. (e) Montevecchi, P. C.; Tundo, A. *J. Org. Chem.* **1981**, *46*, 4998–4999.

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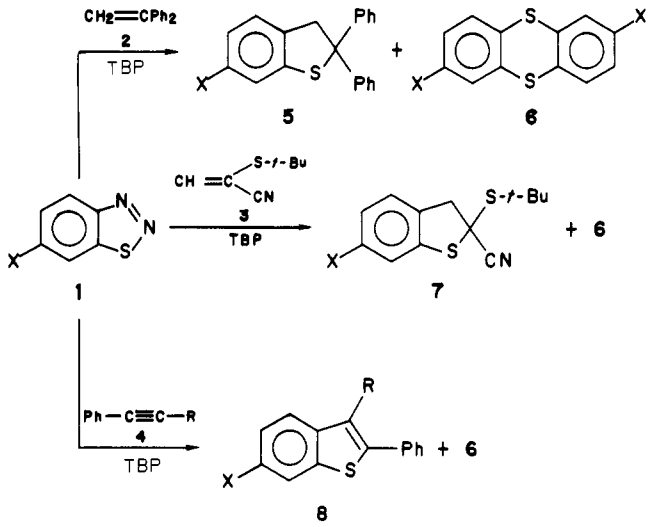
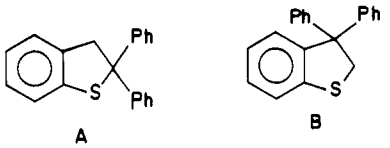
Scheme I[a]



[a] a, X = H; b, X = Cl; c, X = OMe. R = H, Ph.

ethylene (3), or the alkynes 4 in boiling di-*tert*-butyl peroxide (TBP) affords the benzo[*b*]thiophene derivatives 5, 7, and 8; small amounts of thiaanthrenes (6) could also be separated from the reaction mixture, as well as products arising from the reaction of the *tert*-butoxy radical with 1,1-diphenylethylene, i.e., 1,1-diphenyl-2-*tert*-butoxyethylene (Scheme I).

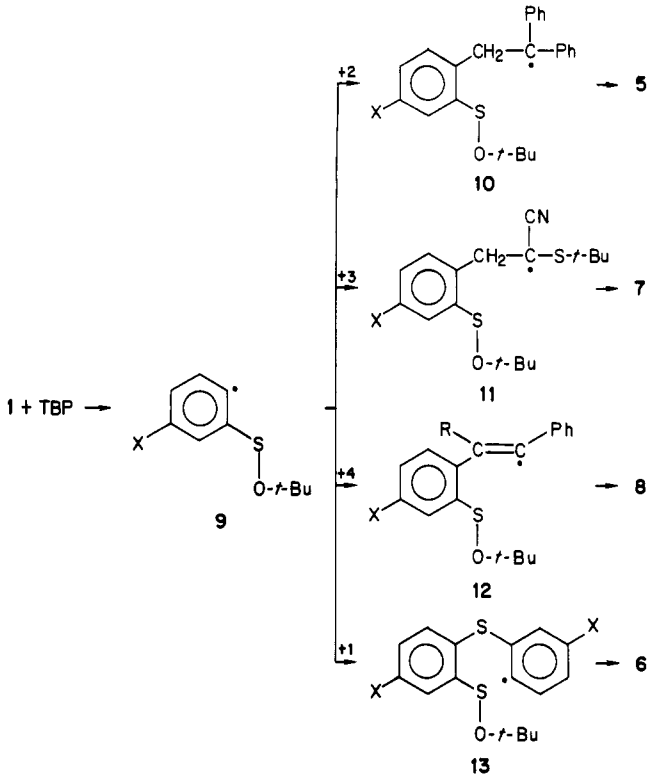
The structure of the cycloadducts 5 has been established by means of spectroscopic techniques. Mass spectral data for **5a** are consistent with both the isomeric structures A and B.



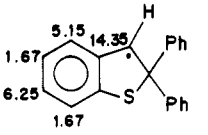
An unambiguous assignment could be made on the basis of the ^{13}C–H coupling constant of the methylene group, which is known to be very sensitive to the nature of the substituents on the carbon atom. Thus, a J_{CH} value of 138 Hz has been found for a CH_2 group bearing a thio substituent,[4] while the same constant is expected to be 124–126 Hz in the absence of heterosubstituents.[5] The experimental value of 125.5 Hz is therefore indicative of structure A.

