

Co-Si bond is vinylsilane tris(cobalt tricarbonyl), a rather unusual compound resulting from the reaction of tetravinylsilane and dicobalt octacarbonyl.⁷

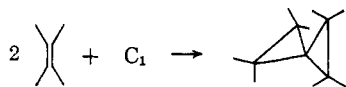
(7) S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, 82 (1962).

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The Chemistry of C₁ Ground State, ³P

Sir:

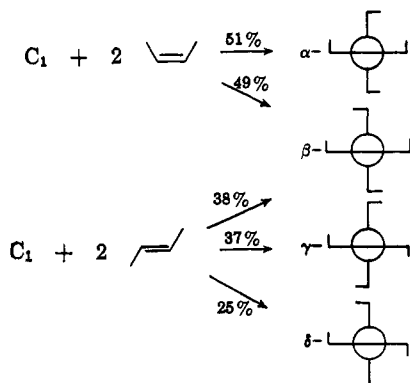
Carbon vapor deposited in paraffin hydrocarbon matrices shows no diminution of C₁ or C₃ content after remaining at -196° for several hours. Additions of methanol to aged matrices result in formation of methylal and 1,3-dimethoxyallene. Additions of olefins result in formation of spiropentanes and bisethanallenes,¹ and *no other product* other than minor components which have a composition indicating they are derived from C₂ + 2olefins.



We report here on the products obtained from the reactions of ground-state C₁ with the *cis*- and *trans*-2-butenes. The spirocyclic product mixtures were analyzed and separated by gas chromatography. They are resistant to permanganate oxidations, and have infrared and mass spectra consistent with the assigned structures of isomeric 1,2,1',2'-tetramethylspiropentanes. Strong spectroscopic evidence has not been adduced for the configurations assigned below; the assignments follow from the assumption of a mechanism for additions, comprising one stereospecific and one nonstereospecific addition.²

The observations for the reactions of *cis*- and *trans*-2-butenes with ground-state carbon atoms can be summarized by Scheme I, the spirocyclic structures being

Scheme I



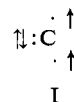
viewed along their major axes. The β -spirocyclic structure is the only common product obtained, no α - being prod-

(1) P. S. Skell and L. D. Wescott, *J. Am. Chem. Soc.*, **85**, 1023 (1963).

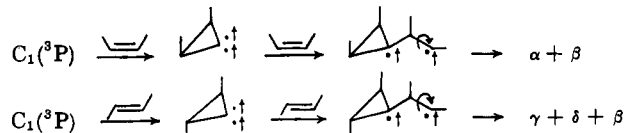
(2) (a) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

uced from *trans*-2-butene, nor any γ - or δ - from *cis*-2-butene.³

A triplet C₁ reagent I, is required for the pictured reaction scheme, and this assignment is in accord with the spectroscopically identified ³P ground state.



That ring formation by stereospecific mode precedes ring formation by the nonstereospecific mode follows from the observation $[\beta/\alpha]_{cis} \neq [(\gamma + \delta)/\beta]_{trans}$. For the reversed sequence of steps these ratios must be identical. Although these considerations do not lead to a unique mechanistic description, the preferred one is



This rationalization is given additional support by the observation that C₁ in singlet D and S states react with 2-butenes to produce spirocyclic products *via* two stereospecific steps.⁴

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

(3) The choice of structures for the γ - and δ -spirocyclic products was made by assigning the more probable reaction mode to the least-hindered structure.

(4) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).
(5) National Science Foundation Cooperative Graduate Fellow, 1963-1965.

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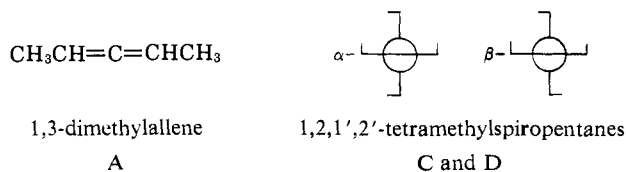
The Chemistry of C₁ Metastable States, ¹D and ¹S

Sir:

A series of experiments in which C₁ was allowed to age in a paraffin hydrocarbon matrix prior to reaction with an olefin revealed a striking alteration of product composition with the age of the C₁. These experiments have revealed the presence of two metastable states in addition to the ³P ground state.¹

Carbon vapor was generated in a carbon arc. In the high vacuum system employed the flight to the wall has a duration of approximately 10⁻⁶ sec. With simultaneous deposition of olefin and carbon vapor the elapsed life of the C₁ (departure from the arc plasma chosen as $t = 0$) is approximately 10⁻⁵ sec. if reaction occurs on contact with the olefin. Under these circumstances the products from C₁ and *cis*-2-butene are those listed (in area %) as A through J (increasing retention times over a dioctyl phthalate gas chromatography column): A, 15; B, 28; C, 12; D, 4; E, 10; F, 2; G, 11; H, 6; I, 3; and J, 9. A, C, and D have been identified and the others are the subjects of current investigations.

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).



