

Exocyclic Alkylidene Carbenes - An *ab initio* Theoretical Study.

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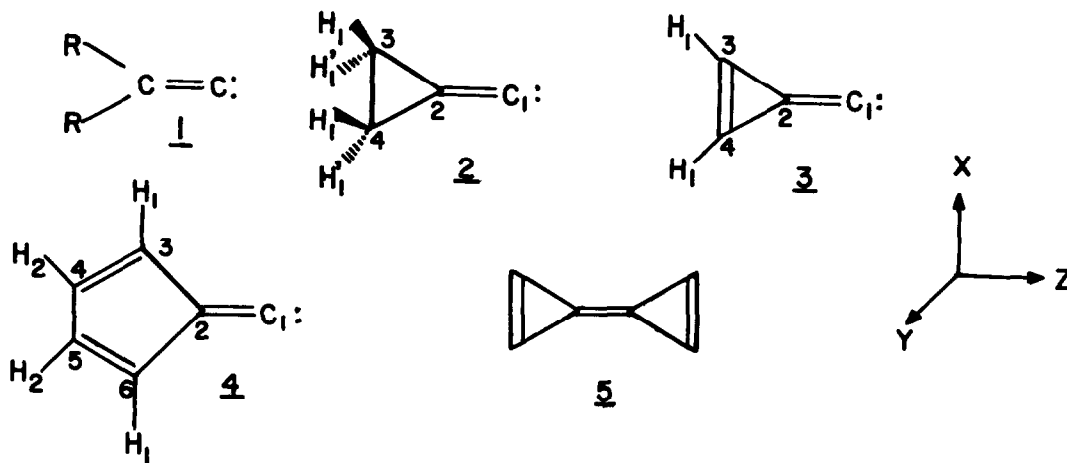
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Summary: *ab initio* calculations were carried out for three exocyclic alkylidene carbenes. Cyclopentadienylvinyl carbene is predicted to be highly electrophilic while the cyclopropenylidenevinyl carbene may provide the first example of a nucleophilic alkylidene carbene.

Unsaturated carbenes 1, where the divalent carbon (carbenic center) is an integral part of an unsaturated system have recently attracted the attention of both experimentalists¹ and theoreticians.² New synthetic methods now provide easy access to this novel and useful class of reaction intermediates.¹ Of special interest synthetically as well as mechanistically are exocyclic alkylidene carbenes such as 2, 3 and 4. Carbene 3 for example, could provide an entry to the unknown 5. In conjunction with experimental efforts to generate 2 - 4 we have also investigated these species computationally in order to provide basic information on their stabilities and to gain insight into their properties. The results are reported in this communication.



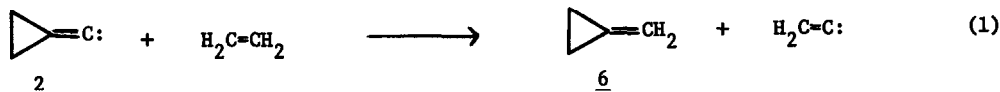
Calculations were carried out using the *ab initio* SCF-MO Gaussian 70^{3a} and Gaussian 76^{3b} series of programs. Complete geometry optimizations, assuming C_{2v} symmetry, were carried out for 2 - 4 with the minimal STO-3G basis set.^{4a} Single point calculations with the optimized STO-3G geometries were carried out using the split-valence 4-31G^{4b} and the augmented 6-31G* (i.e. containing d-type functions on carbon)^{4c} basis sets. Only the singlet electronic states of 2-4 are considered here because the corresponding triplets are considerably higher in energy. The optimized geometries and the total energies of the singlet carbenes 2 - 4 are given in Table 1.

Table 1: Optimized Geometries^a (STO-3G) and Total Energies of the carbenes 2, 3 and 4.

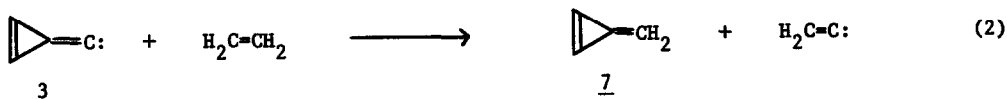
Paramets ^b	<u>2</u>	<u>3</u>	<u>4</u>
r(C ₁ -C ₂)	1.287	1.295	1.320
r(C ₂ -C ₃)	1.493	1.475	1.489
r(C ₃ -C ₄)	1.499	1.284	1.328
r(C ₄ -C ₅)	—	—	1.482
r(C ₃ -H ₁)	1.09	1.078	1.080
r(C ₄ -H ₂)	—	—	1.081
<H ₁ C ₃ C ₄	—	151.92	128.20
<H ₁₁ C ₃ C ₄ ^c	151.91	—	—
<H ₁ C ₃ H ₁₁	114.28	—	124.04 ^d
Energy (STO-3G)	-151.73240	-150.47108	-226.53803
Energy (4-31G)	-153.39584	-152.15673	-229.03511
Energy (6-31G [*])	-153.62634	-152.39582	—

^a Assuming C_{2v} symmetry. ^b Bond lengths in Å, bond angles in degrees, total energies in hartrees. ^c H₁₁ is the bisector of the H₁C₃H₁₁ angle. ^d The H₂C₄C₅ angle.

