Hydrogenolysis of Benzo[b]thiophenes and Related Intermediates over Cobalt Molybdena Catalyst

By

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INTRODUCTION

The chemistry of sulfur removal from high molecular weight heterocyclic sulfur compounds has become of increasing interest with the refining of high boiling and residual petroleum fractions. Benzothiophenes have long been recognized as major constituents of heavier fractions. The first isolated and identified member of this family was the parent compound, benzo[b]thiophene, I (1). Subsequently, 22 alkylbenzo[b]thiophenes have been identified in a 200-250°C distillate of Wasson, Texas crude oil (2,3). Five compounds in this group, 2-methyl- (II), 3-methyl- (III), 2,3-dimethyl-, 2,4-dimethyl- and 2,7-dimethyl- benzo[b]thiophene, comprise over 80% of the benzothiophenes present in the 200-250°C distillate fraction.

Little quantitative information is available concerning the behavior of this type of fused 2-ring heterocyclic sulfur molecule under hydrogenative processing conditions (4). It has been reported that the hydrogenolysis of benzothiophene I with Raney nickel (2,5), palladium on alumina (6,7), molybdenum disulfide (8,9), and cobalt molybdena (10,11) gives ethylbenzene and ethylcyclohexane, or a mixture of these two compounds. Over molybdenum disulfide in the liquid phase, I is converted in 2 hours at 425°C

and 41 atmospheres to ethylbenzene in 90% yield (9) while at 340°C and 100 atmospheres, a lower temperature and higher pressure, I reacts just as easily (93% conversion) to give ethylbenzene in 80% yield and ethylcyclohexane in 8% yield (8). Cobalt molybdena is equally as effective, giving 91% sulfur free product in 8 hours at 400°C and 1 atmosphere (10,11). In contrast, almost no information is available on the hydrogenolysis of alkyl benzo[b]thiophenes. Likewise, little is known on the mechanism of this reaction. Cawley conjectured some years ago in comments to the work of Hoog, et. al. (11b) that 2,3-dihydrobenzo[b]thiophene(IV)is an intermediate in this reaction (12). There is as yet still no evidence regarding this supposition.

Evidence regarding the relative ease with which thiophene and benzo[b]thiophene desulfurize is contradictory. Landa and Mrnkova (8) found I was more easily desulfurized than thiophene. Yamada (9), on the other hand, found the opposite, while Papadopoulos and Wilson (10) found their reactivity nearly equivalent.

The lack of information on the chemical behavior of these important petroleum constituents has led us to an examination of the hydrogenolysis of benzo[b]thiophenes over a commercially available cobalt molybdena catalyst. The various benzothiophenes examined here are clearly representative of those found in petroleum since all were identified in Wasson, Texas, crude oil (2). In addition, various possible intermediates have been examined under the same conditions to further elucidate the sequence of steps involved in desulfurization.

EXPERIMENTAL

All melting points were obtained on a Fisher-Johns melting point block. The infrared spectra were determined with a Perkin-Elmer Model 337 grating spectrophotometer as either neat liquids or suspensions in potassium bromide pellets. The NMR spectra were determined on a Varian Model A-60 NMR spectrometer, using tetramethylsilane as the internal reference. The mass spectra were obtained with a CEC Model 21-103 mass spectrometer at an ionizing potential of 70 ev using an all glass inlet system. Gas-liquid partition chromatography was performed with an F&M Model 810 gas chromatograph using a 12 ft., 1/8 in. o.d. column packed with 20% Carbowax 20 M on Chromosorb W. Preparative separations were done either on this chromatograph or on a Hewlett Packard Model 775 preparative gas chromatograph.

A. Materials

Catalyst. The cobalt molybdena was Harshaw CoMo 0601 supported on an alumina surface (S. A. 160 m^2/g. CoO, 3%; MoO_3, 10.0%). The noble metal catalysts were 0.29% Pd, 0.32% Rh and 0.60% Pt on non-acidic alumina compositions (13). The catalysts were ground to 8/14 mesh particles and pretreated in hydrogen at 500-550°C for three hours immediately prior to use.

Benzo[b]thiophenes. 3-Methylbenzo[b]thiophene was prepared by the method of Werner (14) and Banfield (15). 1-Phenylmercapto-propanone-2 was prepared from thiophenol and 1-chloro-2-propanone and cyclized to 3-methylbenzo[b]thiophene; n_D^{20} 1.6237 [Lit. (16) n_D^{20} 1.6252]; Mw(MS) 148: sulfone, mp 140° [Lit. (14) 146-146.5°].

The following compounds were also prepared by the above method: 2,3-dimethylbenzo[b]thiophene, n_D^{20} 1.6071 (Lit. (14) n_D^{20} 1.6170) Mw(MS) 162; 2,3,7-trimethylbenzo[b]thiophene, mp 50 (Lit. (14) mp 51-2°) Mw(MS) 176: sulfone, mp 192° (Lit. (14) 190-191°); 3,7-dimethylbenzo[b]thiophene, $bp_{1.0}$ 92°, n_D^{20} 1.6069 (Lit. (15) bp_{12} 122-4, n_D^{15} 1.6090) Mw(MS) 162.

2-Methylbenzo[b]thiophene was produced from α(o-carboxylphenylmercapto) propionic acid [mp 196° (Lit. (17) mp 193-195°)] by the method of Hansch and Lindwall (18), mp 40° (Lit. (20), mp 51-52), Mw(MS) 148: sulfone, mp 107° (Lit. (20) 108.5-110°).

7-Methylbenzo[b]thiophene was synthesized by the method of Sunthankar and Tilak (21); $bp_{0.5}$ 56°, n_D^{20} 1.6110 (Lit. (21) bp_4 110-115°. 2,7-Dimethylbenzo[b]thiophene was prepared in a similar fashion $bp_{0.3}$ 66-67° (Lit. (20) bp_{11} 132-136°) n_D^{20} 1.6054, Mw(MS) 162.

