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# AMBIDENT NUCLEOPHILES

## I. REACTION OF SODIUM DIISOPROPYLPHOSPHOROTHIOATE WITH SOME HALIDES OF GROUP IV

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## Summary

The ambident nucleophile diisopropylphosphorothioate, $(Me_2CHO)_2POS^-$ reacts with halides of silicon, germanium and tin to yield *O*-bonded derivatives $(Me_2CHO)_2P(S)OMR_3$ (M = Si, Ge, Sn; R = Me, Ph). These findings are discussed in terms of the energetics of the isomerisation:

$(Me_2CHO)_2P(S)OMR_3 \rightarrow (Me_2CHO)_2P(O)SMR_3$.

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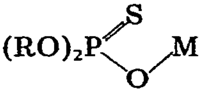
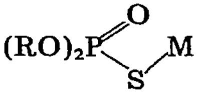
## Introduction

Dialkylphosphorothioate anions $(RO)_2PSO^-$ are ambident nucleophiles, and can react with halides to yield either *O*-bonded (I) or *S*-bonded (II) products:



(I)



(II)

Thus with haloalkanes, *S*-alkylation occurs [1,2], while with acyl halides, *O*-acyl products result [3]; methyl chloroformate gives a mixture of products resulting from both *O*- and *S*-substitution [4]. Reaction of *O,O*-diethylphosphorothioate with phosgene yields carbonyl sulphide and *O,O*-diethylphosphorochloridate, $(EtO)_2P(O)Cl$ but there is uncertainty whether this reaction involves initial *O*- or *S*-substitution; mechanisms for both pathways have been proposed [2,4].

Attack at centres other than carbon may also give products which are either *O*-bonded or *S*-bonded: thus reaction of the diethylphosphorothioate ion with either $(EtO)_2P(O)Cl$ [5-7] or $(CH_3C_6H_4)_2P(S)Cl$ [8] gives the *O*-bonded isomer $(EtO)_2P(S)OP(X)R_2$. Reaction with sulphenyl chlorides R′SCl, on the other hand,

TABLE 1

DIAGNOSTIC INFRA-RED FREQUENCIES ($cm^{-1}$)

| | $\nu$(P—OC) | $\nu$(P—OM) | $\nu$(P=S) |
|---|---|---|---|
| $(Me_2CHO)_2POSSiMe_3$ | 1100 | 985 | 770 |
| $(Me_2CHO)_2POSSiPh_3$ | 1120 | 1000-970 | 840 |
| $(Me_2CHO)_2POSGePh_3$ | 1100 | 990 | 795 |
| $(Me_2CHO)_2POSSnMe_3$ | 1100 | 985 | 770 |
| $(Me_2CHO)_2POSSnPh_3$ | 1075 | 980 | 770 |

yields the *S*-bonded species $(RO)_2P(O)SSR'$ [9].

Apart from the reaction with sulphenyl halides there appears to be no report of the reactions of dialkylphosphorothioate anions at centres other than carbon or phosphorus. The reactions of such an anion towards some halides of Group IV are now reported.

## Results

Sodium diisopropylphosphorothioate, $(Me_2CHO)_2POS^- Na^+$, reacts with trialkyl- and triaryl-halides of silicon, germanium and tin to give good yields of products $(Me_2CHO)_2POSMR_3$ (M = Si, Ge or Sn; R = $CH_3$ or $C_6H_5$). The products have been characterised by analysis, and by their infrared, NMR, and mass spectra; the spectroscopic evidence allows a distinction to be made between the possible isomeric forms of the products.

