*5,6,7,8-Tetrahydro-*D*-monapterin-dihydrochlorid* (*IV*)5). Die Darstellung, ausgehend von II [5], erfolgt analog zu III mit gleicher Ausbeute. – ^{1}H-NMR. (2,9 N DCl): 4,95–4,15, *m*, 7 H: H–C(6), 2 H–C(7), H–C(1′), H–C(2′) und 2 H–C(3′). (1,5 N NaOD): 4,55–3,75, *m*, 7 H: H–C(6), 2 H–C(7), H–C(1′), H–C(2′) und 2 H–C(3′). – ^{13}C-NMR.: IV zeigt im Prinzip eine analoge Duplikation der Signale wie III (vgl. Fussnote 7). Unter gleichen Bedingungen (3,0 N NaOD, pD > 13,5) sind jedoch bei IV die Differenzen der unterschiedlichen chemischen Verschiebungen kleiner und daher teilweise nicht beobachtbar. Änderungen der Bedingungen (1,5 N NaOD, pD = 10,6) ergeben neue chemische Verschiebungen und Signalaufspaltungen. (1,5 N NaOD)6): 161,84, 161,65, C(4); 154,11, C(2); 152,80, 152,52, C(8a); 99,94, 99,62, C(4a); 71,77, 71,45, 70,97, C(1′) und C(2′); 63,91, C(3′); 51,53, 51,13, C(6); 42,88, C(7). (3,0 N NaOD)6): 167,20, 167,00, C(4); 158,15, C(2); 151,92, C(8a); 101,80, C(4a); 71,96, 71,77, C(1′) und C(2′); 64,72, C(3′); 52,41, 52,20, C(6); 43,39, 43,00, C(7). – FD. [*m/e* (rel. %)]: 258 (M^++H, 100), 257 (M^+, 7). – UV. (sauerstofffreies H_2O, pH = 4,3): λ_{max} = 267 nm (ε = 9600). – DC.: Lsgm. A: Rf = 0,11; Lsgm. B: Rf = 0,30; Lsgm. C: Rf = 0,10.

$C_9H_{15}N_5O_4, 2HCl$	Ber.	C 32,74	H 5,19	Cl 21,48	N 21,22%
(330,17)	Gef.	,, 31,22	,, 5,41	,, 22,00	,, 20,09%

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[1] 54. Mitt.: *E. Khalifa, P. K. Sengupta, J. H. Bieri & M. Viscontini*, Helv. *59*, 242 (1976).
[2] *H. Rembold & W. L. Gyure*, Angew. Chem. *84*, 1088 (1972); *R. L. Blakley*, 'The Biochemistry of Folic Acid and Related Pteridines', Wiley, New York 1969.
[3] *L. Jaenicke & C. Kutzbach*, Fortschr. Chem. org. Naturstoffe *21*, 183 (1963); *W. E. Frei*, Dissertation, Universität Zürich 1971; *M. Viscontini & Y. Furuta*, Helv. *56*, 1819 (1973).
[4] *M. Viscontini & R. Provenzale*, Helv. *51*, 1495 (1968).
[5] *M. Viscontini, R. Provenzale, S. Ohlgart & J. Mallevialle*, Helv. *53*, 1202 (1970).
[6] *A. Bobst & M. Viscontini*, Helv. *49*, 875 (1966).
[7] *L. Ernst & W. Trowitzsch*, Chem. Ber. *107*, 3771 (1974).
[8] *G. Müller & W. v. Philipsborn*, Helv. *56*, 2680 (1973).
[9] *U. Ewers, H. Günther & L. Jaenicke*, Chem. Ber. *106*, 3951 (1973).
[10] *W. Frick, R. Weber & M. Viscontini*, Helv. *57*, 2658 (1974).

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28. Organic Phosphorus Compounds 68
The Direct Synthesis of Tri(alkyl- and arylseleno)phosphites and of Tris(*p*-anisyltelluro)phosphite [1]

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(19. XI. 75)

Summary. White phosphorus reacts with organic diselenides in a dipolar aprotic solvent in the presence of a base with the formation of tri(alkyl- or aryl-seleno)phosphites in good yield.

$$P_4 + 6\,RSeSeR \xrightarrow{B} 4\,(RSe)_3P$$

Tri(methylseleno)phosphite shows a ^{31}P-chemical shift = −107 ppm ($J_{P,^{77}Se}$ = 233 Hz). It is readily oxidized in air to the corresponding selenophosphate, $(CH_3Se)_3P{=}O$, ^{31}P-chemical shift = −16 ppm.

