

Condensed Thiophenes from Sulfur Bridging. I. Phenanthro[4,5-*bcd*]thiophene (1)

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Treatment of phenanthrene with hydrogen sulfide and an alumina catalyst at 630° gives phenthro[4,5-*bcd*]thiophene (XVII). Spectral properties of XVII, its sulfoxide, and its sulfone are presented. Other examples of the direct insertion of a sulfur bridging atom into an aromatic molecule are reviewed.

The synthesis of a condensed aromatic compound bearing an internal, catenated thiophene ring, can be effected by means of a dehydro-1,4-cycloaddition reaction between a biaryl-type compound and either elemental sulfur or a sulfur donor. This process accomplishes direct insertion of a sulfur atom bridge between the two aromatic rings which are joined through the pivotal bond of the biaryl substrate. In the simplest case, biphenyl is thus transformed into dibenzothiophene. Three different methods have been used for this reaction: namely (a) treatment with sulfur and aluminum chloride at 100-265° in a Friedel-Crafts type of reaction (4), (b) heating with sulfur at 190-320° (without added catalyst), and (c) treatment with hydrogen sulfide and a heterogeneous catalyst at *ca.* 630°.

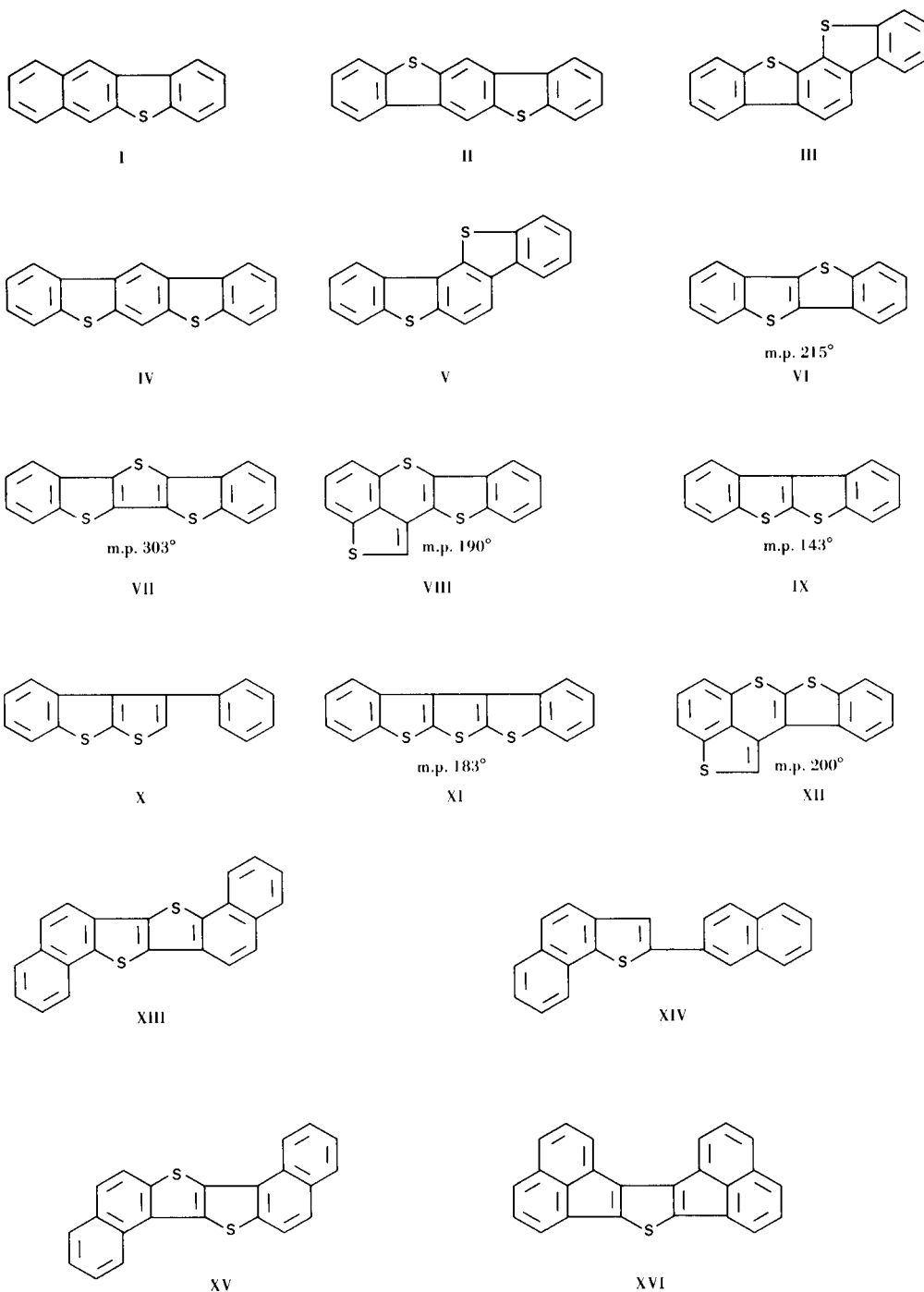
Method (a) was employed to convert biphenyl into dibenzothiophene in good yield (60-80%) (5). With this method, however, other substrates gave mixtures from which pure products were isolated only in small amounts. Thus, the transformations 2-phenylnaphthalene → I (6); *p*-terphenyl → II (2%) and III (1%) (7); *m*-terphenyl → IV (3%), V (2%), and II (< 1%, probably formed by preliminary isomerization of substrate) (8); 3-phenylbenzo[*b*]thiophene → VI (5%, by isomerization) (9); and 2,2'-bisbenzo[*b*]thiophene → VII (16%) (8) have been reported. Also 2,3'- and 3,3'-bisbenzo[*b*]thiophenes formed VII plus a second product assigned structure VIII (from dehydro-1,5-cycloaddition) (9).

