undesirable β-epimers of both **10** and **12** were the kinetically preferred products we sought to establish conditions for epimerization. Thus warming of chromatographically pure β-**10** in THF containing *N,N*-diisopropylethylamine gave pure α-**10** (>95%). Finally 4-acetoxy-2-azetidinone (**13**)[14] was reacted with 2-methyl-3-buten-2-ol in the presence of zinc acetate in refluxing benzene[15] followed by *tert*-butyldimethylsilylation to produce **14** (36%). This was converted into **15** and subsequently **16** (67%) in the usual way. Cyclization of **16** proceeded smoothly in the presence of tetrabutylammonium fluoride and ozone to stereoselectively provide the oxadethiapenam **17**[15,16] (64%) accompanied by the C-2 epimer (14%).

The concise syntheses of **10**, **12**, and **17** using (phenylthio)nitromethane (**1**) are noteworthy in that the method is potentially of general utility in the construction of diverse bicyclic β-lactams containing the carboxylic acid moiety.[17] Both a detailed study of the stereochemistry of reaction and its extension to highly functionalized systems of biological interest are current objectives.

Acknowledgment. We thank the Atlantic Richfield Foundation, Northwestern University, and Pfizer Central Research for generous support.

Registry No. 1, 60595-16-6; 2, 69477-87-8; 3, 96746-22-4; 4, 92339-69-0; 5a, 5661-55-2; 5b, 96746-23-5; 6 (isomer 1), 96746-24-6; 6 (isomer 2), 96746-25-7; 7, 96746-26-8; 8, 96746-27-9; 9, 96746-28-0; 10 (isomer 1), 96746-29-1; 10 (isomer 2), 96746-30-4; 11a, 74373-13-0; 11b, 96746-31-5; 12 (isomer 1), 96746-32-6; 12 (isomer 2), 96746-33-7; 13, 28562-53-0; 14, 96746-34-8; 15, 96746-35-9; 16, 96746-36-0; 17 (isomer 1), 96746-37-1; 17 (isomer 2), 96746-38-2; potassium phthalimide, 1074-82-4; acetaldehyde, 75-07-0; 1,6-heptadiene, 3070-53-9; 2-methyl-3-buten-2-ol, 115-18-4.

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[14] Clauss, K.; Grimm, D.; Prossel, G. *Leibigs Ann. Chem.* **1974**, 539.

[15] Brown, A. G.; Corbett, D. F.; Howarth, T. T. *J. Chem. Soc., Chem. Commun.* **1977**, 359.

[16] Derivatives of the oxadethiapenam ring system are reported elsewhere. For examples, see ref 15 and Kobayshi, T.; Iwano, Y.; Hirai, K. *Chem. Pharm. Bull.* **1978**, *26*, 1761.

[17] Recently Hanessian has described the application of nitromethane in the synthesis of a penem. See: Hanessian, S.; Bedeschi, A.; Battistini, C.; Mongeli, N. *J. Am. Chem. Soc.* **1985**, *107*, 1438.

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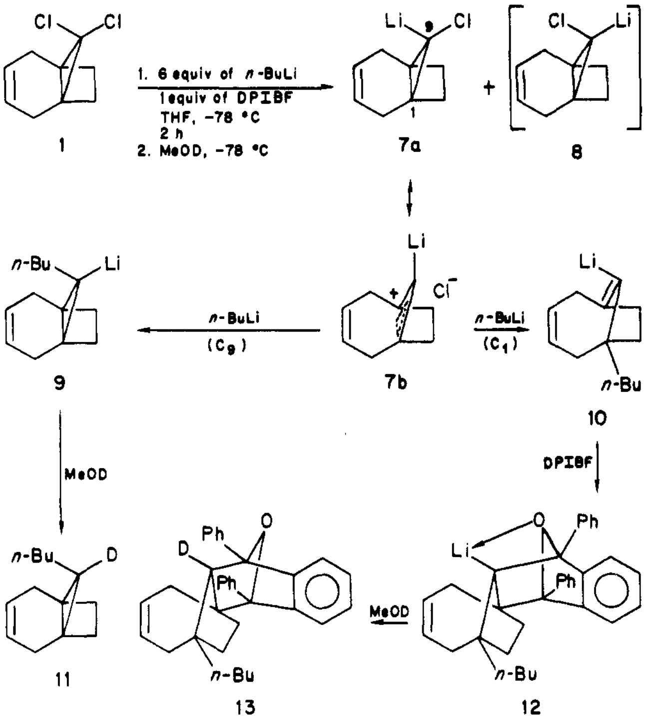
Electrophilic Carbenoids. Formation and Trapping of an Anti-Bredt Vinyllithium

