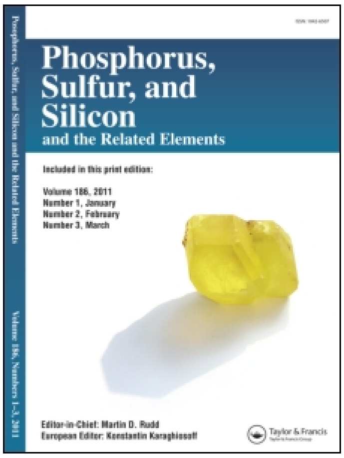

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POLYCYCLIC THIOPHENES FROM THE DIRECT INSERTION OF HETEROSULFUR BRIDGES INTO VINYLARENES, BIARYLS, AND ANGULARLY CONDENSED ARENES

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POLYCYCLIC THIOPHENES FROM THE DIRECT INSERTION OF HETEROSULFUR BRIDGES INTO VINYLARENES, BIARYLS, AND ANGULARLY CONDENSED ARENES

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There are three synthetic methods for direct introduction of a heterosulfur bridging atom into a vinylarene, biaryl, or angularly condensed arene to form a polycyclic thiophene. Two methods employ elemental sulfur, with or without a catalyst (aluminum chloride). The third method, which uses hydrogen sulfide and a heterogeneous catalyst (usually a metallic oxide) at 450–630°, is reviewed in detail. Thus, results on 20 different substrates (including a number of compounds bearing pyridine rings) are presented. Experimental observations which concern mechanistic aspects of the reaction are summarized and interpreted. For most substrates it is suggested that an ECEC mechanism prevails, whereby an adsorbed sulfide ion attacks a π-electron-deficient, adsorbed substrate to form a dihydro intermediate, which then undergoes aromatization. The substrate is adsorbed onto the catalyst either *via* the π-electrons or n-electrons (for some pyridine compounds). Type of adsorption and/or relative reactivities of ring positions may control isomeric ratios of products. For 2- and 4-vinylpyridines as substrates it is proposed that 1,2-addition leads to β-pyridylethanethiols and bis-(β-pyridylethyl) sulfides, which undergo thermal cyclization.

The sulfur bridging reaction as a laboratory and, also possibly, a natural route to the formation of polycyclic condensed thiophenes found in the environment is discussed.

1 INTRODUCTION

There is considerable current interest in the syntheses and characterizations of condensed thiophenes as reference compounds for identification of components of fossil fuels and other organic materials of geochemical origin. Synthetic samples are also desired for use in devising methods of isolation or removal of the natural compounds from their groundmasses. Unfortunately, at this time, only three parent thiophene compounds, viz. thiophene (**1**) itself, benzo[*b*]thiophene (**2**), and dibenzothiophene (**5**), are commercially available.

This paper enumerates the structural types of condensed thiophenes which have now been isolated or tentatively identified in environmental sources and discusses methods for syntheses of the parent compounds by means of direct insertion of a heterosulfur bridge into a precursor molecule (oftentimes a hydrocarbon). Particular attention is directed toward a catalytic method which employs hydrogen sulfide as the source of sulfur atoms. This method has been used in a number of studies conducted at the University of Oregon. The possibility that the synthetic method simulates the formation of condensed thiophenes in geological processes is considered.

2 THIOPHENE COMPOUNDS IN THE ENVIRONMENT

The presence of (**1**),[1a] (**2**),[2a,3] and (**5**)[2,4] in liquid fossil fuels is well documented. It has been estimated that 70% of the sulfur compounds in crude oils are thiophenes and that bi- and tricyclic compounds are more prevalent than monocyclic ones.[5] It is likely that most of the sulfur present in shale oils is of the thiophene type.[6] In fact Pailer *et al.*[7] have identified parent compounds and/or derivatives of (**1**–**11**) in a selected shale oil sample. Kruber *et al.*[8–10] reported the isolations of (**7**), (**12**), and (**13**) from coal tar, though the identification of (**13**) has been questioned.[11] Compound (**12**) was also obtained from high boiling petroleum distillates.[12] Tentatively identified in a liquid mixture from coal


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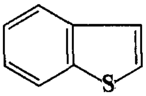
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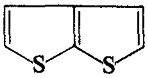
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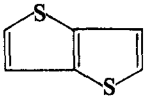
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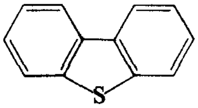
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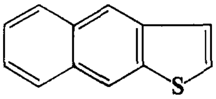
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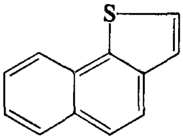
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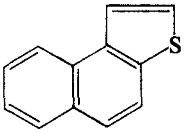
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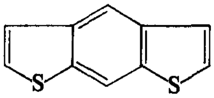
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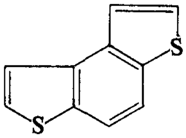
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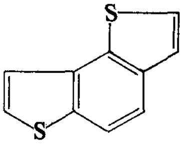
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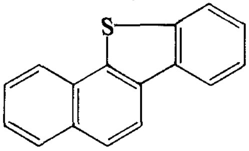
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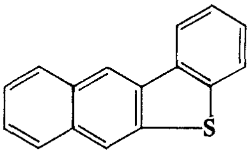
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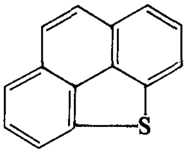
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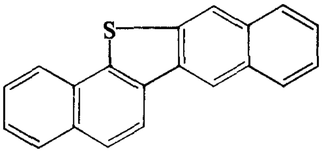
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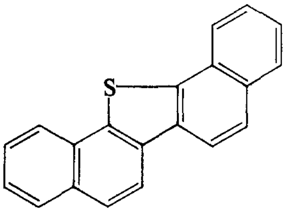
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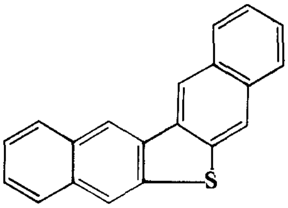
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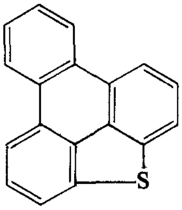
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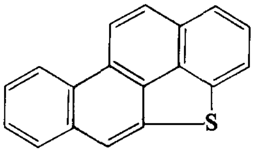
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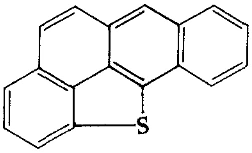
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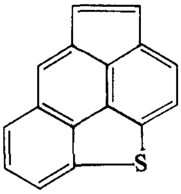
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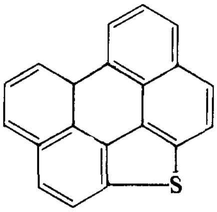
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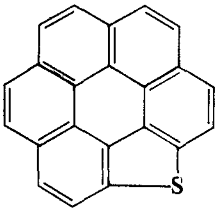
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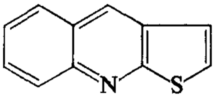
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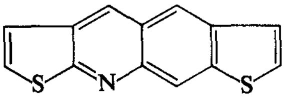
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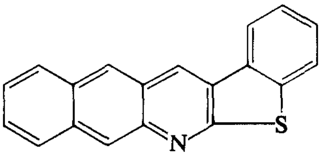
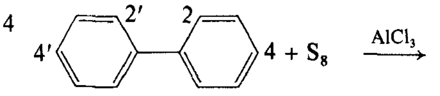

