necessary to determine independently photosynthetic electron turnover rate, as well as new chlorophyll synthesis, have yet to be performed. Beyond this, a double isotope tracer (deuterium and tritium) experiment is required to estimate the isotope effect both for magnitude and direction. Finally, the possible ambiguity introduced by cochromatography of a highly labeled photoproduced contaminant, itself of intrinsic interest if such exists, must be evaluated.

In view of the time required to complete these various operations, it seems wise to make known these preliminary results.

[11] Charles F. Kettering International Fellow, 1964–1965.

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Received April 18, 1966

A Four-Membered Arsenic Ring[1]

Sir:

The homocyclic compounds $(CH_3As)_5$ and $(C_6H_5As)_6$ have been demonstrated by X-ray crystallography.[2,3] We wish now to report the synthesis and properties of $(CF_3As)_4$, which seems to be the first clearly recognized example of an As_4 ring compound.

Synthesis and Purification. Mercury acted upon CF_3AsI_2 (2-day shaking, sealed tube at 25°) to produce a liquid–solid mixture from which the solid was separated by a magnetic separatory funnel[4] and purified by crystallization from hexane at −78°, in a filtering Λ-tube.[5] Recrystallization yielded a sample melting in a 0.1° range at 98.2°, under autogenous pressure. Further evidence of purity was the normal behavior of the vapor–tension data, which determined the equation $\log P = 12.4514 - 4003/T$. Averages of log P and $1/T$ for pairs or triplets of closely adjacent points are shown in Table I. Included are points observed after cooling from higher temperatures, all in good agreement.

Formula. The molecular formula $(CF_3As)_4$ agrees with the observed vapor-phase molecular weight: found, 579; calcd, 576. The 27 strongest mass spectrum peaks[6] all were assignable to fragments containing no atoms other than As, C, and F. The three highest m/e ratios (with parenthetical relative intensities on an arbitrary scale) were assignable as $(CF_3As)_4^+ = 576$ (58), $(CF_3)_3As_4^+ = 507$ (107), and $(CF_3)_2As_4F^+ =$ $(CF_3)_3As_2(CF_2)_2^+$ (?) = 457 (30), confirming the As_4 group. Others were 362 (10), 324 (34), 318 (20), 312 (4), 299 (29), 274 (37), 268 (10), 262 (12), 243 (11), 231 (10), 225 (42), 219 (57), 219 (57), 181 (29), 175 (8), 169 (17), 150 (81), 144 (13), 137 (8), 125 (12), 113 (55), 106 (16), 94 (30), 75 (40), 69 (60), and many weaker peaks.

Table I. Volatility of Solid $(CF_3As)_4$

Temp, °C	43.65	53.1	60.8	67.7	74.95	81.1
P_{obsd}, mm	0.65	1.51	2.93	5.15	9.00	13.9
P_{calcd}, mm	0.65	1.52	2.92	5.11	8.95	14.2

Table II. Infrared Comparison of $(CF_3As)_4$ with $(CF_3P)_4$[a]

Suggested assignments	$(CF_3As)_4$	$(CF_3P)_4$
C–F, 2 × ν_2	2277 (0.38)	2302 (0.53)
C–F, $\nu_1 + \nu_2$	2246 (0.60)	2285 (0.45)
C–F, 2 × ν_1	2225 (0.73)	2256 (1.2)
C–F, ν_2 + CF_3, δ–e	1865 (0.19)	1893 (0.20)
C–F, ν_1 + CF_3, δ–e	1842 (0.27)	1871 (0.36)
C–F, ν_2 + CF_3, δ–a	1665 (0.17)	1685 (0.12)
C–F, ν_1 + CF_3, δ–a	1643 (0.07)	1665 sh (0.06)
C–F, ν_2 + E–CF_3, ν_2	1455 (0.08)	1624 (0.06)
C–F, ν_1 + E–CF_3, ν_2	1430 (0.11)	1607 (0.05)
C–F, ν_2 + E–CF_3, ν_1	1425 (0.11)	1580 (0.04)
C–F, ν_1 + E–CF_3, ν_1	1400 (0.09)	1565 sh (0.03)
2 × CF_3, δ–e	1438 (0.11)	1461 (0.10) (or 308 + 1154?)
308 + 1135	. . .	1444 (0.08)
CF_3, δ–a + δ–e	1257 (1.6)	1277 (1.6)
CF_3, δ–e + E–CF_3, ν_2	1039 (2.6)	1213 (2.2)
CF_3, δ–e + E–CF_3, ν_1	1024 (1.8)	1173 (24)
C–F, ν_2	1140 (500)	1154 (270)
C–F_1, ν_1	1117 (250)	1135 (118)
CF_3, δ–e	728 (23)	742 (9)
CF_3, δ–a	527 (0.17)	534.5 (0.55)
E–CF_3, ν_2	310 (5)	471 (0.5)
E–CF_3, ν_1	295 (2)	436 (9.0) 432 (8.0)
P–CF_3, ρ	. . .	308 (2.0)

