

ticeable from Table II is that all mercury(II) complexes having fewer than two halide ligands react at the diffusion limit, and this high reactivity can be essentially "turned off" by loading the solution with halide ligand. Thus, while mercury(II) is noted for high reactivity toward sulfur in proteins, this is dependent upon the state of complexation of the mercury. As previously noted,<sup>5</sup> if mercury(II) is preincubated with sulfur ligands, the high Lewis acid reactivity disappears. Certainly in our chemical system, once the mercury(II) complexes with the sulfur moiety, it is effectively removed from the reaction scenario. Future work will examine the effect of ligands other than halide; however, a much more reactive system will have to be found to examine the more interesting case of thio ligands.

We have attempted to elucidate a quantitative relationship, using approaches often used to establish linear free energy relationships, but have been unsuccessful so far. One problem with the data in Table II is that they are not extensive enough. As additional data emerges, we are hopeful that the reactivities of metal complexes can be quantified.

**Mechanism of Hydrolyses Promoted by Mercury(II).** As the prior discussion emphasizes, the mechanism of these hydrolyses promoted by mercury(II) involves as much inorganic chemistry as organic; indeed, the very close similarity of the rates of hydrolysis of the *S*-ethyl and *S*-phenyl *O,S*-acetals implies that carbon-sulfur bond heterolysis is not part of the kinetics, since it is known that such heterolysis exhibits a substantial difference in reactivity toward Brønsted acids.<sup>7</sup> The mechanism for the diffusion controlled processes was shown in Scheme VI; the mechanism proposed for the other processes is illustrated using  $\text{HgX}_2$ .

The absence of substantial difference in rate between

the two *O,S*-acetals implies that the dissociation of  $\text{X}^-$  is not concerted with carbon-sulfur heterolysis, and therefore the mechanism is shown as occurring stepwise. The plausibility of this mechanism can be demonstrated by evaluating reasonable preequilibrium constants and dissociation rate constants. The preequilibrium involves association of a soft sulfur center—a good model from Chart I would be association of a soft iodide. An estimate of  $10^3$  to  $10^4$  is reasonable. The rate constant for the rate determining step in Scheme VII will vary with  $\text{X}^-$ ; using the measured rate constants from Table II and a preequilibrium constant of  $10^4$  gives  $k_{\text{rds}}$  of  $10^2$ , 10, and  $10^{-2}$  for chloride, bromide, and iodide dissociations, respectively. While these are certainly consistent with the  $k_{\text{dis}}$  values given in Scheme IV for the dihalide, they are best viewed as minimum values, since the models assumed were chosen most conservatively. The point is not to calculate the specific constants in Scheme VII but to demonstrate that perfectly reasonable values of the constants combine to produce the observed rate constant.

It is important to recognize that the rate-limiting step in Scheme VII arises because the  $\text{HgX}_2$ -acetal complex dissociates the neutral acetal preferentially to the negatively charged halide (i.e., the first step is an equilibrium) and the subsequent complex undergoes carbon-sulfur heterolysis preferentially to reassociation with halide (i.e., the second step is not reversible kinetically). We are currently examining systems which are more likely to show rate-limiting carbon-sulfur heterolysis.

**Acknowledgment.** This work was supported by basic research and equipment grants from the National Science Foundation (CHE-8421082, CHE-9020804, and PRM 7919451).

## Desulfurization of Benzo- and Dibenzothiophenes with Nickel Boride

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Nickel boride, prepared from the reduction of nickel chloride hexahydrate with sodium borohydride in methanol-tetrahydrofuran, reduces benzothiophenes to alkylbenzenes and dibenzothiophenes to biphenyls. The reaction is rapid at or below room temperature and does not require protection from the atmosphere. Best results are obtained when the nickel boride is generated in situ in the presence of the sulfur compound. Hydroxyl, carboxyl, ester, and amino groups are unaffected while chloro, bromo, and nitro substituents are also reduced under these conditions. A short-lived intermediate, possibly a nickel hydride species, appears to be required in the desulfurization. Complexation of the substrate to the nickel boride surface, followed by stepwise reduction of the two C-S bonds, occurs. The faster disappearance of dibenzothiophene containing the lighter <sup>32</sup>S isotope compared to that with <sup>34</sup>S ( $k(^{32}\text{S})/k(^{34}\text{S}) = 1.005$  to  $1.006$ ) suggests that C-S bond cleavage is the rate-determining step.

