sorbing, and $KMnO_4$-positive product in addition to the starting diester 7. The solution was extracted with $CH_2Cl_2$ (4 × 15 mL), and the extracts were dried ($MgSO_4$) and evaporated to give a syrup which was chromatographed on a loose layer of silica gel,[28] 2 mm thick, 2 × 20 cm in solvent system $S_3$. The strongly UV-absorbing band of **9** was eluted and the eluate was evaporated to give a syrup which soon crystallized, 9 mg (8%), mp 109–110 °C: UV max (ethanol) 204 nm (ε 6 250); $^1H$ NMR ($CDCl_3$) 6.84 (d, 1, $H_2$, $J_{2,3}$ = 2), 5.53 (dt, $H_5$, $J_{5,4}$ = 7), 5.24 (dd, 1, $H_3$, $J_{3,2}$ = 2, $J_{3,4}$ = 7), 3.793 and 3.787 (2s, 6, COOMe), 3.06 (t, 1, $H_4$, $J_{4,3}$ = $J_{4,5}$ = 7); EI-MS, *m/e* (relative intensity) 217 (0.2, M + 1), 199 (M - $H_2O$ + 1, 2.7), 184 (4.9, M - MeOH), 166 (100.0, 184 - $H_2O$). Additional peaks: 155 (13.0), 139 (50.8), 123 (25.7), 111 (42.2), 97 (15.4), 83 (20.8), 69 (37.8), 59 (33.3). CI-MS, *m/e* (relative intensity) 217 (15.4, M + H), 199 (100.0, M + H - $H_2O$), 167 (96.3, M + H - $H_2O$ - MeOH), 139 (14.0). Sample recovered from $^1H$ NMR was analyzed. Anal. Calcd for $C_9H_{12}O_6 \cdot {}^1/_4CDCl_3$: C, 45.11; H, 5.11 (includes 0.2% D). Found: C, 45.10; H, 5.42. The same product was obtained when α-chymotrypsin was omitted from the reaction mixture.

**Dimethyl 2α,3α-Dihydroxy-5β-*tert*-butoxy-1β,4β-cyclopentanedicarboxylate (12).** A solution of diester **5** (1.5 g, 4.5 mmol) in 0.75 M HCl in methanol (25 mL) was kept for 90 min at room temperature. TLC ($S_3$) showed the presence of a polar component (component **12**) and starting material **5**. Triethylamine (2.7 mL) was added with ice-cooling, the mixture was evaporated, and the residue was partitioned between water (25 mL) and $CH_2Cl_2$ (2 × 25 mL). The organic phase was dried ($Na_2SO_4$) and evaporated. The residue was chromatographed on a silica gel column (15 g) in solvent system $S_3$ to give compound **12** (0.59 g, 45%), mp 145–150 °C, homogeneous on TLC ($S_3$) in addition to starting material **5** (0.73 g, 49%). An analytical sample was obtained by crystallization from cyclohexane–ethanol (6:1), mp 145–150 °C: IR 3360 and 3250 (OH), 1735 (CO); $^1H$ NMR ($C_3SOCD_3$) 4.79 (d, 2, OH), 4.61 (t, 1, $H_5$), 4.32 (qt, 2, $H_2$ + $H_3$), 3.56 (s, 6, MeO), 2.93 (q, 2, $H_1$ + $H_4$), 0.97 (Me of *t*-Bu, s, 9); $^{13}C$ NMR 170.60 (CO), 74.19 (>CO of *t*-Bu), 72.37 ($C_2$ + $C_3$), 70.84 ($C_5$), 56.08 ($C_1$ + $C_4$), 51.00 (MeO), 27.54 (Me of *t*-Bu). Anal. Calcd for $C_{13}H_{22}O_7$: C, 53.78; H, 7.64. Found: C 54.02; H, 7.68.

**Acknowledgment.** Thanks are due to Drs. Robin Hood, D. P. Lin, and Ole Mols from the Central Instrumentation Facility, Department of Chemistry, Wayne State University, for mass and NMR spectra. The work described herein was supported in part by U.S. Public Health Service Research Grant CA 32779 from the National Cancer Institute, Bethesda, MD, and in part by an institutional grant to the Michigan Cancer Foundation from the United Foundation of Greater Detroit.

**Note added in proof:** An alternate binding model of PLE comprising two hydrophobic sites one of which is capable of interacting with a nonhydrolyzable ester group has been proposed: Lam, L. K. P.; Hui, A. H. F.; Jones, J. B. *J. Org. Chem.* **1986**, *51*, 2047. Sabbioni, G.; Jones, J. B. *Ibid.* **1987**, *52*, 4565. A possible hydrophilic site has not been considered.

**Supplementary Material Available:** A complete description of the crystallographic experiment and tables of pertinent crystallographic data for compound **8** (8 pages). Ordering information is given on any current masthead page.

# On the Mechanism of the Thermal Decomposition of 1-Bromo-1-(trimethylstannyl)cyclopropanes

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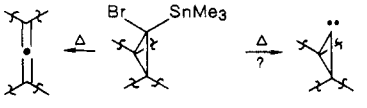
A mechanistic study of the thermolysis of compounds **4a** and **4b** is reported. In methanolic benzene, **4a** reacts entirely via formation of norcaranylidene (**8**), while **4b** gives no carbene but rather ring-opening to a cycloheptenyl ion. The pathway for carbene formation is discussed. Under less polar conditions (cyclohexene), carbene formation from **4a** and ionic ring-opening from **4b** still predominate. However, **4b** now gives some carbenic product.

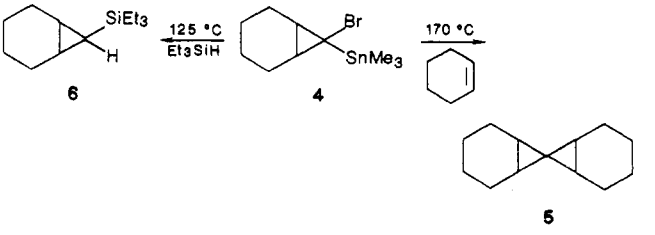
## Introduction

In 1975, Seyferth reported[1] that heating α-bromo-α-(trimethylstannyl)cyclopropanes **1** in solution provided a possible route to cyclopropylidenes **2**. Irrespective of mechanism, most of the variants of **1** tested gave ring-opening to allenes **3** (including all the monocyclic examples of **1**). Only the norcarane system **4** produced divalent




3 1 2

carbon transfer products (e.g., **5**, **6**) with olefins or $Et_3SiH$. Seyferth concluded that the mechanism of the divalent carbon transfer reaction was unclear, there being several disturbing features observed mitigating against a simple carbene mechanism (e.g., **6** was formed as a 1:1 mixture of epimers).



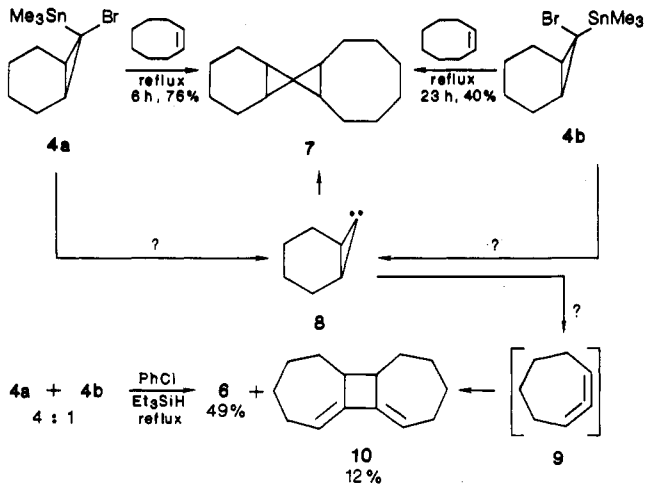

6 4 5

Among the noteworthy observations of Seyferth were the differential reactivities of **4a** and **4b**, with the former considerably more reactive at 83 °C in refluxing cyclohexene. In refluxing cyclooctene (146 °C), **4a**, and **4b** both gave **7**, but in different yields. But whether both precursors gave **7** via a common carbene intermediate (**8**) was unclear. In addition, a 4:1 mixture of **4a**:**4b**, when heated at 170 °C in cyclohexene, gave a 33% isolated yield of **5**. Lastly, the same **4a**:**4b** mixture in chlorobenzene/$Et_3SiH$ (125 °C) afforded, in addition to **6**, 12% of allene dimer **10**. Did **10** arise via the pathway **8** → **9** → **10**?

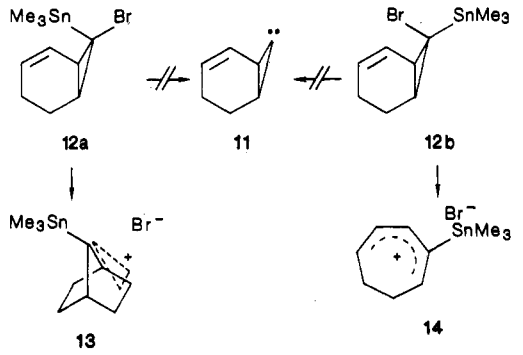
Despite the uncertainties, we had hoped to use this method as an entry to norcarenylidene (**11**). However,

(1) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1975**, *91*, 31.

