

AMBIDENT NUCLEOPHILES

VII*. REACTIONS OF DIISOPROPYL-PHOSPHITE, -PHOSPHOROTHIOATE, -PHOSPHORODITHIOATE, AND -PHOSPHOROSELENOATE WITH CHLOROPHENYLPHOSPHINES

C. GLIDEWELL

Chemistry Department, University of St. Andrews, Fife KY16 9ST (Great Britain)

(Received July 18th, 1977)

Summary

The (1,2) ambident nucleophilic anion diisopropylphosphite $(RO)_2PO^-$ ($R = Me_2CH$) reacts with $Ph_{3-n}PCl_n$ ($n = 1,2$) to yield P-P bonded derivatives $Ph_{3-n}P[P(O)(OR)_2]_n$. The (1,3) ambident nucleophilic anions diisopropylphosphorothioate $(RO)_2POS^-$, and diisopropylphosphorodithioate $(RO)_2PS_2^-$ react with $Ph_{3-n}PCl_n$ ($n = 1,2$) to yield $Ph_{3-n}P[XP(Y)(OR)_2]_n$ ($X = O, Y = S$; and $X = Y = S$, respectively): the analogous diisopropylphosphoroselenoate $(RO)_2POSE^-$ reacts with Ph_2PCl to give $Ph_2P[OP(Se)(OR)_2]$, but $PhP[OP(Se)(OR)_2]_2$ was too unstable to be characterised. Assignments of constitution are made, based on ^{31}P NMR data: the thermodynamics of isomerisation are discussed.

Introduction

The anion Ph_3SiO^- reacts with Ph_2PCl to yield the rearranged derivative, formally of phosphorus(V), $Ph_2P(O)SiPh_3$ [1]: similarly the (1,2) ambident nucleophile $(RO)_2PO^-$ ($R = Me_2CH$ throughout this paper) reacts with Ph_3SiCl to yield [1] the phosphorus(V) derivative $(RO)_2P(O)SiPh_3$. Consequently the reactions of the nucleophiles $(RO)_2PO^-$, $(RO)_2POS^-$, $(RO)_2PS_2^-$, and $(RO)_2POSE^-$ with the substrates Ph_2PCl and $PhPCl_2$ have been investigated in order to determine whether similar rearrangements to yield phenylphosphorus(V) species occur. The reactions of PCl_3 with $(RO)_2POS^-$ [2], $(RO)_2PS_2^-$ [3] and $(RO)_2POSE^-$ [4] have been reported previously: no rearrangements were observed, but neither was any rearrangement observed in the reaction of PCl_3 with Me_3SiO^- [1].

* For part VI see ref. 3.

Experimental

The salts $[(RO)_2POS]Na$, $[(RO)_2PS_2]K$ and $[(RO)_2POSe]Na$ were prepared by standard methods [5,6]: $[(RO)_2PO]Na$ was prepared by reaction of sodium with $(RO)_2PHO$ in anhydrous ether, and the solution was used without prior isolation of the salt.

Reactions were conducted, usually on 0.01 M scale, by adding to a solution of the salt in anhydrous ether or nitromethane, a solution in the same solvent containing the stoichiometric quantity of the chlorophenylphosphine. After stirring during 24 hours at room temperature, the precipitated alkali chloride was removed by centrifugation, and the solvent was then removed under reduced pressure, at or below room temperature, to yield the products.

The products were viscous, involatile, liquids which crystallised only on prolonged (>3 months) storage at $-30^\circ C$. Derivatives of $(RO)_2PO$ and $(RO)_2PS_2$ were colourless, derivatives of $(RO)_2POS$ were pale yellow, and derivatives of $(RO)_2POSe$ were deep orange-yellow. No homogeneous product could be isolated from the reaction of $[(RO)_2PO]Na$ with PCl_3 : $[(RO)_2POSe]_2PPh$ and $[(RO)_2POSe]PPh_2$ both decomposed rapidly with loss of selenium, so that neither could be analysed: spectral data were, however, recorded for $[(RO)_2-POSe]PPh_2$ immediately after preparation. Microanalytical data for new compounds are in Table 1.