(26)

hydrogenation[13] were (**2**), (**5**), "naphthobenzothiophene" (**12** and/or **13**), (**14**) and "dinaphthothiophene" (one or more of the isomers **15**–**17**). Seven condensed thiophenes, viz. (**5**), (**12**), (**14**), a benzo-[*def*]naphthobenzothiophene (**18**, **19**, or **20**), and compounds (**21**–**23**) (or isomers thereof), were identified in carbon blacks by combined gas chromatography–mass spectrometry.[14] Compounds bearing both a thiophene ring and a furan, pyrrole, or pyridine ring are also indicated in petroleum[15] and liquefied coal.[16] Clerc and O'Neal[17] suggested that under electron impact a sample of asphalt fragmented to produce ions of the thienopyridines (**24**–**26**) (or their isomers), while Winniford and Bersohn[18] and Wiser[19] speculated that crude oil asphaltene and coal contain complex molecules bearing thiophene and carbocylic structures as well as nitrogen and/or oxygen heterocyclic rings. Blumer *et al.*[20] found mass spectral evidence for the presence of the "thienologs" of several major series of polycyclic aromatic hydrocarbons in samples of soils and recent marine sediments. In particular they identified (**5**), a "naphthothiophene", and a "benzonaphthothiophene" as present.

3 SYNTHETIC METHODS

Three different methods have been described for the direct introduction of a sulfur bridging atom into a hydrocarbon precursor molecule to yield a thiophene ring structure by the process of dehydro-1,4-cycloaddition. These are (a) use of elemental sulfur plus a Lewis acidic catalyst, (b) use of elemental sulfur plus heat (without added catalyst), and (c) use of hydrogen sulfide plus a heterogeneous catalyst (usually at elevated temperature).[21] These are the best available methods for the syntheses of (**5**), (**1**), and (**2**), respectively, on a large scale. Therefore, it is not surprising that the methods have been investigated for the syntheses of more complex molecules.

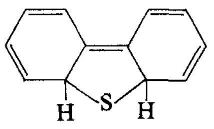
Method (a) is illustrated by the conversion of biphenyl (**27**) into (**5**) by means of aluminum chloride catalyst at 100–265° (Eq. 1).[22] Olah[23] refers to this transformation as a Friedel–Crafts-type reaction,



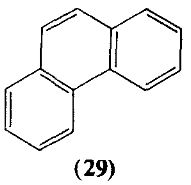
(**27**)

$4\,(\mathbf{5}) + 4H_2S$ (1)

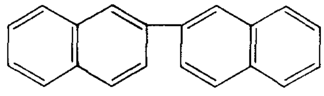
(60–80%)



(**28**)



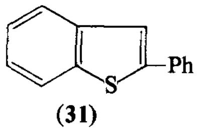
(**29**)



(**30**)

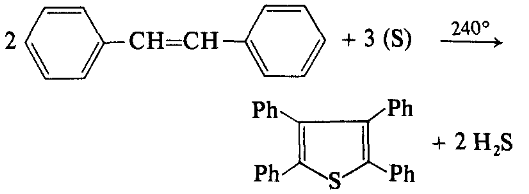
but typical Friedel–Crafts reactions on (**27**) give substitution at C-4 and C-4', not at C-2 and C-2'.[24] While the mechanism of this reaction has not yet been investigated, the alternative possibility of a catalyzed 1,4-sulfur insertion (cheletropic reaction) at position 2 and 2' appears attractive.[25] Dehydrogenation of the expected intermediate (**28**) by means of elemental sulfur should occur readily.[26] Method (a) with aluminum chloride and substrates other than (**27**) has generally given poor yields of desired *S*-bridged products.[21,27] Both phenanthrene (**29**)[28] and 2,2'-binaphthyl (**30**),[29] for example, reacted under these conditions to evolve hydrogen sulfide, but no organosulfur products were isolated. Apparently no attempt to use Lewis acids other than aluminum chloride has yet been reported, though it has been found that no reaction occurs between biphenyl and sulfur at 270° (method b) if the catalyst is omitted.[21] In contrast, at 668° in the presence of a chromia–silica–alumina catalyst, styrene plus elemental sulfur do produce benzo[*b*]-thiophene (**2**) in 3% yield.[30]

Method (b) is used for the commercial synthesis of thiophene (**1**) in 8% yield (for a single pass) from C_4 hydrocarbons in the vapor phase at 565°.[1b] It is presumed that butane and butene first yield 1,3-butadiene which reacts further with either elemental sulfur or hydrogen sulfide (*vide infra*). Oftentimes the thiophene produced results from condensation of an unequal number of molecules of hydrocarbon substrate and atoms of sulfur. For example, acetylene plus sulfur produces (**1**)[1c] plus very small amounts of thienothiophenes (**3**) and (**4**),[31] while toluene forms 2-phenylbenzo[*b*]thiophene (**31**) plus other products, stilbene yields 1,2,3,4-tetraphenylthiophene (**32**) (Eq. 2), and styrene gives 2,4- and



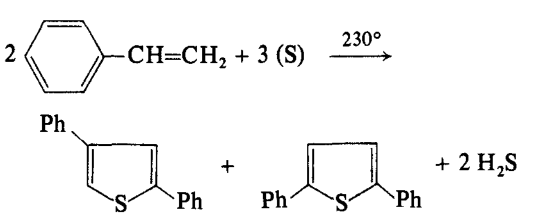
(**31**)

2,5-diphenylthiophenes (**33** and **34**, respectively) (Eq. 3).[32] Horton[32] postulated that compounds (**31–34**) result from initial free-radical attack by a sulfur atom bearing two unpaired electrons onto the hydrocarbon substrate. The resultant chain reaction is terminated by cyclization of an intermediate adduct to form a thiacyclopentane ring. Dehydrogenation of the thiacyclopentane by means of additional sulfur atoms completes the thiophene synthesis.