The reductive desulfurization of various types of organosulfur compounds is of importance both in the laboratory and in industry. In the former case, many synthetic procedures are based upon transformations that utilize a sulfur-containing functionality that must then be reductively removed in the final step. Moreover, the fuel processing industry is faced with increasingly stringent requirements for fuels with low sulfur content in response to mounting concerns over acid rain. Consequently, there

is considerable interest in both areas in new methodology that can efficiently reduce C-S bonds to C-H bonds.

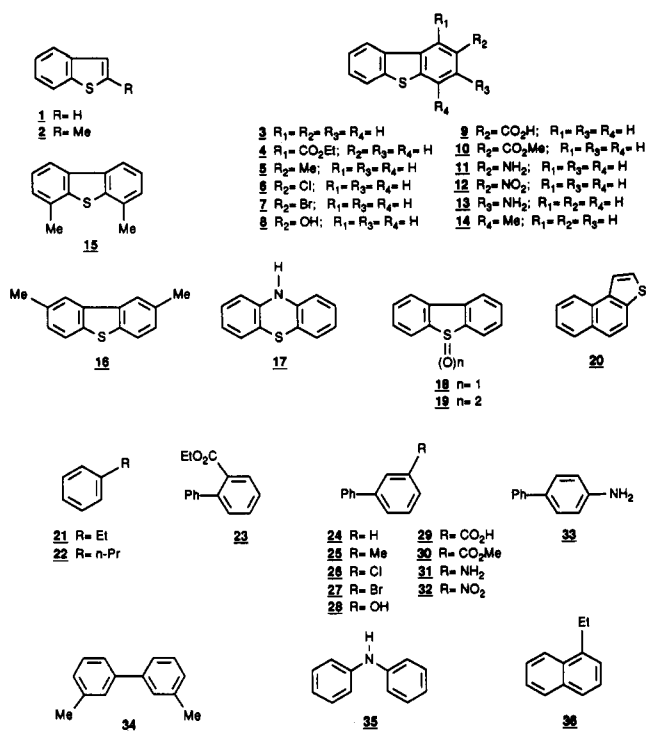
Polycyclic aromatic sulfur compounds such as benzo- and dibenzothiophenes are of special relevance because of their widespread occurrence in fossil fuels and the fact that they are particularly difficult to remove by conventional hydrodesulfurization methods.<sup>1</sup> Furthermore, the sulfur atom of such heterocycles has a strong directing effect towards metalations, alkylations, acylations, and other reactions.<sup>2</sup> Subsequent desulfurization then provides

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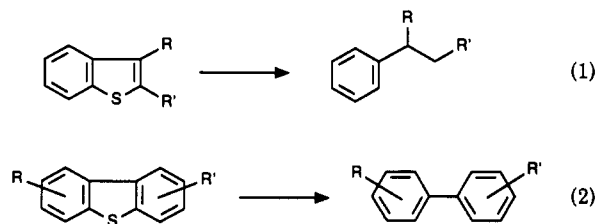
<sup>†</sup>Department of Physics and Astronomy.

(1) Angelici, R. J. *Acc. Chem. Res.* 1988, 21, 387.

Chart I



regioselective entry to variously substituted arenes, bi-phenyls, and related compounds (eqs 1 and 2).



Apart from commercial hydrodesulfurization procedures, a number of other reductive desulfurization methods have been reported for compounds such as thiols, sulfides, and their congeners.<sup>3</sup> Examples include the use of alkali metals,<sup>4</sup> tin hydrides,<sup>5</sup> metal carbonyls,<sup>6</sup> Raney nickel,<sup>7</sup> nickel-aluminum alloy,<sup>8</sup> and reducing agents derived from transition metals and lithium aluminum hydride,<sup>9,10</sup> sodium hydride,<sup>11</sup> Grignard reagents,<sup>12</sup> or sodium borohydride.<sup>9</sup> The latter include nickel boride, a fine, black solid that is easily prepared by the reduction of Ni(II) salts

