

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

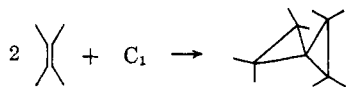
(7) S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, **82** (1962).

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## The Chemistry of C<sub>1</sub> Ground State, <sup>3</sup>P

Sir:

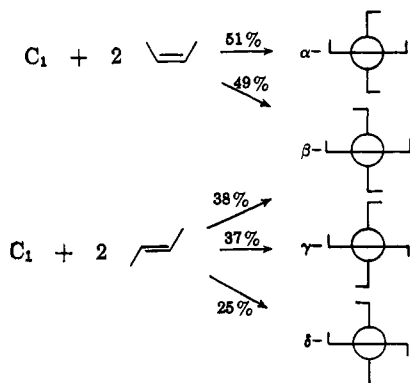
Carbon vapor deposited in paraffin hydrocarbon matrices shows no diminution of C<sub>1</sub> or C<sub>3</sub> content after remaining at -196° for several hours. Additions of methanol to aged matrices result in formation of methylal and 1,3-dimethoxyallene. Additions of olefins result in formation of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



We report here on the products obtained from the reactions of ground-state C<sub>1</sub> with the *cis*- and *trans*-2-butenes. The spiro-pentane 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'-tetramethylspiro-pentanes. 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.<sup>2</sup>

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

Scheme I



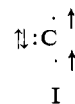
viewed along their major axes. The  $\beta$ -spiro-pentane is the only common product obtained, no  $\alpha$ - being prod-

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

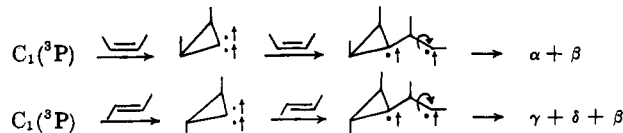
(2) (a) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

uced from *trans*-2-butene, nor any  $\gamma$ - or  $\delta$ - from *cis*-2-butene.<sup>3</sup>

A triplet C<sub>1</sub> reagent I, is required for the pictured reaction scheme, and this assignment is in accord with the spectroscopically identified <sup>3</sup>P 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 C<sub>1</sub> in singlet D and S states react with 2-butenes to produce spiro-pentanes *via* two stereospecific steps.<sup>4</sup>

*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  $\gamma$ - and  $\delta$ -spiro-pentane 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 C<sub>1</sub> Metastable States, <sup>1</sup>D and <sup>1</sup>S

Sir:

A series of experiments in which C<sub>1</sub> 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 C<sub>1</sub>. These experiments have revealed the presence of two metastable states in addition to the <sup>3</sup>P ground state.<sup>1</sup>

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<sup>-6</sup> sec. With simultaneous deposition of olefin and carbon vapor the elapsed life of the C<sub>1</sub> (departure from the arc plasma chosen as  $t = 0$ ) is approximately 10<sup>-5</sup> sec. if reaction occurs on contact with the olefin. Under these circumstances the products from C<sub>1</sub> 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).