

The photochemistry can be done in rigid medium at liquid nitrogen temperature, in fluid solution at low temperature (-20 to -196°), and at room temperature. Not all can be converted to a photochemical colored form at room temperature but, for example, lapachenole can. Further, in the latter case reversibility exists for several cycles, but after these, the colored form remains with little fading. Some compounds can be converted at low temperature and not completely fade when warmed to room temperature, as, for example, alloevodionol and lapachenole. The photochemical colored forms vary in color, being shades of yellow, pink, green, and violet. The colored form of the pyran is yellow.

The importance of this discovery is the implication of such photochemical behavior in plant systems. Chromenes and pyrans occur in a wide variety of sources, including leaves.⁵ Thus, the roles of these chemical classes can be conceived to be as (1) photochemical memory storage devices and (2) precursors to synthesis of more complex molecules through the photochemical production of a reactive colored form. Further subtopical considerations include their role in regulatory processes, such as growth, germination, budding, fruiting, photoperiodisms, and phototropism.

More detailed investigation of the spectroscopy and photochemistry of the chromenes and pyrans, as well as other molecules, is in progress. It could be anticipated that investigation of these systems would open exciting new avenues of understanding of plant processes. It is hoped that this communication, in part, will stimulate such studies.⁶

(5) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworth and Co. (Publishers) Ltd., London, 1963.

(6) We wish to acknowledge the generosity of several people for samples of compounds. Individual acknowledgement will be given in later publications. This research was sponsored by the U. S. Air Force, Systems Engineering Group, Wright-Patterson Air Force Base, Ohio, Contract AF 33(615)-1733.

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Some Chemistry of the C₂ Molecule

Sir:

During studies of the reactions of carbon vapor with alcohols and halocarbons, large quantities of acetylene and smaller quantities of ethylene have been observed. This is in marked contrast to work in this laboratory with olefins¹ and hydrocarbons,² where little or no acetylene and ethylene are observed.

Acetylene has been reported in reactions involving "hot" carbon atoms with olefinic hydrocarbons,³ saturated hydrocarbons,^{4,5} and alkyl halides.⁵ In these cases acetylene is formed by insertion or addition of

(1) P. S. Skell and R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(2) R. Engel and P. S. Skell, *ibid.*, **87**, 4663 (1965).

(3) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(4) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Chem. Phys.*, **41**, 3267 (1964).

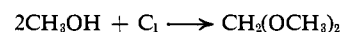
(5) H. Ache and A. Wolf, *J. Am. Chem. Soc.*, **88**, 888 (1966).

energetic ¹⁴C atoms followed by fragmentation of the "hot" intermediate to acetylene and other products.

Under our conditions, condensed-phase, thermal equilibration of hot intermediates is rapid, thus precluding most fragmentation reactions. For this reason a different mechanism is implicated for acetylene formation. We wish to report that acetylene and ethylene produced under our conditions have a C₂ precursor.

The reaction system used has been described.⁶ The C₂ molecules are generated, along with C₁ and C₃, from a 16-v carbon arc under vacuum (1×10^{-4} mm). Reactions occur in condensed phase at liquid nitrogen temperature. Products were isolated by vapor phase chromatography, and their retention times and infrared and mass spectra were compared with those of known compounds.

The major products obtained when carbon vapor and methanol are deposited on a -196° surface under high dilution conditions ($\text{CH}_3\text{OH}/C_{\text{vap}} = 600$) are acetylene, ethylene, and dimethoxymethane. The latter product is simply derived from C₁.



Two labeling experiments demonstrated that the carbon atoms of acetylene and ethylene products are derived from the electrode carbon. Carbon-14-enriched graphite electrodes⁷ were used as sources of carbon vapor. The relative molar ¹⁴C contents indicate two times as much ¹⁴C in the acetylene and ethylene as in the dimethoxymethane (see Table I).

Table I

Product	Relative molar radioactivity ^a		% of carbon found as product
	¹⁴ C _{vap} + ¹² C _{vap} / ¹² CH ₃ OH	¹⁴ CH ₃ OH	
Dimethoxymethane	1.00	2.00	14.6
Acetylene	1.90	0.14	19.2
Ethylene	1.91	0.14	1.2

^a (Millicuries/millimole)_{C₂H₂} or C₂H₄ / (millicuries/millimole)_{standard}.

Reaction of ¹²C carbon vapor with ¹⁴C-labeled methanol provided a complimentary result (see Table I), low relative ¹⁴C content for the acetylene and ethylene. These results are best explained if C₂ is the precursor of acetylene and ethylene.

Insertion of C₁ followed by fragmentation, a favored process with "hot" carbon atoms,^{4,5} is eliminated as the major source of acetylene and ethylene since one carbon atom would be derived from the electrode and the other from the methanol. The "hot" atom process may account for the deviations from whole integer relative reactivities.

Methine, CH, has been postulated as an intermediate from "hot" carbon atoms and organic substrates.⁸ It is highly improbable that methine is the major pre-

(6) P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. Engel, *ibid.*, **87**, 2829 (1965).

(7) Graphite electrodes were dipped into ¹⁴C-labeled fructose solutions acidified with H₂SO₄, charred, and then fired at high temperature.

(8) (a) G. Stöcklin and A. P. Wolf, Proceedings of the Conference on Method of Preparing and Storing Labeled Molecules, Brussels, Euratom, 1963; (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964); (c) A. P. Wolf and G. Stöcklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 32C; (d) J. Nichols, C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **88**, 1065 (1966).

cursor of our acetylene and ethylene since the high dilution conditions would require a long lifetime for CH in frozen methanol to account for these products by bimolecular combination. Experiments to provide conclusive proof are being considered.

