

part of the radical spectrum is being observed. Figure 1 shows that the high-field lines of the radical are somewhat decreased in intensity relative to the low-field lines of the radical. This communication between the hyperfine levels of the radicals probably arises from nuclear relaxation and will be discussed in a subsequent publication.

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-2086 and by the Air Force Office of Scientific Research under Grant AFOSR-70-1852.

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Received August 4, 1972

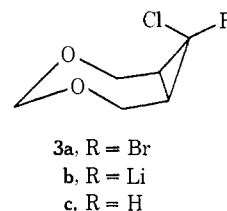
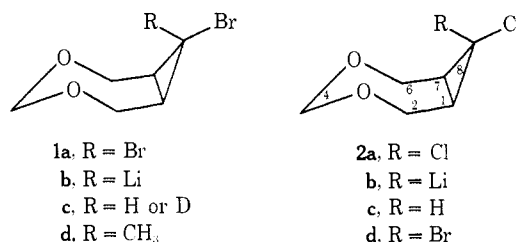
Carbenoids with Neighboring Heteroatoms. IV. Electrophilic Reactions of Epimeric α -Chlorocyclopropyllithium Compounds¹

Sir:

We wish to report, in preliminary form, our observations on the thermally induced electrophilic reactions of carbenoids which are epimeric at the carbenoid center. Earlier studies on α -haloalkyllithium compounds have provided kinetic² and other evidence³ which implicates these reagents as the reacting species in the addition of certain "chlorocarbenes" to carbon-carbon double bonds. More pertinent to the present work was the observation, by Goldstein and Dolbier,⁴ of a halogen-dependent primary deuterium isotope effect in the intramolecular C-H insertion reaction of α -haloneopentyllithium compounds, a result which implicated carbenoids as key intermediates in this electrophilic reaction, as well. In this communication we demonstrate the dependence of the course of the C-H insertion reaction on the stereochemistry of the substituents at the carbenoid carbon atom.

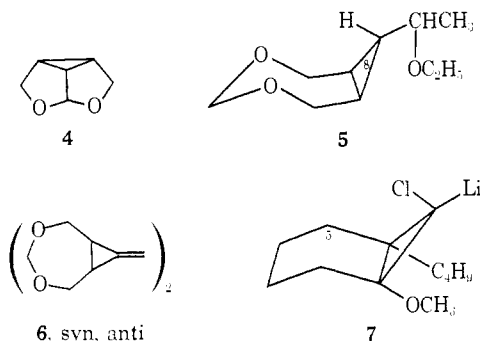
The precursors to the epimeric carbenoids used in this work, namely bromochlorocyclopropanes **2d** and **3a**, were synthesized as follows. The reaction of ethereal dibromocyclopropane **1a**⁵ (mp 56–57.5°) with methyllithium–LiBr at –20 or –78° afforded carbenoid **1b** in high yield as evidenced by the 90% yield of **1c** (nmr H-8 at δ 3.23 (t, $J_{\text{trans}} = 4.7$ Hz)) obtained upon water or D₂O quench of the reaction. In a similar manner, dichlorocyclopropane **2a**⁵ gave, upon reaction with butyllithium,⁶ chlorocarbenoid **2b**, as evidenced by the 70% yield of **2c** (nmr H-8 at δ 3.44 (t, $J_{\text{trans}} = 4.0$ Hz)) obtained after a water quench of the reaction. Chlorination of bromocarbenoid **1b** under narrowly

controlled conditions (**1a** plus butyllithium at –78° in 20:80 ether–THF, followed by a rapid addition of excess CCl₄ and a quench 7 min after the addition) gave **3a** (mp 55–56.5°) in 40–50% yields. The bromination of chlorocarbenoid **2b** with BrCCl₃ was more easily accomplished to yield **2d** (mp 59–61.5°) in 48% yield. While several vpc columns gave identical retention times for **2d** and **3a**, the mixture melting point of **2d** with **3a** was depressed, and chemical-shift differences were apparent when spectra of the pure compounds were compared. The successive reactions at –78° of **2d** with methyllithium and methanol gave **2c** (98%) while the same reaction sequence with **3a** gave a new monochloro compound, **3c** (nmr H-8 at δ 3.58 (t, $J_{\text{cis}} =$



7.5 Hz); mass spectrum $M^+ - Cl$ at 113.0595; ~80% yield).⁷ Thus, the bromochlorocyclopropanes **2d** and **3a** were shown to be isomers with their structures as indicated.

Carbenoids **1b** and **2b** were stable in ether below –20° while, in contrast, carbenoid **3b** yielded products of electrophilic reaction slowly even at –78°. The products of thermal decomposition in ether of the three



carbenoids prepared from methyllithium (without lithium bromide) are given in Table I. As can be seen from the data those carbenoids with exo halogen gave high yields of intramolecular C-H insertion (**4**, mp 44.5–46°) while that carbenoid with endo halogen gave, almost exclusively, products of intermolecular reactions (**5**, H-8 $J_{\text{trans}} = 5.5$ Hz determined using Eu(DPM)₃ with decoupling; *syn*-**6**, mp 209.5–211°; *anti*-**6**, mp 126.5–127.5°). Under more dilute conditions and at higher

(7) With the exception of **3c** and the carbenoids, all compounds gave elemental analyses, or displayed molecular ions, within the prescribed limits. Also, nmr, ir, and mass spectra were consistent with the proposed structures.

