

cleophilic enolate **4** would serve in the relatively unexplored role of an electrophile in the above reaction. Indeed, when the epoxy enolate **4** ( $G = \text{Li}$ ) was treated with  $\text{Me}_2\text{CuLi}$  and the resulting product subjected to acidic hydrolysis, 6-methylcyclohex-2-enone (**8**,  $R = \text{Me}$ ), the product of  $\text{S}_{\text{N}}2'$  attack, was obtained in 65% yield, free of any regioisomeric product. That the regiochemical course ( $\text{S}_{\text{N}}2$  vs.  $\text{S}_{\text{N}}2'$ ) of this addition can be cleanly controlled by the type of organometallic reagent used was demonstrated by the reaction of the same epoxy enolate **4** ( $G = \text{Li}$ ) with methylolithium which provided, after acidic workup, only the product of  $\text{S}_{\text{N}}2$  addition, i.e., 2-methylcyclohex-2-enone (**3**,  $R = \text{Me}$ ) in 99% yield.<sup>13</sup>

Further synthetic and mechanistic aspects of this chemistry are reflected, in part, in Table I. In general, it is seen that organocuprate reagents, irrespective of their hybridization, react in an  $\text{S}_{\text{N}}2'$  fashion with both epoxy enol ethers and epoxy enolates, while the corresponding organolithium and organomagnesium reagents react with the enolates to provide the products resulting from an  $\text{S}_{\text{N}}2$  mode of attack. Of particular note in the latter group is the reaction of the lithium enolate of *tert*-butyl acetate with **4** ( $G = \text{Li}$ , Scheme I; cf. Table I, entry 14) which provides the basis for a convenient solution to the hydroxymethylene lactone problem associated with numerous natural products which exhibit cytotoxic activity.<sup>14</sup>

Several important substrate related variations are also revealed in the tabulated data and support studies. In general, this methodology is applicable to five- and six-membered ring systems. However, the change from cyclic to acyclic epoxy enolate substrates reveals an important mechanistic feature in that the latter, as evidenced in the case of the enolate of mesityl oxide epoxide, failed to react. Presumably, counterion coordination by the bidentate substrate results in an unfavorable orbital alignment between the enolate  $\pi$  system and the allylicly disposed carbon-oxygen bond.<sup>15</sup> Variations in the leaving group can also be made (e.g., entries 18-22) although, once again, the acyclic system is unreactive if the group, such as benzoyloxy, can strongly coordinate the counterion. However, with a halide group, and presumably other weakly or noncoordinating groups, both acyclic and cyclic systems (i.e.,  $\alpha$ -halo ketone enolates) function equally well as enolonium ion equivalents. Finally, it is synthetically noteworthy that the group on oxygen can be widely varied. Thus, in addition to enolates and silyl enol ethers, the readily prepared enol phosphates<sup>7</sup> function as particularly effective substrates for cuprate reagents (Table I, entry 11). Since reduction of the hydroxy enol phosphate product **11** provides only *trans*-4-methylcyclohex-2-enol (**12**), the epoxy ketone functionality serves, through this chemistry, as a readily available cycloalkadiene monoepoxide equivalent whose reactions are stereo- and regio-

controlled. This regioselectivity is contrasted by the reaction of the parent cyclohexadiene monoepoxide with  $\text{Me}_2\text{CuLi}$  which provides allylic alcohol **12** as well as the product of  $\text{S}_{\text{N}}2$  opening in a nearly regiorandom manner.<sup>6a,b</sup>

In summary, this chemistry provides a convenient source of enolonium ion, dienolonium ion, and diene monoepoxide equivalents which service a number of important objectives in synthesis.<sup>16</sup> Further studies on this fundamentally novel enolate chemistry are in progress.

**Acknowledgment.** This investigation was supported by Grant CA 21136, awarded by the National Cancer Institute.

(16) It is noteworthy that this method also allows for regiospecific generation of enolates as demonstrated by the trapping of **5** ( $G = \text{M} = \text{Li}$ ) as its bis(trimethylsilyl) ether.