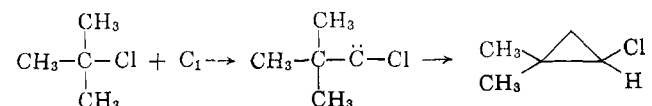
There is a common precursor of acetylene and ethylene, stable at -196° on a neopentane matrix, as shown by the time-delay technique.⁹ Methanol was added to these matrices between 10 sec and 4 hr of their preparation. Over this time span, the C_2H_2/C_2H_4 ratio remained constant and the yield based on carbon vapor, although much less reliable, was also constant. Blank experiments omitting methanol confirmed the earlier results of no appreciable amount of acetylene and ethylene.

1-Propanol was also studied by the technique employing carbon electrodes enriched in ^{14}C . The ratios of specific activities were compared to the major C_1 product, di-*n*-propoxymethane (see Table II). Again the molar activity of C_2H_2 and C_2H_4 is twice that of the C_1 product.

Table II

Product	Rel act.	% of carbon found as product
Di- <i>n</i> -propoxymethane	1.00	14.4
Acetylene	2.04	14.7
Ethylene	1.61	7.5

Acetylene and ethylene are also formed in the simultaneous deposition of carbon vapor and *t*-butyl chloride (also other alkyl halides) on a -196° surface. A major product, identified earlier,¹⁰ in the *t*-butyl chloride experiment is 1-chloro-2,2-dimethylcyclopropane, derived from $C_1(^1S)$ and $C_1(^1D)$.



When *t*-butyl chloride was studied by the technique employing carbon electrodes enriched in ^{14}C , the ratios of the specific activities again implicate C_2 as the precursor of acetylene and ethylene (see Table III).

Table III

Product	Rel act.	% of carbon found as product
1-Chloro-2,2-dimethylcyclopropane	1.00	11.3
Acetylene	1.98	6.0
Ethylene	1.81	0.4

We believe that the above evidence demands a common C_2 precursor to acetylene and ethylene formation. The C_2 molecule is reacting in hydrogen abstraction reactions with the substrate. The C-H bonds in C_2H and C_2H_2 are among the strongest bonds formed by hydrogen atoms.¹¹

(9) P. S. Skell and R. Engel, *J. Am. Chem. Soc.*, **87**, 2493 (1965).

(10) P. S. Skell and R. F. Harris, *ibid.*, **87**, 5807 (1965).

(11) M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962).



The C-H and O-H bond dissociation energies in methanol are given as 92 ± 2 and 102 ± 2 kcal/mole, respectively.¹²

We do not have an explanation for the failure to obtain C_2H_2 from reactions of alkanes and carbon vapor.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research.

(12) J. Kerr, *Chem. Rev.*, **66**, 465 (1966).

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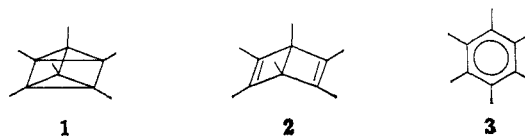
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Hexamethylprismane

Sir:

Tetracyclo[2.2.0.0.2.^{6,0,3,5}]hexane (prismane) was introduced conceptually 97 years ago as Ladenburg's structure for benzene,¹ but until the present time no representative of this ring system has been isolated in pure form.² We now report the preparation and some of the properties of hexamethylprismane (1).

Irradiation at 2537 Å of a dilute butane solution of hexamethylbicyclo[2.2.0]hexa-2,5-diene (2) yields mixtures of 2, hexamethylbenzene (3), and 1. The prismane yield passes through a maximum (~20%) and then diminishes to zero because (1) it too is readily



photoisomerized to mixtures of the three valence tautomers and (2) hexamethylbenzene formation is effectively irreversible at 2537 Å.³ Largely crystalline, the prismane-rich irradiation product is fractionally sublimed, pressed on filter paper to remove adhering 2, and sublimed twice more to give pure hexamethylprismane as volatile white plates, mp $89-90.5^\circ$. *Anal.* Calcd: C, 88.82; H, 11.18. Found: C, 89.08; H, 10.94.

The rather simple infrared spectrum of this hydrocarbon displays maxima (KBr) at 3.42, 6.95, 7.31, 9.61, and 12.54 μ . Its ultraviolet spectrum reveals only end absorption, but the tail is very substantial for a saturated hydrocarbon: ϵ_{230} 990, ϵ_{250} 139, and ϵ_{270} 33 (isooctane). The mass spectrum is dominated by the p and p - 15 (loss of methyl) peaks at *m/e* 162 and 147, relative intensity 55:100. A single sharp line at δ 0.97 constitutes the pmr spectrum (CCl_4) of hexamethylprismane.

When the tetracyclic hydrocarbon was heated 0.5 hr at 129° in a carefully cleaned Pyrex capillary, one-third of it was transformed into a ~2.4:1 mixture of the bicyclic (2) and aromatic (3) tautomers. Powdered Pyrex was found to accelerate the isomerization, par-

(1) A. Ladenburg, *Chem. Ber.*, **2**, 140 (1869).

(2) A tri-*t*-butylprismane has been obtained in 82% purity by K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(3) Though true irreversibility has not been demonstrated, no net conversion of 3 to 1 or 2 is detectable under the reaction conditions.