(2)

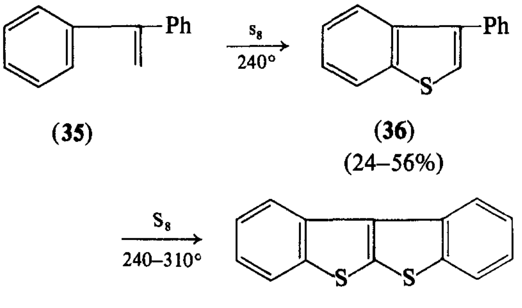
(32) (58%)



(3)

(33) (main product) **(34)** (minor product)

1,1-Diphenylethene (**35**) reacts with one or two atoms of sulfur to yield 3-phenylbenzo[*b*]thiophene (**36**) and **37**, respectively.[33] Apparently compound (**36**) is an intermediate on the route (**35** → **37**) (Eq. 4) since the ratio of yields (**37**/**36**) increases with increasing ratio of S_8/(**35**)[33] and (**36**) is separately transformed into (**37**) under similar conditions.[34] Other examples of method (b) have been presented previously.[21]

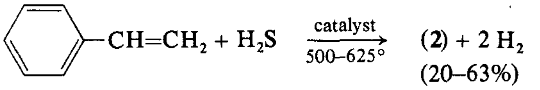


(35) **(36)** (24–56%)

(4)

(37) (20% from **36**) (25–54% from **35**)

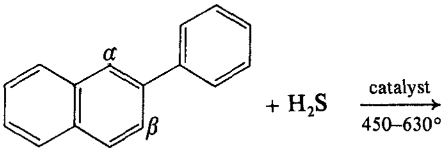
The most frequently used method for direct insertion of a heterosulfur bridging atom is (c), of particular interest in this review. Examples of the transformations effected are shown in Eqs. 5–7. Further consideration of this method is presented in Section 4.



(20–63%) (Ref. 35) (5)

$$(\mathbf{29}) + H_2S \xrightarrow[430\text{–}630^\circ]{\text{catalyst}} (\mathbf{14}) + 2\,H_2 \quad (\text{Refs. } 21, 36) \quad (6)$$

(29–39%)



(38) (**12**) + (**13**) + $2H_2$ (Ref. 11) (7)

(9–26%) (1–6%)

4 ASPECTS OF THE CATALYZED REACTION WITH HYDROGEN SULFIDE

4.1. *Nature of the Catalyst Used*

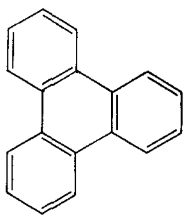
Various metallic oxides and sulfides (or mixtures of them) have been used as catalysts for effecting sulfur-bridging by means of hydrogen sulfide. In most studies the catalyst contained alumina, either alone or as the major component (carrier) in a mixture with Cr_2O_3, ThO_2, Fe_2O_3, FeS, Cr_2O_3–SiO_2, Cr_2O_3–MgO, or CoO–MoO_3.[21,35–37] Even a small amount (13%) of alumina in an aluminosilicate catalyst produced bridging.[21] For conversion of 1,3-butadiene plus hydrogen sulfide into thiophene (8–32% yield at 500–600°), iron pyrite (FeS_2) was effective.[38] In fact thiophene (12–31% yield) was also obtained variously from ethene, butenes, or butanes plus hydrogen sulfide and oxide catalysts.[39] Before use, oxide catalysts are usually conditioned (activated) by treatment with hydrogen sulfide alone or in admixture with hydrogen gas or methanol.[40–42] At the University of Oregon the catalysts that have been employed most extensively are Harshaw Cr-0101T (2% MgO/12% Cr_2O_3/86% Al_2O_3) activated by hydrogen sulfide alone (designated catalyst Cr-1 here)[42] and Harshaw CoMo-0603T (3% CoO/12% MoO_3/85% Al_2O_3), either activated by hydrogen sulfide alone (designated CMA-2) or by hydrogen sulfide–methanol (designated CMA-1).[41] Use of Cr-1 or CMA-2 is accompanied by the formation of elemental sulfur and fine catalyst particles in the product mixture. Contrariwise, use of CMA-1 largely avoids both of these contaminants. During the activation process the catalyst is partially sulfided and some of the metallic ions [e.g., Cr(III), Mo(VI), Fe(III)] are reduced.[44] The characteristic color (green, blue, brown; respectively) of the original catalyst is changed to black.

4.2 Reaction Methodology

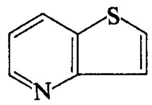
In general the reaction is conducted in a flow system consisting of a vertically mounted reactor tube packed with pelletized, conditioned catalyst (maintained at a constant temperature in the range of 450–630° by means of an external furnace). A neat liquid substrate or a solution of a solid substrate in benzene is added dropwise to the top of the tube while a stream of hydrogen sulfide gas (carrier and reactant) flows through the system. Effluent materials are passed successively into ice- and air-cooled traps (to collect solids and liquids) and concentrated aqueous NaOH solution (to remove unreacted H_2S). The extent of sulfur bridging is judged approximately by the rate of bubbling (due to hydrogen gas evolution) noted in the NaOH solution. Both the traps and the spent catalyst are examined for the presence of reaction products. By-products isolated and identified include elemental sulfur, recovered starting material, and small amounts of biphenyl and dibenzothiophene (**5**)—from reaction of the benzene solvent. While an odor, indicating the possible presence of thiol products in the traps, is apparent, no thiols were obtained from isolation experiments.

