described above. The deuterium content of the 1,2-pentadiene was determined from the mass spectrum recorded at 10.2 eV, corrected by comparison to the spectrum of a 1,2-pentadiene standard.

Reaction with Methyl Ether-d_0–Methyl Ether-d_6 Mixture. Methyl ether-d_6 was prepared by a Williamson ether synthesis using methyl iodide-d_3 and methanol-d_4 obtained from Stohler Isotopic Chemicals. Mass spectral analysis at 16 eV showed the compound to be >95% d_6. This compound was then mixed with an equimolar quantity of methyl ether-d_0, and the deuterium distribution of the mixture was determined from the 16-eV mass spectrum.

The work-up procedure used for the methyl ether-d_0–methyl ether-d_6 substrate–product mixture was identical with that used in the methyl ether reaction described above. The deuterium content of the resulting methoxyallene was determined from the 16-eV mass spectrum, which was corrected for fragmentation by comparison to the spectrum of a methoxyallene standard.

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Formation of Vinylidene Intermediates in the Reaction of Diatomic Carbon with Propylene

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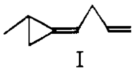
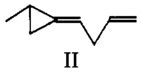
Abstract: Diatomic carbon reacts with two molecules of propylene to form 5,6-methane-1,4-heptadienes. The reaction involves a singlet state C_2 precursor and a vinylidene intermediate.

In the course of our investigations of the reactions of carbon vapor species with olefins we have found that C_2 undergoes the reactions characteristic of singlet carbenes, carbon–hydrogen bond insertion and addition to a double bond.

When carbon vapor from a low intensity carbon arc[1] was codeposited with a large excess of propylene in a vacuum at −196°, 5,5-methano-1,4-heptadienes (I and II) were isolated by gas chromatography on work-up.[2] The two geometrical isomers (I and II) accounted for ~5% of the C_2 estimated to be in the arc.[3] Some acetylene was formed. Products resulting from reaction of C_2 with a single molecule of propylene were 1-penten-4-yne (IV) in 4% yield, 2-methylbutenyne (V) in 1% yield, and 1-pentyne (VI) in 2% yield.

Both compounds I and II gave an *m/e* 108 in the 70-eV mass spectrum. The nmr spectrum of the most easily isolable isomer showed a complex olefinic absorption of four protons between τ 4.0 and 5.5, a complex absorption at τ 7.1, corresponding to two allylic hydrogens, a methyl doublet at τ 8.9 which overlaid the three ring protons absorbing between τ 7.5 and 9.2. The ring and methyl region is almost identical with the spectrum of 2,3:5,6-dimethano-3,4-heptadiene (III),[1] which has this same structural unit. The spectrum of the second geometrical isomer, though less pure, was almost identical with the first. The ir spectra of I and II were identical and gave absorptions at 3.23, 3.35, 3.40, 6.1, 7.5, 7.7 and 11.0 μ. When a mixture of both isomers was hydrogenated with an atmosphere of H_2 over PtO_2,[4] *n*-octane, 3-methylheptane, and 2-methylheptane were found in the ratio of 2.2:1.0:1.0, respectively. These hydrocarbons correspond to cleavage at each of the positions on the ring.


I


II


III

To verify the source of the products I and II, one of the electrodes used in the arc was ^{14}C enriched[5] and the relative radioactivity per mole was compared to compound III, which has a known C_3 precursor.[1] The results are listed in Table I. Since its molar activity is $^2/_3$ that of III, I and II must have C_2 precursors.

Table I. Reaction of Propylene with Carbon-14 Enriched Carbon Vapor

Product	Rel activity/mol
I and II	1.8 2.2
III	[3.00]
IV	1.8
V	2.0
VI	1.5

Two equivalent processes can lead to I and II. If C_2 adds to the double bond of propylene in one step, the resulting vinylidene, A, must insert into the allylic carbon–hydrogen bond of a second propylene molecule (path A). On the other hand, an initial insertion would produce a different vinylidene, B, which would then add to the double bond of a second propylene molecule (path B). No products could be found which would correspond either to two insertions or two additions to the double bond. Path B would produce an intermediate with a hydrogen atom β to the carbene site. The parent vinylidene is known to rearrange to acetylene[6] but when this species is produced by the

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[1] P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

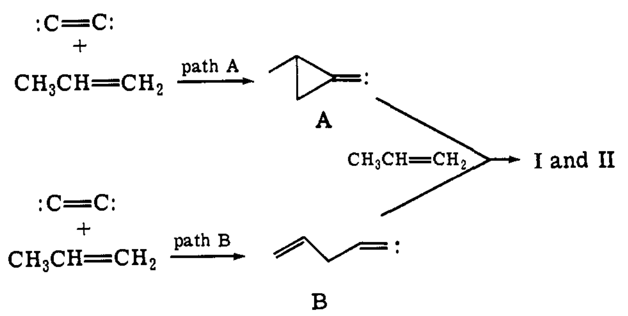
[2] A 20 ft × 0.25 in. 7.5% silicone rubber (SE-30) column on 45–60 mesh Gas Chrom Z at 80° was used.

