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Desulfurization of Dibenzothiophene by Nickel(0) Complexes: Evidence for Electron Transfer in Oxidative Additions[1]

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Two equivalents of the complex (2,2′-bipyridyl)(1,5-cyclooctadiene)nickel(0) cleave dibenzothiophene in homogeneous media to form nickel-substituted biphenyl derivatives and nickel sulfide. The cleavage proceeds more readily in THF than in benzene solution, and excess amine (either bipyridyl or pyridine) retards the reaction. Neither biphenylene nor 2-phenylbenzenethiol was a detectable transient in the desulfurization process. The possible fleeting formation of biphenylene was ruled out by a study of the desulfurized products obtained from the 2,8-dimethyl and the 3,7-dimethyl derivatives of dibenzothiophene. A possible role of nickel hydride in some of the C–S bond cleavage is suspected from the observed effects of either acid or $LiAlH_4$ used in the workup of the reaction mixture. The reaction is not catalytic in nickel when an excess of $LiAlH_4$ is used; this indicates that Ni(0) cannot be regenerated from NiS under these conditions. The observed cleavage of ~50% of the dibenzothiophene by 2 equiv of $(C_{10}H_8N_2)Ni(C_8H_{12})$ is ascribed to the gradual formation of $(C_{10}H_8N_2)_2Ni$, which is ineffectual in cleaving dibenzothiophene. Finally, the relative reactivity of the dibenzothiophenes (dibenzothiophene > 2,8-dimethyldibenzothiophene ≫ 3,7-dimethyldibenzothiophene), the relative effectiveness of amine donors or solvents, and the observed hydrogen abstraction from the solvent are interpreted in terms of an electron-transfer mode of action by the nickel(0) desulfurizing agent.

The desulfurization or organic compounds has recently gained increasing attention in two quite diverse fields, namely, synthetic fuels and organic synthesis. In the former area, the production of environmentally acceptable fuels from coal or petroleum involves the removal of organically bound sulfur, such as sulfides or mercaptans, from the final product. In the latter area, organic synthetic methodology currently utilizes a variety of sulfur-containing groups to achieve a broad range of selective reactions, but after the reaction the adjuvant sulfur group must be removed.[2] In synthetic fuel production some form of hydrodesulfurization, which uses transition-metal catalysts and hydrogen gas at elevated temperatures and pressures, is most often employed,[3] while in organic synthesis heterogeneous reactions with metals such as Raney nickel,[4] molybdenum,[5] titanium,[6] or alkali metals[7] often serve to cleave sulfidic or sulfonyl groups.[8]

Despite the undeniable importance of desulfurization, relatively little is known about the mode of action of various desulfurizing processes.[9] Accordingly, we have undertaken a mechanistic study of the cleavage of aryl sulfides by low-valent transition-metal complexes, with the hope of uncovering the factors that foster desulfurization reactivity. Initially, nickel(0) complexes were chosen that are soluble in hydrocarbons or ethers, so as to study desulfurization in a homogeneous medium. Dibenzothiophene was selected as a model substrate, since such a nucleus is one of the sulfides most resistant to desulfurization in the purification of synthetic fuels.[10]

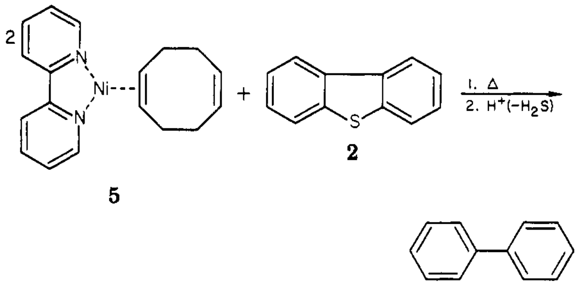
Results

Desulfurization of Dibenzothiophene. (a) Effect of 2,2′-Bipyridyl. The air-sensitive yellow complex bis(1,5-cyclooctadiene)nickel(0) (**1**) was found to give <2% of biphenyl (**3**) when heated with dibenzothiophene (**2**) in a 2:1 molar ratio at 55–60 °C for 48 h. When, however, **1** was treated with 1 equiv of 2,2′-bipyridyl (**4**), complex **5** was then formed,[11] which led to cleavage of **2** in a 45% yield (eq 1;[12] for structure in solution see ref 11).

Table I. Effect of Ligand on the Desulfurization Activity of Bis(1,5-cyclooctadiene)nickel(0) on Dibenzothiophene

amine	% yield of biphenyl
2,2′-bipyridyl	45
4-(dimethylamino)pyridine[a]	21
ethylenediamine	17
1,10-phenanthroline	16
pyridine[a]	14
hexamethylphosphorus triamide	14
N,N,N′,N′-tetramethylethylenediamine	8
1,8-bis(dimethylamino)naphthalene	7
N,N′-dimethylpiperazine	4

[a] Two equivalents per equivalent of $(C_8H_{12})_2Ni$.



5 2 3 (1)

The 2:1 reactant ratio of nickel complex **5** and dibenzothiophene proved to be optimal: a 1:1 ratio gave only an 11% yield of biphenyl and a 3:1 ratio did not improve the yield of biphenyl. In fact, an excess of 2,2′-bipyridyl over that needed to form **5** was detrimental to desulfurization: when 1 equiv of **4** was added to a 2:1 reaction mixture of **5** and **2**, the conversion to biphenyl dropped

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(1) Part 7 of the series "Organic Chemistry of Subvalent Transition Metal Complexes". Part 6: Eisch, J. J.; Han, K. I. *Adv. Chem. Ser.* **1979**, *No. 173*, 195.