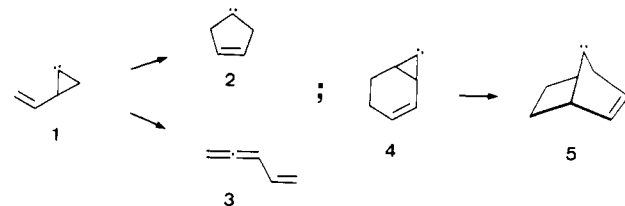
### Temperature Dependence of Carbene-Carbene Rearrangements. A New Method for the Generation of Carbenes<sup>1</sup>

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Among carbene-carbene rearrangements with a skeletal reorganization of the type **1**  $\rightarrow$  **2**,<sup>2</sup> the 7-norcar-2-enylidene-7-norbornenylidene rearrangement **4**  $\rightarrow$  **5**<sup>3</sup> is the least understood.



This reaction, discovered by Skattebøl,<sup>3</sup> is known to give *syn*-7-bromo-7-methylnorbornene (**6**) on treatment of 7,7-dibromonorcar-2-ene (**7**) with methylolithium at  $-78^\circ\text{C}$  as nearly the exclusive product. The mechanism for the stereoselective formation of **6** is still unsettled.<sup>4</sup> This rearrangement has recently been reinvestigated.<sup>5,6</sup> The decomposition of potassium *anti*-7-norcar-2-enylidene<sup>5</sup> and 7-*exo*-norcar-2-ene-*N*-nitrosoarene<sup>6</sup> in methanol gave *anti*-7-methoxynorbornene and *endo*-2-methoxytricyclo[4.1.0.0<sup>3,7</sup>]heptane which probably derive from the 7-norbornenyl cation thought to arise from protonation of the re-

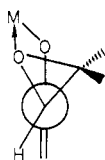
(11) The enol ether spectrum was recorded in THF at 25.2 MHz at ambient temperature. The enolate was prepared in a manner similar to that used for its reactions with organometallic reagents. The enolate showed only an insignificant temperature dependence of its chemical shifts from  $-60$  to  $-20^\circ\text{C}$ .

(12) (a) House, H. O.; Prabhu, A. U.; Phillips, W. V. *J. Org. Chem.* **1976**, *41*, 1209. (b) Jackman, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954. (c) Meyer, R.; Gorrichon, L.; Maroni, P. *J. Organomet. Chem.* **1977**, *129*, C7. (d) Lauterbur, P. G. *Tetrahedron Lett.* **1961**, 274.

(13) The *trans*-3-hydroxy-2-methylcyclohexanone<sup>4a</sup> can be isolated by column chromatography with some loss due to dehydration.

(14) (a) Chavdarian, C. G.; Woo, S. L.; Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1976**, 1769. (b) Grieco, P. A.; Nishizawa, M.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* **1976**, *98*, 1612. (c) Danishefsky, S.; Schuda, P. F.; Kitahara, T.; Etheredge, S. J. *Ibid.* **1977**, *99*, 6066. (d) Kiecznykowski, G. R.; Schlessinger, R. H. *Ibid.* **1978**, *100*, 1938. (e) Iio, H.; Isobe, M.; Kawai, T.; Goto, T. *Ibid.* **1978**, *100*, 1940.

(15) A reasonable representation of the unreactive chelated epoxy enolate is depicted below. Geometrical constraints preclude the formation of such chelated structures for the cyclic epoxy enolates.



(1) Carbene Rearrangements, part 7. Part 6: Brinker, U. H.; König, L. *J. Am. Chem. Soc.* **1981**, *103*, 212.

(2) (a) Skattebøl, L. *Chem. Ind. (London)* **1962**, 2146. (b) Kirmse, W. *Org. Chem. (N.Y.)* **1971**, *1*, 465. (c) Baird, M. S.; Reese, C. B. *Tetrahedron Lett.* **1976**, 2895. (d) Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; pp 159-165. (e) Holm, K. H.; Skattebøl, L. *Tetrahedron Lett.* **1977**, 2347. (f) Butler, D. N.; Gupta, I. *Can. J. Chem.* **1978**, *56*, 80. (g) Schoeller, W. W.; Brinker, U. H. *J. Am. Chem. Soc.* **1978**, *100*, 6012. (h) Brinker, U. H.; Fleischhauer, I. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 396. (i) Jäggi, F. J.; Ganter, C. *Helv. Chim. Acta* **1980**, *63*, 214. (j) Schleyer, P. v. R.; Grubmüller, P.; Maier, W. F.; Vostrowsky, O.; Skattebøl, L.; Holm, K. H. *Tetrahedron Lett.* **1980**, 921. (k) Jones, W. H. *Org. Chem. (N.Y.)* **1980**, *42*, Chapter 3. (l) Brinker, U. H.; Fleischhauer, I. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 304.

