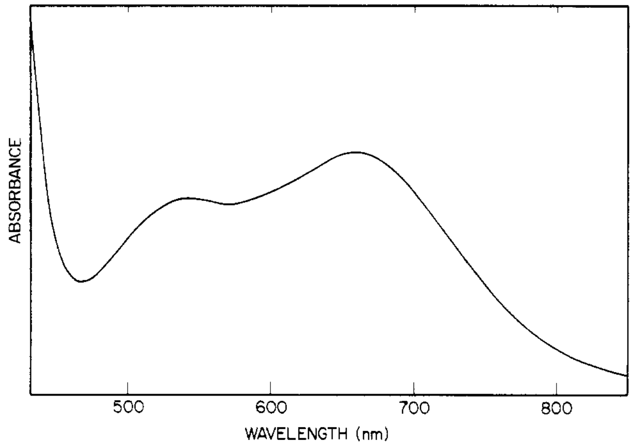


Figure 2. Electronic spectrum of $Re(CO)_3(P\text{-c-}Hx_3)_2\cdot$ in benzene. (ϵ_{max} ~5×10^2 M^{-1} cm^{-1}).

inary, but quite accurate in reproducing the parallel region) are summarized in Table I. There are two distinct rhenium species present, one in considerably higher concentration than the other. Each shows coupling to Re, which has two isotopes,[15] ^{185}Re (37.05%) and ^{187}Re (62.93%), for which $I = {}^5/_2$. The magnetic moments differ by only 1% so the different isotopes do not account for the two observed species.

If the second species were an impurity, we would expect its relative concentration to vary with the preparation or with change in sample handling. No such variation was observed. In attempts to obtain clear ^{31}P coupling information, we obtained EPR spectra at 4 K both by CW and electron spin echo techniques and also ran CW spectra at 77 K at 3.4 GHz without any improvements in resolution. Fortunately, the phosphorus superhyperfine structure is evident in the fourth parallel Re hyperfine line of the major species, showing the 1:2:1 triplet expected from two essentially equivalent ^{31}P centers. Under increased gain, the corresponding line of the minor species has the same characteristics (see Figure 1). Finally, it should be noted that the EPR parameters of both species are analogous to those for $Mn(CO)_3L_2\cdot$ radicals.[10,16]

The major species is assigned a square-pyramidal structure, with phosphine ligands in basal positions, most probably in a trans disposition. A trans ligand arrangement should cause the spectrum to deviate from axial symmetry, but such deviation cannot be detected without extensive refinement, in progress. The contribution of the minor species to the spectrum is apparently constant from one preparation to another. It is most likely an isomer of the major species; it might correspond to a cis configuration of the phosphines in a distorted square-pyramidal structure.

The room-temperature solution mixture was reacted with excess $HSn(n\text{-}C_4H_9)_3$, to form the rhenium hydride $HRe(CO)_3L_2$. The ^1H NMR spectrum (benzene-d_6) revealed one apparent triplet ($J(^1H\text{-}^{31}P) = 20$ Hz) centered at δ -6.23. This result suggests that if there are two isomers of $Re(CO)_3L_2\cdot$, they interconvert rapidly at room temperature and that one (presumably the trans basal form) reacts more rapidly with the hydrogen atom source.

The UV-visible spectrum in benzene (Figure 2) consists of two broad absorptions at 540 and 665 nm (ϵ ~5×10^2 M^{-1} cm^{-1}). The electronic spectra of the $Mn(CO)_3L_2\cdot$ radicals have been discussed[11] in terms of simple one-electron d-d transitions. While $Mn(CO)_5\cdot$ shows a single absorption band,[17] the effect of phosphine substitution is to split the degeneracy of the d orbitals and shift one transition to longer wavelength. $Re(CO)_5\cdot$ shows a single electronic absorption band at 535 nm.[18] Thus, the change in the electronic spectrum upon substitution of $Re(CO)_5\cdot$ parallels that seen for $Mn(CO)_5\cdot$, except that the transitions are shifted to higher energy as expected for the third-row metal.

