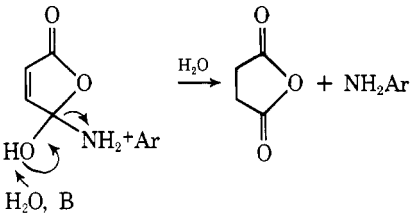
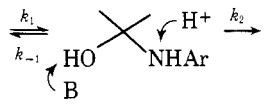


the concerted reaction are the zwitterion, which would result from stepwise decomposition of IH^+ by initial loss of a proton from oxygen, and protonated maleic anhydride, which would result from initial loss of the amine from IH^+.

Our results would indicate that once a tetrahedral addition product of an amide has been produced, two factors will promote decomposition in the direction of amine expulsion for any compound. These are (1) removal of the hydroxylic proton and (2) protonation of the amine functionality. Other aspects of rate differences probably will be inherent to the substrate and nucleophilic catalyst. The relative sizes of k_1 and k_{-1} will



I

determine the concentration of I, if $k_2 \ll k_{-1}$. Obviously, in the case of formation of an enzyme-substrate derivative, k_1/k_{-1} can be extremely favorable and internal bases can supply the function of B. The rate of protonation of I at the amine will probably be diffusion limited so that this feature of catalysis will not evolve as a kinetic factor for the enzyme. Rather, the apparent basicity of the amine should be increased without at the same time increasing the strength of the C-N bond. We are currently investigating chemical means through which this may be accomplished.

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(2) Fellow of the Alfred P. Sloan Foundation.
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Carbenoids with Neighboring Heteroatoms. V. Nucleophilic Reactions of Lithium Carbenoids of the *exo*-8-Halo-3,5-dioxabicyclo[5.1.0]octyl System[1]

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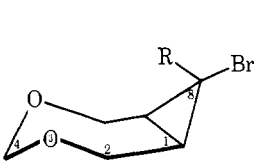
Abstract: The α-haloorganolithium compounds **1b, 2b,** and **3b** were prepared from the *gem*-dihalocyclopropanes by stereoselective halogen–lithium exchange using methyl- or butyllithium. The nucleophilic properties of these carbenoids were studied by reactions with the electrophiles H^+, D^+, CH_3I, benzophenone, and halogenating agents. The chlorination (CCl_4) of **1b** and bromination ($BrCCl_3$) of **3b** provided stereoselective routes to the epimeric bromochlorocyclopropanes **3d** and **6a.** Factors influencing the nucleophilic reactivity of **1b** and **2b** are discussed.

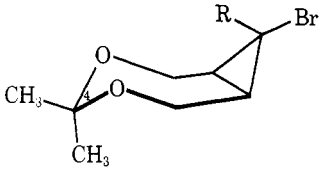
In previous papers in this series[2] we have reported on the stereoselective synthesis of stabilized lithium carbenoids and some of their nucleophilic and electrophilic reactions. In this and the accompanying paper[3] we report, in turn, on nucleophilic and electrophilic reactions of lithium carbenoids in the 3,5-dioxabicyclo[5.1.0]octyl system, a study which ultimately led to the individual preparation of epimeric α-chlorocyclopropyllithium reagents, and the first direct observation of the effect on electrophilic reactivity of stereochemical change at a carbenoid carbon.

The requisite crystalline *gem*-dihalocyclopropanes **1a, 2a,** and **3** were prepared in low to moderate yields by dihalocarbene addition to the corresponding olefins, which, in turn, were prepared from *cis*-2-butene-1,4-diol by the method of Bannock and Lappin.[4] The acetals, **1a** and **3a,** were relatively stable toward hydrolysis of that function if reasonable work-up precautions were taken with regard to pH and temperature. Ketal **2a,** however, required basic conditions at all times, even to the extent of using K_2CO_3 (rather than Na_2SO_4) as drying agent in addition to using it as an additive during purification of **2a** by sublimation.

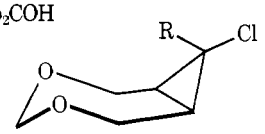
Nucleophilic Reactions of Carbenoids 1b and 2b. Treatment of ethereal **1a** at −78 or −20 °C with methyllithium–lithium bromide gave a suspension of the carbenoid **1b** in high yield as evidenced by the formation of monobromo compound **1c** in 90% yield upon water or methanol quench of the reaction. The



1a, R = Br
b, R = Li
c, R = H
d, R = D
e, R = CH_3
f, R = $(C_6H_5)_2COH$



2a, R = Br
b, R = Li
c, R = H
d, R = $(C_6H_5)_2COH$



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

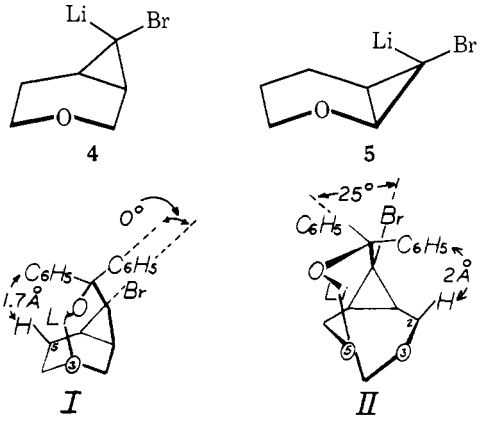
NMR signal for H-8 of **1c** was a triplet at τ 6.77 with J = 4.7 Hz, a coupling constant indicative of trans coupling across a cyclopropane ring. After the solution was stirred at −78 °C for 7.5 h, a D_2O quench gave **1d** in about 90% yield, the NMR spectrum of which showed no signal at τ 6.77.

