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.

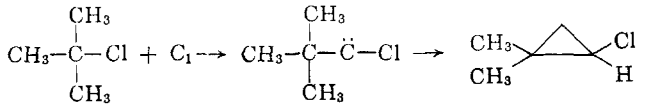
There is a common precursor of acetylene and ethylene, stable at −196° on a neopentane matrix, as shown by the time-delay technique.[9] Methanol was added to these matrices between 10 sec and 4 hr of their preparation. Over this time span, the $C_2H_2/C_2H_4$ ratio remained constant and the yield based 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-*n*-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 $C_1(^1D)$.



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + C_1 \dashrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{C}-Cl \rightarrow$

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]

$$C_2 + H \longrightarrow C_2H \qquad \Delta H = 132 \text{ kcal/mole}$$
$$C_2H + H \longrightarrow C_2H_2 \qquad \Delta H = 114 \text{ kcal/mole}$$

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.

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[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).

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

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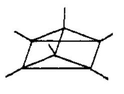
## Hexamethylprismane

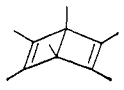
*Sir:*

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**).

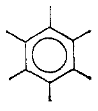
Irradiation at 2537 A of a dilute butane solution of hexamethylbicyclo[2.2.0]hexa-2,5-diene (**2**) yields mixtures of **2**, hexamethylbenzene (**3**), and **1**. The prismane yield passes through a maximum (∼20%) and then diminishes to zero because (1) it too is readily photoisomerized to mixtures of the three valence tautomers and (2) hexamethylbenzene formation is effectively irreversible at 2537 A.[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°. *Anal.* Calcd: C, 88.82; H, 11.18. Found: C, 89.08; H, 10.94.



**1**



**2**



**3**

The rather simple infrared spectrum of this hydrocarbon displays maxima (KBr) at 3.42, 6.95, 7.31, 9.61, and 12.54 $\mu$. Its ultraviolet spectrum reveals only end absorption, but the tail is very substantial for a saturated hydrocarbon: $\epsilon_{230}$ 990, $\epsilon_{250}$ 139, and $\epsilon_{270}$ 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 $\delta$ 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-

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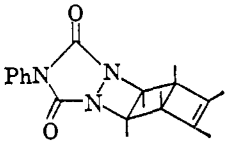
[1] A. Ladenburg, *Chem. Ber.*, 2, 140 (1869).

[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).

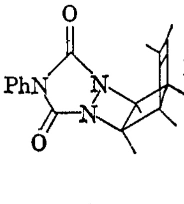
[3] Though true irreversibility has not been demonstrated, no *net* conversion of 3 to 1 or 2 is detectable under the reaction conditions.

ticularly in the direction of hexamethylbenzene; hence unimolecular decomposition of the prismane may proceed significantly slower than the reported rate and may well yield exclusively the Dewar benzene. Hexamethylprismane is immediately isomerized to **2** and **3** by boron trifluoride etherate in carbon tetrachloride, and more slowly by Lindlar catalyst in benzene[4] to **2**, **3**, and yet another valence tautomer, hexamethylbenzvalene.

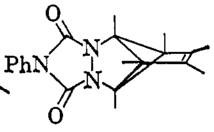
Dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione (**4**) and tetracyanoethylene attack the prismane extremely rapidly at room temperature. The major product from the azo compound and **1** is a 1:1 adduct (*Anal.* Calcd: C, 71.19; H, 6.87; N, 12.45. Found: C, 71.18; H, 6.84; N, 12.46) whose pmr spectrum ($CDCl_3$) consists of a narrow five-proton multiplet centered at δ 7.43 and three needle-like six-proton singlets at δ 1.72, 1.46, and 0.84. Structures **5**, **6**, and **7** are all consistent with the pmr and other spectral data for the adduct, and all are mechanistically feasible candidates. When this compound is treated with osmium tetroxide and pyridine in deuteriochloroform, the methyl region of its pmr spectrum undergoes a sudden change: as the original three signals disappear, four narrow singlets emerge at δ 2.19, 1.76, 1.30, and 1.12 (area ratio, 1:1:2:2). This result eliminates from consideration structures **5** and **6**, as either osmate ester from either isomer should show three methyl signals of equal area. Structure **7**, however, is fully consistent with the new pmr pattern since formation of the pyridine-complexed osmate ester **8** destroys the equivalence of one of the pairs of methyls.



