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ORGANO-PHOSPHORUS COMPOUNDS—IV
THE PREPARATION OF ISOMERIC TETRA-ALKYLDIPHOSPHINES AND TETRA-ALKYLDIPHOSPHINE MONOSULPHIDES, A NEW CLASS OF PHOSPHORUS COMPOUNDS(1)

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Abstract—Organic substituted diphosphine disulphides are reduced by tributylphosphine, when heated in the ratio 1:2 to give excellent yields of tetra-alkyldiphosphines. In this reaction, tetra-alkyldiphosphine disulphides of the type RR′P(S)–(S)PRR′ yield two isomeric diphosphines, the structure of which has been proved without question by nuclear magnetic resonance (n.m.r.) and chemical reactions. It is believed this to be the first time that such isomerism has been observed with triply connected phosphorus compounds.

If tetra-alkyldiphosphine disulphides are caused to react with tributylphosphine in the ratio 1:1 at elevated temperatures a new class of phosphorus compounds, the tetra-alkyldiphosphine monosulphides are produced. The structures and some of the chemical reactions of these compounds are discussed. A number of new n.m.r. chemical shifts are reported.

Although diphosphine, $H_2P–PH_2$, has been known for a long time, the first organic substituted diphosphine $(C_6H_5)_2P–P(C_6H_5)_2$ originally described in 1888(2) was thoroughly investigated only recently.(3) It was prepared by the following reaction:

$$(C_6H_5)_2PH + ClP(C_6H_5)_2 \rightarrow (C_6H_5)_2P–P(C_6H_5)_2 + HCl \qquad (1)$$

Later Issleib and Seidel(4) extended this method to the preparation of aliphatic diphosphines. Other methods for preparing tetra-alkyldiphosphines involve the reduction of tetra-alkyldiphosphine disulphides. As reducing agents, Zn-dust,(5)† Na,(6) Fe, Cu(7) and most conveniently tertiary phosphines(8a,c) have been used, especially n–tributylphosphine, which is available commercially.

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* On leave of absence during 1960 from Monsanto Research S.A., Zürich.

† We observed that with Zn dust as a desulphurizing agent many by-products are formed, caused probably by a decomposition reaction(8a). This observation was confirmed by H. Nöth,(9). The boiling point of 54·5°C for P, P′–dimethyl-P, P′–diethylphosphine, reported in our preliminary communication,(8a) is erroneous. This is the boiling point of methylethylphosphine $CH_3(C_2H_5)PH$. The correct boiling point of $CH_3(C_2H_5)P–P(C_2H_5)CH_3$ is 188–190°C at normal pressure. We believe that the boiling point of $(n–C_3H_7)_2P–P(C_3H_7–n)_2$ given by Kuchen(5) as 108°C is also wrong. This is probably the boiling point of dipropylphosphine $(n–C_3H_7)_2PH$. The correct boiling point of $(n–C_3H_7)_2P–P(C_3H_7–n)_2$ is 144–145°C/16 mm Hg.(6)

(1) Part 3 of this series L. Maier, *Ber. Dtsch. Chem. Ges.* **94**, 3056 (1961).

(2) C. Dörken, *Ber. Dtsch. Chem. Ges.* **21**, 1509 (1888).

(3) W. Kuchen and H. Buchwald, *Ber. Dtsch. Chem. Ges.* **91**, 2871 (1958).

(4) K. Issleib and W. Seidel, *Ber Dtsch. Chem. Ges.* **92**, 2681 (1959).

(5) W. Kuchen and H. Buchwald, *Angew. Chem.* **71**, 162 (1959).

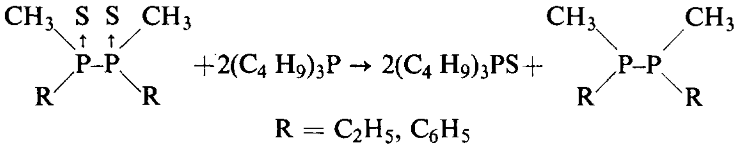
(6) K. Issleib and A. Tzschach, *Ber.* **93**, 1852 (1960).

(7) H. Niebergall, *Angew. Chem.* **72**, 210 (1960).

