

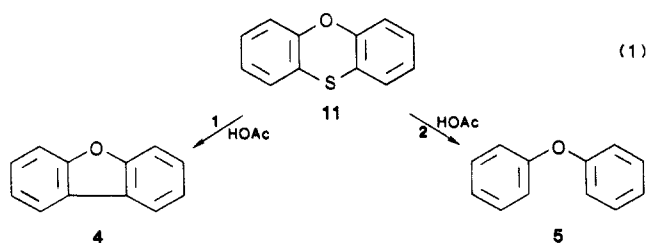
Hydrodesulfurization of Organosulfur Heterocycles by Metal Hydride–Nickel(0) Complexes: Accelerated Single-Electron Transfer in Carbon–Sulfur Bond Cleavage¹

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Abstract: The novel nickel complex, $\text{LiAlH}_2(\text{THF})_n\text{C}_{10}\text{H}_8\text{N}_2\cdot\text{Ni}$ (**2**), which results from the interaction in a THF solution of (2,2'-bipyridyl)(1,5-cyclooctadiene)nickel (**1**) with LiAlH_4 in a 1:1 molar ratio is a powerful desulfurizing agent in homogeneous solution for such aromatic sulfur heterocycles as dibenzothiophene (**3**), phenoxathiin (**11**), phenothiazine (**12**), and thianthrene (**13**). When employed in a 2:1 molar ratio with the heterocyclic substrate, **2** produces the corresponding ring-opened desulfurization products (biphenyl, diphenyl ether, diphenylamine, and benzene, respectively) in high yields. In contrast, **1** effects predominantly ring contraction during desulfurization and yields dibenzofuran, carbazole, and dibenzothiophene from **11**, **12**, and **13**, respectively. From considerations of relative desulfurization rates for substituted dibenzothiophenes, deuterium labeling experiments, and the chemical reactivity differences for **1** and **2**, it is concluded that these reagents desulfurize via single-electron-transfer mechanisms and that radical anions are crucial reactive intermediates. The greater reactivity of **2** is ascribed to its anionic nickel character.

Recently, well-defined nickel(0) complexes have been shown to desulfurize organic compounds in homogeneous media below 100 °C and in the absence of dihydrogen.^{2–5} Such a finding can be of great value in organic synthesis, where sulfur-containing intermediates must be desulfurized under mild conditions.^{4,5} Moreover, the study of such soluble nickel(0) desulfurizing reagents can provide deep insight into the mode of action for heterogeneous transition-metal desulfurization catalysts, which normally require the use of dihydrogen under pressure and of temperatures over 350 °C.^{6–8} Thus, the THF-soluble complex (2,2'-bipyridyl)(1,5-cyclooctadiene)nickel (**1**) was found to desulfurize dibenzothiophene (**3**) at 55–60 °C and to convert **3** into a mixture of biphenyl and biphenylnickel derivatives.⁹ Such a heterocycle is most resistant to more conventional desulfurization reagents. However, the prior interaction of nickel complex **1** with lithium aluminum hydride generated a different and more powerful desulfurizing reagent **2**.² That nickel reagents **1** and **2** are distinctly different chemical reactants is evident in their individual reactions with phenoxathiin (**11**): whereas **11** is smoothly desulfurized by **1** with ring closure to dibenzofuran (**4**), **2** converts **11** into diphenyl ether (**5**) in equally high yield (eq 1).²



Accordingly, the present study was undertaken in order to establish the chemical nature of the novel nickel reagent **2**, to evaluate its reactivity toward aromatic sulfur heterocycles, and to understand its mechanism of reaction.

Table I. Hydrodesulfurization of Dibenzothiophenes by (2,2'-Bipyridyl)(1,5-cyclooctadiene)nickel (**1**) and Lithium Aluminum Hydride in Tetrahydrofuran

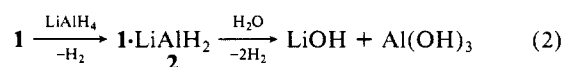
dibenzothiophene	1:LAH ^a molar ratio	yield of biaryl, % ^b
unsubstituted	0:1	<1
	1:1	40
	2:1	41
	2:2	95 ^{c,d}
	2:3	90
2,8-dimethyl	2:2	82
3,7-dimethyl	2:2	68

^a Ratio is based in each reaction upon 1 molar equiv of the dibenzothiophene being allowed to react with $n:m$ molar equiv of reagent **1** and LiAlH_4 . ^b All reactions were conducted at the same concentration of the dibenzothiophene for 48 h at 55–60 °C and then worked up with glacial HOAc. ^c Reaction also was run that employed LiAlD_4 , and the workup used HOAc. Resulting biphenyl was 60.4% d_0 , 25.3% d_1 , and 14.3% d_2 . ^d Reaction also was run that employed LiAlH_4 , and the workup used DOAc. Resulting biphenyl was 94.5% d_0 , 2.3% d_1 , and 3.2% d_2 .