0022-3263/88/1953-0942$01.50/0 

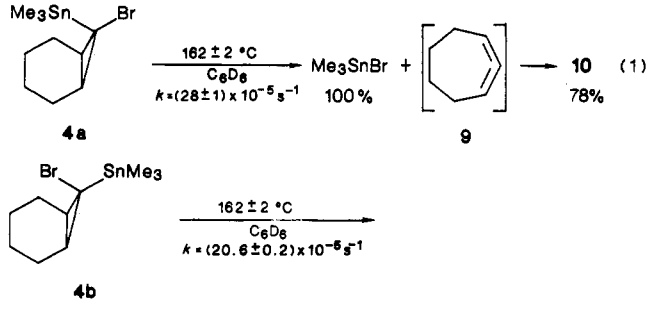


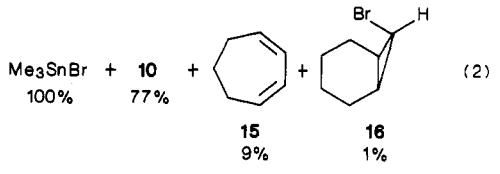

neither isomer of **12** gave **11** upon heating in solution (either in benzene or in methanol); rather, cationic ("carbenoid") rearrangements were encountered.[2] We thus decided to investigate the solution chemistry of the epimers of **4**, with the hope of clarifying when a free cyclopropylidene intermediate (**2**) may be expected.

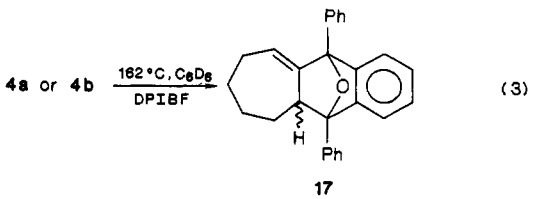



## Results

**A. Reactions in Benzene.** The results of heating a 0.04 M solution of **4a** or **4b** in benzene-$d_6$ at 162 ± 2 °C (sealed tube) are shown in eq 1 and 2. Also indicated are




(2) Warner, P. M.; Herold, R. D. *Tetrahedron Lett.* **1984**, *25*, 4897.

**Table I. Rate Constants for the Decomposition of 4 in Cyclohexene[a] at 162 ± 2 °C**

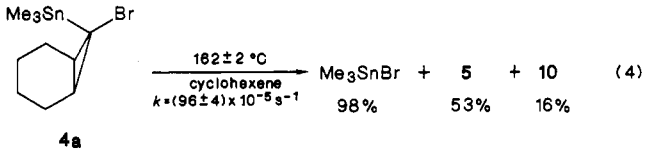
| run[b] | reactant | solvent[c] batch no. | $10^5k$ ($s^{-1}$) |
|---|---|---|---|
| 1 | **4a**, 0.11 M | 1 | 108 ± 1 |
| 2 | **4a**, 0.08 M | 1 | 90 ± 1 |
| 3 | **4a**, 0.06 M | 2 | 31 ± 4 |
| 4 | **4a**, 0.04 M | 2 | 27 ± 3 |
| 5 | **4a**, 0.05 M | 3 | 96 ± 4 |
| 1 | **4b**, 0.07 M | 1 | 7.8 ± 0.1 |
| 2 | **4b**, 0.05 M | 1 | 8.0 ± 0.2 |
| 3 | **4b**, 0.04 M | 2 | 5.3 ± 0.3 |
| 4 | **4b**, 0.03 M | 2 | 4.9 ± 0.04 |
| 6 | **4b**, 0.04 M | 3 | 4.7 ± 0.1 |

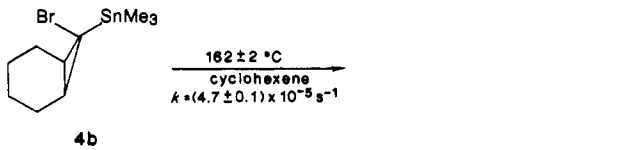
[a] Base-washed glassware was used throughout. After dissolution, each sample was sealed under $N_2$, and the kinetics were followed via $^1H$ NMR. [b] **4a** and **4b** were mixed together in runs 1–4. The same batch of starting material was used for runs 1 and 2 and runs 3 and 4. [c] Solvent batch 1 was distilled under Ar and refrigerated over $K_2CO_3$, while no. 2 and no. 3 were distilled from sodium benzophenone ketyl and refrigerated over Na, under Ar.

the observed first-order rate constants for the loss of **4** (measured by NMR); **4a** was slightly more reactive. When a 0.6 M solution of the mixture **4** was heated as above, **10** was diminished by ca. 50% and replaced by six compounds whose formulae corresponded to trimers of **9** (GC-MS analysis).

As expected, the reaction of a 0.3 M solution of **4a** or **4b** in the presence of 1 equiv of diphenylisobenzofuran (DPIBF) afforded a 30% isolated yield of the two stereoisomers of **17** (see eq 3) in a 6:1 ratio; **17** is the known[3] adduct of **9** and DPIBF. As previously,[3b] the endo isomer of **17** predominated.

**B. Reactions in Cyclohexene.** When sealed solutions of **4a** (0.06 M) and **4b** (0.05 M) in cyclohexene were heated at 162 ± 2 °C (6 h), the products were found to be those shown in eq 4 and 5, with the yields based upon unre-



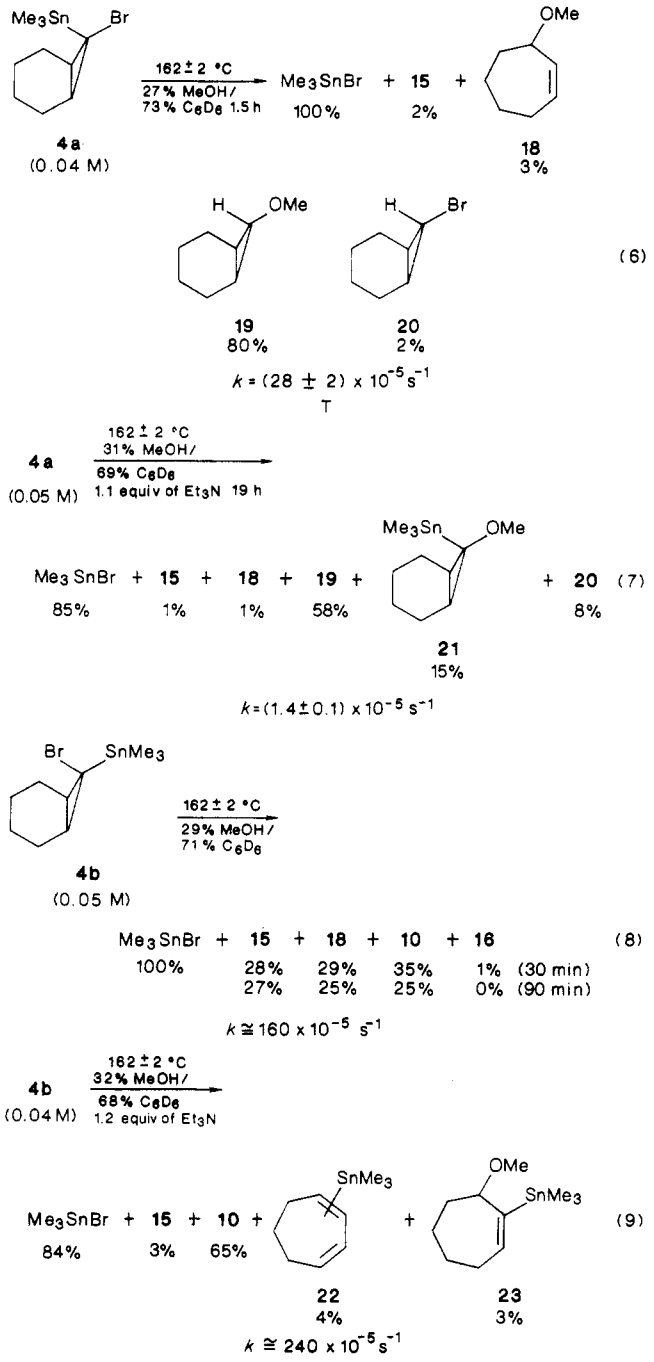




covered starting material. The first-order rate constants for the disappearance of **4** are again cited; **4a** was about 20 times more reactive than **4b**, which is in accord with Seyferth's results.[1]

However, significant rate fluctuations were noted as a function of the batch of cyclohexene used (all solvents used were reagent grade or better). This behavior was previously noted[2] for **12** and led to the use of $Et_3N$ to stabilize the kinetics (see Results, part D). As can be seen from the data in Table I, **4a** was subject to greater rate fluctuations.

