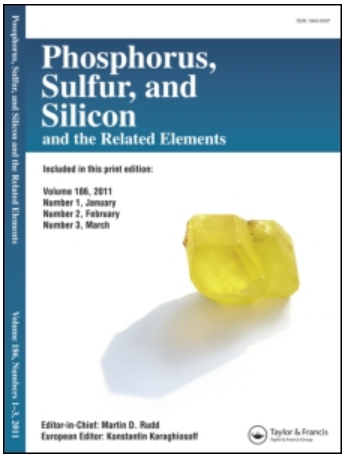

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SOME PHOSPHORYLATED DERIVATIVES OF 1- AND 2-ADAMANTANOLS AND 1-ADAMANTYLAMINE

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SOME PHOSPHORYLATED DERIVATIVES OF 1- AND 2-ADAMANTANOLS AND 1-ADAMANTYLAMINE

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The phosphorylation of 1- and 2-adamantanols and of 1-adamantylamine with $POCl_3$, $PSCl_3$, $PhOP(O)Cl_2$, $4\text{-}ClC_6H_4OP(O)Cl_2$, and PCl_3 is described and the conversion of the obtained phosphorochloridates into a number of derivatives such as phenylhydrazides, diamidates, hydrazides, hydrazones and azides is reported.

INTRODUCTION

Previous studies have described the phosphorylation of *cis*- and *trans*-4-*t*-butylcyclohexanol and *l*-menthol[1–3], *exo*- and *endo*-norborneol,[4] borneol and isoborneol,[5] and their conversion into a range of phosphorylated derivatives. Such compounds are of interest as potential pesticides and in this paper the work has been extended to an investigation of the phosphorylation of the tricyclic compounds 1- and 2-adamantanol and 1-adamantylamine.

DISCUSSION

1- and 2-Adamantanols were phosphorylated with phosphorus oxychloride, thiophosphoryl chloride, phenyl phosphorodichloridate and *p*-chlorophenylphosphorodichloridate to give the expected chloridates in all cases, except for the reaction of 1-adamantanol with phosphorus oxychloride (Schemes 1, 2 and 3).

The phosphorochloridates were converted into a number of derivatives such as phenylhydrazides, diamidates, hydrazides, hydrazones and azides. Selected pyrophosphates and pyrophosphoramidates were also prepared from the appropriate chloridates.

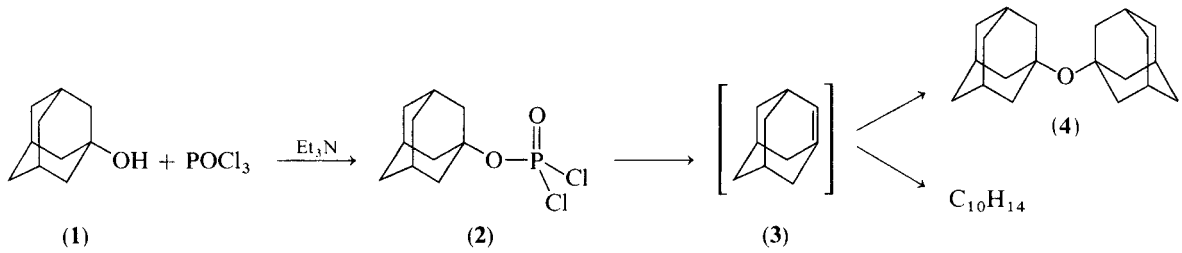
Reaction of 2-adamantanol with phosphorus trichloride gave 2-adamantylphosphorodichloridite which was characterised as the N,N′-diphenyldiamidite (Scheme 3).

1-Adamantylamine was phosphorylated with phosphorus oxychloride, phenylphosphorodichloridate and *p*-chlorophenylphosphorodichloridate to give the expected phosphoramidic chlorides which were converted to the phosphorohydrazides. These with methyl and phenylisocyanates afforded the N-substituted carbamoyl derivatives. Selected hydrazones, azides, amidic phosphates and pyrophosphoramides were also obtained (Scheme 4).

