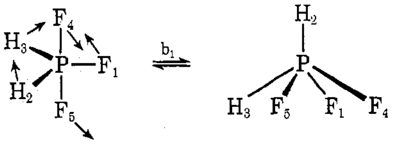
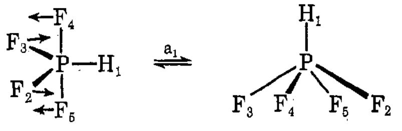

I II

gesting that intramolecular ligand exchange indicated by nmr data proceeds *via* the Berry process.[14,22]


III IV

Finally, the normal mode descriptions for HPF_4 and H_2PF_3 are compared with those for CH_3PF_4 in Table IV. The initial frequency assignments by Downs and Schmutzler[7] for CH_3PF_4 have been altered in Table IV. In line with the potential field refinement[23] resulting from electron diffraction work on more symmetric trigonal bipyramids including CH_3PF_4, a lower frequency associated with an equatorial relative to an axial bending mode is suggested. Consequently, assignments of the corresponding modes for both the a_1 and b_1 species of CH_3PF_4 have been interchanged compared to the original[23] mode designations. On this basis, the tabulated frequencies compare favorably between HPF_4 and CH_3PF_4. The effect of the introduction of the proton relative to the methyl group is seen as an increase in frequency of the equatorial in-plane and equatorial out-of-plane bend of b_1 and b_2 species, respectively.

Relative to HPF_4, both the equatorial and axial PF stretches of a_1 species of H_2PF_3 are at a considerably higher frequency and suggests a mode description for H_2PF_3 containing a greater degree of mixing with the PH stretching coordinate of the same species. The latter seems reasonable for the more highly protonated fluoride. A comparison of frequency assignments for related molecules has been given elsewhere.[24]

Acknowledgment.—Grateful appreciation is expressed for support of this work by a grant from the National Science Foundation. We also wish to thank Dr. Robert Larkin for assistance in obtaining the laser Raman spectra.

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(22) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(23) (a) L. S. Bartell, *Inorg. Chem.*, **9**, 1594 (1970); (b) R. R. Holmes and J. A. Golen, *ibid.*, **9**, 1596 (1970).

(24) R. R. Holmes and M. Fild, *J. Chem. Phys.*, **53**, 4161 (1970).

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Synthesis of the Two Isomeric *N*-Methyl-1,2,4,6,3,5-thia(VI)triazadiphosphorines

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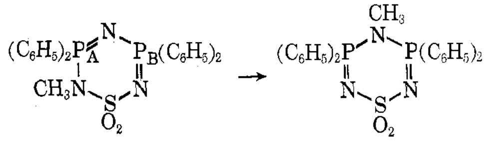
The two isomers corresponding to a methyl group being positioned at the N′ and N″ atoms in the cyclic molecule $S(O_2)N'P(C_6H_5)_2N''P(C_6H_5)_2N$ have been prepared by ring-closure reactions. The compound having the methyl group on the N′ was obtained from iminobis(chlorodiphenylphosphonium) chloride and *N,N′*-dimethylsulfamide or by metathesis from iminobis(methylaminodiphenylphosphonium) chloride and sulfuryl chloride. The other compound, with the methyl group on the N″, was synthesized from bis(chlorodiphenylphosphazo) sulfone and heptamethyldisilazane. ^1H and ^{31}P nmr spectra as well as ir spectra are utilized as structure proofs.

Introduction

Several six-membered ring systems, containing phosphorus, nitrogen, and sulfur are known.[2,3] Since only a few compounds with an endocyclic sequence S–N–P–N–P–N have been prepared,[4–7] the possibility of obtaining isomers of the forms I and II by specific ring-closure reactions seemed worthy of attention and constitutes the scope of the present work.