Further evidence in favor of structure A is provided by the change of the ^{13}C chemical shift at the CH_2 and CPh_2 carbons observed after oxidation of the cyclic sulfide to the corresponding sulfone. It is known that sulfur oxidation causes a deshielding of the α-carbon and a shielding of the β-carbon.[6] From the ^{13}C chemical shift[7] in the sulfide and sulfone, 49.8 and 39.7 ppm for $^{13}CH_2$, and 70.1 and 76.5 ppm for $^{13}CPh_2$, respectively, it can be inferred that the methylene group is β to sulfur. We may also add that the reaction of **5a** with photolytically generated *tert*-butoxy radicals leads to a radical species whose ESR spectrum, invariant in the temperature range from −50 to

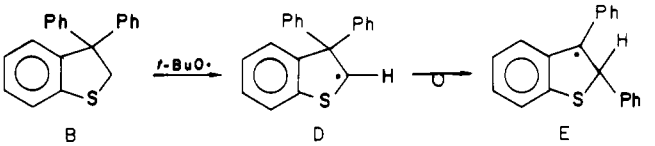
Scheme II



70 °C, has been interpreted in terms of the following hyperfine splitting constants: *a* (2 H) 1.67, *a* (1 H) 5.15, *a* (1 H) 6.25, and *a* (1 H) 14.35 G. Since these couplings are nicely accounted for by a radical having structure C[8] it can be deduced that its precursor possesses structure A.



In fact, hydrogen abstraction from B will produce radical D which would presumably rearrange to E. Neither of these radicals is expected to show a spectrum consistent with the measured hyperfine splitting constants.

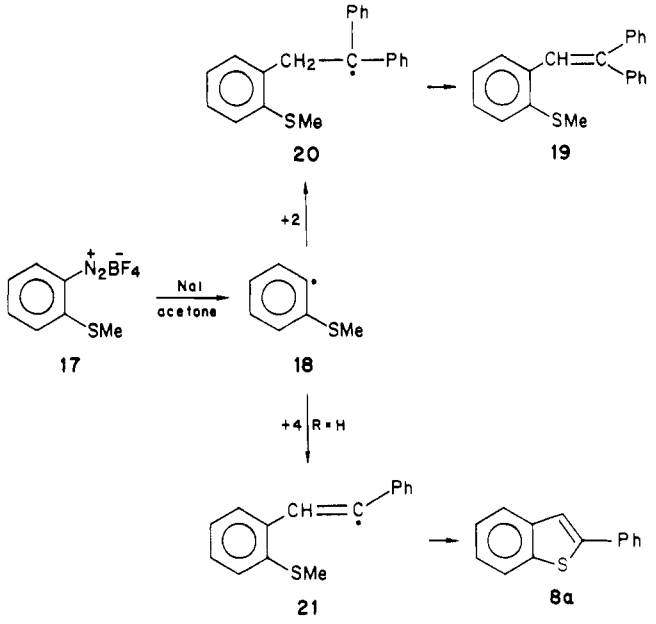


For the ring-substituted adducts 5 and 7 mass spectral data are in agreement with the proposed structures; the choice between the isomeric cycloadducts A and B has been made by analogy with **5a**.

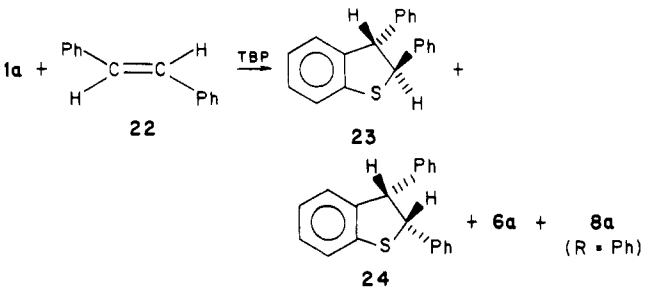
In line with the results of previous studies by us[3] and other authors[9] and with the fact that no reaction occurs between benzothiadiazole and diphenylethylene below 200 °C, it is suggested that the products obtained during the reaction of 6-X-1,2,3-benzothiadiazoles with 2, 3, and 4 arise from the S_H2 attack of the *tert*-butoxy radical at the sulfur atom of 1 with cleavage of the S–N bond. The subsequent loss of nitrogen gives rise to the radical intermediate 9 which adds to the less substituted carbon of

(4) Lunazzi, L.; Taddei, F. *Spectrochim. Acta Part A* **1967**, *23A*, 841–844.
(5) Goldstein, J. H.; Watts, V. S.; Rattet, L. S. "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsly, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1972; Vol. 8, pp 103–162.
(6) Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 108–114.
(7) The ^{13}C and ^1H NMR spectra were recorded with a 100-MHz Varian XL 100 spectrometer.
(8) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *Tetrahedron* **1983**, *39*, 2715–2718.
(9) Suehiro, T.; Tashiro, T.; Nakausa, R. *Chem. Lett.* **1980**, 1339–1342.