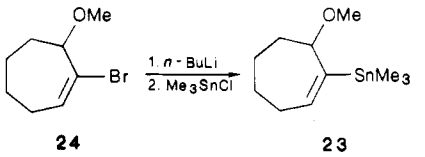
**C. Reactions in Methanol/Benzene.** When sealed solutions of **4a** (0.04 M) and **4b** (0.05 M) were heated in methanolic benzene (v/v mixtures) at 162 ± 2 °C, the products (yields determined by GC, corrected) and rates were as shown in eq 6 and 8. Note that after a 30-min

(3) (a) Wittig, G.; Meske-Schüller, J. *Liebigs Ann. Chem.* **1968**, *711*, 76. (b) These authors[3a] obtained a 10:1 ratio of endo:exo DPIBF adduct from **9** (generated from 1-bromocycloheptene) at 40 °C.




reaction time, 6% of **4b** was recovered. If the solvent batch 2 entries in Table I are the most representative of the "truth", then there appears to be very little rate effect on **4a**, whereas **4b** shows itself to be much more sensitive to changes in solvent polarity. We will return to this point later.

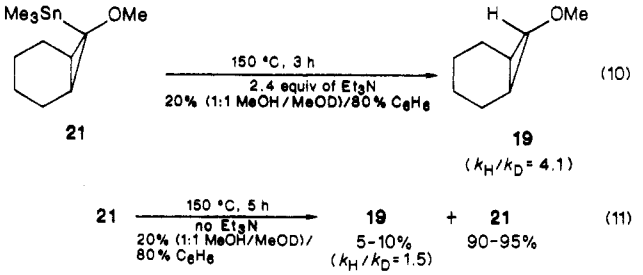
Since there were some apparent acid cleavage products (**16**, **20**) formed, the reactions were repeated in the presence of $Et_3N$ buffer (eq 7 and 9). While **16** disappeared, the amount of **20** actually increased. In view of the results for **21** (eq 10), it is apparent that $Et_3N$ stimulates the production of **20** from **4a**. Also, some new, tin-containing products were observed. Diene **22** was a 1.3:1 mixture of isomers, the structures of which were assigned only on the basis of GC-MS and mechanistic logic. Compound **23**, however, was independently synthesized from **24**;[4] the synthetic material had a GC retention time and a mass spectrum identical with those of **23** from the product mixture (but very diffrent from those of **21**).




Since these reactions appeared ionic in nature, we next probed the effect of varying the base concentration and the solvent polarity. The results of these experiments are shown in Tables II and III, respectively.

Although the production of **21** increased almost linearly with [MeOH], a time-resolved product study later showed that while the loss of **4a** was cleanly first order, the production of **19** and **21** was non-linear; indeed, **21** was slowly being converted to **19**. The data, summarized in Table IV, include the observed $k_H/k_D$'s for **19**. (It was separately shown that in MeOD/benzene **19**-*d* was produced, with the deuterium atom solely, within $^1H$ NMR limits, at $C_7$.)

Indeed, when **21** was directly heated, the results were as shown in eq 10 and 11.




**D. Some Kinetic Effects of Added Amines.** From the rate constants in eq 6 and 7, as well as the data in Table IV, it can be surmised that added $Et_3N$ slowed the decomposition rate of **4a**. We sought to explore this phenomenon a bit more carefully. Table V shows some effects of added amines on the reaction rates of **4a**, **4b**, **12a**, and **12b**.

Noteworthy is the dramatically large inhibitory effect of $Et_2NH$ on **4a**, *despite the formation of no new products*; the reactivity of **4b**, however, is almost unaffected by $Et_2NH$. Perhaps amines form a stable complex with **4a** (or **12a**), thereby creating a preequilibrium which must be surmounted for decomposition to occur. To probe this, a benzene solution of **12a** in the presence of 2 equiv of $Et_3N$ ($[Et_3N]$ = 0.14 M) was examined by $^1H$ NMR between room temperature and 120 °C. *No new peaks were observed*, despite the fact that decomposition of **12a** was strongly inhibited under these conditions. Furthermore, decomposition of **12a** at 162 ± 2 °C showed clean first-order kinetics in the presence of $Et_3N$ when followed to >3 half-lives [0.09 equiv of $Et_3N$, $k = (20 \pm 2) \times 10^{-5}$ s$^{-1}$; 0.52 equiv of $Et_3N$, $k = (6.3 \pm 0.1) \times 10^{-5}$ s$^{-1}$]. *No $Me_3SnBr$ catalysis* (or other catalysis) or induced rearrangements via electrophilic additions were observed for either **12a** or **4a**. On the other hand, addition of $SnCl_4$ did strongly accelerate the decomposition of **12a**.

## Discussion

The norcaryl system was the only one found to undergo net divalent carbon transfer in the Seyferth study.[1] It is thus important to know whether a carbene is formed in this case, either from **4a**, **4b**, or both.

Already in benzene solution a small dichotomy can be seen between the chemistry deriving from **4a** and **4b** (other than a net reactivity difference). For one, **4b** produces **15**,

(4) Arct, J.; Prawda, A.; Kozyriev, V. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 1978, *26*, 523.

**Table II. Effect of Amines on the Products from 4 in Methanolic Benzene at 162 ± 2 °C**

| reactant, M | amine, M | MeOH/$C_6D_6$[a] | major product yields,[b] % | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 19 | 21 | 20 | 10 | 22 | 23 |
| **4a**, 0.05 | $Et_3N$, 0.06 | 31:69 | 58 | 15 | 8 | | | |
| **4a**, 0.04 | $Et_3N$, 0.11 | 29:71 | 65 | 14 | 4 | | | |
| **4a**, 0.05 | Proton sponge,[c] 0.05 | 32:68 | 57 | 18 | 5 | | | |
| **4b**, 0.04 | $Et_3N$, 0.05 | 32:68 | | | | 65 | 4 | 3 |
| **4b**, 0.03 | $Et_2NH$, 0.76 | 30:70 | | | | 64 | 4 | 4 |

[a] Solvent ratios by volume. [b] GC yields, corrected, based on unrecovered reactant. [c] 1,8-Bis(dimethylamino)naphthalene.

**Table III. Effect of Methanol Concentration on the Decomposition Rates of and Products from 4 in Methanolic Benzene at 162 ± 2 °C**

| reactant, M | $[Et_3N]$ | [MeOH] | major product yields,[a] % | | | | | | | $k_{rel}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20 | 19 | 21 | 10 | 15 | 22 | 23 | |
| **4a**, 0.05 | 0.06 | 7.7 | 8 | 58 | 15 | | | | | (1.0) |
| **4a**, 0.05 | 0.05 | 14.8 | 4 | 46 | 31 | | | | | 3.3 |
| **4a**, 0.04 | 0.05 | 17.3 | 2 | 42 | 35 | | | | | 6.4 |
| **4a**, 0.03 | 0.03 | 24.7 | 1 | 38 | 41 | | | | | 16.1 |
| **4b**, 0.04 | 0.04 | 3.5 | | | | 71 | 9 | 1.5 | 1.5 | 45.7 |
| **4b**, 0.04 | 0.05 | 7.9 | | | | 65 | 2.5 | 4 | 3 | 171 |
| **4b**, 0.04 | 0.04 | 12.3 | | | | 70 | 2 | 1.5 | 3 | |
| **4b**, 0.04 | 0.04 | 17.5 | | | | 75 | 0 | 0.5 | 1.5 | |

[a] GC yields, corrected, based on unrecovered reactant.

**Table IV. Time-Resolved Product Formation from 4a in 80% Methanolic Benzene[a] at 162 ± 2 °C**

| run | reactn time (h) | product yields,[b] % | | | $k_H/k_D$[c] |
|---|---|---|---|---|---|
| | | **4a** | 21 | 19 | |
| 1[d] | 1 | 66 | 12 | 12 | 3.2 |
| 1 | 3 | 9 | 15 | 18 | 3.4 |
| 1 | 5.5 | 1 | 12 | 29 | 3.7 |
| 1 | 22 | 0 | 6 | 32 | 4.1 |
| 2[e] | 0.5 | 87 | 5 | trace | |
| 2 | 2 | 66 | 9 | 6 | 2.9 |
| 2 | 3 | 59 | 22 | 15 | 3.1 |
| 2 | 17 | 10 | 43 | 46 | 3.2 |
| 3[f] | 1 | 52 | | 48 | 1.6 |
| 3 | 3 | trace | | 94 | 1.9 |

[a] The solvent composition was (v/v) 10% MeOH/10% MeOD/80% $C_6H_6$. [b] Corrected GC yields. [c] For **19**, determined by GC-MS. [d] 0.88 equiv of $Et_3N$. [e] 1.1 equiv of $Et_3N$. [f] No $Et_3N$.