Results

Nature of the Interaction between (2,2'-Bipyridyl)(1,5-cyclooctadiene)nickel and LiAlH_4 (6**): Formation of **2**.** Desulfurization studies with dibenzothiophene (**3**) have shown that the most active desulfurizing agent resulted when 1 mol of **3** in THF solution at 55 °C was treated with 2 molar equiv of a 1:1 ratio of nickel reagent **1** and LiAlH_4 . Under these conditions a 95% yield of biphenyl was obtained. Use of 3 mol of LiAlH_4 reduced the yield of biphenyl somewhat (90%), but the use of only 1 mol of LiAlH_4 markedly lowered the yield (41%). Therefore, a reaction ratio of 1:2:2 for **3**, **1**, and LiAlH_4 is optimal for desulfurization (Table I).

Accordingly, the reaction between 1:1 molar ratios of nickel reagent **1** and LiAlH_4 in THF solution was studied separately at 25 °C. Addition of LiAlH_4 in THF to a deep-violet solution of **1** led to the evolution of 1 molar equiv of dihydrogen and the formation of a red-violet solution of **2**. Hydrolysis of this solution gave 2 molar equiv of dihydrogen. Thus, all the available hydrogen of the LiAlH_4 was accounted for; specifically, none had been consumed through addition of an Al–H bond to either the bipyridyl or the cyclooctadiene (eq 2).



The deep-red solution of **2**, upon evaporation in vacuo, yielded a black solid **2** which was soluble in THF. By MS, NMR, and

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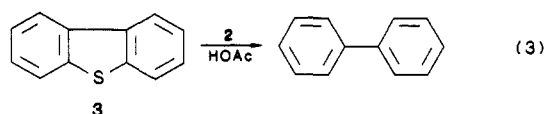
(9) Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Org. Chem.* **1983**, 26, 2963.

Table II. Effect of Various Amines on the Hydrodesulfurizing Activity of a 1:1 Combination of Bis(1,5-cyclooctadiene)nickel and Lithium Aluminum Hydride on Dibenzothiophene

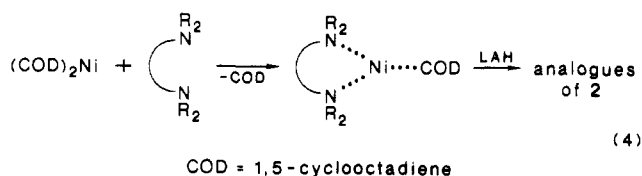
amine ^a	yield of biphenyl, % ^b
ethylenediamine	97
2,2'-bipyridyl	95
hexamethylphosphorus triamide	95
<i>N,N,N',N'</i> -tetramethylethylenediamine	85
pyridine ^c	58 ^d
	82 ^d
	35 ^d
<i>N,N'</i> -dimethylpiperazine	79
1,8-bis(dimethylamino)naphthalene	71
1,10-phenanthroline	68
4-(dimethylamino)pyridine	53

^aIn all cases, except with pyridine, 2 mol of the amine, 2 mol of (COD)₂Ni, and 2 mol of LiAlH₄ were allowed to react with 1 mol of dibenzothiophene. ^bAll reactions were conducted at the same concentration of dibenzothiophene for 48 h at 55–60 °C and then worked up with glacial HOAc. ^cIn this case 4 mol of pyridine and 2 mol of (COD)₂Ni were employed. ^dIn these successive runs, 1.0, 2.0, and finally 3.0 mol of LiAlH₄ were used per 2 mol of (COD)₂Ni and 4.0 mol of pyridine.

IR analyses, **2** was shown to contain 2,2'-bipyridyl and tetrahydrofuran but no cyclooctadiene. Attempts to obtain crystals of **2** suitable for an X-ray structure determination have been thus far unsuccessful.¹⁰ Nevertheless, the gas evolution and spectral studies permit us to conclude that **2** has the stoichiometry LiAlH₂(THF)_n·C₁₀H₈N₂·Ni. Indeed, black solid **2** could be redissolved in THF and heated with 0.5 molar equiv of **3** at 55 °C to give almost a quantitative conversion to biphenyl (eq 3).



Generation of Nickel Complexes Analogous to 2 by Use of Other Amines. Substitution of other chelating diamines for 2,2'-bipyridyl in the formation of the nickel complex and subsequent reaction with 1 molar equiv of LiAlH₄ led to desulfurizing agents comparable in reactivity to **2** (eq 4, Table II). That analogues of **2** made



with TMEDA, HMPA, or ethylenediamine are desulfurizing agents of comparable reactivity to **2** permits us to draw two conclusions: (1) the aromatic unsaturation of the bipyridyl plays no decisive role in modifying the Al–H bond reaction¹¹ and (2) the formally displaceable hydrogens of the amino groups in ethylenediamine do not interfere with the desulfurizing activity. Even pyridine could replace bipyridyl in forming effective analogues of **2**, if 2 equiv were employed. This effect was also noticed with diamines incapable of forming chelating complexes. 4-(Dimethylamino)pyridine, for example, gave relatively low yields of desulfurization (53%) when used in a 1:1 ratio with (COD)₂Ni but was more effective when used in a 2:1 ratio. The reactivity of *N,N'*-dimethylpiperazine, when used in a 1:1 ratio with (COD)₂Ni, deserves comment. The high yield of desulfurization (79%) indicates that it functions as a chelating diamine in its boat conformation.

