

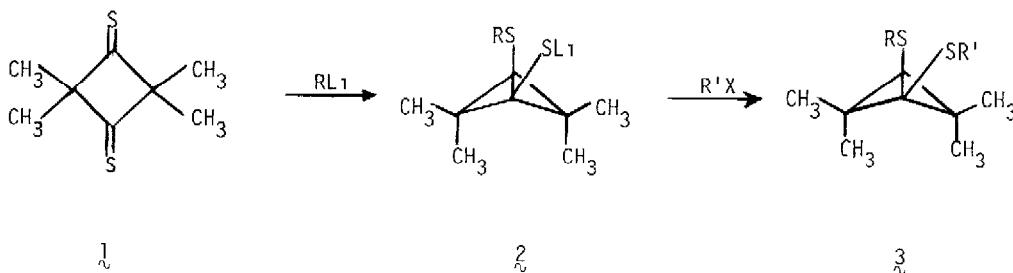
THE ADDITION OF METHYLLITHIUM TO 2,2,4,4-TETRAMETHYLCYCLOBUTAN-1-ONE-3-THIONE THE GENERATION AND CAPTURE OF A BISHOMOENOLATE ANION

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**Abstract** Methylolithium added to 2,2,4,4-tetramethylcyclobutan-1-one-3-thione to produce lithium 3-methylthio-2,2,4,4-tetramethylbicyclo[1.1.0]but-1-oxide. This bishomoenolate was alkylated on carbon by methyl iodide, but retained the bicyclo[1.1.0]butane skeleton when silylated with chlorotrimethylsilane. The ease of oxidation of a series of 1,3-diheteroatom substituted bicyclo[1.1.0]butanes was determined.

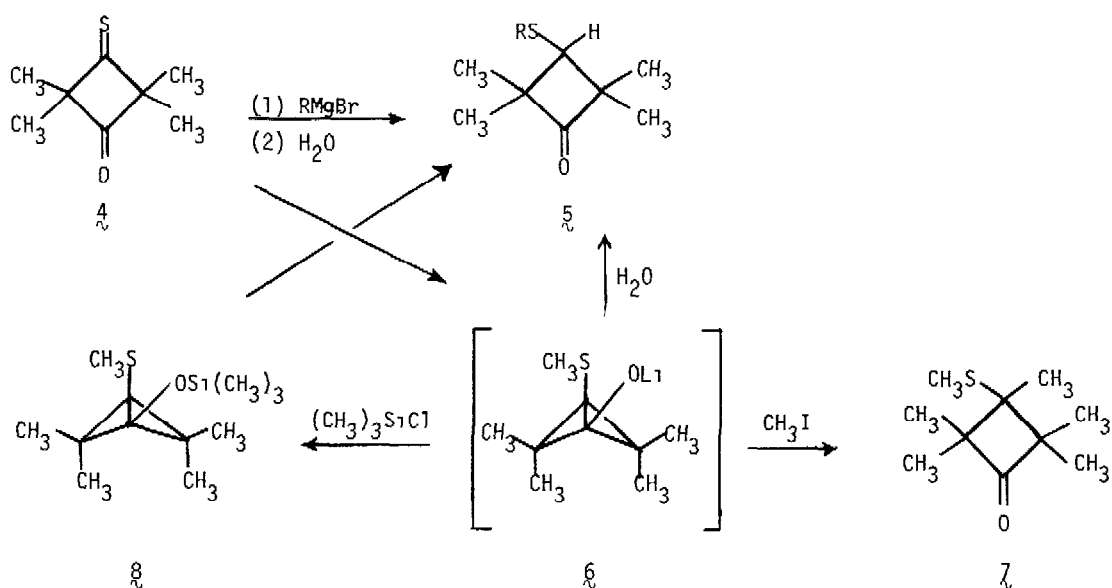
Recently, we reported that 2,2,4,4-tetramethylcyclobutan-1,3-dithione (**1**) reacted with organolithium reagents to give **2** which on alkylation yielded **3**.<sup>1</sup> These results made us suspect that related studies reported<sup>2</sup> for the addition of organometallic reagents to 2,2,4,4-



tetramethylcyclobutan-1-one-3-thione (**4**) might have been mechanistically misinterpreted. We now wish to reinterpret this literature and to report the capture of a bishomoenolate anion by chlorotrimethylsilane.

Literature reports<sup>2</sup> indicate that **4** reacted with alkylmagnesium bromides to produce **5** after hydrolysis. The rationale which was provided in explanation of this observation attributed the selective attack at sulfur to steric hindrance of attack at the carbonyl carbon. Our experience with **1** suggested that a more likely explanation might involve the addition of the organometallic reagent to **4** to yield the bishomoenolate anion, **6**, which on hydrolysis would produce **5**. This hypothesis would explain the apparent lack of reactivity of the carbonyl

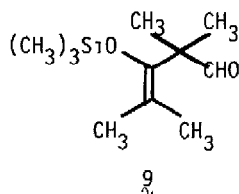
function of  $4$ , since the carbonyl would be tied up as a bishomoenolate anion. In addition,



this hypothesis would be consistent with the known transannular electronic interactions of the thiocarbonyl and carbonyl moieties of  $4$ .<sup>3</sup>

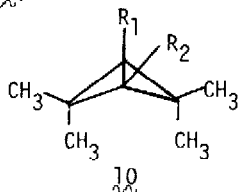
Treatment of  $4$  with methyllithium followed by aqueous workup gave  $5$  ( $R=CH_3$ ) in analogy to the literature report. When the methyllithium addition was followed by methyl iodide addition rather than aqueous workup, we obtained a 69% yield of  $7$ .<sup>4,5</sup> Neither the isolation of  $5$  nor of  $7$  provided evidence for the intermediacy of  $6$ . However, when chlorotrimethylsilane was added in place of methyl iodide we obtained a 76% yield of the bicyclo[1.1.0]butane derivative,  $8$ . The structural assignment of  $8$  was based on correct elemental analysis, and on mass spectral, IR, and NMR data. The proton NMR ( $CCl_4$ ) showed peaks at  $\delta$  2.09 (3H, s), 1.25 (6H, s), 1.11 (6H, s), and 0.15 (9H, s). Carbon NMR (benzene- $d_6$ ) showed absorptions at  $\delta$  -0.1, 17.8, 22.0, 23.3, 36.8, 54.4, and 72.8.