Use of method (b) has not been reported with biphenyl (see Experimental) though it has effected the conversions 3-phenylbenzo[*b*]thiophene → IX (20%); X → XI (20%), and 3,3'-bisbenzo[*b*]thiophene → XII (51%) (9) without attendant skeletal rearrangement. For a substrate of the alkylarene type, *in situ* formation of an aryl-substituted condensed thiophene may well precede sulfur bridging, as exemplified by the transformation 2-methylnaphthalene → [dehydrodimer → XIV] → XIII (or an isomer) (25% overall yield) (9-11). Analogously, structure XV has been postulated (12a,13) for a product obtained from 1-methyl-

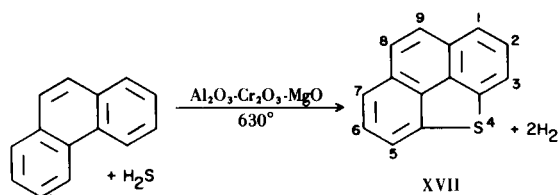
naphthalene (10), and acenaphthene → XVI (14). The isolation of both 2-phenylbenzo[*b*]thiophene and an incompletely identified product C₁₄H₈S₂ (m.p. 209°, possibly VI) from treatment of toluene with sulfur (11,12b) is consistent with the suggested pathway. Dimerization must also occur in the reaction benzo[*b*]thiophene → C₁₆H₈S₃ (m.p. 190-193°, perhaps VIII or XII) (15).

Only a single instance of the use of method (c) to accomplish sulfur bridging, *viz.* the conversion of biphenyl into dibenzothiophene (29% yield for a single pass), by means of hydrogen sulfide and an alumina-chromia-silica catalyst in a flow system was found in the literature (12c,16). We have undertaken further study of method (c) as a synthetic route to various sulfur-bridged products. An investigation of alternative catalysts for formation of dibenzothiophene indicated that alumina bearing thoria or chromia gave considerably higher yields than pure alumina or alumina-silica, while ferrous sulfide was completely inactive (Table I, Experimental). In fact, Harshaw catalyst Cr-0101T (alumina-chromia-magnesia), which had shown some activity for conversion of 4-vinylpyridine and hydrogen sulfide into thieno[2,3-*c*]pyridine at 500-550° (17a), seemed to be slightly better than other alumina-based catalysts tried (59% yield of dibenzothiophene for a single pass). We therefore selected this catalyst for use with other substrates (*vide infra*). It might be noted, however, that variation in yield with the nature of the reactor packing, and especially the failure to achieve any reaction with ferrous sulfide, is strong evidence that the reaction is, indeed, heterogeneously catalyzed. In fact, ferrous sulfide plus elemental sulfur likewise gave no reaction with biphenyl at 630° under the same conditions. Therefore, method (c) is not equivalent to method (b) in its mechanistic aspects.