Table I. Desulfurization of Benzo- and Dibenzothiophenes with Nickel Boride

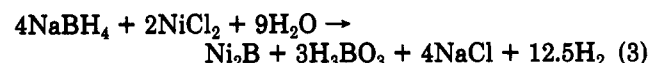
substrate	moles Ni(II) per mole substrate <sup>a,b</sup>	time (min) <sup>c</sup>	product (yield, %) <sup>d</sup>
1	7	15	21 (73)
	14	15	21 (82)
2	14	15	22 (62)
3	7 <sup>e</sup>	60	24 (69)
	14	60	24 (83)
4	14	60	23 (78) <sup>f</sup>
5	14	60	25 (75)
6	7	15	24 (20) + 26 (35) + 3 (25)
	14	60	24 (55) + 26 (30)
7	7	15	24 (38) + 27 (4) + 3 (47)
	14	60	24 (77) + 3 (11)
8	14	60	28 (70) <sup>f</sup>
9	14	60	29 (74) <sup>f</sup>
10	7	15	30 (68) <sup>f</sup>
11	14	60	31 (81)
12	7	15	31 (44) + 11 (40)
	14	60	31 (82)
13	14	60	33 (85) <sup>f</sup>
14	7	15	25 (20)
	14	60	25 (35)
	21	60	25 (63)
15	7	15	34 (6)
	30	60	34 (29)
16	7	15	34 (35)
	14	60	34 (69)
17	14 <sup>e</sup>	60	35 (68) <sup>f</sup>
18	14	60	24 (75) + 3 (6)
19	14	60	24 (22)
20	7	15	36 (60)
	14	60	36 (75)

<sup>a</sup>Three moles of NaBH<sub>4</sub> were used per mole of NiCl<sub>2</sub>·6H<sub>2</sub>O.

<sup>b</sup>The solvent was 3:1 MeOH-THF unless otherwise indicated.

<sup>c</sup>Reactions performed for 15 min were at 0 °C and those performed for 60 min were at room temperature. <sup>d</sup>Yields were determined by GC, using an internal standard, unless otherwise indicated. <sup>e</sup>The solvent was 1:2:1 MeOH-THF-H<sub>2</sub>O. <sup>f</sup>Isolated yield.

with sodium borohydride,<sup>13</sup> usually in protic solvents as shown in eq 3. Although it has proved difficult to char-



acterize,<sup>14</sup> nickel boride ("Ni<sub>2</sub>B") is a useful reducing agent for a variety of functional groups.<sup>9</sup> Its low cost, ease of preparation and handling, nonpyrophoric nature, and simple removal from a reaction mixture by filtration make it a particularly convenient reagent. Several reports of desulfurizations effected with nickel boride have appeared in the literature.<sup>15</sup> In some of the earlier cases, the pro-

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(3) For a general review, see: Luh, T.-Y.; Ni, Z.-J. *Synthesis* 1990, 89.

(4) See inter alia: (a) Gilman, H.; Dietrich, J. J. *J. Org. Chem.* 1957, 22, 851. (b) Ignasiak, T.; Kemp-Jones, A. V.; Strausz, O. P. *J. Org. Chem.* 1977, 42, 312. (c) Maercker, A. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 972.

(5) Neumann, W. P. *Synthesis* 1987, 665.

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cedures employed required elevated temperatures and long reaction times. Furthermore, examples to date encompass a relatively narrow range of substrates, none of which include the reductively recalcitrant benzo- and dibenzothiophenes. We now report a protocol where nickel boride functions as an effective reagent for the rapid desulfurization of the latter compounds under remarkably mild conditions.<sup>16</sup>

## Results and Discussion

**Reaction Conditions and Scope.** The results of our desulfurizations are listed in Table I and the structures of substrates and products are shown in Chart I. Typically, the sulfur compound and nickel(II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) were stirred in methanol-THF (3:1) at 0 °C or at room temperature and sodium borohydride was added in small portions. The immediate formation of nickel boride was observed, accompanied by the vigorous evolution of hydrogen. Desulfurization occurred rapidly and the spent nickel boride was easily removed by filtration. The reactions were carried out in a simple, open Erlenmeyer flask without the need for protection from the atmosphere.