4.3 Preparative Experimental Results

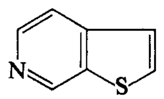
Data for preparative runs on the 20 different starting materials which have been used in the reaction are presented in Table I. In cases where the substrate was treated under various reaction conditions only the run which gave the largest yield of sulfur-bridged product(s) is shown. Good yields of (**2**) and (**5**) were obtained from styrene and biphenyl, respectively (runs 3 and 5) and may reflect, in part, the high stability of the products toward thermolysis and hydrodesulfurization.[3,4,53] In contrast, it was shown that the benzonaphthothiophene (**12**), formed from 2-phenylnaphthalene (**38**), is chemically unstable both under the reaction conditions of run 6 and at the reaction temperature *per se*. Its isomer (**13**) is even less stable under reaction conditions.[11] The substrates phenanthrene (**29**) and triphenylene (**39**) lead to *peri*-condensed[54] thiophenes (**14**) and (**18**), respectively. While multistep, straightforward preparations of (**12**), (**13**),[55] and various other *kata*-condensed[54] thiophenes are reported,[2b] compound (**18**) has not been obtained by another method and only a degradative approach to (**14**) is otherwise reported.[56] It might be noted that the *peri*-condensed compound thiacoronene (**23**), which should be capable of synthesis by method (c), has already been prepared by two alternative procedures.[57] As yet, method (c) has not been investigated as a means of introducing more than one sulfur bridge into an aromatic molecule, e.g. to form (**62**) and/or (**63**) from (**39**).



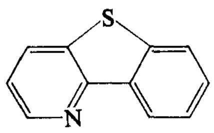
(**39**)



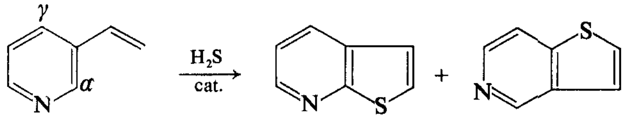
(**40**)



(**41**)

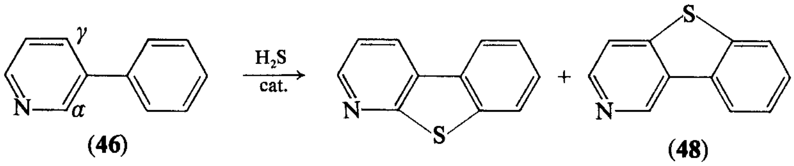


(**42**)



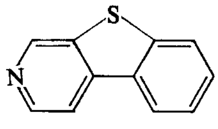
(**43**) (**44**) (main product) (**45**)

(8)



(46) **(47)** **(48)** (not detected)

(9)



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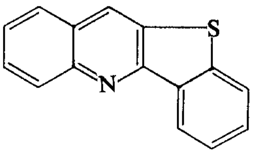

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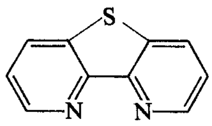

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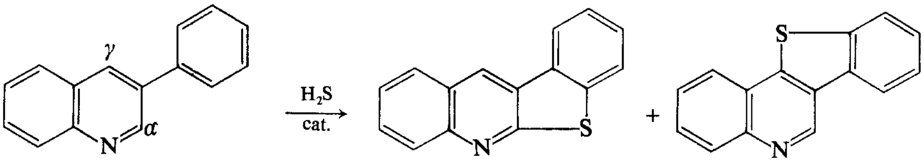
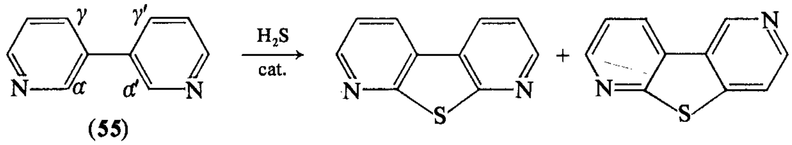


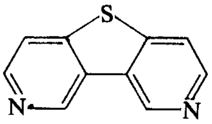
(52) **(53)** (main product) **(54)**

(10)

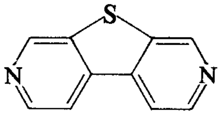


(55) **(56)** (main product) **(57)**

(11)



(58)
(not detected)



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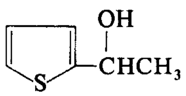

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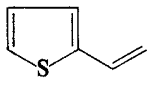

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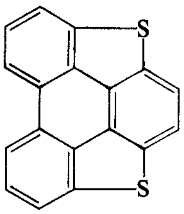

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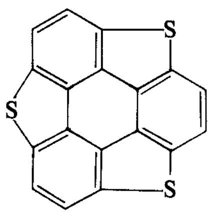


(63)

TABLE I

Preparative runs for sulfur bridging by means of H_2S and a catalyst

Run no.	Starting material	Reaction temp., °C	Catalyst used[a]	Products and yields (mole%)[b]	Reference numbers[c]
1[d]	1,3-butadiene	600	FeS_2	**(1)** (32)[e]	38
2[d]	1-butene[f]	600	Al_2O_3–Fe_2O_3	**(1)** (29)	39
3[d]	styrene	625	Al_2O_3–FeS	**(2)** (63)	35 (45, 46)
4[d]	ethylbenzene	593	Al_2O_3–Cr_2O_3–SiO_2	**(2)** (23)	45 (47)
5	biphenyl	550	CMA-1	**(5)** (63)[g, h]	48 (45)
6	2-Ph-naphthalene **(38)**	500	CMA-1	**(12)** (24), **(13)** (1.4)[i]	11
7	phenanthrene **(29)**	600	CMA-2	**(14)** (28)[j]	36 (21)
8	triphenylene **(39)**	500	CMA-1	**(18)** (18)[j]	49
9[d]	2-vinylpyridine[k]	630	Cr-1	**(40)** (3)[l]	50 (51)
10[d]	3-vinylpyridine[m] **(43)**	630	Cr-1	**(44)** (6), **(45)** (1)[l]	52
11[d]	4-vinylpyridine **(64)**	500	Cr-1	**(41)** (15)[l]	42
12	2-Ph-pyridine	630	Cr-1	**(42)** (22)[g]	37
13	3-Ph-pyridine **(46)**	630	Cr-1	**(47)** (25)[g], **(48)** (none)	37
14	4-Ph-pyridine	630	Cr-1	**(49)** (1.6)	37
15	2-Ph-quinoline	630	Cr-1	**(50)** (18)	37
16	3-Ph-quinoline **(52)**	630	Cr-1	**(53)** (12), **(54)** (5)	37
17	2,2′-bipyridine	630	Cr-1	**(51)** (11)[n]	37
18	3,3′-bipyridine **(55)**	630	Cr-1	**(56)** (12)[n], **(57)** (3)[n], **(58)** (none)	37
19	4,4′-bipyridine	630	Cr-1	**(59)** (3)[n]	37
20	1-(2-thienyl)ethanol **(60)**[o]	630	Cr-1	**(4)** (*ca.* 30)	50

[a] See part 4.1 for information on catalysts Cr-1, CMA-1, and CMA-2.