I II

Experimental Section

Materials.—All solvents used were Spectrograde quality and practically water free. Sulfamide (Alfa) was used as received. Practical grade sulfuryl chloride was redistilled before use and the fraction boiling at 69–70° (757 Torr) retained. Methylamine (Matheson) was dried by passage over KOH pellets. The other starting compounds, *i.e.*, *N,N′*-dimethylsulfamide,[8] iminobis(chlorodiphenylphosphonium) chloride,[9] $[(C_6H_5)_2PCl]_2N^+Cl^-$ (III), and heptamethyldisilazane[10] were prepared according to the literature. Diphenyltrichlorophosphorane is best prepared as given below.

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(1) Postdoctoral Research Fellow, 1970–1972.

(2) S. Pantel and M. Becke-Goehring, "Sechs- und achtgliedrige Ringsysteme in der Phosphor-Stickstoff-Chemie," Springer-Verlag, Berlin, Heidelberg, New York, 1969, p 259 ff.

(3) I. Haiduc, "The Chemistry of Inorganic Ring Systems," Vol. II, Wiley-Interscience, London, New York, Sydney, Toronto, 1970, p 813 ff.

(4) M. Becke-Goehring, K. Bayer, and T. Mann, *Z. Anorg. Allg. Chem.*, **346**, 143 (1966).

(5) R. Appel, D. Hännsgen, and B. Ross, *Z. Naturforsch. B*, **22**, 1354 (1967).

(6) U. Bieller and M. Becke-Goehring, *Z. Anorg. Allg. Chem.*, **380**, 314 (1971).

(7) U. Klingebiel and O. Glemser, *Chem. Ber.*, **104**, 3804 (1971).

(8) M. Bermann and J. R. Van Wazer, submitted for publication in *Synthesis*.

(9) E. Fluck and F. L. Goldmann, *Chem. Ber.*, **96**, 3091 (1963).

(10) R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, **5**, 58 (1957).

Analyses.—Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained on a Mel-Temp melting-point block and are uncorrected.

Spectra.—Infrared (ir) spectra were recorded on KBr pellets (0.5%) with a Beckman IR-10 spectrometer. ^1H nuclear magnetic resonance (nmr) spectra were obtaind with a Varian A-60 spectrometer in $CDCl_3$ solutions with TMS as internal standard. The ^{31}P nmr spectra were run with a Varian XL-100-15 spectrometer, operating at a frequency of 40.55 MHz and locked onto the deuterium resonance of D_2O. The samples were contained in 12-mm o.d. tubes into which was concentrically inserted, using Teflon spacers, a 5-mm o.d. tube containing the D_2O. ^{31}P spectra were decoupled from the protons and chemical shifts are reported *vs.* external 85% H_3PO_4.

Preparation of $(C_6H_5)_2PCl_3$.—In a 1-l., three-necked flask (equipped with a paddle stirrer, a condenser with $CaCl_2$ tube, and a gas-inlet tube), which was previously flushed with dry nitrogen, was placed 55.0 g of $(C_6H_5)_2PCl$ in 40 ml of carbon tetrachloride. Dry chlorine was passed over the cooled solution (*ca.* 0°) and a white precipitate of $(C_6H_5)_2PCl_3$ was formed immediately. Chlorine was passed over the solution until the precipitate turned slightly yellow (due to excess chlorine which cannot be removed later). A few milliliters of $(C_6H_5)_2PCl$ was added until discoloration was achieved and the extremely hygroscopic $(C_6H_5)_2PCl_3$ was filtered (in a glove box) and dried *in vacuo*. The yield is practically quantitative and the product is pure, white crystals, mp (capillary) 194–197° dec (lit.[11] mp 194–200°).

Preparation of Iminobis(methylaminodiphenylphosphonium) Chloride, $[(C_6H_5)_2P(NHCH_3)]_2N^+Cl^-$ (IV).—With exclusion of moisture, 9.2 g of III was added to *ca.* 120 ml of liquid methylamine (exothermic reaction) and the excess of methylamine was removed from the clear solution by warming to room temperature. The resulting white, nonhygroscopic solid was finely ground and extracted with 100 ml of methylene chloride. Filtration afforded 2.47 g of CH_3NH_3Cl (96.2% of theory); concentration of the solution to *ca.* 40 ml gave upon cooling 7.35 g (81.5% of theory) of IV, pure white crystals, mp 213–214° dec.