In a similar vein, an ethereal solution of **2b** was produced by reaction of dibromocyclopropane (**2a**) with 1 equiv of methyllithium–lithium bromide at −78 °C as evidenced by the formation of **2c** in 81% yield upon methanol quenching of the reaction. In **2c** the H-8 NMR signal was a triplet at τ 6.90 with J = 4.0 Hz, a result which, again, indicated trans coupling across a cyclopropane ring.

Carbenoid **1b** failed to react with methyl iodide (or methyl bromide) at −78 °C and at −15 °C when the reaction solvent was ether. The addition of tetrahydrofuran (THF) to the reaction, however, dissolved **1b** and permitted methylation to proceed, yielding **1e** in 75% yield. The low solubility of **1b** is judged *not* to be a key factor in its reluctance to react with methyl iodide since the ether soluble carbenoid **2b** also failed to react with methyl iodide unless THF was present in the reaction solution. The effect of THF is, presumably, to "loosen" the Li atom of **1b** and **2b** from coordination with the ring oxygen atoms, a process which must occur in order for methylation to occur.

The reaction of **1b** with the electrophile benzophenone did not proceed to a measurable extent in ether at −78 °C over 7.5 h. At −15 to −8 °C, however, a 3.3-h reaction gave adduct **1f** in 13% yield. At −78 °C again, after first removing methyl bromide in vacuo from a preparation of **1b**, the addition of benzophenone followed by tetrahydrofuran gave adduct **1f** in 41% yield.

In an initially surprising result, carbenoid **2b** reacted with benzophenone in a 9-h reaction at −78 °C to give **2d** in 39% yield (crude) without the benefit of added THF. Shorter reaction times reduced the yield of **2d**. These data indicate that carbenoids **1b** and **2b** are intermediate in reactivity between 7-*exo*-bromo-3-oxabicyclo[4.1.0]hept-7-yllithium (**4**), which could not be brought to react with benzophenone,[5] and 7-*exo*-bromo-2-oxabicyclo[4.1.0]hept-7-yllithium (**5**), which reacted rapidly at −78 °C in ether giving a high yield of product.[5] An explanation of the inertness of **4**[5] was based on the primary assumption that the Li atom of **4** remained bonded to the ring oxygen of **4** in the transition state of benzophenone adduct formation. Taking this assumption leads to the formation of I, with its attendant, rather severe, nonbonded interactions,[6] as the structure of the initial product of reaction between **4** and benzophenone. The crowded nature of I may preclude its formation regardless of whether the addition of



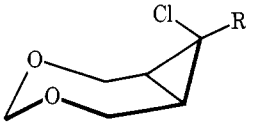
4 **5**

I *II*

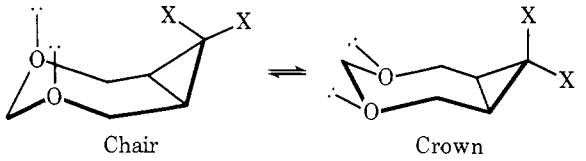
the organolithium reagent to benzophenone is irreversible (crowded transition state) or reversible (unfavorable K_{eq}). Extending this assumption to the case of **2b** leads to II as the structure for the initial benzophenone adduct. Models of II[6] suggested a less severely crowded product and, hence, a faster rate of reaction of **2b** compared with **4**. By comparison with I and II, the adduct of benzophenone and the fast-reacting 2-oxa-carbenoid (**5**) is free of undue strain. Further, if structure **2b** reflects the conformation of the carbenoid, then two oxygens are available for coordination with the Li atom, and one of these bonds must be broken to form II. This factor can also contribute to the reduction in reactivity of **2b** relative to **5**. The fact that the presence of the better-coordinating solvent, THF, is required for reaction of **1b** with benzophenone at −78 °C, while not required for the same reaction of **2b**, is taken as evidence that the Li atom in **1b** is more tightly bound intramolecularly to oxygen than in **2b**. Perhaps the presence of a pseudo-axial CH_3 at C-4 in structure **2b** destabilizes the conformation shown, effectively lowering the barrier to conformational isomerization to a twist form in which only one ring oxygen can be coordinated to Li. In fact, while the NMR spectrum of **1c** is consistent with a chair conformation,[3] the CH_2 portion of the spectrum of **2c**, resembling that of the ring-opened hydrolysis products of **1a** and **2a**, suggests a flexible (twist) conformation for that compound.[3] Presumably, **1c** and **2c** reflect to some extent, the relative conformational porperties of their respective carbenoids.[3] Thus, based on what in known about the effect of *gem*-dimethyl substitution (relative to H substitution) on barriers to conformational change,[8] this is a reasonable explanation for the relative reactivities of **1b** and **2b** toward benzophenone.

***exo*-8-Chloro-3,5-dioxabicyclo[5.1.0]oct-8-yllithium (3b).** The reaction of ethereal dichlorocyclopropane (**3a**) with *n*-butyllithium required 2 equiv of butyllithium for complete lithium–chlorine exchange at −78 °C.[5] At −16 °C, or with added THF at −78 °C, the exchange stoichiometry was 1:1 butyllithium:**3a**. The major product of exchange was **3b** since methanol quench of the reaction gave **3c**, with the now familiar H-8 triplet (τ 6.56, J_{trans} = 4.0 Hz).