(8) (a) L. Maier, *Angew. Chem.* **71**, 575 (1959); (b) L. Maier, *Ber. Dtsch. Chem. Ges.* **94**, 3043, (1961); (c) G. W. Parshall, *J. Inorg. Nucl. Chem.* **14**, 291 (1960).

1. *Stereoisomeric organic substituted diphosphine*

The reduction of asymmetric tetraalkyl- or dialkyl-diaryldiphosphine disulphides with tributylphosphine yields asymmetric diphosphines according to Equation (2);



$$(CH_3)(R)P(\rightarrow S)-P(\rightarrow S)(CH_3)(R) + 2(C_4H_9)_3P \rightarrow 2(C_4H_9)_3PS + (CH_3)(R)P-P(CH_3)(R) \qquad (2)$$

$$R = C_2H_5, C_6H_5$$

In investigating the ^{31}P nuclear magnetic resonance (n.m.r.) spectra of diphosphines which are believed to exhibit two different organic groups on each phosphorus, we found two distinct peaks of the same intensity. Fig. 1 gives the n.m.r. spectra of P,P′-dimethyl-P, P′-diphenyldiphosphine and P, P′-dimethyl-P, P′-diethyldiphosphine.

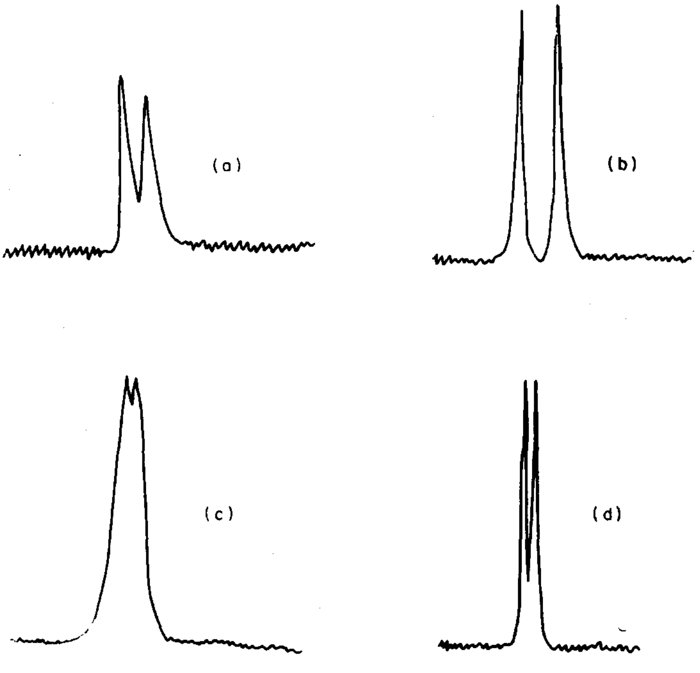
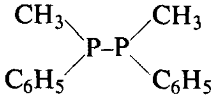
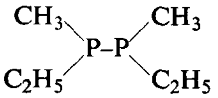


FIG. 1.—a. ^{31}P nuclear magnetic resonance spectrum of



b. same spectrum decoupled

c. ^{31}P nuclear magnetic resonance spectrum of

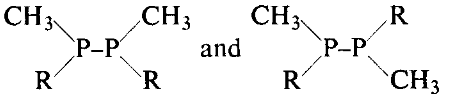


d. same spectrum decoupled

Although two peaks with the same area can be clearly seen (*a*, *c*) in the normal spectra their resolution is not as good as in the spectra *b* and *d* because of the spin–spin splitting of the hydrogens attached to the carbon atoms with the phosphorus. This makes the peaks somewhat broader and not as high as in *b* and *d*.

However, using the spin decoupler to superimpose a radiofrequency so as to decouple the spin–spin splitting of the hydrogens attached to the carbon atoms with the phosphorus, the two peaks become much sharper and higher and the resolution increases (spectra *b*, *d*). The separation of the two peaks changes with the groups attached to the phosphorus atoms. The two peaks in P, P′–dimethyl P, P′–diphenyldiphosphine are separated by 3·5 p.p.m. while in P, P′-dimethyl–P, P′–diethyldiphosphine the separation is 1·5 p.p.m. The existence of two peaks of the same area for these asymmetric diphosphines can be explained on the basis that:

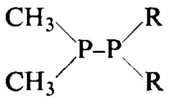
(1) two isomeric forms are present in a 1 : 1 ratio



(I)

R = C_2H_5, C_6H_5 or

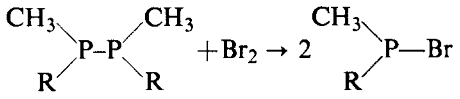
(2) rearrangement occurred to give a structure of the following type:



(II)

Four or more peaks would normally be expected for structure II, although two peaks would be possible for a certain combination of chemical shifts and the P–P coupling constant.

