bromide. The reaction mixture was quenched at 7 min and worked up to give 82 mg of light yellow oil, 80% pure **6c** (by VPC and NMR analysis). When corrected for aliquots withdrawn during monitoring of the reaction, this represents a recovered yield of 70%. Some of this material was purified by preparative VPC (column E) for mass spectrometric and NMR analysis: NMR τ 4.80 (d, $J_{gem} = -7.5$ Hz, H_4), 5.38 (d, $J_{gem} = -7.5$ Hz, H_4), 5.48 (q, $J_{gem} = -13.5$ Hz, $J_{vic} \sim$ 8 Hz with additional splitting, exo H on C_2 and C_6), 6.14 (q, $J_{gem} = -13.5$ Hz, $J_{vic} \sim$ 10–11 Hz with additional splitting, endo H on C_2 and C_6), 6.42 (t, $J_{vic} = 7.5$ Hz, H_8), 8.2 (broad m, $H_{1,7}$); mass spectrum, expected for $M\cdot^+ - Cl$, 113.0603 (found: 113.0595).

References and Notes

(1) (a) The generous support of the National Science Foundation through Grants GP-9543 and 28381 is acknowledged with appreciation. (b) Paper IV: K. G. Taylor and J. Chaney, *J. Am. Chem. Soc.*, **94**, 8924 (1972).

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Carbenoids with Neighboring Heteroatoms. VI. Electrophilic Reactions of α-Chlorocyclopropyllithium Compounds Which Are Epimeric at the Carbenoid Center[1a,b]

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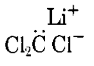
Abstract: The epimeric α-chlorocyclopropyllithium compounds **2b** and **3b**, prepared by Li–Br exchange on the epimeric bromochlorocyclopropanes, were thermolyzed, and the products of electrophilic reaction were characterized. Carbenoid **2b**, with exo Cl, cleanly gave a product of intramolecular C–H insertion, while **3b**, with endo Cl, cleanly gave products of intermolecular reaction when bromide ion was absent from the reaction mixture. Possible causes of this reactivity difference are examined with the conclusion that the differing stereochemistry at the carbenoid carbon atoms is responsible.

Numerous studies have been made (and reviewed[2]) dealing with structure–reactivity relationships in electrophilic reactions of carbenes and carbenoids. The reactions most extensively studied have been the cyclopropane-forming cycloaddition[2,3] and the C–H insertion reactions,[2,4] and with both reaction types, α-haloorganometallic compounds (carbenoids) have been implicated as reactive intermediates in a variety of cases. Most pertinent for this present work was that of Goldstein and Dolbier[4a] who observed a halogen-dependent primary deuterium isotope effect in the intramolecular γ-C–H insertion reaction of α-haloneopentyllithium compounds. Their comparison of intramolecular and intermolecular isotope effects allowed the conclusions that either (1) no intermediate (e.g., a carbene or "carbene complex") intervened between the α-halolithium reagent and the γ-C–H insertion products, or (2) an intermediate was present, having been formed by way of a fully established preequilibrium. Goldstein and Dolbier preferred a mechanism consistent with conclusion 1. It should be noted, however, that mechanisms consistent with conclusion 2 have been proposed for the cyclopropane-forming cycloaddition reaction. Thus, Kobrich, Buttner, and Wagner[5a] have evidence that dichlorocarbene (see A) reacts with olefins in the rate-determining step of dichlorocyclopropane formation, with A having been formed from trichloromethyllithium by a rapidly established prior equilibrium. [Structures B ("carbene-salt complex")[3c] and C ("carbene complex having an ionized C–Cl bond")[2b,d] have also been proposed as the reactive intermediate in this same reaction.]

$LiCl + :CCl_2$

A



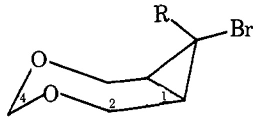
$\overset{Li^+}{Cl_2\dot{C}}\,Cl^-$

B

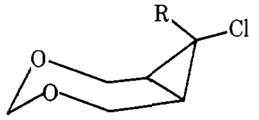
$Cl^-, Li—{}^+CCl_2$

C

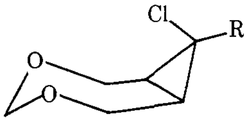
Upon our observation that the thermolysis of bromocarbe-