1H NMR spectra were recorded in $CDCl_3$ solution, using a Varian HA-100 spectrometer: ^{31}P NMR spectra were recorded at 32.19 MHz using a Varian CFT-20 spectrometer, with proton decoupling and Fourier transform. The internal reference was D_3PO_4 which also activated the frequency-lock: the isotopic chemical shift $\delta(D_3PO_4) - \delta(H_3PO_4)$ was +0.29 ppm; all ^{31}P shifts are reported relative to 85% H_3PO_4 , with downfield shifts positive.

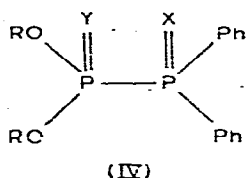
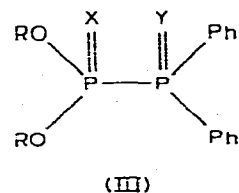
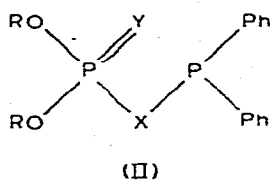
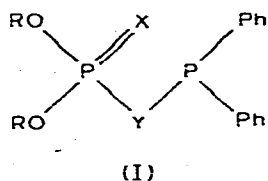
TABLE I
MICROANALYTICAL DATA

Compound	Formula	Analysis (Found (calcd.) (%))	
		C	H
$[(RO)_2PO]_2PPh$	$C_{18}H_{33}O_6P_3$	49.6 (49.3)	7.9 (7.6)
$[(RO)_2POS]_2PPh$	$C_{18}H_{33}O_6P_3S_2$	42.8 (43.0)	6.8 (6.6)
$[(RO)_2PS_2]_2PPh$	$C_{18}H_{33}O_4P_3S_4$	40.4 (40.4)	6.3 (6.2)
$[(RO)_2PO]PPh_2$	$C_{18}H_{24}O_3P_2$	61.2 (61.7)	7.1 (6.9)
$[(RO)_2POS]PPh_2$	$C_{18}H_{24}O_3P_2S$	56.3 (56.5)	5.9 (6.3)
$[(RO)_2PS_2]PPh_2$	$C_{18}H_{24}O_2P_2S_2$	54.5 (54.3)	6.6 (6.1)
$[(RO)_2POSe]PPh_2$	$C_{18}H_{24}O_3P_2Se$	50.8 (50.4)	6.2 (5.6)

Results and discussion

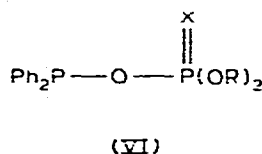
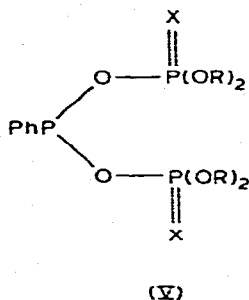
NMR data are presented in Table 2. The integrated proton spectra served to confirm the identities of phenyl-containing species. The phosphorus spectra enable unambiguous assignments of constitution to be made.

For derivatives of $(RO)_2PXY$ ($X, Y = O, S, Se$), four distinct structure types are possible (I–IV); the lack of $^1J(PP)$ enables structures III and IV to be ruled out



immediately, as does also the observation that in $[(RO)_2PXY]_2PPh$, the two $(RO)_2PXY$ groups contain identical phosphorus atoms: structures based on types III and IV would require different ^{31}P chemical shifts for the two $(RO)_2PXY$ groups.