(3) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107.

(4) However, for a related system see: (a) Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 3981. (b) *Ibid.* **1979**, 4141.

(5) Holm, K. H.; Skattebøl, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480.

(6) Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1873.

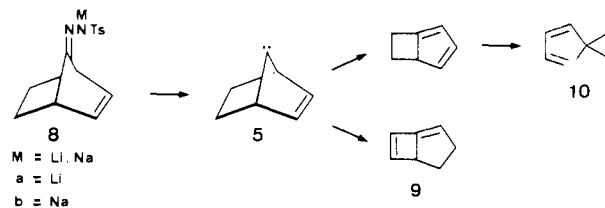
Table I. Product Distribution from Decomposition of 7, 8a, 8b, 11, and 12

compd	T, °C	P, torr	conditions	9	10	0.3	2.7	3.8	1.0	93	93.5	14.7	6.6	20.5	29.9	60.1	37	66	67.6	55.9	yield, 9+10	9:10	total isolated yield, %	ref
7	0		MeLi <sup>a</sup> 1.1 M ether	0.5	0.5				1.0						1.0						1.0	1:1	95	c
12	0		MeLi <sup>a</sup> 1.1 M ether	0.5	1										1.5						1.5	1:2	95	c
11	265-275	5 × 10 <sup>-3</sup>	gas phase	1	0.1			3.8							1.1						1.1	10:1	8 <sup>b</sup>	c
			hot tube																					
7	100	5 × 10 <sup>-3</sup>	MeLi <sup>a</sup> on glass turnings	25.1	4.8				0.3			14.7			29.9						29.9	5.2:1	55	c
12	100	5 × 10 <sup>-3</sup>	MeLi <sup>a</sup> on glass turnings	47.5	12.6							6.6		20.5	60.1						60.1	3.8:1	90	c
8a	190	5 × 10 <sup>-2</sup>		33.5	3.5										37						37	9.6:1	50	7a,b
8b	180			56	10										66						66	5.6:1	80	7c
8a	275	1.5-4.5 × 10 <sup>-4</sup>		62.4	5.2			0.3							67.6						67.6	12:1	70	c
8b	275	1.5-4.5 × 10 <sup>-4</sup>		51	4.9										55.9						55.9	10.4:1	60	c

<sup>a</sup> Made from CH<sub>3</sub>Br and lithium. <sup>b</sup> Only hydrocarbons. <sup>c</sup> This work.

arranged carbene 5.<sup>5,6</sup> Furthermore, the reaction of a compound containing 7 as a structural subunit with methyl lithium at 0 °C has been reported.<sup>4</sup> The formation of the product corresponding to 6 has been attributed to a mechanism involving carbenium ions, thus bypassing a carbene-carbene rearrangement of the type 4 → 5.

Moss,<sup>7</sup> however, found that 7-norbornenylidene (5), generated by Bamford-Stevens reaction of the lithium salt of the corresponding tosylhydrazone (8a) at 190 °C, affords hydrocarbons 9 and 10 (Table I). In stark contrast to this, the aforementioned



reactions all have in common that 9 and 10,<sup>8</sup> the typical products expected from the rearranged carbene 5, are totally missing.

We report here that (1) indeed 9 and 10 are formed from the decomposition of three different precursors (7, 11, 12) in yields up to 60%. (2) The reaction of 1, generated from two different precursors, shows a temperature dependence, i.e., the reaction becomes more selective with higher temperature.<sup>9</sup> From the temperature-dependent product ratios of the reaction of 1,<sup>10</sup> the difference of the enthalpy of activation  $\Delta\Delta H^\ddagger$  and the entropy of activation  $\Delta\Delta S^\ddagger$  of the competing cyclopropylidene-allene (1 → 3) and carbene-carbene rearrangement (1 → 2) has been determined. (3) A new method was developed in order to generate 1, 4, and 5 from the respective geminal dibromides in a "gas phase" at temperatures between 24 and 170 °C.