<u>2,3-Dihydrobenzo[b]thiophene</u>. Oxidation of benzo[b]thiophene with hydrogen peroxide and acetic acid gave benzo[b]thiophene 1,1-dioxide, mp 139° (Lit. (22) 142-3°) that was hydrogenated over 10% Pd on carbon in ethanol to give 2,3-dihydrobenzo[b]thiophene 1,1-dioxide, mp 91° (Lit. (23) mp 91-92°). This was treated with lithium aluminum hydride in ether to give 2,3-dihydrobenzo[b]thiophene (24), bp_5 94-96°. (Lit. (25) bp_6 93°); n_D 1.6195 (Lit. (25) n_D^{25} 1.6195); infrared is identical with earlier data (25).

<u>2,3-Dihydro-2,3,7-trimethylbenzo[b]thiophene</u>

2,3,7-Trimethylbenzo[b]thiophene 1-dioxide in ethanol was reduced over 10% palladium on charcoal at 120°C and 750 psig hydrogen. The solvent was removed and the resulting material chromatographed over silica gel. Non-sulfone contaminants were removed with benzene and the product was then eluted with 50% benzene - 50% methanol.

This material was treated with lithium aluminum hydride in tetrahydrofuran for 1.5 hours. The deoxygenated product was separated by chromatography on silica gel. Two major products were isolated by preparative gas liquid chromatography consistent with threo- and erythro-2,3-dihydro-2,3,7-trimethylbenzo[b]thiophene.

First product: Mw(MS) 178; NMR $\delta_{2\text{-}CH_3}$ & $_{3\text{-}CH_3}$ = 1.1-1.7 ppm (6), $\delta_{7\text{-}CH_3}$ = 2.1-2.3 (3), $\delta_{2\text{-}H}$ = 3.2-3.8 (1), $\delta_{3\text{-}H}$ = 2.7-3.2 (1), $\delta_{H\ aromatic}$ = 6.7-7.2 (3), $J_{H_2\ H_3}$ = 8.0 Hz. Sulfone: mp 69-69.5°C. Integral ratios are shown in parentheses.

Second product: Mw(MS) 178; NMR $\delta_{2\text{-}CH_3}$ and $_{3\text{-}CH_3}$ = 1.0-1.4 ppm (6), $\delta_{7\text{-}CH_3}$ = 3.0-3.6 (3), $\delta_{2\text{-}H}$ = 3.2-3.8 (1), $\delta_{3\text{-}H}$ = 3.6-4.2 (1), $\delta_{H\ aromatic}$ = 6.7-7.2 (3), $J_{H_2\ H_3}$ = 6.8 Hz.

2-Ethylthiophenol. This compound was prepared by the method of Kwart and Evans (26). The oil product was dissolved in hexane and extracted with 10% sodium hydroxide. The base soluble material after acidification and distillation was found to be the desired product [bp 208° at 760 mm or 72° at 5 mm (Lit. (27) 208° at 1 atm.); n_D^{20} 1.5660].

The hexane soluble material proved to be 2-ethylphenyl methyl sulfide, bp_5 87°; n_D 1.5700. Anal. Calcd. for $C_9H_{12}S$; C, 71,00; H, 7.94; S, 21.05. Found: C, 70.74; H, 8.03; S, 20.7.

Benzo[b]thiophene, β-phenylethyl mercaptan, and ethyl phenyl sulfide were obtained from commercial sources and required no further purification.

4,5,6,7-Tetrahydrobenzo[b]thiophene was prepared by the Clemmensen reduction of 4-keto-4,5,6,7-tetrahydrobenzo[b]thiophene; bp_5 75° (Lit. (28) bp_3 53-58°); n_D 1.5555 (Lit. (29) n_D^{20} 1.5572).

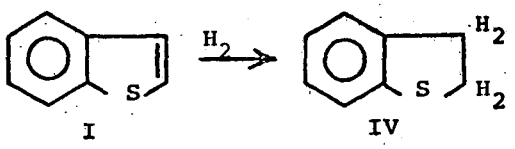
B. Apparatus, Procedure and Analysis

A continuous flow reactor system was employed. Reactants (diluted to 50% wt. in hexane) were flashed into the carrier gas and

passed through the catalyst bed. 100 mm of the tubular reactor length (140 mm x 22 mm) consisted of a quartz preheater maintained at the same temperature as the catalyst bed. The reactant flow was maintained by a syringe pump. The reactor effluent was passed through a water condenser and the liquid condensate analyzed. Product recoveries were excellent with little coke accumulation during the reaction. Analysis of the hydrocarbon and sulfur containing fractions was made by gas-liquid chromatography on a Carbowax 20M supported column. Positive identification of the products was accomplished by comparing retention times with authentic samples and by obtaining mass spectra of samples isolated by preparative chromatography and comparing them with known spectra. Conversions and product distributions are based on recovered condensate, where detector response is uncorrected except as determined by experimental means for I, IV and ethylbenzene where dector response is proportional to molar ratios.

RESULTS AND DISCUSSION

Both sulfur containing and sulfur free (hydrocarbon) products were formed in the gas phase hydrogenolysis of methyl and polymethyl substituted benzo[b]thiophenes at 1 atmosphere and 400°C over cobalt molybdena. Under these conditions benzo[b]-thiophene (I) was converted to ethylbenzene and hydrogen sulfide (Table 1). Over alumina supported noble metal catalysts, 2,3-dihydrobenzo[b]thiophene (IV) was also a major product. No other species (other than those in equation 1) were observed in amounts greater than 1% of the product mixture.



$+ PhCH_2CH_3 + H_2S$ (1)

The true catalytic nature of this reaction is obvious from two observations. First, the thermal stability of I, and presumably the other benzo[b]thiophenes, is evident from the absence of any reaction over nonacidic alumina under like conditions at 400°C. Secondly, the importance of hydrogen in this reaction is illustrated by the lack of any reaction of I over cobalt molybdena in nitrogen at 400°C.