However, structure II could be ruled out since upon going to higher frequencies with the n.m.r. spectrometer (from 16·2 to 24·3 Mc/s) the separation of the two peaks remained the same in p.p.m. If the two peaks were caused by P–P spin splitting, as in structure II, the separation in p.p.m. of the two peaks would have changed. Further evidence for structure I was obtained by cleaving the asymmetric diphosphines with bromine; only one product, a mixed dialkyl- or alkylarylbromophosphine was produced.



(3)

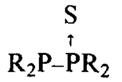
R = C_2H_5, C_6H_5

It is interesting to note that both the meso and the racemic tetra-alkyldiphosphine disulphides(8a,b) gave on reduction with tributylphosphine the asymmetric diphosphines in a 1 : 1 ratio. This means that either the reduction temperature is high enough to effect conversion, or a breakage of the P–P bond is involved to give first a dialkylphosphine radical ($CH_3RP\cdot$), which would then combine with another dialkylphosphine radical in a statistical manner to give a 1 : 1 mixture of the asymmetric diphosphines.

We believe this to be the first time that stereoisomers have been observed with triply connected phosphorus compounds. Separation of the two isomers could not be achieved by distillation.

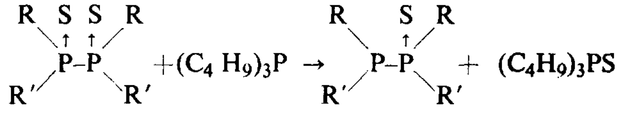
2. *Tetra-alkyldiphosphine monosulphides*

When the tetra-alkyldiphosphine disulphides were made to react with tributylphosphine at 170°C at exactly a 1 : 1 ratio a new class of phosphorus compounds, the tetra-alkyldiphosphine monsulphides



$$R_2P-\overset{\overset{S}{\uparrow}}{P}R_2$$

were obtained in nearly quantitative yield. Only a very small amount of the completely reduced diphosphine disulphide, the tetra-alkyldiphosphine and traces of unreduced diphosphine disulphide were present.



(4)

(III)

R = CH_3, C_2H_5
R′= CH_3, C_2H_5, C_6H_5

The structure of III was proved unequivocably by n.m.r. Since this is an AB type compound, the theory predicts⁽¹⁰⁾ that the spectrum consists of a pair of doublets, the doublet splitting being equal to the spin-coupling constant. Indeed, a spectrum of this kind was obtained. Fig. 2 gives the n.m.r. spectrum of tetramethyldiphosphine monosulphide and dimethyl-diethyldiphosphine monosulphide. The undecoupled spectrum indicated two pairs of peaks, but especially spectrum *c* is not too well resolved because of spin–spin splitting of the hydrogens attached to the carbon atoms with the phosphorus. However, the decoupled spectrum shows clearly that we have two pairs of peaks, whereby the inner peaks (4, 5) being larger in area than the outer peaks (2, 7 b and 1, 7 d). It should be pointed out that the entire spectrum cannot be decoupled at one superimposed frequency. The negative part of the spectrum, attributable to the quadruply connected phosphorus compounds (peak 2–4a or 1–4b) decouples at a different frequency than the positive part of the spectrum assignable to triply connected phosphorus compounds. The spincoupling constant (*J*) (No. of cycles between 2 and 4, 1 and 4, or 5 and 7) was measured as 243 c/s. Knowing *J*, the relative intensities of the four observed peaks can be calculated according to the following equations:

$$C \cdot \sin\theta = \tfrac{1}{2}J \qquad (5)$$

and

$$C = [1/2(\gamma_0\delta)^2+J^2]^{\frac{1}{2}} \qquad (6)$$

This equation solved according to Hamiltonian gives the energies for the transitions⁽¹⁰⁾:

	Energy	*Relative intensity*
$5 \to 2$	$\frac{1}{2}J+C$	$1-\sin\theta$
$7 \to 4$	$-\frac{1}{2}J+C$	$1+\sin\theta$
$4 \to 2$	$\frac{1}{2}J-C$	$1+\sin\theta$
$7 \to 5$	$-\frac{1}{2}J-C$	$1-\sin\theta$

⁽⁹⁾ H. NÖTH, *Z. Naturforsch.* **15 B**, 327 (1960).