7-Bromo-7-(trimethyltin)norcar-2-ene (11)<sup>11</sup> was synthesized in 60–65% yield from 7<sup>3</sup> via metalation (MeLi, THF, -100 °C) followed by addition of trimethyltin chloride at -90 °C<sup>12</sup> (Scheme I). The ratio of the stereoisomers of 11 (98:2) was determined by VPC. Crystallization from pentane left over the main isomer<sup>11</sup> (mp 4.5–6 °C) of unknown stereochemistry. 7,7-Dibromonorbornene (12)<sup>11</sup> was prepared from 7,7-dimethoxynorbornene<sup>13</sup> in 40% yield by reaction with boron tribromide.<sup>14</sup>

Reaction of 7 with methyl lithium in ether at 0 °C gave as reported<sup>3</sup> nearly exclusively 6. However, minor amounts of 7-bromonorcar-2-ene (two isomers; ca. 1%) and 9 and 10 (ca. 1%) could be detected. The presence of 12-crown-4-ether or *N,N,N',N'*-tetramethylethylenediamine did not increase the yield of 9 and 10.<sup>4,15</sup> Likewise, the reaction of 7,7-dibromonorbornene (12) with methyl lithium at 0 °C yielded only small amounts of 9 and 10.<sup>16</sup> However, due to the instability of 9 under the reaction

(7) (a) Moss, R. A.; Dolling, U. H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, 931. (b) Moss, R. A.; Dolling, U. H. *Ibid.* **1972**, 5117. (c) Murahashi, S. I.; Okumura, K.; Maeda, Y.; Sonoda, A.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2420.

(8) There is implicit proof for the formation of 10 from bicyclo[3.2.0]-hepta-1,3-diene. Hamer, N. K.; Stubbs, M. E. *Tetrahedron Lett.* **1972**, 3531. Oda, M.; Breslow, R. *Ibid.* **1973**, 2537.

(9) A similar finding was noticed in a different reaction: Brinker, U. H.; Streu, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 631.

(10) (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125. (b) Giese, B.; Meister, J. *Ibid.* **1978**, *17*, 595. Giese, B.; Lee, W. B.; Meister, J. *Liebigs Ann. Chem.* **1980**, 725.

(11) Satisfactory elemental analyses were obtained on all new compounds. Selected spectral data are as follows. 11: mp 4.5–6 °C (pentane); <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.2 (s, 9 H,  $J^{117,119}\text{Sn-H} = 52\text{--}55$  Hz, Me<sub>3</sub>Sn), 1.5–2.4 (m, 6 H), 5.45–6.2 (m, 2 H); IR (CCl<sub>4</sub>) 3020, 2980, 2920, 1640, 1450, 1190, 1070 cm<sup>-1</sup>. 12: mp 60–61 °C (pentane); <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.95–1.3 (m, 2 H), 2.1–2.5 (m, 2 H), 3.1–3.3 (m, 2 H), 6.1 (t, 2 H); IR (CCl<sub>4</sub>) 3070, 2980, 2950, 1325, 710 cm<sup>-1</sup>. 13: (two isomers) <sup>1</sup>H NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.15 (s, 9 H), 0.2 (s, 9 H), 0.8–1.7 (m, 2 H), 1.8–2.3 (m, 1 H), 4.8–6.0 (m, 3 H); IR (CCl<sub>4</sub>) 3080, 2980, 2920, 1635, 1440, 1195, 910 cm<sup>-1</sup>.

(12) (a) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1973**, *55*, C53. (b) Seyferth, D.; Lambert, R. L., Jr.; Massol, M. *Ibid.* **1975**, *88*, 255.

