high level of antineoplastic activity (PS system). Studies concerned with uncovering such constituents and their mode of action will be continued. Presently, bryostatin 1 is being evaluated by using a selection of the U.S. National Cancer Institute's experimental solid tumor systems.

Acknowledgment. We are pleased to acknowledge very necessary financial support provided by Contract N01-CM-97262 with the Division of Cancer Treatment, NCI, National Institutes of Health, DHW, Grant No. CA16049-01 through 07 awarded by the National Cancer Institute, DHW, Mary Dell Pritzlaff, the Olin Foundation (Spencer T. and Ann W.), the Fannie E. Rippel Foundation, Eleanor W. Libby, the David Ware Waddell Foundation, Pearl Spear, and Robert B. Dalton. For other very helpful assistance we are pleased to thank Drs. J. D. Douros, J. J. Einck, D. Gust, J. L. Hartwell, R. R. Inners, L. W. Knapp, P. Lohavanijaya, M. I. Suffness, J. M. Schmidt, and J. Wtischel, Jr., M. A. Carlson, B. L. Norfleet, K. M. Welch, the Smithsonian Institution Oceanographic Sorting Center, and the National Science Foundation Regional Facility at the University of South Carolina (CH78-18723). The Cornell chemists gratefully acknowledge support provided by NIH CA24487 (J.C.), and the National Science Foundation (predoctoral fellowship to E.A. and funds for the Cornell Chemistry Computing Facility).

Registry No. 1, 83314-01-6.

Supplementary Material Available: List of observed and calculated structure factor magnitudes and calculated phase angles (38 pages). Ordering information is given on any current masthead page. For other supplementary information please refer to ref 11 and 16.

1,3-Dilithiopropanes

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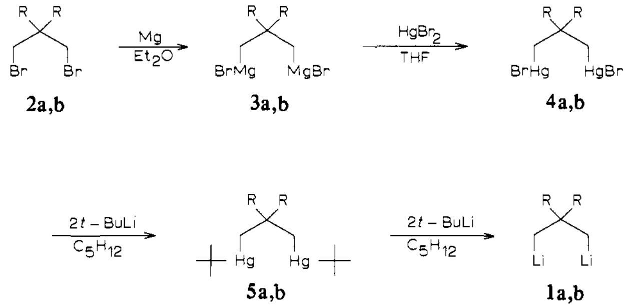
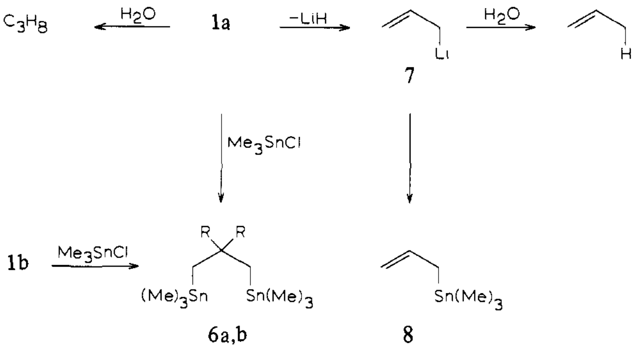
In a classical investigation, West and Rochow[1] established that dilithio derivatives can be prepared from α,ω-dibromoalkanes and lithium metal in ether only if four or more methylene groups separate the two functions. In the reaction of lithium with dibromomethane, only 6% bis(trimethylsilyl)methane was obtained after quenching with trimethylchlorosilane. On the other hand, 1,2-dibromoethane and 1,3-dibromopropane in a similar reaction gave no products indicative of the corresponding dilithio derivatives, although reaction did take place. More recently, Shimp and Lagow came to similar conclusions when performing this reaction with lithium vapor.[2] Likewise, our own attempts to prepare 1,3-dilithiopropane (**1a**, Scheme I) from 1,3-dichloropropane or 1,3-dibromopropane (**2a**) by reaction with lithium metal or *tert*-butyllithium were unsuccessful. Only aromatic,[3] conjugated,[4] and specially functionalized[5] 1,3-dilithium compounds have been described so far. We report here the first synthesis and some properties of the simple aliphatic 1,3-dilithium compound (**1a**) and its 2,2-dimethyl derivative **1b**.

Scheme I[a]



[a] a, R = H; b, R = Me.

Scheme II[a]



[a] a, R = H; b, R = Me.

