cooling, the resulting dark oil was dissolved in $CHCl_3$ and washed with 5% HCl. The HCl washings were made basic with Na_2CO_3 and then extracted with $CHCl_3$. The extracts were washed with water, dried over anhydrous K_2CO_3, and concentrated. Chromatography on alumina, eluting with EtOAc, gave 0.72 g (40%) of **2b** as an oil which showed spectral properties identical with the material obtained by method A above.

3,3′-Trimethylene-2,2′-bipyridine (2c). Method A. In the manner described above for **2b**, a mixture of 2.0 g (12.4 mmol) of **4c**,[11] 1.3 g (18.3 mmol) of β-aminoacrolein, and 30 mg of anhydrous NH_4OAc in 20 mL of ethylene glycol was heated at 140 °C for 19 h. After this time an additional 50 mg of NH_4OAc was added, and the mixture was heated at 150 °C for 5 h. Workup provided 2.1 g of a reddish oil which was chromatographed on 40 g of silica gel, eluting with CH_2Cl_2 (1L), 1:1 EtOAc–CH_2Cl_2 (200 mL), and EtOAc (1 L). From the EtOAc fraction was obtained 0.29 g (12%) of a solid which showed a single peak by VPC (same conditions as for **2b** at a retention time of 26 min). Isolation of this peak gave pure **3c**, mp 140–141 °C: ^1H NMR (100 MHz, $CDCl_3$) δ 8.71 (dd, $H_{6,6'}$, $J_{5,6}$ = 4.7, $J_{4,6}$ = 1.3 Hz), 7.57 (dd, $H_{4,4'}$, $J_{4,5}$ = 7.6, $J_{5,6}$ = 1.3 Hz), 7.24 (dd, $H_{5,5'}$), 2.41 (dd, α-CH_2-, J = 6.7, J = 1.3 Hz), 2.12 (t of t, β-CH_2-, J = 6.7, J = 13.4 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 156.9 (C-2), 148.4 (C-6), 136.6 (C-4), 135.2 (C-3), 123.2 (C-5), 32.4 (α-C), and 29.8 (β-C); IR (KBr) 2932, 1562, 1422, 900, 820, 803, and 758 cm^{-1}; MS, m/e (relative intensity) 196 (35, M), 195 (30), 178 (12), 139 (18), 117 (88), 115 (100), 91 (76). Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.57; H, 6.16; N, 14.27. Found: C, 79.80; H, 5.90; N, 14.20.

Method B. Following the same procedure outlined above for **2b**, 0.94 g (4.3 mmol) of **5c** was heated at 180 °C for 50 h, and the crude product was chromatographed on alumina, eluting with EtOAc, to provide 0.3 g (36%) of **2c**. Recrystallization from EtOAc/hexane provided a solid, mp 136–138 °C, which showed identical spectral properties with the material obtained by method A above.

3,3′-Tetramethylene-2,2′-bipyridine (2d). Following the procedure described as method B for **2b** above, 1.0 g (4.3 mmol) of **5d** was heated at 180 °C for 50 h and the crude product chromatographed on 30 g of alumina, eluting with EtOAc, to provide 0.6 g (66%) of **2d** which gave white crystals upon recrystallization from $CHCl_3$, mp 140–142 °C: ^1H NMR (300 MHz, $CDCl_3$), 8.62 (H_2), 7.59 (H_4), 7.29 (H_3) [the typical pyridyl H–H splittings are complicated by long range couplings], 2.73 (m, α-CH), 2.21 (m), 2.11 (m), 1.53 (m, β-CH); ^{13}C NMR (75 MHz, $CDCl_3$), 155.6 (C-2), 147.0 (C-6, J_{CH} = 179 Hz), 137.0 (C-3), 137.0 (C-4, J_{CH} = 166 Hz), 123.1 (C-5, J_{CH} = 162 Hz), 31.0 (α-C, J_{CH} = 128 Hz), 28.3 (β-C, J_{CH} = 131 Hz); IR (thin film) 3050, 2910, 2925, 2850, 1564, 1420, 1138, 1092, 1075, 788, and 758 cm^{-1}; MS, m/e (relative intensity) 211 (M + 1, 24), 210 (M, 84), 195 (18), 182 (54), 181 (100); m/e calcd for $C_{14}H_{14}N_2$ 210.1157, found 210.1148.