Anal. Calcd for $C_{26}H_{28}ClN_3P_2$: C, 65.09; H, 5.85; Cl, 7.39; N, 8.76; P, 12.91. Found: C, 64.16; H, 5.51; Cl, 7.74; N, 8.49; P, 12.97.

Ir 3020–3000 (vs), 2900 (m), 2860 (m), 2770 (s), 1580 (w), 1470 (m), 1420 (s), 1410 (m), 1285 (s), 1270 (s), 1210 (vs), 1150 (s), 1090 (vs), 1060 (vs), 1005 (m), 975 (s), 905 (w), 870 (s), 820 (m), 735 (s), 700 (vs), 660 (vs), 605 (w), 530 (vs), 510 (s), 480 (vs) cm^{-1}.

Nmr (proton spectrum) $\tau_{C_6H_5}$ 1.99, 2.15, 2.47 (complex multiplet), τ_{NH} ~3.25 (broad signal), τ_{CH_3} 7.67 (d, d), $J_{PNCH_3} = 15.7$ Hz, $J_{NHCH_3} = 5.5$ Hz; (phosphorus spectrum) δ_P −20.4 ppm (in CH_3OH) (lit.[12] −20.9 ppm).

Preparation of Bis(chlorodiphenylphosphazo) Sulfone, $SO_2(N{=}P(C_6H_5)_2Cl)_2$ (V).—The quantities of 43.28 g of $(C_6H_5)_2PCl_3$ and 7.12 g of $SO_2(NH_2)_2$ were suspended in 300 ml of 1,2-dichloroethane and slowly heated with stirring. A clear solution was formed at *ca.* 50° and HCl was evolved at reflux temperature. Refluxing for 3 hr and stripping off the solvent yielded a yellowish, heavy oil which could not be made to crystallize. The yield is quantitative.

Anal. Calcd for $C_{24}H_{20}Cl_2N_2O_2P_2S$: C, 54.05; H, 3.78; Cl, 13.29; N, 5.25; P, 11.61; S, 6.01; O, 6.00. Found: C, 54.68; H, 3.88; Cl, 13.16; N, 5.35; P, 10.81; S, 6.11; O, 6.01 (by difference).

Nmr δ_P −41.8 ppm (in C_6H_6).

Preparation of 1,1-Dioxo-2-methyl-3,3,5,5-tetraphenyl-1,2,4,-6,3,5-thiatriazadiphosphorine (I). A. From III and *N,N'*-Dimethylsulfamide.—An amount of 23.4 g of III was dissolved in 150 ml of chloroform containing 23 ml of triethylamine; then 5.91 g of *N,N'*-dimethylsulfamide was added and refluxed with stirring for 3 hr. The solvent was stripped from the dark-brown solution and the resulting heterogeneous precipitate extracted three times with 200 ml of boiling benzene. Removing of the solvent from the combined, filtered solution yielded a foamy mass. Addition of 40 ml of acetonitrile afforded, upon standing in the refrigerator, white crystals of I, yield 16.2 g (69% of theory), mp 160–161° dec.

Anal. Calcd for $C_{25}H_{23}N_3O_2P_2S$: C, 61.09; H, 4.72; N, 8.55; P, 12.60; S, 6.52; O, 6.51. Found: C, 61.38; H, 5.20; N, 8.78; P, 12.53; S, 6.41; O, 5.70 (by difference).