We have recently reported kinetics studies of the reaction of CO with $Mn(CO)_3L_2\cdot$ radicals.[12] These studies suggest an associative pathway for ligand substitution by CO. The rate of substitution showed a marked decrease for the bulkiest ligands. Although $P\text{-c-}Hx_3$ is much bulkier (cone angle = 170°)[9] than $P(i\text{-}Bu)_3$ (cone angle = 142°), preliminary experiments indicate that the rate of reaction of CO with $Re(CO)_3(P\text{-c-}Hx_3)_2\cdot$ is at least 200 times faster than with $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$. The higher rate for the associative process at rhenium is presumably due to larger size as compared with manganese.

Acknowledgment. This research was supported by the National Science Foundation through Research Grants NSF CHE 81-19525 to T.L.B. and CHE 80-20443 to R.L.B.

Registry No. $Re(CO)_3(P\text{-c-}Hx_3)_2$, 85565-69-1; $Re_2(CO)_8(P\text{-c-}Hx_3)_2$, 65531-96-6.

---

[15] Creber, K. A. M.; Wan, J. K. S. *Chem. Phys. Lett.* **1981,** *81,* 453.

[16] Rattinger, G. B.; Walker, H. W.; Belford, R. L.; Brown, T. L., unpublished work in progress on detailed analysis of $Mn(CO)_3L_2\cdot$ EPR spectra.

[17] (a) Waltz, W. L.; Hackleberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978,** *100,* 7259. (b) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Ibid.* **1981,** *103,* 7515.

[18] Meckstroth, M. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982,** *104,* 1842.

Addition of Alkynyllithium Reagents to the S–S Bond of (μ-Dithio)bis(tricarbonyliron): Equilibria between Open S-Centered and Bridged C-Centered Anions

Dietmar Seyferth,* Gary B. Womack, and Li-Cheng Song[1]

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 3, 1983

Summary: Alkynyllithium reagents cleave the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ to give $(\mu\text{-}RC{\equiv}CS)(\mu\text{-}LiS)Fe_2(CO)_6$ complexes which apparently are in equilibrium with products of intramolecular S^- addition to the α and/or β carbon atom of the $RC{\equiv}C$ group. With alkyl halides and acetyl chloride S-alkylation or S-acylation was observed. Protonation and reactions with group 4 organometallic halides gave "closed" products, while reaction with methylmercuric chloride gave both "open" and "closed" products.

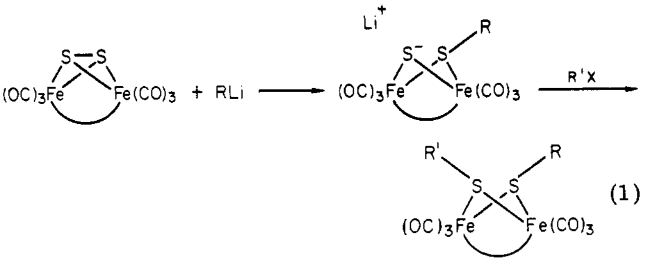
We have reported that the S–S bond of (μ-dithio)bis(tricarbonyliron) undergoes nucleophilic cleavage by or-

---

[1] Visiting Scholar at M.I.T., 1979–1982, on leave from Nankai University, Tian-Jin PRC.

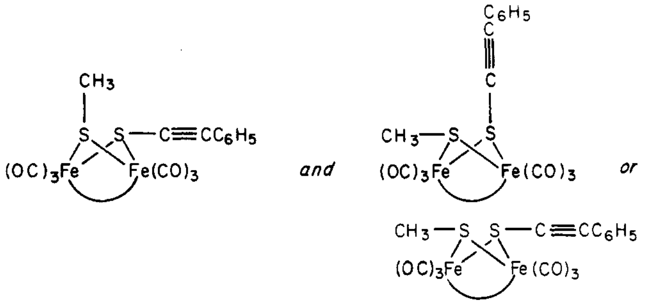
0276-7333/83/2302-0776$01.50/0

ganolithium reagents to give green THF solutions of sulfur-centered anionic complexes (eq 1).[2,3] In further de-



