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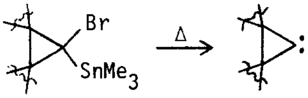
SKATTEBOL TYPE REARRANGEMENT VIA α-BROMOTRIMETHYLSTANNYL CYCLOPROPANE THERMOLYSIS. WHAT IS THE MECHANISM?

Philip M. Warner* and Robert D. Herold
Chemistry Department, Iowa State University
Ames, IA 50011

Summary: Solution thermolysis of the epimers **5** gave rise to separate sets of products, including, for one, Skattebol-type rearrangement. However, neither epimer produced a free carbene.

We[1] have been interested in the Skattebol rearrangement,[2] whereupon a vinylcyclopropylidene or vinylcyclopropylidenoid rearranges to the corresponding cyclopentenylidene (oid) (e.g., **3** → **4**). In 1975, Seyferth[3] reported that thermolysis of α-bromotrimethylstannylcyclopropanes (**1**) might afford a route to the difficultly accessible free cyclopropylidenes (**2**). While we had hoped to generate free **3** from **5**, we now report the thermolysis of **5** does not produce **3**, but does give rise to a Skattebol-type rearrangement.



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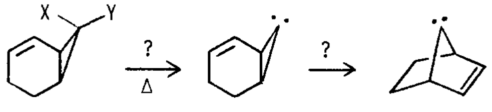
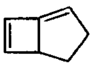


5a, X=Me$_3$Sn
Y=Br
b, X=Br
Y=Me$_3$Sn

3 4



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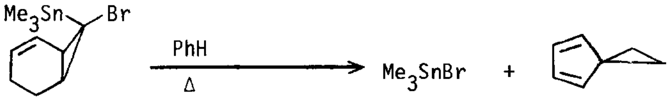
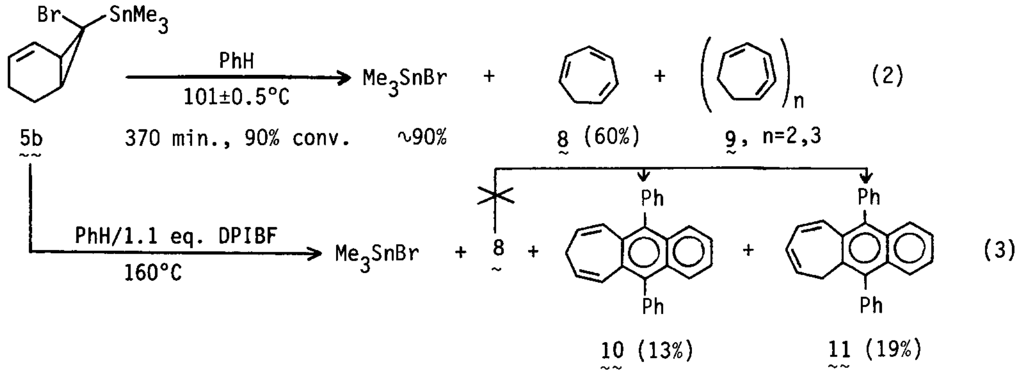
Pyrolysis of **5a**[1a] in benzene solution gave Me_3SnBr and spirodiene **7**[4,5](see eqn. 1), while similar treatment of **5b**[1a] produced Me_3SnBr, cycloheptatriene (**8**), and dimers[6] and trimers[6] of **9** (eqn. 2). When **5b** was heated in the presence of diphenylisobenzofuran (DPIBF), two adducts[7] (**10** and **11**) replaced the oligomers of **9** in the product mixture (eqn. 3).

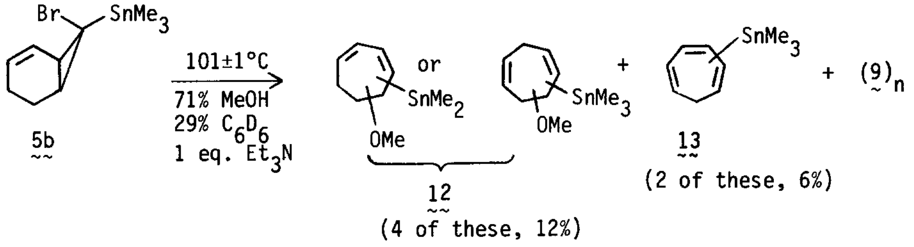


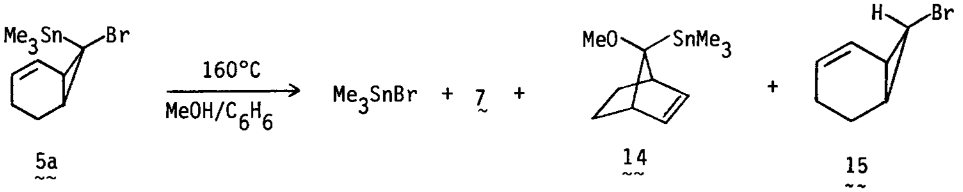
5a 7 (1)

