Acknowledgment. I thank Paul Zinke and Dave Shubert for their capable assistance in the completion of this work and Martin Ashley for obtaining the spectra utilized to determine the stereo- and regiochemistry of the products. Acknowledgment is also made to the Research Corp., to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (GM 31013-02) for support of this research.

Note Added in Proof: Professor E. Negishi has informed us of their study of allylmetalations of alkynylsilanes. Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761.

Registry No. 1, 18925-10-5; **2a**, 3844-94-8; **2b**, 77113-48-5; **2c**, 2170-06-1; **2d**, 88083-69-6; **2e**, 62896-55-3; **2f**, 18387-60-5; **2g**, 14630-42-3; (*E*)-**4a**, 88083-70-9; (*Z*)-**4a**, 88083-71-0; (*E*)-**4b**, 88105-48-0; (*Z*)-**4b**, 88083-72-1; **4c**, 88083-73-2; **4d**, 88083-74-3; **4e**, 88083-75-4; **4f**, 88083-76-5.

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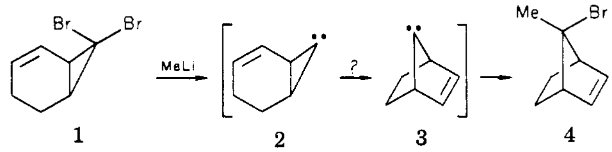
Skattebol-Type Rearrangement of Lithium Carbenoids at Low Temperatures

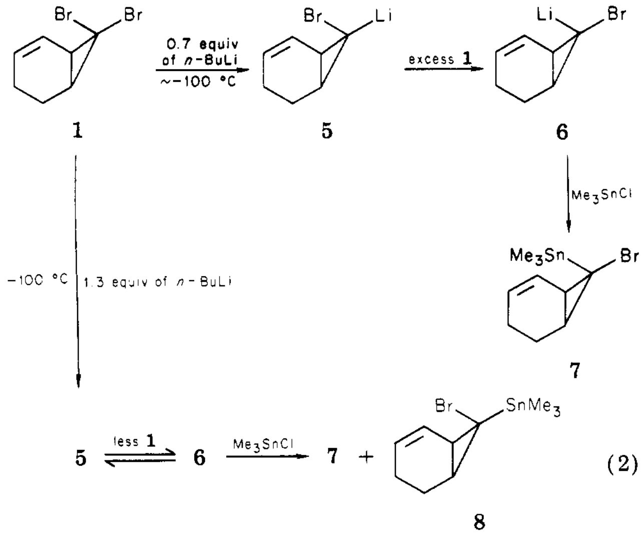
Summary: The Skattebol rearrangement of carbenoids with well-defined stereochemistry at low temperatures is discussed.

Sir: In contrast to the situation for carbonium ions, carbanions, and radicals, the direct rearrangement of one carbene to another has not been compellingly demonstrated.[1,2] Perhaps the earliest proposal of a direct carbene–carbene rearrangement involves the vinylcyclopropylidene to cyclpentenylidene rearrangement (Skattebol rearrangement), as exemplified in eq 1.[3] However, we[4] demonstrated, utilizing a tricyclic analogue of 1, that this rearrangement involves carbenoids rather than free carbenes. In 1981, Brinker[5] showed that passing 1 over MeLi-coated glass chips in the gas phase at ≥24 °C produced the same products as obtained from 3 generated from 7-norbornenyltosylhydrazone.[6] It may thus be tempting to conclude that 2 did indeed rearrange to 3. As is demonstrated herein, such need not be the case at all.



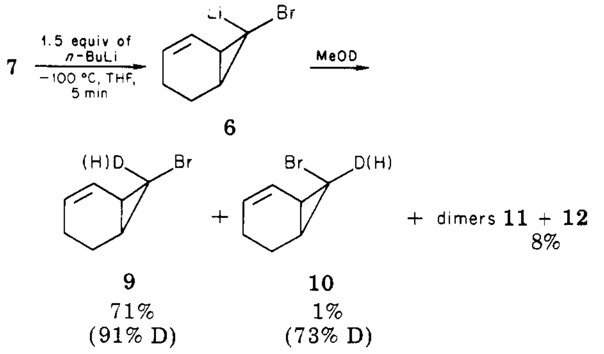
(1)

Our investigation of the carbenoids derived from 1 originated with the isomeric organotin compounds 7 and 8,[5,7] which were themselves made by stannylation of the lithiocarbenoids derived from 1 at ca. −100 °C. As shown (eq 2), the carbenoids present, as reflected by the stannanes formed, were dependent upon the conditions utilized. With a deficiency of n-BuLi (excess of 1), the initial carbenoid 5, was rapidly transformed into the more stable 6. When n-BuLi was present in excess, the 5 to 6 conversion became incomplete, thereby affording both 7 and 8. Importantly, this demonstrated that 6 is thermodynamically more stable than 5. This pattern is the same as Seyferth found for the saturated counterparts of 5 and 6.[7b]