(2) Magnus, P. D. *Tetrahedron* **1977**, *32*, 2019.

(3) Leading reference: Kalinowski, D. R; Teeuwen, H.; DeBeer, V. H. J.; Gates, B. C.; Schuit, G. C. A.; Kwart, H. *J. Catal.* **1978**, *55*, 129.

(4) Hauptmann, H.; Walter, W. F. *Chem. Rev.* **1962**, *63*, 347.

(5) Alper, H.; Blais, C. *Fuel* **1980**, *59*, 670.

(6) Mukaiyama, T.; Hayashi, M.; Narasaka, K. *Chem. Lett.* **1973**, 291.

(7) (a) Gilman, H.; Esmay, D. L. *J. Am. Chem. Soc.* **1953**, *75*, 2947. (b) Eisch, J. J. *J. Org. Chem.* **1963**, 28, 707. (c) Gilman, H.; Dietrich, J. J. *J. Org. Chem.* **1957**, *22*, 851. (d) Ignasiak, T.; Kemp-Jones, A. V.; Strauz, O. P. *J. Org. Chem.* **1977**, *42*, 312.

(8) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

(9) Bonner, W. A.; Grimm, R. A. *Org. Sulfur Compd.* **1966**, *2*, 35.

(10) Aitken, J.; Heeps, T.; Steedman, W. *Fuel* **1968**, *47*, 353.

(11) Dinjus, E.; Gorski, I.; Uhlig, E.; Walther, H. *Z. Anorg. Allg. Chem.* **1976**, *422*, 75. An H^1 NMR study of **5** in solution showed that only one double bond is coordinated to the nickel atom.

(12) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C51.

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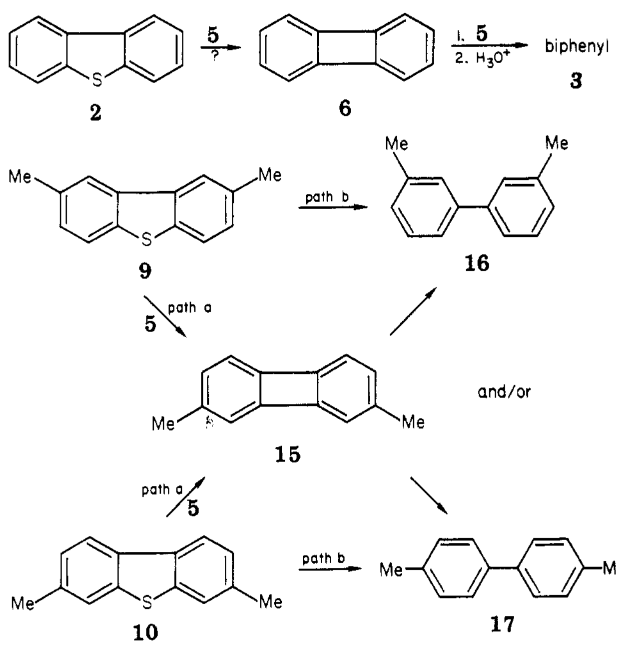
Scheme I



from 45% to <10% (Table III).

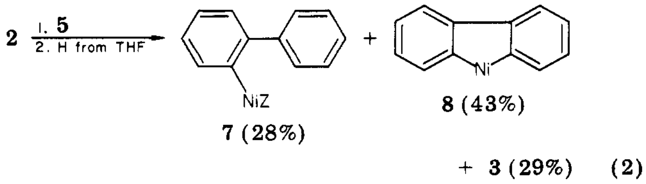
(b) Effect of Other Donors. As is evident from Table I, the activating effect of 2,2′-bipyridyl on the desulfurizing action of nickel(0) complexes was maximal. Particularly noteworthy was the much inferior activation shown by 1,10-phenanthroline, a close structural analogue of 4, and by the mononuclear pyridines.

Even with 5 itself, the solvent employed led to significant variations in desulfurization: C_6H_6, 19%; C_5H_5N, 12%; THF, 45%.

(c) Time Study of Products. The desulfurization reaction depicted in eq 1 was sampled periodically over 48 h. A hydrolytic workup showed the presence of only dibenzothiophene and biphenyl. No biphenylene or 2-phenylthiophenol could be detected. When the acid used for the workup was not carefully deoxygenated some 2-hydroxybiphenyl was then isolated. This product undoubtedly stemmed from the oxidation of a 2-biphenylylnickel intermediate (7, eq 2).

The failure to detect biphenylene in this time study does not rule out its transient existence in the desulfurization process. In a separate experiment, an authentic sample of biphenylene (6) was shown to undergo cleavage with 5 and to yield biphenyl upon hydrolysis (Scheme I). Hence, 6 might be formed from 2 and quickly destroyed.

(d) Deuterium Labeling. When the reaction of 5 with 2 was worked up with CH_3CO_2D, the isolated biphenyl was 29% undeuterated, 28% monodeuterated at C_2, and 43% dideuterated at C_2 and $C_{2'}$. These results indicate the presence of organonickel precursors 7 and 8 in the desulfurization mixture (eq 2).[13] From a similar desulfur-



ization conducted in benzene solution the relative percentages of 3/7/8 obtained were 80:13:17.

Table II. Variation in Protolytic Treatment of the Desulfurization of Dibenzothiophene[a]

acid	% yield biphenyl (3)	 dibenzothiophene (2)
H_3PO_4 (85%)	19	70
HCl (6 N)	20	71
HCl (12 N)	29	70
HCOOH	37	60
CH_3COOH	45	53

[a] Two equivalents of 5 per equivalent of 2 for 48 h at 55–60 °C.