Ir 3060 (w), 1590 (w), 1485 (m), 1440 (s), 1290 (vs), 1230–1210 (vs, b), 1150 (vs), 1120 (vs), 1030 (m), 995 (m), 930 (w), 855 (vs), 805 (s), 770 (s), 750 (s), 730 (vs), 690 (vs), 630 (s), 605 (m), 545 (vs), 530 (vs), 510 (vs) cm^{-1}.

Nmr (proton spectrum) $\tau_{C_6H_5}$ 2.32, 2.42, 2.65 (complex multiplet), τ_{CH_3} 7.08 (d), $J_{P_ACH_3} = 10.0$ Hz; (phosphorus spectrum) (proton decoupled, in CH_2Cl_2) δ_{P_A} −22.2 ppm (d), δ_{P_B} −34.8 ppm (d), $J_{P_AP_B} = 6.2$ Hz, ratio $P_A{:}P_B = 1{:}1$ (theoretical value 1:1).

B. From IV and SO_2Cl_2.—An amount of 5.6 g of IV was dissolved in 100 ml of chloroform containing 4 ml of triethylamine and a solution of 1.76 g of SO_2Cl_2 in 20 ml of $CHCl_3$ was added dropwise over a period of 10 min (exothermic reaction). Refluxing for 3 hr and working-up, as under A, gave 3.1 g (54.1% of theory) of I, which is identical in melting point, mixture melting point, and nmr spectra to the compound obtained above.

Preparation of 1,1-Dioxo-4-methyl-3,3,5,5-tetraphenyl-1,2,4,-6,3,5-thiatriazadiphosphorine (II).—In a 1-l., three-necked, round-bottomed flask equipped with a double-jacket condenser with a long $CaCl_2$ tube, a thermometer, magnetic stirrer, and a dropping funnel was placed 32.6 g of $SO_2(N{=}P(C_6H_5)_2Cl)_2$ (V) in 250 ml of benzene. The solution was warmed to 35° under stirring and a solution of 10.83 g of heptamethyldisilazane in 50 ml of benzene was added dropwise over a period of 30 min so that the temperature of the system did not rise over 45°. A small amount of a white precipitate was formed which redissolved. Vacuum (*ca.* 50 Torr) was applied with a suction pump through the $CaCl_2$ tube and the mixture was held for 2 hr under gentle reflux (temperature between 25 and 30°). After this period of time, only trace amounts of $(CH_3)_3SiCl$ were detected by gas chromatography. The yellow solution was decanted from the decomposition products and/or by-products (*ca.* 2 g) and the solvent was stripped off to yield 27.25 g (92% of theory) of a heavy oil, or sometimes a foamy mass, or a mixture of both. This crude product was taken up in 70 ml of benzene and the resulting solution was added dropwise to an intensely stirred excess of ether (500 ml). The off-white precipitate was filtered and dried *in vacuo* at room temperature, yield 19.9 g (66.2% of theory), dec pt *ca.* 75°.

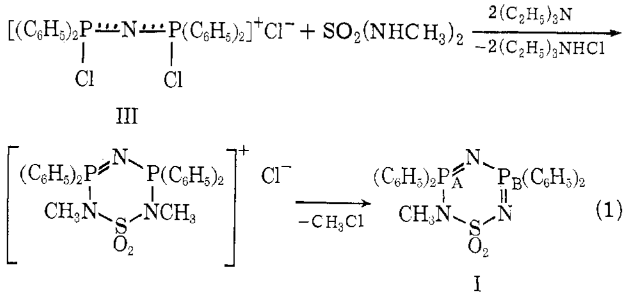
Anal. Calcd for $C_{25}H_{23}N_3O_2P_2S$: C, 61.09; H, 4.72; N, 8.55; P, 12.60; S, 6.52; O, 6.51. Found: C, 61.45; H, 5.05; N, 8.16; P, 12.75; S, 6.29; O, 6.30 (by difference).

Ir 3060 (m), 1590 (m), 1485 (m), 1440 (s), 1260–1150 (vs, b), 1000 (s), 855 (vs, b), 750 (s, sh), 730 (s), 690 (vs), 540–510 (vs, b) cm^{-1}.