Halogenation of Carbenoids 1b and 3b. The chlorination of bromocarbenoid **1b** and the bromination of carbenoid **3b** were investigated for the purpose of providing epimeric bromochlorocyclopropanes (**6a** and **3d**, respectively) as starting materials for the preparation of epimeric carbenoids (**6b** and **3b**, respectively). Prior to settling on this approach to epimeric carbenoids we made several attempts to obtain significant exchange of the exo halogens of **1a** and **3a**. The NMR spectra of **1a** and **3a** clearly indicated a *crown* rather than *chair* (or more appropriately: chaise-lounge) conformation as the major conformational isomer for **1a** and **3a**.[3] In the *crown* conformation, the oxygen nonbonding electrons are not in the proper orientation for assisting in halogen–metal exchange of the endo halogen. This raised the possibility that carbenoid **1b** was not



6a, R = Br
b, R = Li
c, R = H

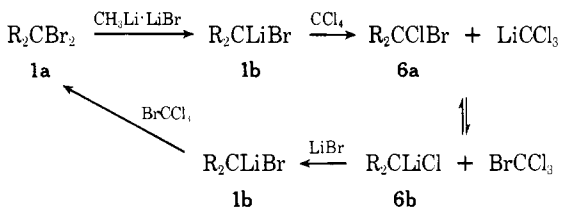


Chair Crown

entirely the kinetically formed carbenoid, but rather the thermodynamic product of the reaction sequence of exo exchange followed by bromide ion-induced or exchange-induced epimerization at C-8. However, **1b** was still the product of exchange when (halide ion)-free butyllithium or phenyllithium, in excess, were used for the reaction. Seyferth[12a] has observed that when 7,7-dibromonorcarane was maintained in excess, exchange with butyllithium at −108 °C produced the lithium carbenoid with the bromine atom in an exo orientation, formed at least in part by exchange-induced epimerization at the carbenoid carbon atom. Carbenoids **1b** and **3b** are probably the kinetic as well as thermodynamic products of the exchange reaction (see below), and while the crown conformation may be the more stable, NMR-observed conformation of **1a** and **3a,** the exchange-directing chair conformation is probably present, available by a crown ⇌ chair interconversion having a low $\Delta G^{\ddagger}$. In this regard it is pertinent to note that chair ⇌ chair interconversion of the related 4,7-dihydro-1,3-dioxepin proceeds with $\Delta G^{\ddagger}$ estimated at less than 7 kcal mol^{-1} (−130 °C)[11] and that the crown and chair conformations of cycloheptene oxide, another bicyclo[5.1.0]octyl-type system, interconvert with a $\Delta G^{\ddagger}$ of 7.9 kcal mol^{-1} (−122 °C).[13]

Returning to the halogenation of carbenoids, chlorocarbenoid **3b** was prepared from **3a** and butyllithium at −78 °C in THF-ether and brominated with bromotrichloromethane, without incident, to give **3d,** mp 59.5–61 °C, in 48% yield. The chlorination of bromocarbenoid **1b** was a different story, however, because the product, bromochlorocyclopropane **6a,** was unstable under the conditions of its preparation. In fact, on one occasion, dibromo compound **1a,** after being completely converted at −78 °C to carbenoid **1b** by methyllithium–lithium bromide, was regenerated in 60% yield (isolated) by *chlorination* of **1b** with carbon tetrachloride. In following the progress of the chlorination reaction, vapor chromatographs of reaction aliquots revealed the initial formation and subsequent disappearance of a peak due to **6a.** Scheme I shows a plausible se-

Scheme I



quence of events which can explain the observed "chlorinative bromination" reaction. Supporting this explanation are the observations that (1) exclusion of lithium bromide suppresses the re-formation **1a;** (2) **6b** reacts with lithium bromide to give **1b;**[3] and while **1b** was never brominated with $BrCCl_3$ in a separate reaction, carbenoid **3b** was. The proposed equilibrium between **6a** and **6b** is believed to favor **6a** since, in earlier experiments, **1a** had not shown any appreciable exchange with $LiCCl_3$.

The best method (of many tried) for the chlorination of **1b** called for the use of butyllithium for the exchange of **1a** in ether:THF (4:1 by volume) at −78 °C, followed by the rapid addition of excess CCl_4, followed, in turn, by a methanol quench of the reaction 7–10 min later. This procedure gave **6a,** mp 55–56.5 °C, in 54% yield.

The bromochlorocyclopropane epimers, **3d** and **6a,** had identical retention times on a variety of VPC columns. A mixture melting point was depressed, however, and the epimers had slightly different NMR spectra. The principal difference was the slight, downfield shift of the cyclopropyl protons of **6a** (τ 7.52) relative to **3d** (τ 7.66). Analogous situations have been reported[14] wherein cyclopropyl hydrogens trans to the most electron-withdrawing substituent are further downfield than the corresponding cis protons. Using this chemical shift difference it was determined that 5–7% of one epimer would be detectable as contamination of the other, making the lower limit of isomeric purity of each 93–95% by this method.

Proof of configuration and higher purity of **3d** and **6a** was obtained by converting each to the corresponding monochloropropanes. Thus, the reaction of ethereal **3d** with methyllithium or methyllithium–lithium bromide at −78 °C, followed shortly by a methanol quench, gave monochloro compound **3c** in 98% yield (as measured by VPC using the internal standard method) containing only a trace, if any, of **6a.** In a like manner, **6a,** which underwent slower exchange than **3d** in ether, was converted in ether–THF to **6c** in 70% isolated yield. In this reaction product mixture, **3d** was present to the extent of less than 3%. The key feature of the NMR spectrum of **6c** was the triplet signal of H-8 seen at τ 6.42, J = 7.5 Hz, consistent with cis coupling across a cyclopropane ring. Also of interest was the lower-field chemical shift of the cyclopropyl protons of **6c** (τ 8.2) relative to their **3d** counterparts (τ 8.5).[13] A low-yield reaction product with a VPC retention time very close to that of **6c** prevented us from obtaining **6c** in analytical purity (maximum purity ~99%). However, a high resolution mass spectrum showed a $M^+ - Cl$ peak at *m/e* 113.0595 (calculated: *m/e* 113.0603). Thus, the bromochlorocyclopropanes **3d** and **6a** are epimers with their configurations as shown.