**Table V. Kinetic Effects[a] of Added Amines at 162 ± 2 °C**

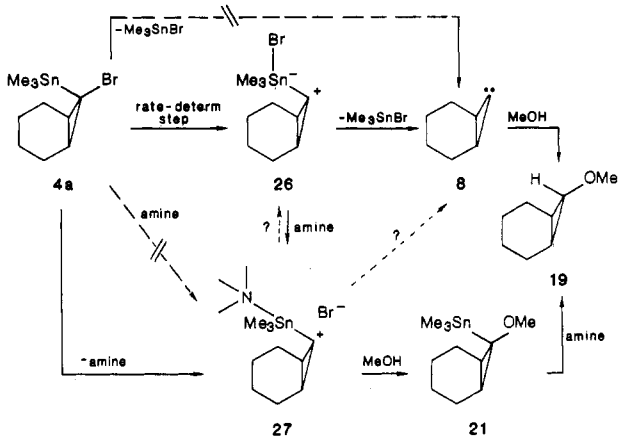
| reactant | solvent | amine, equiv | $k$(no amine)/$k$(amine) |
|---|---|---|---|
| **4a** | cyclohexene | $Et_3N$, 0.3 | 2.7 |
| **4a** | cyclohexene | $Et_3N$, 0.5 | 9.0 |
| **4a** | 29% MeOH/71% $C_6D_6$ | $Et_3N$, 1.1 | 20 |
| **4a** | $C_6D_6$ | $Et_2NH$, .3 | >56 |
| **12a** | benzene | $Et_3N$, 1 | >50 |
| **4b** | cyclohexene | $Et_3N$, 0.8 | 1.9 |
| **4b** | cyclohexene | $Et_3N$, 0.3 | 0.9 |
| **4b** | 30% MeOH/70% $C_6D_6$ | $Et_3N$, 1.2 | 0.9 |
| **4b** | $C_6D_6$ | $Et_2NH$, 3 | 1.2 |
| **12b** | $C_6D_6$ | $Et_3N$, 1 | 1.2[b] |

[a] Rates followed by $^1H$ NMR. [b] At 101 ± 1 °C.

whereas **4a** does not. If **4a** leads solely to carbene 8 and ultimately to **10**, then **15** must arise from a different pathway. A logical choice is ionic ring-opening, as depicted in Scheme II.

The shift to cyclohexene solvent, which is only very slightly less polar than benzene, produces a more sharply focussed product dichotomy (eq 4 and 5). Given the rate variabilities (Table I, eq 6, 8), it is clear that **4b** is more kinetically affected and in the direction expected for an ionic reaction. (As mentioned before, the batch 2 solvent runs suggest virtually no kinetic effect on **4a**.) However, the product distribution is not yet completely dichotomous, so the possibility that both epimers give at least some

**Scheme I**[a]




[a] See text for why long-dashed arrow routes are eliminated.

carbene (8) must still be entertained. We shall return to this point.

**A. Methanolic Solvents.** The critical results obtain in methanolic benzene. Completely dichotomous products are formed from **4a** and **4b** when the methanol concentration is as low as 3.5 M. It should also be noted that the dipole moment of methanol decreases rapidly with temperature (relative to benzene or cyclohexene), such that an $\epsilon \approx 32$ at room temperature translates into $\epsilon \approx 15$ at 162 °C. Thus, the modest polarity increase results in virtually no rate effect on the decompositin of **4a**. This is consistent with initial bromine migration to form ylide **26**[5] (where the cyclopropyl ring would not be expected to open[7]) or concerted loss of $Me_3SnBr$ to give carbene 8 (see

(5) (a) Pentavalent tin ate complexes have been proposed[5b,c] and observed[5d] as reaction intermediates, although we are unaware of any ylidic ate complexes. Nevertheless, recent calculations[5e] in the corresponding Si system makes it likely that **26** is stable relative to the corresponding ion pair (where Sn regains tetravalency). (b) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063. (d) Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102. (e) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889.

(6) (a) Sawyer, A. K. *Organotin Compounds*; Marcel Dekker, Inc.: New York, 1972; Vol. 3, p 630–631. (b) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press, Inc.: Elmsford, New York, 1982; Chapter 11.

Scheme I). Consonant with this interpretation, the rate of decomposition of **4a** in 20% *tert*-butanolic benzene [$\epsilon$(*t*-BuOH) $\approx$ 11 at 25 °C] is (25 ± 2) × $10^{-5}$ $s^{-1}$. And the $k_H/k_D$ = 1.74 for formation of the *tert*-butoxy analogue of **19** is consistent with the intermediacy of carbene **8**. As in other solvents, $Et_3N$ has a large decelerative effect on the decomposition rate of **4a**.

As depicted in Scheme II, **4b** is thought to react via ionization and ring-opening in MeOH/benzene. The rate increase observed for **4b** (eq 8) is consistent with this idea. But the **4b**/**4a** rate ratio is only about 6, far below the *endo*-7-bromonorcaryl/*exo*-7-bromonorcaryl rate ratio of about 12 000.[8] Is it, therefore, possible to exclude a carbon–bromine heterolysis as the rate-limiting step for decomposition of **4a**? In order to evaluate the expected rate ratio for ionization of **4a** and **4b**, one must know the $\alpha$-stabilizing effect of trimethylstannyl—which is unknown. But in a recent papter,[9a] $\alpha$-trimethylsilyl has been shown to be just slightly less effective than $\alpha$-methyl in its ability to stabilize a tertiary ion (i.e., to accelerate a $k_c$ process).

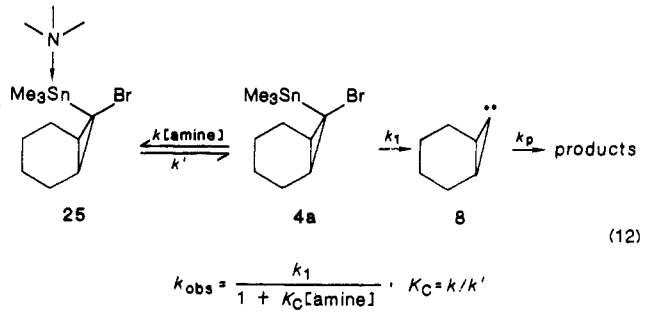
Su[8] has shown that *endo*-7-norcaryl systems ionize in a $k_\Delta$-like fashion, whereas *exo*-7-norcaryls ionize in a $k_c$-like fashion. He has also shown that an $\alpha$-methyl group would accelerate the endo solvolysis by only a factor of 300,[10] while the *exo*-7-norcaryl solvolysis should be accelerated by about $10^7$.[11] Therefore, the expected *endo*-7-bromo-7-methylnorcaryl/*exo*-7-bromo-7-methylnorcaryl rate ratio is $\sim(12\,000)(300)/10^7 = \sim 0.4$! If $\alpha$-trimethylstannyl mimics $\alpha$-trimethylsilyl,[9b] then a **4b**/**4a** rate ratio of 6 for ionization would be quite reasonable. (An accelerative effect of $\alpha$-$Me_3Sn$ has been observed for **4b**—vide infra.)

The electrophilic catalysis (by $SnCl_4$) seen for **12a** is more consistent with an intermediate like **26**.

Now, let us consider the products from **4a**. The one of mechanistic import is **19**.[13] Since **19** is the product from **8** when **8** is generated via the diazo precursor route,[14a] and since **21** is not the source of **19** (eq 11), the only reasonable route to **19** is via norcaranylidene (**8**).[15] If **15** and **18** do arise via ring-opening of **8** (to **9**), then **8** is trapped at least 16 times faster than ring-opening under the conditions of eq 6 (but see the last 2 entries of Table IV for an indication that trapping may be even more preferable to ring-opening).

How may the effect of added amines be explained? From the data in Table V, one can see that amine additives are doing *more than neutralizing* adventitious Lewis acid catalysts. There is a specific inhibitory effect which increases approximately linearly with amine concentration. And the amine cannot be simply sequestering $Me_3SnBr$, since the linear rates and high yields of the latter indicate it does not act as a catalyst nor is it transformed into one.

One possibility would be that amines complex the starting material (**4a**) as shown in eq 12. If so, **4a** would

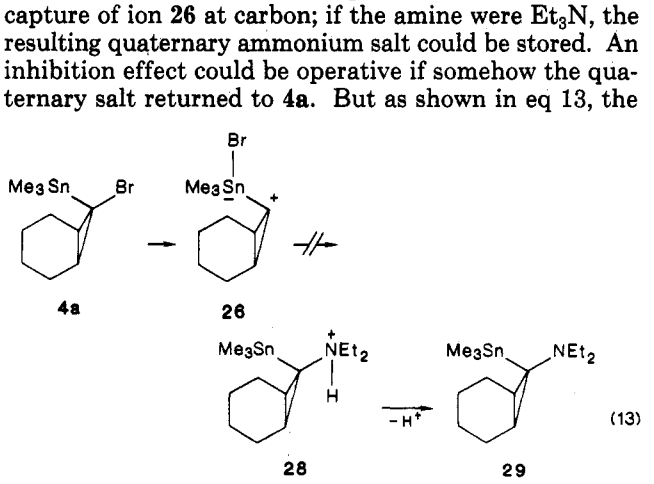



(12)

$$k_{obs} = \frac{k_1}{1 + K_C[\text{amine}]}, \quad K_C = k/k'$$

have to be "stored" as a complex, **25**, even though tin does not apparently form stable ate complexes unless strongly electron-donating and electron-withdrawing groups are in the apical positions.[6] In the event (see Results, part D), using **12a**, no analogue of **25** was observed by $^1H$ NMR, although $K_C$ for **12a** would be 11 ± 3 $M^{-1}$, and the complex should have predominated over **12a**, were it to have been formed.