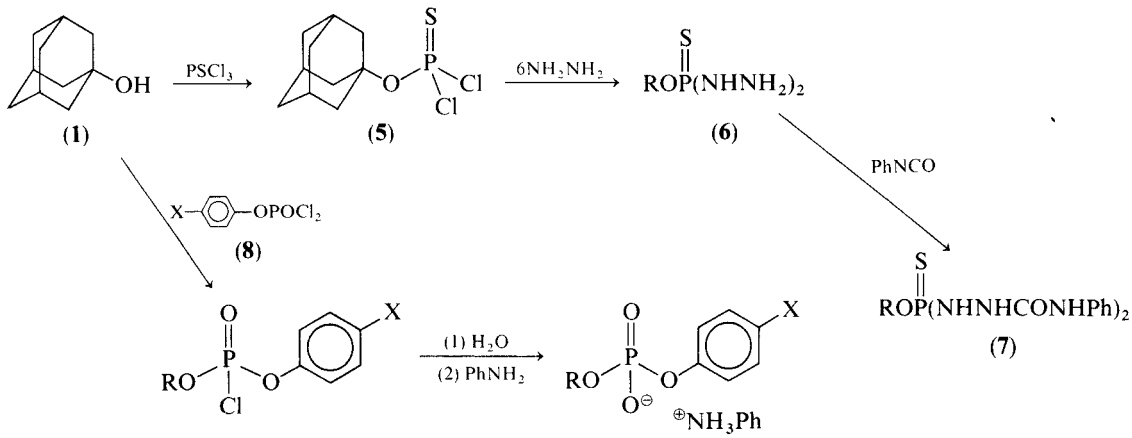
1-Adamantanol (1) (Scheme 1) with phosphorus oxychloride gave an unknown compound of empirical formula $C_{10}H_{14}$ and some *bis*(1-adamantyl)ether (**4**). The reaction probably occurs *via* the phosphorodichloridate (**2**) and adamantene (**3**) which by addition of 1-adamantanol gives the ether (**4**) (cf. ref. 6). Adamantene is unstable and readily dimerises to cyclobutane derivatives[7], but these were not indicated in the mass spectrum of the unknown compound.

Pyrophosphates were readily obtained by treatment of the phosphoramidic chlorides with aqueous pyridine; thus the N-phenylphosphoramidic chloride (**15a**) gave P^1,P^2-dianilino-P^1, P^2-di(2-adamantyl) pyrophosphate (**16a**) while the analogous N-cyclohexyl compound (**15b**) afforded the corresponding pyrophosphate (**16b**). 2-Adamantyl O - phenylphosphorochloridate (**19**) was similarly converted to the pyrophosphate (**16c**). The P^1,P^2-dianilinopyrophosphate (**16a**) was hydrolysed (boiling aqueous sodium hydroxide) and acidification gave the N-phenylamidic phosphate (**15j**).

2-Adamantanol (**13**) was phosphorylated with phosphorus trichloride to the phosphorodichloridite (**22**) which was characterised by treatment with aniline to give the N,N′diphenyldiamidite (**23**). Hydrolysis of 2-adamantyl phosphorodichloridite