Derivatives of $(RO)_2POS$ which contain *O*-bonded thione groups (I: $X = S$, $Y = O$) have $\delta(P) > 58$ ppm while those containing *S*-bonded thiol group (II: $X = S$, $Y = O$) have $\delta(P) < 30$ ppm [2]: on this basis $[(RO)_2POS]_2PPh$ and $[(RO)_2POS]PPh_2$ are assigned the structures V and VI respectively ($X = S$).



Derivatives of $(RO)_2POSe$ which are *O*-bonded and contain $\geq P=Se$ fragments have $^1J(PSe) > 850$ Hz [4] while *Se*-bonded species containing $\geq P=O$ fragments have $^1J(PSe) < 550$ Hz [4]. Consequently $[(RO)_2POSe]PPh_2$ is assigned structure VI ($X = Se$); $[(RO)_2POSe]_2PPh$ was too unstable for the recording of its phosphorus spectrum, but $[(RO)_2POSe]_3P$ also adopts [4] the *O*-bonded struc-

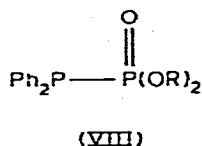
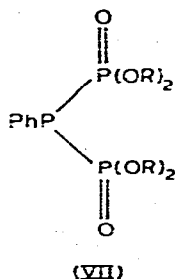
TABLE 2
 NMR DATA

Compound	$\delta(\text{CH}_3)^a$	$\delta(\text{CH})^a$	$\delta(\text{C}_6\text{H}_5)^a$	$\delta(\text{P}_I)^b$	$\delta(\text{P}_{\text{unique}})^c$
$[(\text{RO})_2\text{POS}]_3\text{P}$ [2]	1.35	4.77	—	59.21	151.71
$[(\text{RO})_2\text{PS}_2]_3\text{P}$ [3]	1.29	4.73	—	81.76	149.58
$[(\text{RO})_2\text{POSe}]_3\text{P}$ [4] ^d	1.37	4.92	—	58.25	155.29
$[(\text{RO})_2\text{PO}]_2\text{PPh}$	1.34	4.71	7.3–7.9	–26.96	60.77
$[(\text{RO})_2\text{POS}]_2\text{PPh}$	1.29	4.91	7.3–7.9	60.66	22.29
$[(\text{RO})_2\text{PS}_2]_2\text{PPh}$	1.38	4.84	7.2–8.1	82.21	60.41
$[(\text{RO})_2\text{PO}]\text{PPh}_2$	1.28	4.65	7.2–8.0	–29.20	14.24
$[(\text{RO})_2\text{POS}]\text{PPh}_2$	1.25	4.68	7.3–8.0	60.94	34.95
$[(\text{RO})_2\text{PS}_2]\text{PPh}_2$	1.34	4.88	7.3–8.0	82.48	33.78
$[(\text{RO})_2\text{POSe}]\text{PPh}_2$ ^e	1.39	4.88	7.2–8.0	52.43	28.18

^a Proton shifts in ppm downfield from Me_4Si . ^b Shift of ligand phosphorus in ppm downfield from 85% H_3PO_4 . ^c Shift of unique phosphorus in ppm downfield from 85% H_3PO_4 . ^d $^1\text{J}(\text{PSe})$ 874.2 Hz. ^e $^1\text{J}(\text{PSe})$ 958.8 Hz.

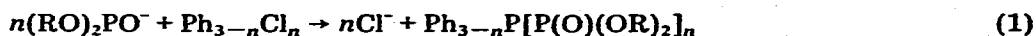
ture. Compounds of $(\text{RO})_2\text{PS}_2$ which contain unidentate ligands (e.g. I: $\text{X} = \text{Y} = \text{S}$) have [3] chemical shifts in the range 73–82 ppm; the values in $[(\text{RO})_2\text{PS}_2]_2\text{PPh}$ and $[(\text{RO})_2\text{PS}_2]\text{PPh}_2$ are consistent with this.

