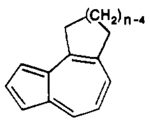
the [6 + 4] cycloaddition. In order to test the efficacy of this substituent effect in intramolecular reactions, we prepared the dienamines **9a–c** and the silyl dienol **9c′** according to the procedures outlined in Scheme II.

The oxidation of the diols **5a** or **5b** with 1 equiv of PCC[6] afforded the corresponding hydroxyaldehydes[7] which undergo the Wittig reaction with 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide[8] and potassium *tert*-butoxide in THF to produce **7a** or **7b**.[9] The synthesis of **7c** begins with ozonolysis of 1-methylcyclohexene (**6**) to produce 6-oxoheptanal; reaction of this ketoaldehyde with the same reagent occurs selectively at the aldehyde moiety to give **7c**. The Wittig reaction gives a mixture of cis and trans alkenes, 7 in each case. The fulvenes **8a** or **8b** were formed from **7a** or **7b** with cyclopentadiene–diethylamine,[10] while the fulvene **8c** was produced from **7c** and cyclopentadiene by using KOH in MeOH–THF.[11] Hydrolysis of the fulvene ketals gives unsaturated aldehydes **8a–c**. The trans isomer of **8** is produced exclusively, even though the cis, trans mixture **7** was used in these reactions. These unsaturated aldehydes can be converted into dienamines **9a–c** with diethylamine and K_2CO_3.[12] The siloxy diene **9c′** was prepared from the aldehyde **8c** with trimethylsilyl chloride and $ZnCl_2$.[13]

The electron-rich dienamines, **9a–c**, were not isolated, but warming solutions of these dienes overnight at 40 °C causes intramolecular cycloadditions, followed by spontaneous elimination of diethylamine, to produce the orange-red[5] dihydroazulenes **10a–c** in good yields (Scheme II).[14,15] The siloxy diene **9c′** produces both the dihydroazulene **10c** and rearrangement products containing the trimethylsiloxy group. These rearrangement products have not yet been characterized.

The carbon skeletons of **10a** and **10b** were verified by dehydrogenation with sulfur in triglyme to give brilliant blue azulenes **11a** and **11b**, in 85% and 38% yields, respectively. The cis stereochemistry of **10a** was indicated by NMR spectroscopy: the protons at the saturated 5–7 fusion are coupled by 6.3 Hz. Dihydroazulene **10b** is a 1:1 mixture of cis and trans isomers which has not surrendered to chromatographic coaxing. The stereochemistry of **10c** was not determined. but a single isomer is formed in the reaction.



11
a: n=5
b: n=6

Thus, the intramolecular [6 + 4] cycloadditions of suitably activated dienylfulvenes can be used to assemble hydroazulenes fused to a third ring. Applications to synthesis and comparisons of stereochemistries to those of analogous Diels–Alder reactions will be forthcoming.

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(7) A more elegant route to appropriate terminally differentiated compounds involves the modified ozonolysis of alkenes: Schreiber, S.; Claus, R. E.; Reagan, J. *Tetrahedron Lett.* **1982**, *23*, 3867.

(8) Cresp, T. M.; Sargent, M. V.; Vogel, P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 37.

(9) New compounds were characterized by spectral methods and by high-resolution mass spectrometry.

(10) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 7129.

(11) Yates, P. *Adv. Alicyclic Chem.* **1968**, *2*, 70.

(12) Hunig, S.; Kahanek, H. *Chem. Ber.* **1957**, *90*, 238.

(13) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

(14) Yields given are for the overall conversion of **8** to **10**. The analogous reaction using pyrrolidine in place of diethylamine is unsuccessful.

(15) Compare the couplings observed for cis- and trans-fused hydrindan systems of 4–6 and ~11 Hz, respectively: Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, *103*, 5200.