The choice of the nickel salt was based upon its good solubility in methanol and on the report that it produces nickel boride with a high surface proportion of boron bonded to nickel, a feature that enhances its reactivity.<sup>14b</sup> However, we also observed that nickel(II) bromide, acetate, sulfate, and sulfamate gave comparable results to those obtained with the chloride in the desulfurization of dibenzothiophene to biphenyl, while nickel(II) nitrate and acetylacetonate produced substantially lower yields of the product. Although neat methanol was a suitable solvent, the addition of THF assisted the dissolution of the substrates. In some cases, the addition of water proved beneficial.

In our previous study of nickel boride-mediated deselenizations,<sup>17</sup> we observed that the reactivity of the reagent decreased rapidly with time. Similarly, when nickel boride was produced in the usual manner and dibenzothiophene was added subsequently, drastically poorer yields of biphenyl were obtained. The deleterious aging effect was evident even with a delay of just 5 min, which resulted in the production of only traces (ca. 1%) of biphenyl instead of the normal yield of 83% shown in Table I. Thus, although reaction times of 15–60 min were typically employed, it appears that the reaction is essentially complete within the first few minutes and it is critical that the organosulfur compound be present in the reaction mixture during the formation of the nickel boride.<sup>18</sup> Although the preparation of the boride according to the stoichiometry of eq 3<sup>9</sup> demands a 2:1 molar ratio of  $\text{NaBH}_4$  to Ni(II), a ratio of 3:1 was employed<sup>17</sup> to compensate for the catalytic decomposition of the borohydride by the newly-formed nickel boride.<sup>13</sup> In contrast to the deselenizations that often proceed efficiently with as little as 2 mol of Ni(II) salt (i.e., 1 mol of  $\text{Ni}_2\text{B}$ ) per mole of selenide, the more robust sulfur compounds in the present study required a substantial excess of the nickel boride reagent and unreacted starting materials accounted for nearly all of the remaining mass balance in the examples in Table I. Sodium borohydride alone failed to desulfurize dibenzo-

thiophene in a control experiment.

Table I also reveals that the desulfurization reaction is not particularly sensitive to electronic effects, as comparable yields were obtained with either electron-donating or electron-withdrawing substituents attached to various positions of the dibenzothiophene nucleus. However, steric hindrance from substituents in the vicinity of the sulfur atom impede the reaction significantly. Thus, 2-methylbenzothiophene (2) afforded a lower yield of *n*-propylbenzene (22) than did benzothiophene (1) of ethylbenzene (21), even with a double amount of the  $\text{Ni}_2\text{B}$  reagent. Similarly, dibenzothiophene (3), 4-methyldibenzothiophene (14), and 4,6-dimethyldibenzothiophene (15) produced decreasing yields of biphenyl (24) and the methyl and dimethyl derivatives 25 and 34, respectively, even in the presence of increased quantities of  $\text{Ni}_2\text{B}$ . On the other hand, methyl substituents that are remote from the sulfur atom (e.g. 5 and 16) had little effect on the yields of the products. The table also indicates that hydroxyl, carboxyl, ester, and amino groups are unaffected by the reaction, whereas reduction of the chloro substituent of 6 is competitive with desulfurization and the reductions of the nitro group of 12 and the bromo substituent of 7 occur preferentially. We also note that dibenzothiophene sulfoxide (18) was smoothly reduced to biphenyl (24) while the corresponding sulfone 19 proved more resistant to desulfurization.