Tri(phenylseleno)phosphite reacts readily with mercury oxide to give the tri(phenylseleno)phosphate, a yellow solid of m.p. 105–110°. It also reacts with sulfur in refluxing benzene solution to give tri(phenylseleno)thiophosphate, also a yellow solid of m.p. 55–58°. However, an attempt to prepare tri(phenylseleno)selenophosphate failed. Under the same conditions as given above,

white phosphorus also reacts with di-*p*-anisyl ditelluride to give tris(*p*-anisyltelluro)phosphite, shiny, rusty brown crystals which decompose rapidly at room temperature, but are stable for several months when kept in acetone solution at – 20°.

Tri(alkyl- or aryl-seleno)phosphites are an unknown class of compounds[1]). Although tri(phenylseleno)phosphite, $(C_6H_5Se)_3P$, was deemed to be formed from phosphorus trichloride and selenophenol, it was not isolated because it was said that it oxidized spontaneously to the corresponding phosphate [2].

$$3\ \mathrm{PhSeH} + \mathrm{PCl_3} \longrightarrow [(\mathrm{PhSe})_3\mathrm{P}] \xrightarrow{[O]} (\mathrm{PhSe})_3\mathrm{PO}$$

In addition, the following system has been described [3].

$$i\text{-PrOC(Se)SeK} + \mathrm{POCl_3} \longrightarrow [i\text{-PrOC(Se)Se}]_2 + \mathrm{PCl_3} \longrightarrow [i\text{-PrOC(Se)Se}]_3\mathrm{P}$$

Furthermore, the chemistry of dialkyl hydrogen selenophosphites which are obtained from the interaction of hydrogen selenide with dialkylchlorophosphites in benzene solution in the presence of a tertiary base such as pyridine or triethylamine, has been investigated in some detail [4].

$$(\mathrm{RO})_2\mathrm{PCl} + \mathrm{H_2Se} + \mathrm{R_3N} \longrightarrow (\mathrm{RO})_2\mathrm{P(Se)H} + \mathrm{R_3N \cdot NCl}$$

We have now found that white phosphorus reacts with organic diselenides in a dipolar aprotic solvent in the presence of a base with the formation of tri(alky- or aryl-seleno)phosphites. The reaction proceeds exceptionally smoothly under very mild conditions. A general procedure is as follows. About 1 ml of 15 N potassium hydroxide is added to a stirred mixture of 1 g atom of finely divided phosphorus and 1.5 mol of diselenide in 500 ml acetone under nitrogen. The reaction is exothermic and the temperature is maintained at 30–50°. After all the phosphorus is consumed ($^1/_2$ to 1 hour) the product is isolated. A very efficient hood is necessary when preparing tri(methylseleno)phosphite because this product has an extraordinary repulsive odor.

$$\mathrm{P_4} + 6\ \mathrm{RSeSeR} \xrightarrow{B} 4\ (\mathrm{RSe})_3\mathrm{P}$$

While the reaction of white phosphorus with dialkylperoxides has not been investigated *per se*, but only in the presence of an olefin [5], it has been reported [6] that dialkyldisulfides react with white phosphorus under similar conditions as the dialkyldiselenides and give a high yield of tri(alkylthio)phosphites.

$$\text{Olefin} + \mathrm{P_4} + (t\text{-BuO})_2 \xrightarrow[7\,h]{150\text{–}160°} \mathrm{R_xP_4O_2H_2} + 2\ \mathrm{C_4H_8}$$

$$\mathrm{P_4} + 6\ \mathrm{RSSR} \longrightarrow 4\ (\mathrm{RS})_3\mathrm{P}$$

Whereas tri(phenylseleno)phosphite is a yellow, crystalline solid which is only slightly soluble in organic solvents, tri(methylseleno)phosphite is a yellow to orange liquid which is soluble in organic solvents and is therefore well suited for NMR.-investigations.

It shows in CCl_4 solution in the ^{1}H-NMR. spectrum a signal for CH_3 centered at 2.17 ppm, $^3J_{P,H} = 7.0$ Hz, $^2J_{^{77}Se,H} = 11$ Hz; and in the ^{31}P-NMR. spectrum a signal at -107 ppm, $^1J_{^{31}P,^{77}Se} = 233$ Hz (neat).

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[1]) After conclusion of our work a paper appeared which described the synthesis of several methylseleno-substituted trivalent phosphorus compounds by reaction of $>$P—Cl with $\geqslant$SiSeCH$_3$ [17].