Thus another mechanism for amine inhibition must be found. Since amines are nucleophilic, one should consider capture of ion **26** at carbon; if the amine were $Et_3N$, the resulting quaternary ammonium salt could be stored. An inhibition effect could be operative if somehow the quaternary salt returned to **4a**. But as shown in eq 13, the




(13)

use of $Et_2NH$ would have inevitably led to new product **29**, which *was not the case*. And since $Et_2NH$ also acted as an inhibitor, amine capture at carbon must be dismissed.

Although unorthodox, we propose that the amine attacks *tin* by nucleophilic displacement by bromide from ylide **26**. Certainly amines are more electron-releasing than bromine, so the conversion of **26** to **27** should be exothermic. It may also benefit from the possibility that the incoming amine may occupy the more favorable axial

(7) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 588.

(8) (a) Cristol, S.; Sequeira, R.; DePuy, C. *J. Am. Chem. Soc.* **1965**, *87*, 4007. (b) Su, T. Ph.D. Dissertation, Princeton University, 1970, pp 148–177.

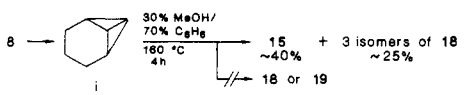
(9) (a) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. (b) For the close similarity between the electron-donating properties of $Me_3Si$ and $Me_3Sn$ as measured by $\sigma$ values, see: Reynolds, W. F.; Hamer, G. K.; Bassindale, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971.

(10) The $\alpha$-methyl effect for cyclopropyl tosylate was measured, and from the close similarity of the $k_{OTs}/k_{Br}$ ratios for cyclopropyl and *endo*-7-norcaryl, it is deduced that the $\alpha$-methyl effect would be about the same for *endo*-7-norcaryl as for cyclopropyl.

(11) The $k_{OTs}/k_{Br}$ ratio for *exo*-7-norcaryl closely resembles that for 2-adamantyl. The latter shows an $\alpha$-methyl rate effect of 3.3 × $10^7$.[12]

(12) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.

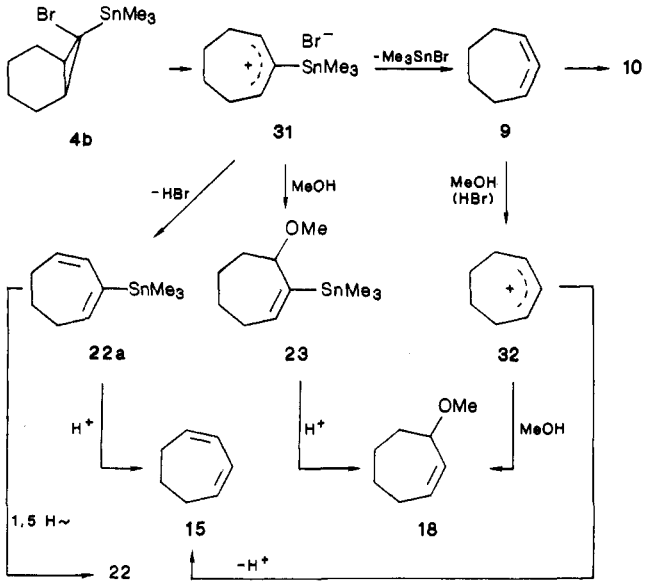
(13) (a) The small amounts of **15** and **18** could have arisen from leakage of ylide **26** (to **33** and then) to the cycloheptenyl system, **31**; from a small amount of ring opening of **8** to **9**; or from i. Thus i is known[14] to be a product from **8** at lower temperatures in MeOH, where it is a minor product. But i would not survive our reaction conditions;[13b] in our hands, i gave ~40% **15** and ~25% of three $C_8H_{14}O$ isomers (not **18** or **19**; possibly 4-methoxycycloheptene and the 2-methoxynorcaranes) upon heating (GC-MS analyses). Thus **15** (2%), but not **18** (3%), could have come from **8** via i. In any event, the hierarchy of reactivities is such that ring-opening of **8** to **9** is competitive with trapping by cyclohexene but not with trapping by methanol. (b) Wiberg, K. B.; Szeimies, G. *Tetrahedron Lett.* **1968**, 1235.



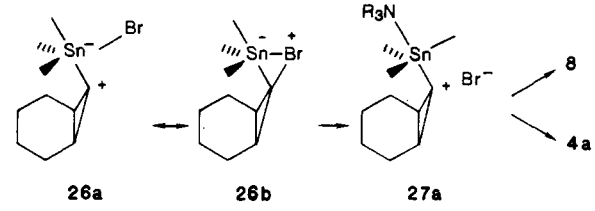

(14) (a) Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1857. (b) To avoid confusion, it should be noted that i is a *major* product when 7,7-dibromonorcarane is treated with alkyllithiums[14c]—but these are *carbenoid* reactions.[14d] (c) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019. (d) Warner, P. M.; Herold, R. D. *J. Org. Chem.* **1983**, *48*, 5411.

(15) The trivial possibility that **19** arises from the solvolysis of destannylation product **20** was dismissed via the appropriate control experiment.

**Scheme II**




position[5] on tin, while the outgoing bromine may be equatorial in **26** [from which position, however, it can more



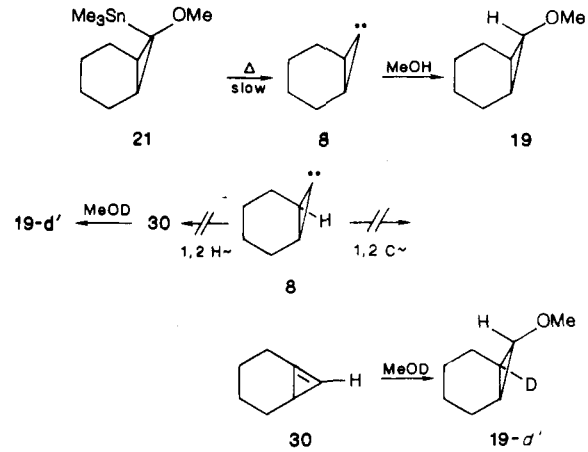

easily stabilize the positive charge on carbon by either a field effect or bridging (see **26a**, **26b**, **27a**)]. Ion pair **27** may partition among return to **4a** (*inhibition*), methanol capture to **21**, and (possibly) formation of carbene **8**.

The kinetic inhibition effect is very important.[16] Since no new intermediate (such as **25**) was seen to build up, inhibition must involve capture of a steady-state intermediate formed *after the rate-determining step*, leading to return to starting **4a**. Amine-mediated transformation of **26** to **27** and then to **4a** satisfies this requirement. On the other hand, direct formation of **27** from **4a** in competition with concerted loss of $Me_3SnBr$ to give carbene **8** *does not lead to inhibition* (but rather to rate acceleration due to formation of **21**), *and is, therefore, excluded.*

The observation of amine inhibition across all solvents studied argues for an ionic process in all cases. We note that **26** does not give **21**. This may argue for the importance of **26b** or similar shielding of carbon from nucleophilic attack.

Whether **27** gives carbene **8** (either of short-dashed arrows in Scheme I) cannot be ascertained. The increase in yield of **21** with increasing methanol concentration (Table III) indicates that **27** is a branch point in terms of product formation. But competitive return (to **4a**) and capture (to **21**) fulfills this mechanistic requirement.

The observed isotope effects ($k_H/k_D$, Table IV, eq 10, 11) are also consistent with Scheme I. In the absence of $Et_3N$, the isotope effect is appropriate for **8**,[17] while in the presence of $Et_3N$ it is intermediate between that for **8** and that for protolysis of **21** (eq 10). Note that the small amount of **19** formed from **21** in the absence of $Et_3N$ shows an isotope effect, indicating that it was formed via **8** (eq 14). Lastly, the MeOD-produced deuterium labeling pattern in **19** (deuterium at $C_7$) allows the elimination of the pathways shown in eq 15.[18]



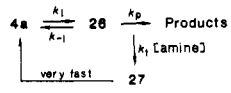

Now, we turn to the mechanistic significance of the products produced from **4b** in the presence of methanol. Since **4b** gives no **19**, it cannot be a source of carbene **8** at all. Yet dimer **10**, from 1,2-cycloheptadiene (**9**), is the major product. Clearly **9** must be arising via a ring-opening process not involving **8**. The only available one is the expected cyclopropyl to allyl cation type (**4b** to **31**, Scheme II; $Br^-$ could be attached to tin in **31**), and this is consistent with the aforementioned rate increase seen for **4b** in methanol (Table III, last column).