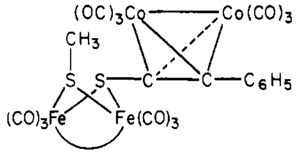
(1)

velopment of this chemistry, we investigated the action of $PhC\equiv CLi$ on $(\mu\text{-}S_2)Fe_2(CO)_6$ (in THF at -78 °C under nitrogen, 30-min reaction time). The resulting green solution was treated with an excess of iodomethane (1 h at -78 °C, 1 h at room temperature) to give a red solution. Removal of solvent followed by column chromatography (silicic acid/pentane) gave red crystals of $(\mu\text{-}CH_3S)(\mu\text{-}C_6H_5C\equiv CS)Fe_2(CO)_6$, mp 80–100 °C dec, as a 1.3:1 mixture of isomers, 1, as indicated by the ^1H NMR spectrum,[4]



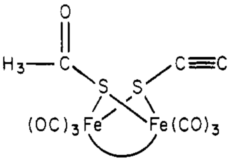
1

in 85% yield. The ^{13}C NMR spectrum confirmed the presence of two isomers and showed that a $C_6H_5C\equiv C$ substituent was present.[4] In another experiment, the major isomer, mp 104–105 °C, was isolated and converted to the $Co_2(CO)_6$ complex 2, mp 124–125 °C, by reaction with an equimolar amount of $Co_2(CO)_8$ in Et_2O. A similar reaction



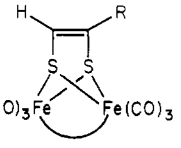
2

of the green solution from the $PhC\equiv CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction with iodoethane gave the ethyl analogue of 1 which also was converted to the $Co_2(CO)_6$ complex analogous to 2. Treatment of the $PhC\equiv CLi/(\mu\text{-}S_2)Fe_2(CO)_6$-derived reagent in similar manner with acetyl chloride gave the novel thioester 3, mp 74–75 °C dec, in 92% yield. Apparently only one isomer was present.[5]



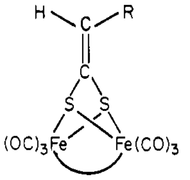
3

Protonation of the $PhC\equiv CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture, with CF_3CO_2H did not give $(\mu\text{-}HS)(\mu\text{-}PhC\equiv CS)Fe_2(CO)_6$, rather the product, obtained in 87% yield, was a dithiolene complex, **4a**.[6] This was found to be a



4a, R = Ph
b, R = SiMe$_3$
c, R = H

general reaction, dithiolene complexes of type 4 being formed in the protonation of the reaction mixtures obtained from $RC\equiv CLi$ (R = alkyl, $CMe=CH_2$) and $HC\equiv CMgBr$ and $(\mu\text{-}S_2)Fe_2(CO)_6$.[7] In contrast, reaction of $LiC\equiv CCO_2Me$ with $(\mu\text{-}S_2)Fe_2(CO)_6$ followed by protonation gave a product with a one-carbon bridge between the sulfur atoms, **5a**, in 51% yield. Both types of products

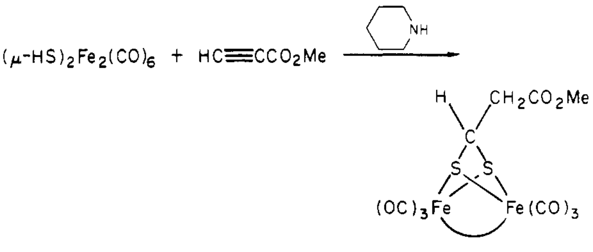


5a, R = CO$_2$Me
b, R = SiMe$_3$

4b (45%) and **5b** (29%) were obtained when the $Me_3SiC\equiv CLi/(\mu\text{-}S_2)Fe_2(CO)_6$ reaction mixture was treated with trifluoroacetic acid.

The assigned structures of complexes 4 and 5 are based in the main on their ^{13}C NMR spectra (Table I). As may be seen, the shieldings of the vinyl carbon atoms not bearing a proton do not vary greatly. The shieldings of the vinylic carbon atoms which do bear a hydrogen atom fall in the region δ_C 133–151 with two exceptions, the last two complexes in Table I, whose $HC=$ signals are found outside this range at higher field.