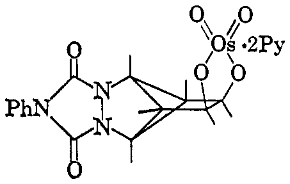
**5**



**6**

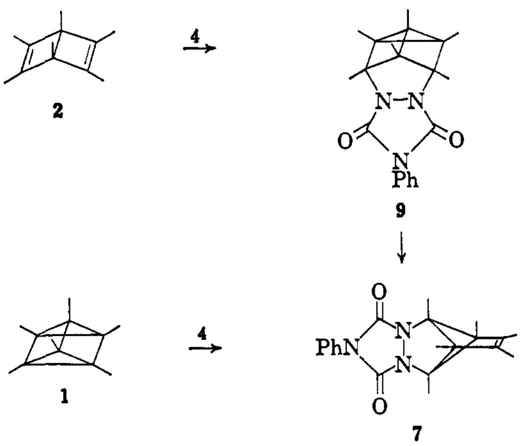


**7**



**8**

Interestingly, the same stable adduct (**7**) is generated more slowly but in good yield from **4** and Dewar benzene (**2**) in acetone. A pmr study has revealed the formation of a labile intermediate adduct on the pathway to **7**. This compound is tentatively formulated as **9** on the basis of its pmr spectrum (which features methyl resonances in $CDCl_3$ at δ 1.79, 1.50, 1.36, and 0.80, relative areas 2:1:1:2) and analogy to homoconjugate addition of dienophiles to norbornadiene.[5] With chloroform instead of the more polar acetone as reaction solvent, the intermediate adduct is far stabler; thus the rearrangement to **7** is probably an ionic process.



The Dewar benzene is produced, often in major amounts, in virtually all of the presently known reactions of hexamethylprismane, regardless of the nature of the reagent or the gentleness of the experimental conditions.[6] This fact suggests that catalysis of the valence tautomerization may require only complexation, not formation of a full-fledged σ bond between hydrocarbon and catalyst. Possibly the key function of the catalyst is to reduce the symmetry of the reacting system, thus weakening the symmetry prohibition[7] against concerted ring opening.

As a consequence of the remarkably efficient aluminum chloride catalyzed trimerization of 2-butyne to Dewar benzene **2**,[8] hexamethylprismane is a readily accessible chemical. We are continuing our investigation of this compound and exploring the scope of the Dewar benzene–prismane photoisomerization.

**Acknowledgment.** The authors wish to thank Dr. G. O. Dudek of Harvard University for determining the mass spectrum of hexamethylprismane, the Danforth Foundation for a fellowship for J. P. L., and the National Science Foundation for financial support of the project.

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[4] It reacts instantly with iodine, but sluggishly with dry methanol; in neither case have the products been adequately characterized.

[5] See, for example, R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 615 (1962), and references contained therein.

[6] The facile catalyzed isomerization of **1** to **2** finds an earlier counterpart in the ring opening of quadricyclanone ketals to norbornadienone ketals at room temperature (D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965)).

[7] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[8] W. Schäfer, *Angew. Chem.*, **78**, 716 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 669 (1966).

[9] Danforth Foundation Fellow, 1962–1966.

[10] This work will comprise a portion of the Ph.D. dissertation o J. P. Lokensgard, University of Wisconsin.

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*Received November 7, 1966*

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## The Photoaddition of 2-Cyclohexenone and Norbornadiene.[1] Studies in Photochemistry. I

*Sir:*

The usual course of the photochemical reaction of unsaturated ketones,[2] esters,[3] or nitro compounds[4]

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[1] Presented to the Chemical Institute of Canada at the Symposium on Synthesis, Banff, Alberta, Aug 1966.

[2] (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); (b) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966); M. Brown, *ibid.*, 340 (1965).