### *Infrared spectra*

*O*-bonded isomers are expected [4] to exhibit in their infrared spectra, bonds assignable to $\nu$(P=S) around 800 and to $\nu$(P—OM) around 1000 $cm^{-1}$, while the spectra of *S*-bonded isomers will contain bonds assignable to $\nu$(P=O) around 1250 and to $\nu$(P—SM) around 590 $cm^{-1}$. None of the products here obtained showed an infrared band which could be assigned to $\nu$(P=O); such a band is prominent in the spectra of both $(Me_2CHO)_2P(O)N(CH_2C_6H_5)SiPh_3$ and $(Me_2CHO)_2P(O)N(CH_2C_6H_5)SnPh_3$ [10], and consequently we believe that its absence in the spectra of the phosphorothioate derivatives is real and not due merely to accidental low intensity. The observed $\nu$(P—OC), $\nu$(P—OM) and $\nu$(P=S) frequencies are recorded in Table 1. The lack of any $\nu$(P=O) absorptions and the observation of $\nu$(P=S) in each case is consistent with each compound's having the *O*-bonded structure.

### *Mass spectra*

The mass spectra of all the compounds described here contained molecular ions. Common features of all the spectra were ions at *m/e* values of 59, 41 and 39, assignable to $Me_2CHO^+$ and its breakdown products $C_3H_5^+$ (allyl) and $C_3H_3^+$ (cyclopropylium). In addition, all the spectra contained a prominent pair of ions at *m/e* 115 and 114; since these are absent from the spectra of $(Me_2CHO)_2P(O)H$ and $(Me_2CHO)_2P(O)N(CH_2C_6H_5)MPh_3$ (M = Si or Sn) [10], we assign them to $H_4PO_3S^+$ and $H_3PO_3S^+$.

The principal features of the mass spectra of the compounds described here, together with that of diisopropyl hydrogen phosphite, are presented in