In the absence of $Et_3N$, **15**, **18**, and **10** are the major products. We doubt that **15** and **18** are formed primarily via **22a** and **23**, since the addition of $Et_3N$ serves mainly to enhance the yield of **9** (**10**) at the expense of **15** and **18**.[19] Also, the majority of **15** and **18** cannot come from solvolysis of protodestannylation product **16** for two reasons: (a) if $Et_3N$ buffers **4b** against destannylation, then a significant rate effect of $Et_3N$ on **4b** ought to be seen, as protolytic destannylation (without $Et_3N$) should proceed at a different rate than solvolysis of **4b** (in the presence of $Et_3N$)–but cf. Table V, entry 8; (b) if **15** and **18** were formed via **16**, then **16** should have built up significantly, since the rate of loss of **4b** was ca. $16 \times 10^{-4}$ $s^{-1}$, while a separate experiment showed that **16** disappeared about 7 times more slowly (**16** does give **15** and **18** upon solvolysis).

Thus we see the major route to **15** and **18** as going via **32**, where $Et_3N$ prevents protonation of **9** (by a catalytic amount of HBr formed from **32**). This may explain why increased [MeOH] has very little effect on the product yields (Table III); the route via **9** is not very susceptible to kinetic intervention by methanol. Importantly, separate experiments established that **15** and **18** did not arise from **10**.

Notably, the observation of some **22** and **23** in the presence of $Et_3N$ (eq 9) means that **31** does have available the reaction channels to **22a** and **23**. One unrealized expectation is that increased amine concentration might alter the **22**:**23**:**9** ratio in favor of **22** (see Table II, last two en-

(16) Steady-state kinetic analysis for part of Scheme I illustrates results.



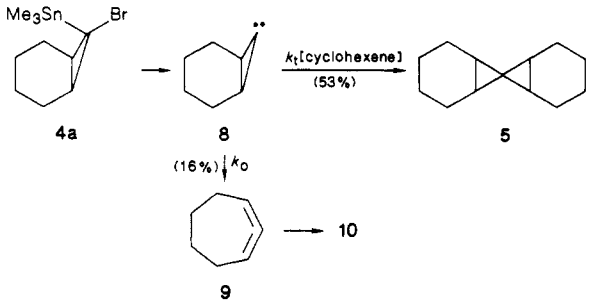

$k_{obsd} = A/(1 + B[amine])$, where $A = k_i k_p/(k_{-1} + k_p)$ and $B = k_t/(k_{-1} + k_p)$ and where $k_i$ is rate-determining

(17) We will soon publish our investigations of the isotope effects for the insertion of **8** into various alcohols over a large temperature range (Chu, I.-S., unpublished).

(18) Oku, A.; Harada, K.; Yagi, T.; Shirahase, Y. *J. Am. Chem. Soc.* **1983**, *105*, 4400.

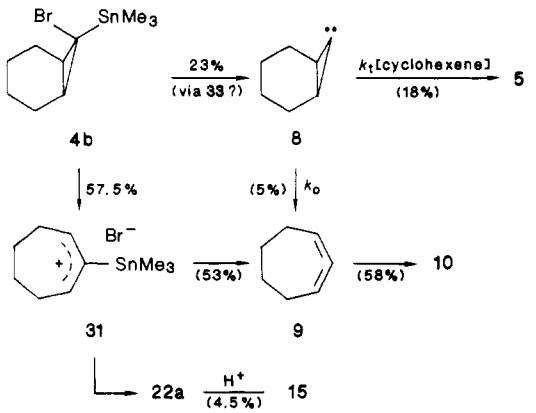
(19) Note the lack of $Et_3N$ inhibition of **4b**; $Et_3N$ capture of **31** cannot regenerate **4b**.

**Scheme III**[a]




[a] $k_o/k_t \cong 3$.

**Scheme IV**



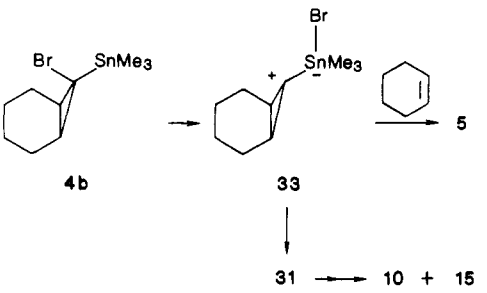

tries). Possibly there are different ion pairs involved in the production of **9**, **22a**, and **23**.

**B. Hydrocarbon Solvents.** Since **4a** yields almost solely carbene **8** in methanolic benzene, there is no reason to think it does otherwise in benzene or cyclohexene (i.e., if methanol does not intercept **26**, cyclohexene and benzene certainly will not). Thus the ratio of olefin adduct **5** to allene dimer **10** may be viewed as the partitioning of carbene **8** between intermolecular capture and ring-opening. While we are still pursuing temperature and [olefin] dependence studies, we can currently say that at 162 ± 2 °C, $k_o/k_t \simeq 3$ (see Scheme III, where [cyclohexene] $\simeq$ 10 M). In benzene, **8** undergoes solely ring-opening.

The reaction paths for **4b** in cyclohexene and benzene are less clearcut. If the adduct **5** were formed solely via **8**, then, based on the partitioning of **8** from **4a**, the pathways would be as shown in Scheme IV. Thus **8** must give only 30% as much **9** as **5** (16%/53%); thus only 5% of **9** can come from **8** in Scheme IV. The remainder, 53%, plus the **15**, must arise via a different route, namely the cationic one (**31**). In all, then, **4b** would partition 57.5% via the cationic pathway and 23% via the carbene pathway, the latter perhaps via direct, synchronous $Me_3SnBr$ extrusion or via a cyclopropyl cation ylide (**33**) which is somewhat slow to open[20] in the less polar cyclohexene.

There are (at least) two other possibilities which avoid the formation of **8** from **4b** (in strict analogy to the situation in methanolic benzene). The first, a bimolecular, rate-determining reaction between **4b** and cyclohexene, seems unreasonable. However, a reaction between ylide **33** and cyclohexene—a carbenoid reaction—seems possible, if unlikely (Scheme V). A potential way to distinguish between **8** and **33** is to study the stereochemistry of the adducts from **4a** and **4b** with an unsymmetrical olefin;[21]

**Scheme V**




the results of such experiments will be reported in due course. A priori, however, it is difficult to see why, if **26** gives **8**, **33** should not.

Lastly, the chemistry of **4b** in benzene must be mechanistically similar to that in cyclohexene—namely mainly, or solely, cationic ring-opening to **9** via **31**.

## Conclusion

We have probed the mechanism of the thermal decomposition of the two epimers of **4**, which is the one system for which Seyferth[1] observed net divalent carbon transfer. Even in nonpolar solvents, the endo isomer (**4b**) reacts primarily (or solely) via an ionic, noncarbenic process. The exo isomer (**4a**) reacts via initial carbon–bromine heterolysis (to give an ylide), followed by $Me_3SnBr$ loss to give norcaranylidene (**8**). The effect of strong Lewis acids (e.g., $SnCl_4$) and especially the inhibitory capabilities of amines support this mechanistic view of the chemistry of **4a**.

The other 1-bromo-1-(trimethylstannyl)cyclopropanes studied by Seyferth,[1] for which allenes were the products, must have reacted chiefly or solely by an ionic ring-opening mechanism (they represent solvolytically more reactive species than **4b**). Only when cyclopropyl cationic ring-opening is greatly impeded can carbene formation be expected.[22] We are continuing our investigation of such cases.

## Experimental Section

**General.** Infrared spectra were recorded on a Beckman IR-4250 or Acculab 2 spectrophotometer. The 90-MHz $^1H$ NMR spectra were obtained on a JEOL FX-90Q spectrometer, the 100-MHz $^1H$ NMR spectra on a Varian HA-100 spectromter, and the 300-MHz $^1H$ NMR spectra on a Bruker WM-300 or a Nicolet NT-300 spectrometer, using the solvents indicated and tetramethylsilane as the internal standard. "NMR yield" refers to a yield measured by 60-MHz $^1H$ NMR integration of the compound relative to a known amount of an internal standard. $^{13}C$ NMR spectra were recorded on a Bruker HX-90, a JEOL FX-90Q, or a Bruker WM-300 spectrometer, as indicated. The GC-MS studies were conducted on a Finnegan 4023 GLC mass spectrometer, and the high resolution mass spectra were measured on an AEI MS 902 mass spectrometer. Analytical GC studies were conducted on a Varian 3700 gas chromatograph. "Corrected GC yield" refers to a yield measured by GC integration of a compound relative to a known amount of an internal standard, with the appropriate correction factors applied.

The following GC columns were used for GC-MS studies: A, DB-1 glass capillary; B, 1.5 ft × 2 mm, 3% OV-101 on Supelcoport, glass; C, SE-30 glass capillary.

The following GC column was used for analytical GC studies: D, 12 ft × 2 mm, 3% OV-1 on Chromosorb W, glass.

**Preparation of *anti*-7-Bromo-*syn*-7-(trimethylstannyl)-bicyclo[4.1.0]heptane (4a) and *syn*-7-Bromo-*anti*-7-(trimethylstannyl)bicyclo[4.1.0]heptane (4b).** Compounds **4a** and **4b** were prepared by the procedure described by Seyferth.[1]

Starting with 0.50 g (1.98 mmol) of 7,7-dibromobicyclo-[4.1.0]heptane, we obtained 0.23 g of crude product. Purification

(20) Reese, C. B.; Stebles, M. R. D. *Tetrahedron Lett.* **1972**, 4427.
(21) Cf. Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; p 288–289.
(22) Runge, A.; Sander, W. *Tetrahedron Lett.* **1986**, *27*, 5835.

via preparative TLC on silica gel (hexane) afforded a 25% yield of **4b** ($R_f$ 0.73) and a 34% yield of **4a** ($R_f$ 0.63).

