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Preliminary communication

EXCHANGE EFFECTS ON THE ^{1}H AND ^{31}P NMR SPECTRA OF CYCLODIPHOSPH(III)AZANE SELENIDES AND TELLURIDES

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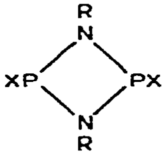
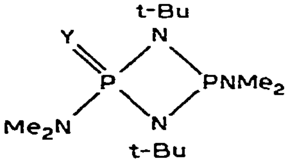
Summary

Oxidation of the isomeric cyclodiphosph(III)azanes, $(Me_2NPNBu\text{-}t)_2$, by selenium and by tellurium gives both isomeric monoselenides but only one monotelluride. Variable temperature ^{1}H and ^{31}P NMR studies provide evidence for restricted rotation about the exocyclic P—N bonds, and in the telluride, of exchange of tellurium between the phosphorus atoms.

During an investigation into the products of oxidation of cyclodiphosph(III)azanes (I, R = t-Bu, X = NMe_2) [1] by selenium and tellurium we have encountered two distinct exchange processes which have a bearing on the lability of phosphorus—chalcogen bonds [2—4] and on barriers to rotation about phosphorus—nitrogen [5,6] bonds.



(I)



(II)

The *cis* and *trans* isomers of I (R = t-Bu, X = NMe_2) are readily oxidised by selenium and by tellurium in benzene solution to give two isomeric monoselenides II (Y = Se), but only one monotelluride could be obtained (Table 1). Attempts to effect complete oxidation were only successful in the case of selenium. The ^{1}H NMR spectra of both isomers of II (Y = Se) showed exchange broadening effects at ambient temperatures, but at ca. 100°C each consisted of two doublets from coupling to the ^{31}P nuclei. On cooling, the

TABLE 1

NMR DATA

Compound[a]		M.p. (°C)	$\delta(P^{III})^b$	$\delta(P^{V})^b$	$\delta(P^{V}NC\underline{H})^{c,d}$	$J(\underline{P}^{V}NC\underline{H})$ (Hz)[c]	$\delta(P^{III}NC\underline{H})^{c,d}$	$J(\underline{P}^{III}NC\underline{H})$ (Hz)[c]
II	(Y = Se)	126–127	111.7	61.0	3.04, 2.60 (282 K)	12.7, 9.8	2.83, 2.78 (331 K)	2.9, 13.7
II	(Y = Se)	102–104	90.5	36.6	3.01 (<210 K)	12.0	2.77, 2.63 (301 K)	13.7, 3.2
II	(Y = Te)	120 (decomp.)	127.7	16.7	3.01, 2.63 ([e])	15.1, 9.7	2.84, 2.77 ([e])	2.7, 14.0

[a] All compounds characterised by elemental analyses and mass spectra. The isomers m.p. 126–127°C and 102–104°C were obtained from *cis* and *trans* isomers of I (R = t-Bu, X = NMe_2), respectively. [b] $CDCl_3$ solutions, relative to external 85% H_3PO_4. [c] 0.1 *M* $CDCl_3$ solutions at ca. −60°C; see Fig. 1 for ambient temperature ^1H NMR spectra of II (Y = Te). [d] Figures in parentheses represent approximate coalescence temperatures. [e] Exchange broadening effects observed in the range 275 ± 40 K.

signals from the dimethylamino-protons attached to the tervalent phosphorus broadened to form two doublets, and in one isomer (m.p. 126—127°C), on further cooling, the dimethylamino-protons attached to the quinquevalent phosphorus exhibited the same phenomenon. In view of recent experiments on the analogous sulphides [7] there is little doubt the nonequivalence of the dimethylamino-protons arises through restricted rotation about the exocyclic P—N bonds and that the barriers to rotation about the tervalent P—N bonds are greater than for P(Se)—N bonds.

By contrast, the ambient temperature ^{1}H NMR spectrum of II (Y = Te) consisted of a single slightly broadened doublet (Fig. 1) and, surprisingly, this

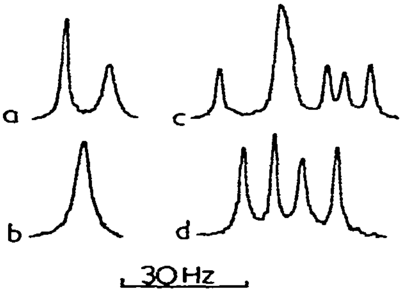


Fig. 1. (a) Ambient temperature ^{1}H NMR spectrum of II (Y = Te), showing dimethylamino-proton signals only (0.1 *M* in $CDCl_3$ solution). (b) As in a, but with irradiation of P^{III} or P^{V} signals. (c) As in a, but at —60°C. (d) As in a at —60°C, with complete ^{31}P decoupling.

collapsed to a singlet at either of two separate ^{31}P decoupling frequencies. This behaviour is attributed to tellurium-atom exchange between the two phosphorus atoms at an intermediate rate on the NMR time scale. The exchange lifetime is less than the spin-lattice relaxation time for the ^{31}P nuclei so that complete ^{1}H-{^{31}P} spin decoupling can be effected by irradiation of either of the two ^{31}P signals. At ca. —60°C the ^{1}H NMR spectrum consisted of four dimethylamino-proton signals showing that both tellurium exchange, and rotation about the exocyclic P—N bonds were slow on the NMR timescale. The former exchange process was concentration dependent, and the latter concentration independent, suggesting that tellurium exchange is at least partly intermolecular. The ^{31}P-{^{1}H} NMR spectrum (saturated solution) is broad at ambient temperatures (line half width ca. 700 Hz) and sharpens at —60°C (width ca. 50 Hz). Rapid exchange of tellurium has recently been observed in aryl-(alkyl-)phosphines [3], $(Me_2N)_3P$/$(Me_2N)_3PTe$ mixtures [2], and in the *cis* isomer of a monotelluride of I (R = Me, X = t-Bu) [4], but the effects of spin relaxation of the type outlined above have not been previously reported.

Tellurium is clearly much more mobile than selenium in these systems, although a 1/1 mixture of I (R = t-Bu, X = NMe_2) and $[Me_2NP(Se)NBu\text{-}t]_2$ [8] rearranges to II (Y = Se) very rapidly (within several minutes) on dissolution in benzene. However, even at ca. 140°C neither monoselenide exhibits selenium exchange on the NMR timescale. At ca. 160°C, when the phosphorus—selenium bond does become labile, the isomer (m.p. 102—104°C) completely isomerises to the isomer (m.p. 126—127°C) which has the same configuration as the single monotelluride obtained. It is apparent, therefore, that the lability of the P—Te bond precludes the formation of more than one isomer of II (Y = Te).

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