(e) Possible Intermediacy of a Nickel Hydride. The type of acid used to hydrolyze the reaction mixtures greatly affected the yield of biphenyl; the yields varied from 19% for 85% H_3PO_4 to 45% for glacial acetic acid (Table II). This variation may in small part be due to the formation of a nickel hydride, through the protonation of a nickel(0) complex,[14] and and the desulfurizing action of such a nickel hydride itself on 2.

As an alternative mode of workup, final treatment of the reaction mixture (eq 1) with $LiAlH_4$ gave a pronounced increase in the biphenyl isolated (N.B.: $LiAlH_4$ alone does not desulfurize dibenzothiophene; cf. ref 12). Subsequent studies showed that $LiAlH_4$ in fact transformed 5 into an even more potent desulfurizing agent. When 2 molar equiv of $(COD)_2Ni$, bipyridyl, and $LiAlH_4$ were combined at the start of reaction, dibenzothiophene could be almost quantitatively converted to biphenyl (93%). In this case, some kind of nickel hydride seems to be involved, although its exact nature is still obscure. A puzzling finding is that when $LiAlD_4$ was used with 5, the biphenyl formed was largely undeuterated (60%). Only 25% of 2-deuterio- and 15% of 2,2′-dideuteriobiphenyls were formed.

(f) Attempts To Regenerate Nickel(0) from Nickel(II) Sulfide in Situ. The use of 0.20 equiv of 5 with 2 equiv of $LiAlH_4$ gave only ~3% of biphenyl. The $LiAlH_4$ was not able to reconvert NiS to a Ni(0) complex under the reaction conditions. Hence, the desulfurization could not be made catalytic in nickel.

When a hydrogen atmosphere was used in place of argon for the reaction of 5 with dibenzothiophene, the desulfurization reaction was markedly retarded (12% of biphenyl). Workup revealed that the hydrogen had reduced 1,5-cyclooctadiene to cyclooctene, thereby consuming desulfurizing agent 5.

Desulfurizations of the Dimethyldibenzothiophenes. The 2,8- and 3,7-dimethyldibenzothiophenes (9 and 10) were subjected to desulfurization by reagent 5, in order to determine the influence of the methyl substituents on the ease of reaction and to discern whether a biphenylene intermediate might be involved (Table III).

Because of reaction complexities, the relative reactivities of dibenzothiophenes 2, 9, and 10 in desulfurization could not be determined by the competition method. Accordingly, individual runs at 55–60 °C for 48 h were carried out, and the percentage conversion to biaryl was measured. Dibenzothiophene was the most reactive (45%), the 2,8-dimethyldibenzothiophene much less reactive (12%), and the 3,7-dimethyldibenzothiophene almost completely unreactive (<3%). 2-Methyldibenzothiophene was intermediate in its reactivity (28% conversion). Furthermore, the 2,8-dimethyl isomer yielded only *m,m′*-bitolyl, while the 3,7-dimethyl isomer produced only *p,p′*-bitolyl.

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[13] The coordination on 7 and 8 cannot be specified, but bipyridyl ligands should stabilize nickel(II) aryls: Wilke, G.; Herrmann, G. *Angew. Chem.* **1966**, *78*, 591.

[14] Jones, K.; Wilke, G. *Angew. Chem.* **1969**, *81*, 534.

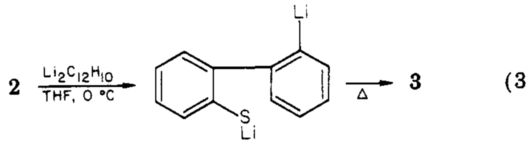
Table III. Desulfurization of Dibenzothiophenes by the (2,2′-Bipyridyl)(1,5-cyclooctadiene)nickel(0) Complex in Tetrahydrofuran

	% yield		
dibenzothiophene	ratio of Bpy/ COD[a]	biaryl	recovd dibenzothiophene
unsubstituted	0:2	<2	98
	1:1	11	87
	2:2	45	53
	3:2	9	90
2-methyl	2:2	28	70
2,8-dimethyl	2:2	12	83
3,7-dimethyl	2:2	3	92

[a] Ratio expresses the equivalents of 2,2′-bipyridyl and of bis(1,5-cyclooctadiene)nickel(0) to 1 equiv of the dibenzothiophene; the reaction conditions were a 48-h period at 55–60 °C and subsequent hydrolysis with glacial acetic acid.

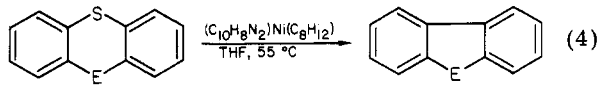
Discussion

Reaction Path. The use of metal desulfurizing agents in homogeneous media offers clear advantages in ease and conversion. The 2:1 adduct of lithium metal and biphenyl in THF, for example, permits almost a quantitative cleavage of dibenzothiophene to the 2′,*S*-dilithio derivative of 2-phenylbenzenethiol (**11**, eq 3);[7b] further heating converts **11** to biphenyl (**3**).



11

With the nickel(0) reagent **5** in homogeneous solution, **2** is converted into biphenyl with no detectable formation of a mercaptide salt similar to **11** (eq 1). In fact, six-membered sulfur heterocycles such as phenoxathin (**12a**), phenothiazine (**12b**), and thianthrene undergo sulfur extrusion and carbon–carbon bond formation when treated with **5** (eq 4).[12]



12a, E = O
b, E = NH
c, E = S

13a–c

The behavior of such six-membered heterocycles raised the possibility that even dibenzothiophene might undergo nickel-promoted desulfurization, not stepwise as with lithium (eq 3), but via direct sulfur extrusion to yield biphenylene (**14**). Subsequently, the biphenylene might then recleave to form biphenyl (**3**, Scheme I). That the conversion of **6** into **3** was feasible under the desulfurization conditions was shown by treating an authentic sample of **6** with **5**. Indeed, biphenyl was found upon workup.