From these observations it can be concluded that the nickel in **2** and its analogues is coordinated by two amine centers.

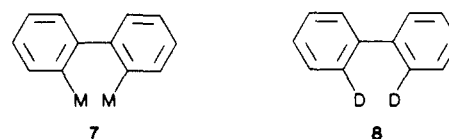
Table III. Desulfurization of Sulfur Heterocyclic Analogues of Dihydroanthracene by Nickel Reagents **1** and **2**

nickel reagent 1^a		
11 , E = O	11a : 79	11b : 3
12 , E = NH	12a : 75	12b : 5
13 , E = S	13a : 55	13b : 15
nickel reagent 2^b		
11 , E = O	11a : 3	11b : 92
12 , E = NH	12a : 5	12b : 65
13 , E = S	13a : 5	13b : 75 ^d

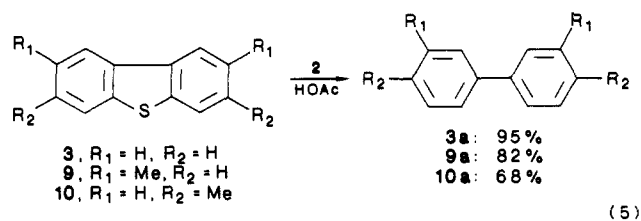
^aReagent was formed from 2 mol each of (COD)₂Ni and 2,2'-bipyridyl; reagent **1** then was allowed to react with 1.0 mol of the heterocycle. ^bReagent was formed from 2 mol of reagent **1** and 2 mol of LiAlH₄; resultant **2** was allowed to react with 1.0 mol of the heterocycle. ^cAll reactions were allowed to proceed at 55–60 °C for 48 h and then worked up with HOAc. ^dBenzene was also formed.

Labeling Studies of Organometallic Intermediates in Desulfurizations with Reagent 2. The desulfurization of dibenzothiophene was conducted with a nickel reagent **2** that was prepared with LiAlD₄. Workup with protic acids gave a biphenyl containing 60.4% d₀-, 25.3% d₁-, and 14.3% d₂-labeled biphenyl. Infrared spectral comparisons showed the deuterons to be in the 2- and 2'-positions.⁹ When a desulfurization reaction was conducted with **2** (i.e., made with LiAlH₄) but the reaction was worked up with deuterated acids, the resulting biphenyl contained only 2.3% biphenyl-d₁ and 3.2% biphenyl-d₂.

These labeling studies show that the isolated biphenyl acquires only about 9% of its hydrogen upon hydrolysis. Of the 91% it acquires prior to hydrolysis, only about 25% comes from the deuterium of the LiAlD₂ unit in **2**. The 75% stems from the medium (either amine or THF). Thus, only a very small proportion of biphenylmetallic intermediates (M = Li, Al, or Ni; **7**) persisted in the desulfurization mixture, and a minor amount of dibenzothiophene has had its sulfur directly displaced by deuterium (**8**) from the LiAlD₂ unit in **2**.



Relative Reactivities in Desulfurizing Dibenzothiophenes. Subjecting **3**, its 2,8-dimethyl isomer **9**, and its 3,7-dimethyl isomer **10** to the desulfurizing action of **2** under identical reaction conditions gave the yields of the corresponding biphenyls summarized in eq 5 (Table I). The reactivity in desulfurization with **2**, therefore, decreases in the sequence **3** > **9** > **10**.



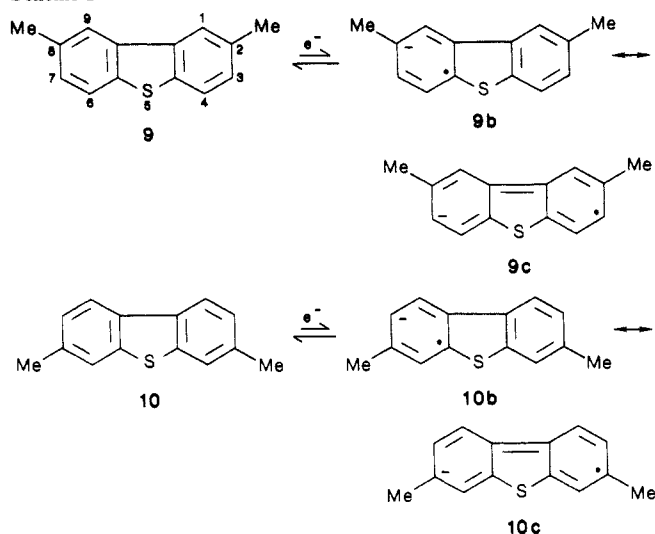
Desulfurization of Sulfur Analogues of Dihydroanthracene. (a) Ring Contraction with Reagent 1. The interaction of 2 molar equiv of nickel reagent **1** with 1 mol each of phenoxathiin (**11**), phenothiazine (**12**), or thianthrene (**13**) gave good to high yields of the monodesulfurized heterocyclic analogue of fluorene (Table III). Small amounts of hydrodesulfurized products **11b**–**13b** accompanied the cyclized sulfur-extrusion products **11a**–**13a**.