Table 1

Hydrodesulfurization of Benzothiophene[a]

Catalyst[b]	Conversion	Products		
		Ethylbenzene	IV	Other
Cobalt molybdena[c]	91-99	96	--	4
Cobalt molybdena[d]	none	--	--	--
Non-acidic alumina	none	--	--	--
Pt on non-acidic alumina	24	92	8	--
Rh on non-acidic alumina	14	84	16	--
Pd on non-acidic alumina	2	75	25	--

a. Conditions: LHSV 0.30; $H_2/I = 3$; 400°C; samples taken after one hour on stream; Pretreat: H_2, 3 Hrs. at 15 cc/min/8cc catalyst at 500°C; I charged as ~50% by weight hexane.

b. For catalyst descriptions see Experimental.

c. In another run with H_2-H_2S pretreat (25 cc/min. H_2, 10cc/min. H_2S at 400°C) observed 99% conversion with same selectivity.

d. Run made in N_2; sample taken at 0.5 hr. on stream.

All of the catalysts we tested were reduced in hydrogen for 3 hours at 500-550°C immediately before use. Since sulfiding had no effect on this reaction the catalysts were used in the oxide state. A similar lack of any affect by sulfiding was observed by Lipsch and Schuit (30) on the thiophene desulfurization.

At a constant hydrogen-reactant ratio for cobalt molybdena the log conversion varies linearly with LHSV (Table 2). It appears that this reaction is not unduly complicated by diffusion problems at the conditions used here. No apparent aging was observed during these 4 hour runs over cobalt molybdena. This agrees with the results of Kolboe who found the same absence of aging for thiophene hydrogenolysis over cobalt molybdena (31). We also found that, with the noble metal catalysts, conversion of I dropped rapidly with time on stream.

Table 2

Effect of LHSV on Benzo[b]thiophene Conversion over Cobalt Molybdena

LHSV	Flow Rate of I	H_2 Rate	Ethylbenzene	I
0.3	1.2 cc/hr.	8 cc/min	83	13
1.0	4.0	25	63	34
2.0	8.0	50	44	54
4.0	16.0	100	18	82[b]

a. Catalyst, 4cc (3.31 g); 400°C; yields in mole percent.

b. Contains 2% IV.

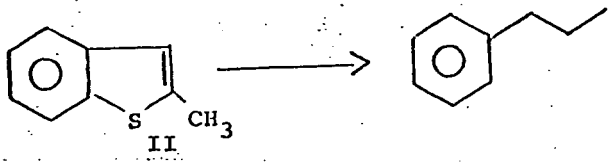
A. Product Characteristics

The product distributions from these reactants are dependent on the number and positions of methyl substituents, and

become increasingly complex as the number of methyl substituents increase in the reactant.

1. Primary Sulfur Extrusion

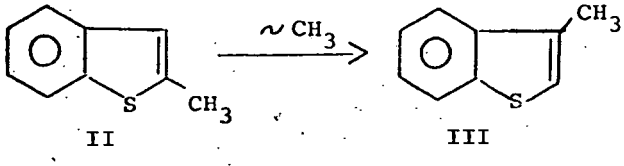
The main hydrocarbon products from this reaction arise from simple, direct sulfur extrusion. This is illustrated in equation 2 below with 2-methylbenzo[b]thiophene (II) which gave n-propylbenzene as the major hydrocarbon product (Table 3).



(2)

2. Alkyl Migration on Thiophene Ring

The major sulfur containing products arise from 1,2-methyl shifts on the thiophene ring. For example, the 3-methylbenzo[b]thiophene (III) produced from II arose by a simple methyl shift from the C-2 to the C-3 position as shown in equation 3.



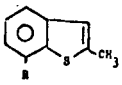
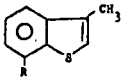
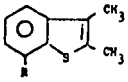
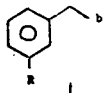
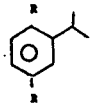
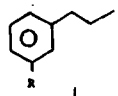
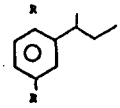
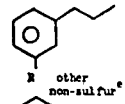
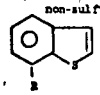
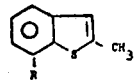
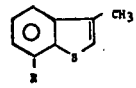
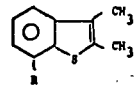
(3)

3. Dealkylation From Thiophene Ring

Sulfur containing products also arise from loss of thiophene ring methyl substituents. For example, I was formed

Table 3

Product Distribution from Hydrogenolysis of Substituted Benzothiophenes[a]

Product								
	H	CH_3	H	CH_3	H	CH_3	H	CH_3
	-	2	.5	2	5	2	4	1
	-	4	.5	.5	.5	-	-	-
	96	86	6	7	10	10	3	1
	-	-	5	3	42[c]	22[c]	2	2
	-	-	75	54[c]	18	10[c]	8	4
	-	-	-	-	-	-	28[c,d]	16[c]
	-	-	-	-	-	-	8	(1)
other non-sulfur[e]	-	0.5(2)	1(2)	4(5)	1(3)	0.5(2)	5(2)	10(4)[f]
	Charge		1	8	2	11	-	2
	-	-	Charge		18[c]	26	15	14
	-	-	9	14	Charge[c]		15	17
	-	-	-	-	-	-	Charge	
other sulfur cpds.[e]	-	7(3)	2(1)	9(3)	3(1)	19(4)	12(3)	32(6)[g]

a. Conditions: CoMo 0501 (Harshaw); 400°C; H_2/benzothiophene 3-5; pretreat, 3 hrs./550°C/H_2; yields are uncorrected vpc data taken after one hour on stream.

b. Max. of 0.5% 2-ethyltoluene, no 4-ethyltoluene as determined on a 5% Bentone 34-5% dinonyl phthalate on chromosorb W column.

c. Trapped from vpc and analyzed by MS.