TABLE 2

MASS SPECTRA

| m/e | Intensity | Assignment | m/e | Intensity | Assignment |
|---|---|---|---|---|---|
| *$(Me_2CHO)_2POH$* | | | *$Me_3SiOSP(OCHMe_2)_2$* | | |
| 166 | 3 | $(Me_2CHO)_2POH^+$ | 270 | 4 | $Me_3SiOSP(OCHMe_2)_2^+$ |
| 150 | 12 | $(Me_2CHO)_2PH^+$ | 211 | 2 | $Me_3SiOSPOCHMe_2^+$ |
| 108 | 82 | $(Me_2CHO)POH_2^+$ | 171 | 18 | |
| 82 | 100 | $H_3PO_3^+$ | 115 | 41 | $H_4PO_3S^+$ |
| 59 | 35 | $Me_2CHO^+$ | 114 | 40 | $H_3PO_3S^+$ |
| 41 | 29 | $C_3H_5^+$ | 83 | 29 | $H_4PO_3^+$ |
| 39 | 18 | $C_3H_3^+$ | 82 | 29 | $H_3PO_3^+$ |
| | | | 59 | 16 | $Me_2CHO^+$ |
| | | | 41 | 100 | $C_3H_5^+$ |
| | | | 39 | 64 | $C_3H_3^+$ |
| *$Me_3SnOSP(OCHMe_2)_2$*[a] | | | *$Ph_3SiOSP(OCHMe_2)_2$* | | |
| 362 | 3 | $Me_3{}^{120}SnOSP(OCHMe_2)_2^+$ | 456 | 2 | $Ph_3SiOSP(OCHMe_2)_2^+$ |
| 347 | 7 | $Me_2{}^{120}SnOSP(OCHMe_2)_2^+$ | 379 | 7 | $Ph_2SiOSP(OCHMe_2)_2^+$ |
| 305 | 10 | $Me_2{}^{120}SnOSPOH(OCHMe_2)^+$ | 276 | 80 | $Ph_3SiOH^+$ |
| 277 | 27 | $Me_3{}^{120}SnOSPO_2H^+$ | 200 | 32 | $H_3OSP(OCHMe_2)_2^+$ |
| 263 | 68 | $Me_2{}^{120}SnOSPO_2H_2^+$ | 199 | 100 | $H_2OSP(OCHMe_2)_2^+$ |
| 245 | 22 | $Me_2{}^{120}SnOSPO^+$ | 181 | 12 | $SP(OCHMe_2)_2^+$ |
| 229 | 19 | $Me_2{}^{120}SnOSP^+$ | 122 | 58 | $SPOCHMe_2^+$ |
| 199 | 18 | ${}^{120}SnOSP^+$ | | | $PhSiOH^+$ |
| 183 | 26 | ${}^{120}SnSP^+$ | 115 | 16 | $H_4PO_3S^+$ |
| 165 | 22 | $Me_3{}^{120}Sn^+$ | 114 | 10 | $H_3PO_3S^+$ |
| 150 | 28 | $Me_2{}^{120}Sn^+$ | 77 | 30 | $Ph^+$ |
| 135 | 40 | $Me^{120}Sn^+$ | 59 | 28 | $Me_2CHO^+$ |
| 120 | 21 | ${}^{120}Sn^+$ | 41 | 44 | $C_3H_5^+$ |
| 115 | 28 | $H_4PO_3S^+$ | 39 | 23 | $C_3H_3^+$ |
| 114 | 32 | $H_3PO_3S^+$ | | | |
| 59 | 85 | $Me_2CHO^+$ | | | |
| 41 | 79 | $C_3H_5^+$ | | | |
| 39 | 100 | $C_3H_3^+$ | | | |
| *$Ph_3GeOSP(OCHMe_2)_2$*[b] | | | *$Ph_3SnOSP(OCHMe_2)_2$*[a] | | |
| 502 | 2 | $Ph_3{}^{74}GeOSP(OCHMe)_2^+$ | 548 | 2 | $Ph_3{}^{120}SnOSP(OCHMe_2)_2^+$ |
| 425 | 7 | $Ph_2{}^{74}GeOSP(OCHMe_2)_2^+$ | 471 | 38 | $Ph_2{}^{120}SnOSP(OCHMe_2)_2^+$ |
| 340 | 43 | $Ph_2{}^{74}GeOSPO_2H^+$ | 387 | 16 | $Ph_2{}^{120}SnOSPO_2H_2^+$ |
| 305 | 88 | $Ph_3{}^{74}Ge^+$ | 351 | 44 | $Ph_3{}^{120}Sn^+$ |
| 261 | 22 | ${}^{74}GeOSP(OCHMe_2)_2^+$ | 274 | 15 | $Ph_2{}^{120}Sn^+$ |
| 228 | 20 | $Ph_2{}^{74}Ge^+$ | 197 | 81 | $Ph^{120}Sn^+$ |
| 183 | 27 | $H_2SP(OCHMe_2)_2^+$ | 122 | 81 | $SP(OCHMe_2)_2^+$ |
| 151 | 100 | $Ph^{74}Ge^+$ | 120 | 81 | ${}^{120}Sn^+$ |
| 115 | 37 | $H_4PO_3S^+$ | 115 | 56 | $H_4PO_3S^+$ |
| 114 | 37 | $H_3PO_3S^+$ | 114 | 56 | $H_3PO_3S^+$ |
| 77 | 91 | $Ph^+$ | 77 | 100 | $Ph^+$ |
| 59 | 37 | $Me_2CHO^+$ | 59 | 38 | $Me_2CHO^+$ |
| 41 | 77 | $C_3H_5^+$ | 41 | 94 | $C_3H_5^+$ |
| 39 | 56 | $C_3H_3^+$ | 39 | 76 | $C_3H_3^+$ |

[a] Ions containing ${}^{120}Sn$ only listed; see text. [b] Ions containing ${}^{74}Ge$ only listed; see text.

Table 2. The assignments in many cases must be regarded as tentative, as the spectra were devoid of metastable peaks. The identification of ions containing germanium or tin was assisted by the isotopic distributions of these elements: no attempt was made to analyse the resulting multiplets. In Table 2, all ions of the germanium or tin compounds refer to species containing the most abundant isotopes, $^{74}$Ge and $^{120}$Sn respectively.