The product, before distillation, contained a signal at -16 ppm in the ^{31}P-NMR. spectrum which probably was due to the presence of $(CH_3Se)_3PO$; this triselenophosphate showed in the ^{1}H-NMR. spectrum a signal for CH_3 centered at 2.31 ppm, $^3J_{P,H} = 13.8$ Hz, $^2J_{^{77}Se,H} = 10.5$ Hz.

On exposure to air tri(methylseleno)phosphite is readily oxidized to the phosphate $(CH_3Se)_3PO$.

Previously ^{31}P-^{77}Se coupling constants have been reported in P_4Se_3 [7] substituted triarylphosphine selenides [8], and some other phosphine selenides [9–11], and selenophosphates [10][11]. Only one tervalent organophosphorus selenium compound, *i.e.*, $(CH_3)_2PSeCH_3$ was investigated previously by NMR.-spectroscopy [12]. In that compound the coupling constants were: $^2J_{P,H} = +7.0$; $^3J_{P,H} = +7.0$; $^2J_{^{77}Se,H} = +10.7$; $^1J_{P,^{77}Se} = -205 \pm 6$ Hz [12].

Comparison of the ^{31}P-*chemical shifts of trimethyl-, tri(methyl-thio)-, and tri(methylseleno)-phosphite*

Compound	^{31}P-chem. shift (ref. 85% H_3PO_4)	Δppm	Ref.	Coupl. const $J_{P,H}$ (Hz)	Ref.
$(CH_3O_3)P$	-141.0		[13]	10.8	[14]
		16.5			
$(CH_3S)_3P$	-124.5		[13]	9.8	[14]
		17.5			
$(CH_3Se)_3P$	-107.0		[a]	7.0	[a]

[a] This work.

Tri(phenylseleno)phosphite reacted readily with mercury oxide to give the tri(phenylseleno)phosphate, a yellow solid of m.p. 105–110° (Lit. [2] m.p. 110°). It also reacted with sulfur in refluxing benzene solution to give tri(phenylseleno)thiophosphate, also a yellow solid of m.p. 55–58°. However an attempt to prepare tri(phenylseleno)selenophosphate by interaction of tri(phenylseleno)phosphite with red selenium in refluxing benzene solution failed. Selenium was not consumed.

$$(PhSe)_3P + HgO \longrightarrow (PhSe)_3P{=}O + Hg$$
$$(PhSe)_3P + S \longrightarrow (PhSe)_3P{=}S$$
$$(PhSe)_3P + Se \not\longrightarrow (PhSe)_3P{=}Se$$

White phosphorus also reacts with di-*p*-anisyl ditelluride in acetone solution in the presence of KOH to give tris(*p*-anisyltelluro)phosphite in shiny, rusty brown crystals. In the crystalline state this compound is unstable and decomposes rapidly at room temperature. However, in acetone solution the compound seems to be stable for several months, if the solution is kept at $-20°$.

$$P_4 + 6\,p\text{-}CH_3OC_6H_4TeTeC_6H_4OCH_3\text{-}p \xrightarrow{OH^-} 4\,(p\text{-}CH_3OC_6H_4Te)_3P$$

Experimental Part[2]

(with Miss *Ch. Frauenknecht* and Mr. *L. Widmer*)

1. *$(C_6H_5Se)_3P$* (I). A mixture of 0.31 g (0.01 mol) of white phosphorus and 30 ml of acetone was heated under nitrogen to 50°. The mixture was stirred vigorously and cooled to 30°, so that

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[2] Microanalyses were carried out by *W. Manser*, ETH Zürich. ^{31}P- and ^{1}H-NMR. spectra were run on an HA 60 IL *Varian* spectrometer using H_3PO_4 or TMS as reference.

the phosphorus solidified in a finely divided state. To this mixture was added with vigorous stirring 4.68 g (0.015 mol) of diphenyl diselenide and 0.01 ml of 15N KOH. The temperature was maintained at 30–35°. All diphenyl diselenide dissolved and the color of the solution turned orange. After 30 min all the phosphorus was consumed and a crystalline slightly yellow precipitate had formed. The supernatant liquid was yellow colored. After standing overnight, the crystals were filtered, washed with acetone, and dried under vacuum. Another crop of yellow crystals was obtained from the mother liquor after concentration and cooling to –21°. Total yield 4,9 g (= 98%), m.p. 91–96°.