The formation of bridged products of types 4 and 5 was rationalized in terms of chemistry similar to the base-catalyzed addition of $(\mu\text{-}HS)_2Fe_2(CO)_6$ to α,β-unsaturated olefinic and acetylenic systems,[8] e.g., eq 2. Thus the



(2)

---

[2] Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508.

[3] Grignard reagents, RMgBr, react similarly to give $(\mu\text{-}BrMgS)(\mu\text{-}RS)Fe_2(CO)_6$ in quantitative yield: Song, L.-C., unpublished work.

[4] ^1H NMR (CD_2Cl_2): δ 1.63 (s, CH_3, axial), 2.15 (s, CH_3, equatorial), 7.38 (m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ_C 8.72 (q, J = 141 Hz, CH_3), 19.6 (q, J = 141 Hz, CH_3), 82.2, 84.3, 88.1, 88.9 (all s, alkynyl C), 122.2 (t, J = 8 Hz, ipso phenyl C), 128.3 (d, J = 162 Hz), 129.0 (d, J = 163 Hz), 132.0 (d, J = 161 Hz) (phenyl C), 207.8, 208.7 (s, FeCO).

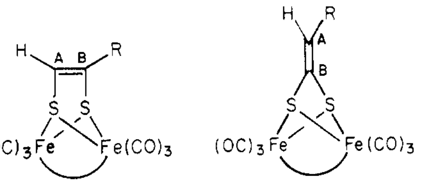
[5] ^1H NMR (CD_2Cl_2): δ 2.40 (s, CH_3), 7.34 (s, C_6H_5). ^{13}C NMR ($CDCl_3$): δ_C 35.5 (q, J = 131 Hz, CH_3), 84.0, 89.4 (s, $C\equiv C$), 122.1 (s, ipso phenyl C), 128.3 (d, J = 156 Hz), 129.1 (d, J = 154 Hz), 132.0 (d, J = 162 Hz) (phenyl C), 198.9 (s, ester $C=O$), 207.5 (s, FeCO).

[6] **4a** is a known compound: Bird, C. W.; Hollins, E. M. *J. Organomet. Chem.* **1965**, *4*, 245. Our product was identical in all respects with theirs.

[7] **4c** was reported earlier: Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 4604. The melting point of our product, 55–56 °C, was in agreement with that reported, 54–55 °C.

[8] Seyferth, D.; Womack, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6839.

Table I. ^{13}C NMR Spectra of



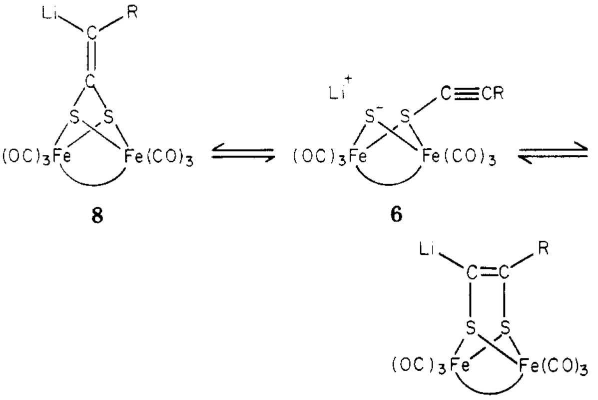
type I

type II

R	type	δ	
		carbon A	carbon B
H^b	I	146.3 (d, J = 190 Hz)	
CH_3	I	134.2 (d, J = 183 Hz)	159.5
n-C_4H_9	I	133.4 (d, J = 183 Hz)	164.4
n-C_5H_{11}	I	133.4 (d, J = 183 Hz)	164.4
C_6H_5	I	134.4 (d, J = 183 Hz)	161.7
$CH_3C{=}CH_2{}^c$	I	135.7 (d, J = 183 Hz)	162.8
$(CH_3)_3Si$	I	150.8 (d, J = 184 Hz)	159.7
$(CH_3)_3Si$	II	115.4 (d, J = 142 Hz)	157.9
$CO_2CH_3{}^c$	II	108.4 (d, J = 169 Hz)	165.3

[a] Solvent used was $CDCl_3$ unless stated otherwise. [b] Solvent was CD_3CN. [c] Solvent was CD_2Cl_2.