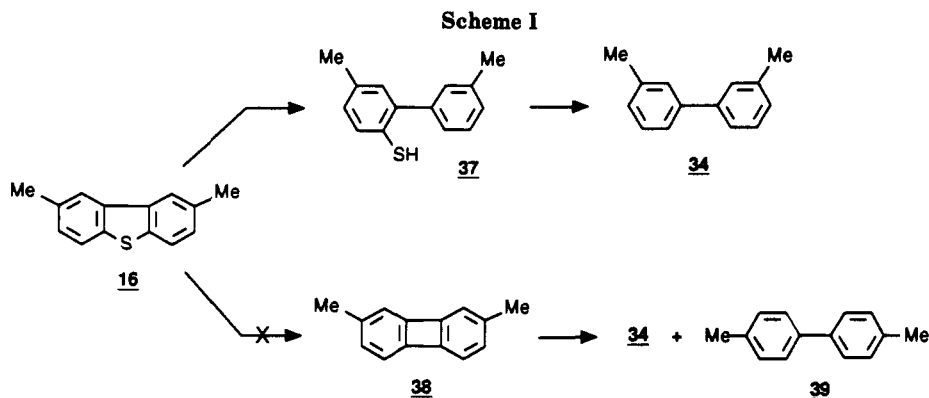
**Mechanism.** During our previous work on deselenization with  $\text{Ni}_2\text{B}$ ,<sup>17</sup> we demonstrated by means of deuterium labeling that the hydrogen atom incorporated into the product during C–Se bond cleavage can originate from either the  $\text{NaBH}_4$  or the protic solvent. Since nickel boride catalyzes the formation of hydrogen gas from  $\text{NaBH}_4$  and the protic solvent under these conditions,<sup>13</sup> it appears likely that dihydrogen is thus first produced and then adsorbed and activated on the nickel boride surface.<sup>15a</sup> This is consistent with the report by Hawthorne and co-workers<sup>14a</sup> that fresh nickel boride has the composition  $(\text{Ni}_2\text{B})_2\text{H}_3$  and that hydrogen is gradually lost when it is heated. However, the much faster loss of reactivity of nickel boride upon aging in both deselenization and the present desulfurization experiments suggests that an essential transient intermediate, and not merely adsorbed hydrogen, is formed on its surface. Although there is no firm evidence concerning the nature of this intermediate, a nickel hydride<sup>19</sup> is a likely candidate. The aging phenomenon is not due to oxidative degradation of the nickel boride by atmospheric oxygen, since the use of an argon atmosphere and careful degassing of the solvent did not prolong the reactivity of the nickel boride in the desulfurization of dibenzothiophene. Attempts to effect desulfurization of the latter with preformed (30 min) nickel boride in the presence of hydrogen gas at pressures of 30–35 atm afforded the low, but significant yield of 18% of biphenyl. This demonstrates that the postulated transient intermediate that is produced during the formation of nickel boride is to some extent regenerated by the treatment of preformed nickel boride with hydrogen gas. However, attempts to use nickel boride catalytically in the presence of hydrogen were unsuccessful, presumably because of the irreversible

(16) Preliminary communication: Back, T. G.; Yang, K. *J. Chem. Soc., Chem. Commun.* 1990, 819.

(17) Back, T. G.; Birss, V. I.; Edwards, M.; Krishna, M. V. *J. Org. Chem.* 1988, 53, 3815.

(18) The aging effect may explain why some of the earlier desulfurizations, using preformed nickel boride, required much more forcing conditions than our protocol, e.g., several hours at 200 °C; see ref 15c.

(19) The formation of transition-metal hydrides from the reduction of their salts with complex hydrides is well known; see: (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* 1972, 72, 231. For examples of other desulfurizations where nickel hydride species have been postulated, see: refs 10a,b and 12c. The formations of transient cobalt hydrides in certain reductions effected with cobalt boride have also been considered, see: (b) Osby, J. O.; Heinzman, S. W.; Ganem, B. *J. Am. Chem. Soc.* 1986, 108, 67. Other types of reactive intermediates, such as Ni(0) species, are also conceivable in the present reactions.



formation of nickel or boron sulfide byproducts. The regeneration of the reactive species by treating nickel boride that had been aged 5 min with fresh  $\text{NaBH}_4$  was also partly successful, affording 10% of biphenyl. We also considered the possibility that contamination of the  $\text{Ni}_2\text{B}$  surface by spectator ions plays a role in the loss of reactivity. However, attempts to wash preformed nickel boride with various solvents and to reactivate it by means of ultrasound failed to restore its desulfurizing capability. It is interesting to note, however, that aged nickel boride is still capable of catalyzing the decomposition of  $\text{NaBH}_4$  and the hydrogenating of olefins,<sup>13</sup> suggesting that these processes do not require the same transient intermediate postulated in desulfurization processes.

The possibility that biphenylene intermediates are formed by the extrusion of sulfur from dibenzothiophene in other types of desulfurization procedures was previously considered by Eisch<sup>20</sup> and Caubère<sup>11b</sup> and their co-workers. This pathway was ruled out in the present case by the observation that 2,8-dimethyldibenzothiophene (16) produced only 3,3'-dimethylbiphenyl (34) and not the 4,4'-dimethyl isomer 39 (Scheme I). Both biphenyls could be formed if the unsymmetrical species 38 was an intermediate. Our results parallel those reported by Eisch using (2,2'-bipyridyl)(1,5-cyclooctadiene)nickel(0) as the desulfurizing species but contrast with those of Caubère, who obtained only 39 with a NiCRA-bpy reagent. Moreover, we observed that the desulfurization of phenothiazine with nickel boride afforded diphenylamine and not carbazole,<sup>21</sup> again demonstrating that C-C bond formation does not accompany reduction of the C-S linkages in the present reactions.