1a, R = Br
b, R = Li
c, R = H
d, R = CH_3



2a, R = Br
b, R = Li
c, R = H
d, R = Cl



3a, R = Br
b, R = Li
c, R = H

Table I. Products of Carbenoid Thermal Decomposition

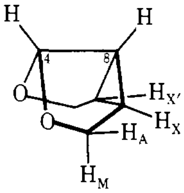
Entry	Carbenoid	Reaction conditions:[a] T, °C (t, h)		% products[b]		
		A	B	**4**	**5**	**6**
1	**1b**[c]	−8 (0.3)	0 (2)	80	Tr	
2	**2b**[d]	−10 (0.2)		26	Tr	
3	**2b**[e]	−78 (1)	22 (1.5)	92	3	
4	**3b**[f]	−78 (2.5)	10 (1)	1	27	61
5	**3b**[g]	−16 (0.2)	−10 (0.5)	23	24	5

[a] Carbenoids were prepared by exchange with ethereal methyllithium (with or without LiBr as noted) and stirred at temperature A for the indicated time, followed by stirring at temperature B and quenching with methanol or water at the indicated time. [b] Yields (±2%) were determined by VPC using internal standards unless otherwise indicated. [c] Methyllithium-LiBr used; other products: **1c** (4%), **1d** (6%). [d] Prepared from **2d** in ether and butyllithium; thermolysis not complete; other products: **2c** (54%), two butyl-containing unknowns (~20%). [e] Prepared from **2a** and methyllithium-LiBr; other products: **2c** (trace). [f] Yields determined by isolation plus VPC; other products: **3c** (1–2%), 3 unknowns (total 4–5%). [g] Reaction run using methyllithium-LiBr; other products: **1c** (13%), **2c** (3%), **3c** (5%); yield of **6** by isolation.

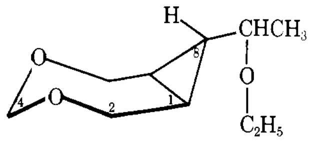
noid **1b** gave, in very clean reaction, intramolecular C–H insertion at C-4, we decided to use the 3,5-dioxabicyclo[5.1.0]-octyl system to test the electrophilic reactivity of epimeric carbenoids, namely **2b** and **3b**. Our hope was that such results would yield additional insight into the role that α-haloorganolithium compounds play in electrophilic reactions. Previous work in the related 4-phenyl-3,5-dioxabicyclo[5.1.0]octyl system by Fraser-Reid,[6] while allowing us the expectation that the thermal reaction of chlorocarbenoid **2b** would parallel that of **1b**, gave no hint as to the possible differential reactivity of **2b** and **3b**.

Preparation and Thermolysis of the Carbenoids. The preparations of carbenoid **1b** from **1a** and carbenoid **2b** from **2a** and **2c** have been previously discussed.[1b] The *endo*-chlorocarbenoid (**3b**) was best prepared at −78 °C in a 10:1 mixture of ether: THF. At this temperature, reaction with bromide ion was relatively slow. When ether was the sole solvent, exchange at −78 °C of the bromine atom of **2a** with methyllithium was faster than that of **3a** and thermolysis of **3b** appeared to be more rapid.

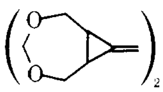
The thermolysis of the carbenoids **1b**, **2b**, and **3b** in ether[7] are reviewed briefly in Table I and the following text. From Table I it can be seen that the two carbenoids with exo halogen gave high yields of intramolecular C–H insertion, compound **4**. That carbenoid with endo halogen gave, almost exclusively, products of intermolecular reactions, **5** and **6**. Under more dilute conditions and at higher formation temperatures, carbenoid **3b** when prepared in the absence of LiBr gave reduced yields of dimers **6** and higher yields of **5** but never more than 3% of **4**. The loss of stereoselectivity in the thermal reactions of carbenoid **3b** (entry 5, Table I) when LiBr was present (as noted by the formation of **4** and **1c**) may well have been due entirely to halide exchange with concomitant carbenoid isomerization (at −16 to −10 °C).