Rather little may be deduced from the mass spectra about the identity of the isomers present. The spectrum of the triphenylsilyl derivative contains ions at *m/e* 276 and 122 which may be tentatively assigned to $Ph_3SiOH^+$ and $PhSiOH^+$ respectively, suggesting that the triphenylsilyl group is *O*-bonded. Similarly all the triphenyl compounds give ions of the form $(Me_2CHO)_nPSH_x^+$: at 181 ($n = 2$, $x = 0$) and at 183 ($n = 2$, $x = 2$) for the silicon and germanium compounds respectively, and at 122 ($n = 1$, $x = 0$) for both the silicon and tin derivatives: these ions may perhaps be indicative of loss of $Ph_3MO$ groups.

*NMR spectra*

All the phosphorothioate derivatives here described gave $^1$H NMR spectra with integrals which accorded with the composition postulated: essential data are presented in Table 3. In $(Me_2CHO)_2P(O)H$ and in the trimethylsilyl and trimethyltin derivatives of the phosphorothioate anion the NMR absorptions due to the isopropyl groups are as expected: in each of the triphenyl compounds the methyl resonance of the isopropyl groups split into two doublets, instead of the one doublet expected, but having the correct total integral and with separations of the order of 5-10 Hz. This is unlikely to be due to coupling of these methyl groups to phosphorus, as it is unobserved in $(Me_2CHO)_2P(O)H$ and the trimethyl compounds: unfortunately, the decoupling conditions required for recording the $^{31}$P NMR spectra precluded the observation of any such coupling. This splitting is unlikely to be caused by the presence of two isomeric forms as it is observed not only for the triphenyl compounds but also for the anion $(Me_2CHO)_2POS^-$ and for the phosphoramidate $(Me_2CHO)_2P(O)NHCH_2C_6H_5$ [10]. A possible rationalisation is in terms of the magnetic non-equivalence of the methyl groups in an isopropoxy fragment attached to a prochiral phosphorus atom: whatever the conformation of the $Me_2CH{-}OPXY$ fragment a slow rotation about the C—O bond can render the two methyl groups magnetically non-equivalent. This suggestion is supported by the observation of two methyl resonances in the $^{13}$C NMR spectra of these compounds. We can, at present, offer no convincing rationalisation for the finding that this non-equivalence of methyl groups is manifested in the $^1$H NMR spectrum for only some of the compounds in question.

The phosphorus chemical shifts (Table 3) of the $Me_3Si$, $Me_3Sn$, $Ph_3Si$ and $Ph_3Ge$ derivatives are all within the range observed [11], —42 to —73 ppm, for compounds of the form $(RO)_2P(S)OR'$: these are all therefore assigned such *O*-bonded structures. The upfield shift in the trimethyl tin compound may be ascribed to an increase in the diamagnetic anisotropy of the bonds to the heavier atom. For the same reason, the triphenyl tin derivative, although its $^{31}$P chemical shift is nearer the range observed [11], —18 to —31 ppm, for compounds of the form $(RO)_2P(O)SR'$, is assigned the *O*-bonded structure $(Me_2CHO)_2P(S)OSnPh_3$: the *S*-bonded isomer might be expected to have a $^{31}$P

TABLE 3

NMR DATA[a]

| | $(CH_3)_2CH$ | $(CH_3)_2CH$ | $C_6H_5$ | $CH_3M$ | $P^b$ |
|---|---|---|---|---|---|
| $H(O)P(OCHMe_2)_2$ | 1.36 | 4.73 | | | −4.2[c] |
| $[OSP(OCHMe_2)_2]^-Na^+$ | 1.27<br>1.32 | 4.60 | | | −53.72 |
| $Me_3SiOSP(OCHMe_2)_2$ | 1.16 | 4.44 | | 0.10 | −60.68 |
| $Me_3SnOSP(OCHMe_2)_2$ | 1.15 | 4.50 | | 0.49 | −47.47<br>$^2J(HC—^{119}Sn)$ 63 Hz<br>$^2J(HC—^{117}Sn)$ 60 Hz |
| $Ph_3SiOSP(OCHMe_2)_2$ | 1.27<br>1.32 | 4.60 | 7.38 (*o,p*)<br>7.60 (*m*) | | −57.94 |
| $Ph_3GeOSP(OCHMe_2)_2$ | 1.04<br>1.15 | 4.61 | 7.43 (*o,p*)<br>7.69 (*m*) | | −59.24 |
| $Ph_3SnOSP(OCHMe_2)_2$ | 1.10<br>1.16 | 4.44 | 7.40 (*o,m,p*) | | −33.66 |