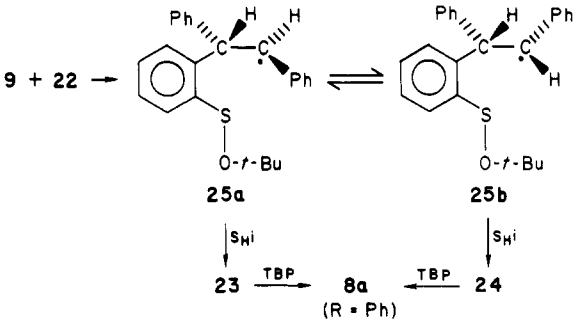
Scheme III



Scheme IV



Scheme V



2, 3, or 4 with formation of the radical adducts **10**, **11**, or **12**. These, via an S_Hi reaction on sulfur, lead to the benzo[*b*]thiophene derivatives **5**, **7**, or **8**. Radical **9** may also give homolytic displacement on the sulfur atom of **1**, the resulting radical **13**, via S_Hi again, leading to thiaanthrene (**6**) (Scheme II).

In principle the formation of the products obtained in the reactions of Scheme I might be rationalized by an alternative route involving the thermolysis of radical **9** to give 5-X-benzene 1,2-thioketocarbene. Benzenesulfenates, in fact, easily undergo thermolysis[10] particularly in the case of *tert*-butyl derivatives. The thioketocarbene could afford the benzo[*b*]thiophene derivatives **5**, **7**, or **8** through cycloaddition to the alkenes **2** and **3** or the alkynes **4**, or thiaanthrene (**6**) through dimerization.

Searching for a possible way to distinguish between these two routes, we investigated the thermolysis of 1,2,3-benzothiadiazole which is known to proceed via benzene 1,2-thioketocarbene,[2b,11] in 1,1-diphenylethylene. The products separated from this reaction were the cycloadduct **5a**, thiaanthrene (**6a**), dibenzo[*c*,*e*]-*o*-dithiin (**14a**), dibenzothiophene (**15a**), 2,3-diphenylbenzo[*b*]thiophene (**8a**, R = Ph), and diphenyl disulfide (**16a**), while the thermolysis in phenylacetylene is reported[2b] to give **14a**, **15a**, **16a**, and **8a** (R = H).

These results suggest that the reaction of **1** with **2**, **3**, or **4**, when performed in TBP, does not involve the intermediacy of thioketocarbene.

With the aim to provide further evidence in support of the mechanism schematized in **II**, 1,1-diphenylethylene and phenylacetylene were allowed to react at room temperature with *o*-(methylthio)benzenediazonium tetrafluoborate (**17**) in acetone solution in the presence of sodium iodide. Quantitative yields of 1,1-diphenyl-2-[2-(methylthio)phenyl]ethylene (**19**) and 2-phenylbenzo[*b*]thiophene (**8a**, R = H),[12] respectively, were obtained from these reactions (Scheme III).

The different energy of the S–Me and S–O-*t*-Bu bonds are taken into account, the results of the latter reactions seem to substantiate the mechanism outlined in **II**. The comparison of radical **10** with **20** and of **12** with **21** leads to the following considerations: the fate of **12** is the same as for **21** since both afford 2-phenylbenzo[*b*]thiophene. Radicals **10** and **20**, on the other hand, behave differently, the former giving the cyclized derivative **5** and the latter the alkene **19**. **12** and **21** being σ radicals, they are scarcely selective and are therefore expected to easily displace from sulfur both the *tert*-butoxy and the methyl groups via S_Hi. The more selective π radicals **10** and **20** follow instead different routes since the energy of the S–O-*t*-Bu and S–Me bonds to be cleaved in the S_Hi reaction is different. Homolytic substitution at sulfur is actually known to take place easily when the leaving group is linked to sulfur by a weak bond.[13]

The reaction of **1** with alkenes in TBP gives cycloadducts in high yields only in the case of radicophilic alkenes.[14] In fact, the main product in the reaction of **1a** with *trans*-stilbene (**22**) was thiaanthrene (**6a**) whereas only small amounts of 2,3-diphenylbenzo[*b*]thiophene (**8a**, R = Ph) and of the corresponding 2,3-dihydro derivatives **23** and **24** were obtained; no traces of *cis*-stilbene were found in the reaction mixture (Scheme IV).