4



5



6, *syn, anti*

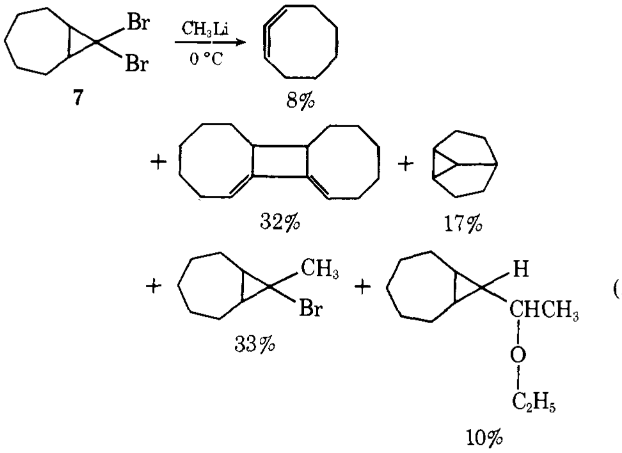
Product Structures. The tricyclic insertion product **4** was characterized by elemental analysis and by analysis of its unequivocal NMR spectrum. In addition to the acetal-H doublet at τ 4.39 (J = 2.8 Hz) and the sextet at τ 7.17 (J = 7.4 and 2.8 Hz) due to the neighboring H-8, there was a distinctive AMXX′ pattern. Referring to structure **4**, H_A with a well-tuned instrument could be resolved from a doublet of triplets (J ~ 2.5 Hz) to a doublet of quartets at 5.93 (J_{AM} = −9.0 Hz, $J_{AX,X'}$ = 2.8 and 2.0 Hz); H_M was a sharp doublet at τ 6.18 (J_{AM} = −9.0 Hz, J_{MX} = $J_{MX'}$ = 0–0.5 Hz); and $H_{XX'}$, being not as well resolved as the signal for H_A, appeared as a doublet of triplets at τ 8.03 (J_{X8} = 7.4 Hz, J_{AX} ~ $J_{AX'}$ ~ 2.4 Hz). Inspection of a molecular model of **4** indicated that the H_M–H_X dihedral angle should be close to 90–100°: also the σ bonds which intervene between H_A and $H_{X'}$ form a W pattern, a structural feature which facilitates coupling over four bonds.[8] The spectrum of **4** displays the same pattern as that reported for the 4-phenyl analogue.[6]

The structure of the solvent-insertion product, **5**, was deduced again from elemental and NMR spectral analyses. In CCl_4, the C-4 methylene group was an AB quartet with the doublets located at τ 5.34 and 5.82 (J_{gem} = −7.5 Hz). The C-2 and C-6 protons showed an "A_2B_2 multiplet" centered at τ 6.11 (Δτ ~ 10–12 Hz, J_{gem} = −14 Hz). A quartet at τ 6.60 (J = 7.3 Hz) and a quintet at τ 6.98 (J = 6.2 Hz) were assigned as signals due to the CH_2 and CH groups of the ethoxyethyl moiety, respectively. The cyclopropyl protons were buried under the CH_3 signals which were centered at about τ 8.8. The addition of 0.15 mol equiv of $Eu(dpm)_3$ to the NMR samples caused significant shifts of all the signals allowing a complete assignment of signals as well as a determination of the stereochemistry at C-8. Thus, the C-4 protons were shifted to τ 0.83 (broad singlet); the C-2, C-6 protons were shifted to τ 2.8 (multiplet); and the CH_2 and CH groups of the ethoxyethyl group were collected in a multiplet at τ 5.96. The cyclopropane-H signals were now visible: H-8 as a somewhat broadened quartet at τ 6.60 (J = 6 Hz) and H-1 and H-7 as an unresolved multiplet at τ 7.27. The CH_3 signals were resolved into a doublet at τ 8.32 (J = 6.5 Hz) and a triplet at τ 8.53 (J = 7.3 Hz). In a double irradiation experiment on this sample, irradiation of the multiplet at τ 2.8 (H's on C-2, C-6) caused the multiplet at τ 7.27 (H's on C-1, C-7) to collapse to a doublet, J = 5.5 Hz, indicative of trans coupling with H-8.[9] Thus, the ethoxyethyl moiety of **5** must occupy an exo position.

Both dimers **6** were isolated as white crystalline solids. Their NMR spectra were similar, each displaying the AB quartet for the H's at C-4, an $A_2M_2X_2$ pattern for the H's on C-2, C-6, and the C-1, C-7 cyclopropane-H multiplet. The isomers gave identical electron impact and chemical ionization mass spectra, and, with the latter technique, peaks at *m/e* 225 for the protonated molecular ions were seen. The absence of vinyl H signals in the NMR spectra of **6** ruled out allene-type dimers as a structural possibility, and the relative simplicity of the spectra was indicative of rather symmetrical structures as would be the case with the bicyclopropylidene skeleton. Molecular models suggested a stronger dipole moment for the syn isomer, and, on this basis, the dimer with the higher melting point has been assigned the syn configuration.