^{1}H-NMR. (in CCl_4): *o*- and *m*-H at 7.14 ppm (*m*, 3.01 H); *p*-H at 7.5 ppm (*m*, 1.99 H).

$C_{18}H_{15}PSe_3$	Calc.	C 43,31	H 3.03	Se 47.45	P 6.21%
(499.19)	Found	,, 43.28	,, 3.09	,, 47.80	,, 5.85%

2. *$(CH_3Se)_3P$* (II). From 2.79 g (0.089 mol) of white phosphorus, 250 ml of acetone, 24.23 g (0.134 mol) of $CH_3SeSeCH_3$ (obtained from Se, NaOH, rongalit and $(CH_3)_2SO_4$ in H_2O according to [15] in 13.4% yield, b.p. 151°) and 0.089 ml of 15N KOH. After stirring for 1 h at 35° a small amount of a greenish powder was filtered, and from the filtrate the solvent evaporated. As a residue a yellow oil was obtained which did not crystallize when cooled to –21°. It was therefore distilled to give 11 g (= 39.43%) II, a yellow oil with a very repulsive odor, b.p. 45–50°/0.1 Torr. ^{1}H-NMR. (in CCl_4): CH_3 at 2.17 ppm ($^3J_{P,H} = 7.0$ Hz, $^2J_{Se,H} = 11$ Hz). – ^{31}P-NMR. (neat): –107 ppm, $J_{P,Se} = 233$ Hz.

Before distillation another signal at –16 ppm could be seen in the ^{31}P-NMR. spectrum which probably was due to the presence of $(CH_3Se)_3PO$. – ^{1}H-NMR. (in CCl_4): CH_3 at 2.31 ppm ($^3J_{P,H} =$ 13.8 Hz; $^2J_{Se,H} = 10.5$ Hz).

$C_3H_9PSe_3$ (312.98) Calc. C 11.51 H 2.89% Found C 12.41 H 3.16%

3. *$(C_6H_5Se)_3P{=}S$* (III). A mixture of 500 mg (1 mmol) of $(PhSe)_3P$ and 32 mg (1 mmol) of sulfur in 20 ml of benzene was refluxed for 7 h. After removing benzene in vacuum, a yellow oil remained as a residue which suddenly crystallized to give yellow crystals, m.p. 54–57° (orange melt). They were recrystallized from ethanol at –21° to give yellow crystals of m.p. 55–58°.

$C_{18}H_{15}PSSe_3$ (531.25) Calc. C 40.69 H 2.84% Found C 42.28 H 3.31%

4. *$(C_6H_5Se)_3P{=}O$* (IV). A mixture of 0.5 g (1 mmol) of $(PhSe)_3P$, 0.216 g (1 mmol) of HgO and 15 ml of benzene was stirred for 4 h. Metallic mercury precipitated. The solution was decanted from the mercury and the solvent evaporated to give 0.45 g of a yellow solid as a residue, which was washed with petroleum ether and dried in vacuum, m.p. 105–110° (Lit. [2] m.p. 110°).

From the wash-petroleum is obtained by evaporation of the solvent a yellow solid of m.p. 57–58° which was identified as diphenyl diselenide.

$C_{12}H_{10}Se_2$ (312.12) Calc. C 46.17 H 3.22% Found C 46.17 H 3.44%

5. (p-*$CH_3OC_6H_4Te)_3P$*) (V). From 0.26 g (0.084 mol) of white phosphorus, 20 ml acetone, a drop of 15N KOH and 4.5 g (0.096 mol) of *p*-$CH_3OC_6H_4TeTeC_6H_4OCH_3$-*p* [16] as described in 1. All the phosphorus was consumed and a dark red solution was obtained. The solution was filtered under argon and the filtrate cooled to –20° for 48 h. Thereby V crystallized out in shiny, rust brown crystals. They were filtered off, washed with cold acetone (–50°) and dried in vacuum (yield 1.65 g = 36.7%). When argon was admitted to the flask at room temperature, the crystals turned beige-white and evolved white fumes. Another crop of crystals was obtained from the mother liquor. These were stored at –20° in acetone solution.

^{1}H-NMR. (in CD_3COCD_3): CH_3 at 3.75 ppm (*s*, 9 H); C_6H_4 at 6.75 ppm (complex *d*, $J_{H,H}$ 8.5 Hz, 6 H) and at 7.67 ppm (complex *d*, $J_{H,H}$ 8.5 Hz, 6 H).