9,10-Dihydro-4,5-methylene-8a,10a-diazoniaphenanthrene Dibromide (6a). A solution of 28 mg (0.165 mmol) of **2a** in 1.5 mL of freshly distilled 1,2-dibromoethane was stirred and heated to reflux for 2 h during which time a precipitate formed. The mixture was cooled and filtered, and the solid thus obtained was washed with acetone and then with ether to afford 54 mg (92%) of **6a** as a green solid, mp >300 °C; ^1H NMR (100 MHz, D_2O) δ 9.19 (d, $H_{1,8}$, $J_{1,2}$ = 6.0 Hz), 9.04 (d, $H_{3,6}$, $J_{2,3}$ = 7.9 Hz), 8.38 (dd, $H_{2,7}$), 5.56 (s, $H_{9,10}$), 4.72 (s, 4, 5-CH_2-).

9,10-Dihydro-4,5-dimethylene-8a,10a-diazoniaphenanthrene Dibromide (6b). Following the procedure described above for **6a**, 30 mg (0.165 mmol) of **2b** afforded 47 mg (77%) of **6b** as a green solid, mp >300 °C; ^1H NMR (100 MHz, D_2O) δ 9.04 (dd, $H_{1,8}$, $J_{1,2}$ = 6.0, $J_{1,3}$ = 1.2 Hz), 8.74 (d, $H_{3,6}$, $J_{2,3}$ = 8.1 Hz), 8.25 (dd, $H_{2,7}$), 5.34 (s, $H_{9,10}$), 3.45 (s, 4,5-CH_2CH_2-).

9,10-Dihydro-4,5-trimethylene-8a,10a-diazoniaphenanthrene Dibromide (6c). Following the procedure described above for **6a**, 32 mg (0.163 mmol) of **2c** afforded 52 mg (83%) of **6c** as a cream color solid, mp >300 °C: ^1H NMR (100 MHz, D_2O) δ 9.18 (dd, $H_{1,8}$, $J_{1,2}$ = 5.9, $J_{1,3}$ = 1.3 Hz), 8.84 (dd, $H_{3,6}$, $J_{2,3}$ = 8.2 Hz), 8.30 (dd, $H_{2,7}$), 5.30 (s, $H_{9,10}$), 2.85 (br m, 4,5-$CH_2CH_2CH_2$-).

9,10-Dihydro-4,5-tetramethylene-8a,10a-diazoniaphenanthene Dibromide (6d). Following the procedure described above for **6a**, 50 mg (0.24 mmol) of **2d** afforded 58 mg (63%) of **6d** as a yellow solid, mp >300 °C: ^1H NMR (300 MHz, D_2O) δ 8.99 (d, $H_{1,8}$, $J_{1,2}$ = 5.8 Hz), 8.72 (dd, $H_{3,6}$, $J_{2,3}$ = 8.3, $J_{1,3}$ = 1.0 Hz), 8.16 (dd, $H_{2,7}$), 5.05 (d of q, $H_{9,10}$), 3.14 (dd, 2H), 2.21 (t, 2 H), 2.12 (t, 2H), 1.66 (quintet, 2H).

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Regiochemistry and Stereochemistry of Nickel-Promoted, Carbon–Carbon Bond-Forming Reactions of Cyclic Sulfur Compounds

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Reactions of methylmagnesium iodide and phenylmagnesium bromide with thianaphthene, dibenzothiophene, thianthrene, and 2,3-dihydrothiapyran in the presence of [1,3-bis(diphenylphosphino)propyl]nickel dichloride have been shown to yield, regioselectively in most cases, ring-opened products in which the carbon–sulfur bonds have been replaced by carbon–carbon bonds. Stereospecific carbon–carbon bond formation has taken place in the reactions of thianaphthene and 2,3-dihydrothiapyran, the products having maintained the cis-olefin configuration of the starting sulfur compounds. Isomerization into the more stable compounds has been observed in some cases.