The reason for this behavior may be due to the different stability of the intermediate radicals **10**, **11**, and **20** with respect to **25**. To this purpose it can be mentioned that spin adducts of aryl radicals with 1,1-diphenylethylene have been found to be easily observable by ESR,[15] while the analogous adducts with *trans*-stilbene could not be

(10) Kharasch, N.; Mc Quarrie, D. P.; Buess, C. M. *J. Am. Chem. Soc.* **1953**, *75*, 2658–2660.

(11) (a) Meier, H.; Bühl, H. *J. Heterocycl. Chem.* **1975**, *12*, 605–606. (b) Bühl, H.; Seitz, B.; Meier, H. *Tetrahedron* **1977**, *33*, 449–452. (c) Wooldrige, T.; Roberts, T. D. *Tetrahedron Lett.* **1977**, 2643–2646. (d) White, R. C.; Scoby, J.; Roberts, T. D. *Tetrahedron Lett.* **1979**, 2785–2788.

(12) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G., unpublished results.

(13) (a) Ingold, K. U.; Roberts, B. P. "Free-Radical Substitution Reactions"; Wiley-Interscience: New York, 1971; pp 200–224. (b) Kampmeier, J. A.; Evans, T. R. *J. Am. Chem. Soc.* **1966**, *88*, 4096–4097. (c) Benati, L.; Montevecchi, P. C.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1272–1276. (d) Benati, L.; Montevecchi, P. C. *J. Org. Chem.* **1976**, *41*, 2639–2640. (e) Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, D. J. *A.C.S. Symp. Ser.* **1978**, *69*, 275–289. (f) Pyror, W. A.; Platt, P. K. *J. Am. Chem. Soc.* **1963**, *85*, 1496–1500. (g) Pyror, W. A.; Guard, H. *J. Am. Chem. Soc.* **1964**, *86*, 1150–1152. (h) Pyror, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 2731–2738.

(14) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917–932.

(15) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 285–290.

detected. Only by reacting the latter alkene with transient radicals centered at elements of the second row, could the corresponding adducts be observed.[8]

The products obtained in the reaction of Scheme IV are consistent with a stepwise process, i.e., addition of the radical **9** to the carbon–carbon double bond of **22** with formation of the radical intermediate **25** having a lifetime long enough to allow the rotation of the terminal CHPh group about the C–C bond. The latter affords the two diastereomers **23** and **24** by S_Hi on sulfur. The aromatic 2,3-diphenylbenzo[*b*]thiophene is likely the result of the dehydrogenation of **23** and/or **24** by *tert*-butoxy radicals (Scheme V).

The proposed diastereomeric structures for **23** and **24** are consistent with mass spectral data and with the finding that both afford quantitatively 2,3-diphenylbenzo[*b*]-thiophene by aromatization with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Their ^{1}H NMR spectra show the expected AB system due to the cycloaliphatic hydrogens, the spin coupling constants being 9.7 and 7.6 Hz for the diastereomers obtained in higher and lower yield, respectively. Although the similarity of the coupling constants do not allow an unambiguous structural assignment, we believe the less hindered isomer **23** to be the one formed in larger concentration.

Experimental Section

1,2,3-Benzothiadiazole[16] (**1a**), 6-chloro-1,2,3-benzothiadiazole[17] (**1b**), 6-methoxy-1,2,3-benzothiadiazole[18] (**1c**), 1-cyano-1-(*tert*-butylthio)ethylene[19] (**3**) and *o*-(methylthio)benzenediazonium tetrafluoborate[20] (**17**) were prepared according to the literature; all the other starting materials are commercially available. The reaction products 2-phenylbenzo[*b*]thiophene[21] (**8a**, R = H), 2,3-diphenylbenzo[*b*]thiophene[22] (**8a**, R = Ph), thiaanthrene[3e] (**6a**), 2,7-dichloro-[3e] and 2,7-dimethoxythiaanthrene[2b] (**6b,c**), dibenzothiophene,[23] dibenzo[*c,e*]-*o*-dithiin,[24] and diphenyl disulfide[25] were identified by mixed melting point determination and spectral data comparison with authentic specimens synthesized as reported in the literature; all the other products were identified by means of their spectral data and elemental analyses.

The ^{1}H NMR spectra were recorded on a varian EM 360L instrument with Me_4Si as an internal standard. Mass spectra were performed with a JEOL JMS-D100 mass spectrometer at an ionization energy of 70 eV.

General Procedure for the Reactions of Benzothiadiazoles with Alkenes or Alkynes in Di-*tert*-butyl Peroxide (TBP). Benzothiadiazole (5 mmol) and alkene or alkyne (25 mmol) in TBP (30 mL) were refluxed for 24 h; the solution was cooled at room temperature and the excess peroxide was removed at reduced pressure. The residue was chromatographed on silica gel (Kieselgel 60, 70–230 mesh ASTM, Merck) and the products were isolated in the reported yields using light petroleum (40–70 °C)/diethyl ether gradient as eluant.