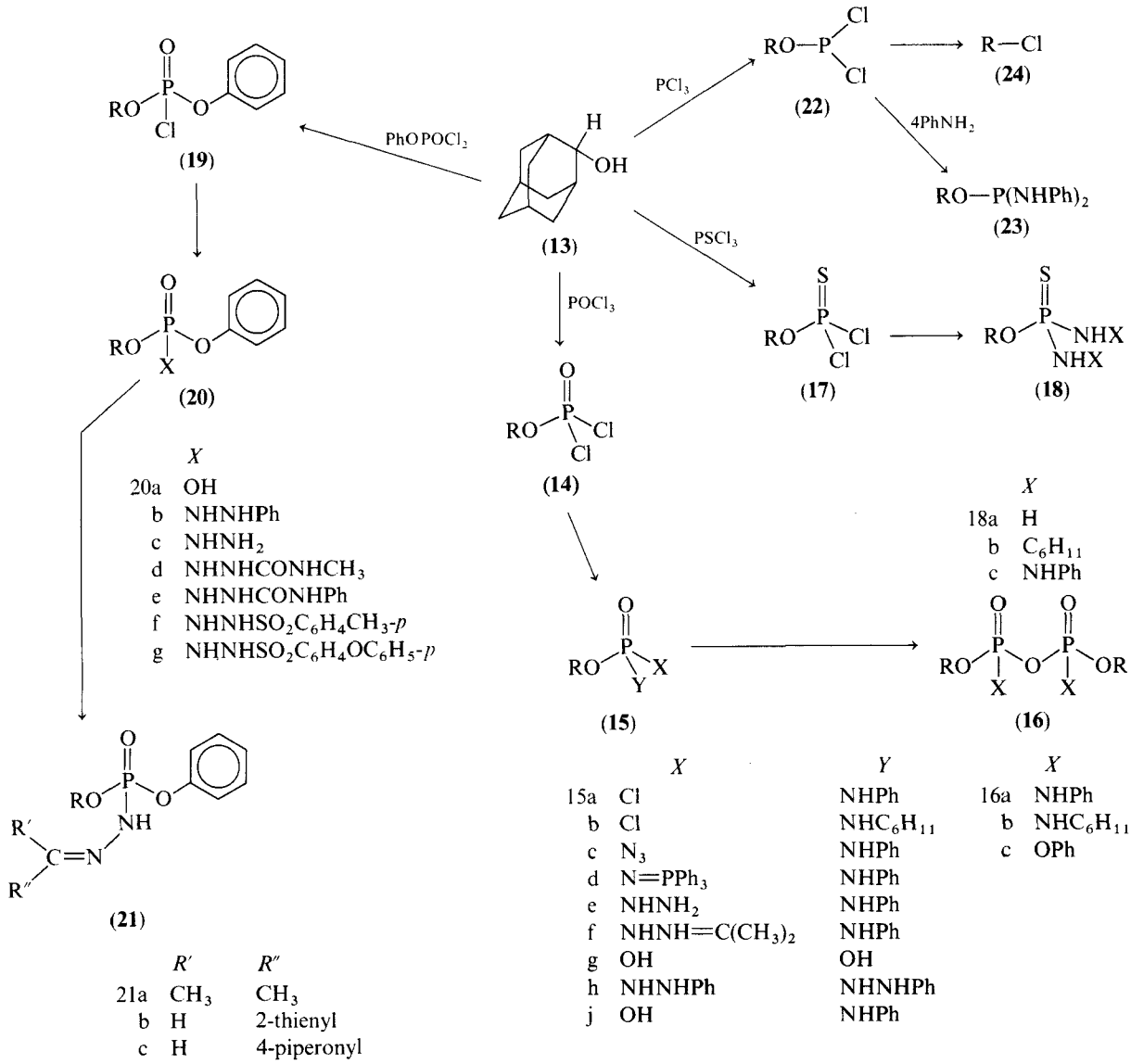
SCHEME 1



	X	Y
10a	H	NH_2
b	H	NHNHCONHPh
c	Cl	NH_2
d	Cl	NHPh

	X	R′	R″
11a	H	CH_3	CH_3
b	Cl	CH_3	CH_3
c	Cl	H	4-piperonyl
d	Cl	H	2-pyridyl
e	Cl	H	2-thienyl

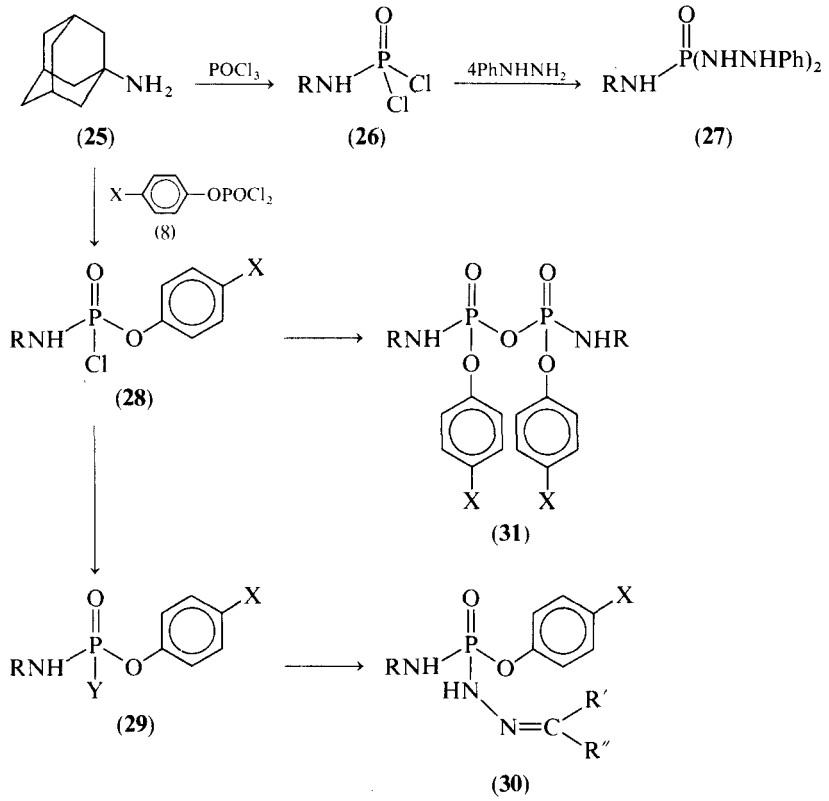
SCHEME 2 (R = 1-adamantyl)



SCHEME 3 (R = 2-adamantyl)

(**22**) (boiling water 6 hr.) gave 2-chloroadamantane (**24**) instead of the expected 2-adamantanol (*trans*-4-*t*-butylcyclohexyl and cholesteryl phosphorodichloridites both gave the corresponding alcohols under these conditions, by hydrolysis of the initially formed phosphites.[8] A competing displacement by chloride ion on the initially formed 2-adamantyl phosphite to produce the insoluble 2-chloroadamantane may well be occuring.

