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ORGANIC CHEMICAL RESEARCH SECTION

LEDERLE LABORATORIES DIVISION MICHAEL J. MARTELL, JR.  
AMERICAN CYANAMID COMPANY  
PEARL RIVER, NEW YORK  
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

COLLEGE OF PHARMACY TAITO O. SOINE  
UNIVERSITY OF MINNESOTA  
MINNEAPOLIS, MINNESOTA  
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

COLLEGE OF PHARMACY LEMONT B. KIER  
UNIVERSITY OF FLORIDA  
GAINESVILLE, FLORIDA

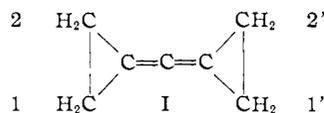
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### CHEMICAL PROPERTIES OF $C_3$ , A DICARBENE

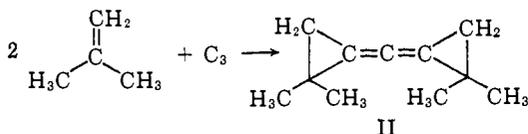
Sir:

We should like to report on the chemical properties of  $C_3$ , a substance which was first detected in the atmosphere of a comet<sup>1</sup> and subsequently identified by optical<sup>2-4</sup> and mass spectroscopic analyses.<sup>5</sup> 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).



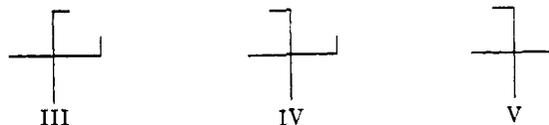
Isobutylene reacts with  $C_3$  to produce 1,1,1',1'-tetramethyl-bis-ethanoallene (II).



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  $4.88 \mu$  in the infrared is attributed to the strained allenic system. Hartzler observed an absorption band at  $4.95 \mu$  for monoethanoallenes.<sup>6</sup> The proton magnetic resonance spectrum shows two unsplit absorptions at 8.67 and 8.72  $\tau$  (referred to tetramethylsilane) with intensities of 1:3, attributed to the cyclopropane  $CH_2$  and the methyl groups, respectively. No vinylic absorption is observed.

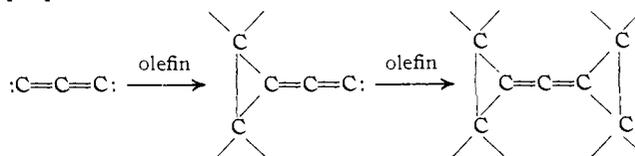
van't Hoff inferred that the two  $CH_2$  groups in allene should lie in orthogonal planes.<sup>7</sup> This prediction

was verified in 1935 independently by Maitland and Mills<sup>8</sup> and by Kohler, Walker and Tishler<sup>9</sup> through resolution of tetrasubstituted allenes into enantiomorphs. The bis-ethanoallenes derived from  $C_3$  and propylene further support this conclusion with an argument based on the number of diastereoisomers. On a Golay column (squalane) these ethanoallenes ( $4.88 \mu$  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  $C_3$  is the major constituent of carbon vapor. The chemical properties of  $C_3$  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.

(7) J. H. van't Hoff, *Bull. soc. chim.*, 23, 295 (1875); "The Arrangements of Atoms in Space," 2nd Ed. (translated by A. Eiloart), Longmans Green & Co., London, 1898.

(8) P. Maitland and W. H. Mills, *Nature*, **135**, 944 (1935).

(9) E. P. Kohler, J. T. Walker and M. Tishler, *J. Am. Chem. Soc.*, **57**, 1743 (1935).

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(11) Esso Research and Engineering Company Fellowship, 1961-1962.

DEPARTMENT OF CHEMISTRY P. S. SKELL<sup>10</sup>  
THE PENNSYLVANIA STATE UNIVERSITY L. D. WESCOTT<sup>11</sup>  
UNIVERSITY PARK, PENNSYLVANIA

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### DEUTERIUM ISOTOPE EFFECTS IN RATES OF METHYLENE RADICAL INSERTION INTO CARBON-HYDROGEN BONDS AND ACROSS CARBON DOUBLE BONDS<sup>1</sup>

Sir:

By the photolysis of ketene in the presence of *cis*-butene-2 and of *cis*-butene-2- $d_8$ , 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 Chesick<sup>2</sup> 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 coördinate.

The reactions of singlet methylene radicals with butene-2 are well known<sup>3,4</sup> 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.

(2) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2448 (1962).