⁽¹⁰⁾ J. A. POPLE, W. G. SCHNEIDER and H. J. BERNSTEIN, *High Resolution Nuclear Magnetic Resonance*, p. 119. McGraw Hill, New York (1959).

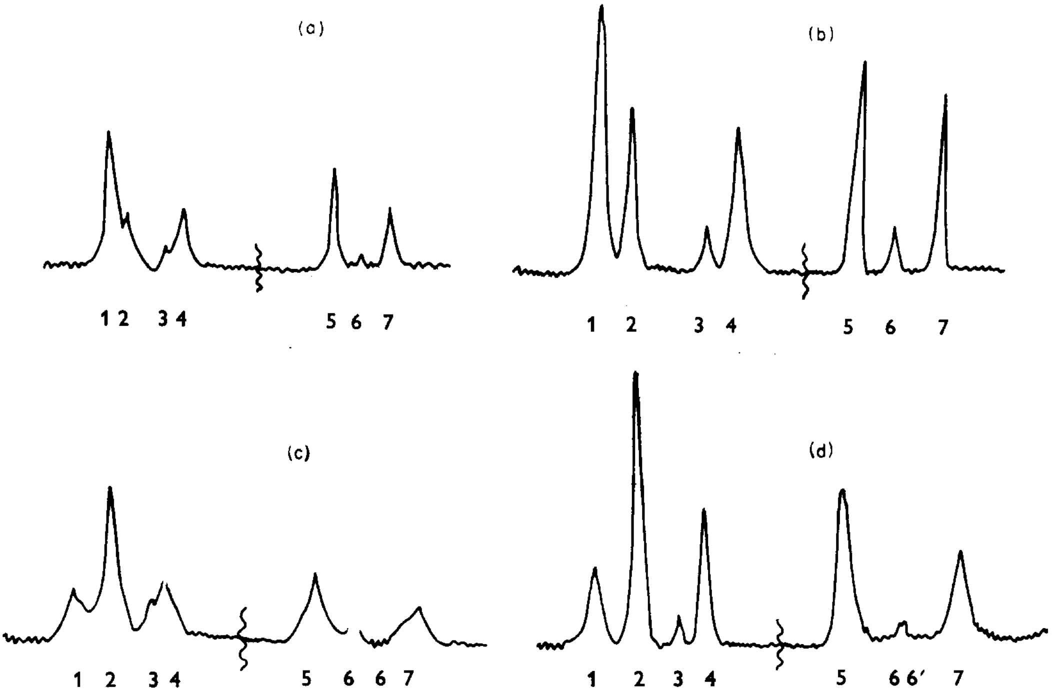
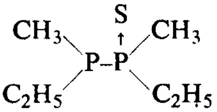


FIG. 2.—a. ^{31}P magnetic resonance spectrum of $(CH_3)_2P{-}\overset{S\uparrow}{P}(CH_3)_2$ (peak 2, 4—5, 7) together with $(C_4H_9)_3PS$ (peak 1), unreduced $[(CH_3)_2PS]_2$ (peak 3) and completely reduced $[(CH_3)_2P]_2$ (peak 6)

b. same spectrum decoupled.

c. ^{31}P magnetic resonance spectrum of

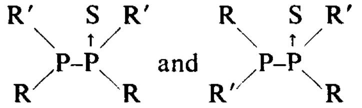


(peak 1, 4—5, 7) together with $(C_4H_9)_3PS$ (peak 2), unreduced $[CH_3(C_2H_5)PS]_2$ (peak 3) and completely reduced $[CH_3C_2H_5P]_2$ (peak 66′).

d. same spectrum decoupled.

Table 1 summarizes the theoretical relative intensities expected for $J = 243$ c/s and $C = 811{\cdot}5$ c/s (C was calculated from the correlation $2C—J = 1380$ c/s whereby $2C—J$ is the distance between the two inner peaks (4 and 5): this gives for sin θ a value of 0·15) with the intensities observed for tetramethyldiphosphine monosulphide and tetraethyldiphosphine monosulphide. The agreement between theory and experiment is excellent.