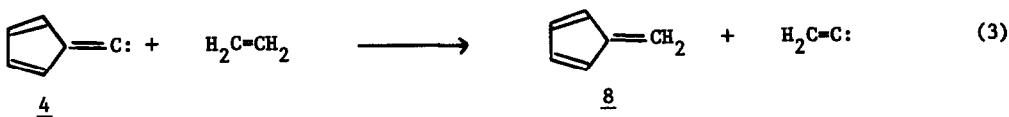
Do exocyclic rings stabilize or destabilize unsaturated carbenes? Comparisons with the parent alkylidene carbene 1, R=H are made by means of the isodesmic reactions 1, 2 and 3 respectively, along with the effect of a gem-dimethyl substituent, given in equation 4.



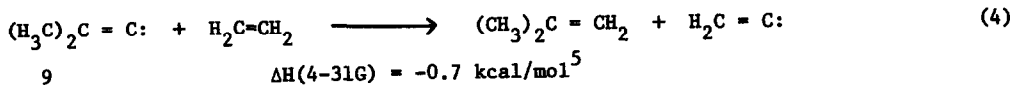
$$\Delta H(6-31G^*) = 4.7 \text{ kcal/mol}^5$$



$$\Delta H(6-31G^*) = -3.2 \text{ kcal/mol}^5$$



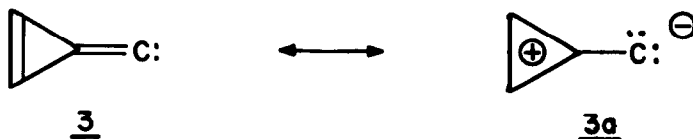
$$\Delta H(4-31G) = -0.4 \text{ kcal/mol}^5$$

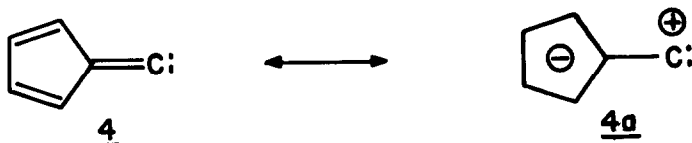


$$\Delta H(4-31G) = -0.7 \text{ kcal/mol}^5$$

Substitution of the β -hydrogens in $H_2C=C:$ by an exocyclic cyclopropane ring stabilizes the carbene by 4.7 kcal/mol; 2 is also more stable than $(CH_3)_2C=C:$ by 5.4 kcal/mol.⁵ The stabilization of 2 results from hyperconjugation between the empty carbenic $2p_x$ orbital and the filled antisymmetric Walsh orbital of the cyclopropane ring.⁶ Hyperconjugation is accompanied by electronic and structural changes: In 2 0.14 electrons (STO-3G) occupy the formally empty $2p_x(C_1)$ orbital compared to only 0.07 electrons in 9. The C_1-C_2 and the C_3-C_4 bonds of 2 are shortened and the C_2-C_3 and the C_2-C_4 bonds are lengthened compared to the corresponding bonds in 6.⁷ The stabilization of 2 is however much smaller than in the isoelectronic cyclopropylidenemethyl cation,⁸ emphasizing that the presence of a charge is essential for efficient hyperconjugation.^{2d} In contrast to 2, 3 is found to be 3.2 kcal/mol less stable than $H_2C=C:$. The destabilizing effect of the exo-cyclopropene ring is not the result of ineffective hyperconjugation or ring strain.⁶ The structural changes in 3 (relative to 7) are similar to those found in 2; 0.11 electrons occupy the $2p_x(C_1)$ orbital of 3. Obviously, destabilizing interactions (see below) outweigh the favorable effect of hyperconjugation, resulting in a net destabilization of 3 compared to 1 and 9. Hyperconjugation is relatively unimportant in 4 as indicated by the relatively low population of the $2p_x(C_1)$ orbital (0.09 electrons) and the similarity of the structures of 4 and 8. The cyclopentadienyl-vinyl carbene 4 is therefore comparable in stability to $H_2C=C:$ and to $(CH_3)_2C=C:$.