Experimental Section

General. Mass spectra were done by Battelle Institute in Columbus, Ohio. All the reactions which involved the use of potassium metal, all dihalo-carbene reactions, and all carbenoid preparations were conducted in an atmosphere of dry nitrogen. The alkyllithium reagents were periodically analyzed by the method of Gilman and Cartledge[15] (see also ref 5).

Analyses by VPC were performed on the following aluminum tubing columns 6 ft × 0.25 in. (unless noted otherwise): A, 6 ft × 0.12 in. 2% UCW 98 on Diatoport S; B, 6 ft × 0.12 in. 10% UCW 98 on Diatoport S; C, 2% UCW 98 on Diatoport S; D, 5% UCW 98 on Diatoport S; E, 10% UCW 98 on Diatoport S; F, 10% SE 30 on Chromosorb W (AW & DMCS); G, 9 ft × 0.12 in. 15% UCW 98 on Diatoport S; H, 5% ethylene glycol adipate on Diatoport S; I, 9 ft × 0.12 in. 10% C-20M on Chromosorb P (NAW); J, 4 ft × 0.25 in. 10% Carbowax and 4% KOH on Chromosorb W (AW & DMCS); K, 15% poly(tetramethyleneglycol ether)-3000 on Chromosorb P (NAW); L, 6 ft × 0.12 in. 10% TEGA on Chromosorb W; M, 5% THEED; and N, (9 ft × 0.25 in.) 20% Carbowax 20M on Chromosorb W (AW & DMCS).

2,2-Dimethyl-4,7-dihydro-1,3-dioxapin. A mixture of 26.4 g (0.30 mol) of *cis*-2-butene-1,4-diol, 29 g (0.50 mol) of acetone, 41.6 g (0.40 mol) of trimethyl orthoformate, 0.06 g (catalytic amount) of *p*-toluenesulfonic acid, and 70 ml of benzene was stirred for 30 min and refluxed for 2 h. Then 14 g (0.24 mol) more of acetone were added, and the mixture was refluxed 2 h longer, cooled, and filtered. Distillation yielded a main fraction, bp 57 °C (14 mm), 22.3 g (58.2% yield) which was pure by VPC (column A): NMR τ 4.47 (t, J = 1.7 Hz, 2

H), 5.58 (d, J = 1.7 Hz, 4 H), 8.70 (s, 6 H), in agreement with the partial spectrum reported by Friebolin.[11]

8,8-Dibromo-3,5-dioxabicyclo[5.1.0]octane (1a). To 400 ml of *tert*-butyl alcohol (distilled from sodium hydride) was added 18.6 g (0.465 mol) of potassium. The mixture was refluxed until total dissolution occurred.

A dry 1-l. Morton flask (high-speed Hirsch stirrer) was charged with 52.5 g (0.515 mol) of 4,7-dihydro-1,3-dioxapin,[4] 98.0 g (0.39 mol) of freshly distilled bromoform, and 125 ml of pentane. Then, the potassium *tert*-butoxide solution was added over 3 h from a dropping funnel to the rapidly stirred, cooled (−20 °C) solution of olefin and bromoform.

The high speed stirring was continued 5 more h at a temperature range of −10 to 5 °C. The resulting light yellow, heterogeneous mixture was quenched with water and worked up to give 11.5 g of reddish oil which partially solidified when cooled to −78 °C. This material was washed with a few milliliters of pentane leaving 9.9 g (9.1%) of light yellow solid ("wet"), mp 53–56 °C after blotting. This was sublimed to give, in almost quantitative recovery, colorless crystals, mp 55–57.5 °C. Several crystallizations from ether–pentane (1:1) gave needle-like crystals: mp 56–57.5; NMR τ 5.02 (d, J_{gem} = −7.0 Hz, H_4), 5.96 (d, J_{gem} = −7.0 Hz, H_4), 5.45 (q, J_{gem} = −13 Hz, J_{vic} ~ 7 Hz plus additional splitting, exo $H_{2,6}$), 6.40 (q, J_{gem} = −13 Hz, J_{vic} ~ 9 Hz plus additional splitting, endo $H_{2,6}$), 7.8 (m, $H_{1,7}$).

Anal. Calcd for $C_6H_8Br_2O_2$: C, 26.50; H, 2.97. Found: C, 26.77; H, 3.06.

***exo*-8-Bromo-3,5-dioxabicyclo[5.1.0]octane (1c).** To a cooled (−78 °C) mixture of 1.85 g (0.673 mmol) of **1a** in 40 ml of ether was added methyllithium–lithium bromide (10 mmol) over 4 min. This heterogeneous mixture was stirred for an additional 17 min and quenched by the slow addition of 1 ml of water. The mixture was washed, dried (K_2CO_3–$MgSO_4$ mixture), and concentrated in vacuo (20 mm) to 0.984 g (75% yield) of pale yellow oil, 85% pure by VPC (column C). Some of the product was distilled, and the major component, **1c**, was further purified by preparative VPC (column C). The VPC yield of **1c** using the above procedure at −20 °C was 90% (column B, internal standard); similarly **1a** plus phenyllithium gave **1c** plus bromobenzene; NMR τ 5.13 (d, J_{gem} = −7.2 Hz, H_4), 5.86 (d, J_{gem} = −7.2 Hz, H_4), 5.72 (d of t, J_{gem} = −13 Hz, $J_{1,2} \sim J_{1,7} \sim 2$ Hz, endo $H_{2,6}$), 6.13 (d, J_{gem} = −13 Hz, $J_{vic} \sim 0$, exo $H_{2,6}$), 6.77 (t, J_{vic} = 4.7 Hz, H_8), 8.41 (m, $H_{1,7}$).