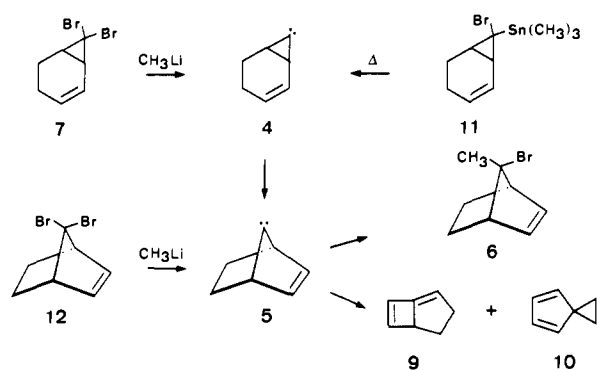
(c) Seyferth, D.; Lambert, R. L. *Ibid.* **1975**, *91*, 31.

(13) Gassman, P. G.; Marshall, J. L. *Org. Synth. Coll.* **1973**, *5*, 424.

(14) Benton, F. L.; Dillon, T. E. *J. Am. Chem. Soc.* **1942**, *64*, 1128.

(15) Moss, R. A.; Pilkwicz, F. G. *J. Am. Chem. Soc.* **1974**, *96*, 5632.

Scheme I



conditions in solution, the very low yield of **9** found from **7** and **12** has to be regarded as a minimum.

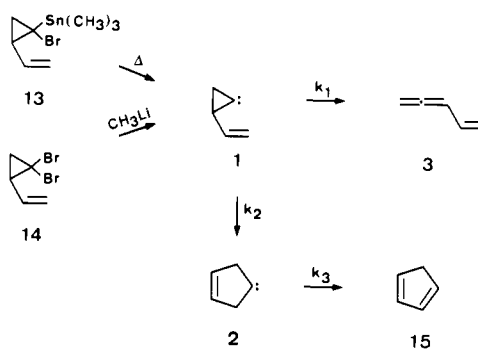
When pyrolyzing the tin compound **11** in the gas phase (flow) at temperatures between 265 and 275 °C, only small portions of **9** and **10** were found<sup>17</sup> (Table I). The high temperature required for the decomposition of **11** turned out to be the major drawback of this method. Thus, when **9** was subjected to the pyrolysis conditions employed, only traces of it "survived" while **10** proved to be stable.

However, when **7** was passed in vacuo through a glass tube, filled with glass turnings coated with methyl lithium<sup>18,19</sup> and heated between 24 and 140 °C, the yield of **9** and **10** increased substantially, reaching a maximum of 30% (Table I). The yield of **9** and **10** in the "gas phase" even doubled to a remarkable 60% when solid **12** was sublimed into the same system in a temperature range of 60–125 °C (Table I). Thus for the production of **9** and **10**, our method is comparable to the Bamford–Stevens reaction of **8a,b** (Table I).

The ratios found for **9** and **10**, out of the reaction of **7** (115 ratios) and **12** (156) observed at different temperatures between 24 and 140 °C, point to a temperature dependence. At all temperatures migration of the ethano bridge<sup>8</sup> in **5** seems to proceed slower than the competing vinyl migration to **9**. With increasing temperature, the formation of **9** becomes slightly more selective [**7**, **9**:**10** (24 °C) 4.8:1; (140 °C) 5.4:1. **12**, (24 °C) 3.5:1; (120 °C) 4.0:1].

We wondered whether the reaction of the parent system **1** would exhibit a more pronounced temperature-dependent product ratio **3**:**15**. Scheme II shows our efforts with the parent system. Reaction of **14** with methyl lithium (1 equiv; THF, -110 °C) via metalation and treatment with trimethyltin chloride at -95 °C resulted in a mixture of both stereoisomers of **13**<sup>11</sup> (ratio 56:44 from VPC analysis) in 70% yield. Pyrolysis of **13** at 260 °C (0.005 torr) afforded the maximum yield (78%) of six hydrocarbons (at 220 °C ca. 3%, at 290 °C ca. 63%). Only 0.4% of cyclopentadiene could be detected which proved to be stable under the reaction conditions employed. Vinylallene (**3**) was by far the main product which, however, partly rearranged to four compounds (0.1–5%). Three of them could be identified as 1-penten-3-yne, *cis*-3-pen-

Scheme II



ten-1-yne and *trans*-3-penten-1-yne.<sup>20</sup> The structure of the remaining product was not determined. The temperature necessary to decompose **13** obviously was too high to produce **15** in quantities larger than a fraction of a per cent (vide infra).