The last five years have witnessed the discovery[1,2] and subsequent general study[3-13] of carbon–carbon bond-forming reactions between alkenyl or aryl sulfides and Grignard reagents in the presence of phosphine-ligated

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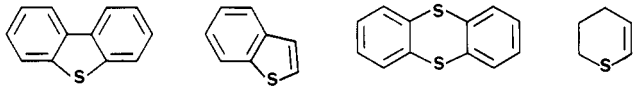
nickel species. In the case of alkenyl sulfides the reaction is highly stereoselective, proceding with nearly complete retention of configuration.[1,2,5-7,9,11] In the aromatic series regiospecific bond formation was observed for reactions of compounds of the Ar(SR)SR′ and ArR(SR′)$_2$ types, the arene–sulfur bond scissions occurring at the least hindered sites.[10] Thio heteroaromatic compounds also undergo nickel-induced reactions with Grignard reagents, giving ring-opened products in which the carbon–sulfur linkages have been replaced by carbon–carbon bonds, e.g., the convenient, one-step synthesis of 1,4-disubstituted 1,3-butadienes from thiophene (as well as from furan, selenophene, and tellurophene).[2,11] Exposure of thianaphthene and dibenzothiophene to an excess of methylmagnesium or phenylmagnesium bromide and a catalytic quantity of bis(triphenylphosphine)nickel dichloride ((tpp)$_2$NiCl$_2$) in refluxing benzene solution has yielded mixtures of *Z* and *E* isomers of *o*-propenyltoluenes or *o*-phenylstilbenes and *o,o*′-ditolyl or *o,o*′-quaterphenyl, respectively.[2] These early experiments revealed little regarding the nature of the reaction intermediates and hence the relative ease of the two carbon–sulfur bond cleavages or regarding the stereochemical course of the thianaphthene reactions.

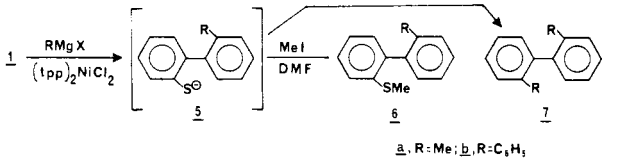
In order to gain some insight into the regio- and stereochemistry of carbon–carbon bond-forming reactions of cyclic sulfur compounds, a more detailed study was needed. Thus an investigation, aiming toward the discovery of experimental conditions favoring optimum regio- and stereoselectivity of the reactions, was undertaken and dibenzothiophene (**1**), thianaphthene (**2**), thianthrene (**3**), and 2,3-dihydrothiapyran (**4**) were chosen as representative starting materials for the study. The structures and relative yields of the reaction products were examined as a function of the nature of the Grignard reagents (used in stoichiometric or excess quantity), the nickel ligands, and the reaction temperature.



1 **2** **3** **4**

Results and Discussion

The first experiments, carried out on dibenzothiophene (**1**), were conducted with stoichiometric quantities of methylmagnesium iodide or phenylmagnesium bromide and a catalytic amount of (tpp)$_2$NiCl$_2$ in benzene solution at room temperature. The reaction progress was monitored by gas-phase chromatography on small aliquots of the reaction mixtures, diluted with a dimethylformamide solution of methyl iodide for the transformation of the products of monomethylation or monophenylation (**5**)[13] into their *S*-methyl derivatives **6**.