Anal. Calcd for $C_6H_9BrO_2$: C, 37.33; H, 4.69. Found: C, 37.32; H, 4.77.

***exo*-8-Bromo-*endo*-8-deuterio-3,5-dioxabicyclo[5.1.0]octane (1d),** which was prepared by quenching the carbenoid **1b** at −78 °C with deuterium oxide after 30 min or 7.5 h, exhibited an NMR spectrum similar to that for **1b** except for the absence of the triplet at 6.77. The yield of **1d** was about 90%.

***exo*-8-Bromo-*endo*-8-methyl-3,5-dioxabicyclo[5.1.0]octane (1e).** To a cooled (−20 °C) stirred solution of 0.45 g (1.7 mmol) of **1a** in 15 ml of ether was added methyllithium–lithium bromide (2.06 mmol), which resulted in a colorless precipitate. An aliquout withdrawn after 7 min was quickly quenched and VPC analysis (column B) showed only **1c.** Methyl iodide (8 mmol) was added, all at once, and after 15 min 3.5 ml of THF was added dropwise over a period of 5 min by which time the reaction mixture became a clear colorless solution. Ten minutes later a quenched aliquot showed that compound **1e** of longer VPC retention time (column B) had been formed and accounted for approximately 95% of the total peak area. The reaction mixture was quenched with water after a total time of 110 min at −20 °C. The usual workup yielded 0.267 g of colorless oil of approximately 87% purity (75% yield). The major peak was purified by preparative VPC (column D): NMR τ 5.20 (d, J_{gem} = −6.0 Hz, H_4), 5.38 (d, J_{gem} = −6.0 Hz, H_4), 5.70 (d of mult, J_{gem} = −13 Hz, mult $w/2 \sim 8$ Hz, $H_{2,6}$), 6.19 (d of mult, J_{gem} = −13 Hz, mult, $W_{1/2} \sim 8$ Hz, $H_{2,6}$), 7.97 (s, CH_3), 8.2 (m, $H_{1,7}$).

An attempted preparation of **1e** from methyl iodide and **1b** under the same conditions except for the absence of THF yielded none of **1e** after 1 h of stirring at −15 °C. However, upon the addition of THF **1e** immediately was formed giving a ratio of **1e** to **1c** of 9:1. Also, **1e** and **1c** were formed as the major products in a ratio of 7:3 when **1b** was prepared at −10 °C in THF as sole solvent (no methyl iodide added).

Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.62; H, 5.26. Found: C, 40.73; H, 5.41.

***exo*-8-Bromo-*endo*-8-(diphenylhydroxymethyl)-3,5-dioxabicyclo[5.1.0]octane (1f).** To a cooled (−20 °C) solution of 0.312 g (1.15 mmol) of **1a** in 35 ml of ether was added methyllithium–lithium bromide (1.59 mmol) which gave **1b** (100%). At 20 min 0.245 g (1.35 mmol) of benzophenone in 2 ml of ether was added and stirring was continued 40 min longer, over which time the temperature increased to −15 °C. Approximately 50% of the ether (supposedly all the methyl bromide formed in the exchange) was distilled in vacuo at this temperature. Thirty minutes later the mixture was cooled to −50 °C and 4.5 ml of THF was slowly added, which gave some clearing of the solution. The temperature was increased to −10 °C over the next 85 min, was stirred at this temperature for 40 min, and was quenched with deuterium oxide. Workup gave 0.483 g of a semisolid material which, when triturated with warm pentane, left 0.135 g (33% yield) of finely divided crystals, mp 194–203 °C dec. Recrystallization (twice) from THF–benzene gave finely divided crystals, pure as indicated by TLC (silica gel): mp 210.5–211 °C dec; ir (KBr) 3330 cm^{-1} (OH); NMR (in Me_2SO-d_6) τ 2.5 (m, 10 aromatic H), 3.33 (s, disappeared in D_2O, OH), 4.77–5.93 (complex m, 4 H at C_2 and C_6), 7.5 (m, $H_{1,7}$).

The VPC yields (column A, internal standard) of **1c** and 3,5-dioxatricyclo[5.1.0.0^{4,8}]octane[3] were 14 and 17%, respectively, based on **1a.** Also, the NMR spectrum showed that the **1c** obtained contained no deuterium. No **1e** was produced.

Attempted preparations of **1f** at −78 °C with reaction times as long as 7.5 h using ether as the sole solvent failed to yield any **1f,** giving 1d (98% VPC, NMR) instead after a D_2O quench. In another attempt to form **1f** at −78 °C, methyl bromide was distilled in vacuo from the reaction mixture and a small amount of THF added. After 2 h at −78 °C, workup gave **1f** as a finely divided crystalline material, mp 202–205 °C dec, (41% yield) after one crystallization from THF–hexane. Another experiment using ether as the solvent at −15 to 8 °C over a reaction period of 3.3 h yielded **1f,** mp 208–209 °C dec, in 13% yield.

Anal. Calcd for $C_{19}H_{19}BrO_3$: C, 60.81; H, 5.10. Found: C, 60.81; H, 5.31.

