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XENON TETRAFLUORIDE[1]

Sir:

The first true compound of xenon, $Xe^+PtF_6^-$, recently was reported by Bartlett.[2] This suggested to us the possibility that under some conditions of temperature and pressure xenon might be oxidized by elemental fluorine. We have now found that xenon and fluorine react readily to form a solid compound XeF_4 that is stable at room temperature.

One part xenon and approximately five parts of fluorine by pressure were mixed in a 130 cc. nickel weighing can. The mixture was heated at 400° for one hour and then cooled rapidly to room temperature with a water bath. The can was weighed before and after admitting the xenon and again after the reaction when the excess fluorine had been pumped off with the can in a $-78°$ bath. The fluorine was pumped through a U-tube in a $-195°$ bath in order to collect any unreacted xenon. No unreacted xenon was found when the reactions were carried out with excess fluorine. A separate experiment with pure xenon had established that it can be caught quantitatively in a $-195°$ bath.

Table I shows the results of formula determinations based on the combining weights of xenon and fluorine.

TABLE I

CHEMICAL FORMULA OF XENON FLUORIDE

Preparation	Xe taken, millimoles	F_2 consumed, millimoles	Atom ratio F/Xe
1	2.248	4.558	4.05
2	1.806	3.539	3.92
3	1.944	3.808	3.91
4	2.745	5.453	3.97

In another method to verify the formula, a weighed sample of the compound was heated in a weighing can with excess hydrogen at 400° to form hydrogen fluoride and xenon. The excess hydrogen was pumped off with the can in a $-195°$ bath. The material was then distilled under high vacuum through two nickel U-tubes in series. The first was in a $-159°$ bath so as to trap the hydrogen fluoride and pass the xenon. The second U-tube was in a $-195°$ bath to trap the xenon. The xenon was transferred to a weighing can and weighed and its identity and purity checked by mass spectrometric analysis. The hydrogen fluoride was weighed, hydrolyzed in a known excess of NaOH and determined both by back titration with HCl and a fluoride analysis. The reduction was found to proceed according to reaction (1)

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF \qquad (1)$$

Total XeF_4 taken: 0.4006 g.; Xe: found 0.2507 g., calculated 0.2537 g.; F: found 0.1435 g., calculated 0.1469 g.; HF: found 7.53 milliequivalents, calculated 7.73 milliequivalents.

Xenon tetrafluoride is a colorless solid. It has a negligible vapor pressure at $-78°$ and roughly 3 mm. at room temperature. It can be sublimed easily at room temperature. Samples of XeF_4 sealed under vacuum in a glass tube grow to large, colorless crystals within a few hours.

The compound is stable at room temperature and has been stored unchanged in nickel or glass vessels for over a week. XeF_4 in a thin-walled Pyrex capillary was observed not to melt up to 100°.

Xenon tetrafluoride appears to be insoluble in and does not react with n-C_7F_{16}.

A preliminary scan of the infrared spectrum of the vapor has been made from 4000 to 400 cm.$^{-1}$, and only one strong band was found. This is at 590 cm.$^{-1}$, in the region where fluorine–metal stretching frequencies usually are found. That there is only one stretching frequency indicates high symmetry of the gaseous molecule, consistent with either a tetrahedral or square planar structure.

Several weighed samples of XeF_4 were hydrolyzed with dilute NaOH and the total amount of evolved gases was determined by *PVT* measurements. Upon hydrolysis with either dilute NaOH or H_2O, a yellow product was formed which slowly dissolved to give a clear, pale yellow solution. One might expect the hydrolysis to proceed according to the reaction

$$XeF_4 + 2H_2O \longrightarrow Xe + O_2 + 4HF \qquad (2)$$

Analysis for total fluoride is in agreement with this equation. However, the amount of gas liberated and the ratio of xenon to oxygen are not in agreement with equation (2). This indicates that the chemistry of hydrolysis is more complex. The nature of the hydrolysis reaction is being investigated further.

Preliminary studies of the reaction of fluorine or XeF_4 with excess Xe at 400° indicate the existence of a lower fluoride of xenon.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] N. Bartlett, *Proc. Chem. Soc.*, 218 (1962).

PRODUCTION AND REACTIONS OF METHYLENE IN THE TRIPLET STATE

Sir:

Unlike singlet methylene,[1–4] the ground state triplet[5] is difficult to generate in the vapor phase.[5,6,7] However, inasmuch as the spin angular momentum is conserved in mercury photosensitized reactions, as believed, it would be expected that in the triplet mercury (Hg 6^3P_1) photosensitized decomposition of ketene and diazomethane triplet methylene

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[1] W. von E. Doering and P. LaFlamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956).

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[4] H. M. Frey, *Proc. Roy. Soc.* (London), **A251**, 575 (1959).

