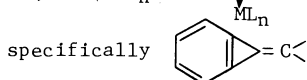


PROPERTIES AND REACTIONS OF UNSATURATED CARBENES

Peter J. Stang

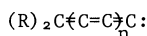
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Abstract - The generation, and some properties and reactions, of unsaturated carbenes; $(R)_2C\dot{C}=C=C$: ($n=0,1,2$) are explored. In particular the following are discussed: a) reaction pathways and transition state geometries of unsaturated carbene-alkene interactions; b) spin multiplicity of extended unsaturated carbenes; c) ylide formation vs. 1,2 vs. 1,4 additions and possible formation of novel persistent diradicals; d) $>C=C \rightarrow ML_n$ vs. $-C\dot{C}-$; e) formation of strained systems,



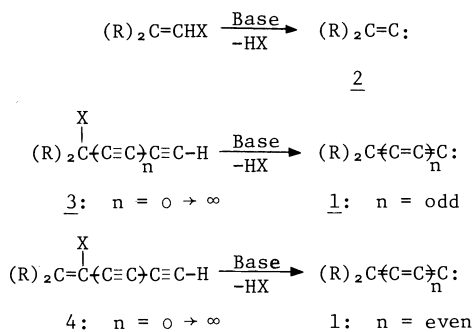
INTRODUCTION

Unsaturated carbenes, 1, are members of a homologous series of reactive intermediates where the carbenic carbon is part of a π -unsaturation:¹



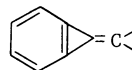
$$\underline{1}: n = 0 \rightarrow \infty$$

The predominant mode of alkylidenecarbene 2 generation is α -elimination from a suitable functionalized ethylene, as shown in Scheme 1. Since appropriately functionalized extended cumulenes are unknown, entry into the higher homologs is best gained² by means of base initiated elimination of suitably functionalized polyalkynes 3 or 4 as illustrated in Scheme 1.



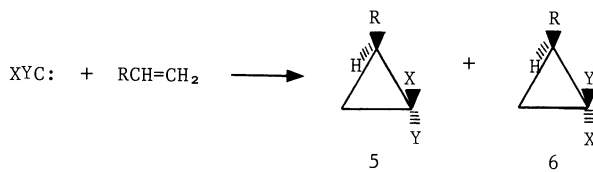
Scheme 1

In this presentation we wish to report some new results as well as pose some questions and challenges to our theoretical colleagues in the field. Emphasis will be placed upon the reactions and behavior of alkylidenecarbenes 2, the first and most investigated member of this family of reactive intermediates. Specifically, we shall discuss five aspects of the chemistry of unsaturated carbenes: a) nature of unsaturated carbene-alkene interactions; b) spin multiplicity of extended unsaturated carbenes; c) ylide formation vs. 1,2 vs. 1,4-addition and possible formation of novel persistent diradicals; d) π -bound vs. carbene-bound transition metal complexes; e) nature and approaches to

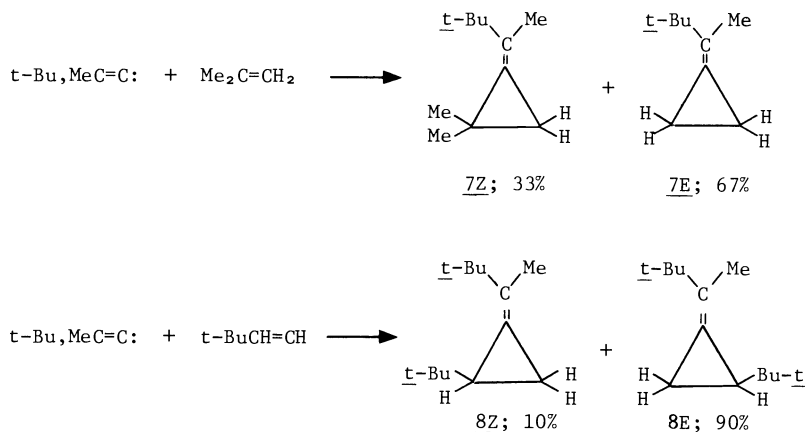


NATURE OF UNSATURATED CARBENE - ALKENE INTERACTIONS.