Alkylidene carbenes can rearrange to the isomeric acetylenes.^{1,9} Are 2, 3 and 4 expected to be thermodynamically stable towards this facile rearrangement process? Our calculations show that 2 and 3 are considerably more stable than the corresponding cyclic acetylenes (e.g at 4-31G 2 is 58.4 kcal/mol more stable than cyclobutyne) so that such a rearrangement is unlikely. Carbene 4 on the other hand is 14 kcal/mol (4-31G) less stable than o-benzyne and rearranged products might be observed. Drastic changes in the electronic properties of the carbenes result when the exocyclic three membered ring is replaced by a five membered ring. All known alkylidene carbenes,¹ like most saturated carbenes,¹⁰ being electron deficient are electrophilic, and possess a positively charged carbenic carbon. Our calculations predict that 4 is a stronger electrophile than other alkylidene carbenes;¹¹ the total charge at C_1 is +0.11 compared with only +0.04 in $(CH_3)_2C=C:$. In 3, on the other hand, C_1 is negatively charged, making it the first example of a nucleophilic (or an ambiphilic^{10,11}) unsaturated carbene; and is therefore expected¹⁰ to behave differently than other alkylidene carbenes. The opposite charges at C_1 in 3 and 4 can be ascribed to contributions of the resonance hybrids 3a and 4a respectively. In 3 the $2p_y(C_1)$ orbital contains 1.03 electrons compared with 0.93 electrons in 9, 0.88 electrons in 2 and only 0.82 electrons in 4. The π -polarization and thus the resulting "aromatic stabilization"⁷ is smaller in 3 than in 7 (but larger in 4 compared to 8).¹² The loss of part of the "aromatic stabilization"⁷ in going from 7 to carbene 3 contributes to the destabilizing effect of the cyclopropene ring (reaction 2)¹³ in alkylidene carbenes. We stress that the π_y electrons, although orthogonal to the carbenic empty $2p_x(C_1)$ orbital, can effect considerably the stabilities and other properties of unsaturated carbenes.





References and Notes

1. For a review see: P.J. Stang, *Chem. Rev.* **78**, 383 (1978).
2. (a) C.E. Dykstra, C.A. Parsons, C.L. Oates, *J. Amer. Chem. Soc.*, **101**, 1962 (1979) (b) C.E. Dykstra and H.F. Schaefer III, *ibid.*, **100**, 1378 (1978); (c) J.W. Kenney III, J. Simons, G.D. Purvis and R.J. Bartlett, *ibid.*, **100**, 6930 (1978); (d) Y. Apeloig and R. Schreiber, *Tetrahedron Lett.*, 4555 (1978); (e) J.H. Davis, W.A. Goddard III, and L.B. Harding, *J. Amer. Chem. Soc.*, **99**, 2919 (1977).
3. (a) W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton and J.A. Pople, QCEP, Program No.236; (b) J.S. Binkley, R.A. Whiteside, P.C. Hariharan, R. Seeger, J.A. Pople, W.J. Hehre and M.D. Newton, QCEP, Program No. 368.
4. (a) W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) W.J. Hehre and J.A. Pople, *ibid.*, **56**, 4233 (1972); R. Ditchfield, W.J. Hehre and J.A. Pople, *ibid.*, **54**, 724 (1971); (c) P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973)
5. The calculated energies of reactions 1-4 were changed only slightly with the other basis sets.
6. The ring strain in 2 and 3 does not effect the calculated energies of equations 1 and 2 as the cyclopropane (or cyclopropene) skeletons appear on both sides of these equations and ring strain cancels out. The energies of equations 1 and 2 apply to reactions in which 2 and 3 are produced from cyclic precursors such as substituted 6 and 7. The ring strain in 2 and 3 is important however in ring opening or rearrangement reactions.
7. W.J. Hehre and J.A. Pople, *J. Amer. Chem. Soc.*, **97**, 6941 (1975).
8. Y. Apeloig, J.B. Collins, D. Cremer, T. Bally, E. Haselbach, J.A. Pople and P.v.R. Schleyer, *J. Org. Chem.*, submitted.
9. H.F. Schaefer III, *Acc. Chem. Res.*, **12**, 288 (1979).
10. R.A. Moss, M. Fedorynski, W.-C. Shieh, *J. Amer. Chem. Soc.*, **101**, 4736 (1979).
11. Arguments which are based on Frontier Orbital considerations¹⁰ lead to similar conclusions. The carbenic lone pair $sp_z(C_1)$ orbital has the highest energy in 3 while the empty $2p_x(C_1)$ orbital is lowest in energy in 4.
12. In the unperturbed $H_2C=C:$ the π -electrons are strongly polarized towards C_2 as the result of electrostatic repulsion by the carbenic lone pair. Unsaturated carbenes therefore resists the accumulation of negative charge at C_1 as in 3a but favor zwitterionic structures such as 4a with positive π -charge at C_1 .¹³
13. A detailed discussion will be presented in the full paper.

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