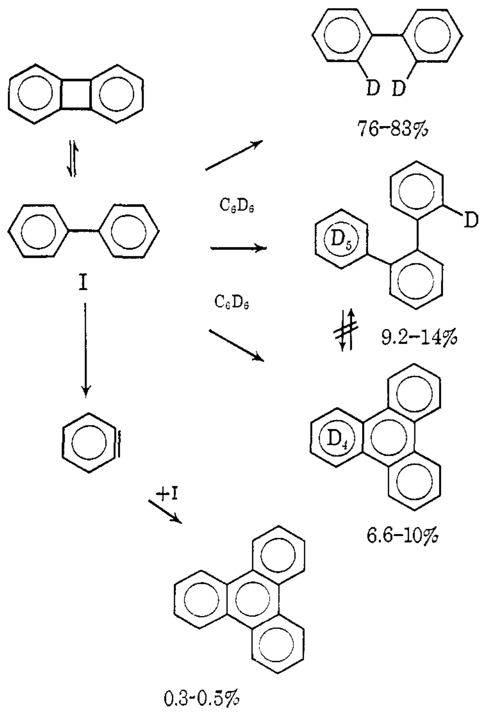

Figure 1. Pyrolysis of biphenylene: products and composition (28–35% yield based on unrecovered biphenylene).

reaction time, biphenylene is gradually consumed without significant formation of tetraphenylene. The nonvolatile portion of the reaction mixture is polymeric.[14]

Thus it seems most likely that efficient dimerization occurs in the liquid phase at higher temperatures as a result of the relatively high steady-state concentration of the diradical, I. At lower temperatures, the concentration of I would be smaller; consequently dimerization would be less favored, and radical addition presumably occurs (Table I, runs 4–6) to give polymeric material.

Other evidence for the intermediacy of I was obtained by vapor-phase pyrolysis of biphenylene (0.1 *M*) in benzene and benzene-d_6, respectively, between 650 and 730° with contact times of 3–5 sec. In benzene at 650°, for example, in addition to unreacted biphenylene (~70%), three major products were obtained: biphenyl, triphenylene (1.3%), and *o*-terphenyl (2.1%).[15a] Only trace amounts of tetraphenylene were detected. At 730°, the results were qualitatively the same but more biphenylene was consumed. However, in the absence of biphenylene, smaller amounts of biphenyl and *o*-terphenyl are formed.[16] When the pyrolysis was conducted in benzene-d_6 (Figure 1) at 650° the biphenyl consisted of mainly d_2 (28%) and d_{10} (57%) species.[16] Biphenyl-d_2 is formed from I and benzene-d_6 by deuterium abstraction, while biphenyl-d_{10} arises mainly from pyrolysis of benzene-d_6.[16,17] The presence of other deuterated species is a result of deuterium–hydrogen exchange[18] between benzene-d_6 and biphenylene[19] and/or biphenyl-d_2. The triphenylene and *o*-terphenyl[20] contained mainly four and six deuterium atoms/molecule, respectively, and more highly deuterated species[19] formed by exchange reactions in the expected amounts. At 730°, the anticipated increase in hydrogen–deuterium exchange was observed.

The presence of triphenylene-d_0 (5.2%) is best explained by the reaction of I with benzyne-d_0 from fragmentation of biphenylene or preferably I. To support this contention, biphenylene was pyrolyzed at 735° in a nitrogen stream. In addition to recovered biphenylene (relative peak area, 100) and tars, the volatile products were biphenyl (44), tetraphenylene (1.2), triphenylene (7.4), and at least six other higher boiling unidentified hydrocarbons (~50). Thus it appears that I is an efficient trap for the benzyne produced since naphthalene-d_4 was not, but triphenylene-d_0 was, observed in pyrolyses conducted in excess benzene-d_6.[3c,d] These results are consistent with those outlined in Figure 1. This may account for the formation of triphenylene by the supposed trimerization of benzyne.[3c,d]

The lack of appreciable further fragmentation (<0.5%) of I in the presence of benzene is not surprising since I undergoes other reactions with benzene (Figure 1). However, in the absence of benzene, in the gas phase where dimerization and other bimolecular reactions are minimized I undergoes more extensive fragmentation to benzyne. This is in closer agreement with electron-impact data.[4]

Acknowledgment. The authors are indebted to Mr. Linwood B. Crider, B. F. Goodrich Company, for mass spectral analyses.

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[14] The nature of this substance is presently under investigation.