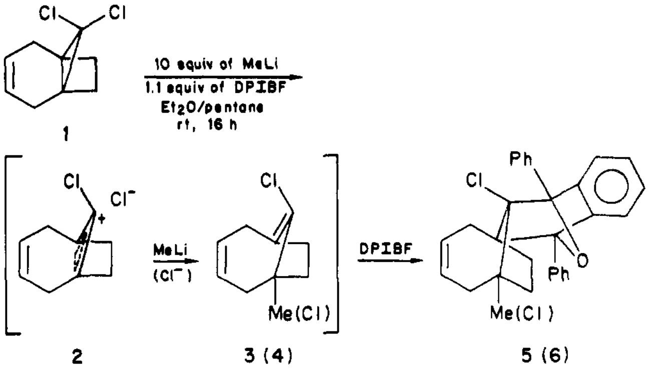
Summary: The reaction of 9,9-dichloro[4.3.1]propell-3-ene (**1**) with excess *n*-BuLi produces a lithium carbenoid which shows exceptional electrophilic reactivity, which includes reaction via cationic ring-opening to afford an anti-Bredt vinyllithium intermediate, **10**.

Scheme I



Sir: We[1] and others[2] have been intensely interested in the properties of bridgehead alkenes. The twisted π-bond structure thereby demanded might be stabilized by the polarizing effect of a lithium substituent. Calculationally,[3] two geminal lithiums lead to energetic equality between the planar and perpendicular olefin structural alternatives, while one lithium leads to a substantial decrease in the π-bond rotation barrier.[3b] Our studies[4] of the electrophilic behavior[5,6] of lithium cyclopropylidenoids has led to a particularly poignant example, which we now report.

When **1**[1i] was treated with excess MeLi in the presence of diphenylisobenzofuran (DPIBF) at room temperature, a slow reaction occurred. Apart from dimers,[1i] the only



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[1] (a) Warner, P.; Peacock, S. *Tetrahedron Lett.* **1983**, *24*, 4169. (b) Warner, P.; Chu, I.-S.; Boulanger, W. *Ibid.* **1983**, *24*, 4165. (c) Warner, P.; Ah-King, M.; Palmer, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 7166. (d) Warner, P.; Peacock, S. *J. Computat. Chem.* **1982**, *3*, 417. (e) Warner, P.; Chang, S.-C.; Powell, D.; Jacobson, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 5125. (f) Warner, P.; Lu, S.; Myers, E.; DeHaven, P.; Jacobson, R. A. *Ibid.* **1977**, *99*, 5102. (g) Warner, P.; Palmer, R. F.; Lu, S. *Ibid.* **1977**, *99*, 3773. (h) Warner, P.; Lu, S. *Ibid.* **1976**, *98*, 6752. (i) Warner, P.; La Rose, R.; Lee, C.; Clardy, J. *Ibid.* **1975**, *97*, 5507.

[2] For reviews, see: (a) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (b) Szeimies, G. *React. Intermed. (Plenum)* **1983**, *3*, 299. (c) See also; Maier, W. F.; Schleyer, P. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

[3] (a) Apeloig, Y.; Schleyer, P.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4332. (b) Nagase, S.; Morokuma, K. *Ibid.* **1978**, *100*, 1661. (c) Laidig, W. D.; Schaefer, H. F. *Ibid.* **1979**, *101*, 7184. (d) Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E. D.; Schleyer, P. *Israel J. Chem.* **1980**, *20*, 43.

[4] (a) Warner, P.; Herold, R. D. *J. Org. Chem.* **1983**, *48*, 5411. (b) Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 3981.

[5] (a) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (b) Seebach, D.; Dammann, R.; Lindner, H. J.; Kitschke, B. *Ibid.* **1979**, *62*, 1143.