Attempts to phosphorylate both 1- and 2-adamantanols with phenyl *N*-phenylphosphoramidic chloride, *N*-pyrrolidinophosphoramidic dichloride and phenyl *N*-pyrrolidinophosphoramidic chloride by boiling the alcohol in toluene and triethylamine with the phosphorylating agent for 12 hr. were unsuccessful and only starting materials were recovered. This lack of phosphorylating power in these reagents reflects the deactivating effect of the adjacent secondary and tertiary nitrogens on the electrophilicity of phosphorus.



	X	Y
29a	H	$NHNH_2$
b	H	NHNHCONHPh
c	Cl	NHPh
d	Cl	NHNHPh
e	Cl	$NHNH_2$
f	Cl	$NHNHCONHCH_3$
g	Cl	NHNHCONHPh
h	Cl	N_3
i	Cl	$N{=}PPh_3$
j	Cl	OH

	X	R′	R″
30a	H	CH_3	CH_3
b	H	H	4-piperonyl
c	Cl	CH_3	CH_3
d	Cl	H	2-thienyl
e	Cl	H	4-piperonyl

SCHEME 4 (R = 1-adamantyl)

TABLE I

Compounds in Scheme 2

No.	M.p.	Yield %	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
7	210–212°	51	$C_{24}H_{31}N_6O_3PS$	55.9	5.9	16.0	56.0	6.0	16.3
9 (X=H)	oil	63[a]							
(X=Cl)	oil	84[a]							
10a	69–73°	20[b]	$C_{16}H_{23}N_2O_3P$	59.4	7.4	8.8	59.6	7.1	8.7
10b	152–156°	67	$C_{23}H_{28}N_3O_4P$	62.4	6.1	9.75	62.6	6.35	9.5
10c	126–130°	77	$C_{16}H_{22}ClN_2O_3P$	54.2	6.1	7.55	53.9	6.2	7.85
10d	152–154°	41	$C_{22}H_{25}ClNO_3P$	63.2	6.2	3.4	63.2	6.0	3.35
11b	130–131°	70	$C_{19}H_{26}ClN_2O_3P$	57.45	6.7	7.2	57.5	6.6	7.1
11c	168–170°	65	$C_{24}H_{26}ClN_2O_5P$	59.2	5.2	5.4	58.9	5.3	5.7
11d	136–138°	63	$C_{22}H_{25}ClN_2O_3P$	59.2	5.9	9.5	59.3	5.6	9.4
11e	118–120°	61	$C_{21}H_{24}ClN_2O_3PS$	56.0	5.4	6.2	55.9	5.3	6.2
12 (X=Cl)	148–153°	57	$C_{22}H_{27}ClNO_4P$	60.6	6.0	3.5	60.6	6.2	3.2

[a] Characterized as solid derivatives

[b] ν_{max}3560, 3360, 3290, 3160 (NH), 1490 (arom C=C), 1200 (P=O), 1000 (P—O— alip), 930, 920 (P—O—C arom) cm^{-1}. T.l.c. (Pr^iOH—$C_6H_5CH_3$—EtOAc 5:1:2.5:1.25, a single spot RF 0.76. In EtOAc-pet ether (1:1), RF 0.45.