(3) H. M. Frey, *Proc. Roy. Soc. (London)*, **A250**, 409 (1959); **A251**, 575 (1959).

(4) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **36**, 1570 (1958).

(1) G. Herzberg, *Astrophys. J.*, **96**, 314 (1942).

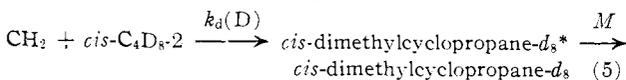
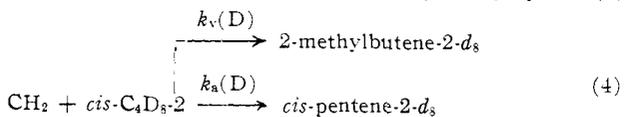
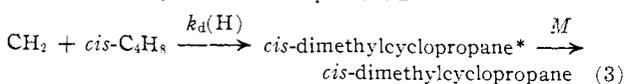
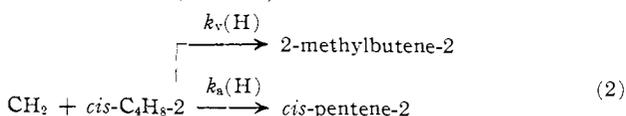
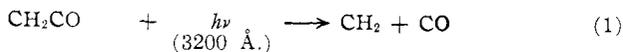
(2) A. E. Douglas, *ibid.*, **114**, 466 (1951).

(3) G. Herzberg, *Mem. soc. roy. sci. Liege, ser. 4*, **15**, 291 (1955).

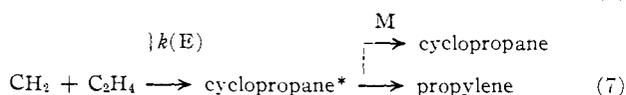
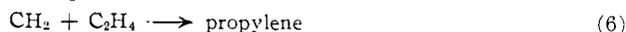
(4) L. Brewer and J. L. Engelke, *J. Chem. Phys.*, **36**, 992 (1962).

(5) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **69**, 100 (1955).

(6) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).



The experiments involve the determination of the rates of allylic and vinylic carbon-hydrogen and carbon-deuterium bond insertion (eq. 2 and 4) relative to carbon-carbon double bond addition (eq. 3 and 5) for *cis*-butene-2 and *cis*-butene-2-*d*<sub>8</sub>, respectively. Ketene-butene mixtures (1:20) were photolyzed for up to 1 hr. in Pyrex reaction vessels with the filtered (~3200 Å.) radiation of a G.E. AH-6 mercury lamp. Product analyses were done by standard gas chromatographic techniques. All gas handling was done in a conventional vacuum system. The relative rates were obtained from the limiting high pressure ratios of each of the various pentenes to the corresponding dimethylcyclopropane, as determined from product composition curves measured over the range of total pressures from 0.3–1500 mm. at 25°, and in the high pressure region at –30°. The relative rates of addition to the carbon-carbon double bond of *cis*-butene-2 and of *cis*-butene-2-*d*<sub>8</sub> were in turn determined by an internal comparison of each butene separately with ethylene, in known mixtures (1:1 butene-ethylene) at ~15 cm. total pressure.



The results are shown in Table I. As seen from Table I, the isotope effects for methylene radical insertion into allylic and vinylic carbon-hydrogen bonds, compared to carbon-deuterium bonds, are factors of

1.96 and 1.55, respectively, *i.e.*, larger than the classical reduced mass factor for carbon-hydrogen and carbon-deuterium isotopes, ~1.37. The observed increases in the isotopic ratio for *k*<sub>i</sub> and *k*<sub>a</sub> in going from 25° to –30°, if not simply the result of experimental error, are small. The secondary isotope effect for double bond addition is small (6–9%).