"open" S-centered anion **6** formed by S–S bond cleavage in $(\mu$-$S_2)Fe_2(CO)_6$ by the action RC≡CLi must be in equilibrium with the "closed" organolithium reagents **7** and/or **8**, with the latter being observed when R can effectively stabilize an adjacent carbanionic center. The diffrence in the types of products observed in alkylation and protonation reactions suggested that examination of other electrophilic substrates might be of interest. Further studies showed that group 4B halides (Me_3SiCl, Ph_3GeBr, Me_3SnCl, Ph_3SnCl, Ph_3PbBr) reacted with RC≡CLi/$(\mu$-$S_2)Fe_2(CO)_6$ reaction mixtures to give bridged products **9** and **10**. The reaction in which methylmercuric chloride was the electrophile used was of particular interest in that both "open" and "closed" products were obtained (eq 3). When aldehydes were the electrophiles used, only "closed" products, **13**, were obtained, as might have been expected.

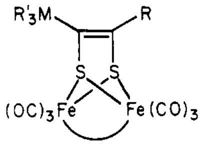


8

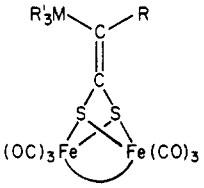
6

7

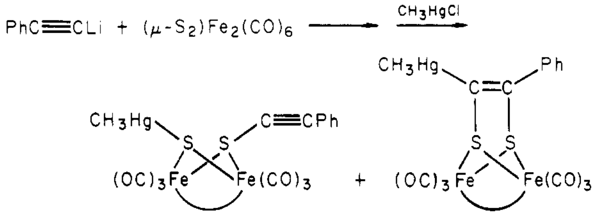
In support of the postulated equilibrium, we have found that a lithium reagent which on reaction with iodomethane gives an "open" product may be generated from a "closed" stannyl-substituted dithiolene complex by the transmetalation reaction[9] (eq 4).



9a, R = H, M = Si, R' = CH_3
b, R = Ph, M = Si, R' = CH_3
c, R = n-C_4H_9, M = Si, R' = CH_3
d, R = Ph, M = Ge, R' = Ph
e, R = CH_3, M = Sn, R' = CH_3
f, R = Ph, M = Sn, R' = CH_3
g, R = Ph, M = Sn, R' = Ph
h, R = n-C_4H_9, M = Sn, R' = CH_3
i, R = Ph, M = Pb, R' = Ph



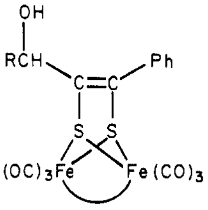
10a, R = CO_2Me, M = Si, R' = CH_3
b, R = CO_2Me, M = Sn, R' = CH_3



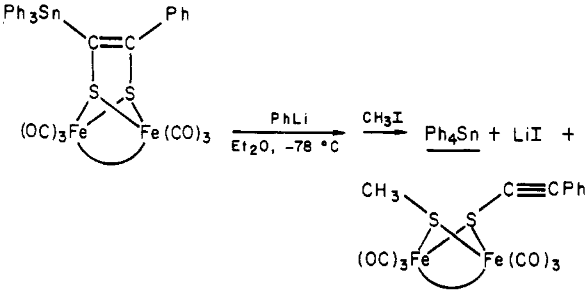
(3)

11 (52%)

12 (16%)



13a, R = Ph
b, R = CH_3
c, R = $(CH_3)_3C$



(4)

59%

At the present stage of our investigation we do not know what the relative amounts of **6**, **7**, and **8** are that are present for any given R under the reaction conditions. The concentration of **7** or **8** need not be large in order to obtain high yields of "closed" product. In some cases it might be that the rate of reaction of the electrophile used is very much greater with **7** or **8** than with **6**. In others it may be that the reaction of the electrophile with **6** is reversible but with **7** or **8** it is not.