Use of phenanthrene as substrate in method (c) has now been found to produce the previously unknown compound phenanthro[4,5-*bcd*]thiophene (XVII), a *peri*-condensed thiophene (39% yield, equation 1). A subsequent paper (18) will be concerned with sulfur bridging in



phenylpyridines, bipyridines, and phenylquinolines by the same method.



Compound XVII readily formed a sulfoxide (XVIII) and a sulfone (XIX). The structure of XVII was established by microanalyses and spectral investigations of these three crystalline compounds. Particularly pertinent, in this regard, are: (a) the presence of mass spectral parent ion peaks at m/e 208, 224, and 240, respectively, in these compounds; (b) the close similarity between ultraviolet spectra of XVII and its hydrocarbon isostere, pyrene (Figure 1); (c) the close similarity in infrared spectral

patterns of XVII and its hydrocarbon analog, 4,5-methylenephenanthrene (XX) (both of point group C_{2v}) in the

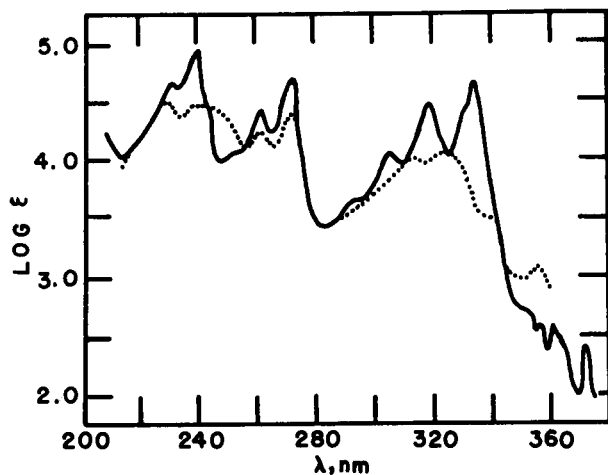
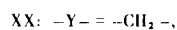
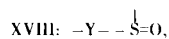
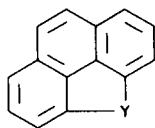
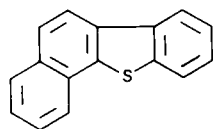


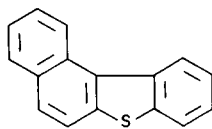
Figure 1. Ultraviolet spectra for pyrene (solid line) (28a) and XVII (dotted line) in 95% ethanol.

aromatic C-H out-of-plane bending region, $670-850\text{ cm}^{-1}$; and (d) the 100 MHz NMR spectrum of XVII, which exhibits a singlet for protons at C-8 and C-9, superimposed on a pattern indicative of an ABC system for the other aromatic protons.

Examination of Figure 1 shows that XVII exhibits the same four regions of ultraviolet absorption as occur for pyrene, but the spectrum of XVII shows a more limited development of fine structure. Badger and Christie (19) noted the similarity of patterns in the ultraviolet absorption spectra of the isosteric pairs, phenanthrene-dibenzothiophene, benz[*a*]anthracene-1, chrysene-XXII, and benzo[*c*]phenanthrene-XXIII (20). It is thus



XXII



XXIII

apparent that a non-bonding pair of electrons on the sulfur atom functions as part of the overall chromophoric π -system in these rigid, planar condensed thiophenes.

According to the theory of Koch and Moffitt (21), one would expect XIX to show "type I" conjugation, which involves overlap of a π molecular orbital of the phenanthrene moiety with a weakly bonding sulfonyl group orbital of the same symmetry and/or with a vacant sulfur 3d atomic orbital. Examination of Figure 2 shows that, indeed, XIX absorbs strongly in the ultraviolet region and that its spectrum is distinctly different from either that of pyrene or that of phenanthrene. In an extension of the