**Pyrolysis of 4a and 4b in Benzene-$d_6$ Solution. 1. 4a.** A 4.8-mg sample of **4a** was dissolved in 0.29 mL of benzene-$d_6$ and placed in an NMR tube. After the tube had been flushed with argon for 2 min, it was sealed under nitrogen and then fully immersed in a preheated oil bath (162 ± 2 °C). After 90 min, the NMR yield of trimethyltin bromide was 81%, and that of recovered starting material was 19%. Also obtained was a 78% corrected GC yield of tricyclo[7.5.0.0$^{2,8}$]tetradeca-1(14),2-diene (**10**), based on unrecovered starting material. A trace (<<1% yield) of *anti*-7-bromo-bicyclo[4.1.0]heptane (**20**) was also identified by comparison of its GC retention time and GC-MS with those of an authentic sample.

**2. 4b.** A 4.3-mg sample of **4b** was similarly reacted. After 120 min, the NMR yield of trimethyltin bromide was 77%, and that of recovered starting material was 23%. The products (corrected GC yields, based on unrecovered starting material) were **10** (77%), *syn*-7-bromobicyclo[4.1.0]heptane, **16** (1%), and cyclohepta-1,3-diene, **15** (9%). Compounds **15** and **16** were both identified by comparison of their GC retention times and GC-MS data with those of authentic samples.

**3. Isolation of the Allene Dimer, Tricyclo[7.5.0.0$^{2,8}$]tetradeca-1(14),2-diene (10).** A 117.3-mg crude sample of **4** (isomeric ratio ca. 1:1) was dissolved in 2 mL of benzene, placed in a test tube, sealed under nitrogen, and heated at 162 ± 2 °C for 240 min. Product **10** ($R_f$ 0.71) was isolated by preparative TLC on silica gel (hexane) in 35% yield. Its NMR spectrum matched the literature spectrum.[1]

**Pyrolysis of 4a and 4b in the Presence of DPIBF. 1. 4a.** A 32-mg (0.09 mmol) sample of **4a** and 26 mg (0.10 mmol) of 1,3-diphenylisobenzofuran (DPIBF) were dissolved in 0.3 mL of benzene-$d_6$. The sample was degassed, sealed under nitrogen in an NMR tube, and then fully immersed in a preheated oil bath at 162 °C for 264 min. NMR analysis showed that the starting material had been ca. 95% converted to trimethyltin bromide and adduct **17**. GC-MS (column A) analysis of **17** showed two peaks in a 6:1 ratio. While the major one showed a weak parent ion, the highest mass fragment observed for the minor isomer corresponded to $P^+ - H_2O$. As expected, no GC-MS peaks for dimer **10** or trimers of **9** were observed.

After the crude product mixture had been air-oxidized for 24 h (in order to transform the unreacted DPIBF to the easily separable 1,2-dibenzoylbenzene), **17** ($R_f$ 0.61) was isolated by preparative TLC on silica gel (10% ether/90% hexane) in 30% yield, as a white solid. (The low yield was probably due to decomposition during the air oxidation.) GC analysis showed that, of the two DPIBF adducts which had been detected in the crude product mixture, only the major one was present in this purified sample. On the basis of spectral comparisons with the reported values,[3] the major isomer of **17** was assigned the endo configuration.

**2. 4b.** Compound **4b** (27 mg) was similarly pyrolyzed in the presence of DPIBF (26 mg). The product mixture was identical by NMR and GC with that obtained above from **4a**. The isolated yield of **17** was again 30%.

**Pyrolysis of 4a and 4b in Cyclohexene Solution. 1. 4a.** Cyclohexene was purified by distillation from sodium benzophenone ketyl and was then stored over sodium, under argon, in a refrigerator.

A 5-mg sample of **4a** was dissolved in 0.26 mL of cyclohexene. The sample was briefly flushed with nitrogen and then sealed under nitrogen in an NMR tube. Next, the tube was fully immersed in a preheated 162 ± 2 °C oil bath. After 360 min of heating, the NMR yield of trimethyltin bromide was 98%, and that of recovered starting material was ca. 0%. Also obtained were the cyclopropanation product **5** and allene dimer **10** (eluted in that order from columns A, B, or C), which were identified by comparison of their GC retention times and GC-MS data with those of authentic samples. Their corrected GC yields were 53% and 16%, respectively.

**2. 4b.** A 4-mg sample of **4b** was similarly pyrolyzed in 0.26 mL of cyclohexene. After 357 min of heating at 162 ± 2 °C, the NMR yield of trimethyltin bromide was 61%, and that of recovered starting material was 36%. Also identified by comparison of their GC retention times and GC-MS data with those of authentic samples were **15**, **5**, and **10**. Their corrected GC yields were 4.5%, 18%, and 58%, respectively, based on unrecovered starting material.

**3. Isolation of the Cyclopropanation Product (5).** A 66-mg sample of a 1.8 to 1 mixture of **4a** and **4b** was pyrolyzed in 0.3 mL of cyclohexene to ca. 100% conversion of the starting material. Preparative TLC on silica gel (hexane) afforded a 25% isolated yield of **5** ($R_f$ 0.88).

**Pyrolysis of 4a and 4b in Methanolic Benzene-$d_6$ Solution. 1. 4a.** A 5-mg sample of **4a** was dissolved in 0.36 mL of 27% methanol/73% benzene-$d_6$ (by volume) in an NMR tube. The sample was briefly flushed with nitrogen and then sealed under nitrogen. Next, the tube was fully immersed in a preheated oil bath and heated at 162 ± 2 °C. After a total of 90 min of heating, the NMR yield of trimethyltin bromide was 75% and that of recovered starting material was 25%. Also identified (by comparison of their GC retention times and GC-MS data with those of authentic samples) were (listed in their order of elution from columns A, B, and C): **15**, **18**, **19**, **20**, **21**, and **10** in corrected GC yields of 2%, 3%, 80%, 2%, ≪1%, and <1%, respectively.

The identity of **19** was established by similarly heating two 14-mg samples of **4a** to 100% and 91% conversion of starting material, respectively. After combination of the two samples, and evaporation of the solvent, **19** was the only product detectable in the crude NMR spectrum. Its identity was verified by comparison of its NMR spectrum and GC retention time with those of an independently prepared sample.[23]

**2. 4b.** A 4-mg sample of **4b** was dissolved in 0.32 mL of 29% methanol/71% benzene-$d_6$ (by volume) and pyrolyzed as above. After 30 min of heating at 162 ± 2 °C, the NMR yield of trimethyltin bromide was 94% and that of recovered starting material was 6%. After another 60 min of heating, the starting material was completely consumed. Also identified (listed in their order of elution from either column A or D) were **15**, **18**, and **10** in corrected GC yields of 27%, 25%, and 25%, respectively.

The identity of **18** was established by heating a 64-mg sample of **4b** in 2 mL of 30% methanol/70% benzene (by volume) in a sealed tube at 162 ± 2 °C for 70 min and then isolating **18** in 7% yield (the low yield was due to the volatility of the product) by preparative TLC on silica gel (10% ether/90% hexane, $R_f$ 0.6). Compound **18** was identified by comparison of its GC retention time and NMR spectrum with those of an independently prepared sample.[24]

**Pyrolysis of 4a and 4b in Methanolic Benzene-$d_6$ in the Presence of Triethylamine. 1. 4a.** A 5-mg (0.016 mmol) sample of **4a** was dissolved in 0.29 mL of 31% methanol/69% benzene-$d_6$ (by volume), along with 0.017 mmol of triethylamine (previously purified by distillation from potassium hydroxide). The sample was then pyrolyzed in a sealed NMR tube at 162 ± 2 °C. After 1140 min, the NMR yield of recovered starting material was 40% and that of trimethyltin bromide was 51%. Also detected (listed in their order of elution from columns A and D) were **15**, **18**, **19**, **20**, **21**, and **10** in corrected GC yields of 1%, 1%, 58%, 8%, 15%, and <1%, respectively, based on unrecovered starting material. (Note that compounds **18** and **19** were separable only on a capillary GC column).