Transition Structure for the Reaction of a Carbenoid, $LiCH_2F$, with Ethylene

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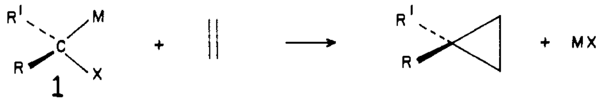
Carbenoids,[1] **1**, are organometallic species that transfer a carbene unit, CRR′, to alkenes to form cyclopropanes.[2] The structures and reactions of carbenoids have been the subject of theoretical[3-8] and experimental studies,[1,2,9-15] but the transition structures of carbenoid reactions remain only the subject of speculation. We wish to report a computational investigation of the reaction of the simplest carbenoid, $LiCH_2F$, with ethylene, and to compare our results with previous proposals[1,9-14] and computed carbene cycloaddition transition structures.[16-21]



M = metal; X = halogen; R,R' = alkyl or halogen

For the Simmons–Smith reaction,[10,11] in which the carbenoid is $IZnCH_2I$, or a solvated or aggregated version thereof, the "butterfly" transition structure, **2**, has been proposed.[10] Here, L and L′ represent "passive" ligands in the reaction. A three-dimensional representation, **3**, was proposed later,[11] in which in-

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(1) Closs, G. L.; Closs, L. E. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 334. Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(2) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; pp 83–128. Marchand, A. P. In "The Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1977; Supplement A, Part 1, pp 553–557, 585–587. Gilchrist, T. L.; Rees, C. W. "Carbenes, Nitrenes, and Arynes"; Thomas Nelson and Sons, Ltd.: London, 1969; pp 85–128. Recent reviews: Siegel, H., *Top. Curr. Chem.* **1982**, *106*, 55. Taylor, K. G. *Tetrahedron* **1982**, *38*, 2752. Moss, R. A.; Jones, M., Jr. "Reactive Intermediates"; Wiley-Interscience: New York, 1981; Vol. 2, p 796. Wulfman, D. S.; Polling, B. "Reactive Intermediates"; Plenum Press: New York, 1980; Vol. 1, Chapter 5. Krief, A. *Tetrahedron* **1980**, *36*, 2531.

(3) Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1979**, 883.

(4) Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4963.

(5) Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 7747.

(6) Vincent, M. A.; Schaefer, H. F., III. *J. Chem. Phys.* **1982**, *77*, 6103.

(7) Rohde, C.; Clark, T.; Kaufman, E.; Schleyer, P. v. R., *J. Chem. Soc., Chem. Commun.* **1982**, 882.

(8) Luke, B. J.; Pople, J. A.; Schleyer, P. v. R.; Clark, T. *Chem. Phys. Lett.*, submitted for publication.

(9) Moss, R. A. In "Carbenes, Vol. I"; Jones, M., Jr., Moss, R. A., Ed.; Wiley-Interscience: New York, 1973.

(10) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc* **1958**, *80*, 5323. See also: Doering, W. v. E.; LaFlamme, P. M. *Tetrahedron* **1958**, *2*, 75. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(11) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347.

(12) Köbrich, G. *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 41. Köbrich, G.; Flory, K.; Drischel, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 513.

(13) Hoeg, D. F.; Lusk, D. I.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 4147.

(14) Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135, 1141.

(15) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 303 and references therein.

(16) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. Hoffmann, R., Hayes, D. M.; Skell, P. S., *J. Phys. Chem.* **1972**, *76*, 664.

(17) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

(18) Houk, K. N.; Rondan, N. G.; Mareda, J., submitted for publication.

(19) Schoeller, W. W. *Angew. Chem.; Int. Ed. Engl.* **1981**, 20, 698.

(20) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

(21) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.

0002-7863/83/1505-6997$01.50/0

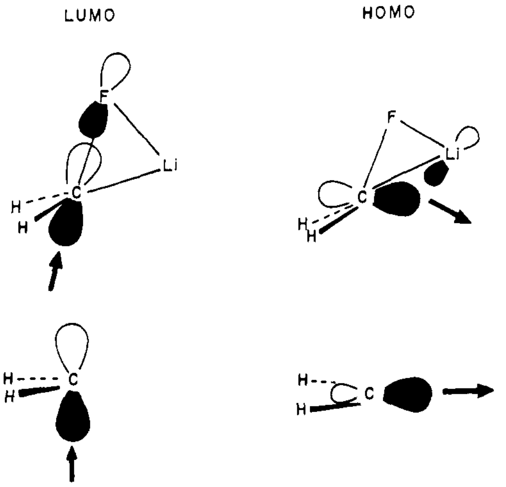
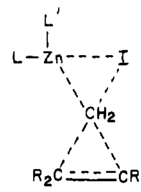


Figure 1. Idealized frontier MO's of the carbenoid, $LiCH_2F$, and CH_2 (arrows represent the preferred direction of approach of a nucleophile to the LUMO or an electrophile to the HOMO).