8,8-Dibromo-4,4-dimethyl-3,5-dioxabicyclo[5.1.0]octane (2a). A dry 1-l. Morton flask equipped with a high-speed mechanical stirrer and cooling bath was charged with 22.3 g (0.174 mol) of 2,2-dimethyl-4,7-dihydro-1,3-dioxapin, 42.5 g (0.168 mol) of bromoform, and 100 ml of pentane. Then potassium *tert*-butoxide solution [9.30 g (0.23 mol) of potassium in 250 ml of alcohol–benzene] was added to the cooled (−10 °C), stirred solution of olefin and bromoform over a 1.5-h period. Vigorous stirring (600–900 rpm) with a Hirsch stirrer was continued 19 h longer at −10 to −5 °C. After the addition of 100 ml of pentane and 100 ml of water, the organic phase was washed with water, the aqueous phase was extracted twice with ether, and the organic phases were combined and dried. Distillation gave 60 ml of dark yellow liquid which was decolorized with charcoal and further evaporated at 48 °C (0.1 mm) to give 8.1 g of **2a,** mp 67–72 °C. Recrystallization from benzene–pentane at −20 °C yielded 2.1 g of **2a** as slightly-yellow prismatic crystals, mp 70–76 °C which, in turn yielded upon sublimation at 70 °C (0.1 mm) 1.9 g of clear crystals, mp 73–75 °C. The above mother liquors yielded, after evaporation of solvent, 4.6 g of **2a** as a "wet" brown solid, which after two sublimations gave 3.9 g of **2a,** mp 69–72 °C. The sublimed material, 5.8 g, constitutes an isolated yield of 11.5%. Subsequent recrystallizations yielded a sample, mp 74–76 °C, for elemental analysis. VPC (column A, internal standard) yields averaged 18%. *Note:* Special precaution must be taken with the crude reaction mixture to prevent hydrolysis of the ketal function: keep basic while wet or moist (K_2CO_3 drying) and avoid temperatures greater than 40 °C; NMR τ 5.6–6.3 ("A_2B_2 quartet" of multiplets J_{gem} = −13 Hz, 4 H at C-2 and C-6), 7.96 (quintet, peak separation = 3 Hz, $H_{1,7}$), 8.72 (s, CH_3), 8.78 (s, CH_3).

Anal. Calcd for $C_8H_{12}Br_2O_2$: C, 32.03; H, 4.03. Found: C, 32.34; H, 4.24.

***cis*-2,3-Di(hydroxymethyl)-1,1-dibromocyclopropane.** Several solid residues were recovered as insoluble or nonvolatile materials from filtrations and sublimations of crude preparations of **2a.** A pure sample of the title compound, mp 101–103 °C, was obtained upon recrystallization from acetone–hexane (1:4 by vol). The cyclopropyl region of the NMR spectrum was obscured due to absorption in that region by the (required) acetone-d_6 solvent. The title compound was also prepared by acidic hydrolysis of **1a** and **2a.**

Anal. Calcd for $C_5H_8Br_2O_2$: C, 23.10; H, 3.10; Br, 61.49. Found: C, 23.16; H, 3.22; Br, 61.47.

An oily diacetate of the preceding diol was prepared using acetic anhydride in pyridine. It was characterized by ir and NMR only: ir

(CCl_4) 1730 cm^{-1} (C=O); NMR ($CDCl_3$) τ 5.4–6.0 ("A_2B_2 quartet" of multiplets, $J_{gem} \sim -11$ Hz, 2 CH_2), 7.8 (singlet superimposed on mult 2 CH_3 plus cyclopropane H).

***exo*-8-Bromo-4,4-dimethyl-3,5-dioxacyclo[5.1.0]octane (2c).** To a cooled (−78 °C) solution of 1.12 g (3.70 mmol) of **2a** in 60 ml of ether was added 6 mmol of methyllithium–lithium bromide over a 0.5-min period. The solution remained clear until quenched (after 3.5 min) with 0.8 ml of methanol. An aliquot removed from the crude mixture indicated that **2c** was formed in 81% yield (VPC, column A, internal standard). The mixture was washed, dried with potassium carbonate, filtered, and concentrated to give 0.57 g of colorless oil (crude yield, 70%). This oil was purified by molecular distillation [pot temp 50–65 °C (8 mm)] followed by preparative VPC (column C): NMR τ 5.7–6.3 ("A_2B_2 quartet" of multiplets, $J_{gem} \sim -13$ Hz, 4 H at C-2 and C-6), 6.90 (t, J_{vic} = 4.0 Hz, H_8), 8.4 (m, $H_{1,7}$), 8.70 (s, CH_3), 8.75 (s, CH_3).

Anal. Calcd for C, 43.46; H, 5.93. Found: C, 43.56; H, 5.91.

***exo*-8-Bromo-4,4-*endo*-8-trimethyl-3,5-dioxabicyclo[5.1.0]octane.** To a stirred solution of 0.19 g (0.6 mmol) of **2a** in 7 ml of dry ether at −78 °C was added 0.8 mmol of methyllithium–lithium bromide. A cold aliquot, quickly quenched by the addition of methanol, was found by VPC (column A) to contain **2c** as the only component. At 5 min, 2.3 mmol of methyl iodide was added. Aliquots withdrawn from the clear solution and quenched at 33 and 44 min showed only **2c.** At 61 min 5 ml of dry THF was added. Aliquots taken at 63 (reaction turbid) and 93 min and at 4 h showed the ratios of the title compound to **2c** to be 0.56, 2.3, and 4.9, respectively. Workup (use K_2CO_3 as drying agent) gave 0.22 g of light yellow oil which was contaminated with THF. The title compound was isolated by preparative VPC (column C). However, the recovery from the VPC collection was very poor, and the column deteriorated after several injections. The NMR spectrum obtained was similar to that of **2c** but it had the expected singlet at τ 8.00 (3 H) and contained no (triplet) signal at τ 6.9 expected for a C-8 proton.