[a] Relative intensities are in parentheses after the frequencies (cm^{-1}). Abbreviations: sh = shoulder; ν = stretching (arbitrary subscripts show different phase patterns); δ = deformation; ρ = rocking; a = asymmetric; e = symmetric; E = As or P.

Infrared Spectrum. The infrared spectrum of $(CF_3As)_4$ vapor is compared with that of $(CF_3P)_4$ in Table II, showing some remarkable similarities; even the assignments of overtones and combinations are parallel. The samples were in heated cells with very thin KBr windows, permitting observation by the Beckman IR7 instrument (with NaCl or CsI optics) down to 275 cm^{-1}, at pressures as high as 100 mm.

Other peaks, possibly assignable when the lower range fundamentals are known, were as follows: for $(CF_3As)_4$, 1376 (0.05), 1353 (0.04), 1322 (0.06), 1285 (0.21), 1226 (1.2), 1197 (2.5), 1090 (12), 1057 (3.3), 1039 (2.6), 1024 (1.8), 993 (0.17), 939 (0.02), 904 (0.02), 850 sh (0.05), 820 (0.09), 785 (0.05), 606 (0.13), and 557 (0.07); for $(CF_3P)_4$, 1485 sh (0.06), 1406 (0.07), 1395 (0.08), 1381 (0.10), 1313 (0.22), 1289 (1.1), 1251 (0.8), 1213 (2.2), 1194 (3.6), 1106.5 (5), 1085 (3), 1069 sh (1.0), 1035 sh (0.12), 1017 (0.13), 994 (0.25), 973 (0.15), 915 (0.02), 901 (0.07), 879.5 (0.09), 862 (0.07), 844 (0.04), 810 (0.03), 785 (0.04), 760 sh (0.05), 702 (0.10), 680 (0.07), 584 (0.08), 569 (0.12), 510 (0.09), and 493 (0.13).

The ultraviolet spectrum of $(CF_3As)_4$ showed broad and equally high peaks at 2240 (ε 3900) and 1970 A

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[1] The major part of this research was performed at the University of Southern California by A. H. Cowley, who wishes to thank the University Research Institute of the University of Texas for financial support during the Fall Semester, 1965. The experimental facilities and supplemental work by Burg were supported by the National Science Foundation through Grant No. GP-3812. The initial synthesis from CF_3AsI_2 and mercury was done by Cullen at the University of Cambridge in 1958; a sample of the mixed product which he made from CF_3AsCl_2 and mercury at the University of British Columbia in 1961 was proved to be the same as that obtained independently at the University of Southern California.

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[5] Similar in principle to that described by A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 726 (1962).

[6] Observed by means of the CEC 21-102 mass spectrometer at the University of Texas. The range scanned was m/e 15–600, with the heated-inlet system left at room temperature.

(ϵ, uncertain background). These are lower wavelengths than found for $(CF_3P)_4$, suggesting a more restricted delocalization of lone-pair electrons than in $(CF_3P)_4$.[7]

Chemical Behavior. The tetramer $(CF_3As)_4$ is sensitive to basic impurities; for example, failure to eliminate water from the container (such as an infrared cell) may lead to a change back to the original solid–liquid mixture. By analogy to the better known $(CF_3P)_n$ system,[7] we assume the slightly less volatile liquid to be the pentamer $(CF_3As)_5$. The action of air upon $(CF_3As)_4$ seems like that of oxygen on $(CF_3P)_4$; a nonvolatile white solid is formed. We have not made a monomer complex analogous to $(CH_3)_3P \cdot PCF_3$,[8] for $(CH_3)_3As$ only dissolves $(CF_3As)_4$, whereas $(CH_3)_3P$ colors it yellow and soon converts it to a nonvolatile brown solid. Basic hydrolysis destroys $(CF_3As)_4$ with nonstoichiometric formation of HCF_3, as might be expected from the behavior of CF_3–As–H compounds.[9]

