the paucity of carbon nucleophiles with pK_a values sufficiently low (pK_a < 17) for participation in the Mitsunobu reaction. The failure of the phenylsulfone (pK_a ~25)[16] in entry 11 to undergo cyclization is relevant in this regard.

General Procedure. Diethyl azodicarboxylate (0.5 mmol) is added dropwise to a stirring solution of triphenylphosphine (0.5 mmol) in anhydrous benzene (5 mL) at room temperature under an inert atmosphere and stirred for 15 min. To the resultant deep red, homogeneous mixture is added a solution of γ-nitroalkanol (0.33 mmol) in benzene (3 mL). Following complete consumption of the reactant (~1 h), the solvent is removed in vacuo and the residue is purified by silica gel chromatography to afford the corresponding α-nitrocyclopropanes in 75–98% yield (Table I).

Acknowledgment. Supported by grants from the USPHS NIH (GM 31278) and the Robert A. Welch Foundation (I-782). Funds for the purchase of a mass spectrometer were provided by NIH (S10 RR05922).

Supplementary Material Available: Spectral and physical data for all α-nitrocyclopropanes in Table I (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963.

Synthesis of Hexalithiobenzene

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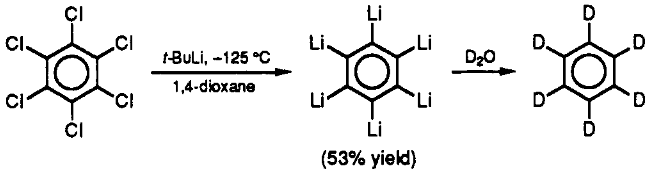
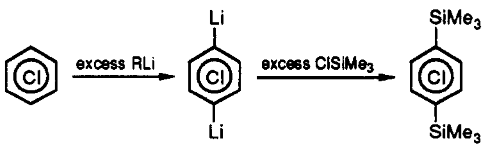
Summary: A new synthesis for hexalithiobenzene starting with hexachlorobenzene is reported.

Recently we reported a new method for preparing polylithium organic compounds by lithium–halogen exchange which appears to be a new general synthesis for such compounds.[1] Previously, in 1978, an experiment in our laboratory established that hexalithiobenzene was a room-temperature stable compound.[2] However low yields (<1%) prevented purification and full characterization.

We now report a convenient laboratory synthesis for hexalithiobenzene in 53% yield.



Previously Henry Gilman and co-workers attempted to prepare hexalithiobenzene using butyllithium and hexachlorobenzene, resulting in only disubstitution.[3] "The formation of pentachlorophenyllithium in the reaction of hexachlorobenzene with n-butyllithium at low temperature was mentioned above. We attempted to achieve polylithiation by treatment of hexachlorobenzene with several equivalents of n-butyllithium or t-butyllithium. No matter how large was the excess of organolithium reagent, after derivatization with trimelthylchlorosilane only 1,4-bis(trimethylsilyl)-2,3,5,6-tetrachlorobenzene, XIV, was obtained (in over 50% yield)."



XIV

To successfully accomplish the hexalithiobenzene synthesis, one must seek conditions which favor lithium–halogen exchange over the competing coupling reactions and in addition create conditions to minimize cross-linking of partially lithium-substituted chlorobenzenes (which are also stable at room temperature).

Thus we have chosen to use *tert*-butyllithium since the bulky reagents are somewhat unfavorable for coupling reactions. The reaction between hexachlorobenzene and *tert*-butyllithium was conducted at the lowest temperature (to minimize vibrational energy leading to lithium–chlorine elimination) compatible with a significant reaction rate (usually less than −105 °C). The *tert*-butyllithium is kept highly concentrated (and in excess) in solution in a stirred round-bottom flask while hexachlorobenzene is slowly added via a solid addition funnel. Thus the halocarbon starting material is reacted very rapidly with the *tert*-butyllithium reagent before cross-linking or coupling reactions occur.