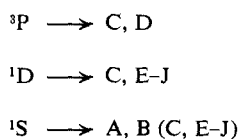
When the arc is operated for 5–10 sec. with paraffin hydrocarbon covering the reaction vessel walls, less than a monomolecular film is deposited. After shutting off the arc, olefin was added at various time intervals and the product composition was determined for each of these experiments. When the C_1 is allowed to age 120 sec. or longer the sole products are C and D in 51:49 ratio, resulting from 3P reacting with *cis*-2-butene.¹

The products from *cis*-2-butene and C_1 aged 9, 17, and 30 sec. revealed that precursors of A and B disappear with a half-life of approximately 2 sec., and the precursors of E through J disappear with a half-life of approximately 15 sec.

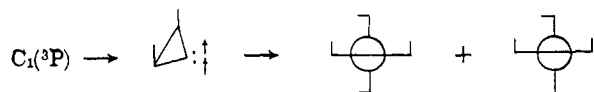
Analysis of spectra from isolated carbon atoms results in a term system with two metastable states 1D and 1S which lie 30 and 60 kcal., respectively, above the 3P ground state.² These forbidden transitions have not been observed. Radiative lifetimes have been predicted³ on purely theoretical grounds: $^1D \rightarrow ^3P$, $\tau_{1/2}$ 2000 sec. and $^1S \rightarrow ^1D$, $\tau_{1/2}$ 2 sec.

Spiropentane formations from 3P carbon atoms and *cis*-2-butene are 100% nonstereospecific in one of the addition steps, leading to equal quantities of C and D. With the metastable forms present C becomes the major product, indicating they react by stereospecific steps only and are therefore singlet.⁴ Since the 10^{-5} sec. free flight from the arc plasma to the walls is long compared to the radiative decay of all higher C_1 states to 3P , 1D , and 1S , these are the only species available for reaction with olefin. It is reasonable to assign to our 2-sec. half-life C_1 the 1S state and to the 15-sec. C_1 the 1D state. The reverse designation is unlikely since the 2-sec. species brings higher energies to the reactants than the 15-sec. species (*vide infra*).

Although it is not yet apparent that 1S carbon atoms do or do not react to produce C and E through J, the chemistry of the three varieties of C_1 can be summarized as follows for reactions with *cis*-2-butene.



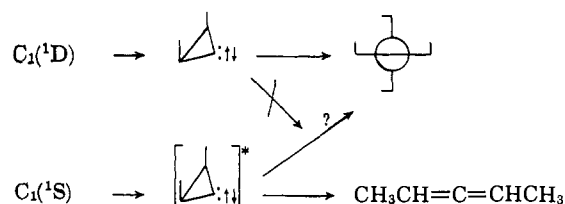
In greater detail for reactions with identified products



(2) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p. 142.

(3) H. Yilmaz, *Phys. Rev.*, **100**, 1148 (1955).

(4) (a) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).



There are a number of striking differences between the work cited here and the atomic carbon work reported by Wolfgang and co-workers.⁵ For example, they find acetylene as a major reaction product with ethylene and we fail to find acetylene from interaction of a mixture of 3P , 1D , and 1S carbon atoms with ethylene.^{5a}

Benson⁶ has suggested that singlet- and triplet-state designations are not required to explain nonstereospecificity in carbene-olefin addition reactions, nonstereospecificity being the resultant of excess energy in the cyclopropane. In condensed phase, dissipation of surplus vibrational energy to neighbors is probably fast compared to rotations about single bonds. Nonetheless, the higher energy C_1 species add stereospecifically and the lower energy species nonstereospecifically.

Acknowledgment. We acknowledge the financial support of the Air Force of Scientific Research and the Army Research Office (Durham).

(5) M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964); J. Durbin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(5a) NOTE ADDED IN PROOF. Professor R. Wolfgang, in response to a preprint of this communication, suggested that the differences in product compositions do not require a reinterpretation of his results to include other excited states. He reports that recent experiments with thermalized carbon atoms in condensed systems show low yields of acetylene.

(6) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(7) National Science Foundation Cooperative Graduate Fellow, 1963–1965.

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The Biosynthesis of Psicofuranine¹

Sir:

A number of nucleoside analogs and antibiotics that contain sugar moieties have been found in nature.^{2,3} Very little is known concerning the biosynthesis of these nucleoside analogs or the sugar portion of these antibiotics. Suhadolnik, *et al.*,⁴ have reported on the direct incorporation of adenosine into cordycepin (3'-deoxyadenosine), while glucose-C¹⁴ has been reported to be the direct precursor of the sugars in erythromycin-A⁵ (L-cladinose and D-desosamine), in novobiosin⁶ (noviose), and in magnamycin⁷ (mycarose). This

(1) This investigation was aided by grant G8685-04 from the National Institutes of Health, United States Public Health Service.

(2) S. S. Cohen, *Science*, **139**, 1017 (1963).

(3) R. U. Lemieux and D. R. Lineback, *Ann. Rev. Biochem.*, **32**, 155 (1963).

(4) R. J. Suhadolnik, G. Weinbaum, and H. P. Meloche, *J. Am. Chem. Soc.*, **86**, 948 (1964).

(5) J. W. Corcoran, *Lloydia*, **27**, 1 (1964).

(6) A. J. Birch, P. W. Holloway, and R. W. Rickards, *Biochim. Biophys. Acta*, **57**, 143 (1962).

(7) H. Grisebach and A. Achenbach, *Angew. Chem.*, **73**, 538 (1961):