Reaction of 1,2,3-Benzothiadiazole (1a) with 1,1-Diphenylethylene (2) in TBP. When the procedure described above was used the following products were obtained: 1,1-Diphenyl-2-*tert*-butoxyethylene[26] (1.5 g): mp 60–62 °C; ^{1}H NMR ($CDCl_3$) δ 1.3 (9 H, s, t-C_4H_9), 6.60 (1 H, s, C=CH), 6.95–7.50 (10 H, m, ArH); mass spectrum, *m/e* (relative intensity) 252 (10, M^+), 196 (100), 178 (9), 167 (44), 165 (73), 152 (25), 57 (32). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.75; H, 8.03. Thiaanthrene (**6a**, 0.1 g, 19% yield): mp 156–158 °C (lit.[3e] mp 157 °C). 2,3-Dihydro-2,2-diphenylbenzo[*b*]thiophene (**5a**, 0.9 g, 63% yield): mp 105–107 °C; ^{1}H NMR ($CDCl_3$) δ 3.8 (2 H, s, CH_2), 6.8–7.45 (14 H, m, ArH); mass spectrum, *m/e* (relative intensity) 288 (100, M^+), 255 (15), 211 (72), 165 (15), 77 (7). Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59; S, 11.11. Found: C, 83.19; H, 5.63; S, 11.16.

Reaction of 1,2,3-Benzothiadiazole (1a) with 1-Cyano-1-(*tert*-butylthio)ethylene (3) in TBP. When the procedure described above was used, the following products were obtained. Thiaanthrene (**6a**, 0.1 g, 19% yield), mp 155–157 °C (lit.[3e] mp 157 °C), and 2,3-dihydro-2-cyano-2-(*tert*-butylthio)benzo[*b*]-thiophene (**7a**, 0.8 g, 64% yield): mp 168–170 °C; ^{1}H NMR ($CDCl_3$) δ 1.6 (9 H, s, t-C_4H_9), 3.53 and 3.73 (2 H, AB, J_{AB} = 15.5 Hz, CH_2), 7.05 (4 H, bs, ArH); mass spectrum, *m/e* (relative intensity) 249 (37, M^+), 193 (41), 166 (35), 160 (100), 57 (88). Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.61; H, 6.06; N, 5.62; S, 25.71. Found: C, 62.64; H, 6.10; N, 5.54; S, 25.61.

Reaction of 1,2,3-Benzothiadiazole (1a) with Phenylacetylene (4, R = H) in TBP. Following the procedure described above, the only reaction product was 2-phenylbenzo[*b*]thiophene (**8a**, R = H, 0.9 g, 85% yield), mp 174–175 °C (lit.[21] mp 175.5–176 °C).

Reaction of 1,2,3-Benzothiadiazole (1a) with Diphenylacetylene (4, R = Ph) in TBP. When the procedure described above was used, the following products were obtained: thiaanthrene (**6a**, 0.35 g, 66% yield), mp 156–157 °C (lit.[3e] mp 157 °C), and 2,3-diphenylbenzo[*b*]thiophene (**8a**, R = Ph, 0.35 g, 25% yield), mp 113–114 °C (lit.[22] mp 113–114 °C).

Reaction of 1,2,3-Benzothiadiazole (1a) with *trans*-Stilbene (22) in TBP. When the procedure described above was used, the reaction gave thiaanthrene (**6a**, 0.4 g, 74% yield), mp 156–157 °C (lit.[3e] mp 157 °C), 2,3-diphenylbenzo[*b*]thiophene (**8a**, R = Ph, 0.15 g, 10% yield), mp 113–114 °C (lit.[22] mp 113–114 °C), and a mixture of the diastereomeric derivatives **23** and **24** (0.1 g, 7% yield); further chromatography of the last mixture gave a white solid and a viscous oil which could not be distilled. Solid (0.07 g, 5% yield): mp 89–91 °C; ^{1}H NMR[7] ($CDCl_3$) δ 4.74 and 5.02 (2 H, AB, J_{AB} = 9.7 Hz, >CHCH<), 6.71–7.47 (14 H, m, ArH); mass spectrum, *m/e* (relative intensity) 288 (100, M^+), 287 (22), 255 (19), 211 (29), 210 (35), 197 (45), 178 (22), 165 (38). Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59; S, 11.11. Found: C, 83.16; H, 5.54; S, 11.05. Oil (0.015 g, 1% yield); ^{1}H NMR[7] ($CDCl_3$) δ 4.88 and 5.27 (2 H, AB, J_{AB} = 7.6 Hz, >CHCH<), 6.65–7.42 (14 H, m, ArH); mass spectrum, *m/e* (relative intensity) 288 (100, M^+), 287 (25), 255 (19), 211 (32), 210 (34), 197 (45), 178 (21), 165 (31).