101 ±0.5°C, 385 min, 88% conv.	85%	76%
162.5±0.5°C, 10 min., 75% conv.	93%	86%



It was immediately obvious that, in contrast to the saturated analog,[3] the disparate product mixtures arising from **5a** and **5b** meant that at most one precursor could be producing a carbene intermediate. Since the halogen in **5b** is in the orientation expected to lead to ionization with concommitant cyclopropane ring-opening, the kinetic effect of solvent polarity was briefly probed. With the less polar Et_3SiH solvent,[8] the rate of **5b** decomposition was slowed relative to benzene by >10-fold; diphenylether produced a ca. 2 fold rate enhancement, while the more polar CD_3CN led to a ca. 12-fold rate enhancement. In all cases the rate effects were more pronounced for **5b** than for **5a** (for which $k(CH_3CN)/k(Et_3SiH) \leq 3$, compared to ≥ 190 for **5b**). Further evidence for the ionic reaction of **5b** was obtained in 29% methanolic benzene-d_6, where, in addition to oligomers of **9**, and a trace of **8** (**8** was stable to these reaction conditions), six tin-containing products were formed (identified by gc-ms only) in ca. 3% yield each. In addition, the reaction rate constant increased 12.6 fold (from that in C_6D_6 with 1 eq. Et_3N) to $(117 \pm 2) \times 10^{-5}$ sec^{-1}.

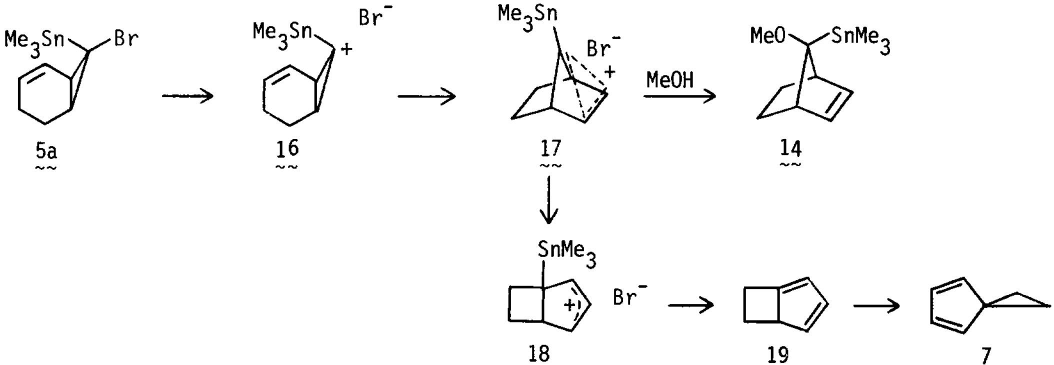




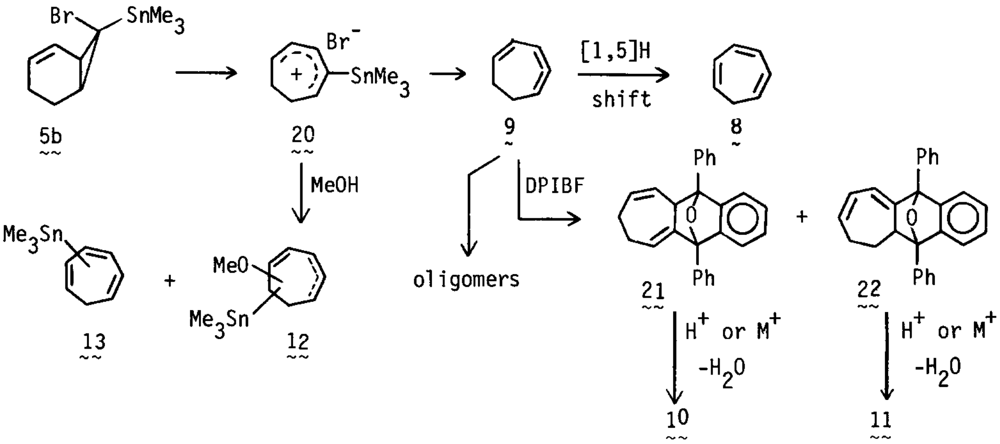
4% MeOH	86%	61%	9%	---
29% MeOH	73%	41%	23%	---
100% MeOH	24%	0%	72%[9]	20%[10]