TABLE II

Compounds in Scheme 3

No	M.p.	Yield (%)	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
15a	143–146°	37	$C_{16}H_{21}ClNO_2P$	59.1	6.3	4.2	59.0	6.45	4.3
15b	oil	57	$C_{16}H_{27}ClNO_2P$	58.2	8.5	4.1	57.9	8.1	4.2
15d	240–242°	44	$C_{34}H_{35}N_2O_2P_2$	72.65	6.35	5.0	72.2	6.2	5.0
15e	132–135°	71	$C_{16}H_{24}N_3O_2P$	60.2	7.5	13.1	59.8	7.5	13.1
15f	178–181°	63	$C_{19}H_{28}N_3O_2P$	62.5	7.4	11.4	63.2	7.8	11.6
15j	168–173°	90	$C_{16}H_{22}NO_3P$	62.5	7.3	—	62.5	7.2	—
16a	230–233°	44	$C_{32}H_{42}N_2O_5P_2$	64.6	7.1	4.45	64.4	7.05	4.7
16b	188–192°	44	$C_{32}H_{54}N_2O_5P_2$	63.2	8.8	4.7	63.2	8.9	4.6
17	157–160°	48	$C_{10}H_{15}Cl_2OPS$	41.7	5.7	—	42.1	5.3	—
18a	190–192°	88	$C_{10}H_{19}N_2OPS$	48.6	8.1	11.7	48.8	7.7	11.4
18c	189–192°	47	$C_{22}H_{29}N_4OPS$	61.5	6.9	13.5	61.7	6.8	13.1
19	oil[a]	60							
20a	139–142°	49[b]	$C_{22}H_{28}NO_4P$	65.7	6.7	3.7	65.8	7.0	3.5
20b	162–164°	40	$C_{22}H_{27}N_2O_3P$	66.3	6.65	7.15	66.3	6.8	7.0
20c	96–99°	87	$C_{16}H_{23}N_2O_3P$	59.6	7.3	8.8	59.6	7.1	8.7
20d	143–146°	85	$C_{18}H_{26}N_3O_4P$	57.0	7.2	11.0	57.0	6.9	11.1
20e	181–183°	91	$C_{23}H_{28}N_3O_4P$	63.0	6.3	9.7	62.6	6.55	9.5
20f	133–136°	29	$C_{23}H_{29}N_2O_5P$	57.8	6.2	5.65	58.0	6.1	5.9
20g	94–98°	37	$C_{28}H_{31}N_2O_6PS$	59.95	5.9	5.1	60.6	5.6	5.05
21a	143–145°	67	$C_{19}H_{27}N_2O_3P$	63.2	7.6	8.1	63.0	7.5	7.7
21b	152–155°	77	$C_{21}H_{25}N_2O_3PS$	60.0	6.2	7.1	60.6	6.0	6.7
21c	129–131°	56	$C_{24}H_{27}N_2O_5P$	63.4	6.3	6.3	63.4	6.0	6.2

[a] Characterized as solid derivatives

[b] ^1H n.m.r. ($CDCl_3$) δ 7.45 br (3H, $\overset{+}{N}H_3^*$), 7.38–7.04, m (10 ArH), 4.52–4.38 br (IH, C*H*OP), 2.16–1.31, m (14 Ad-H). T.l.c. (EtOAc-pet ether 1:1), R_F 0.55.

TABLE III

Compounds in Scheme 4

No.	M.p.	Yield (%)	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
27	168–170°	62	$C_{22}H_{30}N_5OP$	64.75	6.8	16.6	64.2	7.3	17.0
28 (X=H)	oil[a]	49							
28 (X=Cl)	oil[a]	67							
29a	140–145°	64	$C_{16}H_{24}N_3O_2P$	59.5	7.6	12.8	59.8	7.5	13.1
29b	105–109°	80	$C_{23}H_{29}N_4O_3P$	62.5	6.6	13.0	62.7	6.6	12.7
29c	224–226°	36	$C_{22}H_{26}ClN_2O_2P$	63.4	6.3	6.9	63.4	6.2	6.7
29d	198–200°	41	$C_{22}H_{27}ClN_3O_2P$	61.3	6.3	9.9	61.2	6.3	9.4
29e	100–102°	73	$C_{16}H_{23}ClN_3O_2P$	54.1	6.5	12.05	54.0	6.5	11.8
29f	171–173°	60	$C_{18}H_{26}ClN_4O_3P$	52.5	6.1	13.5	52.4	6.3	13.6
29g	214–217°	63	$C_{23}H_{28}ClN_4O_3P$	58.6	5.8	12.1	58.2	5.9	11.8
29h	112–114°	59	$C_{16}H_{20}ClN_4O_2P$	52.4	5.3	15.1	52.4	5.5	15.3
29i	192–195°	43	$C_{34}H_{35}ClN_2O_2P_2$	67.7	6.1	4.55	67.9	5.8	4.7
29j	155–161°	50	$C_{16}H_{21}ClNO_3P$	56.6	6.2	4.4	56.2	6.2	4.1
30a	158–159°	58	$C_{19}H_{28}N_3O_2P$	62.9	7.8	11.8	63.2	7.8	11.6
30b	199–203°	51	$C_{24}H_{28}N_3O_4P$	63.75	6.25	9.6	63.6	6.2	9.3
30c	146–148°	76	$C_{19}H_{27}ClN_3O_2P$	58.0	6.7	10.5	57.7	6.8	10.6
30d	193–196°	63	$C_{21}H_{25}ClN_3O_2PS$	55.9	5.9	9.4	56.1	5.6	9.3
30e	168–170°	80	$C_{24}H_{27}ClN_3O_4P$	59.3	5.5	8.2	59.1	5.5	8.6
31 (X=H)	159–164°	37	$C_{32}H_{42}N_2O_5P_2$	64.3	7.0	4.6	64.4	7.05	4.7
31[b] (X=Cl)	214–216°	22	$C_{32}H_{40}ClN_2O_5P_2$	57.7	5.8	4.0	57.7	6.0	4.2

[a] Characterised as solid derivatives

[b] ^{1}H n.m.r. ($CDCl_3$) δ 7.4–7.05 m (8H, ArH) 5.5–5.3 (2H; NH*), 2.66–1.15 (30H, Ad-H).

