

and C_4D_{10} vs. CH_4 as $2.27/1.88 = 1.21$. We assume 1.26 ± 0.05 as an average value.

The more extended measurements on the isotope effect in abstraction confirm the earlier results,⁷ and indicate that the preference for abstraction of H over D by tritium is qualitatively in the proper direction for the suggested dependence of hot abstraction on bond energy,⁶ and of sufficient magnitude to account for the observed changes in HT/RT for various alkane molecules. If the observed isotope effect on the substitution reaction arises primarily from some origin other than carbon-hydrogen bond energy, measurements of the ratio of deuterium abstraction to deuterium replacement can give a misleading estimate of the possible magnitude of bond energy effects on the abstraction reaction itself.^{4,5}

The observation of probability integral isotope effects favoring H over D by 20–30% for both hydrogen abstraction and substitution in alkane systems suggests that similar effects are probably also in operation with other target molecules. Such isotope effects with the molecules CH_3F and CD_3F , taken separately, would account quite satisfactorily for the lower hot tritium yields observed for both abstraction and hydrogen substitution in the deuterated species, without the necessity for postulating appreciable differences in moderator effects for the two molecules.^{4,5} With this change in explanation for the isotopic variations observed for the methyl fluorides, no significant discrepancies would remain in such isotopic experiments.

Since the observed yield of CD_3T from CD_3F is also less than that of CH_3T from CH_3F , a probability integral isotope effect (in this case, a secondary isotope effect) presumably also exists in the energetic substitution of T for F.

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THE STRUCTURE OF ARGEMONINE; IDENTIFICATION AS (-)-N-METHYLPAPAVINE

Sir:

Argemonine, $C_{21}H_{25}NO_4$, $[\alpha]^{24D} -187.93^\circ$ ($CHCl_3$), is one of three related alkaloids found in the perennial plants *Argemone hispida* G. and *Argemone munita* Dur. and Hilg. subsp. *rotundata* (Rydb.) G. B. Ownb.¹ Kier and Soine^{1d,e} and Shamma² provisionally proposed tetramethoxylated aporphine structures (I)³ for argemonine based on its oxidation to N-methyl-m-hemipinimide and upon its exhaustive Hofmann elimination to a non-nitrogenous product, which was subsequently oxidized to what was believed to be a tetramethoxy biphenyltricarboxylic acid.^{1d}

Our examination of argemonine by mass spectrometry confirmed the molecular formula and molecular weight and, in addition, showed a large fragmentation peak at m/e 204, which probably corresponds to a N-methyl-6,7-dimethoxyisoquinolinium cation. Two aporphine alkaloids, bulbocapnine and glaucine, gave much different results, however, undergoing dehydrogenation in the metal inlet at 200° extremely rapidly, presumably to give fully aromatic structures.

The ultraviolet spectrum of argemonine (λ_{max} 287 $m\mu$ ($\log \epsilon$ 4.01)) is substantially different from known aporphines⁴ which have several intense peaks at

(1) (a) T. O. Soine and O. Gisvold, *J. Am. Pharm. Assoc. (Sci. Ed.)*, **33**, 185 (1944); (b) J. W. Schermerhorn and T. O. Soine, *ibid.*, **40**, 19 (1951); (c) L. B. Kier and T. O. Soine, *ibid.*, **49**, 187 (1960); (d) L. B. Kier and T. O. Soine, *J. Pharm. Sci.*, **50**, 321 (1961); (e) T. O. Soine and L. B. Kier, *ibid.*, **51**, 1196 (1962).

(2) M. Shamma, *Experientia*, **18**, 64 (1962).

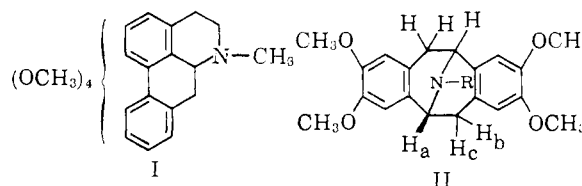
(3) R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. 4, Academic Press, Inc., New York, N. Y., 1954 p. 119; Vol. 7, 1960, p. 427.

(4) M. Shamma, *Experientia*, **16**, 484 (1960).

300–310 $m\mu$, 268–282 $m\mu$ and 220 $m\mu$. The intensities are usually higher also, being in the range of $\log \epsilon$ 4.2 or more.⁴ This difference prompted Shamma² to propose alternate methoxyl arrangements to explain this phenomenon.

The n.m.r. spectrum of argemonine exhibited striking symmetry; the four aromatic protons and four methoxyls being arranged in two groups of two each. Published spectra of aporphine alkaloids,⁵ as well as those re-examined by us, readily revealed the lack of similarity to the spectrum of argemonine. This high degree of symmetry of the n.m.r. spectrum, the optical activity and the other spectral evidence mentioned, point uniquely to structure II (R = CH_3) as argemonine.