[15] (a) Typical data. (b) Other hydrocarbons are also formed. Two of them were tentatively identified as 1- and 2-phenylbiphenylenes *via* mass spectrometry. On the basis of glpc and mass spectral data *o*-, *m*-, and *p*-terphenyl were also present.[16]

[16] G. M. Badger, *Progr. Phys. Org. Chem.*, 3, 1 (1966).

[17] (a) The portion of biphenyl from I and benzene-d_6 amounts to 38.2% (3.7% d_1, 28.3% d_2, 5.5% d_3, and 0.7% d_4) and that from dimerization of benzene-d_6 and possibly phenyl-d_5 radicals (from I and benzene-d_6) amounts to 59.3% (2.1% d_9, 57.2% d_{10}).

[18] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).

[19] Biphenylene (84% d_0, 14% d_1, 1.5% d_2, and 0.2% d_3) *recovered* from pyrolysis in benzene-d_6 at 650° exhibited, as expected, less deuterium–hydrogen exchange than that at 730° (49% d_0, 32% d_1, 14% d_2, 3.9% d_3, 0.9 d_2, and 0.4% d_5). The levels of exchange observed parallel that in all of the reaction products.

[20] Under these conditions triphenylene and *o*-terphenyl are essentially (<1%) noninterconvertible, and tetraphenylene does not fragment.

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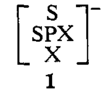
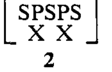
New Phosphorus–Sulfur Chemistry

Sir:

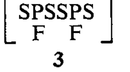
A new class of anionic substituted thiophosphates has been prepared by the reactions of certain types of metal salts with tetraphosphorus decasulfide. These preparations were effected in heterogeneous systems using media such as water, acetonitrile, or 1,2-dimethoxyethane. Three structural species were obtained as exemplified by **1–3**.[1] The type of product, isolated


$$\left[\begin{array}{c} \text{S} \\ \text{SPX} \\ \text{X} \end{array}\right]^-$$

1


$$\left[\begin{array}{c} \text{S S} \\ \text{SPSPS} \\ \text{X X} \end{array}\right]^{2-}$$

2


$$\left[\begin{array}{c} \text{S \ \ S} \\ \text{SPSSPS} \\ \text{F \ \ F} \end{array}\right]^{2-}$$

3

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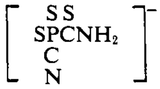
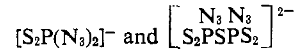
[1] Sample analytical data for these salts are as follows: *Anal.* Calcd for $(n\text{-}C_3H_7)_4N^+S_2P(N_3)_2^-$ (mp 75–76.5°): C 39.4; H, 7.7; N, 26.8; P, 8.5; S, 17.5. Found: C, 39.5; H, 7.8; N, 26.6; P, 8.6; S, 17.7. Calcd for $(n\text{-}C_3H_7)_4N^+S_2PCN(CSNH_2)^-$ (mp 114–115° dec): C, 45.7; H, 8.2; N, 11.4; P, 8.4; S, 26.2. Found: C, 45.9; H, 8.2; N, 11.3; P, 9.0; S, 26.5. Calcd for $[(n\text{-}C_3H_7)_4N^+]_2[S_2P(N_3)SP(N_3)S_2]^{2-}$ (mp 157°): C, 42.5; H, 8.3; N, 16.5; P, 9.1; S, 23.6. Found: C, 42.4; H, 8.7; N, 16.3; P, 9.2; S, 23.7.

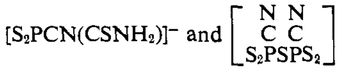
from what appears to be a rather complex reaction between P_4S_{10} and the metal salt, is dependent not only on the solvent employed but also on the work-up procedure. For example, the reaction of sodium fluoride or sodium azide in water gives as one of the products divalent anions of the type **2.** In acetonitrile, sodium fluoride or sodium azide gives primarily univalent anions of type **1.**[2] Sodium cyanide also reacts under these conditions to give a species tentatively characterized as