[5] G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

[6] F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

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should be formed. In view of this we have now carried out such experiments with ketene and found that triplet methylene is formed, as shown by its nonstereospecific reactions with butene-2[3,6,7,8] and lack of random CH insertion reactions.

We have studied reactions of triplet methylene generated in this manner with *cis*- and *trans*-butene-2 and isobutene. In all experiments the ratio of ketene to olefin was 1:10. At lower pressures the product composition varied as a result of secondary reactions of the non-stabilized "hot" adduct, as is also observed in the reactions of singlet methylene.[4] Steady values were obtained in the case of *cis*- and *trans*-butene-2 at approximately 50 cm. and, in the case of isobutene, at about 20 cm. The composition of the products in the high pressure region, expressed as percentage of the total C_5 compounds, is shown in the table.

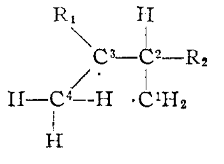
TABLE I

	Dimethyl-cyclopropane			Pentene-2		2-Me[a]	3-Me[b]	2-Me[c]
Reactant	*cis*-1,2	*trans*-1,2	1,1	*cis*	*trans*	B-1	B-1	B-2
trans-Butene-2	13.5	51.9	..	5.6	18.7	0.7	6.8	2.8
cis-Butene-2	21.6	31.3	..	19.3	12.3	0.7	8.1	3.7
cis-Butene-2[d]	28.1	27.1	..	17.0	16.5	..	10.5	4.0
Isobutene	..	..	91.0	..	..	6.5	0.5	2.3

[a] 2-Methylbutene-1. [b] 3-Methylbutene-1. [c] 2-Methylbutene-2. [d] The values obtained from diazomethane photolysis in the presence of excess inert gas (ref. 7).

Unlike singlet methylene, the triplet is seen to react nonstereospecifically with butene-2 and to give far more dimethyl-cyclopropane and 3-methylbutene-2. In the case of *cis*-butene-2 the results can be compared with those obtained from diazomethane photolysis in the presence of excess inert gas,[7] with which they agree reasonably well. In the isobutene reaction, comparison with singlet methylene[9,10] shows a large increase in the amount of 1,1-dimethylcyclopropane with corresponding reduction in the yields of other products.

The suggested mechanism for reaction of triplet methylene with olefins involves initial formation of a triplet addition complex (biradical I), in which partial rotation around the original carbon–carbon double bond is permitted and is responsible for the nonstereospecific formation of addition products.



(I)

In the biradical I, $R_1 = H$ and $R_2 = CH_3$ for *cis*- and *trans*-butene-2, and $R_1 = CH_3$ and $R_2 = H$ for isobutene. Closure of the $C^1C^2C^3$ ring gives the corresponding dimethylcyclopropane. Since there is no evidence for random insertion of triplet methylene into CH bonds, the olefinic C_5 products must be formed by rearrangement. This could occur by migration of H, and perhaps of CH_3 as well, in the biradical, *i.e.* (1) hydrogen migration from C^4 to C^1 (probably *via* a cyclic intermediate); (2) hydrogen migration from C^2 to C^1 (1,2-shift of hydrogen); (3) hydrogen migration from C^2 to C^3 (1,2-shift of hydrogen); (4) methyl migration from C^2 to C^1 or to C^3 (1,2-shift of methyl, occurring perhaps partly or entirely externally).

The products from these migrations in the case of *cis*- or *trans*-butene-2 would be (1) 3-methylbutene-1, (2) 2-methyl-butene-2, (3) 2-methylbutene-1 and (4) *cis*- and *trans*-pentene-2 and 3-methylbutene-1, and in the case of isobutene, (1) 2-methylbutene-1, (2) 2-methylbutene-2 and (3) 3-methylbutene-1. Examination of the product composition shows that the probability of these reactions appears to be in the order (4) > (1) > (2) > (3) for *cis*- and *trans*-butene-2 and (1) > (2) > (3) for isobutene. In the case of isobutene (4) is structurally not possible. This rearrangement scheme is consistent for the three olefins so far examined, but should of course be verified on a much larger number of examples. Further studies of the reactions of triplet methylene are in progress.

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A NEW CARBOCYCLIC STEROID STRUCTURE: 12,18-CYCLOSTEROIDS

Sir:

The steroid molecule has been subjected to the most varied chemical and photochemical transformations. Among the most interesting recent changes have been those involving the angular methyl groups,[1] resulting in the inclusion of the C-19 methyl group in cyclopropano[1j] and cyclobutano[1j] structures and the C-18 methyl group in cyclobutano[1d] and cyclopentano[1c] structures. Phyllanthol,[2] cycloartenol, cyclolaudenol, and cycloeucalenol[3] possess the angular methyl groups in the cyclopropano arrangement.

We wish to present herein the synthesis of the interesting pentacyclic 12,18-dehydrosteroidal ring system and the interconvertibility of the latter with the conanine structure.

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