A new approach to **1** was made possible by our finding[6] that 1,3-bis(bromomagnesio)propane (**3a**)[7] could, under special conditions, be prepared directly and conveniently from **2a**; by reaction of $HgBr_2$ in THF with **3a**, **4a** was obtained.[6] Addition of 2 equiv of *tert*-butyllithium to **4a** in pentane at 0 °C gave **5a** in a rapid reaction, after which precipitated LiBr was removed by filtration. The filtrate was a solution of pure **5a**[8] in pentane, but on attempts to isolate **5a**, it disproportionated to di-*tert*-butylmercury and a nearly insoluble (oligomeric?) material, presumably $(CH_2CH_2CH_2Hg)_n$. Addition of 2 further equiv of *tert*-butyllithium to the solution of **5a** lead to a slow reaction (several hours at room temperature) and the precipitation of a white powder that contained **1a**, together with **7** and LiH. **1a** was characterized by hydrolysis to propane and reaction with trimethylchlorostannane to **6a**;[6] in these reactions, **7** was converted to propene and **8**, respectively (Scheme II). Presumably, the preparation of **1a** can also be achieved by treating **4a** directly with 4 equiv of *tert*-butyllithium; so far, we did not explore this variant because it would furnish a precipitate that, besides **1a**, **7**, and LiH, also contains large amounts of LiBr.

We had anticipated that **1a** would be unstable and decompose spontaneously to allyllithium (**7**) by elimination of LiH. The analogous slow elimination of HMgBr had been observed in **3a** at room temperature;[6] a process that is facilitated through activation of the β hydrogen by the *two* carbon-metal bonds.[9] Normally, primary alkyllithium compounds eliminate LiH at a measurable rate only above ca. 100 °C.[10] However, the effectiveness of β-hydrogen activation in **1a** is quite spectacular: at 20 °C the half-life of **1a** is 1 h at the utmost, as estimated by monitoring the amount and ratio of propane and propene after

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(6) (a) Seetz, J. W. F. L.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 1497. (b) Half-life of **3a** in the reaction mixture after its formation from **2a**: $t_{1/2}$ = ca. 40 days at 25 °C.

(7) Costa, L. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 2390.

(8) **5a**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.26 (s, $^3J_{HgH}$ = 107 Hz, 18 H, *t*-Bu), 1.27 (m, 6 H).

(9) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651 and references cited therein.

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hydrolysis. A relatively small ratio of propane:propene (30:70) was found after 5 min, suggesting that besides from **1a**, **7** is also formed by alternative modes of reaction between *tert*-butyllithium and **5a**.[11] Even when the reaction was carried out at -60 °C, **1a** was accompanied by considerable amounts of **7**. In light of these results, it would appear that the synthesis of **1a** from lithium and 1,3-dichloropropane, claimed in the patent literature[12] but supported by little experimental evidence, is highly unlikely.

It could be expected that a 1,3-dilithium compound not containing β hydrogen would be (more) stable. We therefore prepared 1,3-dilithio-2,2-dimethylpropane (**1b**) by an analogous route (Scheme I). Slow addition (2 days) of 1,3-dibromo-2,2-dimethylpropane (**2b**)[13] to magnesium in diethyl ether yielded 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**3b**, 18% yield), practically free from any organometallic impurities and completely stable in solution. Addition of a solution of $HgBr_2$ in THF to the solution of **3b** in THF gave **4b**.[14] When a suspension of **4b** in pentane was treated with 2 equiv of *tert*-butyllithium, a solution of **5b**[15] and a precipitate of LiBr were formed, which were separated by filtration. On addition of 2 more equiv of *tert*-butyllithium to the clear filtrate, **1b** gradually deposited during 1 week at room temperature. After shorter periods of time, unreacted **5b** was still present. Therefore, we conclude that the essential step of this reaction, i.e., the addition of *tert*-butyllithium to **5b** to form an unstable -ate compex, is retarded by extreme steric hindrance in the adduct. **1b** was collected in pure form by decanting and washing with pentane as a white powder (70–80% yield); it was characterized by its NMR spectrum (vide infra) and by reaction with trimethylchlorostannane to give **6b**[16] as the sole product (Scheme II).

It turned out that **1b** was indeed a rather stable compound. Not only did it not show signs of decomposition in the solid state, but also it was soluble in diethyl ether. Somewhat to our surprise, these solutions were found (NMR) to be fairly stable at room temperature for several weeks ($t_{1/2}$ = 70 days), a finding quite exceptional for a primary alkyllithium.[17] The ^{1}H NMR spectrum in Et_2O-d_{10} was in agreement with the proposed structure: at room temperature, broad ^{1}H resonances were found at δ -0.74 (s, 4 H, CH_2) and 1.15 (s, 6 H, CH_3). As the solution cooled, complicated, reversible dynamic effects were observed in the ^{1}H NMR spectrum (cf. ref 6 for similar phenomena with **3a**); they are presently under investigation.

Registry No. 1a, 13439-59-3; **1b**, 83528-95-4; **2a**, 109-64-8; **2b**, 5434-27-5; **3a**, 62934-64-9; **3b**, 83528-98-7; **4a**, 82773-71-5; **4b**, 83528-96-5; **5a**, 83542-61-4; **5b**, 83542-62-5; **6a**, 35434-81-2; **6b**, 83528-97-6; **7**, 3052-45-7; **8**, 762-73-2; Me_3SnCl, 1066-45-1; *t*-BuLi, 594-19-4; $HgBr_2$, 7789-47-1.

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(11) We thank a referee for valuable comments on this possibility.