Treatment of **23** or **24** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in boiling benzene for 2 h always afforded quantitatively 2,3-diphenylbenzo[*b*]thiophene (**8a**, R = Ph), mp 113–114 °C (lit.[22] mp 113–114 °C).

Reaction of 6-Chloro-1,2,3-benzothiadiazole (1b) with 1,1-Diphenylethylene (2) in TBP. Following the procedure described above the reaction gave 2,7-dichlorothianthrene (**6b**, 0.1 g, 14% yield), mp 184–186 °C (lit.[3e] mp 185–186 °C), and 2,3-dihydro-2,2-diphenyl-6-chlorobenzo[*b*]thiophene (**5b**, 1.3 g, 81% yield), mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (2 H, s, CH_2), 6.9–7.4 (13 H, m, ArH); mass spectrum, *m/e* (relative intensity) 324 (40, $M^+ + 2$), 322 (100, M^+), 245 (66), 210 (47), 165 (33). Anal. Calcd for $C_{20}H_{15}ClS$: C, 74.40; H, 4.68; Cl, 10.98; S, 9.93. Found: C, 74.32; H, 4.69; Cl, 11.04; S, 9.89.

Reaction of 6-Chloro-1,2,3-benzothiadiazole (1b) with 1-Cyano-1-(*tert*-butylthio)ethylene (3) in TBP. When the procedure described above was used, the following products were obtained: 2,7-dichlorothiaanthrene (**6b**; 0.2 g, 28% yield), mp 185–186 °C (lit.[3e] mp 185–186 °C), and 2,3-dihydro-2-cyano-2-(*tert*-butylthio)-6-chlorobenzo[*b*]thiophene (**7b**; 0.9 g, 64% yield); mp 103–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.6 (9 H, s, t-C_4H_9), 3.53 and 3.75 (2 H, AB, J_{AB} = 15 Hz, CH_2), 7.05 (3 H, bs, ArH); mass spectrum, *m/e* (relative intensity) 285 (13, $M^+ + 2$), 283 (30, M^+), 227 (37), 200 (24), 194 (53), 157 (20), 57 (100). Anal. Calcd for $C_{13}H_{14}ClNS_2$: C, 55.01; H, 4.97; Cl, 12.49; N, 4.93; S, 22.59. Found: C, 55.07; H, 4.92; Cl, 12.40; N, 5.00; S, 22.55.

(16) Jacobson, P.; Janssen, H. *Liebigs Ann. Chem.* **1893**, *277*, 218–231.
(17) Kirby, P.; Soloway, S. B.; Davies, J. H.; Webb, S. W. *J. Chem. Soc. C* **1970**, 2250–2253.
(18) Poesche, W. H. *J. Chem. Soc. B* **1971**, 368–373.
(19) Gundermann, K. D.; Thomas, R. *Chem. Ber.* **1956**, *89*, 1263–1270.
(20) Roe, A. *Org. React.* **1949**, *5*, 193–226.
(21) Horton, A. W. *J. Org. Chem.* **1949**, *14*, 761–770.
(22) Capozzi, G.; Melloni, G.; Modena, G. *J. Chem. Soc. C* **1970**, 2621–2625.
(23) Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1939**, *3*, 108–119.
(24) Barber, H. J.; Smiles, S. *J. Chem. Soc.* **1928**, 1141–1149.
(25) Lecher, H. *Chem. Ber.* **1915**, *48*, 524–536.
(26) This alkene was obtained in all the reactions involving 1,1-diphenylethylene and TBP; being a side product, the yields were not calculated.

Reaction of 6-Chloro-1,2,3-benzothiadiazole (1b) with Phenylacetylene (4, R = H) in TBP. When the procedure described above was followed, the reaction gave 2,7-dichlorothiaanthrene (**6b**, 0.3 g, 42% yield), mp 184–186 °C (lit.[3e] mp 185–186 °C), and 2-phenyl-6-chlorobenzo[*b*]thiophene (**8b**, R = H, 0.6 g, 49% yield), mp 202–204 °C; mass spectrum, *m/e* (relative intensity) 246 (40, $M^+ + 2$), 244 (100, M^+), 212 (7), 208 (24), 165 (22). Anal. Calcd for $C_{14}H_9ClS$: C, 68.71; H, 3.71; Cl, 14.48; S, 13.10. Found: C, 68.65; H, 3.78; Cl, 14.54; S, 13.02.

