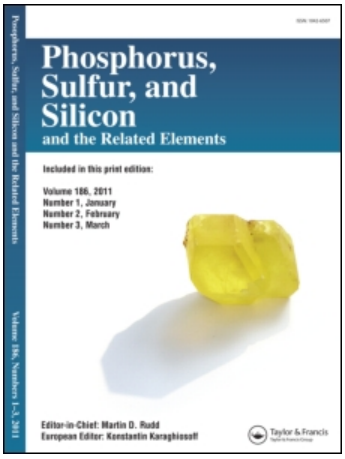

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SOME DERIVATIVES OF 4-*t*-BUTYLCYCLOHEXYL AND 1-MENTHOL-PHOSPHOROCHLORIDATES

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SOME DERIVATIVES OF 4-*t*-BUTYLCYCLOHEXYL AND 1-MENTHOL-PHOSPHOROCHLORIDATES

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cis and *trans*-4-*t*-Butylcyclohexanol and 1-menthol have been converted to the phosphorodichloridates with phosphorus oxychloride. Similar reaction with thiophosphoryl chloride afforded the phosphorodichloridothioates. By using 2 mol equivs. of 4-*t*-butylcyclohexanol, analogous condensations gave the corresponding phosphochloridates and chloridothioates, but with 1-menthol the reaction was unsuccessful. The various chloridates were characterized by preparation of a wide range of derivatives, e.g. amidates, azides, hydrazides, and hydrazones. These compounds are of interest as potential pesticides and their spectral features are discussed.

INTRODUCTION

Commercial 4-*t*-butylcyclohexanol (**1**) has been phosphorylated with phosphorus oxychloride to the phosphorodichloridate (**2**; X = O) (50% yield) as previously described.[1,2] Phosphorylation of the pure *trans*-isomer gave an appreciably higher yield (87%) of the dichloridate.

Reduction of 4-*t*-butylcyclohexanone with lithium tri-sec-butylborohydride ("L-Selectride") gave the *cis*-alcohol,[3,4] which, with phosphorus oxychloride at −10°, afforded the *cis*-phosphorodichloridate (69%). An analogous reaction with thiophosphoryl chloride gave the *cis*-phosphorodichloridothioate (**2**; X = S). When phosphorus oxychloride was reacted with *trans*-4-*t*-butylcyclohexanol (2 mol equivs.) the phosphorochloridate (Table I, **15**; X = O, Y = Cl) was obtained; an analogous reaction with thiophosphoryl chloride afforded the phosphorochloridothioate (**15**; X = S, Y = Cl).

1-Menthol (2-isopropyl-5-methylcyclohexanol) was phosphorylated with phosphorus oxychloride to the corresponding phosphorodichloridate (**40**; X = O, Y = Z = Cl); the reaction with thiophosphoryl chloride similarly gave the phosphorodichloridothioate (**40**; Table II, X = S, Y = Z = Cl). The various chloridates were reacted with selected nucleophilic reagents such as amines, hydrazine, and azide ion to give a wide range of derivatives, e.g. amidates, hydrazides, hydrazones and azides which served to characterize the chloridates and are also of interest as potential pesticides.