EXPERIMENTAL

I.r. spectra were determined as liquid films or Nujol mulls using a Perkin Elmer 237 spectrometer. N.m.r. spectra were measured with a Varian A60A and Perkin Elmer HA 100 spectrometers using tetramethylsilane as internal standard. In the n.m.r. spectral data signals marked with an asterisk are removed by treatment with D_2O. Mass spectra were measured with an AE1 MS9 spectrometer at 70 eV.

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. T.l.c. was carried out on silica gel G plates developed with iodine vapour. Microanalyses were carried out by Butterworth Microanalytical Consultants Ltd., Teddington, England.

Attempted phosphorylation of 1-Admantanol (1) A solution of 1-adamantanol (1.52g) and triethylamine (1.01g; 1 mol. equiv.) in toluene (50 ml) was added dropwise over a period of 30 min. to a stirred solution of phosphorus oxychloride (1.53g; 1 mol. equiv.) at room temperature. The mixture was stirred for 1 hr, heated under reflux for 15 hr, and allowed to cool. Triethylamine hydrochloride (0.3g) was filtered off, and the filtrate evaporated *in vacuo*. The residue was dissolved in petroleum ether (b.p. 40–60°, 50 ml) and the ice-cold solution was decanted from a brown oil which had separated. Evaporation produced a solid (1.3g). T.l.c. (chloroform-petroleum ether (b.p. 40–60°) 2:3) showed two spots R_F 0.92, 0.58. Column chromatography (45g silica-gel 60–120 mesh; elution with chloroform-petroleum ether (b.p. 40–60°) 2:3) separated the components. The first was an unknown solid (0.75g) m.p. 141–143° (R_F 0.92). (Found: C, 89.8; H, 10.3 $C_{10}H_{14}$ requires C, 89.8; H, 10.45%). ν_{max}2680, 2655, 2620 (bridgehead C—H) 1350, 1345d, 1300, 1295d, 1105, 1035, 982, 835, 810, 770, 692 cm^{-1}.

N.m.r. δ ($CDCl_3$) 2.14 (8H), 1.69 (6H). M.s. shows a molecular ion at 134. This component was also obtained on repeated recrystallisation of the crude product from petroleum ether (b.p. 60–80°) and from methanol, m.p. 141–3°. The second component was *bis*(1-adamantyl)ether (4) (0.4g) m.p. 158–161° (lit[9] m.p. 179–182°). (Found: C, 83.9; H, 10.4. Calc. for $C_{20}H_{30}O$: C, 83.9; H, 10.5%). ν_{max}2680, 2655, 2620 (bridgehead C—H), 1360, 1352, 1348, 1345, 1320, 1318, 1300, 1280, 1260, 1190, 1180, 1120, 1103, 1095, 1090, 1075, 995, 980, 950, 940, 875, 822, 812 cm^{-1}. N.m.r. δ ($CDCl_3$) 2.09 (4H), 1.92 (6H), 1.61 (5H). M.s. shows a molecular ion at 286.

1-Adamantyl phosphorodichloridothioate (5) A solution of 1-adamantanol (1) (5.0g; 1 mol. equiv.) and pyridine (2.6g; 1 mol. equiv.) in toluene (125 ml) was gradually added during 30 min. to a stirred solution of thiophosphoryl chloride (5.58g; 1 mol. equiv.) in dry toluene (100 ml). The mixture was boiled under reflux for 24h, cooled, and pyridine hydrochloride (3.4g) filtered off. The filtrate was evaporated at 40°/7mm and triturated with petroleum ether (b.p. 60–80°, 150 ml). After removal of traces of solids, the filtrate was washed with water (3 × 100 ml), sodium bisulphite solution (2 × 75 ml), dried ($MgSO_4$) and evaporated. Recrystallisation from petroleum

ether (b.p. 40–60°) gave the *phosphorodichloridothioate* (5.2g, 55%) m.p. 198–202°. (Found: C, 417; H, 5.5. $C_{10}H_{15}Cl_2OPS$ requires C, 42.1; H, 5.3%). The Lassaigne test was positive for P,S and Cl. ν_{max} 2675, 2650, 2625, 995, 980 (P—O—C), 845 (P=S) cm^{-1}. T.l.c. (ethyl acetate-petroleum ether (b.p. 60–80°) 1:1) showed a single spot, R_F 0.79.