TABLE I  
RATE CONSTANT RATIOS FOR THE REACTION OF METHYLENE  
WITH *cis*-BUTENE-2 AND *cis*-BUTENE-2-*d*<sub>8</sub>

	25°	–30°	Average
<i>k</i> <sub>i</sub> (H)/ <i>k</i> <sub>d</sub> (H) <sup>a</sup>	1.35	1.5 <sup>b</sup>	
<i>k</i> <sub>i</sub> (D)/ <i>k</i> <sub>d</sub> (D) <sup>a</sup>	0.80	0.9 <sup>b</sup>	
[ <i>k</i> <sub>i</sub> (H)/ <i>k</i> <sub>d</sub> (H)]/[ <i>k</i> <sub>i</sub> (D)/ <i>k</i> <sub>d</sub> (D)]	1.68	1.69	
<i>k</i> <sub>d</sub> (H)/ <i>k</i> (E) <sup>c</sup>	1.01	0.92	
<i>k</i> <sub>d</sub> (D)/ <i>k</i> (E) <sup>c</sup>	0.94	0.84	
<i>k</i> <sub>d</sub> (H)/ <i>k</i> <sub>d</sub> (D)	1.07	1.09	1.08
<i>k</i> <sub>i</sub> (H)/ <i>k</i> <sub>i</sub> (D)	1.80	1.84	1.82
<i>k</i> <sub>v</sub> (H)/ <i>k</i> <sub>a</sub> (H) (per bond)	–	–	1.21
<i>k</i> <sub>v</sub> (D)/ <i>k</i> <sub>a</sub> (D) (per bond)	–	–	1.52
<i>k</i> <sub>a</sub> (H)/ <i>k</i> <sub>a</sub> (D)	–	–	1.96
<i>k</i> <sub>v</sub> (H)/ <i>k</i> <sub>v</sub> (D)	–	–	1.55

<sup>a</sup> *k*<sub>i</sub> = 6*k*<sub>a</sub> + 2*k*<sub>v</sub>. <sup>b</sup> Ratios containing some extrapolation errors due in large part to presence of minor fraction of triplet methylenes, such that the ratio of the ratios in line 3 is more accurate. <sup>c</sup> Each comparison with ethylene was made in duplicate. The ratio of the ratios given in line 6 is more accurate than these individual values for the same reason as in footnote *b*.

That the last effect is close to unity seems quite reasonable in view of the very low or zero activation energy for the addition reaction.<sup>5,6</sup> A very small secondary isotope effect has also been reported recently for H addition to the double bond of propylene-*d*<sub>6</sub>.<sup>7</sup> For the somewhat slower insertion reactions, the two primary isotope effects are appropriately higher and both are consistent with the idea that C–H bond extension is important in the activated complex; unfortunately, the energetics of this methylene radical system are still somewhat uncertain.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WASHINGTON  
SEATTLE 5, WASHINGTON

J. W. SIMONS<sup>8</sup>  
B. S. RABINOVITCH

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- (5) G. B. Kistiakowsky and K. Sauer, *J. Am. Chem. Soc.*, **78**, 5699 (1956).  
(6) W. B. Demore, H. O. Pritchard and N. Davidson, *ibid.*, **81**, 5874 (1959).  
(7) M. Takahasi and R. J. Cvetanovic, *Can. J. Chem.*, **40**, 1037 (1962).  
(8) General Electric predoctoral fellow.

## BOOK REVIEWS

**Regular Solutions.** By JOEL H. HILDEBRAND, Professor of Chemistry, Emeritus, University of California, Berkeley, and ROBERT L. SCOTT, Professor of Chemistry, University of California, Los Angeles. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1962. x + 180 pp. 15.5 × 23.5 cm. Price, \$7.00.

Hildebrand's first paper on solutions appeared in 1909, "The Color of Iodine Solutions," including of course the violet of the royal family of regular solutions, although they were not christened as regular until twenty years later. In 1961, he published a review article, "Solubility," in *This Journal*, and the first edition (206 pages) of the book with this title appeared in 1924. The second edition (203 pages), which came out in 1936, omitted an unimportant chapter on electrolytes. The third edition (488 pages), "Solubility of Nonelectrolytes," in 1950 has Scott as co-author. Now in 1962 they publish, "Regular Solutions" (180 pages). Although it is about on schedule for a fourth edition, it is more a sublimation. Scott's contribution to the third edition is obvious and important, but it is hard to detect any

further contributions to the current book. It seems to be pure Hildebrand.

The chapters and appendices are titled: Preface, The Regular Solution Concept, Thermodynamic Relations, Entropy of Mixing, Regular Solutions of Gases in Liquids, The Liquid State, Intermolecular Forces, Heat of Mixing, Volume Changes on Mixing, Regular Solutions of Solids, Liquid-Liquid Mixtures, Summary and Critique; List of Symbols, The Acentric Factor and Critical Data, Solubility of Gases and Entropy of Solution, Solubility of Iodine and Its Dependence on Temperature at 25°C., Solubility Parameters.

Anyone interested in solutions, and every chemist must be, should read this book. One should go from the preface and first chapter immediately to the tenth—"Summary and Critique." The intervening chapters may be read in any order.

We cannot give a better picture of this book than the first two "conclusions" of the summary.

"1. A pure liquid, if composed of non-polar, symmetrical, compact molecules, has a structure of maximum randomness, as