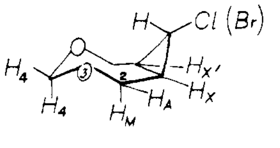
Discussion

First, it is interesting to contrast the reactivity of carbenoid **1b** with the one obtained from 8,8-dibromobicyclo[5.1.0]octane[10] (**7**), the all-carbon analogue of **1a**. The addition of **7** to excess methyllithium at 0 °C produced the product array shown in reaction 1. The most notable difference is the lack of formation of allene-derived products with carbenoid **1b** (as well as with carbenoids **2b** and **3b**). Previous work[11,12] has indicated that electron-donating substituents, if they are bound directly to the three-membered ring, facilitate the ring opening of α-bromocyclopropyllithium compounds to yield allene. In the cases of **1b**, **2b**, and **3b**, two electron-withdrawing $ROCH_2$ groups are bound to the cyclopropane ring, and, in comparison with **7**, allene formation is thereby retarded. Thus, a transition state for allene formation is indicated in which positive charge develops at the β and/or β′ carbon atoms of the opening three-membered ring.

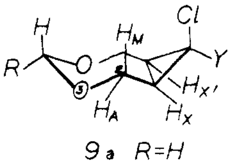


(1)

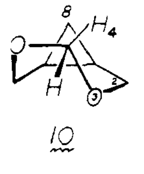
Secondly, while chlorocarbenoids **2b** and **3b** differ in stereochemistry at C-8, they probably also differ in conformation as well. The work of Moore and King[13] has indicated, and the later work of Paquette, Zon, and Taylor[14] has confirmed, that intramolecular C–H insertion of 7-norcaranylidenes occurs with syn-axial C–H bonds. Thus, if **2b** and **3b** have different preferred conformations, this would be expected to alter their relative reactivity patterns. Servis and Anet[15] have examined the conformations of cycloheptene oxide and found two principal interconverting conformers, a "chair" and a "crown" conformer (akin to **8** and **9**, respectively), with the former being the more stable conformational isomer (ΔG (−122 °C) = 0.2 kcal mol^{-1}, $\Delta G^{\ddagger}$ = 7.9 kcal mol^{-1}). Examination of the NMR spectra of compounds **1, 2,** and **3** reveals, likewise, two principal conformations, the chair (or perhaps, chaise-lounge) conformer, **8**, and crown conformer, **9**, either of which is the preferred one under certain structural circumstances. Thus, monohalo compounds **1c** and **2c** with the C-8 hydrogen atom in an endo configuration give NMR spectra with the AMXX′ portion[16] very similar to that of tricyclic ether **4** (see Figure 1). The most notable spectral similarities between, for example, **2c** and **4** were (1) the evidence for long-range coupling between H_A and $H_{X'}$ rendering the signal for H_A of **2c** a doublet of triplets with $J_{AX} \sim J_{AX'} \sim 2$ Hz, and (2) the low coupling constant between H_M and H_X estimated from $W_{1/2}$ measurement of the somewhat broadened (with respect to **4**) H_M doublet to be 1–1.5 Hz ($J_{gem} = -13$ Hz). (In the XX′ spectral region, differences are seen that reflect the different H-8 configurations.) Thus, the vicinal-H dihedral angle between H_AH_X and H_MH_X in **1c** and **2c** must be similar to those in **4**, a situation which indicates that the major conformation of **1c** and **2c** is the chair conformation **8**. In view of the relative thermal stability of carbenoids **1b** and **2b**, we propose that **8** is the conformation of these carbenoids, wherein the endo Li atom can be solvated intramolecularly by the ring oxygen atoms. Simple rotation about the C-2–O-3 bond converts chair **8** to twist conformation **10**, a process which transforms H-4 to a pseudo-axial conformation, now accessable for the C–H insertion reaction.



8



9a R=H
Y=H, Cl, Br
b R=C_6H_5
Y=Cl



10

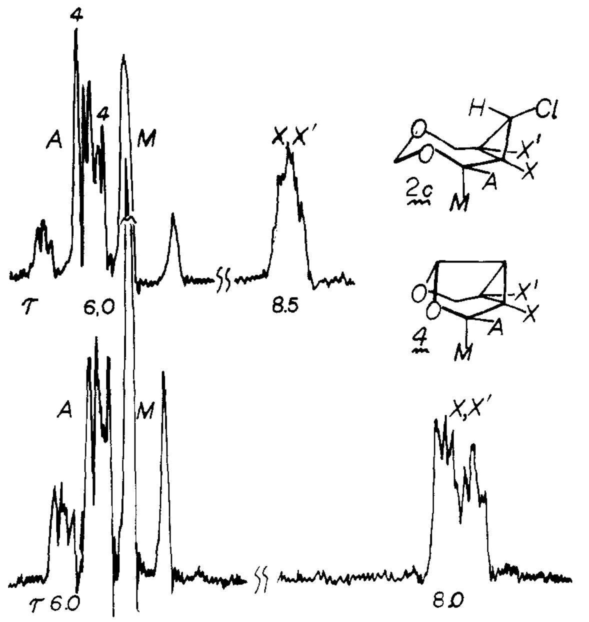


Figure 1. The AMXX′ portions[16] of the proton NMR spectra of **4** (lower trace) and **2c** (upper trace). The signals labeled as 4 in the upper trace are due to one of the C-4 protons of **2c**; see text for discussion of spectral similarities and differences.