One of the major unanswered questions in unsaturated carbene chemistry is the exact mode of approach of the carbene towards the π -system of alkenes and the precise nature of the transition state in carbene-alkene addition reactions. The stereochemical outcome of the addition of a dissymmetrically substituted carbene to an unsymmetrical olefin is a reflection of the path of approach and consequent transition state geometry of the carbene-olefin interaction. In the case of regular carbenes such a reaction results in the unequal formation of syn, 5 and anti, 6 adducts:



Whereas the potential surface of methylene³ and related⁴ carbene cycloadditions to olefins, and their transition states, has been theoretically investigated, no comparable data exists for alkylidenecarbenes. A priori the only prediction that can be made for alkylidene-carbene-olefin interactions is that the least motion linear approach is symmetry forbidden and therefore an unlikely high energy process. Moreover, any approach and transition state must account for at least two known experimental facts.¹ The regiochemistry¹ of addition of a dissymmetric carbene to unsymmetrical olefins depicted in Scheme 2 and the unusual relative reactivity summarized⁵ in Table 1.



Scheme 2

Table I Relative Reactivity of $(\text{CH}_3)_2\text{C=C:}$ with Various Olefins at -20°C .

Substrate	Relative Reactivity
<u>cis</u> -2-butene	8.7
2-methyl-2-butene	2.7
<u>trans</u> -2-butene	1.6
1-butene	1.5
isobutylene	1.0
2,3-dimethyl-2-butene	0.25

Extensive calculations⁶ indicate that the preferred approach of the carbene to an olefin is the anti, semi-perpendicular one, shown in Figure 1a, with the large carbenic substituent pointing up and away from the olefin; resulting in the formation of the favored (major) E-adduct. Whereas the minor Z-isomer arises from the anti, semi-perpendicular approach shown in Figure 1b. The calculated difference in energy between these two approaches is a function of both the olefinic (R) and carbenic (L,S) substituents but for R=t-Bu and L=t-Bu, S=Me it is 5.0 kcal/mole.⁶ All other approaches and pathways are higher in energy.

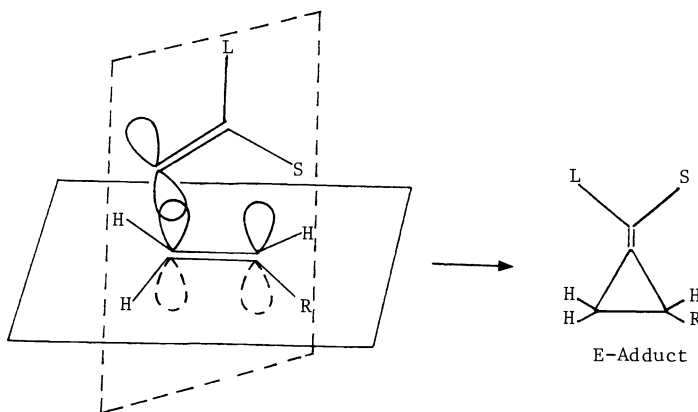


Figure 1a

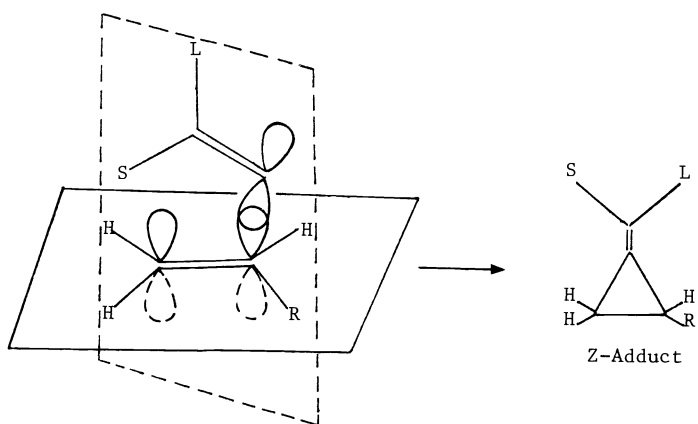
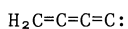


Figure 1b

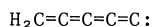
Such an approach explains not only the observed regiochemistry of Scheme 2 but also the unusual reactivity of Table 1. Namely, that a cis olefin reacts faster than a trans one; that 1-butene reacts faster than isobutylene and that the electronically richest, but sterically most crowded, tetramethylethylene reacts slowest.