(1) (a) The generous support of the National Science Foundation through Grants GP-9543 and 28381 is acknowledged with appreciation. (b) Paper III: K. G. Taylor, W. H. Hobbs, M. S. Clark, and J. Chaney, *J. Org. Chem.*, **37**, 2436 (1972).

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(6) In ether solvent at –78°, 2 equiv of butyllithium was required for complete reaction of **2a**. At –20°, or with small amounts of THF present at –78°, the exchange reaction stoichiometry was 1:1.

Table I. Products of Carbenoid Thermal Decomposition

Entry	Carbenoid	Reaction conditions ^a		% products ^b		
		A	B	4	5	6
1	1b ^c	-8 (0.3)	0 (2)	80	Trace	
2	2b ^d	-10 (0.2)		26	Trace	
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 methyl-lithium (no LiBr unless 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 ($\pm 2\%$) were determined by vpc using internal standards unless otherwise indicated. ^c Methyl-lithium-LiBr used; other products: 1c (4%), 1d (6%). ^d Prepared from 2a and butyllithium; other products: 2c (54%), two butyl-containing unknowns ($\sim 20\%$). ^e Prepared from 2d, other products: 2c (trace). ^f Yields determined by isolation plus vpc; other products: 3c (1-2%), three unknowns (total 4-5%). ^g Reaction run using methyl-lithium-LiBr; other products: 1c (13%), 2c (3%), 3c (5%); yield of 6 by isolation.

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 is present may well be due entirely to halide exchange with concomitant carbenoid isomerization. The presence of bromide ion had little effect on the stereochemistry of the thermal reaction of bromocarbenoid 1b. Carbenoid 2b has yet to be tested in the presence of bromide ion.

The above results complement the deuterium isotope results of Goldstein and Dolbier⁴ and further indicate that in the transition state of α elimination LiX is bound to carbon tightly enough to influence the stereochemical outcome of these electrophilic reactions.

In the above we have emphasized the stereochemical difference at C-8 between 2b and 3b. It should be noted that these carbenoids differ in thermal stability and, most probably, in state of aggregation and conformation as well. The role of the first two effects is not understood but the importance of the last effect on intramolecular C-H insertion reactions of "cyclopropylidines" is well documented.⁸ Thus, if both oxygen atoms are coordinated with Li in 2b, then the resulting conformation of 2b (as shown) should preclude insertion at C-2 (or C-6). However, expecting that 3b should have a conformation similar to that of 3a which, by nmr, is different from that shown, we conclude that intramolecular C-H insertion at C-2 and C-4 (or C-6) is not conformationally precluded and that other factors, among them the stereochemistry at C-8, must dictate the product distribution.

Finally, while with the present carbon skeleton C-H insertion cleanly takes place on the side opposite the departing halogen, this may not be generally true. For example, we have already observed that carbenoid 7 yields C-H insertion at C-5 in 51% yield.^{1b} Further

work on the stereochemistry of reactions of 2b and 3b at higher temperatures is in progress.

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Received August 11, 1972

Lifetime of the ⁴T_{2g} State of Tris(2,4-pentanedionato)chromium(III) Reexamined

Sir:

Observation of a relatively rapid relaxation between the ¹A and ⁵T states of an iron(II) complex¹ has prompted reexamination of slower intersystem crossing processes reported for metal complexes. A rate constant of $1.2 \times 10^5 \text{ sec}^{-1}$ for intersystem crossing from the photoexcited ⁴T_{2g} state to the ²E_g state of Cr(acac)₃ has been inferred² from an apparent maximum in the observed luminescence intensity as a function of time at 77°K. We have reinvestigated the luminescence of this complex and find no evidence of such a maximum. Under the conditions of our experiment, this implies a lower limit of 10^7 sec^{-1} for the rate constant for intersystem crossing to the ²E_g state.

Tris(2,4-pentanedionato)chromium(III)³ was purified by recrystallization and characterized by elemental analyses and its visible absorption spectrum.⁴ A $10^{-2} M$ solution in 1:1 methanol-ethanol was degassed and sealed *in vacuo* in a silica cell which was immersed directly in liquid nitrogen to form a clear glass. A pulsed dye laser was used as the excitation source.⁵ The output wavelength of the dye laser was determined with a Spex 1700 III spectrograph to be 593 nm with a band width of 2 nm. The luminescence was observed through a Corning 2-64 filter and a Jarrell-Ash 1/4 meter monochromator with a spectral band width of approximately 30 nm. An RCA C31034A photomultiplier tube with a flat relative sensitivity to 840 nm and a Tektronix 454 oscilloscope with a photodiode external trigger completed the detection system.

Typical results are presented in Figure 1. On the slowest time scale, Figure 1c, a phosphorescence decay is observed with a lifetime at $431 \pm 9 \mu\text{sec}$, corresponding to a rate constant of $2.3 \times 10^4 \text{ sec}^{-1}$ at 77°K. This is in excellent agreement with the lifetime of 420 μsec reported⁶ at 85°K but somewhat longer than the lifetime of 360 μsec previously reported² at 77°K. We observed lifetimes as short as 180 μsec in preliminary experiments when the sample was not directly immersed in liquid nitrogen but was cooled by thermal contact with a reservoir at 77°K. This reflects the expected temperature dependence of the phosphorescence lifetime and suggests that in the previous experiment² the sample temperature was somewhat greater than 77°K. The wavelength of maximum luminescence was observed to be 785 nm, in good agreement with the reported⁷ value of 777 nm, considering the wide band

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