The chemistry described in this communication allows

---

(9) The transmetalation reaction is applicable to good advantage to the preparation of vinylic lithium reagents: Seyferth, D.; Weiner, M. A.; Vaughan, L. G.; Raab, G.; Welch, D. E.; Cohen, H. M.; Alleston, D. L. *Bull. Soc. Chim. Fr.* **1963**, 1364.

facile dithio ligand construction on the $Fe_2(CO)_6$ framework. It has potential for useful application in the synthesis of novel organosulfur compounds since methods are known for the release of organosulfur ligands from their $Fe_2(CO)_6$ complexes.[10]

We are continuing synthetic studies on the general theme of this communication and also are carrying out further experiments designed to probe the $7 \rightleftharpoons 6 \rightleftharpoons 8$ equilibrium. All products were characterized spectroscopically (IR, ^1H, often ^{13}C NMR, and EI-MS) and by C/H analysis (±0.3%).

Acknowledgment. This work was supported in part by the National Science Foundation.

Registry No. 1 (isomer 1), 85552-96-1; 1 (isomer 2), 85611-51-4; 1 (isomer 3), 85611-52-4; 1 ethyl analogue, 85551-98-3; **2**, 85552-97-2; **2** ethyl analogue, 85552-99-4; **3**, 85553-00-0; **4a**, 85553-01-1; **4b**, 85553-02-2; **4c**, 12079-70-8; **4** (R = CH_3), 8553-20-4; **4** (R = n-C_4H_9), 85553-21-5; **4** (R = n-C_5H_{11}), 85553-22-6; **4** (R = $C(CH_3){=}CH_2$), 85553-23-7; **5a**, 85553-03-3; **5b**, 85553-04-4; **9b**, 85553-05-5; **9c**, 85553-06-6; **9d**, 85553-07-7; **9e**, 85553-08-8; **9f**, 85553-09-9; **9g**, 85553-10-2; **9h**, 85553-11-3; **9i**, 85553-12-4; **10a**, 85553-13-5; **10b**, 85553-14-6; 11, 85553-15-7; 12, 85553-16-8; **13a**, 85553-17-9; **13b**, 85553-18-0; **13c**, 85553-19-1; $(M{-}S_2)Fe_2(CO)_6$, 14243-23-3; Me_3SiCl, 75-77-4; Ph_3GeBr, 3005-32-1; Me_3SnCl, 1066-45-1; Ph_3SnCl, 639-58-7; Ph_3PbBr, 894-06-4; $PhC{\equiv}CLi$, 4440-01-1; CF_3CO_2H, 76-05-1; $LiC{\equiv}CCO_2Me$, 72036-29-4; $Me_3SiC{\equiv}CLi$, 54655-07-1; CH_3HgCl, 115-09-3; acetyl chloride, 75-36-5; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; 2,2-dimethylpropanal, 630-19-3.

---

(10) Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

A Novel Regiospecific Alkylation of the Aromatic Nucleus via Lithium Trialkylborohydrides and Aryl Sulfones[1]

Herbert C. Brown,* Suk-Choong Kim,[2] and Sundaram Krishnamurthy[3]

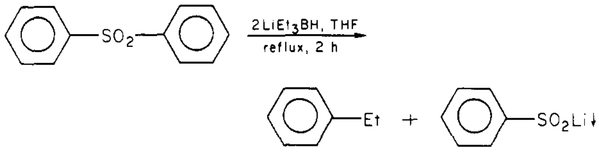
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received January 24, 1983

Summary: Lithium triethylborohydride readily reacts with diphenyl sulfone in refluxing tetrahydrofuran (THF) to provide the unexpected alkylation product ethylbenzene in good yield (75–92%). The reaction appears to proceed satisfactorily for the introduction of other primary alkyl groups, such as n-butyl and isobutyl, and no rearrangement of the alkyl group is observed. Further, the alkylation is highly regiospecific—the alkyl group introduced enters at the original position occupied by the sulfone substituent. The new alkylation reaction provides a convenient means for the specific introduction of the alkyl group into the aromatic nucleus.