Chemical evidence for the structure of  $8$  was provided by its facile hydrolysis to  $5$ . Treatment of  $8$  with aqueous methanol resulted in the complete conversion of  $8$  into  $5$ . In addition, when  $8$  was passed through a column of basic alumina, small amounts of  $9$  were obtained in addition to  $5$ . It is interesting to note that  $9$  would formally result from cleavage of the  $C_1-C_3$  and  $C_2-C_3$  bonds of  $8$ , a process which is reminiscent of the "retrocarbene" cleavages observed in certain transition metal complex promoted rearrangements of bicyclo-

[1.1.0]butanes<sup>6</sup>

Our original interest in the preparation of 3a ( $R=R'=CH_3$ ) was an outgrowth of our studies of the electrochemical oxidation of highly strained polycyclic molecules<sup>7,8</sup>. In view of our detailed investigation of the oxidation of methylated derivatives of bicyclo[1.1.0]butane, we became interested in the effect of heteroatom substitution at  $C_1$  and  $C_3$  of this highly reactive ring system. This led us to evaluate the ease of oxidation of the series of 2,2,4,4-tetramethylbicyclo[1.1.0]butane derivatives<sup>9</sup> listed in Table 1. Measurements were made by single-sweep voltammetry (sweep rate 100 mV/s) on a Princeton Applied Research Model 174 polarographic analyzer equipped with platinum electrodes. All measurements were made in high-

Table 1. Half-wave Potentials for the Oxidation of Derivatives of 2,2,4,4-Tetramethylbicyclo[1.1.0]butane (10)



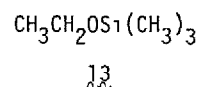
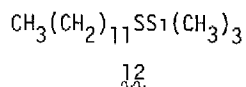
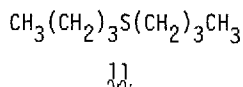
Compound	$R_1$	$R_2$	$E_{1/2}$ vs SCE ( $\pm 0.02V$ ) <sup>a</sup>
<u>10a</u>	H	H	1.57 <sup>b</sup>
<u>10b</u>	CH <sub>3</sub>	H	1.20 <sup>b</sup>
<u>10c</u>	CH <sub>3</sub>	CH <sub>3</sub>	0.93 <sup>b</sup>
<u>10d</u>	CH <sub>3</sub> S	H	0.96
<u>10e</u> (3a)	CH <sub>3</sub> S	CH <sub>3</sub> S	0.57
<u>10f</u> <sup>c</sup>	CH <sub>3</sub> S	(CH <sub>3</sub> ) <sub>3</sub> SiS	0.71
<u>10g</u> (8)	CH <sub>3</sub> S	(CH <sub>3</sub> ) <sub>3</sub> SiO	0.44

(a) The values cited assume that the measured electrode potentials are kinetically shifted (due to follow-up reactions) relative to the *reversible* potentials for each compound studied. (b) Values taken from ref. 8. (c) For the mode of preparation of 10f see ref. 9.

purity acetonitrile containing 0.1 M tetraethylammonium fluoroborate as the supporting electro-

lyte Substrate concentration was  $ca\ 10^{-3}M$

As can be seen from the data in Table 1, the presence of a heteroatom at the bridgehead of a bicyclo[1.1.0]butane skeleton has a significant effect on the ease of oxidation of the molecule. One might question whether this oxidation involves the removal of an electron from the orbital associated with the C<sub>1</sub>-C<sub>3</sub> bond of the bicyclo[1.1.0]butane or the removal of a non-bonding electron from one of the heteroatoms. While this question cannot be answered rigorously at this time, it is evident that either the presence of the heteroatom substantially raises the energy level of the HOMO of the bicyclo[1.1.0]butane nucleus<sup>8</sup> or that the attachment of a bicyclo[1.1.0]butane moiety greatly increases the ease of oxidation of the heteroatom. For comparison purposes half-wave oxidation potentials of 11, 12, and 13 were measured<sup>10</sup> and found to be 1.54 V, 1.53 V, and >2.5 V, respectively. It is clear that the heteroatom groups of 11,



12, and 13 are considerably more resistant to oxidation than are compounds 10d through 10g. The great ease of oxidation of 10g compared to 10d and 13 suggests that the primary site of oxidation may still be the C<sub>1</sub>-C<sub>3</sub> bond of the bicyclo[1.1.0]butane.<sup>8</sup>

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#### References and Notes

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- 4 Satisfactory spectral data and elemental analyses and/or exact mass molecular weights were obtained on all new compounds unless otherwise specified.
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- 9 Compound 10f was prepared from 2 (R=CH<sub>3</sub>) through quenching with chlorotrimethylsilane.
- 10 Oxidation potentials for simple sulfides have previously been determined, but not under our experimental conditions. For examples see P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, 116, 1499 (1969)

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