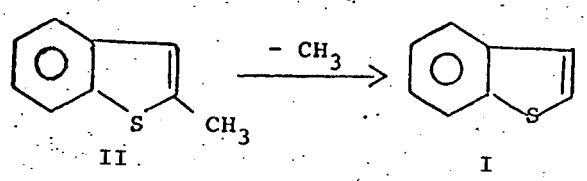
d. The small m/e 92 intensity (3% of m/e 91) excludes significant quantity of isobutylbenzene (m/e 92 is 67% of m/e 91) and n-butylbenzene (m/e 92 in ~65% of m/e 91).

e. Number of peaks shown in parentheses.

f. Two of these peaks were trapped by vpc. Molecular weights in one were 148 and 162 and in the other were 162 and 142 (possibly dimethylindanes).

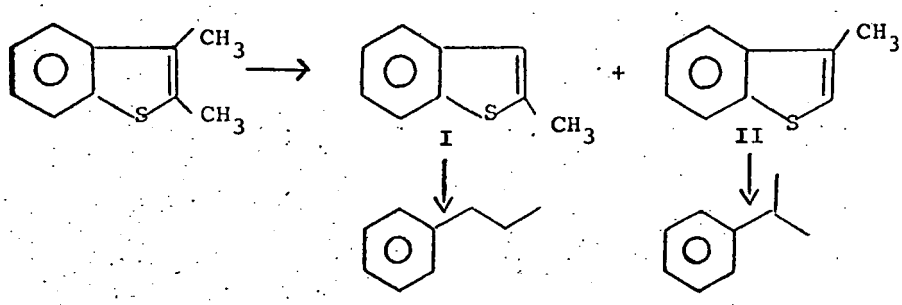
g. No 2,3-dihydro-2,3,7-trimethylbenzothiophenes are present.

from II by simple dealkylation of the 2-methyl substituent as shown in equation 4.



(4)

These dealkylation products were usually formed in smaller amounts than those produced via equation 3. This, of course, does not apply where both thiophene positions are occupied and the path in equation 3 is impossible. For example, II and III found in the product from 2,3-dimethylbenzo[b]thiophene, as shown in equation 5, resulted from monodemethylation reactions. These were the major sulfur products since simple 1,2-methyl shifts were not permitted in the reactant.

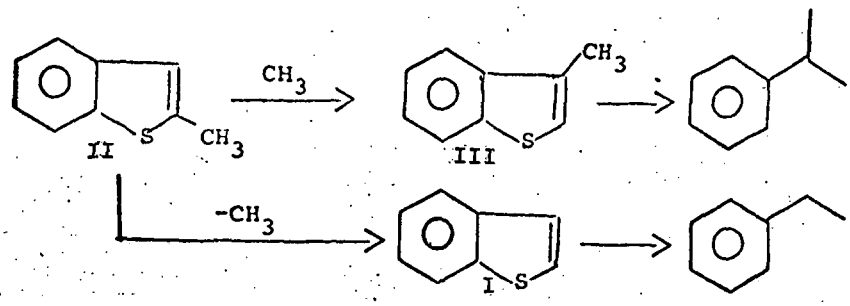


(5)

4. <u>Secondary Sulfur Extrusion</u>

Hydrocarbon products resulting from simple sulfur extrusion of <u>rearranged</u> and demethylated sulfur products are found in somewhat lesser amounts than the directly formed extrusion product in equation (3). This is illustrated by equation 6 where

the cumene and ethylbenzene formed from II resulted from sulfur extrusion of the methyl rearranged and dealkylated products, III and I, respectively.

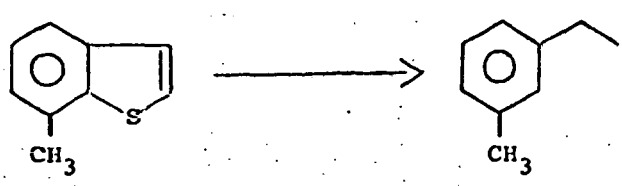


(6)

The same explanation is applied to the formation of n-propylbenzene and cumene from 2,3-dimethylbenzo[b]thiophene illustrated in equation 5.

5. Relative Inertness of Alkyl Substituents on Benzene Ring

Methyl substituents on the benzene ring of benzo[b]thiophene neither rearrange nor dealkylate under the conditions used in this study. The products are the same as those from non-six-ring substituted benzo[b]thiophenes except that each product bears an appropriately placed methyl substituent. For example, 7-methylbenzo[b]thiophene gave only 3-ethyltoluene (equation 7). Neither the ortho or para isomer was produced. The product distributions in Table 3, where the 7-methyl and the non-six-ring substituted benzo[b]thiophenes are compared, attest to this fact.



(7)

Applying these relationships permits us to predict with some certainty the products from hydrogenolysis of any other methyl- or polymethyl-benzo[b]thiophene. Using 3,7-dimethylbenzo[b]-thiophene from Table 3 as an example, we found the predictions and results agree, namely:

1. 3-isopropyltoluene was the major hydrocarbon product (compare with equation 2);
2. 2,7-dimethylbenzo[b]thiophene and 7-methylbenzo[b]-thiophene were the major sulfur containing products (compare with equations (3) and (4) respectively);
3. lesser amounts of 3-n-propyltoluene and 3-ethyl-toluene than the major hydrocarbon product were formed (compare with equation (5);
4. no loss or migration of the methyl group originally attached to the benzene ring of the 3,7-dimethylbenzo[b]-thiophene occurred.

The same applies to other examples chosen from Table 3.

B. Alternative Mechanisms

Although various alternative explanations may be applied to explain certain products, generally on close examination they are less tenable than those already postulated. For example, if ethylbenzene, formed from II, had arisen via cracking of n-propyl-benzene, toluene should have been an even more abundant product than it was, since such a mechanism would have favored toluene over ethylbenzene. The concentration of ethylbenzene in the product was, in fact, 8 times greater than toluene. An equally unlikely

mechanism is the formation of ethylbenzene via cumene cracking since benzene would have been expected as the favored product. Again, the yield of ethylbenzene was some 8 times greater than that of benzene.

