cleophilic enolate 4 would serve in the relatively unexplored role of an electrophile in the above reaction. Indeed, when the epoxy enolate 4 (G = Li) was treated with Me_2CuLi and the resulting product subjected to acidic hydrolysis, 6-methylcyclohex-2-enone (8, R = Me), the product of $S_N 2'$ attack, was obtained in 65% yield, free of any regioisomeric product. That the regiochemical course $(S_N 2 \text{ vs. } S_N 2')$ 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 = Li) with methyllithium which provided, after acidic workup, only the product of $S_N 2$ addition, i.e., 2-methylcyclohex-2-enone (3, R = Me) in 99% yield.13

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 $S_N 2'$ 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 S_N2 mode of attack. Of particular note in the latter group is the reaction of the lithium enolate of tert-butyl acetate with 4 (G = 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.14

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 π system and the allylically disposed carbon-oxygen bond.¹⁵ 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., α -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 silvl enol ethers, the readily prepared enol phosphates⁷ function as particularly effective substrates for cuprate reagents (Table I, entry 11). Since reduction of the hydroxy enol phosphate product 11 provides only trans-4methylcyclohex-2-enol (12), the epoxy ketone functionality serves, through this chemistry, as a readily available cycloalkadiene monoepoxide equivalent whose reactions are stereo- and regio-

(13) The trans-3-hydroxy-2-methylcyclohexanone^{4a} 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) Kieczykowski, 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.

controlled. This regioselectivity is contrasted by the reaction of the parent cyclohexadiene monoepoxide with Me₂CuLi which provides allylic alcohol 12 as well as the product of S_N2 opening in a nearly regiorandom manner.^{6a,b}

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.¹⁶ 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 = M = Li) as its bis(trimethylsilyl) ether.

Temperature Dependence of Carbene–Carbene Rearrangements. A New Method for the Generation of Carbenes¹

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Received December 24, 1980

Among carbene-carbene rearrangements with a skeletal reorganization of the type $1 \rightarrow 2^{2}$, the 7-norcar-2-enylidene-7norbornenylidene rearrangement $4 \rightarrow 5^3$ is the least understood.



This reaction, discovered by Skattebøl,³ is known to give syn-7bromo-7-methylnorbornene (6) on treatment of 7,7-dibromonorcar-2-ene (7) with methyllithium at -78 °C as nearly the exclusive product. The mechanism for the stereoselective formation of $\mathbf{6}$ is still unsettled.⁴ This rearrangement has recently been reinvestigated.^{5,6} The decomposition of potassium anti-7norcar-2-enediazotate⁵ and 7-exo-norcar-2-ene-N-nitrosourea⁶ in methanol gave anti-7-methoxynorbornene and endo-2-methoxytricyclo[4.1.0.0^{3,7}]heptane which probably derive from the 7norbornenyl cation thought to arise from protonation of the re-

(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.; Skattebol, L. J. Am. Chem. Soc. 1977, 99, 5480.

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

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⁽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 °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.

⁽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 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, Chanter 3. (1) Rrinker, U. H.: Fleischhauer, I. Angew. Chem., Int. Ed. Engl. Chapter 3. (1) Brinker, U. H.; Fleischhauer, I. Angew. Chem., Int. Ed. Engl. 1980, 19, 304

