ADDITION OF TRIMETHYLSILYLLITHIUM AND TRIMETHYLSTANNYLLITHIUM TO A HINDERED CYCLOPROPYL ENONE

Richard T. Taylor\* and James G. Galloway Hughes Chemical Laboratories, Miami University, Oxford, Ohio 45056

<u>Abstract.</u> Addition of Me<sub>3</sub>SiLi or Me<sub>3</sub>SnLi to  $\underline{1}$  affords cyclopropyl cleavage to the ring expanded system ( $\underline{2}$  and  $\underline{3}$ ).

Organosilicon and organotin alkalis represent an interesting approach to the preparation of organosilicon and tin compounds.<sup>1</sup> Extensive studies on the mechanism of substitution of the organotin species for halogens have been carried out and the results interpreted in terms of SN2, halogen-metal exchange, electron transfer and other mechanisms.<sup>2</sup> While both trimethylsilyllithium and trimethylstannyllithium are known to add to most  $\alpha,\beta$ -unsaturated carbonyls in a conjugate fashion,<sup>3-5</sup> Still concluded, on the basis of the reactivity of 1,2-addition intermediates, that the silyl anion added via an electron-transfer mechanism and the stannyl anion through nucleophilic attack.<sup>6</sup> The change in mechanism was attributed to a difference in oxidation potential (although both are good reducing agents) and the lesser steric requirements of the stannyl group.<sup>4</sup>

House has used the ring opening of the cyclopropyl enone <u>1</u> as a probe for electron transfer in cuprate reactions.<sup>7</sup> Although other interpretations of House's results have been advanced,<sup>8</sup> we have investigated the action of Me<sub>3</sub>SiLi and Me<sub>3</sub>SnLi on <u>1</u> and report the results herein.

Treatment of <u>1</u> with Me<sub>3</sub>SiLi or Me<sub>3</sub>SnLi in THF/HMPA according to the method of Still<sup>3,4</sup> (from reaction of Me<sub>3</sub>MMMe<sub>3</sub> and CH<sub>3</sub>Li) each afforded a single addition product in 72% and 86% isolated yields, respectively.<sup>9</sup> NMR analysis<sup>10</sup> suggested that the modes of addition were analogous for both metalloid species and were consistant with cyclopropyl cleavage. That ring opening with expansion (to <u>2</u> and <u>3</u>) took place to the exclusion of the expected mode (<u>4</u> and <u>5</u>) was demonstrated by alternate synthesis.



Aldol condensation of 3-trimethylsilylmethylcyclohexanone( $\underline{6}$ )<sup>11</sup> with pinacolone followed by acid dehydration<sup>7</sup> afforded the three double bond isomers.<sup>9</sup> GC/MS analysis<sup>12</sup> demonstrated that none of the three products corresponded to the previously prepared silyl adduct.

Treatment of 3-trimethylsilylcyclohexanone(7) with ethyl diazoacetate followed by hydrolysis/decarboxylation afforded the ring expanded products(8 and 9) in 2:1 ratio and moderate yield,<sup>9,13</sup> with the structure of 9 confirmed by addition of Me<sub>3</sub>SiLi to cycloheptenone.<sup>3</sup> Treatment of 8 with pinacolone, in the previously described fashion, likewise afforded three isomers. One of these isomers proved identical, by GC/MS, to the silyl addition product 2.



Reaction through this mode of ring opening was rather unexpected. Addition at the more hindered carbon is uncharacteristic of nucleophilic attack.<sup>8</sup> However, electron transfer is also expected to afford the other products ( $\underline{4}$  and  $\underline{5}$ ), based upon treatment of  $\underline{1}$  with Li/HMPA/tBuOH, which afforded  $\underline{10}$ , alternatively synthesized in the usual way from 3-methylcyclohexanone<sup>9</sup> and identified in GC/MS analysis.



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HMPA is not necessary for this reaction. Addition of  $\underline{1}$  to Me<sub>3</sub>SnLi generated in THF, or to a solution of pure crystalline Me<sub>3</sub>SiLi<sup>14</sup> in THF gave the same ring expansion products previously obtained. It is also of interest to note that little deconjugation or cis-trans isomerization of  $\underline{1}$  could be observed, indicating that acid-base reaction of these anions was not competitive with the addition.

Our current view is that the metalloid systems differ from the Li/HMPA/tBuOH system in the steric requirements of the reducing agent. Since electron transfer should require interaction between the  $\pi$  system of the enone and the anionic species, the endo cyclopropyl hydrogen (<u>11</u>) would be expected to hinder reduction from the face syn to the cyclopropyl group. The resultant



metalloid radical would then be located in a position to assist opening of the cyclopropyl ring in the observed fashion. That the direction of approach of a reagent can affect the mode of bond cleavage in a strained system has been previously proposed<sup>15</sup>. Less sterically demanding reagents (such as Li/HMPA) or those that do not proceed through an electron transfer mechanism would not be affected in this fashion and could undergo the conventional ring opening reaction.<sup>16</sup>

## Footnotes and References

1.	See	Ε.	Negishi	ι, '	'0r8	ganometall	lice	s in Or	ganic	S	ynthesis	, v	01.1";	Wiley,	New	York,	1980	; p.412.
2.	G.	F.	Smith,	н.	G.	Kuivila,	R.	Simon,	and 1	L.	Sultan,	<u>J</u> .	Amer.	Chem.	<u>Soc</u> .,	<u>103</u> ,	833	(1981)

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- 6. W. C. Still and A. Mitra, Tetrahedron Lett., 2659 (1978).
- 7. H. O. House and K. A. J. Snoble, J. Org. Chem., 41, 3076 (1976).
- 8. C. P. Casey and M. C. Cesa, J. Amer. Chem. Soc., 101, 4236 (1979).
- Satisfactory C and H analyses were obtained for all new compounds (as isomer mixtures for condensations).
- 10. For the silyl adduct <u>2</u>: δCCl<sub>4</sub>(CHCl<sub>3</sub> = 7.25): 5.15 (m,1); 3.18 (br s,2); 2.20-1.20 (m,5); 1.20-0.70 (m,13,inc. s at 1.12); 0.07 (s,9).
  For the tin adduct <u>3</u>: δCCl<sub>4</sub> (CHCl<sub>3</sub> = 7.25): 5.25 (m,1); 3.23 (brs,2); 2.10-1.30 (m,5); 1.20-0.80 (m,13,inc. s at 1.07); 0.12 (s,9,inc, Sn sidebands).
- 11. R. T. Taylor and J. G. Galloway, J. Organometal. Chem., 220, 295 (1981).
- GC/MS analyses were carried out on a Hewlett-Packard HP5993 instrument equipped with 6 ft x 1/8 inch column of 2% OV-11 on Chromosorb W.
- 13. P. F. Hudrlik, et al, J. Amer. Chem. Soc., 102, 6894 (1980) report much greater selectivity in Baeyer-Villager reactions of such systems. Presumably, our case involves a transition state with much less positive charge on the migrating group. The synthetic utility of this particular reaction is somewhat attenuated by the formation of several byproducts from which separation was quite tedious.
- 14. We thank Professor E. A. Sadurski (Ohio Northern University) for a sample of pure, crystalline MegSiLi.
- 15. L. A. Paquette and G. Zon, J. Amer. Chem. Soc., 96, 224 (1974).
- 16. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for the support of this research.

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