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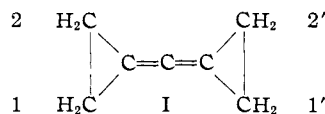
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CHEMICAL PROPERTIES OF C₃, A DICARBENE

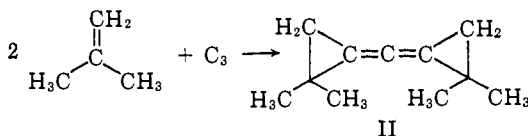
Sir:

We should like to report on the chemical properties of C₃, a substance which was first detected in the atmosphere of a comet¹ and subsequently identified by optical²⁻⁴ and mass spectroscopic analyses.⁵ We are not aware of any prior description of chemical properties of this substance.

Carbon vapor produced *in vacuo* (10⁻³ to 10⁻⁵ mm.) reacts at a liquid nitrogen-cooled surface with olefins to produce homologs of the parent substance bis-ethanoallene (I).



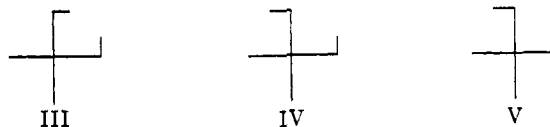
Isobutylene reacts with C₃ to produce 1,1,1',1'-tetramethyl-bis-ethanoallene (II).



This substance is the major product of the reaction, obtained in approximately 40% yield based on bulk carbon vaporized. Distillation under high vacuum serves to separate II from isobutylene and condensed carbon, and with gas chromatography a pure product is isolable. A parent peak is observed in a low voltage (15 v.) mass spectrum at 148 mass units. A strong absorption band at 4.88 μ in the infrared is attributed to the strained allenic system. Hartzler observed an absorption band at 4.95 μ for monoethanoallenes.⁶ The proton magnetic resonance spectrum shows two unsplit absorptions at 8.67 and 8.72 τ (referred to tetramethylsilane) with intensities of 1:3, attributed to the cyclopropane CH₂ and the methyl groups, respectively. No vinylic absorption is observed.

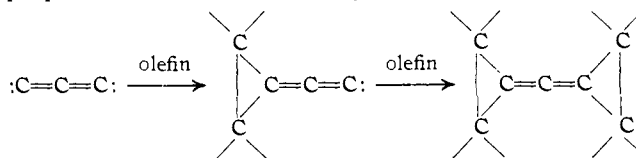
van't Hoff inferred that the two CH₂ groups in allene should lie in orthogonal planes.⁷ This prediction

was verified in 1935 independently by Maitland and Mills⁸ and by Kohler, Walker and Tishler⁹ through resolution of tetrasubstituted allenes into enantiomorphs. The bis-ethanoallenes derived from C₃ and propylene further support this conclusion with an argument based on the number of diastereoisomers. On a Golay column (squalane) these ethanoallenes (4.88 μ absorption, parent peak in mass spectrum at 120) are resolved into three components, the trace showing intensities of 1:2:1. Viewed from either end along the axis defined by the allenic carbon atoms, the cyclopropane rings define orthogonal planes. Step-wise random addition should give three isomers III, IV and V, in the ratio of 1:2:1



respectively, thus identifying structure IV for the more abundant product.

These findings offer a chemical proof that C₃ is the major constituent of carbon vapor. The chemical properties of C₃ are tentatively summarized as follows.



The temperatures and pressures in these experiments closely approximate cometary ambient conditions. Other experiments in progress attempt to duplicate reactions which may be occurring on comets.

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DEUTERIUM ISOTOPE EFFECTS IN RATES OF METHYLENE RADICAL INSERTION INTO CARBON-HYDROGEN BONDS AND ACROSS CARBON DOUBLE BONDS¹

Sir:

By the photolysis of ketene in the presence of *cis*-butene-2 and of *cis*-butene-2-*d*₃, the relative rates of methylene radical addition across the double bond, and the relative rates of insertion into the allylic and vinylic carbon-hydrogen and carbon-deuterium bonds of the butene reactants have been determined at 25° and -30°. The only previous report on such effects is a recent mention by Chesick² of a ratio of 1.3 for the relative rates of insertion into C-H and C-D bonds. These insertion ratios seem of considerable value in helping to determine whether C-H extension is important in the definition of the reaction coordinate.

The reactions of singlet methylene radicals with butene-2 are well known^{3,4} and those of importance in this work are given in eq. 1 through 5.

(1) This work was supported by the Office of Naval Research.

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