In contrast, those compounds with endo halogen atoms, **1a**, **2a**, **3d**, **3a**, and **3c**, all have NMR spectra with AMXX′ portions[16] which are quite complex and which are strikingly similar to the appropriate spectral regions of **9b**,[6] (see Figure 2) whose solid-state conformation has been shown to be a crown conformation as shown.[17] In fact, the only differences among the spectra just mentioned are minor chemical shift differences and the superposition of the upfield H-4 doublet on the H_A signals of **1a**, **2a**, **3a**, and **3c**. Also, in the case of **3c**, the signals for H-8 and H_M partially overlap. Computer analysis of the spectrum of **9b** gives the coupling constants indicated in the experimental section, and the substantial coupling between H_M and H_X confirm the large H_M–H_X dihedral angle imparted by conformation **9**.

gem-Dimethyl substitution at C-4 might be expected to destabilize conformations **8** and **9** relative to **10**, in which neither methyl group occupies an axial-like position. Consistent

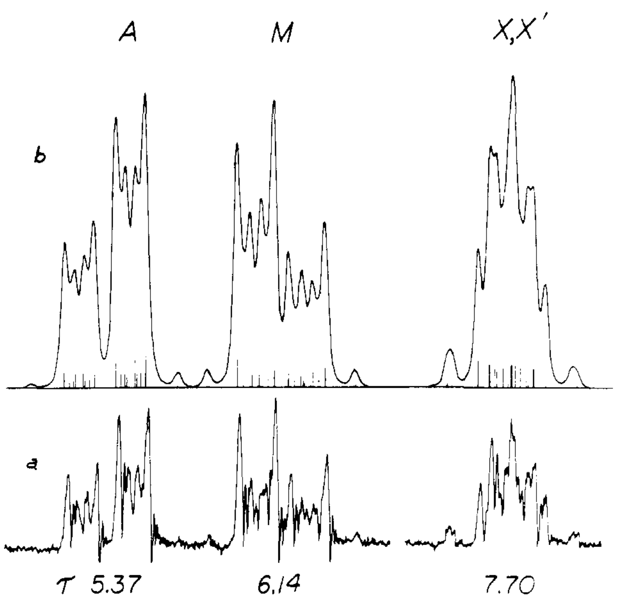


Figure 2. The AMXX′ portion[16] of (a) the proton NMR spectrum and (b) the simulated spectrum of compound **9b.** The similarities and minor differences of this spectrum with those of compounds **9a** are discussed in the text. The spectrum of **2a** was temperature independent from +70 to −70 °C.

with this suggestion we note that the AMX portion of 4,4-dimethyl-*exo*-8-bromo-3,5-dioxabicyclo[5.1.0]octane[1b] represents a merging of the spectra for **8** and **9** and begins to resemble the spectra of acyclic analogues[1b] (see Figure 3).

In conformation **9,** H_M, $H_{M'}$ and H_{4n} are axially disposed and hence accessable for intramolecular C–H insertion. Again, C-2, O-3 rotation converts **9** to **10** in which H_4 is somewhat nearer to C-8 and still accessible for C–H insertion. We propose crown conformation **9** as the major conformation of carbenoid **3b** and note that with three axial H's available, intramolecular C–H insertion is not conformationally precluded.

However, Kirmse[2a,18] has noted that a γ-methoxyl group substituent (carbene carbon is α) markedly reduced the rate of γ-C–H insertion (cyclopropane formation) of carbenes generated by thermal decomposition of tosylhydrazone salts, a result which contrasts with observations on intermolecular insertion reactions. Also, the results of Paquette and coworkers[14] seem to indicate that a γ-methoxyl substituent retards γ-C–H insertion but that a δ-methoxyl substituent *enhances* δ-C–H insertion. On this basis it might be argued that H_M and $H_{M'}$ of **9** are, by a substituent effect, precluded from participation in a C–H insertion reaction. By the same token, H-4, an ϵ substituent, should be enhanced in its proclivity to participate in such reactions, and a variety of intramolecular ϵ-C–H insertions have been observed.[2a,6,10,14,19]

Thus, we see (at present) no conformational or substituent effect that should preclude intramolecular C–H insertion by carbenoid **3b,** nor any such effect which should preclude intermolecular reaction by carbenoid **2b.** Hence, we are drawn to conclude that the reactivity differences of **2b** and **3b** results from their differing stereochemistry at C-8 which, in turn, leads to different electrophilic reaction pathways. The cleanly intramolecular pathway of **2b** together with the cleanly intermolecular nature of the reactions of **3b** demonstrates that a reversibly formed intermediate such as a free carbene[5a,20] or a carbene complex having an ionized C–Cl bond[2b,21] is not a common intermediate in these electrophilic reactions. From the thermolysis of **2b** in the presence of LiBr (see entry 3, Table I), **2c** could be detected in the product mixture, but no products of ligand exchange,[20b] **1c** and **1d,** were present. The results with **1b** and **2b** support the conclusions of ref 4a.