| iotal Mated Md, % ref | <u>95 c</u> | 95 c | 8 ⁰ c | L | 55 C | 90 c | 50 7a,b | 80 7c | 70 c | 60 c | |
|-----------------------------|--------------------------------|--------------------------------|--------------------|----------|-------------------------------------|-------------------------------------|--------------------|------------|----------------------------|--------------------------|--|
| 9:10 yix | 1:1 | 1:2 | 10:1 | , c | 5.2:1 | 3.8:1 | 9.6:1 | 5.6:1 | 12:1 | 10.4:1 | |
| yield, 9 + 10 | 1.0 | 1.5 | 1.1 | | 29.9 | 60.1 | 37 | 6 6 | 67.6 | 55.9 | |
| H | | | | | | 20.5 | | | | | |
| CH3 BH | 93 | 93.5 | | | 14.7 | 9.9 | | | | | |
| | 1.0 | | | | 10.5 | | | | | | |
| $\overline{\mathcal{A}}$ | | | | | 0.3 | | | | | | |
| | | | 3.8 | | | | | | 0.3 | | |
| | | | 2.7 | | | | 0.8 | S | 1.1 | 0.9 | |
| | | | | | | 0.1 | 0.5 | 9 | 1.1 | 2.7 | |
| | | | | | | | 0.5 | | | | |
| a | 0.5 | 1 | 0.1 | | 4.8 | 12.6 | 3.5 | 10 | 5.2 | 4.9 | |
| | 0.5 | 0.5 | 1 | | 25.1 | 47.5 | 33.5 | 56 | 62.4 | 51 | ţk. |
| conditions | MeLi, ^a 1.1 M ether | MeLi, ^a 1.1 M ether | gas phase | hot tube | MeLi ^a on glass turnings | MeLi ^a on glass turnings | 1 | | | | nly hydrocarbons. ^c This wo |
| P, torr | | | 5×10^{-3} | | 5×10^{-3} | 5×10^{-3} | 5×10^{-2} | | 1.5-4.5 × 10 ⁻⁴ | $1.5-4.5 \times 10^{-4}$ | Ar and lithium. b O |
| T, °C | 0 | 0 | 265-275 | | 100 | 100 | 190 | 180 | 275 | 275 | e from CH, I |
| compd | - | 12 | 11 | | 2 | 12 | 8a | 8b | 8a | 8b | a Made |

arranged carbene 5.5,6 Furthermore, the reaction of a compound containing 7 as a structural subunit with methyllithium at 0 °C has been reported.⁴ 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,⁷ 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 10,8 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.⁹ From the temperature-dependent product ratios of the reaction of 1,¹⁰ the difference of the enthalpy of activation $\Delta \Delta H^{\dagger}$ and the enthropy of activation $\Delta \Delta S^*$ of the competing cyclopropylidene-allene (1 \rightarrow 3) and carbene-carbene rearrangement (1 \rightarrow 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)¹¹ was synthesized in 60-65% yield from 7³ via metalation (MeLi, THF, -100 °C) followed by addition of trimethyltin chloride at -90 °C¹² (Scheme I). The ratio of the stereoisomers of 11 (98:2) was determined by VPC. Crystallization from pentane left over the main isomer¹¹ (mp 4.5-6 °C) of unknown stereochemistry. 7,7-Dibromonorbornene (12)¹¹ was prepared from 7,7-dimethoxynorbornene¹³ in 40% yield by reaction with boron tribromide.¹⁴

Reaction of 7 with methyllithium in ether at 0 °C gave as reported³ nearly exclusively 6. However, minor amounts of 7bromonorcar-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 10.4,15 Likewise, the reaction of 7,7-dibromonorbornene (12) with methyllithium at 0 °C yielded only small amounts of 9 and 10.¹⁶ However, due to the instability of 9 under the reaction

(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); ¹H NMR (60 MHz, CCl₄) δ 0.2 (s, 9 H, J ^{117,119}Sn-H = 52–55 Hz, Me₃Sn), 1.5–2.4 (m, 6 H), 5.45-6.2 (m, 2 H); IR (CCl₄) 3020, 2980, 2920, 1640, 1450, 1190, 1070 cm⁻¹. 12: mp 60-61 °C (pentane); ¹H NMR (60 MHz, CCl₄) δ 1070 cm⁻¹. 12: mp 60-61 °C (pentane); ¹H NMR (60 MHz, CCl₄) 3
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 (CCl₄) 3070, 2980, 2950, 1325, 710 cm⁻¹. 13: (two isomers) ¹H NMR (60 MHz, CCl₄) δ 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 (CCl₄) 3080, 2980, 2920, 1635, 1440, 1195, 910 cm⁻¹. (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., Jr55, 131. (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 P. 4. - Piklewing: F. G. J. Am. Chem. Soc. 1974, 96, 5632.

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

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

^{(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.

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 found¹⁷ (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 methyllithium^{18,19} 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 bridge⁸ 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 methyllithium (1 equiv; THF, -110 °C) via metalation and treatment with trimethyltin chloride at -95 °C resulted in a mixture of both stereoisomers of 13^{11} (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-penCommunications to the Editor



ten-1-yne and *trans*-3-penten-1-yne.²⁰ 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 methyllithium in solution according to the literature^{2a,3} 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".¹⁸ 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-2vinylcyclopropanes²¹ 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 $k_1:k_2^{22}$ (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 Skattebøl²³ 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.