Cumene in the product may have formed from II through n-propylbenzene side chain isomerization, which is known to occur to a slight extent under these conditions. However, the presence of III in the product from the 2-isomer (II) and the observed similar relative hydrodesulfurization rates for these isomers (see conversion data in Table 4 below) require that at least some of the cumene comes via the hydrodesulfurization route in equation 5. It seems likely that these routes occur concurrently, with the sulfur extrusion route probably being favored.

C. Conversion - Hydrodesulfurization: Structure Effects

Although in these cases great similarity in product types and distributions exist, a wide range of conversions of the individual benzothiophenes was observed. Conversion, was not necessarily related to hydrodesulfurization. For example, of the 47% 2,3,7-trimethylbenzothiophene that reacted (Table 4), only 16% was converted to sulfur free products.

Table 4

Conversion and Hydrodesulfurization Selectivity of Methyl- and Polymethyl-benzo[b]thiophenes

Position (Me group)	none	7	2	2,7	3	3,7	2,3	2,3,7
Conversion[a-1]	91-99	60	74	54	43	47	39	47
Hydrodesulfurization[a-2]	91-99	57	66	43	32	24	15	16
Selectivity (%)[b]	100	95	89	80	75	51	38	34

a. Reported as percent reactant (1) converted and (2) desulfurized.
b. Hydrodesulfurization/conversion x 100.

Several characteristics are readily apparent on examining these data. Generally an increase in the number of attached methyl groups decreased both conversion and hydrodesulfurization selectivity. Secondly, the presence of methyl substituents on the thiophene ring positions markedly lowered the hydrodesulfurization activity. Thirdly, a 3-methyl group caused a larger decrease in hydrodesulfurization selectivity than a 2-methyl substituent. An aromatic methyl substituent had a consistent but less pronounced effect. Therefore, the hydrodesulfurization selectivity sequence follows the order: $7\text{-}CH_3 > 2\text{-}CH_3 > 3\text{-}CH_3$. The consistent effect of an aromatic methyl group on the hydrodesulfurization selectivity is shown by comparing the following hydrodesulfurization yields:

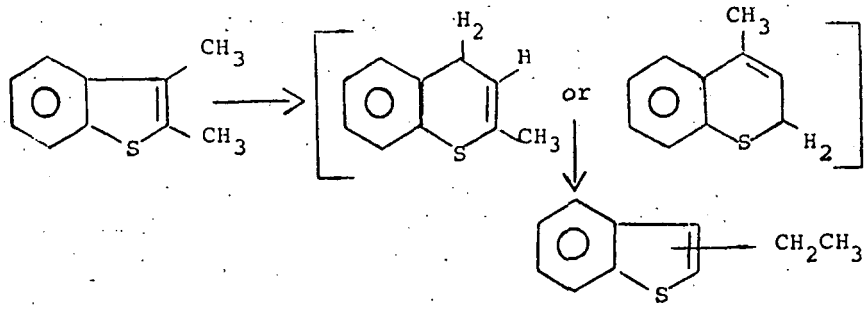
Benzo[b]thiophene	$> 7\text{-}CH_3$
$2\text{-}CH_3$	$> 2,7\text{-}(CH_3)_2$
$3\text{-}CH_3$	$> 3,7\text{-}(CH_3)_2$

We found that the hydrodesulfurization selectivity of the 2,3,7-trimethyl derivative is about the same as that of 2,3-dimethylbenzo[b]thiophene.

D. Unidentified Products

The 2,3-dimethyl compounds yielded more hydrocarbon and sulfur containing products than any of the other reactants examined (see Table 3). They also gave more unidentified products than any of the other reactants. If simple 1,2-methyl shifts were the sole mechanism by which rearrangement products arose, then the abundance of other unidentified materials appears inconsistent with the rather limited number of conceivable products that could form. The

multiplicity of unidentified products may result from a ring expansion mechanism such as the one shown below involving thiachromene type intermediates. Products such as ethylbenzo[b]-thiophenes and thiachromenes could originate by this mechanism.



The multiplicity of unidentified hydrocarbon products from these 2,3-dimethyl substituted benzo[b]thiophenes appears to parallel the unidentified sulfur containing products in the same way that most of the hydrocarbon products are related to sulfur containing products for substrates having up to one thiophene methyl substituent.

E. Intermediates

1. Dihydrobenzo[b]thiophenes

Evidence of dihydrobenzo[b]thiophenes in these reactions at 400°C and one atmosphere pressure can be found both at low temperatures and at very high flow rates. At 400°C and 0.3 LHSV the noble metal catalysts gave 2,3-dihydrobenzo[b]thiophene (IV) in rather low yield while cobalt molybdena gave none. Only at

higher space velocities (4 $hr.^{-1}$) did any IV appear, and then in only 2% yield (Table 2). At 300°C over cobalt molybdena the amount of IV in the product was equal to the ethylbenzene formed. No other products were present (Table 5). Therefore, the presence of IV in the product mixtures is consistent with it being an intermediate in this reaction.

Table 5

Hydrodesulfurization at Lower Temperature over Cobalt Molybdena[a]

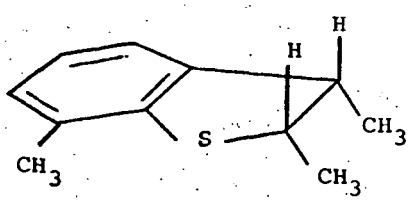
Reactant[b]	Temp.	$PhCH_2CH_3$	V	IV	I	$PhCH_2CH_2SH$
I	300	10	--	9	80	--
IV	290	8	--	74	18	--
2-CH_3CH_2PhSH (V)	290	94	5	0.1	1	--
$PhCH_2CH_2SH$ (VI)	300	91[c]	--	--	--	9

a. H_2/HC = 3-5/1; LHSV = 2.4.