Thus, **14** was treated with methyl lithium in solution according to the literature<sup>2a,3</sup> in the temperature range between -78 and +35 °C. At 35 °C difficulties arose due to polymerization of **3** and **15**. However, as with **7** and **12**, smooth decomposition took place when **14** was passed in vacuo (0.005 torr) between 24 and 130 °C through the "MeLi tube".<sup>18</sup> Over the whole temperature range the yield of **3** and **15** was rather constant with formation of the enines only in trace amounts. Also less than 1% of 1-bromo-2-vinylcyclopropanes<sup>21</sup> were formed everytime. At 104 °C 85% of **15** and **3** was found. There is a decrease of the ratio of **15**:**3** with increase of temperature, i.e., the formation of **3** becomes more selective with higher temperatures.

For a discussion of this phenomenon, two principle types of reactions for the formation of **3** and **15** from **14** have to be discussed. (1) **3** and **15** are formed from two different intermediates (not shown here). (2) **3** and **15** have a common intermediate (Scheme II). In both cases the ratio of **3** and **15** only depends on the ratio of the rate-determining constants  $k_1:k_2$ <sup>22</sup> (Scheme II). Therefore, from only the observed temperature dependence of the ratio **3**:**15**, a decision in favor of one of the two mechanistic alternatives (1 or 2) cannot be made. However, both the unpublished work of Skattebøl<sup>23</sup> and the present work favor a reaction path in which the vinylcyclopropylidene (**1**) is a common intermediate in the formation of **3** and **15**. The ratio  $\ln(k_1/k_2)$  can be expressed by the following equation.

$$\ln(k_1/k_2) = \Delta\Delta H^\ddagger / RT + \Delta\Delta S^\ddagger / R$$

$$k_1/k_2 = [\mathbf{3}]/[\mathbf{15}]$$

The ratios  $\ln k_1/k_2$  determined in solution<sup>24</sup> (4) as well as in the "gas phase" (34) [VPC analysis; 38 points at 28 temperatures (from -75 to +170 °C)] give a reasonably straight line with a correlation coefficient of  $r = -0.95$ ;  $\Delta\Delta H^\ddagger = 1.6$  kcal/mol  $\pm$  7%;  $\Delta\Delta S^\ddagger = 5.4$  cal/(mol K)  $\pm$  8%. At the isokinetic temperature ( $T_{is} \sim 30$  °C) equal amounts of **3** and **15** are formed in the reaction of **14**. The carbene-carbene rearrangement **1**  $\rightarrow$  **2** proceeds more easily at lower temperatures than the competing ring opening to the allene. However, at higher temperatures the entropy term is gaining decisive influence. Due to lesser sterical requirements, the ring opening to the allene is favored. This also explains the low yield of cyclopentadiene (**15**) found from the reaction of **13** at 260 °C.

(16) The reaction of 1,2,3,4,7,7-hexachloronorbornene with methyl lithium was found to give 1,2,3,4,7-pentachloro-7-anti-methylnorbornene as sole product. Alexander, R.; Davies, D. I. *J. Chem. Soc., Perkin Trans. I* 1973, 83.

(17) In contrast to our results, **9** and **10** were not detected in the flow pyrolysis of 7-anti-bromo-7-syn-(trimethyltin)norcar-2-ene (**11**) at 450 °C. Professor P. Warner, Iowa State University, personal communication.

(18) (a) The procedure of preparing the MeLi tube ( $l = 25$  cm,  $\phi = 2.5$  cm) for the reaction of **7** and **14**: Under argon atmosphere 35 g glass turnings ( $\phi = 4$  mm) and 20 mL of an ethereal solution of methyl lithium (1.4 M) were combined. The solvent was removed on a rotavapor at room temperature. The coated glass turnings were filled into the tube (argon!), which was then heated up externally while being connected to a pump. After ca. 12 h the ether had escaped and the final vacuum arrived at 0.005 torr. (b) For the decomposition of **12** a packed tube of 50 cm length was used. (c) Different MeLi tubes sometimes gave different product yields.