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

 $k_1/k_2 = [3]/[15]$

The ratios $\ln k_1/k_2$ determined in solution²⁴ (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; $\Delta\Delta H^* = 1.6$ kcal/mol \pm 7%; $\Delta\Delta S^* = 5.4$ 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 enthropy 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 methyllithium 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. 1 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.

Professor P. Warner, Iowa State University, personal communication. (18) (a) The procedure of preparing the MeLi tube $(l = 25 \text{ cm}, \phi = 2.5 \text{ cm})$ for the reaction of 7 and 14: Under argon atmosphere 35 g glass turnings $(\phi = 4 \text{ mm})$ and 20 mL of an ethereal solution of methyllithium (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 packet 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 methyllithium: 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 methyllithium. 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 Δ^3 -cyclopentenone tosylhydrazone at 275 °C, no vinylallene (3) could be detected. Brinker, U. H.; Ritzer, 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"²⁵ affording nearly exclusively 6, while in the "gas phase" the typical products of 5 become dominant.²⁶ Carbenoid chemistry the alkyllithium 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), $\Delta \Delta H^*$ and $\Delta \Delta S^*$ 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.

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

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Received November 18, 1980

Isotropic carbon-13 chemical shifts of methylenes in threemembered rings are well-known to be anomalously upfield (~ 20 ppm) from other aliphatic chemical shifts. Recently this laboratory reported the chemical shift tensor for the methylene in cyclopropene¹ (Table I), where it was found that the unusually highfield isotropic shift of 2.3 ppm from Me₄Si was a consequence of only one component (σ_{33}) appearing at a rather surprising high-field value of -59 ppm from Me₄Si. 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 patterns² 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 13 C cross-polarization (CP) spectrum of matrix-isolated cyclopropane containing a pair of adjacent carbon-13 nuclei will reflect the 13 C- 13 C dipolar coupling.³ 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. 13 C Shift Tensors for CH₂ in Cyclopropane and Cyclopropene^a

| | $\sigma_{iso}(liq)$ | σ11 | σ22 | σ33 | |
|---------------------------|---------------------|-----|-----|-----|--|
| cyclopropane | -3.8 | 22 | 2 | -36 | |
| cyclopropene ^b | 2.3 | 40 | 29 | -59 | |

^a All shifts in ppm from external Me₄Si. Estimated errors ± 2.5 ppm. ^b Reference 1.



Figure 1. (a) Experimental ¹³C spectrum taken at 20.12 MHz. (b) Simulation using the parameters in the inset. σ_{11} and σ_{22} are oriented on each carbon as shown. σ_{33} is perpendicular to the plane of the drawing. Note that when H_0 is along σ_{11} for one of the ¹³C'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 ¹³C-labeled cyclopropane for the matrix experiment was synthesized from diethyl malonate-1,3- ^{13}C (Merck and Co. Inc., 90 atom % ¹³C) as outlined in the sequence of reactions in (1). The ring-closure step was accomplished by a specially activated Zn-Cu reagent.⁴

The principal axes of the ¹³C chemical shift tensor are easily specified by the local $C_{2\nu}$ symmetry at the carbon nucleus⁵ 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_2 axis (Figure 1). It should be noted that the two ¹³C nuclei in cyclopropane do not constitute a simple A_2 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 by³

$$v_{a\pm}(\theta,\phi) = \frac{v_1 + v_2}{2} - \frac{A}{2} \pm C \qquad P_{a\pm}(\theta,\phi) = 1 \pm B/C$$
$$v_{b\pm}(\theta,\phi) = \frac{v_1 + v_2}{2} + \frac{A}{2} \pm C \qquad P_{b\pm}(\theta,\phi) = 1 \pm B/C$$
$$A = D(1 - 3\cos^2\theta) + J$$

(4) Hassner, A.; Krepski, L. R. J. Org. Chem. 1978, 43, 2879.
(5) Buckingham, A. D.; Malm, S. Mol. Phys. 1971, 22, 1127.

⁽²⁶⁾ Seebachs' ¹³C 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.

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Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. J. Am. Chem. Soc. 1980, 102, 6672.
 Pausak, S.; Pines, A.; Waugh, J. S. J. Chem. Phys. 1975, 59, 591.

⁽²⁾ Pausak, S.; Pines, A.; Waugh, J. S. J. Chem. Phys. 1975, 59, 591 (3) Zilm, K. W.; Grant, D. J. Am. Chem. Soc., in press.