SPIN MULTIPLICITY OF EXTENDED UNSATURATED CARBENES.

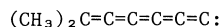
Both experimental⁷ and theoretical⁸ data agree that alkylidencarbenes, 2, possess a singlet ground state with a calculated singlet-triplet energy splitting of 45-51 kcal/mole. The calculated singlet-triplet energy difference for $H_2C=C=C:$ is 36 - 48 kcal/mole depending on the method of calculation.⁸ The greater s-character of the carbenic carbon (compared to methylene) and the correlation effects arising from $\sigma^2 \rightarrow \pi^2$ and $\pi^2 \rightarrow \pi^2$ configuration interactions of the valence electrons are responsible for the stabilization of the singlet in unsaturated carbenes. Based upon these two calculations and the trends derived from them the next two homologs 9 and 10 are also predicted to possess a singlet ground state. Indirect experimental data⁹ confirm the singlet nature of 9. However, no



9



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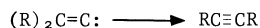


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experimental data, nor explicit calculations exist on the true spin multiplicity, and more specifically the exact singlet-triplet energy differences, of extended carbenes beyond 3-carbons, despite the fact that carbenes with 5¹⁰ and 6-carbons¹¹ are readily available experimentally. Hence, reliable ab initio calculations on the spin multiplicities of extended unsaturated carbenes 9, 10, 11 and beyond, would be most welcome. In particular, as such carbenes are extended is there a possible cross over to triplet ground state, where does it occur? What are the calculated energy splittings and hence can one hope to see low lying triplet chemistry even if the ground state remains a singlet?

YLIDE FORMATION VS. 1,2- VS. 1,4-ADDITION.

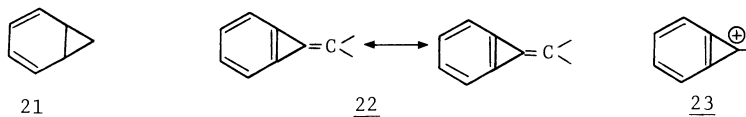
alkylidene carbene transition metal complexes 20 have been reported.¹⁵ These two species are of course isoelectronic, with the organic moiety in each case acting as a two electron donor ligand but differing greatly in bonding and structural features. It is well known of course that in the case of the uncomplexed species, the acetylene is thermodynamically much more stable than the carbene with the latter rearranging to the former with little or no activation energy (at least where R=H or C₆H₅):



The question is, what is the effect of metal complexation on this stability and rearrangement? Little is known about this question, although some preliminary calculations by Schaefer¹⁶ on some very simple model systems, indicate that metals may well stabilize the carbene at the expense of the acetylene. This is in accord with experimental data whereby such carbene complexes are generally made by either photo or base initiated acetylene π -complex isomerizations,¹⁷ and the existence of the parent alkylidene carbene complex (20: R=H) as a stable isolable compound.¹⁸ Once again this area could greatly benefit from better and more extensive theoretical, as well as, experimental investigations.



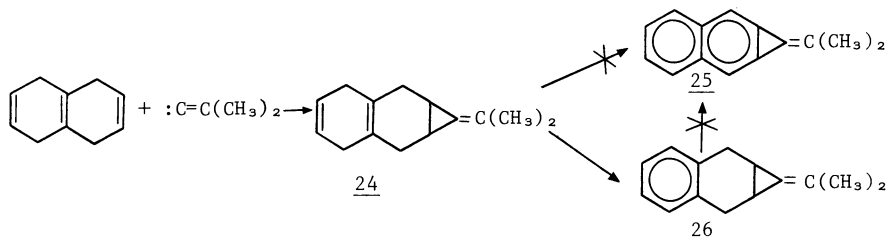
Cyclopropenes 21 are well known,¹⁹ highly strained, interesting compounds. The analogous



alkylidene system 22 would be expected to be even more strained and interesting. Such a system may be looked upon as a hybrid of an annulated benzene, a diene substituted triafulene and a [3]-radialene. Although no such compounds are known to date the highly strained carbenium ion 23 related to and derived from 21 is known.²⁰

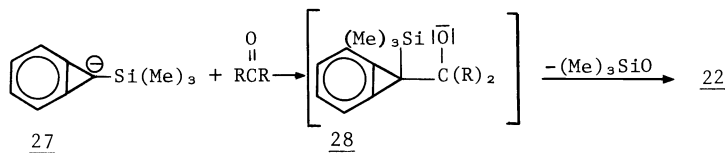
To our knowledge theoretical calculations on both 22 and 23 are also lacking. Molecule 22 would seem to be a particularly attractive candidate for such an investigation.