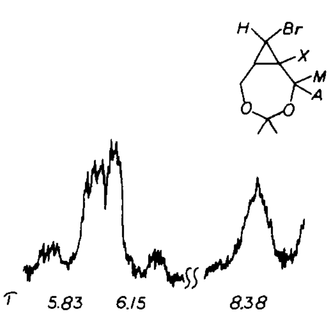


Figure 3. The AMX portion[16] of the proton NMR spectrum of *exo*-8-bromo-4,4-dimethyl-3,5-dioxabicyclo[5.1.0]octane.

Were such an intermediate to have intervened in the case of **3b,** isomerization to the more thermodynamically stable **2b** in the absence of added nucleophile would be an expected result. Thus, (*Z*)-2-phenyl-1-chloro-1-propenyllithium was found[2b,21] to isomerize to the more stable *E* isomer without the benefit of added chloride ion and little if any such isomerization was observed in the reaction recorded as entry 4 of Table I. However, in reactions of **3b** conducted at higher temperature (see Experimental Section), significant amounts of the epimeric chloride **2c** (but never more than 3% of **4**) were formed. Also, it could be argued that entry 5 of Table I gives evidence that bromide ion has trapped an intermediate that has an ionized C–Cl bond, but a valid alternate interpretation of these results is that **3b** suffered displacement of chloride by bromide ion.[22] Further experiments are required to distinguish these pathways.

In any event, the results reported herein establish carbenoid-center stereochemistry as an important parameter in carbenoid electrophilic reactivity.

Experimental Section

General. For general procedures, see ref 1b.

3,5-Dioxatricyclo[5.1.0.0^{4,8}]octane (4). An ethereal solution of methyllithium-LiBr (∼40 mmol) was added dropwise in two batches to a stirred solution of 5.90 g (21.7 mmol) of **1a** in 65 ml of ether at −8 to 0 °C, yielding a heavy white precipitate. After stirring at 0 °C for a total of 22 h the reaction mixture was quenched by the addition of cold water. VPC analysis (column B) indicated a major component accounting for 79% of the total peak area. The organic phase was dried (K_2CO_3, then K_2CO_3-$MgSO_4$ mixture), and a VPC analysis of the organic phase (internal standard, *m*-bromoanisole) and the water phase [internal standard, bis(2-ethoxyethyl) ether] revealed the presence of 39.9 and 35.7% yields, respectively, of **4.** When this total was corrected to account for aliquots previously withdrawn for monitoring the reaction, the yield of **4** was 80%. Other products were **5** (trace), **1c** (4%), and **1d** (6%). Recovery of **4** by distillation of the organic phase was poor. The aqueous phase was saturated with sodium chloride and extracted with methylene chloride. Drying and careful evaporation of the methylene chloride gave a solid, which was recrystallized from the minimum amount of pentane and sublimed (40 °C, 0.5 mm) to yield 0.44 g of **4,** mp 44.5-46 °C. Further recrystallization and sublimation did not improve the melting point. Other similarly performed reactions in more dilute solutions gave comparable yields: NMR ($CDCl_3$) τ 4.39 (d, J = 2.8 Hz, H-4), 5.93 (d of q, J_{gem} = −9.0 Hz, J_{AX} = 2.8 Hz, $J_{AX'}$ = 2.0 Hz, H_A), 6.18 (d, J_{gem} = −9.0 Hz, $J_{AX} \sim J_{AX'}$ = 0-0.5 Hz, H_M), 7.17 (t of d, $J_{8,4}$ = 2.8 Hz, $J_{8,X}$ = $J_{8,X'}$ = 7.4 Hz, H_8), and 8.03 (d of t, $J_{X',8}$ = 7.4, $J_{AX} \sim J_{AX'}$ = 2.4 Hz).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.18; O, 28.55. Found: C, 64.00; H, 7.15; 0, 28.90.