Initially surprising was the fact that reaction of **5a** in MeOH provided evidence not for trapping of carbenes, **3** or **4**, but rather for an ionic intermediate, **17**, which gave **14**.[12] Generation of **4** from its Li tosylhydrazone salt[4] (150°-155°, diglyme[13]) verified that **4** was not formed from **5a**. In solution (and similar to its gas phase behavior[2c,4]), authentic **4**

Scheme I



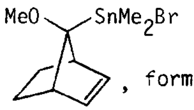
Scheme II



gave 28-29% **6** (as its DPIBF adducts), and only *ca*. 1% **7**.

Schemes I and II summarize the reactions of **5**. Dehydration of **21** and **22** has been effected.[14] **Neither 5a nor 5b affords a carbene in solution, although a Skattebol-style rearrangement occurs from 5a--via a cationic mechanism.**

References and Notes

1. (a) Warner, P. M.; Herold, R. F. J. Org. Chem., **1983**, 48, 5411; (b) Warner, P. M.; Chang, S.-C. Tetrahedron Lett., **1978**, 3981.
2. (a) Holm, K. H.; Skattebol, L. J. Am. Chem. Soc., **1977**, 99, 5480; (b) Kirmse, W.; Jendralla, H. Chem. Ber., **1978**, 111, 1873; (c) Brinker, U. H.; Ritzer, J. J. Am. Chem. Soc., **1981**, 103, 2116; (d) Holm, K. H.; Skattebol, L. Tetrahedron Lett., **1977**, 2347, and references therein.
3. Seyferth, D.; Lambert, R. L., Jr. J. Organomet. Chem., **1975**, 91, 31.
4. Moss, R. A.; Dolling, U.-H.; Whittle, J. R. Tetrahedron Lett., **1971**, 931. These authors report the gas phase chemistry of **4**, including formation of **7**.
5. Some samples of **5a** reacted faster (Lewis acid catalysis; details to be reported separately). In those cases, the yield of **7** was somewhat higher (up to 95%), since during longer reaction times, **7** was partially consumed due to its thermal lability and/or acid sensitivity.
6. GC-MS showed at least 4 dimers (12 [2 + 2] allene dimers are possible) and 3 trimers; these were not investigated further.
7. **10** + **11** (these were separable by capillary GC only): mp 164-170°C; PMR (CCl_4: δ 7.28-6.93 (m, 14H), 6.9-5.6 (m, 4H), 3.00 (d, J = 6 Hz, CH_2 of **11**), 2.50 (t, J = 6 Hz, CH_2 of **10**); gc-ms spectra of **10** and **11** were identical. Anal. Calcd for $C_{27}H_{20}$: m/e 344.1565; found: m/e 344.1553.
8. The reason for using this solvent will be discussed separately.
9. Some 44% of **14** was found as 

, formed presumably via HBr induced cleavage of **14**. Reluctance to develop anionic character at the 7-norbornenyl position[11] may account for the protic cleavage of a methyl group.
10. Product **15** was presumably formed via HBr induced cleavage of **5a**.
11. Bowman, E.S.; Hughes, G. B.; Grutzner, J. B. J. Am. Chem. Soc., **1976**, 98, 8273.
12. **14**: 300 MHz PMR (C_6D_6): δ 5.68 (t, J = 2.2 Hz, 2H), 2.94 (s, 3H), 2.66 (m, 2H), 1.87 (m, H^{5+6}_{exo}), 0.98 (m, H^{5+6}_{endo}), 0.16 (s, 9H); CMR (C_6D_6): δ 135.6 (6.0), 53.7 (1.5), 48.1 (5.0), 22.3 (5.5), -7.5 (2.1); 2D NOE PMR revealed an NOE between the vinyl and $SnMe_3$ H's, but none between the MeO and exo CH_2 H's. Anal. Calcd for $C_{10}H_{17}OSn$ (P-15): m/e 273.0301; found: m/e 273.0304 (the P^+ was present, but too weak to measure accurately).
13. It was verified that **5a** gave only **7** in diglyme, too.
14. Since subsequent experiments made **21** and **22** available (each as a mixture of endo and exo

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