Both aromatic and aliphatic sulfones are generally inert to metal hydride and complex metal hydride reducing agents.[4,5] During the course of our exploratory study of the reducing characteristics of lithium triethylborohydride[6] with organic compounds containing representative functional groups, it was observed that di-n-butyl sulfone, a dialkyl sulfone, was completely inert to this reagent under standard reaction conditions (0 °C, THF, $LiEt_3BH$/substrate = 4/1).[7] Surprisingly, diphenyl sulfone, a diaryl sulfone, reacted at a slow but significant rate (0.93 equiv of $LiEt_3BH$ consumption in 24 h). The reaction underwent a series of color changes accompanied by the formation of a white precipitate characterized as lithium benzenesulfinate. GLC analysis of the reaction mixture soon revealed the complete absence of the expected reduction products—diphenyl sulfoxide and diphenyl sulfide; instead, there was present ethylbenzene. Interestingly, we are achieving alkylation of the aromatic nucleus instead of reducing the sulfone functionality! Alkali-metal trialkylborohydrides are exceptionally powerful hydride reducing agents for organic functional groups.[5,7,8] However, the present reaction appears to involve the facile transfer of an alkyl group from the triethylborohydride moiety rather than the usual hydride transfer. Consequently, we became interested in exploring this reaction in detail.

In refluxing THF, lithium triethylborohydride (2 equiv) reacted rapidly with diphenyl sulfone. GLC analysis of the reaction mixture at the end of 30 min indicated the formation of ethylbenzene in 71% yield, a value which did not change appreciably (3 h, 75%) with longer reaction times.[9] The white precipitate, which readily dissolves in water, was isolated (93% yield) and characterized as lithium benzenesulfinate[10,11] (eq 1). However, the residual hydride analysis by hydrolyzing a known aliquot of the reaction mixture indicated that only 0.5 equiv of hydride ($LiEt_3BH$) had been consumed. Attempts to establish the stoichiometry by various other methods were not successful.[12] Possibly a reactive hydride species is being generated during the course of this reaction.



(1)

The alkylation is highly regiospecific. The reaction of lithium triethylborohydride with di-p-tolyl sulfone yields exclusively p-ethyltoluene completely free from the corresponding ortho and meta isomers (GLC, ^1H NMR, and IR) (eq 2).

---

(1) Presented in part at the IMEBORON IV, Salt Lake City and Snowbird, UT, July 1979; Abstract No. 19.

(2) Graduate research assistant on Grant No. DA-ARO-D-31-124-73-G148, supported by the U.S. Army Research Office (Durham). Present address: Hahn Jung Chemicals, Inc., Incheon, Korea.

(3) Present address: Research Laboratories, Eastman Kodak Company, Rochester, NY 14650.

(4) Gaylord, N. G. "Reductions with Complex Metal Hydrides"; Interscience: New York, 1958, pp 845–851.

(5) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567–607.

(6) Super-Hydride (lithium triethylborohydride) is now commercially available as 1 M solution in THF from Aldrich Chemical Co., Inc., Milwaukee, WI. L-Selectride is also available from Aldrich Chemical Co., Inc.

(7) Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1–12.

(8) (a) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55–60. (b) Brown, H. C.; Krishnamurthy, S. *Ibid.* **1979**, *12*, 3–11.

(9) GLC analyses were performed on a Varian Model 1200 gas chroamtograph (FID) using either 5% SE-30 or 5% Carbowax 20M column, 6 ft × 0.125 in. employing an internal standard.

(10) Lithium benzene sulfinate, mp >200 °C, exhibited an almost indentical pattern in IR absorption with that of sodium benzene sulfinate.

(11) Lindberg, B. J. *Acta Chem. Scand.* **1967**, *21*, 2215–2234.

(12) Reaction of 1 equiv of diphenyl sulfone with 0.5 equiv of $LiEt_3BH$ in refluxing THF (2 h) indicating the recovery of 48% sulfone and the formation of 34% ethylbenzene roughly indicating that the reaction requires 1 equiv of the reagent.

0276-7333/83/2302-0779$01.50/0