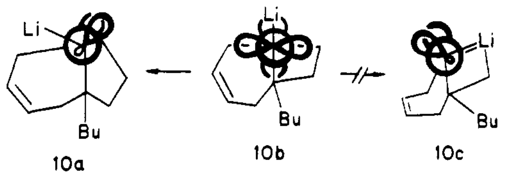
[6] Carbenoid additions to olefins are examples of electrophilic carbenoid behavior; see: (a) Mareda, J.; Rondan, N. G.; Houk, K. N.; Clark, T.; Schleyer, P. *J. Am. Chem. Soc.* **1983**, *105*, 6997. (b) Luke, B. T.; Pople, J. A.; Schleyer, P.; Clark, T. *Chem. Phys. Lett.* **1983**, *102*, 148. (c) Schleyer, P.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

0022-3263/85/1950-2605$01.50/0

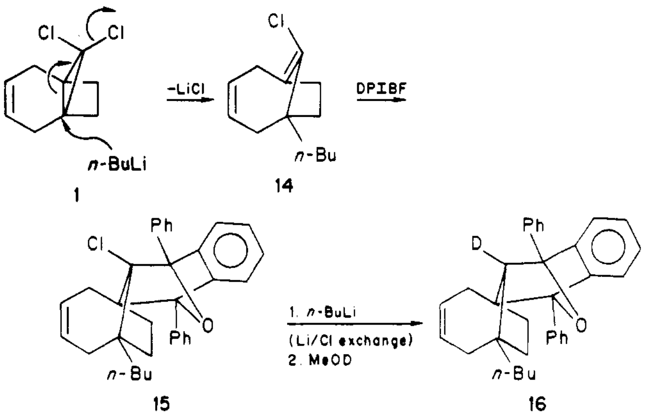
major products were endo[7] adducts **5**[8] and **6**,[8] isolated in 13–22% and 11–18% yields, respectively. Their formation was obviously another[1i] example of the solvolytic behavior of **1**, with MeLi and Cl^- acting as nucleophiles to give intermediates **3** and **4**.

We next investigated the reaction of **1** with *n*-BuLi/THF. After a few experiments, it became clear that **1** did not rapidly react with 2 equiv of *n*-BuLi in the presence of 1 equiv of DPIBF over the range from −95 °C to −25 °C. In fact, for reasons that are unclear, but probably related to aggregate effects, **1** remained substantially unreacted when stirred with ca. 2.5 equiv of *n*-BuLi/1 equiv of DPIBF for 2 h at −25 °C. However, **1** reacted completely with 5–6 equiv of *n*-BuLi/1 equiv of DPIBF after 2 h at −78 °C![9] The major products, following an MeOD quench at −78 °C, were **11**[10] and **13**,[11] isolated in 34% and 37% yield, respectively. Scheme I summarizes our proposed mechanism for formation of these products.[17]

Thus initial exchange would lead to carbenoids **7** and **8**. Although no products directly attributable to **8** were found, it seems likely that **8** would have been rapidly equilibrated to the more stable **7**[12] (perhaps via bimolecular reaction with **1**[13]). Resonance form **7b** emphasizes the highly polar[5] nature of especially this carbenoid;[14] attack at C_9 would yield **9** via an invertive process,[15,16] while collapse at C_1 would produce **10**. While aggregated,[18] the stereochemistry of **10** should still be controlled by π-bonding (based on calculations,[3b,1i] the rehybridized[1c] π-bonded form of **10**, **10a**, may lie ∼20 kcal/mol below the perpendicular form, **10b**; **10c**, which is *trans*-cyclopentenoid, should be only ∼10 kcal/mol more stable than **10b**). Although **10a** would react exclusively from the



2-carbon bridge side, **10b** might do likewise; the precise structure of **10** thus remains unresolved. The exo stereochemistry of **13** is explicable on the basis of oxygen–lithium interaction in the transition state leading to **12** (and the interaction may be with >1 Li). This point is crucial, since the alternative mechanism shown below should produce the unobserved endo isomer of **13**, namely, **16**. Also, Li/Cl exchange of **15** would not have occurred, since **5** did not react with *n*-BuLi at −78 °C.