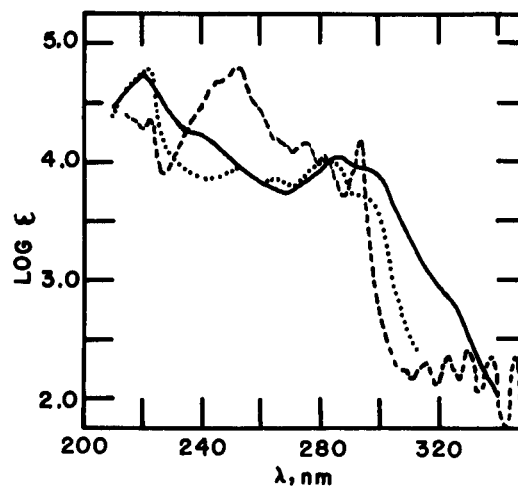


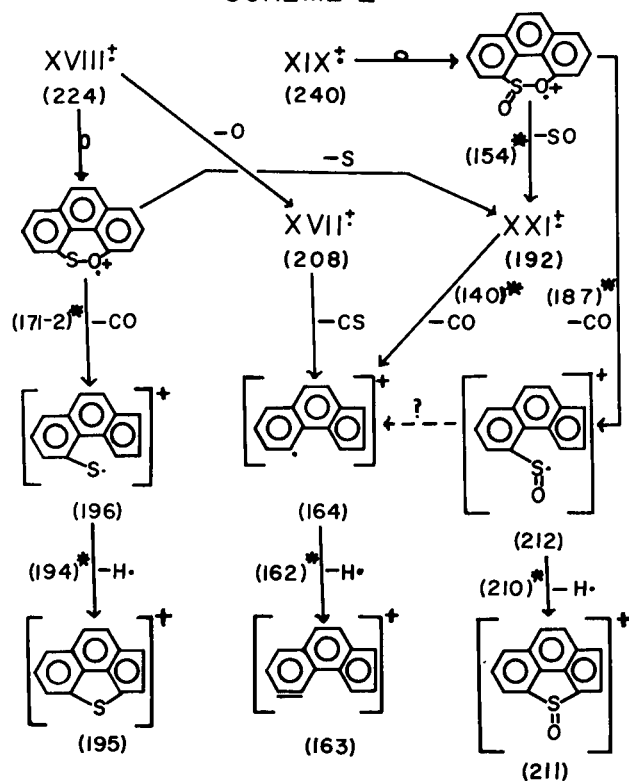
Figure 2. Ultraviolet spectra for phenanthrene (broken line) (28b), sulfoxide XVIII (solid line), and sulfone XIX (dotted line) in 95% ethanol.

theory, Koch (22) predicted that due to a lower degree of symmetry the sulfinyl group should show less conjugating power than the sulfonyl group and, hence, the ultraviolet spectra of sulfide, sulfoxide, and sulfone congeners should differ (with the sulfoxide spectrum, perhaps, intermediate to the others). This prediction is not substantiated for XVIII, which shows a spectrum closely similar to that of XIX (Figure 2). In the dibenzothiophene series the spectra of all three congeners are similar, while in the series XXIII only the sulfoxide and sulfone spectra resemble one another closely throughout the range of wavelength studied (19). It is apparent at this time that in the sulfoxides of these three series the non-bonding electron pair on the sulfur atom contributes very little to absorption of ultraviolet light by the molecule.

Scheme 1 accounts for the majority of the pertinent peaks found in the mass spectra of XVII-XIX. The fragmentation scheme is similar to ones reported for the dibenzothiophene series (23). Thus, sulfide XVII elimi-

nates HCS in two successive steps. Sulfoxide XVIII either loses an oxygen atom to enter the fragmentation pathway of XVII or rearranges to a cyclic sulfenate ester, which then loses a sulfur atom to produce an ion of mass number 192 (*vide infra*) or (more likely) eliminates HCO in two steps. Ions of mass numbers 195 and 196 have counterparts in the dibenzothiophene system. Sulfone XIX loses little oxygen directly [1% relative abundance for (M-16) peak; 5% for (M-32) peak]. Instead, it mainly rearranges to a cyclic sulfinate ester which either eliminates HCO directly or eliminates SO and then HCO. Most of the elimination steps are corroborated by the presence of

SCHEME I



peaks for metastable ions. The ion of mass number 192 is presumed to have the structure of XXI, a heterocycle analogous to dibenzofuran (postulated in the fragmentation pathway of dibenzothiophene sulfone). From considerations of steric strain, the ion of mass number 164 is presumed to lose a hydrogen atom to give an arylene structure (as shown) rather than to form a 4-membered ring (as proposed in the dibenzothiophene series). The analogous transformations of the dibenzothiophene and XVII systems on electron impact again serve to corroborate the structures assigned to XVII-XIX.