Reaction of 6-Methoxy-1,2,3-benzothiadiazole (1c) with 1,1-Diphenylethylene (2) in TBP. When the procedure described above was used, the following products were obtained: 2,7-dimethoxythiaanthrene (**6c**, 0.3 g, 43% yield), mp 134–135 °C (lit.[2b] mp 134–135 °C), and 2,3-dihydro-2,2-diphenyl-6-methoxybenzo[*b*]thiophene (**5c**, 0.8 g, 52% yield): mp 95–96 °C; ^1H NMR ($CDCl_3$) δ 3.65 (3 H, s, OCH_3), 3.80 (2 H, s, CH_2), 6.35–7.45 (13 H, m, ArH); mass spectrum, *m/e* (relative intensity) 318 (100, M^+), 241 (46), 227 (15), 197 (11), 165 (17), 77 (9). Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70; S, 10.07. Found: C, 79.29; H, 5.75; S, 9.95.

Reaction of 6-Methoxy-1,2,3-benzothiadiazole (1c) with 1-Cyano-1-(*tert*-butylthio)ethylene (3) in TBP. When the procedure described above was used, the following compounds were obtained: 2,7-dimethoxythiaanthrene (**6c**, 0.35 g, 50% yield), mp 134–136 °C (lit.[2b] mp 134–135 °C), and 2-cyano-6-methoxybenzo[*b*]thiophene (0.2 g, 21% yield): mp 83–84 °C; ^1H NMR ($CDCl_3$) δ 3.90 (3 H, s, OCH_3), 6.85–7.75 (4 H, m, ArH); mass spectrum, *m/e* (relative intensity) 189 (100, M^+), 174 (63), 156 (12), 146 (61). Anal. Calcd for $C_{10}H_7NOS$: C, 63.47; H, 3.73; N, 7.40; S, 16.94. Found: C, 63.36; H, 3.70; N, 7.49; S, 16.87. Also obtained was 2,3-dihydro-2-cyano-2-(*tert*-butylthio)-6-methoxybenzo[*b*]thiophene (**7c**, 0.2 g, 14% yield): mp 85–86 °C; ^1H NMR ($CDCl_3$) δ 1.60 (9 H, s, *t*-C_4H_9), 3.48 and 3.66 (2 H, AB, J_{AB} = 16 Hz, CH_2), 3.75 (3 H, s, OCH_3), 6.40–7.10 (3 H, m, ArH); mass spectrum, *m/e* (relative intensity) 279 (65, M^+), 223 (59), 196 (39), 190 (100), 189 (80) 57 (62). Anal. Calcd for $C_{14}H_{17}NOS_2$: C, 60.18; H, 6.13; N, 5.01; S, 22.95. Found: C, 60.13; H, 6.18; N, 4.95; S, 23.08.

Reaction of 6-Methoxy-1,2,3-benzothiadiazole (1c) with Phenylacetylene (4, R = H) in TBP. When the procedure described above was followed the reaction gave 2,7-dimethoxythiaanthrene (**6c**, 0.4 g, 65% yield), mp 134–135 °C (lit.[2b] mp 134–135 °C), and 2-phenyl-6-methoxybenzo[*b*]thiophene (**8c**, R = H, 0.4 g, 33% yield): mp 157–159 °C (lit.[27] mp 59 °C); ^1H NMR ($CDCl_3$) δ 3.85 (3 H, s, OCH_3), 6.80–7.70 (9 H, m, ArH); mass spectrum, *m/e* (relative intensity) 240 (100, M^+), 225 (59), 197 (38), 165 (17), 120 (18). Anal. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03; S, 13.34. Found: C, 74.87; H, 5.08; S, 13.40.

To confirm the real structure of the 2-phenyl-6-methoxybenzo[*b*]thiophene obtained in this reaction, the product (0.3 g) was refluxed in absolute ethanol (100 mL) with Raney nickel (6 g) for 1 h; the mixture was filtered and the metal washed with ethanol. The alcoholic solution, after removal of the solvent, gave 1-phenyl-2-(4-methoxyphenyl)ethane (0.24 g, 90% yield), mp 59–61 °C, identical in all respects with an authentic specimen.[28]

2,3-Dihydro-2,2-diphenylbenzo[*b*]thiophene 1,1-Dioxide. To a solution of 2,3-dihydro-2,2-diphenylbenzo[*b*]thiophene (**5a**, 0.7 g) in acetic acid (15 mL) was added 36% hydrogen peroxide (3 mL) and the reaction mixture was refluxed for 30 min. After cooling, the solution was poured into water and a solid separated in white crystals which were filtered and recrystallized from ethanol (0.65 g, 85% yield): mp 180–182 °C; ^1H NMR ($CDCl_3$) δ 4.0 (2 H, s, CH_2) 7.0–7.70 (14 H, m, ArH); mass spectrum, *m/e* (relative intensity) 320 (25, M^+), 256 (62), 255 (47), 179 (69), 178 (100), 165 (55), 77 (29). Anal. Calcd for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.00. Found: C, 74.85; H, 4.98; S, 10.03.