[b] Based on the amount of starting material used. Unless otherwise indicated, yields refer to isolated products.

[c] Data given are from the first reference shown. Important additional data are reported in parenthesized references.

[d] No solvent was used in the run.

[e] Isolated as a crystalline derivative.

[f] Ethene or mixed C_4 hydrocarbons may also be used.

[g] From gas chromatographic analysis of the crude product mixture.

[h] The yield has been corrected for the formation of **(5)** from the benzene solvent used.

[i] The combined yield of **(12)** and **(13)** was 33% by gas chromatography.

[j] After purification via the *S*-oxide.

[k] 2-Ethylpyridine gives a lower yield of **(40)** under these conditions.

[l] Analyzed by a combination of gas chromatographic and nmr methods.

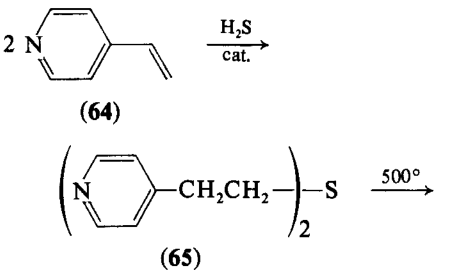
[m] Contained 8% of 3-ethylpyridine.

[n] From nmr analysis of the crude product mixture.

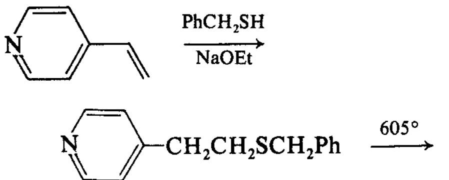
[o] Compound **(60)** is probably dehydrated to 2-vinylthiophene **(61)** before reaction with hydrogen sulfide.

As noted from runs 9–19, replacement of a phenyl ring in styrene or biphenyl by a pyridyl ring, or replacement of the naphthyl ring of **(38)** by a quinolyl ring decreases the yield of bridged products. This trend may be ascribed to the tenacious adsorption of azine nitrogen atoms onto alumina[58] (or other part of the catalyst), with attendant loss by retention or decomposition of the substrate and/or product(s).

Runs 6, 10, 13, 16, and 18 (cf. Eq. 7–11, respectively) illustrate that isomeric preferences occur in product formation when the substrate molecule may undergo bridging in 2 or 3 different ways. Thus, **(38)** gives cyclization mainly into the α-position of the naphthalene ring. Also cyclization into the pyridine ring occurs more readily at the α-position than the γ-position. [Note: In run 18, α,α'-, $>\alpha,\gamma'$-, $>\gamma,\gamma'$-cyclization.] Comparison of runs 12–14 and of runs 17–19 shows that particularly low yields of products result for cyclization between a 4-substituent and a β-position of the pyridine ring. Cyclization between a 2-substituent and a β-position, however, produces a much higher yield. The 15% yield of **(41)** obtained from 4-vinylpyridine (run 11) is rationalized in terms of the formation of intermediate **(65)**,[42, 59] which undergoes thermolytic cyclization (Eq. 12, *vide infra*). In fact, this interpretation led to a preparative synthesis of **(41)** *sans* heterogeneous catalyst (Eq. 13).[42] Analogously 2-vinylpyridine gives **(40)** in 27% overall yield.[60]



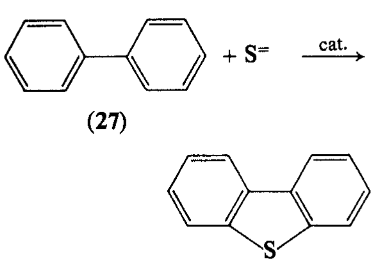
(64) **(65)** (41) (12)



(66) (98%) **(41)** (13) (58%)

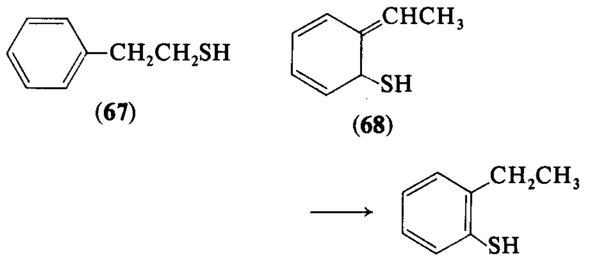
4.4 Reaction Mechanisms

From the fact that hydrogen gas is evolved in the sulfur bridging reaction (cf. Eqs. 5–7) it is apparent that an oxidation-reduction process is involved. On the basis of general theory of heterogenous catalysis by semiconductors[61,62] this indicates that the catalyst serves as a reservoir for electrons, i.e. acts as an electron-transfer agent. Formally, one can write a balanced ion-electron oxidation half-reaction (Eq. 14), wherein the catalyst is also considered a transfer agent for sulfur and hydrogen, but the chemical natures of the active species involved are not necessarily meant to be sulfide ions and hydrogen molecules *per se*.