However, an attempt to detect biphenylene during the course of desulfurizing dibenzothiophene failed. Consequently, as a rigorous test for the fleeting formation and destruction of such a biphenylene intermediate, the products formed from the individual desulfurizations of 2,8-dimethyldibenzothiophene (**9**) and of 3,7-dimethyldibenzothiophene (**10**) were scrutinized. Were a biphenylene involved, both **9** and **10** would form the same intermediate (**15**). The subsequent destruction of **15** by **5** would yield the same composition of bitolyls **16** and **17** (path a, Scheme I). On the other hand, were **15** not involved, then each dimethyldibenzothiophene would yield only its own bitolyl (path b, Scheme I: **9** → **16**; **10** → **17**). Experiment showed that the latter outcome obtained, so the role of biphenylene as an intermediate can be confidently ruled out.

Ligands on Nickel(0). From the observation that a 1:1 ratio of amine to $(C_8H_{12})_2Ni$ gives a maximum desulfurizing activity it can be concluded that both the amine and dibenzothiophene are coordinated to the nickel(0) in its reactive form (**18**, eq 5). An excess of amine competes with the thiophene for coordination on nickel (**18** vs. **19**).

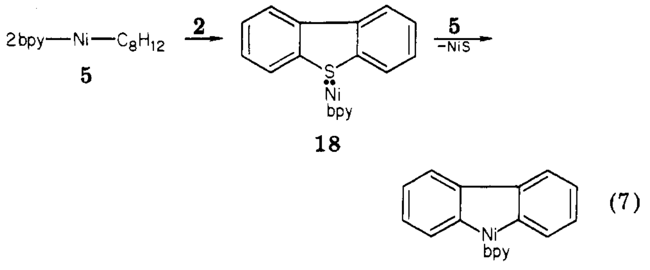
$$\begin{tikzcd} \underset{\mathbf{1}}{(C_8H_{12})_2Ni} \arrow[r, "bpy", "-C_8H_{12}"'] & \underset{\mathbf{5}}{bpy\text{-}Ni\text{-}C_8H_{12}} \arrow[r, "\mathbf{2}"] \arrow[d, "bpy"] & \underset{\mathbf{18}}{bpy\text{-}Ni\text{-}\mathbf{2}} \\ & \underset{\mathbf{19}}{(bpy)_2Ni} & \end{tikzcd} \qquad (5)$$

In fact, the eventual cessation of desulfurization (~45% conversion with **2**) can be explained by the accumulation of bipyridyl in the reaction mixture as **5** is consumed. The fully coordinated nickel in **19** cannot coordinate with sulfides and hence is unreactive.[15] The surprisingly low reactivity of 1,10-phenanthroline and other amines in desulfurization (Table I) can be ascribed to the equilibrium between the amine–olefin complex **20** and the diamine complex **21** (eq 6). Attempts with phenanthrolines to isolate complex **20** have failed; only complex **21** is obtained.[11]

$$\mathbf{1} \xrightarrow[-C_8H_{12}]{\text{amine}} \underset{\mathbf{20}}{\text{amine-Ni-}C_8H_{12}} \overset{\text{amine}}{\rightleftharpoons} \underset{\mathbf{21}}{(\text{amine})_2\text{Ni}} \qquad (6)$$

In the same vein, the observed solvent effects can be rationalized: the greater donor character of pyridine over THF will tend to make pyridine compete with the sulfur substrate for coordination sites on nickel. On the other hand, the nonpolar benzene may suppress the formation of polar complexes **5** and **18** and favor nonpolar complexes **1** and **19**.

Stoichiometry. The maximum reactivity of 2 equiv of the bipyridyl–olefin complex **5** suggests that 1 equiv forms bipyridyl–sulfide complex **18**, and this is attacked by a second equivalent of **5** (eq 7). Evidence for the initial formation of **8** lies in the deuteration studies, where over 40% of the biphenyl formed was found to be dideuterated at C_2 and $C_{2'}$.



5

18

8

Also, such nickel heterocycles have been obtained by us by the action of nickel(0) complexes on biphenylene.[16] That such aryl nickel compounds are prone to homolysis of their carbon–nickel bonds is well recognized.[17] In THF solution **8** partly decomposes, and the resulting biphenyl acquired ~43% of its protons from the solvent; in benzene solution, a nondonor medium, over 80% of **8** undergoes such homolysis (deuterium content

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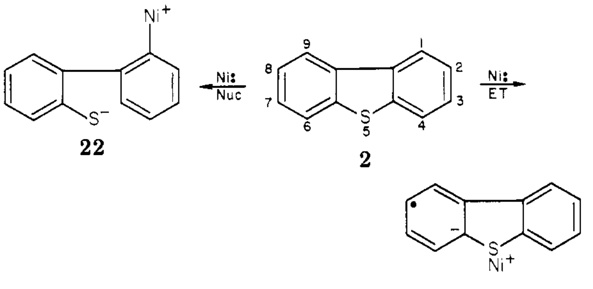
[15] This compound has been prepared: Misoni, A.; Uchida, Y.; Yamagishi, T.; Kageyama, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1438.

[16] Eisch, J. J.; Aradi, A. A.; Piotrowski, A. Third International Symposium on Homogeneous Catalysis, Milan, Italy, Aug 31, 1982.