(b) Hydrodesulfurization with Reagent 2. With nickel reagent **2** the proportions of products **11a**–**13a** to **11b**–**13b** were reversed: the hydrodesulfurized structures became the principal products, while the cyclized products were minor in amount (Table III). In addition, thianthrene gave rise to benzene. This diverging

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(11) The authors are aware that LiAlH₄ is known to hydraluminate pyridine bases: Lansbury, P. T.; Peterson, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 2236.

Scheme I



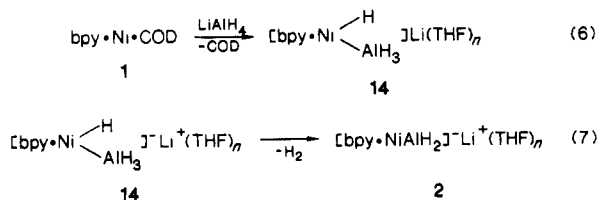
compound	yield of biaryl, %	$E_{1/2}$, V (reduction)
unsubstituted dibenzothiophene	95	2.432
2,8-dimethyl derivative	82	2.452
3,7-dimethyl derivative	68	2.563

chemical behavior between reagents 1 and 2 again indicates that 2 is the much stronger desulfurizing agent.

Discussion

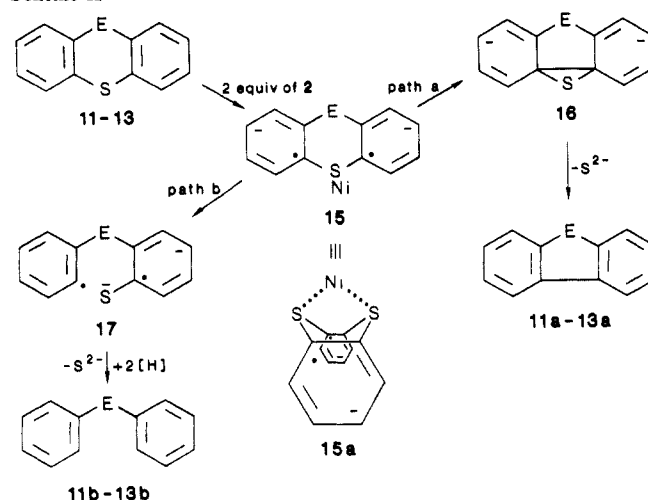
The mode of generating nickel reagent 2 demonstrates that it is neither just an activated form of lithium aluminum hydride nor just a nickel hydride. First of all, heating either dibenzothiophene or phenoxathiin with pure LiAlH_4 in THF for prolonged periods gave only traces of biphenyl (13b) or diphenyl ether (11b). Secondly, using LiAlD_4 to prepare 2 gave a desulfurizing agent that introduces <25% deuterium into the biphenyl formed from dibenzothiophene. Thirdly, attempts to produce analogues of 2 from nickel(II) salts and metal hydrides (LiAlH_4 , $i\text{-Bu}_2\text{AlH}$, or NaBH_4), a known route to nickel hydrides,¹² generate decidedly inferior desulfurizing agents.

Although a definitive structure for 2, especially with respect to its molecular size, must await its X-ray crystal analysis, considerable information is available on complexes of nickel(0) and complex metal hydrides.^{13,14} The tendency of such hydrides to form hydridic donor bridges with $\text{Ni}(0)$ centers suggests that reagent 1 and LiAlH_4 undergo an oxidative addition (eq 6) and that 14 then eliminates dihydrogen to form 2 (eq 7). Reagent 2 is probably dimeric, since analogous complexes with chelating phosphines, P_2NiBH_2 , are known to be dimeric.¹⁵



However, the mode of reaction of 2 does not agree with the view that it functions as a nucleophilic source of a metal (Ni or Al) or of hydrogen. If such nucleophilic attack were central to desulfurizing dibenzothiophene, then the deuterium labeling studies would have observed a much higher content of 2,2'-dideuterio-biphenyl in the product. Such dideuterated biphenyl would have arisen from the presence of 7 or 8 prior to hydrolysis. That the

Scheme II



preponderance of the hydrogen in the biphenyl came from the solvent, not from the LiAlH_4 nor the HOAc used upon workup, rules out any simple nucleophilic attack of 2 upon the sulfur heterocycle.