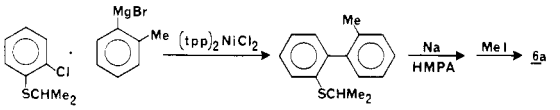


5 **6** **7**

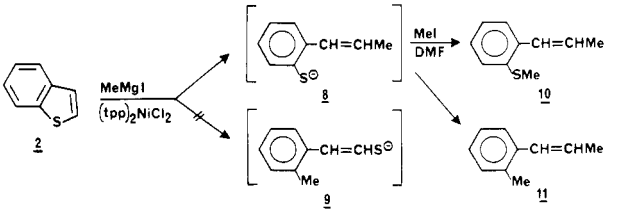
a, R = Me; **b**, R = C_6H_5

Whereas in the reaction of methylmagnesium iodide a mixture of mono- and disubstitution products (**6a** and **7a**, respectively) was observed even at an early reaction stage, no evidence for the presence of the monosubstitution product **6b** could be found in the reaction of phenylmagnesium bromide. Thus even under mild conditions the reactions showed no selectivity. Thus in the first case the reagent did not discriminate between the starting material (**1**) and intermediate **5a**, the two reactions proceeding with comparable rates, and in the second case the intermediate **5b** was more reactive than the starting compound.

The identity of the S-methylated monosubstitution product **6a** was confirmed by the following independent synthesis.[8,14]



The reaction of thianaphthene (**2**) with methylmagnesium iodide and (tpp)$_2$NiCl$_2$ at room temperature was interesting in that it was found to proceed in a stepwise manner. The first step was regiospecific, involving bond scission between carbon 2 and sulfur and yielding intermediate **8**. Thus the reactivity of the starting compound **2** was distinctly higher than that of intermediate **8**. No evidence was found pointing to the intermediacy of compound **9**, the product of initial arene–sulfur bond cleavage. The exclusive formation of intermediate **8** was expected on the basis of the well-documented fact that the sulfur displacement of alkenyl sulfides is faster than that of aryl sulfides.[1,2,6] This fact also explained the observed difference in behavior of dibenzothiophene (**1**) and thianaphthene (**2**).



2 **8** **10** **9** **11**

The thianaphthene reaction proved to be nonstereospecific, as the S-methylated product **10** consisted of a 1:1 mixture of *o*-(*Z*)- and *o*-(*E*)-propenylthioanisoles. Hence a more efficient catalyst was needed. Previous observations had shown that [1,3-bis(diphenylphosphino)propyl]nickel dichloride (dpppNiCl$_2$) is more efficient than (tpp)$_2$NiCl$_2$ in promoting the conversion of carbon–sulfur into carbon–carbon bonds. Thus, for instance, in contrast to the inertness of *p-tert*-butylthioanisole toward ethyl-

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(8) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Wenkert, E. *Tetrahedron Lett.* **1982**, 4629.
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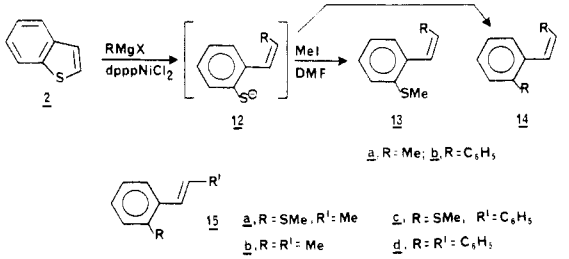
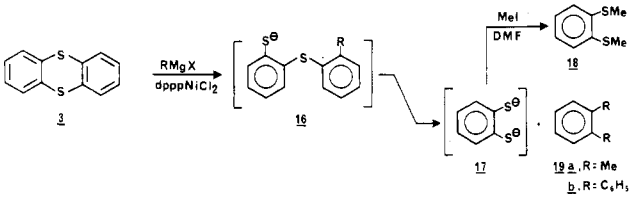
(10) Tiecco, M.; Testaferri, L.; Tingoli, M.; Wenkert, E. *Tetrahedron* **1983**, *39*, 2289.
(11) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1984**, 617.
(12) Wenkert, E.; Hanna, J. M., Jr.; Leftin, M. H.; Michelotti, E. L.; Potts, K. T.; Usifer, D. *J. Org. Chem.* **1985**, *50*, 1125.
(13) For the sake of simplicity the monosubstitution products (e.g., **5**) are portrayed as free thiolate anions, even though they undoubtedly are associated with the magnesium or nickel counter ions.
(14) Maiolo, F.; Testaferri, L.; Tiecco, M.; Tingoli, M. *J. Org. Chem.* **1981**, *46*, 3070.