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(14) **4b**: mp 171 °C dec ($CHCl_3$); ^{1}H NMR (250 MHz, Me_2SO-d_6) δ 1.15 (s, $^4J_{HgH}$ = 18.1 Hz, 6 H, CH_3), 2.07 (s, $^2J_{HgH}$ = 211.2 Hz, 4 H, CH_2); ^{13}C NMR (62.89 MHz, Me_2SO-d_6) δ 56.5 (t, $^1J_{CH}$ = 132.0 Hz, $^1J_{HgC}$ = 1656.3 Hz, $^3J_{HgC}$ = 148.9 Hz, CH_2), 38.6 (s, $^2J_{HgC}$ = 61.6 Hz, quaternary C), 36.5 (q, $^1J_{CH}$ = 123.3 Hz, $^3J_{HgC}$ = 163.6 Hz, CH_3). Anal. $C_5H_{10}Br_2Hg_2$: C, H, Hg.

(15) **5b**: colorless liquid obtained by GLC; slowly disproportionates under polymerization; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.04 (s, 6 H, C(2)–CH_3), 1.24 (s, 4 H, CH_2), 1.29 (s, $^3J_{HgH}$ = 106 Hz, 18 H, *t*-Bu); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 30.87 (q of sept, $^1J_{CH}$ = 124.5 Hz, $^3J_{CH}$ = 6.1 Hz, $^2J_{HgC}$ = 20.1 Hz, CH_3 of *t*-Bu), 39.6 (s, quaternary C of *t*-Bu), 40.0 (q, $^1J_{CH}$ = 119.5 Hz, $^3J_{HgC}$ = 62.9 Hz, C(2)–CH_3), 60.9 (s, C(2)), 65.6 (t, $^1J_{CH}$ = 124.5 Hz, $^1J_{HgC}$ = 540.8 Hz, $^3J_{HgC}$ = 74.2 Hz, CH_2).

(16) **6b**: colorless liquid obtained by GLC; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, $^2J_{SnH}$ = 49 and 51.5 Hz, 18 H, Sn–CH_3), 1.04 (s, 6 H, C–CH_3), 1.10 (s, $^2J_{SnH}$ = 53.5 Hz, 4 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ -8.2 (q, $^1J_{CH}$ = 128.2 Hz, $^1J_{SnC}$ = 301.5 and 316.2 Hz, Sn–CH_3), 33.5 (t, $^1J_{CH}$ = 124.5 Hz, $^1J_{SnC}$ = 349.2 and 366.2 Hz, $^3J_{SnC}$ = 41.5 Hz, CH_2), 34.6 (q, $^1J_{CH}$ = 124.5 Hz, $^3J_{SnC}$ = 31.7 Hz, (C–CH_3), 35.9 (s, $^3J_{SnC}$ = 20.8 Hz, quaternary C). Anal. $C_{11}H_{28}Sn_2$: C, H, Sn.

(17) **Note Added in Proof**: Prof. P. von R. Schleyer has informed us that ab initio calculations (3-21G) reveal symmetrical double lithium 1,3-bridging to stabilize **1b** by 24.6 kcal mol^{-1} relative to the open extended form, which may explain the unusual stability of **1b** (or an oligomeric cluster derived thereof).

Experimental Observations of Large Interactions of π^* Orbitals through Four Bonds

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Analysis of orbital interactions (OI) in terms of through-space (TS) and through-bond (TB) components has contributed significantly to our understanding of the nature of interactions between remote groups in molecules.[1,2] One expects OITB to diminish with increasing number of intervening σ bonds and that these interactions are of longer range than OITS.[1] However, only two systematic experimental studies of this attenuation have been reported; one on the σ-type lone-pair splittings along a series of diiodopolyacetylenes[3] and the other on the π,π interactions in the series of "norbornylogues".[4,5] From these limited data it appears that OIT-*n*-B are attenuated more slowly with increasing number, *n*, of intervening σ bonds than expected on the basis of theoretical predictions. In fact, the latter study showed that π,π interactions may be even larger for OIT-4-B than for OIT-3-B.[4]

To date, no experimental studies of through-bond-*dominated* π^*,π^* interactions (π^*-OIT-*n*-B) have been reported.[6] Such a study would be timely in light of the suggestion that OITB involving π^* MO's is responsible for the enhanced reactivity of the double bonds in nonconjugated dienes toward Birch reduction.[2a,7] We have therefore embarked on a systematic study of π^*-OIT-*n*-B by using electron transmission spectroscopy (ETS)[8] as a probe of the anion states and report in Figure 1 ET spectra for the series of compounds **2**–**8**, the structures of which are indicated in the figure. The vertical attachment energies (-EA) are indicated by vertical lines. The details of the method and the assumptions inherent in the association of the structure with the vertical EA's are discussed elsewhere.[8,9]

The EA's and the IP's of compounds **2**–**8**, together with those of ethylene,[10] *cis*-2-butene,[10] cyclohexene,[6] norbornene, and norbornadiene[6] (**1**) are summarized in Table I, and these data

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