***exo*-8-(1-Ethoxyethyl)-3,5-dioxabicyclo[5.1.0]octane (5).** A solution of methyllithium in ether (1.3 ml, 0.5 mmol) was added to ethereal **3a**[1b] at −15 °C. The reaction was stirred for a total of 7 min during a temperature rise to −8 °C and then was quenched by adding methanol. VPC analysis (column B; internal standard, tetradecane) indicated the formation of **5** (37%), **2c** (19%), **3c** (6%), and **4** (2.9%). Dimers **6** were isolated in about 5% yield. No other major products could be detected by VPC on columns A–C, E, G, and I–L, and no other major products were in evidence from NMR analysis of the crude reaction mixture. For preparative purposes, a larger-scale version of the aforementioned reaction was run. After washing and concentrating the mixture, compound **5** was isolated by preparative VPC (column D); NMR ($CDCl_3$) τ 5.34 (d, $J_{\text{gem}} = -7.5$ Hz, H-4), 5.82 (d, $J_{\text{gem}} = -7.5$ Hz, H-4), 6.11 ("A_2B_2 multiplet", $\Delta\tau \sim 10$–12 Hz, signal $W_{1/2} \sim 34$ Hz, $J_{\text{gem}} = -14$ Hz, 4 H on C-2 and C-6), 6.60 (q, $J = 7.3$ Hz, CH_2 of ethoxyethyl group at C-8), 6.98 (quintet, $J = 6.2$ Hz, CH of ethoxyethyl group at C-8), and 8.85 (m, H-1, H-7, CH_3 groups of ethoxyethyl group); NMR ($CDCl_3$) with 0.15 mol equiv of $Eu(dpm)_3$[23] added, τ 0.83 (bs, 2 H at C-4), 2.8 (m, 4 H at C-2 and C-6), 5.96 (m, 3 H, CH_2 and CH of ethoxyethyl group), 6.60 (q, $J = 6$ Hz, 1 H at C-8), 7.27 (m, 2 H at C-1 and C-7), 8.32 (d, $J = 6.5$ Hz, CH_3–CH of ethoxyethyl group at C-8), and 8.53 (t, $J = 7.3$ Hz, CH_3CH_2 of ethoxyethyl group at C-8); irradiation of the multiplet at τ 2.8 resulted in the collapse of the multiplet at τ 7.27 to a doublet, $J_{\text{trans}} = 5.5$ Hz.

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74. Found: C, 64.65; H, 9.77.

***syn*- and *anti*-$\Delta^{8,8'}$-Bis(3,5-dioxabicyclo[5.1.0]octylidene) (6).** A cooled (−78 °C) solution of 0.66 g (2.93 mmol) of **3a**[1b] in 23 ml of ether was treated (by rapid addition) with 4.23 mmol of ethereal methyllithium. The resulting heterogeneous mixture was stirred 2.5 h at −78 °C and then allowed to warm to 10 °C over a 1-h period, at which time the reaction was quenched with 10 ml of water. The water quench only partially dissolved the white solids suspended in the ethereal reaction mixture, leaving an organic solid (sparingly soluble in ether) suspended in the aqueous phase. After separating the ether phase, the aqueous phase was extracted with methylene chloride. Both the ether and methylene chloride phases were dried (K_2CO_3) and evaporated to yield 0.252 g of "wet" solid and 0.137 g of solid, respectively. Both solids were triturated with 50 ml of warm hexane leaving a total residue of 95 mg (29%) of finely divided solid, *syn*-**6**, mp 205–210 °C. Dimer *syn*-**6** was further purified by recrystallization from the following series of solvent pairs: methylene chloride/ethyl acetate (mp 208.5–212 °C), acetonitrile/methylene chloride (mp 207.5–211.5 °C), and again, methylene chloride/ethyl acetate (mp 209.5–211.5 °C). The hexane triturate was concentrated to 5 ml volume and cooled (−20 °C) to yield, in two crops, 103 mg (31%) of *anti*-**6**, mp 120–126 °C. Dimer *anti*-**6** was purified by recrystallization from hexane, sublimation [70 °C (0.2 mm)] and recrystallization from ether/hexane, to give colorless needles, mp 127.5–129.5 °C. Evaporation of the hexane filtrate and VPC analysis gave **5** (27%), **4** (1%), and **3c** (2%).