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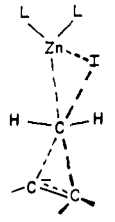

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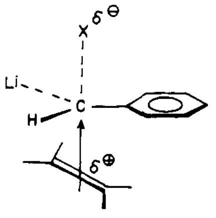

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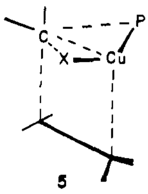

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version of the methylene carbon must occur during the reaction. The HCH fragment is linear in the proposed transition structure.

Table I. 3-21G Energies of Stationary Points on the $LiCH_2F$–Ethylene Surface

structure	total energy, au	relative energy, kcal/mol
$LiCH_2F$ (6)[a] ethylene (7)[a]	−145.09508 −77.60099	0
$LiCH_2F$–ethylene complex (8)	−222.71587	−12.4
transition structure (9)	−222.67007	16.3
LiF–cyclopropane complex	−222.77779	−51.3
cyclopropane[a] LiF[a]	−116.40121 −106.35419	−37.2[b]

[a] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University, Pittsburgh, PA, 1981. [b] This value is −54.6 kcal/mol at 6-31G*. See ref 8.

Köbrich proposed a similar "butterfly" for CCl_2 transfer from $LiCCl_3$, preceded by complexation of the electrophilic Li with the π bond.[12] Such coordination of RLi to π systems is now well-known from theoretical studies.[22,23] Hoeg et al. gave a similar formulation, but the carbenoid was represented as a pair of ions, Li^+ and Cl^-, coordinated on the backside of CCl_2.[13] Closs has proposed the transition structure **4** for the reactions of arylcarbenoids with alkenes.[1] The π bond acts as a nucleophile, causing an S_N2-like displacement of halogen from the carbenoid. For copper carbenoid reactions, Moser proposed coordination of copper with the alkene in the transition state,[14] as represented in **5**.

A consideration of the electronic structures of carbenoids leads to a prediction of a transition structure related more to the Closs formulation than to the traditional "butterfly" mechanism. Figure 1 compares the idealized frontier molecular orbitals of $LiCH_2F$ to those of CH_2. The LUMO of the carbenoid is a σ^*_{CF} orbital that resembles quite closely the LUMO of methylene. As in the Closs formulation, nucleophiles should preferentially interact in the direction indicated by the arrow in Figure 1. The HOMO is more or less a carbanion-type lone-pair orbital, or a highly polarized σ_{CLi} orbital, which is responsible for the "carbanionoid"[16] character of haloorganometallics. Again, the resemblance to the methylene HOMO is obvious. Reaction with an electrophile should occur in the indicated direction.