Experimentally, we have recently embarked²¹ upon the preparation of 22 and related compounds by three different approaches:



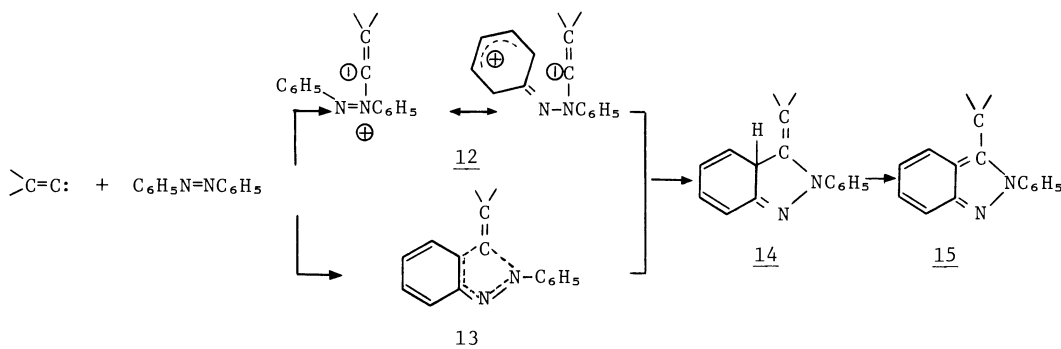
Addition of alkylidene carbene 2 to tetrahydronaphthalene gives 24 which upon reaction with DDQ gives only 26 and upon forcing conditions only tar with none of the desired 25 being observed.²¹

Similar reaction of 2 with 1,4-cyclohexadiene followed by allylic halogenation and exhaustive dehydrohalogenation might give 22. Likewise reaction of the known²² anion 27 with an appropriate ketone followed by the Peterson reaction of the intermediate 28 should be a most promising route to 22:



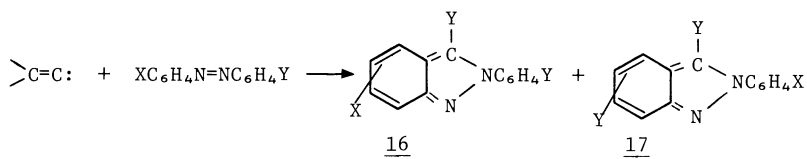
Unfortunately to date we have been unable to complete these reactions.

Some time ago we reported on the interaction of alkylidene-carbenes 2 with azobenzene, giving a 2-indazole 15 as a product.¹² At the time we proposed two major possible pathways, via either an ylide, 12, or a concerted 1,4 Woodward-Hoffmann allowed cycloaddition process 13; to intermediate 14, followed by a hydrogen shift and product formation, as shown in Scheme 3.



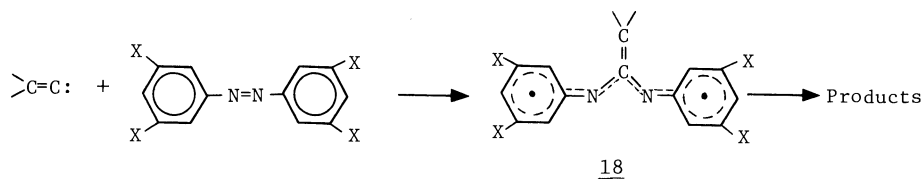
Scheme 3

In an attempt to decide between these two possible pathways we examined the effect of ring, (one in each ring) substituents on the reaction.¹³ Substitution of a single ring or two different substituents results in two products 16 and 17 where the ratio of the products is a measure of the influence of the substituent:



As it turns out the influence of substituents is very small with the product ratio 16/17 only varying over the range of 30/70 to 60/40.¹³ This makes proper interpretation very difficult and theoretical potential surface calculations would be most desirable. In fact the entire area of possible carbene-substrate ylide formation vs. 1,2 vs. 1,4 addition could greatly benefit from appropriate theoretical calculations.