One gram of C_6Cl_6 (3.5 mmol) was slowly added to a slurry consisting of 40 mL of pentane, 49.6 mL (84 mmol) of 1.7 M *tert*-butyllithium, and 28.7 mL (337 mmol) of 1,4-dioxane, maintained at −125 °C. The reaction mixture was allowed to stir for 24 h. While other solvents are also useful, 1,4-dioxane has proven to be the most effective solvent for halobenzene reactions studied to date with respect to maximizing the lithium–halogen exchange reaction.

After 24 h (the optimum reaction time) the products were derivatized by addition of excess D_2O and the reaction temperature was slowly raised to room temperature. The deuteration products were analyzed by GC/MS. C_6D_6 was identified by ^{13}C and ^{1}H NMR and by HRMS ($C_6D_6^+$ m/z, calcd 84.084611, found 84.086183). Other products are polymeric species from cross-linking and coupling reactions.

Mass spectral data were obtained directly on the new hexalithiobenzene compound using laser desorption ionization/Fourier transform ion cyclotron resonance (LDI/FTICR) with a Nicolet Analytical Instruments FTMS 2000 spectrometer. Due to significant space charge distortion and high pressures (10^{-5} to 10^{-7} Torr) within the system, accurate mass detection was not possible.[4] Intense mo-

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(1) Baran, J. R., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 9003.

(2) Shimp, L. A.; Chung, C.; Lagow, R. J. *Inorg. Chim. Acta* **1978**, *29*, 77.

(3) Haiduc, I.; Gilman, H. *Revue Roumaine de Chimie* **1971**, *16*(6), 907.

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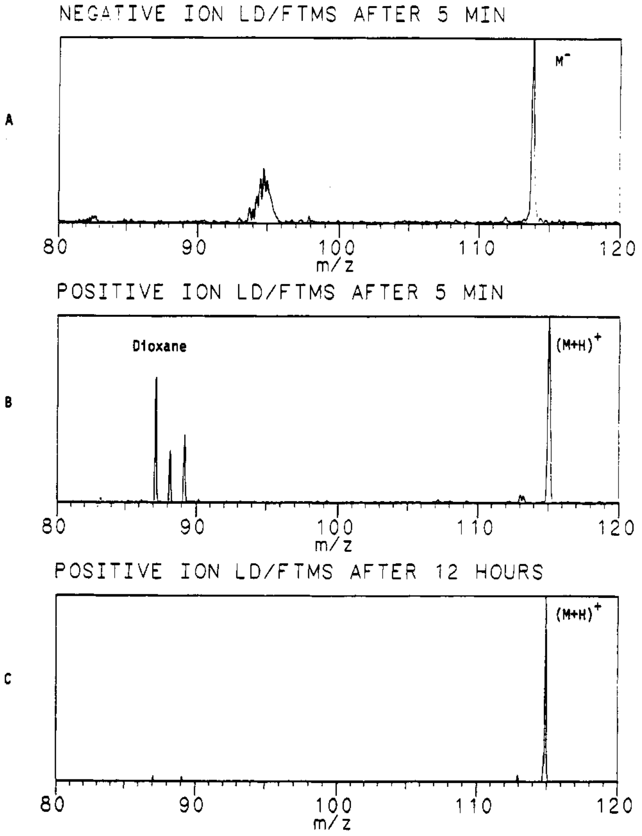
NEGATIVE ION LD/FTMS AFTER 5 MIN

POSITIVE ION LD/FTMS AFTER 5 MIN

POSITIVE ION LD/FTMS AFTER 12 HOURS

Figure 1.

lecular ion peaks for C_6Li_6 were obtained in both negative ion and positive ion modes. In the negative ion mode, *m/z* 114 $(C_6Li_6)^-$ dominated the spectrum (Figure 1a). In positive ion [chemical ionization (CI)] mode, *m/z* 115 $[(C_6Li_6+H)^+]$ dominated the spectrum (Figure 1b). After 12 h in vacuum, the 1,4-dioxane had been completely removed and the prominent mass in the positive ion spectrum was still *m/z* 115 (Figure 1c). These are the expected peaks for the compound in the respective ionization modes. The low resolution mass spectra do not exhibit the expected Li isotope patterns. Space charge conditions that exist in the high pressure regime used for the experiment are known to have a strong tendency under the space in LDI experiments for the neighboring peaks to colesce.[4] It appeared that the excess *tert*-butyllithium was also pumped off in the vacuum over time, leaving a gray-white material which was seen through a viewing port and is probably hexalithiobenzene. The white hexalithiobenzene reacted violently when exposed to air, yielding black decomposition products.