Provided that, during the preparation, an "umbrella-type" inversion of the molecule occurs at the triply connected phosphorus atom to give:



(IV)

tetra-alkyldiphosphine monosulphides with two different groups on the phosphorus atoms should theoretically give 8 peaks in the m.m.r. with the four inner peaks being larger in area than the four outer peaks. In reality only four peaks (the two

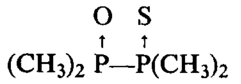
TABLE 1.—THE CALCULATED RELATIVE INTENSITIES FOR J = 243 c/s AND C = 811·5 c/s ARE COMPARED WITH THE INTENSITIES OBSERVED FOR $(CH_3)_2P\text{-}\overset{\overset{S}{\uparrow}}{P}(CH_3)_2$ AND $(C_2H_5)_2P\text{-}\overset{\overset{S}{\uparrow}}{P}(C_2H_5)_2$

Peak	Calc. relative intensities	Observed for $(CH_3)_2P\text{-}\underset{\underset{S}{\downarrow}}{P}\text{-}(CH_3)_2$	$(C_2H_5)_2P\text{-}\underset{\underset{S}{\downarrow}}{P}(C_2H_5)_2$
2	0·85	0·85	0·81
4	1·15	1·17	1·14
5	1·15	1·18	1·13
7	0·85	0·85	0·85
Intensity ratio	1·353	1·37	1·33

inner ones being large) were observed. This might be due to the fact that molecular inversion did not occur (perhaps being prevented by the bulky sulphur atom) or the n.m.r. resolution was not high enough to resolve the eight peaks.

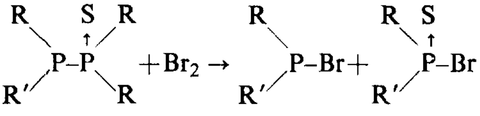
3. *Properties of the tetra-alkyldiphosphine monosulphides*

Tetramethyldiphosphine monosulphide could be distilled without decomposition under reduced pressure. However, because of the closeness of the boiling points no quantitative separation from tributylphosphine sulphide was achieved. The compound ignites in air. Oxidation with O_2 in acetone solution caused destruction of the molecule and no compound of the structure



$$(CH_3)_2\overset{\overset{O}{\uparrow}}{P}\text{—}\overset{\overset{S}{\uparrow}}{P}(CH_3)_2$$

could be identified. However, a chemical proof of the structure was obtained by cleavage of the diphosphine monosulphides with bromine in benzene solution.



(7)

A 1:1 mixture of dialkylbromophosphine and dialkylthiophosphinic bromide was obtained.

EXPERIMENTAL

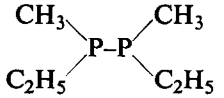
The tetra-alkyldiphosphine disulphides $[(CH_3)_2PS]_2$,(11) $[(C_2H_5)_2PS]_2$,(12) $[CH_3(C_2H_5)PS]_2$ and $[CH_3(C_6H_5)PS]_2$(8a,b) were prepared as described in the literature, and carefully purified by recrystallizing them several times.*

* The main impurities, which are dialkylthiophosphinic acids, $R_2P(S)SH$ and $R_2P(S)OH$, were first removed by treatment with alkaline solution.(12a) It was found in this work that they are reduced by $(C_4H_9)_3P$ to give a secondary phosphine (R_2PH).

(11) (a) M. I. KABACHNIK and E. S. SHEPELEVA, *Izvestia Akad. Nauk* 56 (1949); (b) H. REINHARDT, D. BIANCHI and D. MOLLE, *Ber. Dtsch. Chem. Ges.* **90**, 1657 (1957).

(12) (a) P. J. CHRISTEN, L. M. VAN DER LINDE and F. N. HOOGE, *Rec. Trav. Chim.* **78**, 161 (1959); (b) K. ISSLEIB and A. TZSCHACH, *Ber. Dtsch. Chem. Ges.* **92**, 704 (1959).