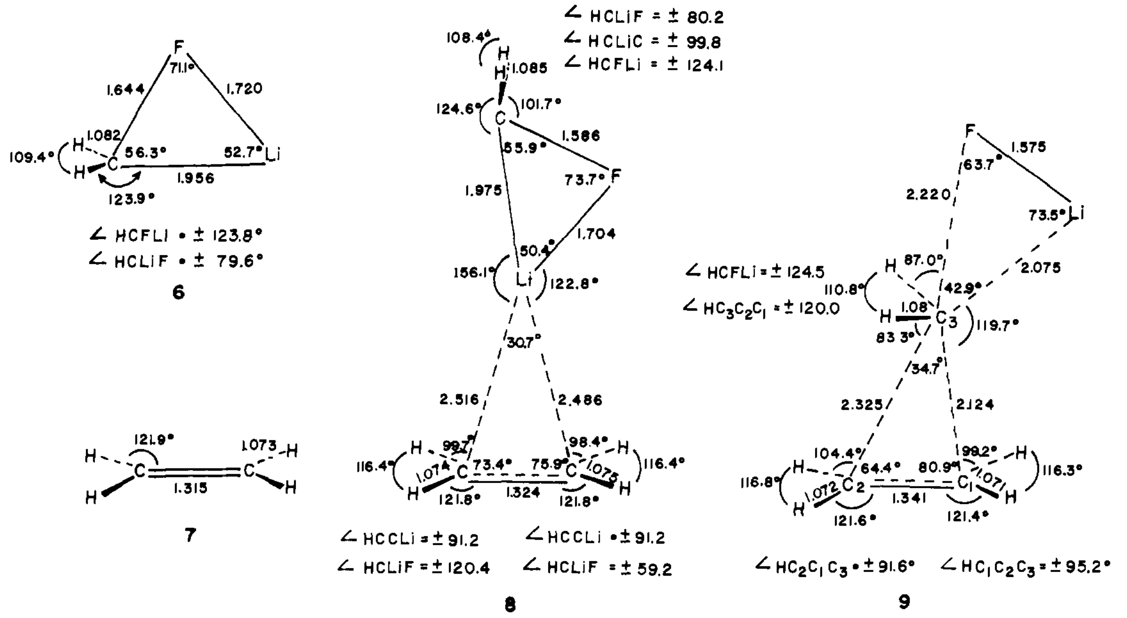

Figure 2. 3-21G structures of isolated $LiCH_2F$ (**6**), ethylene (**7**), the carbenoid–ethylene complex **8**, and the transition structure **9**.

Theoretical investigations were carried out using ab initio gradient techniques[24] and the 3-21G basis set.[25] The computed structures of the reactants, an organolithium–ethylene complex, **8**, and the transition structure **9** are shown in Figure 2. Energies of the various species are given in Table I. The $LiCH_2F$ carbenoid and ethylene form a complex, **8**, which has only slight distortions from reactant geometries and Li–C (ethylene) distances (2.49 and 2.52 Å) only slightly different from those of the LiH complex.[23] Although such a complex is expected to be stable in the gas phase, it is not expected to be present in solution, where the carbenoid is undoubtedly aggregated and solvated.[7,15] Similarly, the products, LiF and cyclopropane, form a complex that is 14.1 kcal/mol more stable than the separated entities. This also would not be expected to be present in solution.

The transition structure **9**, is related to the "butterfly" **3** but the CH_2 group is in a plane nearly parallel to the ethylene plane, like the arrangement proposed by Closs. The methylene fragment is aligned so that the LUMO can interact in an electrophilic sense with the ethylene HOMO on one side and simultaneously with a fluorine lone-pair on the other side. Li^+ is loosely associated with the lone-pair HOMO on the methylene and bonded more strongly to the departing fluoride. The CF bond is stretched by 0.58 Å (35%), while the CLi bond is stretched by 0.12 Å (6%) and the LiF length is shortened by 0.14 Å (8%). The LiF moiety is substantially "decomplexed", freeing the carbene character of CH_2. Transition structure **9** also resembles the transition structure for isomerization of the carbenoid to the nearly linear isomer, H_2CLiF,[3,6] which would have very strong electrophilic properties. Other carbenoids, such as Cl_3CLi, undergo isomerization to higher energy isomers (Cl_2CLiCl) with great ease.[5] The transition structures for carbenoid cycloadditions involving more nucleofugic halogens are expected to have lower activation energies but involve less advanced C–X bond breaking and earlier transition structures.

The CH_2 group does not invert (in the sense implied by **3**) during the reaction. Indeed, the carbenoid transition structure **9**, is quite similar to the transition structures for free halocarbene cycloadditions,[17,18] except that the carbene fragment of **6** is less strongly bound to ethylene in the transition structure.

Although carbenoids are expected to be aggregated[7] and solvated in solution,[15] the essential features of the methylene-transfer cycloaddition revealed by **9**, namely a carbene-like transition structure with advanced C–X bond breaking and loose coordination of Li^+ to electron-rich centers, are expected to be maintained in solution reactions.

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Registry No. 6, 59189-61-6; **7**, 74-85-1; **8**, 87555-38-2; LiF, 7789-24-4; cyclopropane, 75-19-4.