$$\left[\begin{array}{c} S\,S \\ SPCNH_2 \\ C \\ N \end{array}\right]^-$$

Structures of these anionic thiophosphates have not been rigorously established; however, infrared and nmr data (H^1, P^{31}, and F^{19}) are consistent with the structures presented in **1** through **3**. In the fluorine-substituted derivatives **1** through **3**, the PF coupling constant does not significantly vary (the values are 1149, 1160, and 1170 for structures **1** through **3**, respectively). There are, however, significant variations in chemical shifts for these compounds, ranging in the fluoro species from +2.3 to −7.4 ppm ($CFCl_3$ reference) for structures **1** and **3**, respectively. The P^{31} resonances are shifted to considerably lower fields than those of their oxygen analogs. For example, the P^{31} resonance of $S_2PF_2^-$ appears at −118 ppm with reference to 85% phosphoric acid. In $P_2S_5F_2^{2-}$, the phosphorus nuclei are strongly coupled, whereas in $P_2S_6F_2^{2-}$, the coupling is too weak to be detected in the P^{31} nmr experiment. Infrared spectra of the tetra-*n*-propylammonium salts of


$$[S_2P(N_3)_2]^- \text{ and } \left[\begin{array}{c} N_3\,N_3 \\ S_2PSPS_2 \end{array}\right]^{2-}$$

examined in Nujol mulls contain strong absorptions in the regions 2100–2130 and 1240–1250 cm^{-1} characteristic of asymmetric and symmetric vibrations, respectively, for the azide grouping. There is no readily identifiable –CN stretching vibration band in the infrared spectra of the tetra-*n*-propylammonium salts of


$$[S_2PCN(CSNH_2)]^- \text{ and } \left[\begin{array}{c} N\;\;N \\ C\;\;C \\ S_2PSPS_2 \end{array}\right]$$

examined in Nujol mulls. The Raman spectrum of a dimethyl sulfoxide solution of the latter salt, however, contains a strong band at 2160 cm^{-1} that may be assignable to the –CN absorption. The NH protons in $S_2PCN(CSNH_2)^-$ are nonequivalent (P^{31} nmr data), presumably because of restricted rotation about the C–N bond. Rotamer lifetimes are relatively long, *ca.* 10^{-2} sec at 120°.

All these new thiophosphates display fairly good stability toward acid and base. Hydronium salts of these anions have been prepared. These salts are weaker acids than hydrochloric acid. Thermal reactivity of the salts seems to be relatively low; for example, in the case of the hydronium salt of $S_2P(N_3)_2^-$, there is only slight evidence of decomposition at room temperature over a period of several months. Hydronium salts of both the $S_2P(N_3)_2^-$ and the $S_2PF_2^-$ anions have been distilled under vacuum and, although some decomposition may have occurred, most of the starting material was recovered, as demonstrated by precipitation as the tetra-*n*-propylammonium salt.

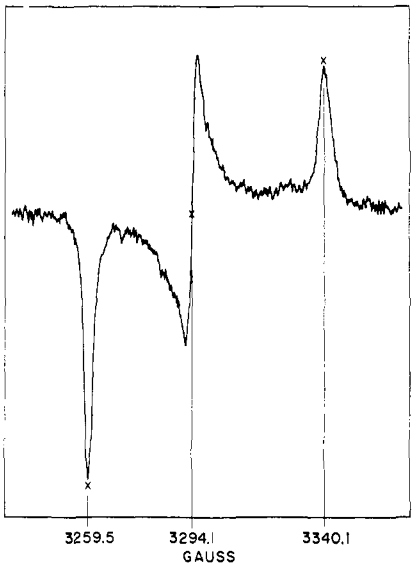


Figure 1. Esr spectrum of the species produced on warming $(n\text{-}C_3H_7)_4N^+S_2P(N_3)_2^-$ to 122° for 5 min. The spectrum was obtained at −155° using a Varian spectrometer with 100-kc modulation operating at 9.3735 kMc/sec.