The n.m.r. spectrum (in $CDCl_3$) is, in part, an ABX system⁶ in which protons H_a couple only with H_b ⁷ and appear as a doublet centering at 5.92 τ ($J_{ab} = 6$ c.p.s.). Protons H_c couple only with protons H_b and are a doublet centering at 7.38 τ ($J_{bc} = 17$ c.p.s.). Protons H_b are split by H_a and H_c and are a pair of doublets centering at 6.47 and 6.58 τ . The aromatic protons are singlets of intensity two each at 3.24 and 3.41 τ and the methoxyl groups are singlets at 6.08 and 6.16 τ . The N-methyl group is a singlet at 7.43 τ .



Structure II has been known in the literature for many years, as N-methylpapavine, a conversion product of papaverine, although its structure was only recently established by Battersby and Binks.⁸ Synthesis of a sample of N-methylpapavine⁸ and comparison of the infrared, ultraviolet, n.m.r. and mass spectra with those of argemonine confirmed their identity.

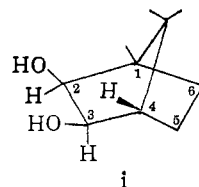
This structure represents a new ring system in nature and furthermore exemplifies a novel type of a benzylisoquinoline alkaloid.

Based on this evidence the structure assigned to the biphenyltricarboxylic acid^{1d} must be in error and its structure is now under investigation.

(5) (a) S. Goodwin, J. N. Shoolery and L. F. Johnson, *Proc. Chem. Soc.*, 306 (1958); (b) I. R. C. Bick, J. Harley-Mason, N. Sheppard and M. J. Vernengo, *J. Chem. Soc.*, 1896 (1961); (c) O. E. Edwards and K. L. Handa, *Can. J. Chem.*, **39**, 1801 (1961); (d) Varian High Resolution N.M.R. Spectra Catalog, Varian Associates, Instrument Division, 1962, spectra 333 and 342.

(6) (a) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 132; (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 90.

(7) This phenomenon has recently been investigated by F. A. L. Anei (*Can. J. Chem.*, **39**, 789 (1961)), and references contained therein) as applied to the bicyclo[2.2.1]heptane system. Thus, 2-exo,3-exo-camphane-2,3-diol (i) exhibits a bridgehead coupling constant of zero ($J_{31} = 0$) with the adjacent proton, as predicted by the Karplus equation (M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959)) where the dihedral angle is 79° .



(8) A. R. Battersby and R. Binks, *J. Chem. Soc.*, 2888 (1955), and references contained therein. Papavine itself (II, R = H) is produced by tin and acid reduction of papaverine. The n.m.r. spectrum of papavine is much like that of N-methylpapavine except that the bridgehead protons are shifted downfield to a doublet centering at 5.55 τ and protons H_c occur as a doublet shifted downfield to 7.25 τ . The NH appears as a singlet at 7.87 τ .

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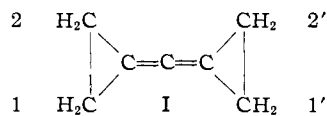
RECEIVED FEBRUARY 5, 1963

CHEMICAL PROPERTIES OF C_3 , A DICARBENE

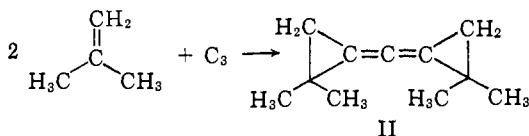
Sir:

We should like to report on the chemical properties of C_3 , a substance which was first detected in the atmosphere of a 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).



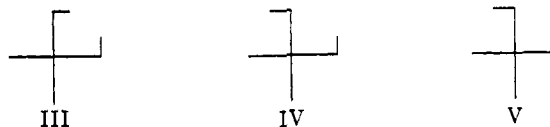
Isobutylene reacts with C_3 to produce 1,1,1',1'-tetramethyl-bis-ethanoallene (II).



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 4.88μ in the infrared is attributed to the strained allenic system. Hartzler observed an absorption band at 4.95μ 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 CH_2 and the methyl groups, respectively. No vinylic absorption is observed.

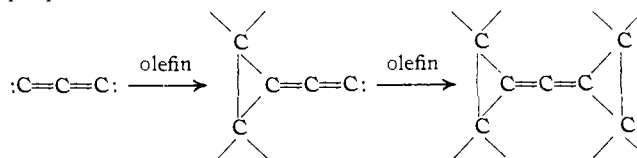
van't Hoff inferred that the two CH_2 groups in allene should lie in orthogonal planes.⁷ This prediction

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 C_3 and propylene further support this conclusion with an argument based on the number of diastereoisomers. On a Golay column (squalane) these ethanoallenes (4.88μ 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).

(10) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR 62-52.

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

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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 coördinate.

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.

(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).