[17] Jolly, P. J.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1, p 151.

of the resulting biphenyl ~20%). That portion of **7** and **8** remaining at workup undergoes deuteration by DOAc. The observed maximal desulfurization of ~50% also agrees with the 2:1 stoichiometry. One equivalent of the nickel(0) is consumed by the formation of **8** and nickel sulfide; the other equivalent is converted into $(bpy)_2Ni$, which is unreactive in desulfurization.

Evidence for Electron Transfer. The oxidation addition reactions of the bipyridyl-nickel(0) complex **5** toward these sulfides have the characteristics of stepwise electron transfer rather than of nucleophilic attack (eq 8).[18]



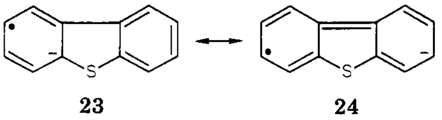
22 **2** **23**

(8)

Electron transfer appears to be operative for these reasons: (a) a donor solvent or strongly donor ligands on nickel(0) promote reaction,[19] just as such solvents do in the formation of alkali metal–unsaturated hydrocarbon adducts;[20] (b) deuterolytic workup of the reaction mixtures gives evidence for hydrogen abstraction by radicals; (c) the effect of methyl substituents on the reactivity of the dibenzothiophene nucleus accords with the intermediacy of radical–anions such as **23**. Points a and c deserve further comment.

In forming the bipyridyl–olefin complex **5** from $(C_8H_{12})_2Ni$ (**1**), the color changes from yellow to bluish violet. Since this absorption can be ascribed to a metal-to-ligand charge-transfer transition,[21] replacement of the olefin by bipyridyl has brought about a marked bathochromic shift in this transition. Such a shift implies a smaller promotional energy for exciting the d electron onto the ligand. Hence, such a d electron may be more readily transferred to either ligand in a bipyridyl–dibenzothiophene complex (**18**). Indeed, **5** is much more reactive in desulfurization than **1**.

The observed reactivity in desulfurization, namely, dibenzothiophene > 2,8-dimethyldibenzothiophene ≫ 3,7-dimethyldibenzothiophene, can be correlated with what is known about electron spin densities of radical–ion **23**.[22a] For dibenzothiophene itself, the hyperfine ESR coupling constants (which are proportional to spin densities) were found to be as follows: C_1, 4.48; C_2, 0.86; C_3, 5.16; C_4, 1.46 G. From this it follows that resonance form **24** is more



23 **24**

important than **23**. Because of electron release, attaching methyl groups to dibenzothiophene should destabilize the radical–anion and hence retard the desulfurization process. Indeed, the polarographic reduction potentials bear out this expectation: the $E_{1/2}$ values for dibenzothiophene, 2,8-dimethyldibenzothiophene, and 3,7-dimethyldibenzothiophene become increasingly negative in this sequence: 2.432, 2.452, and 2.563 V.[22b] Putting one and then two methyl groups at C_2 and C_8 does diminish the desulfurization (45% to 28% to 12%). But such retardation should be maximal when such groups are attached at C_3 and C_7. This expectation is in fact realized (45% to 3%, Table III).

The striking increase in desulfurizing potency by combining bipyridyl complex **5** with $LiAlH_4$ may be related to the foregoing electron-transfer process, for relatively little deuterium incorporation is observed (~30%) when $LiAlD_4$ is employed. Were a form of nucleophilic, hydridic attack on the carbon–sulfur bond involved, a preponderance of deuterium incorporation into the biphenyl would have resulted. But more information is required before a clear mechanistic picture emerges.

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrometer (Model 457) equipped with sodium chloride optics. Proton magnetic resonance spectra (^1H NMR) were obtained with a Varian spectrometer (Model EM-360) on neat samples or on 10% solutions in pure solvents. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Vapor-phase chromatographic analysis (VPC) and isolations were carried out on an F&M chromatograph (Model 720) equipped with a 12 ft × 0.25 in. column of 10% UC-298 on Chromosorb W. Mass spectra of solids and liquids were initially obtained with a Du Pont spectrometer (Model 21-491B) and subsequently through the mass spectral facility at Cornell University. Elemental analyses were perfored by the Spang Microanalytical Laboratory, Ann Arbor, MI.

General Procedures. All preparations and reactions involving air- and moisture-sensitive organometallic compounds were conducted under an anhydrous, oxygen-free atmosphere, which was nitrogen for organolithium compounds and argon for organonickel reagents. The appropriate techniques for the transfer, reaction, analysis, and purification of such reagents have been recently described in detail.[23]

The yields of desulfurization reactions were determined by the isolation and weighing of the crude products and the analysis of the mixture of VPC. *p,p'*-Bitolyl was employed as an internal standard. Response factors were determined on pure samples of all components encountered in such analyses. For identification and spectral analyses the individual components were separated or collected by column or gas–liquid chromatography.

Starting Materials. Solvents. Commercial solvents were purified according to recommended published procedures.[23] Tetrahydrofuran (THF), ethyl ether, benzene, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), hexamethylphosphoramide (HMPA), toluene, and triethylene glycol dimethyl ether (triglyme) were distilled under nitrogen after being heated at reflux over sodium–potassium alloy.[24]

Reagents. Pyridine was rendered anhydrous by heating over BaO and distilling. Similar distillation or recrystallization was used to purify 2,2'-bipyridyl, 4-(dimethylamino)pyridine, ethylenediamine, 1,10-phenanthroline, 1,8-bis(dimethylamino)naphthalene, and *N,N'*-dimethylpiperazine.