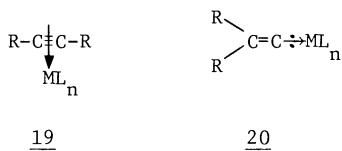
In the course of these studies we may have discovered the formation of novel persistent diradicals 18 via the addition of 2 to tetrasubstituted azobenzenes with strongly electron withdrawing substituents such as X=Cl or CF₃:



However, confirmation of these unusual intermediates awaits further experimentation.

π -ACETYLENE VS. ALKYLIDENECARBENE TRANSITION METAL COMPLEXES.

Numerous π -acetylene transition metal complexes 19 are known.¹⁴ Likewise, recently



CONCLUSION

Unsaturated carbenes 1 are novel versatile reactive intermediates with interesting properties and chemistry. In this presentation we have focused on some challenging questions and problems in this field with emphasis on the interaction of theory and experimental mechanistic organic chemistry, the main topic of this forum. Modern theory could provide considerable insight into the interpretation of existing data as well as guidance for fruitful, future experimentation.

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REFERENCES

1. For reviews and key references see: P.J. Stang, Chem. Rev., 78, 383 (1978); Accounts Chem. Res., 11, 107 (1978); H.D. Hartzler in "Carbenes," R.A. Moss; M. Jones, Jr., Eds., Vol. II, Chapt. 2, Wiley-Interscience; New York, 1975.
2. P.J. Stang, Accounts Chem. Res., submitted.
3. R. Hoffmann, J. Am. Chem. Soc., 90, 1475 (1968); R. Hoffmann, D.M. Hayes, P.S. Skell, J. Phys. Chem., 76, 664 (1972).
4. N.G. Rondan, K.N. Honk, R.A. Moss, J. Am. Chem. Soc., 102, 1770 (1980).
5. P.J. Stang, J.R. Madsen, M.G. Mangum, D.P. Fox, J. Org. Chem., 42, 1802 (1977).
6. P.J. Stang, D.P. Fox, Y. Apeloig, M. Karni, J. Am. Chem. Soc., submitted.
7. P.J. Stang, M.G. Mangum, J. Am. Chem. Soc., 97, 1459 (1975).
8. J.W. Kenney, J. Simons, G.D. Parris, R.J. Bartlett, J. Am. Chem. Soc., 100, 6930 (1978), and references therein.
9. P.J. Stang, T.E. Fisk, J. Am. Chem. Soc., 103, 4638 (1981).
10. W.J. leNoble, S. Basak, S. Srivastava, J. Am. Chem. Soc., 103, 4638 (1981).
11. P.J. Stang, M. Ladika, J. Am. Chem. Soc., 103, 6437 (1981).
12. P.J. Stang, M.G. Mangum, J. Am. Chem. Soc., 99, 2597 (1977).
13. P.J. Stang, G.H. Anderson, unpublished observations.
14. J.P. Collman, L.S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", Univ. Science Books, Calif. 1980.
15. C.P. Casey "Reactive Intermediates" Vol. 2, M. Jones, Jr., R.A. Moss, Eds., Wiley-Interscience, New York, N.Y., 1981, Chapt. 4 pp 135-174 and references therein.
16. H.F. Schaefer, Accounts Chem. Res., 12, 288 (1979).
17. Inter alia: A.B. Antonova, et.al., J. Organomet. Chem., 137, 55, 69 (1977) G.M. Dankins et.al., Chem. Comm., 1120 (1980).
18. K. Folding, J.C. Huffmann, L.N. Lewis, K.G. Caulton, Inorg. Chem., 18, 3483 (1979).
19. B. Halton, Chem. Rev. 73, 113 (1973), W.E. Billups, Accounts Chem. Res. 11, 245 (1978).
20. P. Müller, Helv. Chim. Acta, 57, 704 (1974) ibid., 56, 500 (1973).
21. B. Halton, P.J. Stang, unpublished observations.
22. C. Eaborn, et.al., J. Organomet. Chem., 124, C27 (1977).