1-Adamantyl phosphorodihydrazinothioate (*6*) A solution of 1-adamantyl phosphorodichloridothioate (0.4g; 1 mol. equiv.) and hydrazine hydrate (0.42g; 6 mol. equivs.) in benzene (40 ml) was heated under reflux for 16 hr. The cold reaction mixture was poured onto ice and stirred for 1 hr. to give the *dihydrazinothioate* (0.35g; 90%). m.p. 184–187°. (Found: C, 43.3; H, 7.6; N, 20.5. $C_{10}H_{21}N_4OPS$ requires C, 43.5; H, 7.6; N, 20.3%). The Lassaigne test was positive for P and S. ν_{max} 3340, 3090 (NH), 2620 (bridgehead C—H), 1610 (NH_2), 980–990 (P—O—C), 845 (P=S) cm^{-1}.

N-1-Adamantylphosphoramidic dichloride (*26*) A solution of 1-adamantylamine (25) (3.02g) and triethylamine (2.02g; 1 mol. equiv.) in toluene (20ml) was added to a stirred solution of phosphorus oxychloride (3.07g; 1 mol. equiv.) in toluene (100ml) at 0°. The mixture was stirred for 1 hr. at 0° and left at room temperature for 16 hr. Triethylamine hydrochloride (2.25g) was removed and the filtrate was evaporated. The residue was crystallised from benzene-petroleum ether (b.p. 60–80°), washed with water, and recrystallised from acetonitrile-petroleum ether (bp. 60–80° to give the *phosphoramidic dichloride* (2.5g, 44%), m.p. 120–124°. (Found: C, 44.9; H, 6.0; N, 5.0. $C_{10}H_{15}Cl_2NOP$ requires C, 44.8; H, 6.0; N, 5.2%). ν_{max} 3180–3160 (NH), 1270, 1250 (P=O), 1115, 1105, 1090 (P—O—C) cm^{-1}. T.l.c. (ethyl acetate-petroleum ether (b.p. 60–80°) 1:1) showed a single spot, R_F 0.56.

Acetone 1-Adamantyl O-phenylphosphorohydrazone (*11a*) 1-Adamantyl O-phenylphosphorohydrazide (0.2g) was boiled under reflux in acetone (20 ml) for 2 hr. to give the *acetone hydrazone* (0.19g, 90%), m.p. 155–159°. (Found: C, 62.95; H, 7.85; N, 7.41. $C_{19}H_{27}N_2O_3P$ requires C, 63.0; H, 7.5; N, 7.7%). ν_{max} 3210 (NH), 1495 (C=C), 1245, 1230 (P=O doublet), 1020 (P—O—C alip), 960 (P—O—C arom.) cm^{-1}. T.l.c. (2-propanol-ethylacetate-toluene-water 5:2.5:1:1.25) showed a single spot, R_F 0.75; and ethyl acetate-petroleum ether (b.p. 60–80°) 1:1 also revealed a single spot, R_F 0.50.

2-Adamantyl dihydrogen phosphate (*15g*) 2-Adamantyl phosphorodichloridate (1.0g) was stirred with distilled water (20 ml) for 15 min., and warmed at 60°–70° for 15 min. After 6 hr. at room temperature, the precipitate was filtered off, and washed with water (100 ml). Recrystallization (acetonitrile) gave the *dihydrogen phosphate* (0.58g, 67%), m.p. 237–242°. (Found: C, 52.0; H, 7.5. $C_{10}H_{17}O_4P$ requires C, 51.7; H, 7.3%). ν_{max} 2320–2290, 1680–1630 (P—OH), 1230 (P=O) 1020 (P—O—C) cm^{-1}. T.l.c. (ethanol) gave a single spot, R_F 0.77.

2-Adamantyl N,N'-diphenylphosphorodihydrazide (*15h*) 2-Adamantyl phosphorodichloridate (2.73g) was added dropwise to a stirred solution of phenylhydrazine (4.32g; 4 mol. equivs.) in acetonitrile (40 ml). The mixture was stirred for 16 hr. and at 0° for 12 hr. The solid was filtered off, washed with water (150 ml), stirred with potassium hydroxide solution (5%; 75 ml) for 6 hr. refiltered, and washed with water and petroleum ether (b.p. 40–60°; 50 ml). Recrystallization (ethanol-petroleum ether (b.p. 60–80°)) gave the *N,N'-diphenylhydrazide* (1.9g, 46%), m.p. 164–166°. (Found: C, 64.0; H, 7.4; N, 13.8. $C_{22}H_{29}N_4O_2P$ requires C, 64.1; H, 7.0; N, 13.6%). ν_{max} 3370, 3330, 3300 (NH), 1205 (P=O), 1020 (P—O—C) cm^{-1}. T.l.c. (ethanol) revealed a single spot, R_F 0.76.