Dibenzothiophene was recrystallized from ethanol, mp 98–100 °C. 3,7-Dimethyldibenzothiophene [mp 147–148 °C (from ethanol)] was prepared from biphenyl in four steps: (a) bromination to yield 55% of 4,4'-dibromobiphenyl, mp 160–162 °C;[25] (b) chlorosulfonation to form 3,7-dibromodibenzothiophene 5,5-di-

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[18] (a) Electron transfer: Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7145. (b) Nucleophilic attack: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630.

[19] Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45.

[20] Eisch, J. J. "The Chemistry of Organometallic Compounds"; Macmillan C.: New York, 1967; p 192.

[21] Lees, A. J., personal communication.

[22] (a) Gerdil, R.; Lucken, E. A. C. *J. Am. Chem. Soc.* **1965**, *87*, 213. (b) Gerdil, R.; Lucken, E. A. C. *Ibid.* **1966**, *88*, 733.

[23] Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol. 2.

[24] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 6, p 1102.

[25] Buckles, R. E.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108.

oxide, mp 308–309 °C;[26] (c) reduction with $LiAlH_4$ in ethyl ether to provide 71% of 3,7-dibromodibenzothiophene;[22] (d) bromine–lithium exchange with *n*-butyllithium at −5 °C in ethyl ether, followed by treatment with dimethyl sulfate.[22] 2,8-Dimethyldibenzothiophene [mp 114–116 °C (from ethanol)] was prepared in two steps from dibenzothiophene: (a) bromination in glacial HOAc to yield 2,8-dibromodibenzothiophene, mp 221–223 °C,[27] (b) bromine–lithium exchange with *n*-butyllithium in ethyl ether at 5 °C, followed by treatment with dimethyl sulfate.[22]

Bis(1,5-cyclooctadiene)nickel (0) was prepared from nickel(II) chloride hexahydrate. The latter nickel salt was converted into anhydrous nickel(II) acetylacetonate,[28] and then a toluene solution of this nickel compound was reduced to nickel(0) by triethylaluminum in the presence of 1,5-cyclooctadiene and 1,3-butadiene.[29] Even with adherence to published directions, this synthesis proved to be difficult or unreliable. Once the separation of black, colloidal nickel begins, it is difficult to get a good yield of reasonably stable $(C_8H_{12})_2Ni$. Traces of free nickel in the product shorten the storage lifetime of the complex. Thus, the following measures must be taken to avoid the onset of nickel metal deposition: (a) thorough purification of all solvents and reagents, especially the scrupulous deoxygenation of all surfaces and liquids; (b) a generous excess of 1,3-butadiene in the media used for the formation *and washing* of the nickel(0) complex, for the butadiene is an excellent scavenger for any nickel metal traces; (c) washing the crude $(C_8H_{12})_2Ni$ with cold ethyl ether (containing butadiene) is superior to using toluene; (d) avoidance of contact between ground-glass joints (with or without grease) and solutions of the nickel(0) complex; (e) keeping all parts of the medium cold (especially upper parts of the reaction vessel) during the reduction of $Ni(acac)_2$ by Et_3Al. Once well-washed and free of solvent and metal traces, the bright yellow crystals of $(C_8H_{12})_2Ni$ are quite stable at 25 °C under argon if they are shielded from light and contact with joint grease. The product can be freed of any metallic nickel by dissolution in pure THF, filtration of the solution though a fine glass frit and cooling at −78 °C to deposit well-formed crystals of the complex.[30]

The deuterated reagents were obtained from the Aldrich Chemical Co: deterium oxide (99.8% D_2O), deuterium chloride (37%, 99.8% D), *O*-deuterioacetic acid (98% CH_3CO_2D), and $LiAlD_4$ (98%).

Products. 3,3′-Bitolyl and 4,4′-bitolyl were prepared by coupling the respective tolyl Grignard reagents with TlBr:[31] 3,3′-bitolyl, bp 153–155 °C (18 mmHg); 4,4′-bitolyl, mp 119–120 °C. Biphenylene was prepared by the thermolysis of benzenediazonium 2-carboxylate, mp 110–112 °C.[32]

2,2′-Dideuteriobiphenyl was prepared by treating a solution of 1.3 mmol of 2,2′-diiodobiphenyl[33] in 4 mL of anhydrous THF at 0 °C with 2.9 mmol of butyllithium in hexane–THF. After warming to 25 °C, the mixture was treated with D_2O and worked up in the usual manner. The deuterated biphenyl was collected by GLC: MS, *m/e* (relative intensity) 1.57 (M + 1, 15.1), 156 (M 100), 155 (44.8), 154 (46.3), 153 (19.5); IR (CS_2) 785 (0.22), 740 (0.15), 705 (0.04), 640 (0.34) cm^{-1}.

2-Deuteriobiphenyl was prepared by treating 2-biphenylylmagnesium bromide in THF with D_2O: MS, *m/e* (relative intensity) 156 (12.9), 155 (100), 154 (30.4), 153 (16.5); IR (CS_2) 785 (0.29), 740 (0.44), 705 (0.22), 640 (0.16) cm^{-1}.

For comparison, the spectral data for undeuterated biphenyl under similar conditions of measurement were: MS, *m/e* (relative intensity) 155 (13.8), 154 (100), 153 (21.4), 152 (12.6); IR (CS_2) 7.85 (0.11), 740 (0.58), 705 (0.55), 615 (0.11). The deuterium content of the biphenyls encountered in this study was determined by use of such reference spectra.