The relative reactivities of the dimethyldibenzothiophenes toward 2 show that the electron-donating methyl substituents retard carbon-sulfur bond cleavage. As with their reduced reactivity toward 1, such retardation can be correlated with the destabilization such methyl groups would confer on radical anion formation (Scheme I). Of the resonance structures, 9b-9c and 10b-10c, 9c and 10c can readily be considered the more important because the electron density can be spread over two aryl rings. Hence, the spin density would be greater at C_3 and C_7 than at C_2 and C_8 . Indeed, such spin densities have been determined from the ESR coupling constants of the dibenzothiophene radical anion and found to vary thus: C_1 , 4.48; C_2 , 0.86; C_3 , 5.16; and C_4 , 1.46 G.¹⁶ Because the electron density of the heterocycle would be enhanced by any attached methyl group, both 9 and 10 should accept electrons less readily from 2 than dibenzothiophene. But methyl groups attached at C_3 and C_7 should exert the maximum destabilization upon the radical anion, since such positions have the highest electron density. The polarographic reduction potentials required to form the radical anion electrochemically bear out this suggestion: the 3,7 isomer is the most difficult to reduce and the parent nucleus the easiest.¹⁷ Hence, these data support the occurrence of single-electron transfer in desulfurizations with 2.

In the desulfurizations of the sulfur analogues of dihydroanthracene, 11-13, by either 1 or 2, evidence is also more consonant with the operation of an SET process. The desulfurization of 11-13 by 1 to give ring contraction provides a particularly graphic example of the generation of diradical anions (15). The intramolecular coupling (path a) of such intermediates appears to be promoted by the boat conformation of the central heterocyclic ring (15a). In turn, such a conformation would be fostered by chelating coordination with the nickel center (Scheme II). Intermediate 15 undergoes principally coupling (16) to yield 11a-13a ultimately. A small proportion undergoes cleavage to 17 and finally to 11b-13b. With the same heterocycles, reagent 2 promotes path b, and the principal products are the open-chain hydrodesulfurized products 11b-13b. Possibly, the greater tendency of reagent 1 to form chelate complex 15 may be responsible for the dominance of ring-closure products 11a-13a over open-chain products 11b-13b.

Finally, in keeping with the generation of radical anions 9b-9c, 10b-10c, 15, and 17 one would expect the hydrogen acquired during such desulfurization to stem principally from the most ready source of hydrogen atoms, namely, tetrahydrofuran.

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(17) Gerdil, R.; Lucken, E. A. C. *J. Am. Chem. Soc.* **1966**, *88*, 733.

On the basis of the foregoing findings, therefore, we conclude that nickel reagents **1** and **2** act as electron sources in such desulfurizations and that the greater activity of **2** may be ascribed to its SET activity being enhanced by its anionic nickel character.

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared spectra (IR) were recorded on a Perkin-Elmer grating spectrometer, Model 457, equipped with sodium chloride optics. Proton magnetic resonance spectra (^1H NMR) were obtained with Varian spectrometers, Model EM-360 or Model HA-100D, 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. 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.

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.¹⁸

The yields of desulfurization reactions were determined by isolating and weighing the crude products and the analysis of the mixture by GLPC. *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.¹⁸ 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.¹⁹

Reagents. Pyridine was rendered anhydrous by refluxing over BaO and then distilling. Similar distillation over an appropriate drying agent or recrystallization was used to purify dibenzofuran, phenoxathiin, phenothiazine, dibenzofuran, 2-phenylbenzofuran, and thianthrene. The pure ligands, 2,2'-bipyridyl, 1,8-bis(dimethylamino)naphthalene, 4-(dimethylamino)pyridine, *N,N'*-dimethylpiperazine, ethylenediamine, and 1,10-phenanthroline, were either recrystallized from dry, deoxygenated solvents or distilled under nitrogen.

3,7-Dimethyldibenzothiophene, mp 147–148 °C (from ethanol), was prepared from biphenyl in four steps: (a) bromination to yield 55% 4,4'-dibromobiphenyl, mp 160–162 °C;⁹ (b) chlorosulfonation to form 3,7-dibromodibenzothiophene 5,5-dioxide, mp 308–309 °C;⁹ (c) reduction with LiAlH_4 in ethyl ether to provide 71% 3,7-dibromodibenzothiophene;⁹ and finally (d) bromine-lithium exchange with *n*-butyllithium at –5 °C in ethyl ether, followed by treatment with dimethyl sulfate.⁹ 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 °C⁹ and (b) bromine-lithium exchange with *n*-butyllithium in ethyl ether at 5 °C, followed by treatment with dimethyl sulfate.⁹

Metal salts, such as the acetylacetonates and halides of Ni(II) were purchased and dried before use. Bis(1,5-cyclooctadiene)nickel was prepared according to a modified procedure recently published.⁹

The deuterated reagents were obtained from the Aldrich Chemical Company: deuterium oxide (99.8% D_2O), deuterium chloride (37%, 99.8% D), *O*-deuterioacetic acid (98% $\text{CH}_3\text{CO}_2\text{D}$), and LiAlD_4 (98%).

