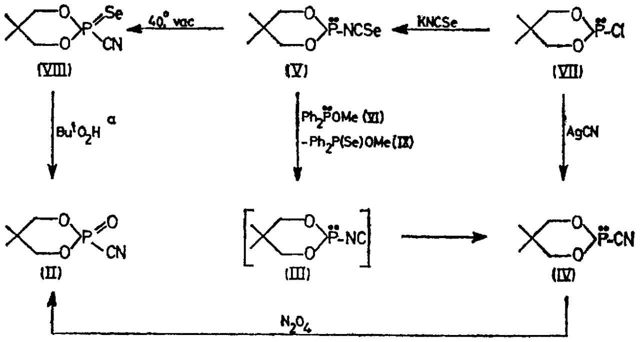
# Deselenization of Dialkyl Phosphoroisoselenocyanatidite

By Wojciech J. Stec,* Teresa Sudoł (Mrs), and Bogdan Uznański

(*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90—362 Łódź, Boczna 5 Poland*)

*Summary* Attempts to distil dialkyl phosphoroisoselenocyanatidite (V) caused its rearrangement to dialkyl cyanophosphoroselenoate (VIII), and treatment of (V) with the phosphinite (VI) gives dialkyl phosphorocyanidite (IV); these observations indicate the thermodynamic instability of the intermediate dialkyl phosphoroisocyanidite (III), which has not been identified by physical methods but is supported by the proposed reaction mechanism.

We have recently reported the rearrangement of dialkyl phosphoroisocyanidate (I) to the isomeric cyanidate (II) which may be explained in terms of the 'hard-soft acid-base' concept.[2] The less hard carbon atom of the cyanide ion attacks the phosphorus atom of the phosphoryl group more readily than the very hard nucleophilic nitrogen atom. Thus dialkyl phosphoroisocyanidite (III) should rearrange to the corresponding phosphorocyanidite (IV) even more readily due to the enhanced soft character of the trivalent phosphorus atom. We have now attempted to synthesise (III) and test its thermodynamic stability. As the most probable way of preparation of (III) we chose deselenization of dialkyl phosphoroisoselenocyanatidite (V) with methyl diphenylphosphinite† (VI).[3] (V) was obtained by the reaction of dialkyl phosphorochloridite (VII) with potassium isoselenocyanate[4] in dimethoxyethane solution. Separation of inorganic salts and removal of solvent left an oily residue, which, by $^{31}P$ n.m.r. spectroscopy was shown to contain mainly one compound (75%, $\delta_{31P} = -106$), contaminated with starting material (VII) (25%, $\delta_{31P} = -147{\cdot}5$). The proton-noise decoupled $^{31}P$ n.m.r. spectrum revealed the triplet (1:1:1) structure of the signal at $\delta_{31P} = -106$ suggesting the presence of a P–N bond in the product,[5] ($^1J_{P-^{14}N}$ 68 Hz). Its isoselenocyanato structure was shown by a strong, broad band in the i.r. spectrum at 1985 cm$^{-1}$ (benzene), characteristic of the NCSe group attached to a P$^{III}$ atom.[4] Attempts to isolate (V) by means of high vacuum short path distillation caused its rearrangement to isomeric dialkyl cyanophosphoroselenoate (VIII), which was isolated *via* sublimation, m.p. = 114—115°; $\delta_{31P}$ $\{^1H\} = -27{\cdot}5$ (singlet), $^1J_{PSe}$ 1040 Hz; i.r. $\nu_{CN} = 2200$ cm$^{-1}$ (weak, sharp), m.s. (70eV), base peak *m/e* = 41, parent ion *m/e* = 239 (21%), 237 (10%).



Scheme. [a] Oxidation performed in 8 mm n.m.r. tube and monitored by $^{31}P$ n.m.r.; (II) was not isolated.

In the light of this rearrangement we decided to perform the deselenization on crude (V). Its treatment with (VI) in benzene solution caused immediate cleavage of the C=Se bond with formation of methyl diphenylphosphinoselenoate (IX)‡ and a second product, ($\delta_{31P} = -100{\cdot}7$; i.r. $\nu_{CN} = 2170$ cm$^{-1}$ (medium, sharp). The deselenization process was independently monitored by i.r. (KBr cell, benzene solution with compensation) and $^{31}P$ n.m.r. (sealed n.m.r. tube). In the i.r. spectrum it was possible to observe the disappearance of the $\nu_{NCSe}$ band of (V) and the simul-

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† When trimethyl or triethylphosphite were used for deselenization of (V), the resulting phosphoroselenoates were found difficult to separate from the reaction mixture due to the similarity of their boiling points to that of (IV).

‡ M.p. 86—87°, $\delta_{31P} = -87{\cdot}5$, $^1J_{PSe}$ 837 Hz, $\delta_{OMe}$ ($^1H$ n.m.r.) 1·9 (int. Me$_4$Si, CDCl$_3$). Negative values of $^{31}P$ n.m.r. chemical shifts are reported for compounds absorbing at lower field than 85% H$_3$PO$_4$, used as external standard.

taneous appearance and increase of intensity of a new band at 2170 cm$^{-1}$ (medium, sharp). The $^{31}$P n.m.r. spectrum recorded 5 minutes after charging of the tube with both reactants (at $-50°$) showed only the presence of (IX) and the product $\delta_{31P} = -100{\cdot}7$ p.p.m.§ The proton-noise decoupled spectrum revealed the singlet nature of both signals. Since (III) was expected in the $^{31}$P $\{^1$H$\}$ n.m.r. spectrum as a (1:1:1) triplet due to spin–spin interaction of $^{31}$P with the $^{14}$N nucleus of the isonitrile group, the product was suspected to have the structure (IV). This was supported by comparison of its spectral ($^1$H, $^{31}$P n.m.r., i.r., m.s.) properties with those of an authentic sample of (IV) obtained independently, by reaction of (VII) with AgCN in acetonitrile solution¶ according to the procedure described by Coskran *et al.*[6] Oxidation of (IV) with $N_2O_4$†† in $CH_2Cl_2$ solution at $-40°$ gave (II) and reaction with KNCSe in dimethoxyethane produced (VIII). Thus the product of deselenization of (V) with (VI), isolated in 60% yield, has the cyanide structure (IV). The presence of a P–N bond in (V) ($^1J_{P-^{14}N}$, $\nu_{NCSe}$) as well as the presence of P–C bond in (IV) (independent synthesis, $\nu_{CN}$) are unambiguous. In the light of our previous work[1] there is no doubt that (III) must be formed by deselenization of (V), but under the reaction conditions, (III) immediately isomerizes to the thermodynamically more stable (IV). It is not certain whether the (III)→(IV) rearrangement is catalysed by the presence of ionic species (traces of KNCSe) or by (VI). The influence of such catalysts has been noticed during our studies on the rearrangement of dialkyl phosphorothiocyanatidates.[7]

The rearrangement, (III)→(IV), supports our predictions based on the 'hard-soft acid-base' concept and provides new information about the stability of acidic isonitriles.

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§ (VII), present in crude (V) also contaminated the final reaction product.

¶ Reaction of (VII) with silver cyanide or cuprous cyanide always gave product (IV) contaminated with the starting chlorophosphite.

†† (II) is obtained in analytically pure form by the reaction of methyl phosphite with cyanogen chloride, yield 85%, m.p. 68—69° (in our previous work[1] erronously given as 79—81° due to contamination with products of hydrolysis).

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