In conclusion, carbenoid **7** shows exceptional electrophilic reactivity, including a cationic ring-opening pathway.[17]

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Registry No. 1, 38325-65-4; 5, 96845-64-6; 6, 96845-65-7; 11, 96865-75-7; 13, 96865-76-8.

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[7] Compounds **5** and **6** are "endo" with respect to the Cl stereochemistry. We use this reference because electronic interactions between the Cl and the diene may account for the predominant stereochemistry. Models do not establish a clear steric preference for either exo or endo approach. We note that furan discriminates by a 4:1 stereochemical margin in its reaction with **4**, although the preferred stereochemistry is unknown.[1i]

[8] (a) **5**: mp 195–196 °C; structure determined by single-crystal X-ray analysis. (b) **6**: mp 183–184.5 °C; structure determined by single-crystal X-ray analysis.

[9] The effect here is unrelated to the overall concentration of *n*-BuLi—rather the molar ratio of *n*-BuLi to **1**. It should be noted that an interaction of some sort (perhaps charge-transfer) occurs between *n*-BuLi and DPIBF; a red-colored solution develops. However, we do not know if all the DPIBF interacts with the *n*-BuLi, whereby the new species formed would have to behave as a diene, equivalent to ordinary DPIBF. In the absence of DPIBF, **1** reacts completely with 2 equiv of *n*-BuLi over 2 h at −78 °C; the complex product mixture has not been fully characterized.

[10] Structural characterization of **11** and its all-protio isomer (**11-9-H**) was effected via NMR. The 300-MHz spectra of **11** and **11-9-H** differed noticeably only by the presence of a triplet at δ 0.65 in the latter case, but not the former. ^{13}C NMR showed the expected nine resonances (δ 123.8, 32.3, 28.4, 25.3, 22.6, 21.0, 19.8, 14.3). The stereochemical assignment followed from a NOSY 2D NMR experiment, wherein the cyclopropyl hydrogen clearly interacted with some of the cyclobutyl hydrogens but not with the vinylic or allylic hydrogens. Anal. Calcd for $C_{13}H_{20}$: *m/e* 176.1565, found *m/e* 176.1568.

[11] **13-9-H**: mp 202–203 °C; structure determined by single-crystal X-ray analysis.

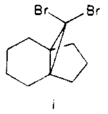
[12] Köbrich and Goyert (Köbrich, G.; Goyert, W. *Tetrahedron* **1968**, *24*, 4327) found a similar result for 7-lithio-7-chloronorcarane.

[13] Seyferth, D.; Lambert, R. L., Jr.; Massol, M. *J. Organomet. Chem.* **1975**, *88*, 255.

[14] (a) Based on the theoretical calculation[14b] that equates the cationic stabilizing effect of an α-Li to that of an α-NH_2, the principal resonance contributor to **7** would have the charge at C-9. (b) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Schleyer, P. *J. Am. Chem. Soc.* **1982**, *104*, 3651.

[15] Such stereochemistry has been confirmed in (a) a related cyclopropylidenoid case (Warner, P.; Chang, S.-C.; Koszewski, N., submitted for publication) and (b) a vinylidenoid case (Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035).

[16] There is no possibility that **9** arises via S_N2 attack of **7** (or **8**) upon *n*-BuCl, followed by Li/Cl exchange. First of all, the 9-butyl-9-chloro-[4.2.1]propell-3-ene would not undergo metal-halogen exchange. Secondly, this point has been investigated for the methylation of i, and only electrophilic carbenoid behavior was found.[15a]



i

[17] A referee has suggested that, alternatively, **14** may be metalated, followed by DPIBF trapping. This provides an alternate route to **10** (the metalation product of **14**) and also requires that the pathway to **11** involves a carbenoid intermediate, while that to **10** does not. While we cannot presently rigorously exclude the pathway via **14**, we note that were it formed, a substantial fraction of **14** should have been trapped to give **15**; **15** was not observed. Another mechanism, involving DPIBF$^{-\cdot}$[9] attack on carbenoid **8**, followed by radical addition across the propellane bond, would yield a bridgehead radical. This radical would have to couple with a Bu· to give **12** and that seems much less probable than H· abstraction.

[18] Aggregated ordinary vinyllithiums are configurationally stable at low temperatures in THF: Knorr, R.; von Roman, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 366.