Products. 3,3'-Bitolyl and 4,4'-bitolyl were prepared by coupling the respective tolyl Grignard reagents with TiBr_4 .⁹ 3,3'-bitolyl bp 153–155 °C (18 mmHg) and 4,4'-bitolyl mp 119–120 °C. Biphenylene was prepared by the thermolysis of benzenediazonium-2-carboxylate, mp 110–112 °C.⁹

2,2'-Dideuteriobiphenyl and 2-deuteriobiphenyl were prepared by methods recently published.⁹ Their mass spectra and that of undeuteriated biphenyl were recorded under identical operating conditions of the mass spectrometer, so that peak intensities could be used to calculate the

deuterium content of the biphenyls encountered in this study.

Diphenyl ether, dibenzofuran, diphenylamine, and carbazole were identified by comparison with authentic samples.

Analytical Procedures. Vapor-phase chromatographic analyses and isolations were achieved with 6-ft \times 0.25-in. columns packed with 10% UC-W98 or SE-30 phases on Chromosorb W or with 10% UC-W98 on Chromosorb P.

Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

The LiAlH_4 solutions in THF were analyzed by measuring the volume of hydrogen evolved and by titrating with a solution of *n*-butyl alcohol in toluene in the presence of 4-phenylazodiphenylamine.²⁰ In gasimetric measurements a correction was made for the vapor pressure of THF.²¹

Interaction of (2,2'-Bipyridyl)(1,5-cyclooctadiene)nickel (1**) with LiAlH_4 .**²² Gas evolution studies were conducted in a 100-mL pear-shaped Schlenk flask, whose side entry bore a three-way stopcock and top entry a rubber septum. The side entry was connected to a calibrated, mercury-filled buret. Aliquots of $(\text{COD})_2\text{Ni}$ (0.5 mmol, 138 mg), an equimolar amount of 2,2'-bipyridyl, and 15 mL of pure THF were placed in the flask. After the violet $(\text{bpy})(\text{COD})\text{Ni}$ complex had formed in solution, the equimolar amount of LiAlH_4 in THF (approximately 1.0 M) was slowly introduced through the septum with a gas-tight syringe. As hydrogen was evolved, the reaction mixture formed a black solution. The collected volume of gas was corrected for the vapor pressure of the THF solution and adjusted to STP. An average of seven runs gave 1.06 ± 0.1 molar equiv of hydrogen. Hydrolysis of the reaction mixtures with 6 N aqueous HCl accounted for 1.02 ± 0.1 molar equiv of additional hydrogen. Hence, all the available hydrogen was evolved, 50% in the reaction with $(\text{bpy})(\text{COD})\text{Ni}$ and 50% upon terminal hydrolysis.

The hydrolyzed, dried organic layers was shown by GLPC analysis to contain only 2,2'-bipyridyl and a 5:1 mixture of 1,5-cyclooctadiene and cyclooctene.

Evaporation of volatile components from an unhydrolyzed reaction mixture under reduced pressure left a crystalline black solid (**2**) that could be redissolved in THF. The mass spectrum of the black solid at 70 eV showed peaks characteristic of 2,2'-bipyridyl and of THF. Neither in the mass spectrum nor in the ^1H NMR spectrum ($\text{THF}-d_6$) was there any sign of a cycloocta derivative. From these gas-evolution and spectral data the black solid **2**²³ is concluded to have the composition $\text{LiAlH}_2(\text{THF})_n\text{C}_{10}\text{H}_8\text{N}_2\text{Ni}$.

Hydrodesulfurization of Dibenzothiophene (3**) with (2,2'-Bipyridyl)-(1,5-cyclooctadiene)nickel (**1**) and Lithium Aluminum Hydride.** (a) **Varying Ratios of Nickel Reagent **1** to LiAlH_4 .** A stirred, deep-violet solution of **1**, prepared from 559 mg (2.03 mmol) of $(\text{COD})_2\text{Ni}$ and 217 mg (2.03 mmol) of 2,2'-bipyridyl in 15 mL of THF, was treated with 77 mg (2.03 mmol) of LiAlH_4 at 25 °C. After gas evolution had subsided, the resulting reddish violet solution was treated with 177 mg (0.96 mmol) of dibenzothiophene and then heated at 55 °C for 48 h. Then the cooled mixture was treated with 6 N aqueous HCl, the organic layer separated and dried over anhydrous MgSO_4 , and the solvent evaporated. By GLPC analysis the residue consisted of 95% biphenyl and 5% **3**.

In reactions of the same 2.0 mM scale, the use of 1.0 mmol of LiAlH_4 gave 41% biphenyl and 59% **3**, while the use of 3.0 mmol of LiAlH_4 produced 90% biphenyl and 10% **3**.