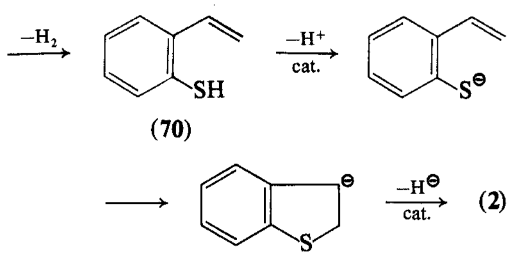
(27) **(5)** $+ H_2 + 2e^-$ (14)

Moore and Greensfelder[35] considered that hydrogen sulfide might add to styrene (Eq. 5) in two different ways, viz. in a 1,2-*anti*-Markovnikov (free radical) manner to give the intermediate **(67)** or in a 1,4-manner to form **(69)**, via **(68)**. They discounted the former mechanism on the basis of their observation that the yield of benzo[*b*]thiophene **(2)** was not altered by use of diluents in the reaction.[46] Hence, the intermediacy of free radicals was believed to be unlikely. Lending credence to the latter mechanism is the observation of Hansch and Blondon[63] that **(69)** does, indeed, cyclize to **(2)** (42% yield) at 450° in the presence of a pre-reduced chromia–alumina catalyst and nitrogen as a carrier gas. Though it is uncertain that the observation is pertinent here, Hansch *et al.*[64] found that a different catalyst (Cr_2O_3–CuO–charcoal) likewise gives dehydrocyclization of **(69)** to **(2)** (68% yield) at 445°, probably via the mechanistic pathway shown here. In fact, at a somewhat lower reaction temperature *o*-mercaptostyrene **(70)** can be isolated. Also, cyclization of the analogous *o*-aminostyrene is fostered by admixing the catalyst with a solid base (CaO or K_2O). As noted later, we now propose a more straightforward modification of this mechanistic pathway.

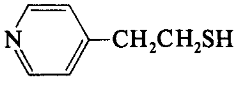


(67) **(68)** **(69)**

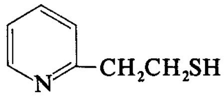
(69)



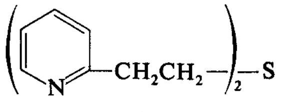
(70)



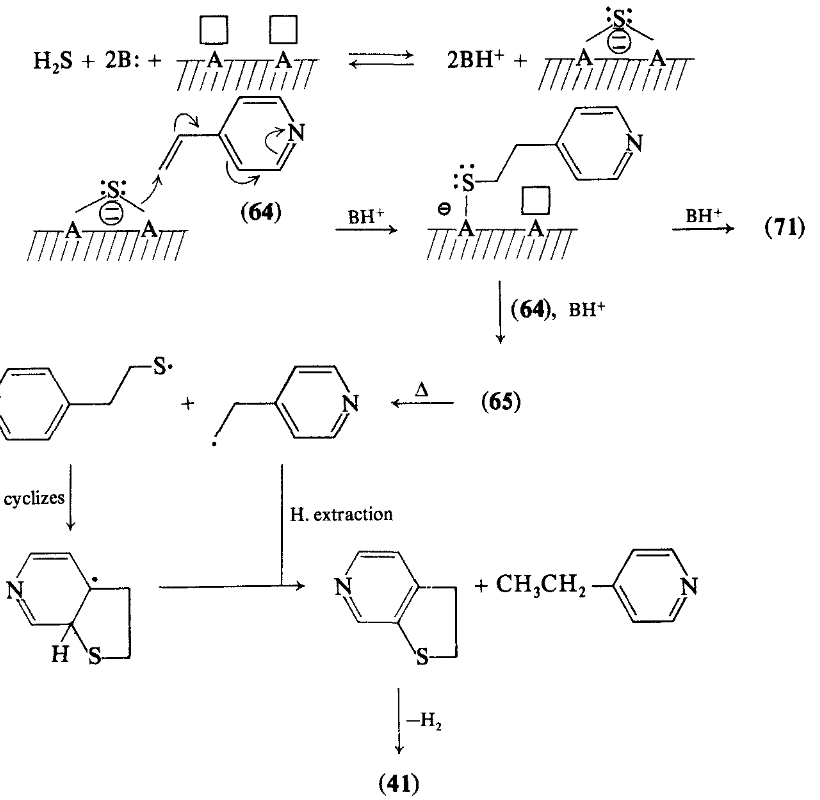
(71)



(72)



(73)



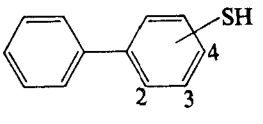
SCHEME 1[a] Partial mechanistic scheme[b] for *S*-bridging of 4-vinylpyridine (**64**) to form thieno[2,3-*c*]pyridine (**41**)

[a] B: and $\overset{\square}{A}$ are Lewis basic and acidic sites, respectively, on the surface of the catalyst.

[b] Alternatively, (**71**) and (**65**) may form from analogous Broñsted acid-base self-catalyzed condensations on a surface (or even in the gas phase).

Isolation of sulfide (**65**) from reaction of 4-vinylpyridine with H_2S (Eq. 12) implies the intermediate formation of thiol (**71**). In fact, in runs with various reactor packings (including glass beads), both (**72**) and (**73**) were identified in the product mixture from 2-vinylpyridine and hydrogen sulfide.[50] In contrast, neither the corresponding isomeric thiol nor the isomeric sulfide was detected in the product mixture from 3-vinylpyridine (in the presence of Cr-1).[50] We interpret these results in the following way. Addition of hydrogen sulfide to 2- or 4-vinylpyridine is either self-catalyzed (Brönsted acid-base interaction) or is catalyzed by Lewis basic and acidic sites on the surface of the heterogeneous catalyst used[65a] (Scheme 1). Thermolysis of the resultant thiol (**72** or **71**) or sulfide (**73** or **65**) effects free-radical cyclization. Subsequent dehydrogenation (thermal and/or catalytic) then yields (**40** or **41**). 4-Ethylpyridine and its hydrogenolysis product 4-methylpyridine are significant by-products formed from (**64**),[42] and the corresponding 2-isomers result from 2-vinvylpyridine.[50] The case of 3-vinylpyridine (**43**), which does not undergo nucleophilic additions readily, will be considered in a general scheme later.