magnesium bromide in the presence of $(tpp)_2NiCl_2$ the sulfur compound was transformed into *p-tert*-butylethylbenzene under the influence of $dpppNiCl_2$.[2] Moreover, the use of the latter nickel species in reactions with secondary Grignard reagents has been shown to decrease greatly the competitive isomerization and reduction processes.[7] As a consequence all further reactions of compounds **1–4** were carried out with the use of catalytic quantities of $dpppNiCl_2$. The reaction of dibenzothiophene (**1**) with a stoichiometric quantity of methylmagnesium iodide at room temperature with $dpppNiCl_2$ gave results similar to those obtained with $(tpp)_2NiCl_2$. The selectivity was still poor, as the monosubstitution product (**6a**) was contamined, even at an early reaction stage, by the disubstitution product (**7a**). After five days a 2:1 mixture of biphenyls **6a** and **7a** in 65% yield was obtained.

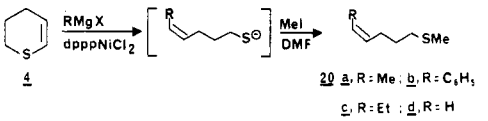
The efficiency of $dpppNiCl_2$ was evident particularly in the case of the reactions of thianaphthene (**2**). A reaction with an equivalent amount of methylmagnesium iodide at room temperature was regio- and stereospecific affording (after S-methylation) *o*-(*Z*)-propenylthioanisole (**13a**) in 84% yield. Reactions with excess of methylmagnesium iodide at 60 °C gave similar results, *o*-(*Z*)-propenyltoluene (**14a**) being the sole product isolated in 62% yield. The isomer purity of products **13a** and **14a** was confirmed by GC and ^1H NMR spectral analyses of these substances and their *E* isomers (**15a** and **15b**, respectively). The reactions of thianaphthene (**2**) with phenylmagnesium bromide led regio- and stereospecifically to *cis*-stilbenes **13b** and **14b**, as demonstrated by GC analyses of reaction mixtures at an early reaction stage. The primary products, however, proved to be configurationally unstable in the reaction medium, suffering partial isomerization into the more stable *trans*-stilbenes. A similar isomerization had been noted for the products obtained from the $dpppNiCl_2$-catalyzed reactions of benzofuran with Grignard reagents.[15] Isomerization of the stilbenes derived from thianaphthene (**2**) occurred also during reaction workup and product isolation, a 2.5:1 *Z*/*E* mixture (70% yield) of **13b** and **15c** and a 1:1 *Z*/*E* isomer mixture (70%) of **14b** and **15d** being obtained from reactions carried out at room temperature and at 60 °C, respectively.



The next experiments concerned thianthrene (**3**). Whereas the first step in reactions of this compound with Grignard reagents presents no problems of regioselectivity, the second step (i.e., the reactions of intermediate **16**), in principle, can take place at three different sites. The reactions of thianthrene (**3**) with excess methylmagnesium iodide or phenylmagnesium bromide in the presence of $dpppNiCl_2$ at room temperature were highly regioselective, affording nearly equimolar amounts *o*-bis(methylthio)benzene (**18**, derived from intermediate **17**) (67% and 65%, respectively) and *o*-xylene (**19a**) (60%) or *o*-terphenyl (**19b**) (60%). Compounds **17** and **19** were present in the reaction mixtures even after short reaction times, indicative of the fact intermediate **16** is undergoing reactions with Grignard reagents at rates comparable with or greater than those of the starting material (**3**). Intermediate **17** reacted slowly with Grignard reagents, affording more substituted benzenes **19**. Thus the reaction of phenylmagnesium bromide (8 equiv) with thianthrene (**3**) in refluxing benzene for 72 h gave *o*-terphenyl (**19b**) in 80% yield.