Both Eisch and Caubère proposed single electron transfer (SET) mechanisms for their respective desulfurizations and observed that dibenzothiophene is substantially more reactive than the 2,8-dimethyl derivative under their conditions. This is presumably due to the destabilizing effects of alkyl substituents upon the radical anion intermediates formed in SET processes. In contrast to their results, a competition experiment between dibenzothiophene (3) and the 2,8-dimethyl derivative 16 showed little difference in their reactivity towards nickel boride, suggesting that SET processes are not involved in the present reactions. The possibility of free-radical intermediates<sup>22</sup> produced by homolysis of the C-Se bond was ruled out in our previous study of  $\text{Ni}_2\text{B}$ -mediated dese-

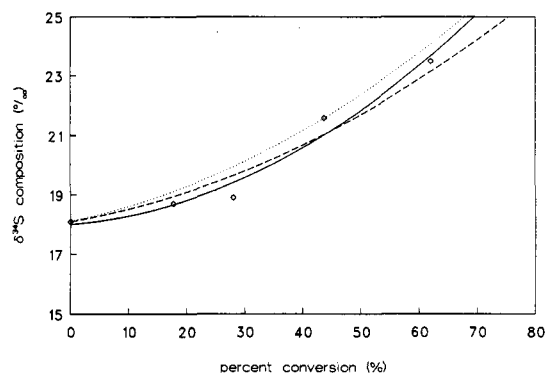


Figure 1. S isotope composition in recovered starting material. The S-isotope composition is reported in terms of the natural abundance  $\delta(^{34}\text{S})$  scale defined in eq 4, where ‰ is parts per

$$\delta(^{34}\text{S}) \text{ (in ‰)} = \left\{ \frac{[^{34}\text{S}/^{32}\text{S}]_x}{[^{34}\text{S}/^{32}\text{S}]_{\text{CDT}}} - 1 \right\} \times 10^3 \quad (4)$$

thousand (per mil),  $^{34}\text{S}/^{32}\text{S}$  is the number ratio of  $^{34}\text{S}$  to  $^{32}\text{S}$  atoms in the sample X or in the international CDT (Canyon Diablo Meteorite Troilite) standard. The solid curve and points represent experimental values, while the upper and lower broken curves represent the theoretical  $^{34}\text{S}$  compositions for  $k(^{32}\text{S})/k(^{34}\text{S}) = 1.006$  and 1.005, respectively, calculated according to ref 23.

lenizations<sup>17</sup> by the failure to observe deuterated products in the presence of labeled hydrogen atom donors such as  $\text{THF-d}_8$ . Similar conclusions in the present instance are made by analogy.

Desulfurization with  $\text{Ni}_2\text{B}$  appears to proceed in a stepwise fashion, probably via the thiol 37 or the corresponding thiolate. Since the reaction mixtures from dibenzothiophenes contain only the corresponding biphenyls along the unreacted starting materials, but no significant amounts of thiol products, we conclude that, as expected, the latter species undergo desulfurization more easily than the original dibenzothiophenes. Initial complexation of dibenzothiophene with nickel chloride prior to addition of the sodium borohydride was ruled out because the UV-vis spectrum of an equimolar solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and dibenzothiophene in methanol was identical to the superimposed spectra of the individual components. However, an attempt was made to determine whether complexation of the dibenzothiophene with the nickel boride or the C-S bond cleavage step was rate-determining. We studied the desulfurization of 17 with varying, but limited amounts of nickel boride, resulting in incomplete reactions. The recovered starting materials were then subjected to mass spectroscopic analysis to determine the ratio of the stable sulfur isotopes. There was a more rapid depletion of the lighter  $^{32}\text{S}$  isotope, resulting in enrichment of  $^{34}\text{S}$  in the recovered starting materials. The  $\delta(^{34}\text{S})$  value of the unreacted starting material increased with the extent

(20) For desulfurizations with a Ni(0) species in the absence of metal hydrides, see: Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Org. Chem.* 1983, 48, 2963.