Mechanistic aspects of sulfur bridging in biaryls and angularly condensed arenes are even less certain. To check on the possibility that an arylthiol is an intermediate, Klemm and Karchesy[48] investigated the three isomeric biphenylthiols (**74**–**76**) as substrates in the bridging reaction. They found that at 450° with CMA-1 as catalyst, (**74**) and biphenyl (**27**) give essentially the same yield (44 ± 2%) of dibenzothiophene (**5**) and this is only slightly less than one obtains (54%) from thermolysis of (**74**)

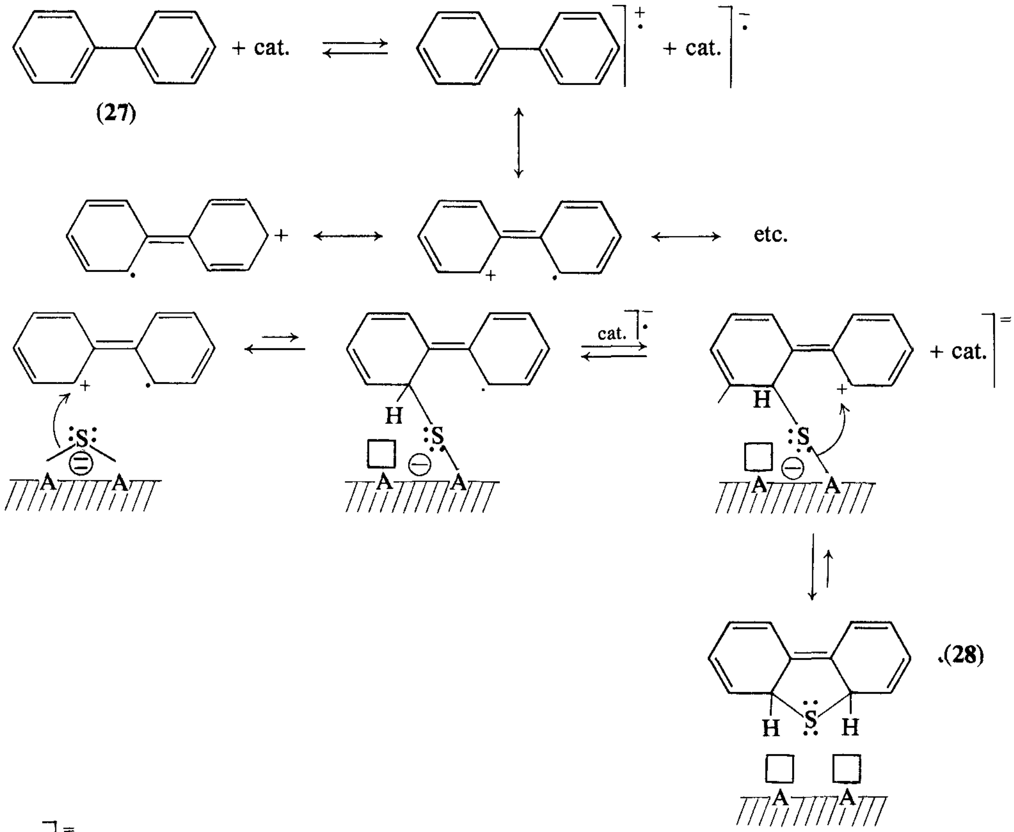


(**74**), 2-isomer
(**75**), 3-isomer
(**76**), 4-isomer

at that temperature. However, even at 550° without a catalyst, (**27**) and hydrogen sulfide do not react. Thus, if one has a reaction sequence of (**27** → **74** → **5**) the first step (thiylation) must be catalyzed, but the second step (cyclization) may be either catalyzed or thermal (or both). More surprising were the results from (**75**) and (**76**) with CMA-1 at 450° since these substrates give higher yields (54% and 86%, respectively) of (**5**) than from (**74**). It was suggested that (**74**–**76**) are strongly adsorbed onto the catalyst surface via the sulfur atom as an anchoring group.[66a] For (**75**) and (**76**) this adsorption facilitates *S*-bridging at the 2,2′-position, which is followed by loss of the anchoring group and desorption of (**5**). Very little (0–2%) direct loss of SH group (desulfurization) to give (**27**) occurs. With alumina at 550°, (**76**) again gives a higher yield (45%) of (**5**) than does (**27**) (27%), but desulfurization (33% yield of **27** from **76**) is also significant. From these results it is apparent that if a biphenylthiol is an intermediate in the reaction the original thiylation process must occur with considerable selectivity at C-2 (and/or C-3).

Kellogg[67] noted that thiyl radicals add to various alkenic systems readily, but that addition to (or substitution into) aromatic systems occurs only in the presence of redox metal ions or molecular oxygen. He suggested that thiyl addition to an aromatic system is reversible and that the rate of dethiylation of the adduct is high (compared to the rate of addition). Thus, it could be that only thiylation at C-2 of (**27**) (or an analogous bridging position in another aromatic substrate) will be observed because subsequent cyclization occurs rapidly and displaces the unfavorable equilibrium.

It is easy to rationalize the use of catalysts



$$\left.\text{cat.}\right]^{=} + 2\text{BH}^{+} \longrightarrow \text{cat.} + 2\text{B:} + \text{H}_2$$

$$(\mathbf{28}) \xrightarrow[\text{cat.}]{\Delta\text{ and/or}} (\mathbf{5}) + \text{H}_2$$

SCHEME 2[a] Hypothetical mechanism for *S*-bridging of biphenyl (**27**) to form dibenzothiophene (**5**)[b]

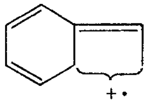
[a] See footnote a in Scheme 1.

[b] Modifications of this mechanism are possible, especially since the source and timing for loss of the second electron may be varied.

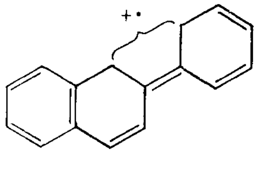
bearing Fe, Cr, or Mo compounds in *S*-bridging since these contain ions which can undergo one-electron redox reactions. Use of ThO_2 is also plausible because of the presence of electrons in conduction bands in the sulfides.[68] Catalysis by alumina alone or aluminosilicate, on the other hand,[21] may require the availability of adventitious molecular oxygen (though no studies have been made on this possibility). Snyder[69] summarized evidence for the action of chromatographic alumina and aluminosilicate in effecting charge transfer from an adsorbed polycyclic arene (e.g. naphthacene or perylene) to the surface (i.e. one-electron redox).