No problems of regioselectivity were expected in the reactions of 2,3-dihydrothiopyran (**4**) in view of the known fact dialkyl sulfides do not undergo carbon–sulfur cleavage.[1,2] The reaction of 2,3-dihydrothiopyran (**4**) with Grignard reagents under the influence of $dpppNiCl_2$ in refluxing benzene proceeded with complete stereospecificity, giving (after methyl iodide treatment) solely cis-olefinic products **20**. Thus, methylmagnesium iodide, phenylmagnesium bromide, and ethylmagnesium bromide produced olefins **20a–c** in 52, 61, and 59% yields, respectively. It is noteworthy that no reduction product (**20d**) emanated from the reaction with ethylmagnesium bromide.



Experimental Section

Melting points were taken on a Reichert micro hotstage and are uncorrected. ^1H NMR spectra of $CDCl_3$ solutions were recorded on a Varian EM-390 spectrometer and ^{13}C NMR spectra of $CDCl_3$ solutions were measured on a wide-bore, broad-band Nicolet NT-200 spectrometer (with Oxford magnet), operating at 50.3 MHz in the Fourier transform mode. The carbon shifts are in part per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) - 76.9$ ppm. Gas chromatographic analyses were performed with a 20-in. 10% UCW 982 column on a Hewlett-Packard 5830A chromatograph. Elemental analyses were recorded on a Carlo Erba Model 1106 Elemental Analyzer.

General Procedure for the Grignard Reactions on the Cyclic Sulfur Compounds. A 3.0 M ethereal solution of methylmagnesium iodide (0.5 mL, 1.5 mmol) was added to a stirred suspension of $(tpp)_2NiCl_2$ or $dpppNiCl_2$ (0.75 mmol) in 15 mL of dry benzene under an atmosphere of helium. After 15 min at room temperature there was added first an ethereal solution of the required Grignard reagent (15.0 mmol) and then a solution of the sulfur compound (7.5 mmol) in 5 mL of dry benzene. The mixture was stirred at room temperture or 60 or 80 °C (see Discussion) for the time periods indicated below. Thereafter it was concentrated to a volume of 5 mL at room temperature under vacuum, cooled in an ice bath, and diluted slowly with 15 mL of dry DMF. A solution of methyl iodide (1.5 mmol) in 2 mL of dry DMF was added dropwise to the cooling mixture and the temperature maintained for 30 min. The mixture was poured into a saturated aqueous ammonium chloride solution and extracted with ether. The extract was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. Chromatography of the residue on 50 g of silica and elution with 200:1 hexane–ether furnished the products.

***o*-Methyl-*o'*-(methylthio)biphenyl (6a)**: 55% yield (by GC analysis); reaction time, 15 h; mp 53–55 °C; ^1H NMR δ 2.10 (s, 3, Me), 2.30 (s, 3, SMe), 6.9–7.4 (m, 8, aromatic Hs).

Anal. Calcd for $C_{14}H_{14}S$: C, 78.44; H, 6.60; S, 14.96. Found: C, 78.15; H, 6.70; S, 15.05.

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o-Bitolyl (7a): 15% yield (by GC analysis); spectrally identical with an authentic sample.[2]

o,o'-Quaterphenyl: 52% yield (reaction time: 15 h); spectrally identical with an authentic sample.[2]

o-(Z)-Propenylthioanisole (13a): reaction time, 45 h; colorless liquid; ^{1}H NMR δ 1.78 (dd, 3, J = 7, 2 Hz, Me), 2.34 (s, 3, SMe), 5.90 (dq, 1, J = 12, 7 Hz, olefinic H), 6.50 (dq, 1, J = 12, 2 Hz, benzyl H), 6.9–7.5 (m, 4, aromatic Hs).

Anal. Calcd for $C_{10}H_{12}S$: C, 73.11; H, 7.38; S, 19.51. Found: C, 73.31; H, 7.12; S, 19.65.

o-(Z)-Propenyltoluene (14a): reaction time, 15 h; colorless liquid; ^{1}H NMR δ 1.75 (dd, 3, J = 7, 2 Hz, olefinic Me), 2.25 (s, 3, ArMe), 5.75 (dq, 1, J = 12, 7 Hz, olefinic H), 6.45 (dq, 1, J = 12, 2 Hz, benzyl H), 7.0–7.3 (m, 4, aromatic Hs).