[3] R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

[4] P. R. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967.

[5] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

[6] H. Okabe and J. R. McNesby, *J. Chem. Phys.*, **36**, 601 (1962).

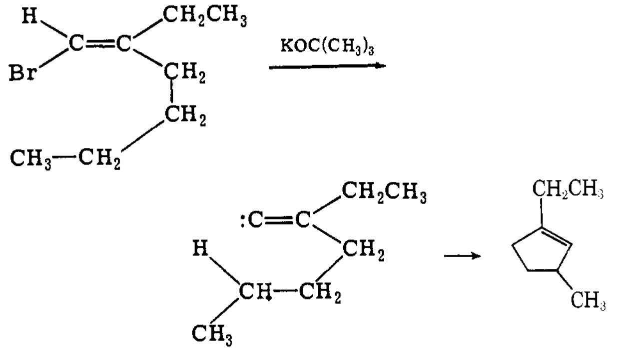


abstraction of two hydrogen atoms by C_2 from an alkane in our system, it lives long enough to react further with an alkylcarbene derived from the same substrate molecule.[7] However, since IV is a significant produce which could arise from rearrangement of vinylidene B, it seems likely that path B would favor rearrangement over addition to a second propylene molecule to form I and II. Thus, path A seems more probable than path B.

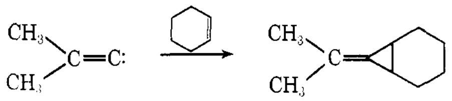
No vinylallene, the product expected[7] from reaction of C_2 with the methyl group of propylene, was formed.

An alternate route to IV, V, and VI involves radical addition to the double bond by either triplet C_2 or an ethynyl radical derived from triplet C_2. With both C_1[8] and C_3[9] we have been aided in the determination of the electronic state of the reacting carbon species through the use of thermal vaporization of the carbon, an alternative method of production which forms only ground-state C_1[10] and C_3.[9] This method is not available for use with C_2, however, since there is a low-lying triplet ($^3\pi_u$) only 1.74 kcal above the ground state ($^1\Sigma_g{}^+$).[11] Any method which produces the singlet will also form a considerable fraction of the triplet. We have, therefore, attempted to use chemical means instead. To this end an equimolar mixture of propylene and 1,3-butadiene was used as substrate. If the intermediate vinylidene (cyclic or acyclic) were a triplet, it should be preferentially trapped by 1,3-butadiene. No crossover products with 1,3-butadiene ($<0.3\%$) could be found, which is in accord with a singlet state precursor. Any attempt to analyze the stereochemistry of the addition step to *cis*- and *trans*-2-butene proved unsuccessful due to the unusual complexity of this reaction.

Both mechanisms (A and B) involve methylenecarbenes (vinylidenes). Intermediates of this type have precedent in the literature, though it is not clear whether those reports are concerned with carbenoids or free carbenes. Both the addition and insertion reactions of vinylidenes have been observed in solution. The addition of potassium *tert*-butoxide to 1-bromo-2-ethyl-1-hexene in hydrocarbon solvent produces a vinylidene which inserts into carbon–hydrogen bonds.[12]



Likewise, vinylidenes produced by addition of lithium ethoxide to 5,5-disubstituted oxazolidones or by action of potassium *tert*-butoxide on 2,2-disubstituted vinyl bromides add to the double bonds of olefins to form cyclopropane rings.[13–17]



Experimental Section

The reaction system employed in this study has been described previously[1] and the modifications required for the production of thermally vaporized carbon have also appeared.[9]

The method employed for the carbon-14 labeling experiment has been described.[5,8]

Products described were isolated by gas chromatography[2] and identified by the spectral properties described in the text of this paper.

Reaction with Propylene–Butadiene Substrate Mixture. The product mixture from reaction of carbon vapor with a propylene–butadiene substrate mixture was compared, by gas chromatography,[2] to the product mixture from reaction with propylene and to that from reaction with butadiene. No products were found which did not appear in products obtained from reaction with each substrate when run separately. This result was confirmed by analysis of the products from the propylene–butadiene reaction, by combined gas chromatography–mass spectrometry.

Acknowledgment. The financial support of the Air Force Office of Scientific Research (Grant No. 1983) is acknowledged with gratitude.

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