Rapid Transfer of Selenium from Tertiary Phosphine Selenides to Tertiary Phosphines

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Summary The title reaction, which is fast on the n.m.r. time-scale and is concentration dependent, resembles more closely the analogous process with phosphine tellurides rather than that with phosphine sulphides.

THE transfer of sulphur atoms from tertiary phosphine sulphides to more basic phosphine molecules is well documented, and finds numerous synthetic applications.[1] An extension of this reaction is the redistribution of sulphur in unsymmetrical methylene-diphosphine monosulphides [equation (1)].[2] With the heavier chalcogens, the transfer of tellurium from phosphine tellurides to the analogous

$$Ph_2P(S)CH_2PMe_2 \xrightarrow{\text{Heat}} Ph_2PCH_2P(S)Me_2 \qquad (1)$$

tertiary phosphine is fast on the n.m.r. time-scale at ambient temperatures.[3,4] Nothing has been reported concerning the transfer of selenium between phosphorus atoms.

We find that the exchange of selenium between tertiary phosphine selenides and the analogous tertiary phosphine is fast on the n.m.r. time-scale at elevated temperatures (Table). Thus the two singlet methyl resonances, produced after ^{31}P decoupling, of mixtures of Ph_2MePSe and Ph_2MeP broaden and coalesce as the temperature is increased. The coalescence covers a wide range of temperatures and is difficult to measure accurately,† but it is obviously concentration dependent. The methylene signals from the mixtures of $Ph_2P(Se)CH_2PPh_2$ and $Ph_2PCH_2PPh_2$, and of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ display similar behaviour. This is consistent with an intermolecular transfer of selenium. Although the coalescence temperatures of Ph_2MePSe with Ph_2MeP and $Ph_2P(Se)CH_2PPh_2$ with $Ph_2PCH_2PPh_2$ are

TABLE. Coalescence temperatures[a]

Components	Concentrations[b]/mol l^{-1} (Coalescence temp./K)							
Ph_2MePSe	0·33	(>447)	0·36	(438)	0·67	(428)	1·0	(418)
Ph_2MeP	0·33		0·72		1·32		2·0	
$Ph_2P(Se)CH_2PPh_2$	0·53	(>438)						
$Ph_2P(Se)CH_2PPh_2$	0·53	(438)	0·67	(418)	1·0	(411)		
$Ph_2PCH_2PPh_2$	0·27		0·67		1·0			
$Ph_2P(Se)CH_2P(Se)Ph_2$	0·67	(>443)						
$Ph_2P(Se)CH_2PPh_2$	0·67							
$Ph_2P(Se)C_2H_4P(Se)Ph_2$	0·20	(398[c])	0·33	(368)				
$Ph_2P(Se)C_2H_4PPh_2$	0·40		0·67					
$Ph_2PC_2H_4PPh_2$	0·20		0·33					

[a] Measured at 60 MHz on a JEOL C60HL spectrometer with noise-modulation of the ^{31}P irradiation field (P^V and P^{III} signals generally separated by *ca.* 1 kHz). Temperatures ±10 K. [b] *o*-Dichlorobenzene solutions. [c] Chlorobenzene solution.

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† We define the coalescence temperature as the lowest temperature at which no valley can be discerned between the individual signals.

comparable, 1,2-bis(diphenylphosphino)ethane with its mono- and di-selenide coalesced at lower temperatures, and $Ph_2P(Se)CH_2PPh_2$ alone or with $Ph_2P(Se)CH_2P(Se)Ph_2$ failed to reach coalescence in the temperature range examined. Obviously the nature of the substituents on phosphorus affects the rate of selenium exchange.

N.m.r. investigations also show that equimolar solutions of $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2PCH_2PPh_2$ react quantitatively to produce $Ph_2P(Se)CH_2PPh_2$ immediately on mixing, whereas $Ph_2P(Se)C_2H_4P(Se)Ph_2$ and $Ph_2PC_2H_4PPh_2$ equilibrate to a 1:2:1 mixture of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ at a similar rate. This difference in the nature of the products is presumably because the more electron deficient P^V atom affects the activity of the P^{III} atom in $Ph_2P(Se)CH_2PPh_2$, but not in $Ph_2P(Se)C_2H_4PPh_2$ where the phosphorus atoms are separated by two CH_2 groups. We find that the analogous reactions of phosphine sulphides are similar [equations (2) and (3)], though much slower. Equilibrium is reached after about 24 h at 160 °C (in the absence of solvent, or in *o*-dichlorobenzene solution) but requires more than 40 days

$$Ph_2P(S)CH_2P(S)Ph_2 + Ph_2PCH_2PPh_2 \rightarrow Ph_2P(S)CH_2PPh_2 \qquad (2)$$

$$Ph_2P(S)C_2H_4P(S)Ph_2 + Ph_2PC_2H_4PPh_2 \rightleftharpoons Ph_2P(S)C_2H_4PPh_2 \qquad (3)$$

at 80 °C in benzene solution. The redistribution of sulphur, selenium, and tellurium[4] between phosphorus atoms in methylene diphosphine systems thus appears to be a general process, of which reaction (1) is but a specific example. Seen in this light, the detection of *ca.* 10% of $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$ amongst the products of reaction (1) is not remarkable.[2] The rate of chalcogen atom transfer between phosphines is seen to increase in the order $S << Se < Te$.

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