Desulfurization Reactions of Dibenzothiophene (2) with Bis(1,5-cyclooctadiene)nickel (1). The reactions were conducted in a 100-mL, two-necked, round-bottomed flask whose necks were fitted with a reflux condenser and a rubber septum. After the apparatus was dried and flushed with argon, the flask was charged with 3.1 mmol of $(C_8H_{12})_2Ni$ and 20 mL of anhydrous degassed THF. The appropriate amount of amine ligand, if any, was introduced and magnetic stirring maintained for 30 min. Then the desired amount of the dibenzothiophene was added and the resulting mixture stirred at 55–60 °C (oil-bath temperature) for 48 h. After the mixture cooled the degassed protolyzing agent was injected. After the solution lightened to the green color of hydrated nickel(II) salts, the organic layer was diluted with ether, separated, washed with water, and dried over $MgSO_4$. Solvent removal and a combination of spectral and GLC analyses on the organic residue ensued.

Specific Variations in Desulfurizing Dibenzothiophene. (a) Oxidation. When the protolytic agent was aqueous HCl and this agent was not carefully deoxygenated under argon, then 3–6% of 2-hydroxybiphenyl was detected and isolated.

(b) Time Study of Products. A reaction mixture of 1.30 g (8.33 mol) of $(C_8H_{12})_2Ni$, 2.29 g (8.33 mmol) of 2,2′-bipyridyl, and 755 mg (4.1 mol) dibenzothiophene in 120 mL of THF was stirred at 55 °C and at various elapsed times, and 10-mL aliquots were withdrawn from the blue-violet solution and protolyzed with glacial acetic acid under argon. The conversion to biphenyl (hours) increased thus: 0% (2 h), 1% (5), 5% (8), 15% (12), 18% (20), 19% (25)8 22% (30), and 23% (44). No product other than biphenyl was observed at any stage. Specifically biphenylene and 2-phenylthiophenol would have been readily observable by GLC.

(c) Protolyzing Agent. A series of mixtures consisting of a 2:2:1 molar ratio of 2,2′-bipyridyl/$(C_8H_{12})_2Ni$/dibenzothiophene (1.66 mmol) in 25 mL of THF was allowed to react at 55 °C for 48 h. Each was worked up with a different deoxygenated protolyzing agent and the organic product then analyzed by GLC. Material balances of the order of 95–99% were achieved. The percentage of biphenyl vs. acid used as follows (percent, acid): 45, HOAc; 37, HCO_2H; 29, 12 N HCl; 20, 6 N HCl; 19, H_3PO_4. Accordingly, glacial acetic acid was used in all workups.

(d) Ligand Substitutions on Nickel(0). A series of desulfurizations were done identically with the one described in section c, except that equivalent amounts of various amines were substituted for the bipyridyl. For amines that had at least two basic nitrogens, 3.32 mmol was employed; for pyridine and 4-(dimethylamino)pyridine, 6.64 mmol was used. The observed conversions to biphenyl are compiled in Table I.

(e) Solvent Effect. Carrying out a 2:2:1 molar interaction of 2,2′-bipyridyl/$(C_8H_{12})_2Ni$/dibenzothiophene in THF for 48 h at 55 °C led to a 45% conversion to biphenyl. When pyridine or benzene was used in place of THF, the conversion to biphenyl fell to 12% or 19%, respectively.

(f) Variation in the Proportion of Bipyridyl (4). When a series of desulfurizations with a 2:1 ratio of $(C_8H_{12})_2Ni$/dibenzothiophene in THF were run, the following variations in the molar equivalents of 2,2′-bipyridyl used caused the conversion to biphenyl to change (equiv of bipyridyl, percent biphenyl): 0, ~1; 1.0, 11; 2.0, 45; 3.0 <10.

(g) Deuterolysis of the Reaction Products. A standard 2:2:1 ratio of bipyridyl/$(C_8H_{12})_2Ni$/dibenzothiophene in THF was allowed to react at 55 °C for 48 h. Treatment of the cooled mixture with CH_3CO_2D and the usual workup led to the isolation of the biphenyl (45%), which was shown by a combination of IR and mass spectral measurements to be composed of undeuterated biphenyl (29%), 2-deuteriobiphenyl (28%), and 2,2′-dideuteriobiphenyl (43%).

A similar reaction, except that benzene was used in place of THF, gave upon deuterolysis a biphenyl (19%) that consisted of 70% undeuterated, 13% 2-deuterated, and 17% of 2,2′-dideuterated hydrocarbon.

(h) Attempts To Observe Catalytic Desulfurization. Treatment of 1 equiv of dibenzothiophene with 0.2 equiv each of bipyridyl and $(C_8H_{12})_2Ni$ in THF and 2 equiv of $LiAlH_4$ gave, at most, 3% of biphenyl.

When a typical 2:2:1 mixture of bipyridyl, $(C_8H_{12})_2Ni$, and dibenzothiophene in THF was permitted to react under a hydrogen, rather than an argon, atmosphere, hydrogen was consumed in reducing 1,5-cyclooctadiene to cyclooctene. The biphenyl obtained upon workup had fallen to 12%.

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(i) Desulfurization with $LiAlH_4$. A blue-violet solution of 217 mg (2.03 mmol) of 2,2′-bipyridyl and 559 mg (2.03 mmol) of $(C_8H_{12})_2Ni$ in 15 mL of THF was admixed with 77 mg (2.03) of $LiAlH_4$. The solution foamed slightly, and a distinct reddening of the initially blue-violet color was noted. After 48 h at 55 °C the usual protolytic workup showed the presence of 93% of biphenyl and 5% of the starting thiophene.

In an identical run, the reaction mixture was treated after 48 h with CH_3CO_2D. The isolated biphenyl consisted of 95% of undeuterated, 2% of 2-deuterated, and 3% of 2,2′-dideuterated hydrocarbon.

In a control run, dibenzothiophene and $LiAlH_4$ in THF at 55 °C for 48 h gave <1% of biphenyl upon workup.