2-Adamantyl N-phenylphosphoramidic azide (*15c*) A solution of 2-adamantyl N-phenylphosphoramidic chloride (2.0g) in acetone (40 ml) was stirred with a solution of sodium azide (0.80g; 2 mol. equivs.) in water (5 ml) for 6 hr. at room temperature. Dilution with ice-water (200 ml) and extraction with ether (2 × 100 ml) gave the azide as a yellow oil (0.8g, 39%). ν_{max} 3170, 3090 (NH), 2160 (N_3), 1230 (P=O), 1010 (P—O—C) cm^{-1}. The azide (**15c**) was characterised by formation of the *triphenylphosphinimine derivative* (**15d**).

2-Adamantyl phosphorodichloridate (*4*) A solution of 2-adamantanol (13) (3.06g) and triethylamine (2.02g; 1 mol. equiv.) in benzene (150 ml) was added with stirring to an ice cold solution of phosphorus oxychloride (3.07g; 1 mol. equiv.) in benzene (30 ml). The mixture was stirred at room temperature for 2 hr. and boiled under reflux for 6 hr. Triethylamine hydrochloride (2.0g) was filtered off, and the filtrate evaporated to give the *phosphorodichloridate* as an oil (4.4g, 83%). ν_{max} 1290 (P=O), 1010, 985 (P—O—C alip.) cm^{-1}. This was characterised by preparation of solid derivatives.

2-Adamantyl N,N'-dicyclohexylphosphorodiamidothioate (*18b*) Cyclohexylamine (0.67g; 4 mol. equivs.) was added to a stirred solution of 2-adamantyl phosphorodichloridothioate (17) (0.5g) in dioxan (25ml). The mixture was heated under reflux for 8 hr. to give the *phosphorodiamidothioate* (0.3g, 42%), m.p. 142–143°. (Found: C, 64.8; H, 9.15; N, 7.5. $C_{22}H_{39}N_2OPS$ requires C, 64.4; H, 9.5; N, 6.8%). ν_{max} 3365 (NH), 1095 (P—N), 1025, 980 (P—O—C), 885 (P=S) cm^{-1}.

P^1,P^2-Di(2-adamantyl)-P^1,P^2-diphenylpyrophosphate (*16c*) A solution of pyridine in water (2.5 ml) was added to a stirred solution of 2-adamantyl O-phenylphosphorochloridate (1.0g) in pyridine (5ml). After 18 hr. the solution was poured onto ice-water (750 ml) and the solid was filtered off, washed with water (100 ml) and dried (P_2O_5, *in vacuo*) to give the *pyrophosphate* (0.2g, 29%), m.p. 118–121° (Found: C, 64.2; H, 7.3. $C_{32}H_{40}O_7P_2$ requires C, 64.2; H, 6.7%). ν_{max} 1275 (P=O), 1010 (P—O—C aliph.) 960 (P—O—P), 945 (P—O—C arom.) cm^{-1}. ^{1}H-n.m.r. ($CDCl_3$) δ 7.3 (10ArH), 4.78–4.62 br (2H, C*H*—OP), 2.18–1.6 br.m. (2OH, Ad—H). T.l.c. (ethyl acetate-petroleum ether (b.p. 70–80°), 1:1) gave a single spot, R_F 0.63.

2-Adamantyl phosphorodichloridite (*22*) 2-Adamantol (10g) was stirred at room temperature with phosphorus trichloride (15 ml) for ½ hr. to give the *dichloridite* (45%), m.p. 185–188°. ν_{max} 1005, 990 (P—O—C) cm^{-1}. (Found: C, 47.4; H, 5.6. $C_{16}H_{15}Cl_2OP$ requires C, 47.4; H, 5.8%). Treatment of the dichloridite with: (a) boiling water (6h) gave 2-chloroadamantane (24) (60%), m.p. 187–190° (from MeOH) (lit[10]. 186–188°). (Found: C, 70.7; H, 8.9. Calc. for $C_{10}H_{15}Cl$: C, 70.4; H, 8.8%). T.l.c. (EtOAc-petroleum ether 60–80° 1:1) showed one spot, R_F 0.74 (b) Aniline (4 mol. equivs.) in petroleum ether (40–60°) at room temperature (12hr.) gave *2-adamanyl-N,N^1-diphenylphosphorodiamidite* (23) (46%), m.p. 264–266°. (Found: C, 72.45; H, 7.4; N, 7.8. $C_{22}H_{27}N_2OP$ requires C.72.1; H, 7.4; N, 7.65%). ν_{max} 3380, 3280 (NH), 1605, 1500 (arom C=C), 1010 (P—O—C) cm^{-1}.

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