For *syn*-**6**: NMR ($CDCl_3$ τ 5.13 (d, $J_{\text{gem}} = -7.0$ Hz, 2 H at C-4 and 4′), 5.51 (d, $J_{\text{gem}} = -7.0$ Hz, 2 H at C-4 and 4′), 5.66 (d of d with further splittings, $J_{\text{gem}} = -13$ Hz, 4 H endo on C-2, C-6, C-2′, and C-6′), 6.44 (d of d with futher splittings, $J_{\text{gem}} = -13$ Hz, 4 H_{exo} on C-2, C-6, C-2′, and C-6′), 7.72 (m, cyclopropane H's); electron impact mass spectrum *m/e* (rel intensity) 179 (5), 163–5 (10), 133–5 (20), 121, 119, 117 (15–25), 103–105 (30–50), 95 (95), 91 (100), 81 (45), 77–79 (50–70); chemical ionization mass spectrum *m/e* 225 (P + 1).

For *anti*-**6**: NMR ($CDCl_3$) τ 5.26 (d, $J_{\text{gem}} = -7.0$ Hz, 2 H at C-4 and 4′), 5.45 (d, $J_{\text{gem}} = -7.0$ Hz, 2 H at C-4 and 4′), 5.76 (d of d with further splittings, $J_{\text{gem}} = -13$ Hz, 4 H_{endo} on C-2, C-6, C-2′, C-6′), 6.30 (d of d with further splittings, 4 H_{exo} on C-2, C-6, C-2′, C-6′), 7.82 (m, cyclopropane H's); electron impact mass spectrum, identical with that of *syn*-**6**; chemical ionization mass spectrum *m/e* 225 (P + 1).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.18. Found: for *syn*-**6** C, 64.72; H, 7.17; for *anti*-**6**; C, 63.94; H, 7.25.

Additional Thermolyses of Carbenoids. A. To a cooled solution (−78 °C) of 42.5 mg (0.185 mmol) of **2a**[1b] in 6 ml of ether was added 0.85 ml (0.28 mmol) of ethereal methyllithium–lithium bromide. The resulting heterogeneous mixture was stirred at −78 °C for 1 h (no reaction) and then warmed to 22 °C over a 1.5-h period. One equivalent of water was added to quench the reaction which was analyzed by VPC (column B[1b]) using tetradecane as internal standard. The results are tabulated in Table I, entry 3.

B. To a cooled (−10 °C) solution of 0.142 g (0.78 mmol) of **2d**[1b] and a weighed amount of tetradecane in 15 ml of ether was added 1.5 ml (1.5 mmol) of butyllithium in pentane. The increasingly turbid solution was stirred a total of 10 min and then quenched by the addition of 1 equiv of methanol. The results of VPC analysis of this reaction are recorded in Table I, entry 2.

C. A solution of methyllithium–lithium bromide (0.5 mmol) was added to ethereal **3a** at −16 °C, and the reaction was stirred at that temperature for 10 min. The mixture was stirred for an additional 30 min while warming to −10 °C and then quenched with methanol. VPC analysis (column B; tetradecane, internal standard) of the reaction gave the results recorded in Table I, entry 5.

NMR Spectrum of 9b. The AA′MM′XX′ portion of the spectrum of **9b**[6] was analyzed and simulated using standard techniques with the computer program LAOCN3. The following chemical shifts (Hz) and coupling constants (Hz) yielded the spectrum shown in Figure 2b: H_A, 279.2 ($J_{AM} = -13.45$, J_{AX} 7.34, $J_{AX'}$ 0.34); H_M, 235.0 (J_{MX} 9.56, $J_{MX'}$ 0.21); H_X, 138.0 ($J_{XX'}$ 11.22); the chemical shifts and associated coupling constants of the symmetrically equivalent A′M′X′ protons and coupling schemes are equal to those listed; all other constants are 0.

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References and Notes

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(9) (a) The usually observed range for J_{trans} in a variety of substituted cyclopropanes is 2.3–8.6 Hz and for J_{cis} is 6.6–12.6 Hz.[9b] Exceptions are encountered when vicinal electronegative substituents are present to reduce both J_{trans} (as low as 0 Hz[9c]) and J_{cis} (as low as 5 Hz[9c]). For a cyclopropane with substituents as those found in **5,** the observed J (5.5 Hz), while on the high side of the J_{trans} range, is outside the range usually observed for J_{cis}.[9b] In analogy, *exo*-7-(2-tetrahydrofuranyl)-bicyclo[4.1.0]heptane is formed when 7-chloro-bicyclo[4.1.0]heptyllithium is thermolyzed in THF.[9d] (b) H. Booth in "Progress in NMR Spectroscopy", Vol. 5, J. W. Emsley, J. Feeny, and L. H. Suttcliff, Ed., Pergammon Press, London, 1969, Chapter 3; (c) T. Ando, H. Yamanoka, and W. Funasaka, *Tetrahedron Lett.*, 2587 (1967); (d) G. Kobrich and W. Goyert, *Tetrahedron*, **24,** 4327 (1968).

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