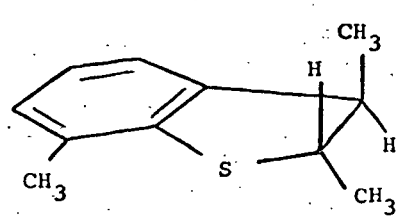
b. Reactants charged as 25% by weight in hexane.

c. Includes 6% styrene in the product.

We also observed the dihydro intermediate from the trimethyl substrate. When 2,3,7-trimethylbenzo[b]thiophene was passed over cobalt molybdena at 290°C only about 1% conversion was observed. In addition to 3-sec-butyltoluene, two other peaks identical with the retention times of erythro- and threo- 2,3-dihydro-2,3,7-trimethylbenzo[b]thiophene were found. These two isomers shown below were prepared separately by the method described



erythro



threo

in the experimental section and are, at present, indistinguishable as to stereochemistry.

When 1% of 2,3-dimethylbenzo[b]thiophene was converted in the same way as noted above, sec-butylbenzene was found along with two peaks in the chromatograph not detected in the 400°C run. The retention times of these 2 peaks were similar to those observed above for the 2,3-dihydro-2,3,7-trimethylbenzo[b]thiophenes, which suggests the presence of erythro- and threo-2,3-dihydro-2,3-dimethylbenzo[b]thiophene. We have not, however, compared these retention times with authentic samples.

When IV was passed over cobalt molybdena under the conditions of this reaction, I and ethylbenzene were the only main products. The product distributions from I (Table 1) and IV (Table 6) were almost identical at 400°C and 0.3 LHSV. Even at

Table 6

Hydrodesulfurization of 2,3- Dihydrobenzo[b]thiophene (IV)[a]

Catalyst	Product Distribution			
	IV	I	Ethylbenzene	Other
Cobalt molybdate	2	1	95	2
Cobalt molybdate[b]	1	8	89	2
Cobalt molybdate[c]	2	68	30	--
Non-acidic Alumina[c]	95	5	--	--
Pt on non-acidic alumina[c]	27	61	12	--
Rh on non-acidic alumina[c]	24	66	10	--
Chromia-alumina[c]	32	58	10	--

a. Conditions: 400°C; LHSV 0.30; H_2/II = 4; samples taken after one hour on stream; IV is charged as a 50% (by weight) mixture in hexane.
b. 350°C.
c. No carrier gas.

~300°C the conversions of I and IV and the yield of desulfurized product were about the same (Table 5). We did observe some departure from apparent equilibrium at 400°C and 4 LHSV where the distributions from reactions of I and IV differed somewhat (Table 7). Since IV is itself a source of hydrogen the different partial pressures of hydrogen in these two reactions could affect the product distribution, although such a large increase in desulfurized product (18 to 40%) would not be expected. Without a large excess of hydrogen a constant ratio of I and IV cannot be anticipated.

Table 7

Comparison of the Hydrodesulfurization of I and IV over Cobalt Molybdena[a]

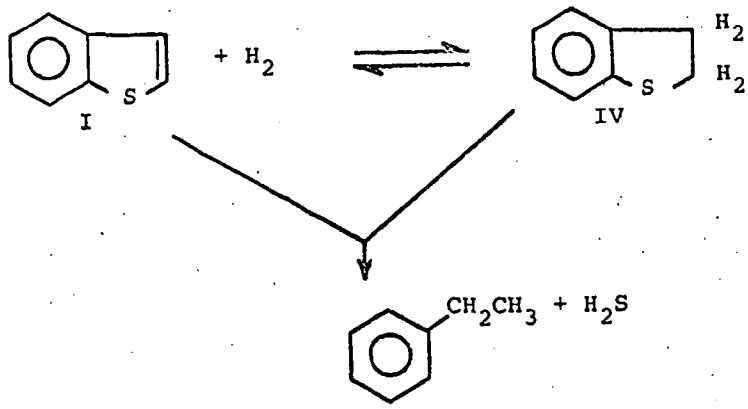
Charge (% wt) 50% in Hexane		Reactant Composition		
I	IV	$PhCH_2CH_3$	I	IV
100	--	18	80	2
50	50	22	70	8
---	100	40	56	3

a. Liquid flow rate: 4 cc/hr., H_2, 25 cc/min; 400°C; LHSV 4.

At 400°C IV will dehydrogenate to the extent of 5% over alumina. Addition of Pt or Rh increases the reaction of IV to 73 and 76%, respectively (Table 6). Although desulfurization was small it was similar to that observed for I over these same catalysts.

Therefore, it appears that equilibrium occurs rapidly between I and IV (as depicted in eq. 8). The desulfurization reaction that gives ethylbenzene is a slow step that drains this

equilibrium state in a non-reversible manner. Since both I and IV form ethylbenzene at comparable rates, to exclude either as a

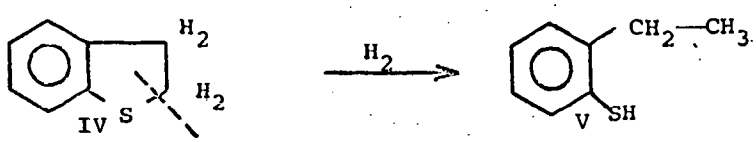


(8)

source of desulfurized product is not possible by our data. If we assume for the present that IV is the source of ethylbenzene, desulfurization may be a multistep process involving first a cleavage of one carbon-sulfur bond to give a discrete mercaptan intermediate followed by a second carbon-sulfur bond cleavage to give hydrocarbon product and H_2S. Alternatively, sulfur may be lost in a one step process involving a synchronous breaking of two carbon-sulfur bonds giving rise to hydrocarbon product directly without involving mercaptan intermediates.