Nmr (proton spectrum) $\tau_{C_6H_5}$ 2.18, 2.32, 2.67 (complex multiplet), τ_{CH_3} 8.81 (t), $J_{PCH_3} = 6.8$ Hz; (phosphorus spectrum) δ_P −28.6 ppm (in $CHCl_3$), −28.2 ppm (in CH_2Cl_2).

Results and Discussion

The formation of 1,1-dioxo-2-methyl-3,3,5,5-tetraphenyl-1,2,4,6,3,5-thiatriazadiphosphorine (I) by a specific ring-closure reaction according to eq 1 proceeds rather smoothly and the ionic intermediate is not isolated. Evidence for I is given by nmr spectroscopy. The ^1H nmr spectrum of the methyl group shows a doublet ($J_{P_ACH_3} = 10$ Hz); and decoupling all the hydrogens while observing the ^{31}P nmr spectrum shows *two* nonequivalent tetracoordinate phosphorus atoms P_A and P_B to be present, with a coupling constant $J_{P_AP_B} = 6.2$ Hz. The assignment of the chem-



III

I

(1)

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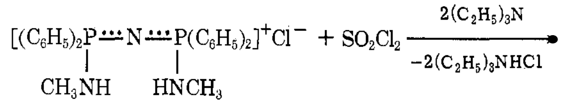
[11] D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **3**, 428 (1964).

[12] A. Schmidpeter and H. Brecht, *Angew. Chem.*, **79**, 946 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 945 (1967).

ical shifts of P_A and P_B has been made as follows: the chemical shift of compound III is δ_P -43.3 ppm[13,14] and of compound IV is δ_P -20.4 ppm. As the electronic environment of P_A is virtually not changed by passing from IV to I, the observed change in chemical shift by this ring closure should be small and $\Delta\delta_{P_A}$ is found to be only 1.8 ppm. The change for P_B [$\Delta\delta_{P_B} = 7.5$ ppm for III → I and $\Delta\delta_{P_B} = 14.4$ ppm for IV → I] is larger, a finding which we attribute to increased $p_\pi \rightarrow d_\pi$ bonding of P_B with N(4) and N(6). Moreover, these arguments show that the methyl group is fixed to one of the two nitrogen atoms adjacent to the sulfur (either N(2) or N(6)), with no positional exchange of the CH_3 group with respect to the P_A and P_B atoms on the nmr time scale at normal room temperature. If there were positional exchange of the CH_3 group between N(2) and N(6), only *one* signal for P_A and P_B should be observable. Furthermore, evidence that the N–P_ANP_BN portion of the ring is planar or that configurations due to ring puckering[15] undergo rapid transformation may be adduced from the fact that no geometrical isomers were detected from the nmr spectra.

The infrared spectrum of I shows the phenyl bands at 3060 cm^{-1} ($\nu_{C_6H_5}$), at 1590 and 1485 cm^{-1} ($\delta_{C_6H_5}$(asym and sym)), and at 770 and 690 cm^{-1} (rocking vibrations). The band at 995 cm^{-1} is assigned to the P–C (phenyl) group; the CH_3 deformation vibration occurs at 1440 cm^{-1}. The characteristic sharp P═N bands are found at 1230–1210 and 1120 cm^{-1} and ν_{P-N} is at 855 cm^{-1}. The ν_{SO_2}(asym) band at 1290 cm^{-1} and the ν_{SO_2}(sym) band at 1150 cm^{-1} are clearly observable (in contrast to II) and the assignment can be made by comparison with the corresponding modes in *N,N'*-dimethylsulfamide;[8] similarly the SO_2 bending mode may be ascribed to the band at 545 cm^{-1}.