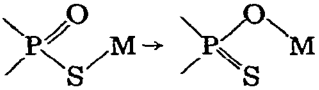
[a] Proton shifts δ in ppm from $Me_4Si$. [b] Phosphorus shifts in ppm from 85% $H_3PO_4$ [c] Ref. 12.

shift near the upper end of the range, say ca. —20 ppm. The phosphorus shift in sodium diisopropylphosphorothioate itself, —53.72, is close to that reported [12], —56.0 ppm, for the diethyl analogue; the slight upfield shift is typical of the effect of increased branching in alkyl substituents [11].

## Discussion

On the basis of their infrared, mass and $^{31}P$ NMR spectra, the products of the reactions of sodium diisopropylphosphorothioate with halides of silicon, germanium and tin all appear to be *O*-bonded isomers $(Me_2CHO)_2P(S)OMR_3$. From the reactions of dialkylphosphorothioate ions with carbon halides both *O*-bonded [3] and *S*-bonded [1,2] compounds have been isolated. However, it is unclear in most of these cases whether the product isolated is the thermodynamically more stable isomer. In the cases of reactions at silicon, germanium or tin, reaction is probably rapid enough to yield the thermodynamically more stable isomer [13,14].

The enthalpy changes for the processes:

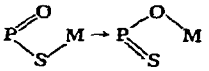


are readily estimated from bond energy terms: $\Delta H = +B(P{=}O) + B(P—S) + B(S—M) - B(P{=}S) - B(P—O) - B(O—M)$; the calculations for M = C, Si, Ge, and Sn are set out in Table 4. Apart from possible differential interactions with the solvent, which we are unable to quantify, the principal contribution to $\Delta S$ for these isomerisations will arise from the molecular vibrations. We estimate [19] $-T\Delta S$ to be no greater than +2 kJ $mol^{-1}$. We conclude that for M = Si, Ge and Sn, the thermodynamically more stable isomer is the *O*-bonded one, while for M = C it is the *S*-bonded isomer.

In the reaction of phosphorothioate anions with carbon halides, the prod-

TABLE 4

BOND ENERGY TERMS (kJ) AND ENTHALPY CHANGES (kJ mol$^{-1}$) FOR REACTION



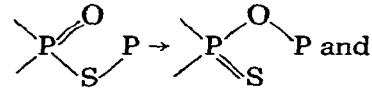
| M | $+B$(P=O) | $+B$(P—S) | $+B$(S—M) | $-B$(P=S) | $-B$(P—O) | $-B$(O—M) | $=\Delta H$ |
|---|---|---|---|---|---|---|---|
| C | +620$^a$ | +218$^a$ | +301$^b$ | −380$^a$ | −368$^c$ | −358$^c$ | +33 |
| Si | +620 | +218 | +294$^d$ | −380 | −368 | −445$^e$ | −61 |
| Ge | +620 | +218 | +243$^d$ | −380 | −368 | −356$^e$ | −23 |
| Sn | +620 | +218 | +240$^d$ | −380 | −368 | −384$^e$ | −54 |

[a] Ref. 15. [b] Ref. 16. [c] Ref. 17. [d] Calculated from Pauling's geometric mean equation [17]. [e] Ref. 18.