As based on these preceding considerations plus analogy to electrochemically initiated aromatic nucleophilic substitution reactions, we now propose a mechanistic pathway for *S*-bridging of styrene, biaryls (including aza- and diazabiaryls), and angularly condensed arenes, as exemplified for biphenyl as a substrate in Scheme 2. This scheme does not apply to 2- and 4-vinylpyridines, but is applicable to 3-vinylpyridine. In our scheme the catalyst (with or without adventitious molecular oxygen) initiates the reaction by abstracting an electron from the π-system (or perhaps from the n-electron pair on the pyridine nitrogen atom in some cases)[70] of the aromatic compound to form a cation radical, which undergoes nucleophilic attack by means of an adsorbed sulfide ion. (Alternatively, attack could be by an adsorbed bisulfide ion, with subsequent loss of a proton.) Loss of a second electron from the half-bridged adduct (probably from the aromatic ring, as shown) to the catalyst is followed (or accompanied) by a second nucleophilic attack (cyclization) to form the intermediate (**28**). It seems likely that biphenyl and the other aromatic hydrocarbon substrates studied are adsorbed flatwise onto the surface of the catalyst.[66b, 71] Thus, sulfur insertion should occur suprafacially and (**28**) should have a *cis*-geometry. The elimination of molecular hydrogen from (**28**), either thermally[72] or catalytically, will then be facile. Molecular hydrogen will also result from interaction of protons (from adsorption of hydrogen sulfide) and electrons on the catalyst surface.

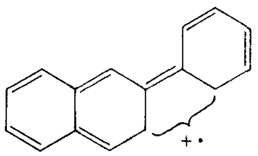
As depicted, the conversion (**27** → **28**) is an example of an ECEC-type mechanism, recognized as the probable pathway for certain oxidative substitutions of arenes by nucleophiles in organic electrochemistry.[73–75] Zahradnik and Beran[76] noted the parallelism between electro-oxidation and catalysis by semiconductors in the formation of radical cations. An unknown factor in this correlation, however, is the extent to which the catalytic surface can lower the ionization potential of the substrate molecule.[69, 77] Pertinent resonance forms of the cation radicals that would be involved in three of the substrate systems used are shown as (**77**–**82**).



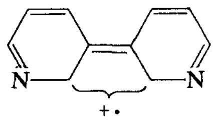
(**77**)



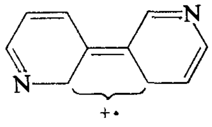
(**78**)



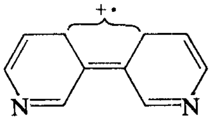
(**79**)



(**80**)



(**81**)



(**82**)

Radical cation (**77**) will yield benzo[*b*]thiophene (**2**). Form (**78**), more stable than (**79**), accounts for the preferential formation of (**12**), compared to (**13**) (Eq. 7).

In contrast to the hydrocarbons the azine compounds may be adsorbed via nitrogen n-electrons (edgewise or tilted geometry), via π-electrons (flatwise), or (at a step in the surface) via both n- and π-electrons.[37, 58] For simplicity we shall assume that all reactive azine molecules discussed here are deficient in π-electrons,[77] but some of these molecules are retained on the catalyst surface primarily through anchoring by means of the non-bonding electrons on the nitrogen atom(s). Thus, for 3,3′-bipyridine (**55**), for example, the reactive cation radicals would be (**80**–**82**). The product yield relationship of (**56** > **57** > **58**) (Eq. 11, run 18) is ascribed either to greater reactivity at the α-position than at the γ-one[65b] toward either nucleophilic or free-radical attack,[78] or to a geometric relationship whereby the molecule is adsorbed edgewise by means of one or both nitrogen atoms to the same surface plane as that which holds the attacking sulfide ion (or to both factors operating at the same time). For edgewise adsorption, form (**82**) would be geometrically disfavored (inasmuch as the adsorbed sulfide ion would be far away from the γ- and γ'-positions) to give facile reaction. Similar arguments can be used with 3-vinylpyridine and 3-

phenylpyridine as substrates. The overwhelming populations of molecules of 4-phenylpyridine and 4,4′-bipyridine should be anchored edgewise, whereby the uppermost rings will remain too remote from the layer of adsorbed sulfide ions to permit bond formation (i.e. bridging) to occur. The very low yields of bridged products which do form from these substrate molecules can then be ascribed to reaction by the small fractions of the total populations which do attain flatwise adsorption. 2-Phenyl-pyridine and 2-phenylquinoline (steric hindrance to *n*-adsorption) and 3-phenylquinoline (large π-system) should be adsorbed flatwise to appreciable extents.[37]

Two additional studies which are consistent with Scheme 2 are the loss of the methyl group during reaction of 4-methylbiphenyl[48] and the complete exchange of deuterium atoms for protium atoms on conversion of decadeuteriobiphenyl into (**5**).[79]

5 GEOCHEMICAL ORIGIN OF CONDENSED THIOPHENES

It is interesting to consider the question of whether or not a sulfur-bridging reaction can account for the origin of condensed thiophenes in geochemical samples. Since the thiophene nucleus is rarely found in present living systems it is presumed that thiophene structures must have been formed by chemical transformations of the geological source material.[5] Organically bound sulfur is presumed to arise from mineral sulfides (e.g. FeS_2), hydrogen sulfide, or elemental sulfur.[80] In fact it has been noted[81] that the sulfur composition of a crude oil is dependent on the original sulfur content of the rocks adjacent to the oil deposit and the extent to which this sulfur has been expelled from the rock (i.e. brought into contact with the crude oil pool), perhaps in one of the aforementioned chemical forms. Bestougeff *et al.*[82] showed that sulfurization of various petroleum fractions occurs (a) with hydrogen sulfide at 80–90°, 18–75 atm. pressure, and especially in the presence of a catalyst (e.g. molecular sieves) or (b) with elemental sulfur at 50–100°. However, the structural natures of the resultant organosulfur compounds were not ascertained. Carruthers and Douglas[83] proposed that dibenzothiophenes in petroleum may arise from 2,2′-dihydroxybiphenyl precursors. It has also been suggested that sulfur replaces oxygen in furans and pyrans, a process which can be effected at 400–450° with hydrogen sulfide and an alumina catalyst in the laboratory.[84] The present paper illustrates the chemical feasibility of producing condensed thiophenes in fossil fuels by direct reaction of hydrogen sulfide or elemental sulfur with aromatic hydrocarbons, but at temperatures considerably higher than those to which crude oil may have been subjected[5,81] over a long period of time. It is clear that the origin of condensed thiophenes in fossil fuels is still uncertain, but that model laboratory reactions may help to establish plausible pathways. We believe that the catalyzed hydrogen sulfide reaction may be one of the natural routes to these compounds.

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