2. <u>2-Ethylthiophenol</u>

A stepwise carbon-sulfur bond cleavage in IV could result in 2-ethylthiophenol (V) (eq. 3) if the bond between C_2 and S were broken as shown in eq. 9.

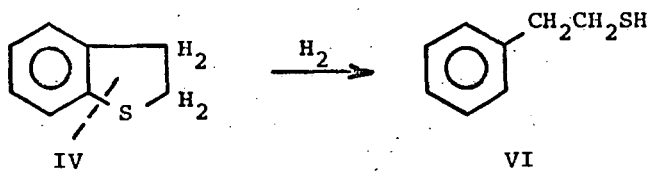


(9)

Such an intermediate has never been detected in our product mixtures. When V was passed over cobalt molybdena in hydrogen at 290°C, 94% was converted to ethylbenzene and 1% to I (Table 5). Since under similar conditions thiophenol is also completely converted to benzene, it appears that the rate of desulfurization of aryl mercaptans, in particular V, is about 30 times faster than that of I * excludes any likely possibility of finding them in the product mixture. The presence of 1% of I in the product can be explained by the reversibility of eq. 9 as is well known (27,32). The reverse reaction in hydrogen apparently is not favored at 400°C.

3. β-Phenylethyl mercaptan

Cleavage of the other carbon-sulfur bond is also possible (eq. 10). β-Phenylethyl mercaptan (VI) might be a likely intermediate although, again, it could not be detected. At 300°C in



(10)

hydrogen it forms ethylbenzene and styrene in greater than 90% yield without any trace of I or IV. VI appears to react at about the same rate as V which is 30 times faster than either that of I or IV.* Since alkyl mercaptans are so easily desulfurized, even

*This can be deduced from the data in Table 5.

in the absence of hydrogen, it is highly unlikely that VI can be found. Indeed, it must be at most only a very short-lived intermediate.

The reversibility of this reaction (eq. 10) at either 300° or 400°C is not likely, although under suitable conditions (600°C) I can be formed (33,34). On examining the reaction somewhat further, it appears that even alumina will catalyze its decomposition, giving styrene primarily. In the presence of a hydrogenation function, however, ethylbenzene is the main product (Table 8). A solid (mp 133-135°C) was observed from the reaction

Table 8

β-Phenylethyl Mercaptan (VI) Hydrogenolysis[a]

Catalyst	Gas	Styrene	Ethylbenzene
Al_2O_3	H_2	84	14
Pt/Al_2O_3	H_2	1	96
Pt/Al_2O_3	N_2	22	74
CoMo	H_2	--	100

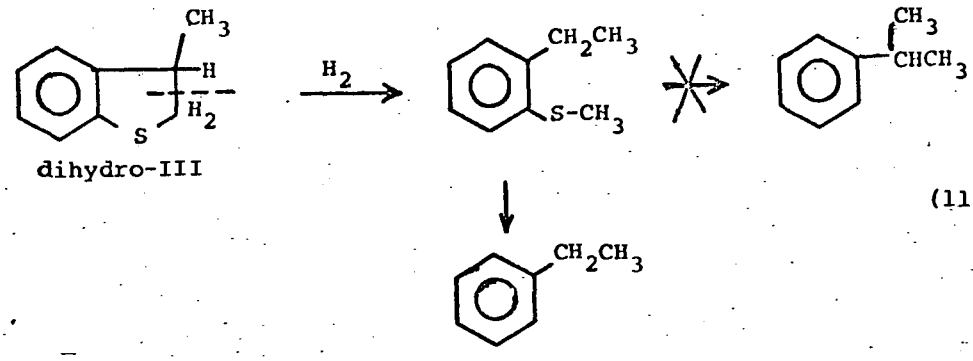
a. 400°C; LHSV 0.30; Conversion 100%; non-acidic alumina (13) was used.

in hydrogen over alumina. Its mass spectrum had a parent ion that was also the base peak at m/e 236. This is suggestive of diphenylthiophene isolated previously in similar systems (33).

OTHER INTERMEDIATES

There are other alternative routes besides those that arise by initial carbon-sulfur bond cleavage. We have examined the possibility of an initial C-C cleavage. If dihydro III were

fragmented as shown here, methyl 2-ethylphenyl sulfide would be formed (eq. 11). In order for this sulfide to fit the product



(11)

distribution, it must desulfurize to give cumene. Under these conditions 2-ethylphenyl methyl sulfide gave no cumene. The only products found were a small amount of I and ethylbenzene (Table 9). Over Pt/Al_2O_3 somewhat more I was formed, but no cumene. This rules out the possibility of an important C_2-C_3 bond-breaking sequence.

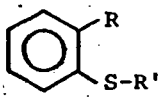


Table 9

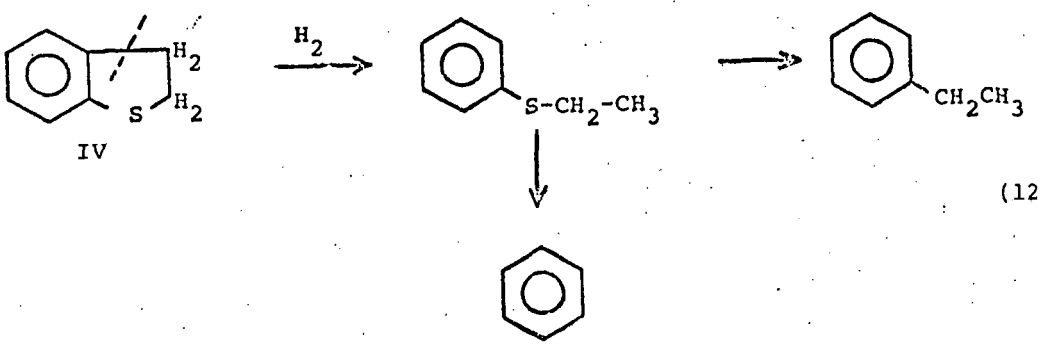
Hydrogenation of Alkyl Aryl Sulfides at 400°C

R	R'	Catalyst	Gas	Conv.	Products: Benzene	Products: $PhCH_2CH_3$	Products: I
H	C_2H_5	Pt/Al_2O_3	H_2	99	99	--	--
H	C_2H_5	Al_2O_3	N_2	41[a]	--	--	--
C_2H_5	CH_3	CoMo	H_2	100[b]	--	99	--
C_2H_5	CH_3	Pt/Al_2O_3	H_2	99[b]	--	89	8

a. Thiophenol was the only product.

b. No 2-ethylthiophenol, cumene or III was detected.