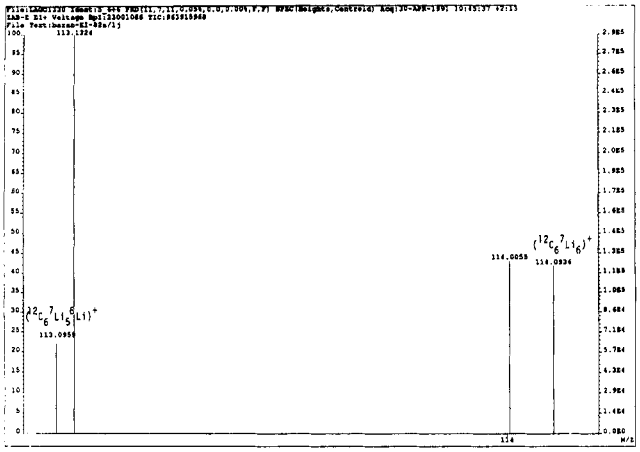

Figure 2. High resolution mass spectrum of C_6Li_6. The peak at 113.1324 comes from the coupling reaction of *tert*-butyl chloride and *tert*-butyllithium. The peak at 114.0055 is a fluorocarbon calibration peak.

High resolution spectra (Figure 2) were also run on a VG Model ZAB2-E high resolution mass spectrometer using electron impact. Peaks for $(C_6{}^7Li_6)^+$ and $(C_6{}^7Li_5{}^6Li)^+$ were observed with the following: ratios $(^{12}C_6{}^7Li_6)^+/(^{12}C_6{}^7Li_5{}^6Li)^+$ calcd 2.0868, obsd 2.047; masses $^{12}C_6{}^7Li_6$ calcd 114.093602, obsd 114.096027; $^{12}C_6{}^7Li_5{}^6Li$ calcd 113.095902, obsd 113.095146.

Hexalithiobenzene should be an exciting new reagent and both its structural chemistry and reaction chemistry should be extraordinarily interesting. With advance notice of our synthesis, Schaefer and Xie have forecast an extremely interesting planar structure for hexalithiobenzene gas-phase monomers with six lithium bridging the carbons, producing a star-like structure.[5]

One of the most surprising features of the new compound hexalithiobenzene is its relatively high vapor pressure. A conventional inlet was used to obtain the high resolution mass spectrum. This high vapor pressure may be indicative of the π system dominating the structure such that polymers, such as dimers, tetramers, and hexamers, may not be major structural features, especially in the gas phase. Perhaps the crystal structure, which is being sought,[6] will be similar to that of benzene rather than polymeric as are most organolithium compounds. If this is true perhaps the calculated molecular structure of Schaefer and Xie[5] will be seen, even in the crystal structure.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9106482) and the Robert A. Welch Foundation (F-700) for support of this work.

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(4) Francl, T. J.; Sherman, M. G.; Hunter, R. L.; Locke, M. J.; Bowers, W. D.; McIver, R. T., Jr. *Int. J. Mass Spectrum Ion Proc.* **1983**, *54*, 189.

(5) Schaefer, H. F., III; Xie, Y. *Chem. Phys. Lett.* **1991**, *179*, 563.

(6) In collaboration with the George Sheldrick group, Göttingen.

N-(*tert*-Butoxycarbonyl)-2-(*tert*-butyldimethylsiloxy)pyrrole: A Promising Compound for Synthesis of Chiral Nonracemic Hydroxylated Pyrrolidine Derivatives

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Summary: *N*-*t*-Boc-2-(*tert*-butyldimethylsiloxy)pyrrole has been synthesized from pyrrole and used to prepare enantiomerically pure pyrrolinones **5**, **6**, **15**, and **16** and polyhydroxylated pyrrolidinones of type **11** and **12**.

The discovery that carbohydrates in which the ring

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