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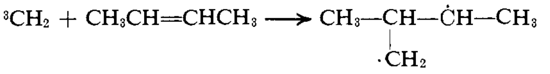
Received May 6, 1966

1,2 Shifts of Methyl Groups in Alkyl Diradicals. Formation of Pentenes in Triplet Methylene Reactions with 2-Butene

Sir:

Photolytically formed methylene reacts with *trans*-2-butene in the gas phase to form a variety of C_5 products, including several pentenes and both 1,2-dimethylcyclopropanes.[1-3] Direct stereospecific insertion by singlet methylene into the C=C bond or into one of the C–H bonds accounts for the formation of *trans*-1,2-dimethylcyclopropane, 2-methyl-2-butene, and *trans*-2-pentene, and isomerization of the excited *trans*-dimethylcyclopropane produces the *cis* isomer and several pentenes in reactions carried out at low gas pressures. At higher pressures, however, pentene products are still observed[4] which cannot readily be rationalized through singlet methylene mechanisms. These products, including *cis*-2-pentene, 2-methyl-1-butene, and 3-methyl-1-butene, have been attributed to the reactions of triplet methylene, both as a lesser contributor in the direct photolysis of ketene or diazomethane and as the major reactant in the presence of inert gases[5-7] or in Hg-photosensitized decompositions of methylene precursors.[8]

One initial step suggested for the reaction of triplet methylene with *trans*-2-butene is reaction 1, with subsequent rearrangement of this diradical required for



$$^3CH_2 + CH_3CH{=}CHCH_3 \longrightarrow CH_3\text{—}\underset{\cdot CH_2}{\underset{|}{CH}}\text{—}\dot{C}H\text{—}CH_3 \qquad (1)$$

the formation of the pentenes. No agreement has existed concerning the nature of such rearrangements, and several possible mechanisms have been suggested,[4] including (a) 1,4-hydrogen shift; (b) 1,2-hydrogen shift; (c) 1,2-methyl shift; and (d) the closing of the diradical to the substituted cyclopropane, followed by reopening of a different ring C–C bond and a 1,2-hydrogen shift. An alternate mechanism for pentene formation involves an initial abstraction reaction by the triplet methylene, followed by methyl–butenyl radical combination.[9]

Additional information about these possible mechanisms can be obtained through tritium labeling of the original methylene and subsequent determination of the intramolecular location of the tritium label. In this situation, the diradical formed in (1) is $CH_3CH(\dot{C}HT)\underset{\cdot}{C}HCH_3$, and the various rearrangements lead to different locations for the tritium atom originally in the methylene group. In our initial experiments we have utilized CHT from the photolysis of CHT=C=O at 3660 A, and have analyzed the C_5 olefinic products for their intramolecular tritium location through the techniques of isotopic radio gas chromatography.[10,11] The reacting methylene is approximately 30% triplet under these conditions.

Two important products for mechanism determination in this system are 3-methyl-1-butene and *cis*-2-pentene. The shift of a methyl group in the triplet diradical would lead to $(CH_3)_2CHCH{=}CHT$ and *cis*-$CH_3CHTCH{=}CHCH_3$, while $CH_3CH(CH_2T)CH{=}CH_2$ would be formed by 1,4-hydrogen shift. The ring-closure and reopening mechanism (d) would produce $CH_3\dot{C}HCHT\dot{C}HCH_3$, and the rearrangement would give both $CH_3CH_2CT{=}CHCH_3$ and $CH_3CHTCH{=}CHCH_3$.[12] The initial abstraction of H by CHT would lead only to alkyl-tritiated forms of 3-methyl-1-butene and *cis*-2-pentene in the subsequent CH_2T–butenyl combination.[13] The intramolecular distribution of tritium between alkyl and olefinic positions is summarized in Table I for 3-methyl-1-butene and *cis*-2-pentene from CHT reactions with *trans*-2-butene under a variety of conditions.

The 3-methyl-1-butene contains tritium activity in both alkyl and olefinic positions, indicating more than one mechanism for its formation. The presence of an olefinic tritium component indicates that 1,2-methyl migration is an important process for the formation of this molecule. While 1,2 shifts of methyl or hydrogen

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(12) A kinetic isotope effect would be anticipated, such that $CH_3CH_2CT{=}CHCH_3$ should predominate.

(13) The ratio gas chromatographic techniques separate the tritiated olefins into an alkyl-*t* group and an olefin-*t* group, but do not distinguish isomeric forms within the two groups.