$C_{21}H_{21}O_3PTe_3$ (734.5) Calc. C 34.31 H 2.86% Found C 33.97 H 3.00%

REFERENCES

[1] Part 67: *W. C. Kaska & L. Maier*, Helv. *57*, 2550 (1974).
[2] *N. Petragnani, V. G. Toscano & M. Moura Campos*, Chem. Ber. *101*, 3070 (1968).
[3] *A. Rosenbaum*, J. prakt. Chemistry *37*, 200 (1968); *A. Rosenbaum, H. Kirchberg & E. Leibnitz*, ibid. *19*, 1 (1963).

[4] *C. Krawiecki, J. Michalski, R. A. Y. Jones & A. R. Katritzky*, Rocz. Chem. *43*, 869 (196
W. Gerrard & H. R. Hudson in 'Organic Phosphorus Compounds', ed. G. M. Kosolapoff
L. Maier, John Wiley and Sons, Inc., Vol. *5*, 113 (1973).
[5] *W. E. Garwood, L. A. Hamilton & F. M. Seger*, Ind. Eng. Chemistry *52*, 401 (1960); U.S. Pa
2731458 (1956); *L. Maier*, in 'Topics in Current Chemistry' *19*, 1 (1971).
[6] *C. Wu*, J. Amer. chem. Soc., *87*, 2522 (1965).
[7] *R. A. Dwek, R. E. Richards, D. Taylor, G. J. Penny & G. M. Sheldrick*, J. chem. Soc. (A) *196*
935.
[8] *R. P. Pinnel, C. A. Megerle, S. L. Manatt & P. A. Kroon*, J. Amer. chem. Soc. *95*, 977 (1973).
[9] *I. A. Nuretdinov & E. I. Liginova*, Izv. Akad. Nauk, SSSR *1971*, 2360.
[10] *W. J. Stec, A. Okruszek, B. Usnanski & J. Michalski*, Phosphorus *2*, 97 (1972).
[11] *W. McFarlane & D. S. Rycroft*, J. chem. Soc. Dalton Trans., *1973*, 2162.
[12] *W. McFarlane & J. A. Nash*, Chem. Commun. *1969*, 913.
[13] *V. Mark, C. H. Dungan, M. M. Crutchfield & J. R. Van Wazer*, in 'Topics in Phosphor
Chemistry', Vol. 5 (1967).
[14] *G. Mavel*, in 'Annual Reports on NMR-Spectroscopy, Vol. 5B (1973).
[15] *M. L. Bird & F. Challenger*, J. chem. Soc. *1942*, 570.
[16] *I. D. Sadekov, L. M. Sayapina, A. Ya. Bushkov & V. I. Minkin*, Žur. Obšč. Chim. *41*, 271
(1971); Engl. transl., p. 2747.
[17] *J. W. Anderson, J. E. Drake, R. T. Hemmings & D. L. Nelson*, Inorg. nucl. Chemistry Letters *1*
233 (1975).

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29. ^{15}N Labelling: Potassium Azide, Tetrazoles and Imidazoles

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(30. IV. 75)

Summary. A simplified high-yield preparation of end-labelled potassium azide from $K^{15}NO$ is described. Treatment of 4-chloropyrimidines with $K^{15}NN_2$ and subsequent gas-phase pyrolysi gives ring-labelled 1-cyanoimidazoles in 80–100% yields. The cyano-groups in the latter ar easily removed by hydrolysis.

^{15}N labelling of *inter alia* heterocyclic compounds is of importance for the elucidation of chemical and biochemical reaction pathways. Such labellings usually require lenghty and/or expensive syntheses. A simple way to introduce ^{15}N-labelled substituents in (hetero)aromatic molecules is *via* nucleophilic substitution with azide ion. Labelled azide is, however, very expensive and not widely distributed.

We now report a simple and inexpensive preparation of end-labelled potassium azide from commercial potassium nitrate, as well as its use in an efficient synthesis of ^{15}N-labelled imidazoles.

1. *Potassium Azide.* End-labelled KN_3 has been prepared by *Clusius & Hürzeler* [1] by the sequence $NaNO_2 \rightarrow C_2H_5ONO \rightarrow KN_3$. The sodium nitrite was obtained by *Clusius & Hoch* [2] by reduction of KNO_3 with mercury. We have adopted these procedures for use with a standard vacuum line, and modified the reaction in such a way that the conversion of KNO_3 to KN_3 is a two-flask operation. The apparatus is shown in Fig. 1, and the procedure is described in detail in the Experimental Part.