(21) Carbazole was the product from the desulfurization of phenothiazine with (2,2'-bipyridyl)(1,5-cyclooctadiene)nickel(0); see: Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* 1977, 139, C51.

(22) Free radical mechanism have been proposed in the reductions of alkyl halides with cobalt aluminide; see ref 19b.

of the reaction, as shown in Figure 1. Theoretical curves for  $\delta(^{34}\text{S})$  are also shown, based on the assumption of a single rate-determining step and first-order kinetics for the disappearance of the reactant in that step. This model indicates a kinetic isotope effect,  $k(^{32}\text{S}) > k(^{34}\text{S})$ , where the  $^{32}\text{S}$ -containing reactant underwent C-S cleavage about 1.005 to 1.006 times faster than that containing  $^{34}\text{S}$ .<sup>23</sup> This in turn is consistent with C-S bond cleavage as the rate-determining step.

**Conclusions.** Nickel boride is easily prepared *in situ* from Ni(II) salts and sodium borohydride and is an effective reagent for the desulfurization of benzo- and dibenzothiophenes under notably mild conditions. The procedure is exceptionally convenient because it can be carried out in a few minutes at room temperature, without protection from the atmosphere, and requires only a simple workup.

Our results are consistent with a mechanism where dihydrogen is produced from the catalytic decomposition of the sodium borohydride in methanol and is first adsorbed on the nickel boride surface. The additional formation of an essential transient intermediate, such as a nickel hydride, is inferred from the rapid loss of reactivity of nickel boride after its preparation. Complexation of the sulfur atom of the substrate to the nickel boride surface is followed by the stepwise reductive cleavage of the two C-S bonds. The cleavage of the first C-S bond is less facile than that of the second and C-S cleavage comprises the rate-determining step in the overall desulfurization process.

### Experimental Section

Nickel chloride hexahydrate (*CAUTION*: Nickel salts are toxic and suspected carcinogens; they should be handled with appropriate care), sodium borohydride, and substrates 1, 3, 17, and 19 were purchased from the Aldrich Co., while literature procedures were used to obtain compounds 2,<sup>24</sup> 4,<sup>25</sup> 5,<sup>26</sup> 6,<sup>27</sup> 7,<sup>28</sup> 8,<sup>29a</sup> 9,<sup>26</sup> 10,<sup>30</sup> 11,<sup>29a</sup> 12,<sup>28</sup> 13,<sup>29a</sup> 14,<sup>30</sup> 15,<sup>31</sup> 16<sup>31</sup> and 18.<sup>28</sup> Compound 20 was a gift from Dr. Peter Clark.

GC analyses were performed on a Varian 3700 chromatograph equipped with a flame ionization detector, a 15-m DB-17 Megabore column (J and W Scientific Co.), and a Varian CDS111C integrator. Yields were measured by integration relative to an internal standard (*n*-decane, *n*-undecane, or *n*-dodecane) and corrections were made for relative response factors. The identities of the products were confirmed by comparison of their GC mass spectra with those of authentic samples. Mass spectra were recorded on either a Kratos MS80 or a VG7070 instrument, except in the case of stable isotope analyses (*vide infra*). Samples of biphenyls 26<sup>27</sup> and 31<sup>29b</sup> were prepared by literature methods, while those of other desulfurization products that were measured by GC were obtained from commercial sources.

The desulfurization of benzothiophene is described below. The other desulfurizations in Table I were performed similarly with minor variations as reported in the Table. Isolated products were

obtained by preparative TLC on Analtech 20 × 20 cm plates coated with 1 mm of silica gel GF or by column chromatography on Merck silica gel (60–200 mesh).

**Typical Procedure: Desulfurization of Benzothiophene (1).** Benzothiophene (127 mg, 0.95 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (1.58 g, 6.65 mmol) were dissolved in 30 mL of methanol and 10 mL of THF in an open Erlenmeyer flask cooled in an ice bath. The solution was magnetically stirred while NaBH<sub>4</sub> (755 mg, 20.0 mmol) was added in portions. (*CAUTION*: A vigorous reaction with hydrogen evolution occurs.) After 15 min, the mixture was filtered through Celite and 100  $\mu\text{L}$  of *n*-undecane (internal standard) was added to the filtrate. GC analysis indicated the presence of 73.6 mg (73%) of ethylbenzene (21), with the same retention time and mass spectrum as an authentic sample.