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(22) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 3651, and references therein. Nagase, S.; Houk, K. N. *Tetrahedron Lett.* **1982**, *23*, 19.

(23) Schleyer, P. v. R.; Kos, A. J.; Kaufman, E., submitted for publication.

(24) Gradient programs: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A., GAUSSIAN 80, QCPE, Indiana University. Hout, R. F., Jr.; Francl, M. M.; Blurock, N.; Pietro, W. J.; Pollack, S. K.; DeFrees, D. J.; Levi, B. A.; Steckler, R.; Hehre, W. J., GAUSSIAN 83, Quantum Program Exchange, Indiana University, Bloomington, IN, to be submitted in 1983.

(25) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

Regiochemistry in Thiocarbonyl Diels–Alder Additions: Reversal of Selectivity by Substituent Effects in Thioaldehydes

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Thiocarbonyl dienophiles, ZC(R)=S where Z = acyl, CN, carboethoxy, etc., react with donor-substituted unsymmetrical dienes to give [4 + 2] cycloadducts with path b selectivity (Scheme I).[1,2] In contrast, carbonyl dienophiles react with high path a selectivity.[1]

It has been reported that certain thioketones,[3a] simple dithioesters,[3b] and thermally generated PhCH=S[3c] show little preference for either path a or b. To probe the relationship between regiochemistry and the effect of thiocarbonyl substituents, we have examined a series of thioaldehydes, ZCH=S, which retain high dienophilic reactivity for Z = alkyl, aryl, H, acyl, etc. As summarized in Table I, the regiochemistry of cycloaddition with electron-rich dienes is reversed for Z = alkyl compared to Z = acyl, CN, etc. Computations for representative thioaldehydes provide an explanation for the variable regiochemistry observed in these [4 + 2] cycloadditions.

Systematic comparisons have been made by using 2-(*tert*-butyldimethylsiloxy)-1,3-butadiene as the trapping agent for thioaldehydes generated by the photochemical method[2e] (Table I). In borderline cases where yields are low due to thioaldehyde self-condensation, the more reactive Danishefsky diene has been employed. To verify that thioaldehydes are generated with similar

Table I. Thioaldehyde Trapping from $PhCOCH_2SCH_2Z$, *hν*, and Diene in Situ

	yields, %				
ZCH=S, Z	1	2	3	4	6
CN^a	4	70			
$COC_6H_5{}^a$	5	59	c	$90^{d,f}$	
$C_6H_5{}^g$	10	5	74^b	*c*	
$CH=CH_2$	trace	*c*	7^b	*c*	92^d
$SiMe_3$	30	3			
H	68	6			73
$C(CH_3)_3{}^e$	4.5	*c*	25^b	*c*	93
$CH_2CH_2C_6H_5$	23	*c*	84^b	*c*	91^d

[a] From ref 1e. [b] Yield after acid treatment to give a 2,3-dihydrothiopyran-4-one. [c] Isomeric adducts not detected. [d] Mixture of stereoisomers. [e] 2,2-Dimethylpropanethial has been shown to survive in solution at 20 °C (ref 5). [f] Yield of adducts estimated by NMR vs. internal standard; chromatography or acid treatment causes elimination to a mixture of unstable 2,4- and 2,6-dihydrothiopyran-3-ones. [g] See ref 3c for similar results.

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(1) Review: Weinreb, S. *Heterocycles* **1979**, *12*, 949.

(2) (a) Vyas, S. M.; Hory, G. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 180. (b) Vyas, D. M.; Hory, G. W. *Can. J. Chem.* **1971**, *49*, 3755. (c) Friedrich, K.; Zamkanei, M. *Tetrahedron Lett.* **1977**, 2139. (d) Vedejs, E.; Arnost, M. J.; Dolphin, J. M.; Eustache, J. *J. Org. Chem.* **1980**, *45*, 2601. (e) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445. (f) Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Chem. Commun.* **1983**, 423.

(3) (a) Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. *Tetrahedron* **1969**, *25*, 871. (b) Beslin, P.; Metzner, P. *Tetrahedron Lett.* **1980**, 4657. (c) Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487.