(j) Desulfurization with $LiAlD_4$. A reaction identical with that in section i, except that $LiAlD_4$ was substituted for $LiAlH_4$, gave upon workup with CH_3CO_2H a mixture of 60% undeuterated biphenyl, 25% of 2-deuteriobiphenyl, and 15% of 2,2′-dideuteriobiphenyl.

Desulfurizations of the Dimethyldibenzothiophenes 9 and 10. Under strictly comparable conditions, both the 2,8- and the 3,7-dimethyl isomers of dibenzothiophene were individually treated with 2 molar equiv of $(C_8H_{12})_2Ni$ and 2,2-bipyridyl in THF, as described in section c above. The 2,8-isomer (**9**) yielded 83% of the starting thiophene and 12% of only *m,m*′-bitolyl, which contained no trace of any *p,p*′-bitolyl: NMR (neat) δ 2.25 (s, 6 H), 6.7–7.13 (m, 8 H); IR (neat) 3020 (s), 2910 (s), 1610 (s), 1480 (s), 1170 (w), 1150 (w), 1130 (w), 890 (m), 770 (vs), 700 (vs). These spectral data were identical with those of an authentic sample.

The 3,7-isomer (**10**) gave a maximum of 3% of *p,p*′-bitolyl containing no detectable amount of the *m,m*′-isomer. Its NMR and IR spectra were superimposable upon those of an authentic sample.

Cleavage of Biphenylene (6). The interaction of 0.93 mmol of $(C_8H_{12})_2Ni$ and 0.78 mmol of biphenylene in 8 mL of THF for 20 h at 50 °C gave upon workup with 6 N HCl only unreacted biphenylene. However, a reaction of 0.5 mmol of biphenylene with 0.58 mmol each of $(C_8H_{12})_2Ni$ and 2,2′-bipyridyl in 7 mL of THF gave, after 20 h at 50 °C and workup with a sequence of $LiAlH_4$ (reaction time of 10 min) and then H_2O, a mixture of 40% of biphenyl and 60% of **6**.

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Registry No. 1, 1295-35-8; 2, 132-65-0; 3, 92-52-4; 5, 55425-72-4; 6, 259-79-0; 9, 1207-15-4; 10, 1136-85-2; 16, 612-75-9; 17, 613-33-2; H, 1333-74-0; $LiAlH_4$, 16853-85-3; 4,4′-dibromobiphenyl, 92-86-4; 3,7-dibromodibenzothiophene 5,5-dioxide, 83834-12-2; 3,7-dibromodibenzothiophene, 83834-10-0; 3,7-dilithiodibenzothiophene, 86456-51-1; 2,8-dibromodibenzothiophene, 31574-87-5; 2,8-dilithiodibenzothiophene, 86456-52-2; nickel(II) chloride, 7718-54-9; nickel(II) acetylacetonate, 3264-82-2; triethylaluminum, 97-93-8; 1,5-cyclooctadiene, 111-78-4; 1,3-butadiene, 106-99-0; 2,2′-dideuteriobiphenyl, 16327-75-6; 2,2′-diiodobiphenyl, 2236-52-4; 2,2′-dilithiobiphenyl, 16291-32-0; 2-biphenylylmagnesium bromide, 82214-69-5; 2-deuteriobiphenyl, 4819-96-9; 2,2′-bipyridyl, 366-18-7; 4-(dimethylamino)pyridine, 1122-58-3; ethylenediamine, 107-15-3; 1,10-phenanthroline, 66-71-7; pyridine, 110-86-1; hexamethylphosphorus triamide, 680-31-9; *N,N,N′,N′*-tetramethylethylenediamine, 110-18-9; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; *N,N′*-dimethylpiperazine, 106-58-1.

Electrochemical Oxidation of Benzophenone Hydrazones

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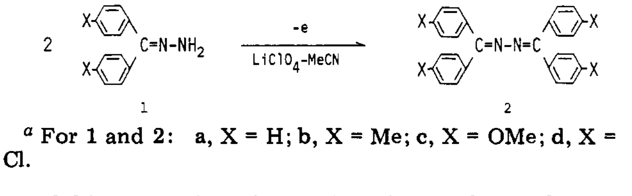
The anodic oxidation of benzophenone hydrazones (**1**) was found to give several products, depending upon the electrolysis conditions employed such as electrode material, temperature, and electrolyte composition. For example, the oxidation using a platinum anode at room temperature in $LiClO_4$–MeCN afforded exclusively benzophenone azines (**2**), whereas in NaOMe–MeOH benzophenone dimethyl acetals (**3**) were formed as the main products. On the other hand, the oxidation using a graphite anode in refluxing MeOH containing NaOMe gave diphenylmethyl methyl ethers (**4**), along with diphenylmethanes (**5**). When the analogous electrolysis was conducted in the presence of methacrylic acid derivatives, corresponding diphenylcyclopropanes (**7**) were obtained in relatively high yields.

The oxidation of ketone hydrazones has been extensively studied by using various oxidizing agents[1] and utilized in a wide variety of synthetic processes;[2] however, only a limited amount of work has been accomplished on the electrochemical oxidation of hydrazones. The only available report has shown that the anodic oxidation of keto arylhydrazones in aqueous acetonitrile gives the parent ketone, whereas with a cyclic hydrazone such as 3,5,5-trimethyl-2-pyrazoline, a rearranged product, i.e., 3,3-dimethylbutan-2-one, is formed.[3]

In this paper, we report the results of macroscale electrolysis of benzophenone hydrazones (**1**) under various

Scheme I[a]



[a] For **1** and **2**: a, X = H; b, X = Me; c, X = OMe; d, X = Cl.

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