The metathetic reaction (eq 2) for compound I is presumed to follow the same pattern.



$$[(C_6H_5)_2\underset{CH_3NH}{P}\cdots N\cdots \underset{HNCH_3}{P}(C_6H_5)_2]^+Cl^- + SO_2Cl_2 \xrightarrow[-2(C_2H_5)_3NHCl]{2(C_2H_5)_3N}$$

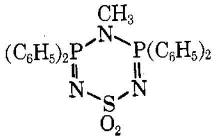
IV

$$I + CH_3Cl \quad (2)$$

1,1-Dioxo-4-methyl-3,3,5,5-tetraphenyl-1,2,4,6,3,5-thiatriazadiphosphorine (II) is obtained according to eq 3, in analogy to similar ring-closure reactions.[4,6,7]

$$SO_2(N{=}P(C_6H_5)_2Cl)_2 + CH_3N(Si(CH_3)_3)_2 \longrightarrow$$

V



$$+2CH_3SiCl \quad (3)$$

II

Evidence for this compound is provided by the triplet of the CH_3 group in the ^1H nmr spectrum (coupling with two identical phosphorus atoms). Clearly only one ^{31}P nmr signal is obtained. Ring formation is indicated by the pronounced change of the phosphorus chemical shift (from -41.8 to -28.6 ppm), as well as by the shift of the CH_3 group signal from τ 7.70 for the three-membered chain $CH_3N[P(C_6H_5)_2]_2$[16] to τ 8.81 for II. The coupling constant ($J_{PNCH_3} = 7.0$ Hz) is significantly lower than that found for somewhat similar ring systems[7,17,18] containing a N═P—N(CH_3)—P═N sequence, where it is *ca.* 14 Hz. These data suggest small (if any) $p_\pi \rightarrow d_\pi$ delocalization for P—N (CH_3), along with strong $p_\pi \rightarrow d_\pi$ bonding for P(3)–N(2) and P(4)–N(5). This postulation infers that there may be virtually no cyclic π system in II in contrast to a rather delocalized π system in I.

As expected, the infrared spectrum of II is simpler than that of I. The different vibration modes for the C_6H_5 and CH_3 groups are found at the same wave numbers as for I, as is ν_{P-N} at 855 cm^{-1}. The prominent absorptions at 1260–1150 and 540–510 cm^{-1} contain the SO_2 and P═N vibrations which we did not separate. This finding is in accord with earlier work[19] on spectra containing $-SO_2N{=}P<$ groups and it emphasizes the ideas outlined above concerning localized strong $p_\pi \rightarrow d_\pi$ bonding for P═N in II.

Acknowledgments.—We thank the National Science Foundation (GP-28698X) for partial financial support of this work and Dr. A. D. F. Toy of the Stauffer Chemical Co. for a generous gift of diphenylphosphinous chloride.

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(13) E. Fluck, *Z. Naturforsch. B*, **20**, 505 (1966).

(14) A. Schmidpeter and H. Groeger, *Chem. Ber.*, **100**, 3979 (1967).

(15) A chair or boat configuration seems unlikely, since the structure determination of a NPNPN unit in $[(C_6H_5)_2P(NH_2)]_2N^+Cl^-$ [J. W. Cox and E. R. Corey, *Chem. Commun.*, 205 (1969)] shows planarity, as do transition metal complexes with this sequence as a ligand [M. R. Churchill, J. Cooke, J. Wormald, A. Davison, and E. S. Switkes, *J. Amer. Chem. Soc.*, **91**, 6518 (1969); A. Davison and E. S. Switkes, *Inorg. Chem.*, **10**, 837 (1971)]. However, a configuration in which the sulfur lies out of the NPNPN plane may perhaps be found.

(16) D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, **4**, 1222 (1965).

(17) A. Schmidpeter and R. Böhm, *Z. Anorg. Allg. Chem.*, **362**, 65 (1968).

(18) W. Lehr, *ibid.*, **371**, 225 (1969).

(19) W. Wiegräbe and H. Bock, *Chem. Ber.*, **101**, 1414 (1968), and quotations therein.