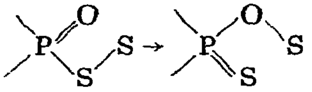
uct is sometimes the thermodynamically more stable isomer: in the reaction with silicon, germanium or tin halides, the product seems always to be the thermodynamically more stable isomer. Formation of the thermodynamically stable isomer is observed also in the reaction of *N*-silyldimethylamine with carbonyl sulphide to yield *O*-silyl-*N,N*-dimethylthiocarbamate [20], and in the reaction of the *N*-benzyl-*O,O*-diisopropylphosphoramidate ion with halides of silicon and tin to give *O*-substitution [10].

Similarly, we calculate $\Delta H$ values for the isomerisation reactions

(*a*)



and (*b*)



as −60 and +69 kJ mol$^{-1}$ respectively, so that reactions of phosphorothioate ions with a phosphorochloridate [5-7] or a sulphenyl halide [9] yield in each case the thermodynamically more stable isomer.

If initial attack is by oxygen, then inversion of configuration of the $R_3M$ group would be expected in the case of M = Si [13]. Further study of this point, and of the stereochemistry of sulphur attack on silicon, is in progress.

## Experimental

Sodium diisopropylphosphorothioate was prepared [21] from diisopropyl hydrogen phosphite [22]. Triphenylbromogermane was prepared by reaction of bromine with tetraphenylgermane [23]. The remaining halides were obtained commercially, triphenylchlorosilane and triphenyltin chloride being recrystallised before use. All reactions were conducted in diethyl ether (dried over Na) under a dry nitrogen atmosphere. $^1$H NMR spectra were obtained using a Varian HA-100 instrument, $^{31}$P NMR spectra were obtained with a Varian XL-100 instrument using wide-band decoupling and $^{13}$C NMR spectra were obtained using a Varian CFT-20 spectrometer with wide-band decoupling.

### *Reactions of sodium diisopropylphosphorothioate*

*(a). With trimethylchlorosilane.* The silane (0.517 g, 4.76 × 10$^{-3}$ mol) and the sodium salt (1.00 g, 4.54 × 10$^{-3}$ mol) were refluxed together in diethyl ether (0.4 dm$^3$) for 12 h. The mixture was filtered through sintered glass, the solvent

evaporated and the product obtained as a pale yellow oil (0.98 g, $3.63 \times 10^{-3}$ mol, 80%). (Found: C, 38.7; H, 8.7. $C_9H_{23}O_3PSSi$ calcd.: C, 39.9; h, 8.6%.)

*(b). With triphenylchlorosilane.* The silane (1.40 g, $4.75 \times 10^{-3}$ mol) and the sodium salt (1.00 g, $4.54 \times 10^{-3}$ mol) were refluxed in diethyl ether (0.4 dm$^3$) for 12 h. The solution was cooled and filtered, and the solvent removed. The product was obtained as an off-white crystalline solid, (2.00 g, $4.39 \times 10^{-3}$ mol, 96%), m.p. 132-134°C. (Found: C, 60.2; H, 5.8. $C_{24}H_{29}O_3PSSi$ calcd.: C, 63.1; H, 6.4%.)

*(c). With triphenylbromogermane.* The sodium salt (1.00 g, $4.54 \times 10^{-3}$ mol) and triphenylbromogermane (1.83 g, $4.77 \times 10^{-3}$ mol) were refluxed in diethyl ether (0.4 dm$^3$) for 12 h. The solution was cooled and filtered and the solvent removed; the mixture was further cooled and centrifuged to yield the product as a viscous oil (1.91 g, $3.81 \times 10^{-3}$ mol, 84%) which defied all attempts to render it crystalline. (Found: C, 57.2; H, 5.7. $C_{24}H_{29}GeO_3PS$ calcd.: C, 57.2; H, 5.8%.)