***exo*-8-Bromo-*endo*-8-(diphenylhydroxymethyl)-4,4-dimethyl-3,5-dioxabicyclo[5.1.0]octane (2d).** To a cooled (−78 °C) solution of 0.37 g (1.23 mmol) of **2a** in 22 ml of ether was added 1.18 mmol of methyllithium–lithium bromide. To the resulting homogeneous, colorless solution was added 0.185 g (1.02 mmol) of benzophenone in 1 ml of ether, giving a yellow coloration which lasted 15 min. The stirring at −78 °C was continued for 9 h during which time the solution remained homogeneous. After a cold quench (D_2O) the usual workup gave 0.436 g of cloudy oil which crystallized after treatment with pentane (−78 °C) to give 175 mg, mp 128–131 °C, of **2d.** The mother liquor yielded an additional 15 mg of **2d,** mp 126–133 °C (39% combined, crude yield). A sample was recrystallized from a methylene chloride–pentane (2:1 by vol) yielding a pure sample: mp 132.5–133 °C; ir (CCl_4) 3350 cm^{-1}, sharp, moderately strong band which remained unchanged upon dilution from 10 to 4% except for a decrease of intensity; NMR τ 2.3–2.8 (m, 10 phenyl H's), 4.33 (s, OH), 5.2–6.1 (m, 4 H on C_2 and C_6), 8.6 (s, 2 CH_3).

Reactions of ethereal **2b** with benzophenone at −78 °C gave lower yields of **2d** when shorter reaction times were used. For example, a 50-min reaction gave **2d,** mp 132–134 °C, in 14% yield.

Anal. Calcd for $C_{21}H_{23}BrO_3$: C, 62.54; H, 5.75. Found: C, 62.49; H, 6.04.

8,8-Dichloro-3,5-dioxabicyclo[5.1.0]octane (3a). To 45.6 g (0.46 mol) of 4,7-dihydro-1,3-dioxapin[4] in 250 ml of pentane at 0 °C was added 73 g (1.35 mmol) of sodium methoxide. To this stirred (mechanical) mixture was added 70 g (0.37 mmol) of ethyl trichloroacetate over a 10-min period, after which time a violent reaction occurred resulting in partial loss of material. The dropwise addition of an additional 30 g (0.16 mol) of ethyl trichloroacetate was continued over a 25-min period. The resulting mixture was stirred for 8 h at 0 °C and quenched by the dropwise addition of 60 ml of water. Workup gave a red oil, which upon dissolution in pentane and cooling (−40 °C) gave 14.7 g of semi-solid material which was sublimed (50 to 65 °C, 0.6 to 0.8 mm) giving 11.6 g of **3a,** mp 51–55.5. Recrystallization from hexane and then ether gave 10 g of white crystalline material, mp 53–56 °C (with prior softening). This, in turn, was sublimed (50 °C, 1 mm) to give 9.55 of prismatic crystals, mp 53.5–55.5 °C (11% yield). Further recrystallization gave an analytical sample mp 54–55.5 °C; NMR τ 4.92 (d, J_{gem} = −7.0 Hz, H_4), 5.67 d, J_{gem} = −7.0 Hz, H_4), 5.42 (q, J_{gem} = −13.5 Hz, $J_{vic} \sim 7$ Hz with further splitting, exo H on C_2 and C_6), 6.26 (q, J_{gem} = −13.5 Hz, $J_{vic} \sim 9$ Hv with further splitting, endo H on C_2 and C_6), 7.8 (m, $H_{1,7}$).

Anal. Calcd for $C_6H_8Cl_2O_2$: C, 39.37; H, 4.40. Found: C, 39.65; H, 4.62.

***exo*-8-Chloro-3,5-dioxabicyclo[5.1.0]octane (3c).** To 0.281 g (1.25 mmol) of **3d** in 20 ml of ether at −78 °C was added 3.6 ml (1.24 mmol) of butyllithium in hexane. This gave immediately a colorless precipitate. The mixture was quenched with methanol after 12 min. The workup, similar to that for **1c,** gave 0.207 g of **3c** of about 80% purity (75% yield). Some of this material was purified by preparative VPC (colume E): NMR τ 5.25 (d, J_{gem} = −7.0 Hz, H_4), 5.95 (d, J = −7.0 Hz, H_4), 5.85 (d of t, J_{gem} = −13.0 Hz, $J_{1,2} \sim J_{2,7}$ = 1.9 Hz, endo H on C_2 and C_6), 6.20 (d, J_{gem} = −13.0 Hz, $J_{vic} \sim 0$, exo H on C_2 and C_6), 6.56 (t, J_{vic} = 4.0 Hz, H_8), 8.5 (m, $H_{1,7}$).

Similarly, **3c** was formed from **3d** and methyllithium or methyllithium–lithium bromide in yields of 95% (VPC, several columns, internal standard). Also, **3c** was formed from **3a** and butyllithium at −16 to −8 °C in ether using a methanol quench. Yield determinations (VPC, internal standard) showed **3c** (54%), 3,5-dioxatricyclo[5.1.0.$0^{4,8}$]octane (26%),[3] plus a butyl-containing unknown (~10%), and traces of other products.