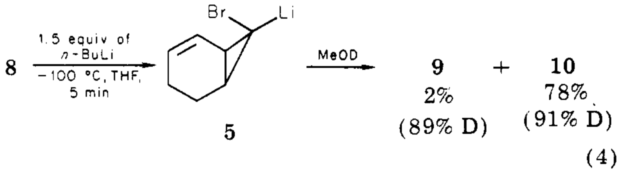


(2)

When 7 and 8 were separately treated with 1.5 equiv of n-BuLi/THF at ca. −100 °C for 5 min, followed by MeOD quenching, the products[8] were as shown in eq 3 and 4.[9]



(3)



(4)

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[1] For possible cases involving diazo precursors, see: (a) Kirmse, W.; Chiem, P. V.; Henning, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 1695. (b) Freeman, P. K.; Swenson, K. E. *J. Org. Chem.* **1982**, *47*, 2040. (c) Brinker, U. H.; Konig, L. *J. Am. Chem. Soc.* **1981**, *103*, 212. (d) Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1873. (e) Holm, K. H.; Skattebol, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480.

[2] (a) Jones' review[2b] cites two types of carbene–carbene rearrangements. In this context, we refer to what he calls type II. The type I, typified by the arylcarbene rearrangements, probably involves an intermediate between the two interconverting carbenes. (b) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.

[3] Skattebol, L. *Tetrahedron* **1967**, *23*, 1107.

[4] Warner, P.; Chang, S.-C. *Tetrahedron Lett.* (a) **1978**, 3981. (b) **1979**, 4141.

[5] Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116.

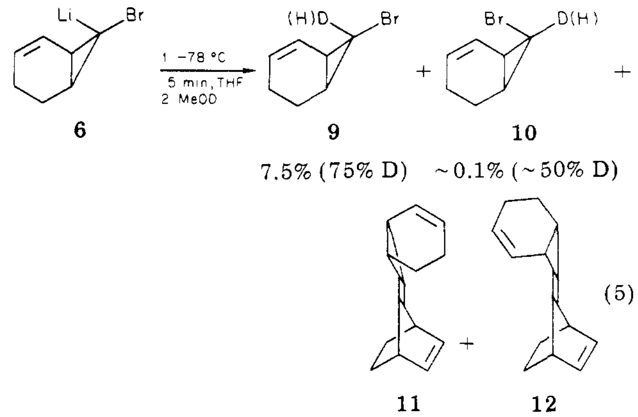
[6] (a) Moss, R. A.; Dolling, U. H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, 931. (b) Moss, R. A.; Dolling, U. H. *Ibid.* **1972**, 5117. (c) Murahashi, S. I.; Okumura, K.; Maeda, Y.; Sonoda, A.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2420.

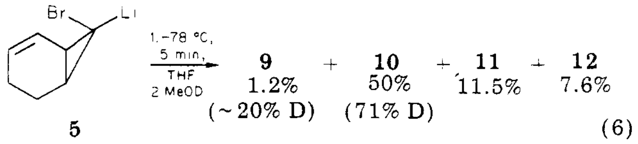
[7] (a) Besides spectroscopic structural evidence, 7 and 8 were separately hydrogenated to their known saturated counterparts.[6b] (b) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1975**, *88*, 287. (c) Seyferth, D.; Lambert, R. L., Jr., Massol, M. *Ibid.* **1975**, *88*, 255.

0022-3263/83/1948-5411$01.50/0

Although **6** rearranged slightly (perhaps via local heating), it is clear that **5** and **6** were both stereochemically stable at ~−100 °C. The percentage of H incorporation was probably due to the small amount of MeOH present in the MeOD, multiplied by a primary isotope effect.

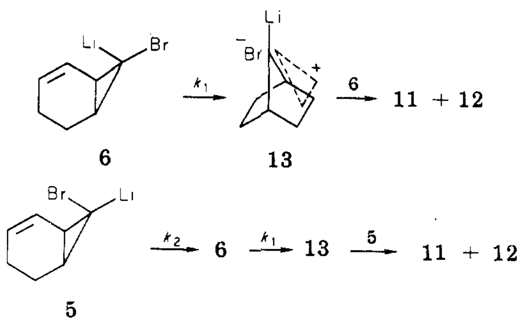
The key experiments involved generating solutions of **6** and **5** at −78 °C and allowing reaction for short time periods, followed by MeOD quenching. The results for 5-min reaction times (average of duplicate runs) are shown in eq 5 and 6. In addition, 3-min runs gave essentially the same results, while **5**, after 20 min at −78 °C, produced 33% dimers[10] (**11** and **12**) and 32% **10** (69 %D incorporation).[11]