Anal. Calcd for $C_{10}H_{12}$: C, 90.83; H, 9.17. Found: C, 90.65; H, 9.10.

o-(Methylthio)-(Z)-stilbene (13b): 55% yield (by GC analysis); reaction time, 45 h; colorless liquid; ^{1}H NMR δ 2.40 (s, 3, Me), 6.65 (4-line AB, 2, J = 12 Hz, olefinic Hs), 6.8–7.5 (m, 9, aromatic Hs).

Anal. Calcd for $C_{15}H_{14}S$: C, 79.59; H, 6.25; S, 14.16. Found: C, 79.68; H, 6.15; S, 14.25.

o-(Methylthio)-(E)-stilbene (15c): 28% yield (by GC analysis); colorless liquid; ^{1}H NMR δ 2.40 (s, 3, Me), 7.25 (4-line AB, 2, J = 17 Hz, olefinic Hs), 7.0–7.6 (m, 9, aromatic Hs).

Anal. Calcd for $C_{15}H_{14}S$: C, 79.59; H, 6.25; S, 14.16. Found: C, 79.80; H, 6.45; S, 14.30.

o-Phenyl-(Z)-stilbene (14b): reaction time, 48 h; mp 58–60 °C; ^{1}H NMR δ 6.41 (4-line AB, 2, J = 12 Hz, olefinic Hs), 7.0–7.5 (m, 14, aromatic Hs).

Anal. Calcd for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.80; H, 6.41.

o-Phenyl-(E)-stilbene (15d): mp 61–63 °C; ^{1}H NMR δ 7.05 (4-line AB, 2, J = 17 Hz, olefinic Hs), 7.1–7.9 (m, 14, aromatic Hs).

Anal. Calcd for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.52; H, 6.51.

o-Bis(methylthio)benzene (18): reaction time, 36 h; spectrally identical with the known compound.[14]

o-Xylene (19a): spectrally identical with a commercial sample.

o-Terphenyl (19b): reaction time, 36 h; spectrally identical with an authentic specimen.[10]

6-(Methylthio)-2(Z)-hexene (20a): reaction time, 15 h; colorless liquid; ^{1}H NMR δ 1.4–1.9 (m, 5, Me, 2 H-5), 2.10 (s, 3, SMe), 1.9–2.4 (m, 2, 2 H-4), 2.50 (t, 2, J = 8 Hz, SCH_2), 5.1–5.7 (m, 2, olefinic Hs); ^{13}C NMR δ 12.7 (C-1), 15.4 (SMe), 25.8 (C-4), 28.8 (C-5), 33.7 (C-6), 124.6 (C-2), 129.4 (C-3).

Anal. Calcd for $C_7H_{14}S$: C, 64.53; H, 10.85; S, 24.62. Found: C, 64.47; H, 11.00; S, 24.80.

6-(Methylthio)-1-phenyl-1(Z)-pentene (20b): reaction time, 3 h; colorless liquid; ^{1}H NMR δ 1.5–1.9 (m, 2, 2 H-4), 2.00 (s, 3, Me), 2.2–2.6 (m, 4, 2 H-3, SCH_2), 5.55 (dt, 1, J = 12, 7 Hz, H-2), 6.35 (dt, 1, J = 12, 2 Hz, H-1), 7.0–7.4 (m, 5, aromatic Hs); ^{13}C NMR δ 15.4 (Me), 27.6 (C-3), 29.3 (C-4), 33.7 (C-5), 126.4 (*p*-C), 128.0 (*o*-C), 128.5 (*m*-C), 129.4 (C-2), 131.6 (C-1), 137.3 (ipso-C).

Anal. Calcd for $C_{12}H_{16}S$: C, 74.93; H, 8.40; S, 16.67. Found: C, 75.02; H, 8.65; S, 16.45.