EXPERIMENTAL (24)

Reaction of Biphenyl with Hydrogen Sulfide.

This reaction was conducted in a flow apparatus as described previously (17b)-packed monel tube, hydrogen sulfide carrier gas, reaction temperature $630 \pm 15^\circ$ (unless otherwise noted), and dropwise addition of biphenyl in benzene solution. A solution of the crude product in cold acetone was filtered to remove sulfur and evaporated to dryness. The residue was analyzed by vpc as described previously (17b) but with a He flow rate of 60 ml./minute; retention times: biphenyl, 5 minutes; dibenzothiophene, 34 minutes. Yield data for various packings are presented in Table I.

Phenanthro[4,5-*bcd*]thiophene (XVII).

Reaction of phenanthrene with hydrogen sulfide was conducted at $630 \pm 15^\circ$ with Harshaw Cr-0101T catalyst (1/8" pellets) in the foregoing manner. A solution of 15 g. of phenanthrene in 55 ml. of benzene was added to the reactor at the rate of 26 drops/minute.

The crude product, collected as previously (17b), was chromatographed by means of 150 g. of Alcoa F-20 alumina and cyclohexane to give a mixture of XVII (39% yield) and unreacted phenanthrene (54% recovery), as determined by nmr analysis. Crystallization of the mixture from petroleum ether ($30-60^\circ$) gave yellow product, m.p. $135-137.5^\circ$. Recrystallizations from ethanol and sublimation at 130° (0.5 mm.) gave white needles of XVII, m.p. $139-140^\circ$.

Anal. Calcd. for $C_{14}H_8S$: C, 80.73; H, 3.87; S, 15.40. Found: C, 80.99; H, 3.88; S, 15.54.

Phenanthro[4,5-*bcd*]thiophene 4-Oxide (XVIII).

To a slurry of 125 mg. (0.6 mmole) of XVII in 4 ml. of acetonitrile-water (3:1 by volume) was added, during a period of 20 minutes, a solution of 177 mg. (0.64 mmole) of iodobenzene dichloride (25) in 3 ml. of acetonitrile. The mixture was stirred for 2 hours, diluted with 15 ml. of water, and extracted with chloroform. Evaporation of the residue (magnesium sulfate) extract and crystallization of the residue from acetone-hexane gave 57 mg. (42% of XVIII, m.p. $191-193^\circ$; obtained as cream-colored needles on further recrystallization from the same solvent, m.p. $200.5-202^\circ$.

Anal. Calcd. for $C_{14}H_8OS$: C, 74.97; H, 3.60; S, 14.30. Found: C, 74.95; H, 3.91; S, 14.02.

Phenanthro[4,5-*bcd*]thiophene 4,4-Dioxide (XIX).

A solution of 104 mg. of XVII in 3 ml. of glacial acetic acid and 1 ml. of 30% hydrogen peroxide was refluxed for 25 minutes. Addition of 10 ml. of water and cooling to -20° produced crystals of XIX, collected by filtration; yield 86 mg. (72%), m.p. $265-267^\circ$; obtained as cream-colored needles, m.p. $271.5-273^\circ$ dec., on recrystallization from acetone.

Anal. Calcd. for $C_{14}H_8O_2S$: C, 69.98; H, 3.36; S, 13.34. Found: C, 69.66; H, 3.17; S, 13.30.

Spectral Investigations of XVII-XIX.

Ultraviolet absorption spectra were determined on ethanolic solutions by means of a Cary Model 15 spectrophotometer: for XVII, λ max 230 nm (log ϵ 4.49), 245 (4.48), 262 (4.22), 272.5 (4.38), 311 (3.99), 325 (4.07), 338 (shoulder, 3.52), 356 (3.10); for XVIII, λ max 220 nm (log ϵ 4.73), 285 (4.06), 298 (shoulder, 3.91); for XIX, λ max 222 nm (log ϵ 4.76), 253 (3.93), 267 (3.88), 282.5 (4.05), 295 (shoulder, 3.72).