*(d). With trimethyltin chloride.* Trimethyltin chloride (0.92 g, $4.62 \times 10^{-3}$ mol) was refluxed for 12 h with the sodium salt (1.00 g, $4.45 \times 10^{-3}$ mol) in diethyl ether (0.4 dm$^3$). The mixture was cooled and filtered; removal of the solvent gave the product as a viscous oil which on further cooling crystallised as a colourless solid (1.20 g, $3.32 \times 10^{-3}$ mol, 73%), m.p. 70°C. (Found: C, 28.3; H, 6.4. $C_9H_{23}O_3PSSn$ calcd.: C, 29.9; H, 6.4%.)

*(e). With triphenyltin chloride.* The sodium salt (1.00 g, $4.54 \times 10^{-3}$ mol) and triphenyltin chloride (1.80 g, $4.67 \times 10^{-3}$ mol) were refluxed together in diethyl ether (0.4 dm$^3$) for 12 h. After cooling the mixture and filtration, removal of the solvent gave a viscous, pale yellow oil which crystallised on further cooling to yield the product (2.32 g, $4.24 \times 10^{-3}$ mol, 93%), m.p. 82-85°C. (Found: C, 52.1; H, 5.3. $C_{24}H_{29}O_3PSSn$ calcd.: C, 52.7; H, 5.3%.)

## References

1 G. Shrader, Chem. Zentralbl., (1958) 13619; (1961) 5943.
2 H.S. Aaron, R.T. Uyeda, H.F Frack and J.I. Miller, J. Amer. Chem. Soc., 84 (1962) 617.
3 B.A. Arbusov and D.K. Jarmukhametova, Izv. Akad. Nauk S.S.S R., Otd. Khim. Nauk, (1958) 1061.
4 J.I.G. Cadogan, J. Chem. Soc., (1961) 3067.
5 B.A. Arbusov, P.I. Alimov, M.A. Zvereva, I.D. Neklesova and M.A. Kudrina, Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk, (1954) 1038.
6 B. Fiszer, J. Michalski and J. Wieczorkowski, Rocz. Chem., 27 (1953) 482.
7 R.A.Y. Jones, A.R. Katritky and J. Michalski, Proc. Chem. Soc., (1959) 321.
8 A. Michaelis, Justus Liebigs Ann. Chem., 315 (1901) 66.
9 O. Foss, Acta Chem. Scand., 1 (1947) 307.
10 I.A. Duncan and C. Glidewell, unpublished.
11 V. Mark, C.H. Dungan, M.M. Crutchfield and J.R. Van Wazer, in "Topics in Phosphorus Chemistry", Vol. V, Interscience, New York, 1967 and references therein.
12 H. Finegold, Ann. N.Y. Acad. Sci., 70 (1958) 875.
13 L.H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965.
14 J.R. Chipperfield and R.H. Prince, J. Chem. Soc., (1963) 3567.
15 S.B. Hartley, W.S. Holmes, J.K. Jacques, M.F. Mole and J.C. McCoubrey, Quart. Rev., 17 (1963) 204.
16 T.L. Cottrell, "The Strengths of Chemical Bonds", Butterworths, London, 1958.
17 D.A. Johnston, "Some Thermodynamic Aspects of Inorganic Chemistry", Cambridge University Press, 1968.
18 E.A.V. Ebsworth, in A.G. MacDiarmid (Ed.), "Organometallic Compounds of the Group IV Elements", Dekker, New York, 1 (1968) 1.
19 J.G. Aston, in H.S. Taylor and S. Glasstone (Eds.), "Treatise on Physical Chemistry", Van Nostrand, New York, 1 (1942) 511.

20 E.A.V. Ebsworth, G. Rocktäschel and J.C. Thomson, J. Chem. Soc. A, (1967) 362.
21 O. Foss, Acta Chem. Scand., 1 (1947) 8.
22 H. McCombie, B.C. Saunders and G.J. Stacey, *J. Chem. Soc.*, (1945) 380.
23 O.H. Johnston, W.H. Nebergall and D.M. Harris, Inorg. Syn., 5 (1957) 76.