(19) The MeLi tube was used at temperatures between 24 and 170 °C. The upper limit resulted from the beginning of thermal decomposition of methyl lithium: Ziegler, K.; Nagel, K.; Patheiger, M. *Z. Anorg. Allg. Chem.* 1955, 282, 345.

(20) Brinker, U. H.; Preis, H.-G., unpublished results.

(21) In principle, 1-bromo-2-vinylcyclopropanes could give **3** and **15** in the reaction with methyl lithium. Boswell, R. F.; Bass, R. G. *J. Org. Chem.* 1975, 40, 2419. However, this proved not to be the case. Brinker, U. H., unpublished results.

(22) There is no reaction **2**  $\rightarrow$  **1**. Thus, on flash pyrolysis of the sodium salt of  $\Delta^3$ -cyclopentenone tosylhydrazone at 275 °C, no vinylallene (**3**) could be detected. Brinker, U. H.; Ritzler, J., unpublished.

(23) Brinker, U. H.; König, L. *J. Am. Chem. Soc.* 1979, 101, 4738, footnote 4.

(24) We thank Dipl. Chem. Ilona Fleischhauer for determining the ratios of **3**:**15** in solution.

In conclusion, our results suggest that the chemistry of **7** and **12** in solution is the chemistry of "carbene complexes"<sup>25</sup> affording nearly exclusively **6**, while in the "gas phase" the typical products of **5** become dominant.<sup>26</sup> Carbenoid chemistry the alkyl lithium way can be shifted toward chemistry expected from free carbenes with our new method. Thus, the geminal dibromides studied in the gas phase give higher yields of hydrocarbons—thought to stem from free carbenes—than in solution. In cases in which a tosylhydrazone cannot be synthesized, the decomposition of geminal dibromides may be an alternative to the Bamford-Stevens reaction. From the product ratios of vinylallene (**3**) and cyclopentadiene (**15**),  $\Delta\Delta H^\ddagger$  and  $\Delta\Delta S^\ddagger$  of the competing cyclopropylidene-allene and carbene-carbene rearrangement **1**  $\rightarrow$  **2** can be determined.

**Acknowledgment.** We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft. We thank K. Gomann for skillful experimental and technical assistance.

(25) Hoeg, D. F.; Lusk, D. I.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 4147.

(26) Seebachs' <sup>13</sup>C NMR experiments demonstrate that there is a smooth transition of carbenoids to carbenes: Seebach, D.; Siegel, H.; Müllen, K.; Hiltbrunner, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 844. Siegel, H.; Hiltbrunner, K.; Seebach, D. *Ibid.* **1979**, *18*, 845.

### Carbon-13 Magnetic Resonance Dipolar Spectroscopy. Orientation of the Chemical Shift Tensor in Cyclopropane

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Isotropic carbon-13 chemical shifts of methylenes in three-membered rings are well-known to be anomalously upfield ( $\sim 20$  ppm) from other aliphatic chemical shifts. Recently this laboratory reported the chemical shift tensor for the methylene in cyclopropene<sup>1</sup> (Table I), where it was found that the unusually high-field isotropic shift of 2.3 ppm from Me<sub>4</sub>Si was a consequence of only one component ( $\sigma_{33}$ ) appearing at a rather surprising high-field value of  $-59$  ppm from Me<sub>4</sub>Si. The other two components were found at typical aliphatic shielding values. We now find that cyclopropane also gives a similar result (Table I). To understand better these shielding phenomena, we undertook a study to determine the orientation of the shift tensor with respect to the molecular frame in cyclopropane. This is usually accomplished by analysis of spectral patterns<sup>2</sup> obtained from a single crystal in various orientations. The experimental difficulties associated with performing such an experiment on a small molecule like cyclopropane make this approach unappealing.