When **3b** was prepared in ether at −78 °C from **3a** and butyllithium, it was found that 2 equiv of butyllithium were required for complete exchange of the starting **3a.** However, in the presence of added THF only 1 equiv was required at −78 °C. Also, it was found that the exchange reaction between **3a** and butyllithium at −78 °C in solvent mixtures of varied ratios of pentane/THF/TMEDA proceeded stereoselectively giving, nearly exclusively, **3c** after methanol quench.

Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.10. Found: C, 48.66; H, 6.05.

***endo*-8-Bromo-*exo*-8-chloro-3,5-dioxabicyclo[5.1.0]octane (3d).** To a cooled (−78 °C), stirred solution of 1.472 g (8.07 mmol) of **3a** in 14 ml of THF and 70 ml of ether was added 6.2 ml of butyllithium (8.05 mmol) in pentane. VPC analysis of an aliquot of this heterogeneous mixture indicated that halogen–metal exchange was incomplete. At 12 min, another 0.4 ml of butyllithium was added; at 20.5 min, 1.5 ml (14 mmol) of bromotrichloromethane was added by syringe giving a yellow suspension. Quenching the reaction at 27 min by the addition of 0.4 ml of methanol resulted in decoloration. Workup gave a yellow oil which crystallized upon addition of a minimum volume of pentane to give 1.01 g of **3d,** mp 57–60 °C. Recrystallization yielded 0.919 g, mp 59.5–61 °C (48% yield), 95% pure by VPC (column A). A sample for elemental analysis was prepared by preparative VPC (column F) followed by sublimation: mp 59.5–61 °C; NMR τ 4.81 (d, J_{gem} = −7.0 Hz, H_4), 5.40 (d, J_{gem} = −7.0 Hz, H_4), 5.29 (q, J_{gem} = −13.5 Hz, $J_{vic} \sim 8$ Hz with further splitting, exo H on C_2 and C_6), 6.18 (q, J_{gem} = −13.5 Hz, $J_{vic} \sim 9$–10 Hz with further splitting, endo H on C_2 and C_6), 7.7 (broad m, $H_{1,7}$).

Anal. Calcd for $C_6H_8BrClO_2$: C, 31.67; H, 3.54. Found: C, 31.57; H, 3.58.

***exo*-8-Bromo-*endo*-chloro-3,5-dioxabicyclo[5.1.0]octane (6a).** To a cooled (−78 °C) solution of 7.00 g (25.7 mmol) of **1a** in 410 ml of ether and 130 ml of THF was added 24 ml of butyllithium in pentane (28.8 mmol). Quenched aliquots taken at 10 and 16 min showed (VPC, column B) **1c** exclusively. To the colorless, homogeneous solution at 20 min was added (all at once) 8 ml (82.4 mmol) of carbon tetrachloride. The resulting colorless suspension was quenched (methanol) 10 min later. Workup gave 4.7 g of semisolid, which upon brief treatment with a small volume of pentane yielded a soft solid. Sublimations (50 °C, 1 mm) and recrystallizations (hexane) gave 3.43 g of **6a,** mp 54–56 °C (54% yield). A sample was further purified for elemental analysis by recrystallization and sublimation: mp 55–56.6; NMR τ 4.80 (d, J_{gem} = −7.5 Hz, H_4), 5.36 (d, J_{gem} = −7.5 Hz, H_4), 5.24 (q, J_{gem} = −13.0 Hz, J_{vic} 8 Hz with further splitting, exo H on C_2 and C_6), 6.10 (q, J_{gem} = −13.0 Hz, $J_{vic} \sim 9$–10 Hz with further splitting, endo H on C_2 and C_6), 7.52 (broad m, $H_{1,7}$).

When carbenoid **1b** was prepared using methyllithium–lithium bromide in ether, treatment with carbon tetrachloride gave **1a,** mp 55–57 °C, in 64% yield.

The epimeric bromo-chloro compounds, **3d** and **6a,** could not be separated by vapor phase chromatography using columns A, B, C, D, F, G, H, I, K, L, M, and N. However, a mixture melted at 51–54 °C and chemical shift differences were noted in the NMR spectra.

Anal. Calcd for $C_6H_8BrClO_2$: C, 31.67; H, 3.54. Found: C, 31.86; H, 3.40.

***endo*-8-Chloro-3,5-dioxabicyclo[5.1.0]octane (6c).** To a cooled (−78 °C) solution of 0.16 g (0.7 mmol) of **6a** in 10 ml of ether and 1.5 ml of THF was added 2.4 ml (0.77 mmol) of methyllithium–lithium

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).

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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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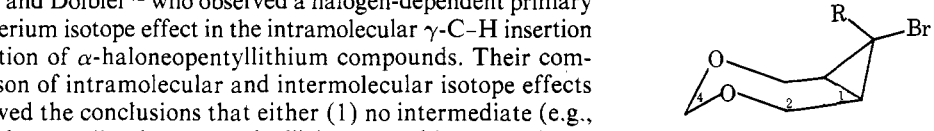
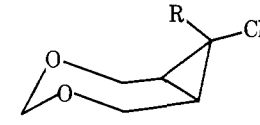
Abstract: The epimeric α-chlorocyclopropyllithium compounds **2b** and **3b**, prepared by Li–Br exchange on the epimeric bromochlorocyclopropanes, were thermolyzed, and the products of electrophilic reaction were characterized. Carbenoid **2b**, with exo Cl, cleanly gave a product of intramolecular 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.]

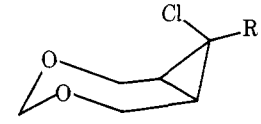


Upon our observation that the thermolysis of bromocarbe-

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