The thermal stability and reactivity of these compounds have not as yet been fully characterized. The cesium salt of $S_2PF_2^-$ begins to degrade at 325°. At 375° in 3 hr, about 10% molar amounts of gas are evolved consisting of SPF_3 and PF_3 in approximately a 2:1 ratio. Thermal degradation of $(n\text{-}C_3H_7)_4N^+S_2PCN(CSNH_2)^-$ at 133–135° yields HCN as the primary gaseous species (1.18 moles of gas per mole of salt). The azide ion $S_2P(N_3)_2^-$ in the form of the tetra-*n*-propylammonium salt exhibited no evolution of nitrogen in the molten state at 80° over a 15-min period. At 101–102° the melt turned blue and nitrogen was evolved slowly. The amount of gas evolved at this temperature in 7.75 hr was about 95% of that expected for complete decomposition of the bis azide derivative to 2 moles of nitrogen. A sample of the salt which has been heated at 122° for 5 min, during which time the melt turned deep blue and evolved a small amount of nitrogen, was quickly chilled to −196° and stored at this temperature for about 3 hr. The esr spectrum of the sample obtained at −155° (Figure 1) closely resembles in appearance and line positions (g_1 = 2.055; g_2 = 2.033; g_3 = 2.005) the low-temperature esr spectra obtained from sulfur dissolved in amines (g_1 = 2.055; g_2 = 2.035; g_3 = 2.003).[3] In that work the spectra were interpreted in terms of noninteracting unpaired electrons (with anisotropic g values) localized on sulfur atoms. At this time a less likely possibility that the spectrum of the products of thermal decomposition of $(n\text{-}C_3H_7)_4N^+S_2P(N_3)_2^-$ reflects the presence of a triplet-state biradical species cannot be ruled out. If this were the case, the 81-gauss separation of the outer two lines would correspond to an electron separation of about 9 A. A half-field resonance signal often observed in triplet-state spectra was not detected in this particular spectrum.

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(2) The S_2PF_2 anion may also be prepared in almost quantitative yield from the reaction $2SPF_3 + 2CsF \rightarrow CsS_2PF_2 + CsPF_6$ using acetonitrile as solvent.

(3) W. G. Hodgson, S. A. Buckler, and G. Peters, *J. Am. Chem. Soc.*, **85**, 543 (1963).

The salts of $S_2PF_2^-$ readily oxidize with bromine to give the new compound $P_2S_4F_4$.[4] The F^{19} and P^{31} nmr spectra and the infrared data are consistent with the structure $F_2(S)PSSP(S)F_2$. This compound reacts with a variety of olefins; for example, it reacts with cyclohexene, to give $C_6H_{10}[SP(S)F_2]_2$,[5] a colorless liquid moderately stable to hydrolytic attack. Additionally, the cesium salt of $S_2PF_2^-$ reacts with a variety of organic halides to give compounds of the type $RSP(S)F_2$ where R is ethyl,[6] benzyl, or isopropyl.

Full details of this area of phosphorus–sulfur chemistry will be reported in a later paper.

Acknowledgment. We are indebted to Drs. M. T. Jones and D. R. Eaton for assistance in the esr interpretations.

(4) *Anal.* Calcd for $P_2S_4F_4$: P, 23.3; S, 48.2; F, 28.5; mol wt, 266. Found: P, 23.5; S, 48.0; F, 28.3; mol wt (cryoscopic in benzene), 260; bp 58–60° (10 mm).

(5) *Anal.* Calcd for $C_6H_{10}S_4P_2F_4$: C, 20.7; H, 2.9; S, 36.8; P, 17.8; F, 21.8. Found: C, 20.9; H, 2.9; S, 37.3; P, 17.5; F, 22.0; bp 104° (0.5 mm).

(6) *Anal.* Calcd for $C_2H_5SPSF_2$: C, 14.8; H, 3.1; S, 39.5; P, 19.1; F, 23.4; mol wt, 162. Found: C, 15.3; H, 3.5; S, 39.1; P, 18.5; F, 23.0; mol wt (cryoscopic in benzene), 157; bp 124°.

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$1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$

Sir:

The polyhedral boranes $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are noted for their unusual stabilities and for the broad scope of their derivative chemistries.[1] The carborane $B_{10}C_2H_{12}$ which is isostructural and isoelectronic with $B_{12}H_{12}^{2-}$ has also received much attention because of its great thermal stability and extensive derivative chemistry.[2] The 1,6 and 1,10 isomers of $B_8H_8(CCH_3)_2$ which are isostructural and isoelectronic with $B_{10}H_{10}^{2-}$ have recently been reported.[3] The chemistry of $B_{10}C_2H_{12}$ differs from that of $B_{12}H_{12}^{2-}$, and the chemistry of $B_8C_2H_{10}$ can be expected to differ from that of $B_{10}H_{10}^{2-}$, both because of the charge differences and the localized effects of the carbon atoms.