The phosphorus spectra of $[(\text{RO})_2\text{PO}]_2\text{PPh}$ and $[(\text{RO})_2\text{PO}]\text{PPh}_2$ are very similar to those reported for $[(\text{EtO})_2\text{PO}]_2\text{PPh}$ [7] and $[(\text{EtO})_2\text{PO}]\text{PPh}_2$ [8], respectively; these compounds are therefore assigned structures containing P–P bonds (VII and VIII).

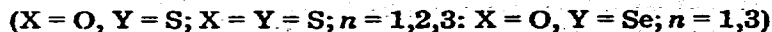


The products of the reactions of $(\text{RO})_2\text{PXY}^-$ with PCl_3 have been shown [2–4] to contain a unique three-connected phosphorus atom, bonded to oxygen in $[(\text{RO})_2\text{POX}]_3\text{P}$ ($\text{X} = \text{S}, \text{Se}$) and to sulphur in $[(\text{RO})_2\text{PS}_2]_3\text{P}$.

On the basis of the NMR assignments, equations 1 and 2 may be written to describe the reactions of $(\text{RO})_2\text{PO}^-$ and $(\text{RO})_2\text{PXY}^-$ with $\text{Ph}_{3-n}\text{PCl}_n$ ($n = 1, 2, 3$):



$$(n = 1, 2)$$



No rearrangements to yield $\text{PhP}(\text{X})\text{=}$ or $\text{Ph}_2\text{P}(\text{X})\text{=}$ species occur in any of these systems.

For the four phosphorus ligands, we may write as examples of the possible isomerisation reactions, equations 3 and 4. When $X = Y = S$, equation 4 repre-



sents the isomerisation of a PSP bridge: $\text{>P}-\text{S}-\text{P}< \rightarrow \text{>P}-\text{P}(\text{S})<$. For the remaining systems the isomerisation process is: $\text{>P}-\text{O}-\text{P}< \rightarrow \text{>P}-\text{P}(\text{O})<$.

A simple bond-energy term calculation shows that the ΔH° terms associated with the isomerisations of POP and PSP bridges are -93 and -153 kJ mol^{-1} , respectively. Hence the $\text{P}-\text{O}-\text{P}$ bridged isomer is thermodynamically the less stable in the $(\text{RO})_2\text{POPPh}_2$ system, consistent with the observation of a $\text{P}=\text{O}$ bonded isomer. However, in the remaining systems, the thermodynamically less stable isomers are formed. Attempts to rearrange the observed kinetically stabilised isomers were found to lead to extensive decomposition: for example storage of $[(\text{RO})_2\text{PS}_2]\text{PPh}_2$ for one month at ambient temperature led to no visible change, but the ^{31}P NMR spectrum was subsequently found to exhibit sixteen resonances in the range $26.6-96.8 \text{ ppm}$, indicating a very complex mode of decomposition, which was not further investigated. $\text{Ph}_{3-n}\text{P}[\text{OP}(\text{Se})(\text{OR})_2]_n$ ($n = 1, 2$) are similarly unstable at room temperature.

References

- 1 I.G.T. Ferguson and C. Glidewell, *J. Chem. Soc. (Dalton)*, in press.
- 2 C. Glidewell, *Inorg. Chim. Acta*, **24** (1977) 255.
- 3 C. Glidewell, *Inorg. Chim. Acta*, **25** (1977) 159.
- 4 C. Glidewell, and E.J. Leslie, *J. Chem. Soc. (Dalton)*, (1977) 527.
- 5 O. Foss, *Acta Chem. Scand.*, **1** (1947) 307.
- 6 N.I. Zemlyanskii, O.A. Prib and B.S. Drach, *Zhur. Obschch. Khim.*, **31** (1961) 880.
- 7 K.M. Abraham and J.R. Van Wazer, *Inorg. Chem.*, **15** (1976) 2322.
- 8 E. Fluck and H. Binder, *Inorg. Nuclear Chem. Lett.*, **3** (1967) 307.