**Desulfurization of Dibenzothiophene (3) with Aged Nickel Boride.** Nickel boride was prepared from 1.4 mmol of NiCl<sub>2</sub>·6H<sub>2</sub>O and 4.2 mmol of NaBH<sub>4</sub> in 10 mL of methanol and 3.3 mL of THF in the usual manner. After a delay of 5 min, 37 mg (0.20 mmol) of dibenzothiophene was added and stirring was continued for 15 min at 0 °C. Workup and GC analysis of the reaction mixture as in the typical procedure indicated the presence of ca. 1% of biphenyl (24) and 99% of starting material 3.

The reaction was repeated as above, except that an additional portion of NaBH<sub>4</sub> (4.2 mmol) was added after the 5-min delay and the addition of dibenzothiophene. In this case 10% of biphenyl and 86% of dibenzothiophene were detected.

**Desulfurization of Dibenzothiophene (3) with Hydrogen under Pressure.** Nickel boride was prepared from 4 mmol of NiCl<sub>2</sub>·6H<sub>2</sub>O and 12 mmol of NaBH<sub>4</sub> in 30 mL of methanol and 10 mL of THF in the usual manner. After 30 min, 106 mg (0.576 mmol) of dibenzothiophene was added and the mixture was stirred in a high-pressure reaction vessel (Parr Instrument Co.) charged with 30–35 atm of hydrogen for 20 h. Workup and GC analysis of the reaction mixture as in the typical procedure indicated the presence of 18% of biphenyl (24) and 82% of the starting material.

**Competition Reaction between Dibenzothiophene (3) and 2,8-Dimethyldibenzothiophene (16).** Sodium borohydride (159 mg, 4.20 mmol) was added to a solution of dibenzothiophene (19 mg, 0.10 mmol), 2,8-dimethyldibenzothiophene (22 mg, 0.10 mmol), and NiCl<sub>2</sub>·6H<sub>2</sub>O (334 mg, 1.41 mmol) in 3:1 methanol-THF at 0 °C. After 15 min, the reaction was worked up as in the typical procedure. GC analysis indicated the presence of biphenyl (24) and the 3,3'-dimethyl derivative 34 in yields of 52% and 41%, respectively, as well as 44% of unreacted 3 and 55% of unreacted 16.

**Determination of the Kinetic Isotope Effect in the Desulfurization of Phenothiazine (17).** For sulfur isotope analyses, samples of unreacted starting materials were isolated as described above for the desulfurization of 17. These were combusted with oxygen at 25 atm in a high-pressure apparatus (Parr Instrument Co.). After combustion, water initially present plus washings of the vessel's interior surfaces was filtered into a beaker containing a 1 N BaCl<sub>2</sub> solution. The resulting BaSO<sub>4</sub> precipitate was filtered, dried, and treated with a 1:1 V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> mixture to produce SO<sub>2</sub> according to a literature procedure.<sup>32</sup> The SO<sub>2</sub> was analyzed for S-isotope composition using a mass spectrometer built with VG Micromass 602 components.

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**Registry No.** 1, 95-15-8; 2, 1195-14-8; 3, 132-65-0; 4, 34724-71-5; 5, 20928-02-3; 6, 68820-91-7; 7, 22439-61-8; 8, 22439-65-2; 9, 20928-05-6; 10, 22099-28-1; 11, 7428-91-3; 12, 6639-36-7; 13, 25288-76-0; 14, 7372-88-5; 15, 1207-12-1; 16, 1207-15-4; 17, 92-84-2; 18, 1013-23-6; 19, 1016-05-3; 20, 233-02-3; 21, 100-41-4; 22, 103-65-1; 23, 19926-49-9; 24, 92-52-4; 25, 643-93-6; 26, 2051-61-8; 27, 2113-57-7; 28, 580-51-8; 29, 716-76-7; 30, 614-32-4; 31, 2243-47-2; 32, 2113-58-8; 33, 92-67-1; 34, 612-75-9; 35, 122-39-4; 36, 1127-76-0; 37, 12007-01-1.

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