A <sup>13</sup>C cross-polarization (CP) spectrum of matrix-isolated cyclopropane containing a pair of adjacent carbon-13 nuclei will reflect the <sup>13</sup>C-<sup>13</sup>C dipolar coupling.<sup>3</sup> As both the splitting produced by the dipolar interaction and the chemical shift depend on the molecular orientation relative to the magnetic field, the

Table I. <sup>13</sup>C Shift Tensors for CH<sub>2</sub> in Cyclopropane and Cyclopropene<sup>a</sup>

	$\sigma_{\text{iso}}(\text{liq})$	$\sigma_{11}$	$\sigma_{22}$	$\sigma_{33}$
cyclopropane	-3.8	22	2	-36
cyclopropene <sup>b</sup>	2.3	40	29	-59

<sup>a</sup> All shifts in ppm from external Me<sub>4</sub>Si. Estimated errors  $\pm 2.5$  ppm. <sup>b</sup> Reference 1.

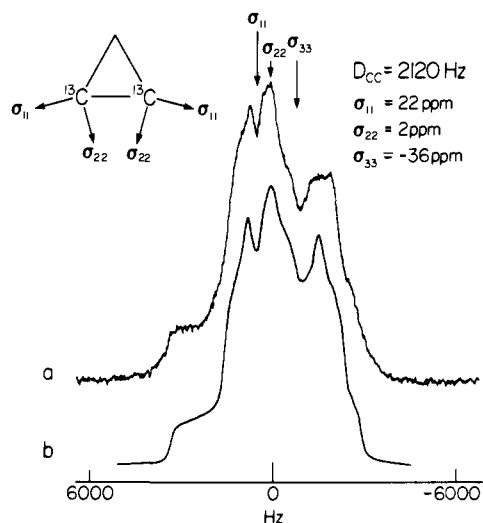
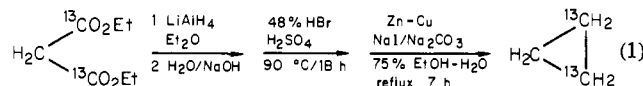


Figure 1. (a) Experimental <sup>13</sup>C spectrum taken at 20.12 MHz. (b) Simulation using the parameters in the inset.  $\sigma_{11}$  and  $\sigma_{22}$  are oriented on each carbon as shown.  $\sigma_{33}$  is perpendicular to the plane of the drawing. Note that when  $H_0$  is along one of the <sup>13</sup>C's, the other resonates at  $3/4\sigma_{22} + 1/4\sigma_{11}$ .

powder pattern produced will contain the information needed to relate the cyclopropane chemical shift tensor to the dipolar vector and thus the molecular frame.

Doubly <sup>13</sup>C-labeled cyclopropane for the matrix experiment was synthesized from diethyl malonate-1,3-<sup>13</sup>C (Merck and Co. Inc., 90 atom % <sup>13</sup>C) as outlined in the sequence of reactions in (1). The ring-closure step was accomplished by a specially activated Zn-Cu reagent.<sup>4</sup>



The principal axes of the <sup>13</sup>C chemical shift tensor are easily specified by the local C<sub>2v</sub> symmetry at the carbon nucleus<sup>5</sup> if intermolecular effects are taken to be negligible. Two axes are constrained to be perpendicular to the two mirror planes and the remaining axis must lie along the C<sub>2</sub> axis (Figure 1). It should be noted that the two <sup>13</sup>C nuclei in cyclopropane do not constitute a simple A<sub>2</sub> spin system in the solid state as the nuclei do not have the same shift at all possible orientations of the field with respect to the molecule because all of the principal shielding axes are not coparallel. When the difference in these resonant frequencies ( $\Delta\nu$ ) is comparable to the dipolar coupling, the spectrum becomes second order in the same sense as a typical AB system. For an AB dipolar coupled system the four transitions and concomitant transition probabilities for any one orientation are given by<sup>3</sup>

$$\nu_{a\pm}(\theta, \phi) = \frac{\nu_1 + \nu_2}{2} - \frac{A}{2} \pm C \quad P_{a\pm}(\theta, \phi) = 1 \pm B/C$$

$$\nu_{b\pm}(\theta, \phi) = \frac{\nu_1 + \nu_2}{2} + \frac{A}{2} \pm C \quad P_{b\pm}(\theta, \phi) = 1 \mp B/C$$

$$A = D(1 - 3 \cos^2 \theta) + J$$

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