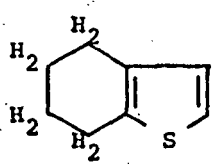
The possibility of cleavage of the C_{aryl} - C_{alkyl} bond (eq. 12) was also eliminated since ethyl phenyl sulfide



(12)

reacts in hydrogen over Pt/Al_2O_3 (Table 9) to give benzene in 99% yield. No ethylbenzene was detected, nor were I and IV found. Presumably cobalt molybdena would act similarly. Since neither ethyl phenyl sulfide or 2-ethylphenyl methyl sulfide gives products consistent with those observed from the respective benzo[b]thiophenes, C-C bond cleavage is apparently unimportant in these reactions.

Other partially hydrogenated structures besides IV are also possible intermediates. Complete or partial hydrogenation of the aromatic ring system to destroy the resonance stabilization of the ring system has been proposed before desulfurization reactions (11). Hydrodenitrogenation reactions are also thought to proceed by this route (35,36). Therefore, 4,5,6,7-tetrahydrobenzothiophene (VII), a partially hydrogenated benzothiophene and thus a possible intermediate, was examined under these conditions at 400°C over



VII

cobalt molybdena. It reacted almost completely, giving I, IV and ethylbenzene (Table 8) which is consistent with the products from I. However, even in the absence of hydrogen, VII was converted easily, although not without a hydrogenation function present. At

Table 10

Reaction of 4,5,6,7-Tetrahydrobenzothiophene (VII)

Catalyst	Temp. °C	Conv.	$PhCH_2CH_3$	I	IV	Other
Cobalt molybdena[a]	400°	92	36	58	3	
Cobalt molybdena[b]	290°	12	22	3	9	(63% other hydrogenated material)
non-acidic alumina[c]	400°	0				
Cobalt molybdena[d]	400°	100	30	67	--	

a. LHSV 4.0; H_2/HC = 4; 50% VII in hexane

b. LHSV 2.4; H_2/HC = 4; 25% VII in hexane

c. LHSV 0.30; N_2 as carrier gas; 50% VII in hexane

d. LHSV 0.30; N_2 as carrier gas N_2/HC = 4, toluene and IV less than 1%. 50% VII in hexane

290°C, however, VII was only 12% converted, 63% being hydrogenated materials not previously observed from I or IV. The behavior at low temperature precludes any possibility of VII being an intermediate in this reaction.

Therefore, in summary our results show that desulfurization may occur by a sequence involving cleavage of one C-S bond to give a mercaptan, followed by cleavage of the second bond to give ethylbenzene. The relative ease of hydrogenolysis of the C-S bonds of either the aryl mercaptans or alkyl mercaptans appears to be about the same under these conditions. In the absence of hydrogen,

however, the alkyl carbon-sulfur bond is broken preferentially since ethyl phenyl sulfide over alumina in N_2 gives phenyl mercaptan in 40% yield as the only product (Table 9). Our data can only conclude that if a stepwise process does occur, then carbon-sulfur bond cleavage would not be selective.

CONCLUSIONS

1. The products from hydrodesulfurization of methyl-substituted benzo[b]thiophenes at atmospheric pressure and 400°C stem from certain common paths, as pointed out and schematically illustrated for 3,7-dimethylbenzo[b]thiophene below.

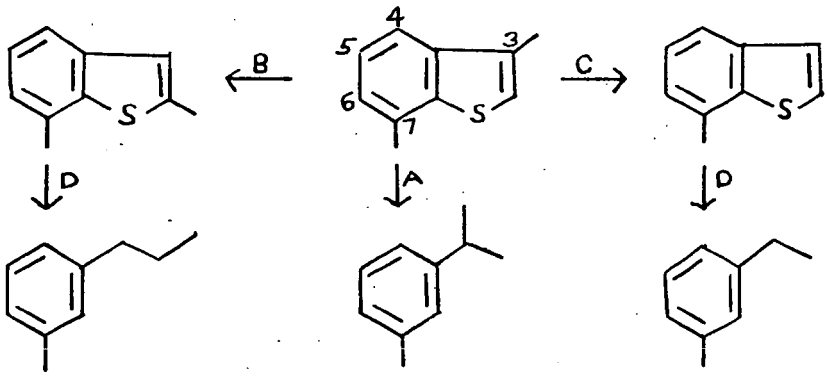
A. Direct sulfur extrusion from the primary reactant.

B. Alkyl group migration on the thiophene ring.

C. Dealkylation from the thiophene ring.

D. Sulfur extrusion from rearranged or demethylated secondary products.

E. Relative inertness of benzene ring methyl groups to dealkylation or migration.



2. Conversions, product distribution and hydrodesulfurization selectivities were highly dependent upon the number and positions of the methyl groups. The greater the number of methyl groups, the lower the conversion. Thiophene methyl groups lower the conversion and hydrodesulfurization selectivities more than a methyl substituent on the benzene ring.

3. Dihydrobenzo[b]thiophenes appear to be intermediates in these reactions. Their detection under certain reaction conditions and their behavior under similar reaction conditions supports this conclusion.

4. The desulfurization step involves C-S bond breaking. No evidence was found for C-C bond breaking.

5. Aromatic ring saturation is not necessary before C_{aryl}-S bond breaking occurs.

ACKNOWLEDGEMENT

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