For the isolation of **21** (*anti*-7-methoxy-*syn*-7-(trimethylstannyl)bicyclo[4.1.0]heptane), pyrolyses were run with 14, 29, and 30 mg of **4a**. Each sample was dissolved, along with 1.1 equiv of triethylamine, in 0.4 mL of 63% to 73% methanolic benzene-$d_6$ and then pyrolyzed in a sealed NMR tube at 162 ± 2 °C. After the starting material was approximately 65% consumed, each tube was opened. The pyrolysates were combined and subjected to purification via preparative TLC on silica gel (10% ether/90% hexane). Compound **21** ($R_f$ 0.64) was isolated in 14% yield, based on unrecovered starting material. The low isolated yield was due to its volatility. 300-MHz $^1$H NMR, Nicolet NT-300 ($C_6D_6$): δ 3.02 (s, 3 H), 1.80 (m, 2 H), 1.55 (m, 2 H), 1.28 (m, 2 H), 1.1 (m, 2 H), 0.99 (m, 2 H), 0.32 (s, with Sn satellites, 9H). A 2D NOE experiment demonstrated that there was a substantial NOE between the trimethylstannyl protons and the exo cyclohexyl ring protons but *none* between the methoxy protons and the exo

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cyclohexyl ring protons, thus allowing the stereochemical assignment. $^{13}C$ NMR ($C_6D_6$): $\delta$ 72.3 (relative intensity, 70), 55.6 (184), 22.4 (433), 22.1 (460), 21.9 (517), −6.9 (242). 70-eV MS (Finnegan GC-MS, column D), $m/e$ (relative intensity): FPTC (first peak of a $^{120,118,116}Sn$ cluster) at 290 ($P^{120Sn}$, 0.01), FPTC at 275 ($P^{120Sn}$ − 15, 0.39), FPTC at 245 ($P^{120Sn}$ − 45, 0.37), FPTC at 165 ($Me_3Sn^+$, 14), 125 (P − $Me_3Sn$, 100), 93 (P − $Me_3Sn$ − MeOH, 27). Anal. Calcd for $C_{11}H_{22}SnO$: 290.0693. Found: 290.0707.

**2. 4b.** A 4-mg (0.012 mmol) sample of **4b** and 0.014 mmol of triethylamine were dissolved in 0.29 mL of 32% methanol/68% benzene-$d_6$ (by volume) and pyrolyzed in a sealed NMR tube. After the sample had been heated at 162 ± 2 °C for 12 min, the NMR yield of recovered starting material was 17%, and that of trimethyltin bromide was 70%. Also identified (listed in their order of elution from columns A and D) were **15**, **22** (tentatively identified as two isomeric (trimethylstannyl)cyclohepta-1,3-dienes, in a 1.3 to 1 ratio), **23** (3-methoxy-2-(trimethylstannyl)cycloheptene), and **10** in corrected GC yields of 3%, 4%, 3%, and 65%, respectively, based on unrecovered starting material. (The GC correction factor for **22** was assumed to be the same as that measured for **21** and **23**.

The isomers of **22** were tentatively identified by GC-MS; based on mechanistic considerations and their degree of unsaturation, other structures are implausible. There were two GC peaks (peak A and peak B) associated with **22**: 70 eV MS (Finnegan GC-MS, column A) for peak A, $m/e$ (relative intensity): FPTC at 258 ($P^{120Sn}$, 1.9), FPTC at 243 ($P^{120Sn}$ − 15, 10.3), 93 (P − $Me_3Sn$, 100); for peak B: FPTC at 258 ($P^{120Sn}$, 1.1), FPTC at 243 ($P^{120Sn}$ − 15, 8.0), 93 (P − $Me_3Sn$, 100).

Compound **23** had the same retention time (column D) and mass spectrum as an independently synthesized sample (see below). Interestingly, the mass spectra of **21** and **23** are very distinct from each other.

**Preparation of 1-(Trimethylstannyl)-7-methoxycycloheptene (23).** In a 25-mL three-necked round-bottom flask equipped with magnetic stirring bar, addition funnel, serum cap, and static Ar inlet was placed a solution 50 mg (0.25 mmol) of **24** in 10 mL of dry THF. The addition funnel was charged with a solution of 54 mg (0.27 mmol) of $Me_3SnCl$ in 5 mL of dry THF. The flask was cooled to −105 °C (Skellysolv B/liquid $N_2$ slush bath), after which 0.15 mL (0.29 mmol) of a 1.9 M *n*-BuLi/hexane solution was syringed dropwise down the side of the flask over a 1-min period, with stirring. The resulting yellowish solution was stirred for an additional 20 min, whereupon the $Me_3SnCl$ solution was added dropwise over a 1-min period. After another 5 min at −105 °C, the solution was allowed to warm to room temperature.

After quenching with a few drops of water and concentration in vacuo to ca. 1 mL, the solution was added to 25 mL of ether. After washing with saturated $NH_4Cl$ solution and saturated NaCl solution, drying ($MgSO_4$), filtration, and concentration in vacuo, **23** was obtained in 34% yield: 60-MHz $^1H$ NMR ($CCl_4$) $\delta$ 0.02 (s, with Sn satellites, 9 H), 0.8–2.3 (m, 8 H), 3.30 (s, 3 H), 3.78 (m, 1 H), 5.83 (td, 1 H, $J_{2,3}$ = 6 Hz, $J_{2,7}$ = 2.5 Hz); 70-eV MS (column A), $m/e$ (relative intensity) FPTC at 275 ($P^{120Sn}$ − 15, 22.1, P not observed), FPTC at 245 ($P^{120Sn}$ − 45, 40.3), FPTC at 165 ($Me_3Sn^+$, 14.3), 151 (SnOMe, 71.7), 125 (P − $Me_3Sn$, 16.1), 95 (36.4), 93 (P − $Me_3SnOMe$ − H, 100). Anal. Calcd for $C_{10}H_{19}SnO$ (P − 15): 275.0458. Found: 275.0459.

**Pyrolysis of Allene Dimer 10 in Methanolic Benzene-$d_6$ in the Presence of 0.1 Equiv of Hydrogen Bromide.** A sample of **10** was prepared by pyrolyzing 4.5 mg of **4a** in 0.30 mL of benzene-$d_6$, as described above; after 180 min at 162 ± 2 °C, the corrected GC yield of **10** was 75%.

To $^3/_4$ of this crude benzene-$d_6$ solution of **10** was added a solution of 0.001 mmol of hydrogen bromide (48% aqueous hydrobromic acid) in 0.10 mL of absolute methanol. The resulting solution (30% methanol/70% benzene-$d_6$ by volume) was sealed in an NMR tube, under nitrogen, and heated, fully immersed in an oil bath, at 162 ± 2 °C for 30 min. At this time, the pH of the solution was still ca. 2, as it had been before the pyrolysis. The corrected GC yield of **10**, based on **4a**, was now 49%. The loss of ca. 35% of the **10** during the heating with hydrogen bromide was probably due to acid-catalyzed polymerization. Importantly, there was no detectable amount of either **15** or **18** in the product mixture.

**Table VI. GC-MS Data for Fully Deuteriated and Undeuteriated Samples of 19, at 20 eV**

| source | int. of $m/e$ 125 | int. of $m/e$ 126 | int. of $m/e$ 127 | int. of $m/e$ 128 |
|---|---|---|---|---|
| **19**, undeuteriated[a] | 7.646 $(P-1)^H$ | 100.000 $P^H$ | 9.131 $(P+1)^H$ | 0.549 $(P+2)^H$ |
| **19**, fully deuterated | 1.621 $(P-2)^D$ | 7.629 $(P-1)^D$ | 100.000 $P^D$ | 8.918 $(P+1)^D$ |

[a] The P − 2 peak at $m/e$ 124 (0.095) was taken as negligible.

**Pyrolysis of 4a in MeOD; Kinetic Isotope Effects.** The deuterium incorporation in **19** was determined by heating a 9-mg sample of **4a** in 0.35 mL of 29% MeOD (99.5+ atom % D)/71% benzene-$d_6$ (by volume) at 162 ± 2 °C to 85% conversion. NMR analysis indicated deuterium incorporation solely at $C_7$ of **19**. GC-MS analysis of this sample, and of an undeuterated sample, indicated that this sample incorporated 100% of one deuterium atom, to within the detection limits of the mass spectrometer (see Table VI). The $(P+1)^D/P^D$ ratio was 0.0892, which is very close to the natural abundance ratio of 0.0891.

Kinetic isotope effects were determined via GC-MS analyses of samples of **19** generated in MeOH/MeOD mixtures, where the % D incorporations were determined by comparison with the fully deuteriated and undeuteriated MS results. Then,

$$\frac{k_H}{k_D} = \frac{\%\ \text{H in } \mathbf{19}}{\%\ \text{D in } \mathbf{19}} \times \frac{[\text{MeOD}]}{[\text{MeOH}]}$$

**Rate Measurements.** Rates were followed by $^1H$ NMR with either $CH_2Br_2$ added as an internal standard or the $Me_3SnBr$ produced used as a standard. In the latter case, an assumption of 100% yield of $Me_3SnBr$ was necessary. This was often the case, or close enough to be preferable to adding something to the reaction mixture which might have affected the rates.

The first-order rate constants and their uncertainties were calculated via a nonlinear least squares analysis program.

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**Registry No. 4a**, 43131-25-5; **4b**, 43131-22-2; **12a**, 88243-90-7; **12b**, 88243-89-4; **19**, 2988-67-2; **19**-$d_{14}$, 112461-15-1; **21**, 112461-11-7; **22** (isomer 1), 112461-12-8; **22** (isomer 2), 112461-13-9; **23**, 112461-14-0; **24**, 68861-56-3; $Me_3SnCl$, 1066-45-1.