Table I. Analyses

Compound	Calculated, %					Found, %				
	B	C	H	N	H[a]	B	C	H	N	H[a]
$B_{10}H_{12}CNH_3$	72.5	8.0	10.1	9.4	....	73.0	8.0	10.1	9.4	..
$(CH_3)_3NHB_{10}H_{12}CH$	56.0	24.9	11.9	7.2	2320	56.1	25.4	12.3	7.2	2358
$B_9H_{11}CN(CH_3)_3$	54.2	26.8	11.3	7.8	..	53.6	27.1	11.3	6.6	..
$(CH_3)_4NB_9H_9CH$	50.4	31.1	11.4	7.2	1970	50.7	31.4	11.9	7.2	2003
$CsB_{11}H_{11}CH$	43.0	4.4	4.4	...	1710	42.6	4.6	4.5	...	1723
$(CH_3)_4NB_{10}H_{10}CH$	52.7	29.2	11.2	6.8	2080	52.8	28.5	11.1	6.8	2090

[a] By evolution, ml/g.

This communication is concerned with the $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ anions. These species comprise the "missing links" in the $B_{10}H_{10}^{2-}$–$B_8C_2H_{10}$ and $B_{12}H_{12}^{2-}$–$B_{10}C_2H_{12}$ series, respectively. It is anticipated that these monobasic carboranes may exhibit some of the chemical properties of both their dibasic borane and neutral carborane analogs. This has already been demonstrated, in part, by the reactions of $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ with *n*-butyllithium to form $1\text{-}B_9H_9CLi^-$ and $B_{11}H_{11}CLi^-$, respectively. The reaction of $1\text{-}B_9H_9CLi^-$ with trimethylchlorosilane has given $1\text{-}B_9H_9CSi(CH_3)_3^-$. Analogous lithio derivatives have been prepared from $B_{10}C_2H_{12}$ and widely exploited.[2]

The preparations of $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ are outlined in the following equations.

$$Na_2B_{10}H_{13}CN^{4} \xrightarrow[\text{ion exchange}]{H^+} B_{10}H_{12}CNH_3 \xrightarrow[NaOH-H_2O]{(CH_3)_2SO_4} B_{10}H_{12}CN(CH_3)_3 \xrightarrow[\text{reflux}]{Na,\,THF} NaB_{10}H_{12}CH + NaB_{10}H_{10}CH \quad (1)$$

The sodium salt of $B_{10}H_{12}CH^-$ is much less soluble in tetrahydrofuran (THF) than is $NaB_{10}H_{10}CH$; separation is therefore readily accomplished.

$$2CsB_{10}H_{12}CH \xrightarrow{300\text{–}320°} Cs\text{–}1\text{-}B_9H_9CH + CsB_{11}H_{11}CH + 2H_2 \quad (2)$$

Alternate syntheses include

$$CsB_{10}H_{12}CH \xrightarrow[180°]{(C_2H_5)_3N\cdot BH_3} CsB_{11}H_{11}CH \quad (3)$$

$$NaB_{10}H_{12}CN\cdot S(CH_3)_2^{4} \xrightarrow[\text{ion exchange}]{H^+} B_{10}H_{11}(OH)CNH_3 \xrightarrow[NaOH]{(CH_3)_2SO_4} B_{10}H_{11}(OH)CN(CH_3)_3 \xrightarrow[H_2O,\,THF]{NaOH} B_9H_{11}CN(CH_3)_3 \xrightarrow[\text{reflux}]{Na,\,THF} \xrightarrow[H_2O]{(CH_3)_4N^+} H_2 + (CH_3)_4N\text{–}1\text{-}B_9H_9CH \quad (4)$$

If the acidification in eq 1 is accomplished with 12 *M* hydrochloric acid instead of by ion exchange, a mixture of $B_{10}H_{12}CNH_3$ and $B_9H_{11}CNH_3$ is obtained.

$$Na_2B_{10}H_{13}CN \xrightarrow[-H_2]{12\ M\ HCl} B_9H_{11}CNH_3 + B_{10}H_{12}CNH_3 \quad (5)$$

Analyses are given in Table I.

The postulate that $1\text{-}B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ are isostructural with $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, respectively, is supported by their B^{11} nmr spectra. The spectrum of $Cs\text{–}1\text{-}B_9H_9CH$ in acetonitrile consists of three doublets of relative intensities 1:4:4 at −11.8 (J = 152 cps), 37.4 (J = 138 cps), and 43.8 ppm (J = 107 cps), respectively, referred to methyl borate. This is in accord with the spectrum expected for the $B_{10}H_{10}^{2-}$

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(1) W. H. Knoth, *J. Am. Chem. Soc.*, **88**, 935 (1966), and references therein.

(2) Carborane chemistry has recently been reviewed: T. P. Onak, *Advan. Organometal. Chem.*, 3, 263 (1965).

(3) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

(4) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).