7-(Methylthio)-3(Z)-heptene (20c): reaction time, 15 h; colorless liquid; ^{1}H NMR δ 0.95 (t, 3, J = 8 Hz, Me), 1.4–1.9 (m, 2, 2 H-6), 2.10 (s, 3, SMe), 1.8–2.3 (m, 4, allyl Hs), 2.50 (t, 2, J = 8 Hz, SCH_2), 5.1–5.6 (m, 2, olefinic Hs); ^{13}C NMR δ 14.2 (C-1), 15.4 (SMe), 20.4 (C-2), 26.0 (C-5), 29.0 (C-6), 33.6 (C-7), 127.8 (C-4), 132.4 (C-3).

Anal. Calcd for $C_8H_{16}S$: C, 66.58; H, 11.20; S, 22.22. Found: C, 66.65; H, 11.30; S, 22.05.

o-Methyl-o'-(methylthio)biphenyl (6a). A 3.0 M ethereal solution of methylmagnesium iodide (0.25 mL, 0.75 mmol) was added to a stirred suspension of 0.38 mmol of $(tpp)_2NiCl_2$ in 10 mL of dry benzene under helium. After 15 min at room temperature a 2.0 M ethereal solution of *o*-tolylmagnesium bromide (5.7 mL) was added and the mixture concentrated to a volume of 8 mL. A solution of 3.8 mmol of *o*-chlorophenyl isopropyl sulfide in 7 mL of dry benzene was added and the mixture heated at 60 °C for 20 h. It then was poured into a saturated ammonium chloride solution and extracted with ether. The extract was dried (Na_2SO_4) and evaporated under vacuum. Chromatography of the residue on 20 g of silica and elution with 200:1 hexane–ether led to 120 mg of starting chloride and 360 mg (68%, based on utilized starting compound) of *o*-methyl-*o'*-(isopropylthio)biphenyl: colorless liquid; ^{1}H NMR δ 1.12 (d, 3, J = 8 Hz, *i*-PrMe), 1.15 (d, 3, J = 8 Hz, *i*-PrMe), 2.10 (s, 3, Me), 3.25 (sept., 1, J = 8 Hz, SCH), 7.0–7.5 (m, 8, aromatic Hs).

Metallic sodium (70 mg, 3 mmol) was added to a stirred solution of *o*-methyl-*o'*-(isopropylthio)biphenyl (240 mg, 1 mmol) in 10 mL of dry HMPA at 100 °C under an atmosphere of nitrogen. After 2 h the resultant solution was cooled to room temperature and a solution of methyl iodide (1.5 mmol) in 2 mL of dry HMPA added. After 15 min the mixture was poured into water and extracted with ether. The extract was washed exhaustively with water and brine, dried (Na_2SO_4), and evaporated under reduced pressure. Chromatography of the residue on silica and elution with pentane gave 180 mg (85%) of biphenyl **6a**.

Olefin Isomerization. The *Z* olefins were exposed to a trace of thiophenol and AIBN without solvent under nitrogen at 90 °C for 1 h. Chromatography of the crude product on silica and elution with pentane gave the corresponding *E* isomers.

o-(E)-Propenylthioanisole (15a): colorless liquid; ^{1}H NMR δ 1.90 (dd, 3, J = 7, 2 Hz, Me), 2.40 (s, 3, SMe), 6.10 (dq, 1, J = 16, 7 Hz, olefinic H), 6.80 (dq, 1, J = 16, 2 Hz, benzyl H), 6.9–7.5 (m, 4, aromatic Hs).

Anal. Calcd for $C_{10}H_{12}S$: C, 73.11; H, 7.38; S, 19.51. Found: C, 73.00; H, 7.48; S, 19.55.

o-(E)-Propenyltoluene (15b): colorless liquid; ^{1}H NMR δ 1.90 (dd, 3, J = 7, 2 Hz, olefinic Me), 2.30 (s, 3, ArMe), 6.10 (dq, 1, J = 16, 7 Hz, olefinic H), 6.55 (dq, 1, J = 16, 2 Hz, benzyl H), 7.0–7.5 (m, 4, aromatic Hs).

Anal. Calcd for $C_{10}H_{12}$: C, 90.90; H, 9.10. Found: C, 91.02; H, 8.95.

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