1. *Preparation of*

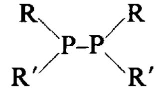


$$(CH_3)(C_2H_5)P\text{–}P(CH_3)(C_2H_5)$$

(V)

A mixture of 12 g of $[CH_3C_2H_5PS]_2$—the high and low melting form[8a, b] gave upon reduction the same 1:1 mixture of stereoisomeric diphosphines—and 23 g of tributylphosphine* was slowly heated in an atmosphere of nitrogen. The mixture became a homogenous liquid at 150°C. Continued heating yielded 8 g of liquid, spontaneously inflammable in air, which on redistillation gave 5·5 g (65·4 per cent.) of clear colourless (V) b.p. 188–190°C at 740 mm Hg. (Found: C, 48·32; H, 11·06. Calc. for $C_6H_{16}P_2$ (150·15): C, 47·99; H, 10·74%). N.m.r. indicated that the reduction of the diphosphine disulphides with tributylphosphine is quantitative. However, due to the high solubility of the tetra-alkyldiphosphines in tributylphosphine sulphide only a 60–70 per cent yield could be obtained by distillation. For n.m.r. investigation mixtures of the diphosphine disulphides and tributylphosphine in the ratio of 1:2·1 (5 per cent excess of $(C_4H_9)_3P$) were sealed under nitrogen in thick-walled Pyrex tubes of 15 mm diameter and heated for 1½–3 hours to 170°C. Heating of the tubes for 20 hr at 170°C did not decompose the tetra-alkyldiphosphines. The tubes were opened under nitrogen and the tetra-alkyldiphosphines were obtained by fractional distillation. Table 2 summarizes the results.

TABLE 2.—BOILING POINTS AND ^{31}P CHEMICAL SHIFTS OF TETRA-ALKYLDIPHOSPHINES



$$RR'P\text{–}PRR'$$

R	R′	b.p. (°C)	Yield (%)	^{31}P chemical shift in p.p.m. relative to 85% H_3PO_4
CH_3	CH_3	38–40/16 mm Hg*	62	+59·5
C_2H_5	C_2H_5	220–3/740 mm Hg†	68	+34·3
CH_3	C_2H_5	188–190/740 mm Hg	65·4	+44·7, +46·2
CH_3	C_6H_5	128–130/0·5 mm Hg‡	70	+38·2, +41·7

* Reported b.p. 140°C.(13)

† Reported b.p. 221–222°C.(4)

‡ m.p. 73–76°C; reported m.p. 75–77°C.(14)

2. *Cleavage of* $[CH_3(C_2H_5)P]_2$ *(V) with bromine*

A solution of 6·9 g of bromine in 20 ml of benzene was slowly added to 6·5 g of V dissolved in 20 ml of benzene. A strong exothermic reaction ensued (excess of bromine has to be avoided, otherwise $CH_3(C_2H_5)PBr_3$ is formed). Fractional distillation of the colourless solution yielded 8·7 g (= 65 per cent.) of $CH_3C_2H_5PBr$, a colourless liquid which fumes heavily in moist air, b.p. 129°C/740 mm Hg, n.m.r. chemical shift—98·5 p.p.m. (reported b.p. 128–129°C/720 mm, chemical shift—98·5 p.p.m.).(15) (Found: C, 23·25; H, 5·20. Calc. for C_3H_8BrP(154·99): C, 23·04; H, 5·47%). In the same way 4·3 g of $[CH_3(C_6H_5)P]_2$ dissolved in 15 ml of benzene with 2·2 g of bromine in 15 ml of benzene gave 4 g (= 61 per cent) of $CH_3C_6H_5PBr$, bp. 65°C/0·5 mm (reported b.p. 215°C/15 mm Hg(16), chemical shift—77 p.p.m.**

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* The tributylphosphine used in these experiments was supplied by Westvaco, Mineral Products Division of F.M.C. Corporation.

** This agreed well with a sample synthesized by an independent method which will be reported in the near future.

(13) A. B. BURG, P. J. SLOTA and W. MAHLER, *Abstracts of Paper presented at 134th meeting of the American Chemical Society*, p. 78 P. September (1958).

(14) J. W. B. REESOR and G. F. WRIGHT, *J. Org. Chem.* **22**, 385 (1957).

(15) H. ULMER, L. C. D. GROENWEGHE, and L. MAIER *J. Inorg. Chem.* **20**, 82 (1961)

(16) G. M. KOSOLAPOFF, *Organophosphorus Compounds*, J. Wiley, New York (1950).