(b) **Use of Pyridine in Place of 2,2'-Bipyridyl.** A solution of 2.0 mmol of $(\text{COD})_2\text{Ni}$ and 4.0 mmol of pyridine in 15 mL of THF was treated with a given amount of solid LiAlH_4 . After gas evolution had ceased, 1.0 mmol of dibenzothiophene was added and the mixture stirred for 48 h at 55 °C. Protolysis with glacial acetic acid and the usual subsequent aqueous workup gave the following results: (1) 1.0 mmol of LiAlH_4 , 58% biphenyl; (2) 2.0 mmol of LiAlH_4 , 82% biphenyl; and (3) 3.0 mmol of LiAlH_4 , 35% biphenyl.

(c) **Use of Various Amines in Place of 2,2'-Bipyridyl.** A series of reactions were carried out in which 2.0 mmol each of $(\text{COD})_2\text{Ni}$, the amine, and LiAlH_4 in 15 mL were allowed to react with 1.0 mmol of **3** for 48 h at 55 °C. Workup as in section b gave the yields of biphenyl listed in Table II.

(d) **Use of Lithium Aluminum Deuteride.** A solution of 403 mg (1.47 mmol) of $(\text{COD})_2\text{Ni}$ and 229 mg (1.47 mmol) of 2,2'-bipyridyl in 15 mL of THF was stirred for 1 h and then mixed with 55 mg (1.47 mmol) of LiAlD_4 . After 50 min the gas evolution had ceased, and then 129 mg

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(22) We are grateful to Stephen R. Sexsmith, who carried out these gasimetric measurements.

(23) We thank Dr. Andrzej M. Piotrowski, who first isolated and characterized solid **2**.

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(0.70 mmol) of dibenzothiophene was added. After 48 h at 55 °C the mixture was worked up, first with glacial acetic acid and then with 6 N aqueous HCl. A sample of the biphenyl (95%) was analyzed by MS and IR measurements. The product was a mixture of 14.3% 2,2'-dideuterio- and 25.3% 2-deuteriobiphenyl, together with 60.4% biphenyl.

(e) **Workup with *o*-Deuterioacetic Acid.** The reaction between (COD)₂Ni, 2,2'-bipyridyl, and LiAlH₄ in 15 mL of THF was conducted on a 1.5 mM scale as in section d. Workup with CH₃CO₂D gave 94.5% biphenyl and a mixture of 2.3% 2-deuterio- and 3.2% 2,2'-dideuteriobiphenyl.

Hydrodesulfurization of Dibenzothiophene (3) with Nickel Salts and Metal Hydrides. (a) **2,2'-Bipyridyl and LiAlH₄.** A solution of 200 mg (0.73 mmol) of nickel(II) acetylacetonate and 113 mg (0.73 mmol) of 2,2'-bipyridyl in 15 mL of THF was treated with 26 mg (0.73 mmol) of LiAlH₄. After the brown solution was stirred for 30 min at 25 °C, 67 mg (0.36 mmol) of 3 was added. The reaction mixture was heated for 48 h at 55 °C and then given the usual protolytic workup. A GLPC analysis showed a 36% conversion to biphenyl.

A reaction in which 6 molar equiv of LiAlH₄ was used with 2 molar equiv each of Ni(acac)₂ and 2,2'-bipyridyl to desulfurize 1 molar equiv dibenzothiophene gave 32% biphenyl.

(b) **Use of NaBH₄.** A reaction analogous to that in section a, except that NaBH₄ was substituted for LiAlH₄, gave a 6% conversion to biphenyl, either in THF (55 °C) or in triglyme (130 °C).

(c) **Use of Diisobutylaluminum Hydride.** A green solution of 290 mg (1.83 mmol) of Ni(acac)₂ and 285 mg (1.83 mmol) of 2,2'-bipyridyl in 15 mL of toluene was stirred while being treated with 260 mg (1.83 mmol) of (*i*-Bu)₂AlH. Then 160 mg (0.87 mmol) of 3 was added to the brown solution. After 24 h at reflux and the usual protolytic workup, a GLPC analysis showed a 38% conversion to biphenyl.

Hydrodesulfurization of 2,8-Dimethyldibenzothiophene (9). A deep-violet solution of 1, prepared from 560 mg (2.03 mmol) of (COD)₂Ni and 220 mg (2.03 mmol) of 2,2'-bipyridyl in 15 mL of THF, was treated first with 80 mg (2.03 mmol) of LiAlH₄ and after 30 min with 212 mg (1.0 mmol) of 9. After 48 h at 55 °C hydrolytic workup gave an 82% yield of 3,3'-dimethylbiphenyl.

Hydrodesulfurization of 3,7-Dimethyldibenzothiophene (10). A reaction mixture of 560 mg (2.03 mmol) of (COD)₂Ni and 220 mg (2.03 mmol) of 2,2'-bipyridyl in 15 mL of THF was treated first with 80 mg (2.03 mmol) of LiAlH₄ and then with 212 mg (1.07 mmol) of 10. After 48 h at 55 °C and the usual workup the GLPC analysis showed a 68% conversion to 4,4'-dimethylbiphenyl but none of the 3,3' isomer.