Thermal Decomposition of 1,2,3-Benzothiadiazole (1a) in 1,1-Diphenylethylene (2). 1,2,3-Benzothiadiazole (1.36 g, 10 mmol) and 1,1-diphenylethylene (3.6 g, 20 mmol) were kept in a "bomb" at 220 °C for 18 h. The crude material was chromatographed on a silica gel column (kieselgel 60, 70–230 mesh ASTM, Merck) eluting with light petroleum (40–70 °C). The following products were obtained: diphenyl disulfide (0.03 g, 3% yield), mp 60–61 °C (lit.[25] mp 60–62 °C), thiaanthrene (**6a**, 0.15 g, 14% yield), mp 156–157 °C (lit.[3e] mp 157 °C), dibenzothiophene (0.027 g, 3% yield), mp 97–99 °C (lit.[23] mp 98–99 °C), dibenzo[*c,e*]-*o*-dithiin (0.043 g, 4% yield), mp 112–113 °C (lit.[24] mp 113 °C), 2,3-diphenylbenzothiophene (**8a**, R = Ph, 0.57 g, 20% yield), mp 113–114 °C (lit.[22] mp 113–114 °C), and 2,3-dihydro-2,2-diphenylbenzo[*b*]thiophene (**5a**, 0.72 g, 25% yield), mp 105–107 °C.

Decomposition of *o*-(Methylthio)benzenediazonium Tetrafluoborate (17) by Sodium Iodide in the Presence of 1,1-Diphenylethylene (2). To a solution of *o*-(methylthio)-benzenediazonium tetrafluoborate[20] (1.15 g, 5 mmol) and 1,1-diphenylethylene (9.0 g, 50 mmol) in dry acetone (50 mL) was added sodium iodide (1.13 g, 7.5 mmol) at room temperature under magnetic stirring. During the addition an intense evolution of nitrogen was observed. The reaction was complete within only a few minutes. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (kieselgel 60, 70–230 mesh ASTM, Merck) using light petroleum (40–70 °C)/diethyl ether gradient as eluant. Besides a large amount of starting diphenylethylene (8.0 g) the reaction gave 1-[(*o*-methylthio)phenyl]-2,2-diphenylethylene (**19**, 0.8 g, 55% yield): mp 120–121 °C; ^1H NMR ($CDCl_3$) δ 2.40 (3 H, s, SCH_3), 6.60–7.35 (15 H, m, ArH and C=CH); mass spectrum, *m/e* (relative intensity) 302 (100, M^+), 287 (70), 255 (19), 254 (20), 211 (13), 210 (15), 77 (9). Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00; S, 10.60. Found: C, 83.31; H, 5.95; S, 10.56.

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Registry No. **1a**, 273-77-8; **1b**, 2364-40-1; **1c**, 1753-90-8; **2**, 530-48-3; **3**, 72314-64-8; **4** (R = H), 536-74-3; **4** (R = Ph), 501-65-5; **5a**, 92013-95-1; **5c**, 92013-96-2; **6a**, 92-85-3; **6b**, 60420-80-6; **6c**, 54815-69-9; **7a**, 92013-97-3; **7b**, 92013-98-4; **7c**, 92013-99-5; **8a** (R = H), 1207-95-0; **8a** (R = Ph), 22751-52-6; **8b** (R = H), 92014-00-1; **8c** (R = H), 92014-01-2; **19**, 92014-02-3; **22**, 103-30-0; **23**, 92014-03-4; **24**, 92014-04-5; TBP, 110-05-4; MeO-*o*-$C_6H_4N_2^+BF_4^-$, 52959-17-8; 2-cyano-6-methoxybenzo[*b*]thiophene, 92014-05-6; 2,3-dihydro-2,2-diphenylbenzo[*b*]thiophene 1,1-dioxide, 92014-06-7; dibenzothiophene, 132-65-0; dibenzo[*c,e*]-*o*-dithiin, 230-26-2.

(27) Banfield, J. E.; Davies, W.; Gamble, N. W.; Middleton, S. *J. Chem. Soc.* **1956**, 4791–4799.

(28) Buu-Hoi, Ng. Ph.; Hoân, Ng.; Xuong, Ng. D. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 285–291.