3. *Preparation of* $(CH_3)_2\overset{\overset{S}{\uparrow}}{P}-P(CH_3)_2$ (VI)

A mixture of 11·5 g of tributylphosphine and 10·5 g of tetramethyldiphosphine disulphide was sealed under nitrogen in a thick-walled Pyrex tube and heated for 20 hr to 170°C (n.m.r. analysis after 3 hr heating indicated that the reduction was not complete after this period). Then the tube was opened under nitrogen and the content fractionally distilled under reduced pressure. A fraction boiling at 65–70°C/0·5 mm contained mostly VI (90 per cent.) but also 10 per cent. of $(C_4H_9)_3PS$ as analyzed by n.m.r. The compound ignites in air and solidifies at room temperature. Other tetra-alkyldiphosphine monosulphides were synthesized similarly and analysed by n.m.r. The results are summarized in Table 3.

TABLE 3.—^{31}P CHEMICAL SHIFT OF TETRA-ALKYLDIPHONPHINE MONOSULPHIDES $RR'P-\overset{\overset{S}{\uparrow}}{P}RR'$

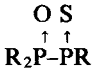
R	R′	^{31}P chemical shift in p.p.m. relative to 85% H_3PO_4*	
CH_3	CH_3	—43·9, —30·3	+54·7, +69·5
C_2H_5	C_2H_5	—62·8, —47·8	+29·5, +44·6
CH_3	C_2H_5	—53·9, —40·2	+40·9, +55·8
CH_3	C_6H_5	—43·7, —33·9	+37·5, +47·4

* The negative shift is due to the quadruply connected phosphorus atom and the positive shift to the triply connected phosphorus atom.

Through careful fractionation P, P'-dimethyl-P, P′-diethyldiphosphine-monosulphide $[CH_3(C_2H_5)\overset{\overset{S}{\uparrow}}{P}-P(C_2H_5)CH_3]$ was obtained in a pure state, b.p. 85–86°C/0·025 mm and analysed. (Found: C, 39·21; H, 8·79; S, 17·74. Calc. for $C_6H_{16}P_2S$(181·2): C, 39·76; H, 8·90; S, 18·11%).

4. *Oxidation of VI with oxygen*

Oxygen was bubbled through a solution of 1 g of VI dissolved in 5 ml of acetone. An extremely exothermic reaction occured. Acetone came to reflux. N.m.r. analysis of the crude product in acetone solution gave nine peaks all on the negative side. The two peaks on the positive side had disappeared. Since for a compound of the structure



$$R_2\overset{\overset{O}{\uparrow}}{P}-\overset{\overset{S}{\uparrow}}{P}R_2$$

only four peaks on the negative side would be expected, the P–P bond was probably oxidized to give a P–O–P bond which hydrolysed partly with trace amounts of water to give phosphinic and monothiophosphinic acid. No isolation of the species was attempted.

5. *Cleavage of* $R_2\overset{\overset{S}{\uparrow}}{P}-PR_2$ *with bromine*

(a) *Cleavage of* $CH_3(C_2H_5)P-\overset{\overset{S}{\uparrow}}{P}(C_2H_5)CH_3$ (VII) *with bromine.* To a solution of 0·9 g of VII in 1 ml of benzene was added 0·7 g of bromine in 1 ml of benzene. An exothermic reaction occurred. N.m.r. analysis showed two peaks of the same area, one at —98·5 p.p.m. ($CH_3C_2H_5PBr$ see experiment 2 and Reference 15) and one at —85 p.p.m.($CH_3C_2H_5P(S)Br$.) The latter compound was also obtained when $[CH_3(C_2H_5)PS]_2$ was cleaved with bromine;(8a) the chemical shift was the same.

(b) *Cleavage of* $(C_2H_5)_2P\text{–}\overset{\overset{S}{\uparrow}}{P}(C_2H_5)_2$ (VIII) *with bromine.* To 0·72 g of VIII in 1 ml of C_6H_6 was added 0·63 g of bromine in 1 ml of benzene. Diethylbromopshophine, $(C_2H_5)_2PBr$, chemical shift —117 p.p.m. (and diethylthiophosphinic bromide (chemical shift—96 p.p.m.), this compound was also obtained when $[(C_2H_5)_2PS]_2$ was cleaved with bromine;(5) the chemical shift was the same) were produced in a 1:1 ratio.

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