Ring Contraction of Sulfur Heterocycles with (2,2'-Bipyridyl)(1,5-cyclooctadiene)nickel (1). (a) **Phenoxathiin (11).** A violet solution of an equimolar mixture of (COD)₂Ni and 2,2'-bipyridyl in THF (10

mL/1.5 mmol of 1) was treated with phenoxathiin and the resulting mixture heated at 55 °C for 48 h. The cooled reaction mixture was treated with glacial acetic acid, and the organic products were isolated in the usual way. For four reactions having the following ratios of 11:1, namely, 1:1, 1:2, 1:3, and 1:4, the corresponding conversions to dibenzofuran, as determined by GLPC analysis, were 15%, 79%, 81%, and 78%. Thus, a 1:2 ratio of 11:1 was most satisfactory. Also, the side production of diphenyl ether increased as the ratio of 11:1 changed: 1:1, 1%; 1:2, 3%; and 1:3, 11%.

(b) **Phenothiazine (12).** Similar to the procedure in section a, the interaction of 3.15 mmol of 1 in 20 mL of THF with 1.5 mmol of 12 yielded a 75% conversion to carbazole and a 5% conversion to diphenylamine.

(c) **Thianthrene (13).** Similar to the procedure in section a, the reaction between 3.2 mmol of 1 and 1.3 mmol of 13 gave 55% dibenzothiophene, 15% biphenyl, and 30% 13.

Hydrodesulfurization of Sulfur Heterocycles (Table III). (a) **Phenoxathiin (11).** To a violet solution of 2.2 mmol each of (COD)₂Ni and 2,2'-bipyridyl in 20 mL of THF was added 2.2 mmol of LiAlH₄. After 60 min at 25 °C 1.0 mmol of 11 was added. The reaction was allowed to proceed for 24 h at 25–30 °C. The usual workup and GLPC analysis showed a mixture of 92% diphenyl ether, 3% dibenzofuran, and 5% 11.

(b) **Phenothiazine (12).** A violet solution of 3.9 mmol of 1 in 20 mL of THF was treated with 6.0 mmol of LiAlH₄. After 60 min of stirring, 1.8 mmol of 12 was added and the mixture heated for 48 h at 55 °C. The usual workup gave 65% diphenylamine, 5% carbazole, and 30% 12.

(c) **Thianthrene (13).** A violet solution of 3.0 mmol of 1 in 20 mL of THF was treated with 3.0 mmol of LiAlH₄, and then 1.4 mmol of 13 was added. After 48 h at 55 °C and the usual workup, the following products were found: 15% biphenyl, 5% dibenzothiophene, benzene, and 13.

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Registry No. 1, 55425-72-4; 3, 132-65-0; 3a, 92-52-4; 9, 1207-15-4; 9a, 612-75-9; 10, 1136-85-2; 10a, 613-33-2; 11, 262-20-4; 11a, 132-64-9; 11b, 101-84-8; 12, 92-84-2; 12a, 86-74-8; 12b, 122-39-4; 13, 92-85-3; benzene, 71-43-2; ethylenediamine, 107-15-3; 2,2'-bipyridyl, 366-18-7; hexamethylphosphorus triamide, 680-31-9; *N,N,N',N'*-tetramethylethylenediamine, 110-18-9; pyridine, 110-86-1; *N,N'*-dimethylpiperazine, 106-58-1; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; 1,10-phenanthroline, 66-71-7; 4-(dimethylamino)pyridine, 1122-58-3.

Do Carbenium Ion Additions toward Alkenes Proceed via π Complexes? A Stereochemical Investigation

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Abstract: Lewis-acid-catalyzed addition reactions of diarylmethyl chlorides with (*E*)- and (*Z*)-2-butene yield the addition products 3a (>84% anti selectivity) and the products 5–7, which are formed via 1,2-H and 1,2-CH₃ shifts. The Markovnikov addition products 3b are generated exclusively from the corresponding reactions with the *E,Z*-isomeric β -methylstyrenes 2b. While the *E* isomer *t*-2b gives the anti adducts *t*-3b predominantly, (*Z*)- β -methylstyrene reacts with low stereoselectivity. In all cases, the yield of anti adducts increases with increasing stability of the attacking diarylcarbenium ion and decreasing solvent polarity. These observations are interpreted in terms of partially bridged intermediates which are attacked by nucleophiles from the backside.

1. Introduction

Electrophilic additions to carbon–carbon double bonds have been studied in great detail.¹ A wide variety of mechanisms has

been detected, and the stereochemical course ranges from high anti^{2a-c} or syn^{2d} stereoselectivity to a complete loss of stereochemical information^{2e} (Scheme I). Concerted and stepwise mechanisms have been reported,^{1,2} and the latter processes might

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