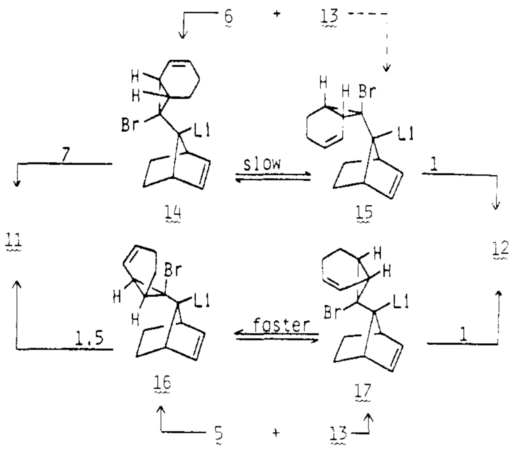
First, it is clear that **6**, although more stable than **5**, rearranges some 15 times faster. The only realistic interpretation for this is that the double bond participates effectively in **6** but not in **5**. Second, the different dimer distributions make it clear that **11** and **12** are products of carbenoid dimerization. If carbenes are to be invoked,[12] then a carbenoid to carbene to carbenoid sequence would be necessary and the less stable carbenoid must produce a carbene more slowly. The more economical explanation involves the sequence shown in Scheme I. Thus double bond participation aids ionization of bromine,[13] leading directly to the rearranged 7-lithio-7-norbornenyl ion pair[14] **13**, which electrophilically attacks **6** to product **11** and **12**. With **5**, epimerization most likely precedes ionic rearrangement; the resulting **13** now must attack **5** to produce **11** and **12**. Kinetic analysis of this scheme gives $k_1/k_2 = 14 \pm 1$.

Scheme I



Scheme II shows our explanation of the dimerization. When **13** attacks **6**, **14** is clearly more favorable than **15**, and elimination from **14** provides **11** predominantly (7:1). On the other hand, attack of **5** by **13** can give two sterically similar rotamers, **16** and **17**. These each eliminate with similar efficiency.

Scheme II



In conclusion, we have shown that Skattebol rearrangement of **1** proceeds through carbenoids with well-defined stereochemistry at −78 °C. From the data, we estimate $\Delta G^{\ddagger} \approx 13$ kcal/mol for the Skattebol rearrangement of **6** at −78 °C. It is reasonable to conclude, although it is not proven, that the higher temperature observations of Brinker[5] can be carbenoid; i.e., they may involve the rearrangement of **6** (formed on the MeLi-coated glass surface) to **13** (written covalently[14]), followed by the dissociation of **13** into LiBr and carbene **3**. Since **13** would be formed on a fixed surface, it would not be able to dimerize, as it otherwise does in THF solution.

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[8] In addition to the compounds shown, 0.5–3% of butylated and/or stannylated additional products were detected by GC/MS.

[9] Treatment of either **7** or **8** with BuLi/Et$_2$O at −95 °C, followed by MeI trapping, gave only methylated and butylated norbornenyl bromides and iodides (related to **4**).

[10] The structures of **11** and **12** were elucidated by the usual spectral and analytical techniques. The stereochemical distinction was made by 300-MHz NMR, where the olefinic protons of the norbornenyl moiety are separated by twice the amount in **11** ($\Delta\delta$ = 0.046 ppm) as in **12** ($\Delta\delta$ = 0.022 ppm).

[11] (a) This corresponds to a first-order rate only ca. $^1/_2$ that observed in the 3- and 5-min runs. This may be due to fast initial reaction due to local heating. (b) In all runs, 3–13% of other products were detected; these consisted of approximately 10 compounds.

[12] (a) We have studied carbenoid generation from the saturated counterpart of **1** at temperatures between −100 °C and 55 °C. As Köbrich concluded[12b] for the corresponding chlorocarbenoids, free carbenes are not in evidence to any appreciable degree. This conclusion is based on our use of Et$_3$SiH as a carbene trap. The saturated analogue of **1** gave no more than ~0.5% of silane insertion products, under conditions where CCl$_2$ was trapped in 63% yield. Furthermore, a large excess of Et$_3$SiH failed to trap carbene **3** during the reactions of **5** and **6**. It is thus unreasonable to postulate a mechanism for dimer formation involving the attack of **3** on **5** or **6**. (b) Köbrich, G.; Goyert, W. *Tetrahedron* **1968**, *24*, 4327.

[13] (a) Lest the reader balk at the idea of nucleophilic displacement of a cyclopropyl bromide, it should be noted that ^{13}C NMR evidence suggests a weak, highly polarized C–Br bond in cyclopropylcarbenoids.[13b] (b) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046.

[14] To emphasize the electrophilic nature of **13**, we have written it as an ion pair; it could also be written as a covalent material, with Br anti to the double bond.