TABLE I

Exploratory Runs for Reaction of Biphenyl with Hydrogen Sulfide at 630°

Catalyst Composition	Catalyst Source and Designation	% Yield (a) of Dibenzothiophene
FeS, 85% min. purity	Baker and Adamson (8-60 mesh)	0
Al ₂ O ₃ (13%)/SiO ₂ (87%)	American Cyanamid Aerocat Catalyst	31
Al ₂ O ₃	Houdry HA 100	33
Al ₂ O ₃	Harshaw Al-0104T	35
Al ₂ O ₃ (90%)/ThO ₂ (10%)	Harshaw Th-0101T	54
Al ₂ O ₂ (95%)/Cr ₂ O ₃ (5%)	Harshaw Cr-0104T	56
Al ₂ O ₃ (81%)/Cr ₂ O ₃ (19%)	Harshaw Cr-1404T	57
Al ₂ O ₃ (86%)/Cr ₂ O ₃ (12%)/MgO (2%)	Harshaw Cr-0101T	59 (b)

(a) Based on total amount of biphenyl charged to the reactor in a single pass. (b) Runs at 580° and 680° gave yields of 55%.

Infrared absorption spectra of XVII and 4,5-methylenephenanthrene were determined in the region of 670-850 cm⁻¹ on potassium bromide pellets by means of a Beckman IR-5A instrument. Strong to very strong bands were found at 696, 745, and 815 cm⁻¹ for XVII and at 692, 751, and 815 cm⁻¹ for the hydrocarbon. Spectra of XVIII and XIX (latter by means of an IR-7 instrument) were measured on chloroform solutions: for XVIII, very strong bands at 1030 (sulfoxide) and 820 cm⁻¹ (two vicinal H); for XIX, strong, sharp bands at 1320 and 1160 cm⁻¹ (close doublet) (sulfone) and medium, sharp bands at 1110 (sulfone?) (26) and 830 cm⁻¹ (two vicinal H).

The mass spectra were determined by means of a CEC Model 21-110 instrument at 70 eV and inlet temperatures of 100°, 160°, and 165°, respectively; for XVII, m/e (relative abundance) (27), 210 (6), 209 (17), 208 (100), 207 (7), 206 (6), 163 (13), 104 (13, M⁺); for XVIII, 226 (7), 225 (16), 224 (100), 210 (5), 209 (13), 208 (77), 207 (8), 206 (6), 196 (17), 195 (39), 192 (11), 170 (7), 163 (17), 152 (7), 150 (5), 112 (10, M⁺), 104 (14, see XVII), 103 (5), 98 (5), 97.5 (8), 87 (5), 76 (5), 74 (5); for XIX, 242 (5), 241 (14), 240 (90), 212 (8), 211 (26), 208 (5), 195 (6), 193 (16), 192 (100), 174 (7), 164 (7), 163 (23), 150 (7), 139 (5), 96 (8), 87 (7), 81.5 (5), 75 (7), 74 (5).

The NMR spectra were determined by means of a Varian Associates HA-100 instrument on deuteriochloroform solutions with tetramethylsilane used for lock signal. Integrations of peak areas were determined by cutting and weighing the spectrograms for sweep widths of 100 Hz. Compound XVII showed a singlet at δ 7.69 ppm (H-8 and H-9) superimposed on a multiplet at 7.4-7.76 (total 6H), and a doublet of doublets at 7.83 (2H, $J = 1.6$ Hz, $J = 7$ Hz, probably H-3 and H-5). Compound XVIII showed a singlet at δ 7.69 ppm (H-8 and H-9) superimposed on a multiplet at 7.3-7.75 (total 4H), and two multiplets of 2H each at 7.75-7.93 and 7.93-8.1. Compound XIX showed a singlet at δ 7.78 ppm (H-8 and H-9) superimposed on a multiplet at 7.4-8.1.

Treatment of Biphenyl with Sulfur.

Refluxing an equimolar mixture of biphenyl and sulfur (at 270°) for 24 hours (with or without added Harshaw catalyst Cr-0101T) gave quantitative recovery of biphenyl.

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