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; $(\mu\text{-}S_2)Fe_2(CO)_6$, 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.

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[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]

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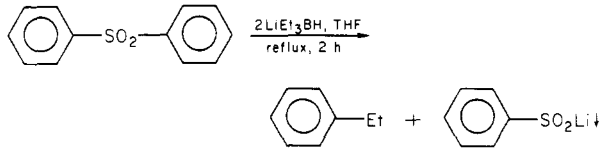
Received January 24, 1983

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).

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[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.

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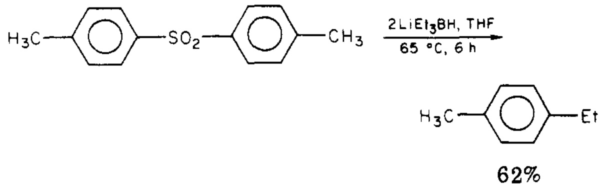
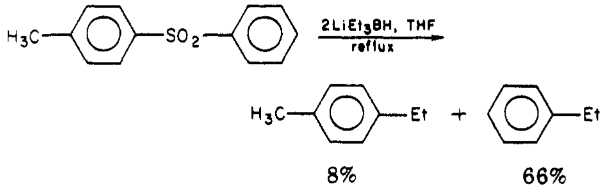


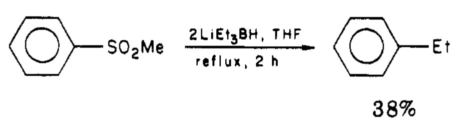
(2)

Electron-releasing substituents appear to retard the rate of alkylation, as evidenced by the diminished reactivity of di-*p*-tolyl sulfone. The sensitivity of the reaction to the nature of substituents is also reflected in the ratio of alkylation products realized with the unsymmetrical diaryl sulfone, phenyl *p*-tolyl sulfone (eq 3).



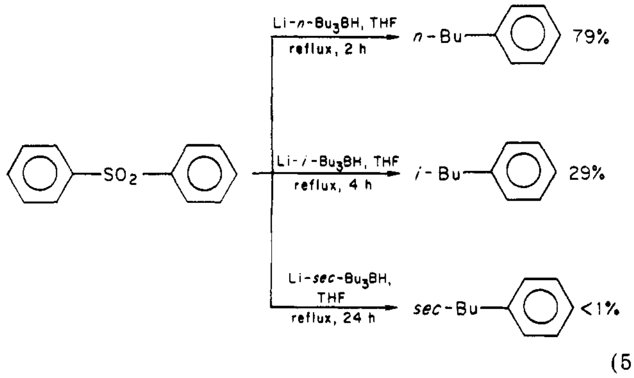
(3)

Alkyl aryl sulfones react more sluggishly, giving lower yields of the desired products (eq 4).



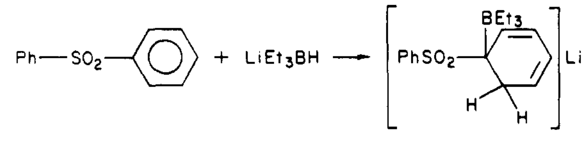
(4)

The reaction appears to be general and applicable to other less hindered trialkylborohydrides bearing primary alkyl substituents (*n*-butyl and isobutyl). Even more important, the alkylation proceeds without detectable rearrangement of the carbon skeleton of the alkyl group, a valuable characteristic. The highly hindered reagent, lithium tri-*sec*-butylborohydride (L-Selectride[6]), failed to give any significant amount of *sec*-butylbenzene (eq 5).

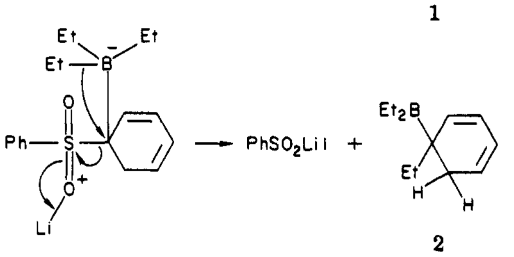


(5)

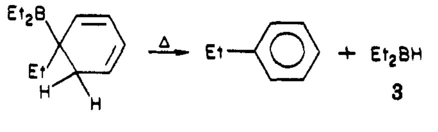
The reaction appears to involve the following stages, consistent with the above experimental observations (eq 6–8).



1 (6)

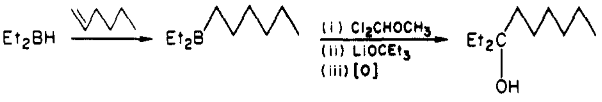


2 (7)



3 (8)

Further, it is possible that the diethylborane (3) thus formed hydroborates the intermediates 1 or 2, thereby lowering the yield of the final product, ethylbenzene. Consequently, trapping the diethylborane produced should enhance the yield of ethylbenzene. Indeed, when the reaction of diphenyl sulfone with lithium triethylborohydride was carried out in the presence of excess 1-octene, the yield of ethylbenzene was increased to 92%; oxidation (NaOH–H_2O_2) of the reaction mixture revealed the presence of an equivalent amount of 1-octanol (>99% isomeric purity). Further evidence for the intermediacy of diethylborane was obtained by the conversion of the diethyl alkylborane produced to the corresponding tertiary alcohol by the DCME reaction[13] (eq 9).



(9)

In conclusion, the reaction of aryl sulfones with unhindered lithium trialkylborohydride provides the first example of trialkylborohydride mediated carbon–carbon bond formation in aromatic systems. The alkylation proceeds regiospecifically without any rearrangement of the alkyl group.

Registry No. Diphenyl sulfone, 127-63-9; lithium triethylborohydride, 22560-16-3; ethylbenzene, 100-41-4; lithium benzenesulfinate, 16883-74-2; di-*p*-tolyl sulfone, 599-66-6; *p*-ethyltoluene, 622-96-8; phenyl p-tolyl sulfone, 640-57-3; methyl phenyl sulfone, 3112-85-4; lithium tributylborohydride, 67335-72-2; lithium triisobutylborohydride, 63717-73-7; butylbenzene, 104-51-8; isobutylbenzene, 538-93-2.

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(13) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* 1973, *38*, 2422–2424.

Homogeneous Catalysis of Hydrogen–Deuterium Exchange Reactions Involving Cyclopentadienyl Complexes of Palladium and Platinum

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Summary: Some cyclopentadienyl complexes of palladium and platinum, when treated with tertiary phosphines, are shown to promote and undergo H–D exchange reactions with a range of deuterated solvents. Two or more routes are involved in the exchange process, one of which depends on base catalysis via zerovalent metal complexes generated during the course of the reactions.

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