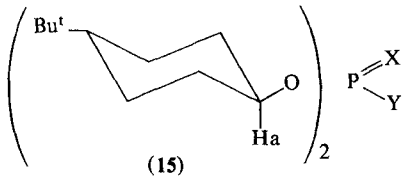
DISCUSSION

Pure *trans*-4-*t*-butylcyclohexanol (**1**)[5] with phosphorus oxychloride at room temperature gave the phosphorodichloridate (**2**; X = O, 87%) whereas commercial 4-*t*-butylcyclohexanol (75:25 *trans/cis* mixture) only gave 50% of the dichloridate.[1,2] This has been converted into a wide range of derivatives (Scheme 1): amidates (**3**); amidic chlorides (**4**); the phosphate (**5**); dihydrazide (**6**, R = H), diphenylhydrazide (**6**; R = Ph) and hydroxyazide (**7**). The amidic chloride (**4**; R = Ph) was converted to the acid (**8**; R = Ph) and the anilinium salt (**9**; R = Ph); the hydrazide (**10**; R^1 = H, R = Ph) (characterized by formation of the acetone, glucose, and furfuraldehyde hydrazones); the phenylhydrazide (**10**; R = R″ = Ph); the azide (**11**), which, with triphenylphosphine, gave the iminophosphorane (**12**; R = Ph); the diamidate (**13**; R = Ph), which, with phenylisocyanate, gave phenylcarbamoyl derivative (**14**; R = Ph). The amidic chloride (**4**; X = O, R = Ph) by controlled hydrolysis (aqueous pyridine) afforded P^1:P^2-di(4-*t*-butylcyclohexyl) P^1:P^2-dianilinopyrophosphate. The cyclohexylamidic chloride (**4**; R = C_6H_{11}) similarly gave the corresponding pyrophosphate, and this amidic chloride (**4**; R = C_6H_{11}) also gave the hydrazide (**10**; R′ = H, X = O; R = C_6H_{11}) and the acetone hydrazone.

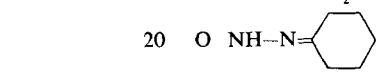
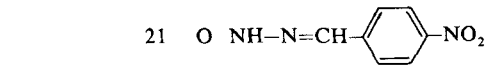
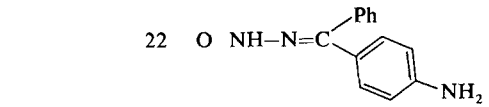
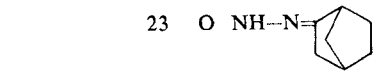
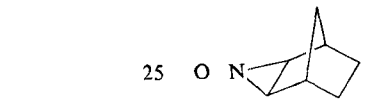
trans-4-*t*-Butylcyclohexanol was also phosphorylated with phenyl phosphorodichloridate to the corresponding phosphorochloridate which was converted

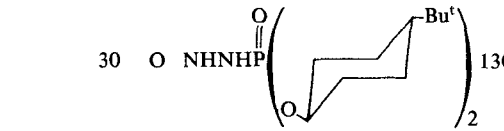
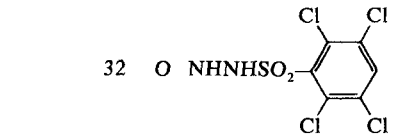
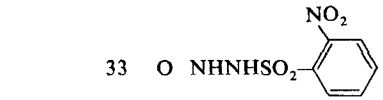
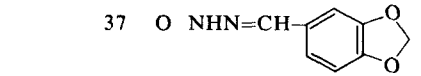
TABLE I

Derivatives of Bis-trans-4-t-Butylcyclohexyl Phosphorochloridate (**15**; X = O, Y = Cl) and the thio analogue (**15**; X = S, Y = Cl)



(**15**)

No.	X	Y	Mp°	Formula	Analysis							
					Found (%)				Required (%)			
					C	H	N	P	C	H	N	P
16	O	$C_6H_{11}NH$	139–142	$C_{26}H_{50}NO_3P$	68.9	11.2	3.1	6.9	68.6	11.0	3.1	6.85
17	O	N_3	44–47	$C_{20}H_{38}N_3O_3P$	60.3	9.5	10.2	—	60.2	9.5	10.5	—
18	O	$NH \cdot NH_2$	165–168	$C_{20}H_{41}N_2O_3P$	61.7	10.4	7.5	—	61.85	10.56	7.2	—
19	O	$NHN{=}CMe_2$	152–153	$C_{23}H_{45}N_2O_3P$	64.3	10.5	6.4	7.0	64.5	10.51	6.5	7.2
20	O		189–190	$C_{26}H_{49}N_2O_3P$	66.6	10.7	5.9	—	66.7	10.5	6.0[a]	—
21	O		230–232	$C_{28}H_{46}N_3O_5P$	62.6	8.8	7.7	—	62.8	8.6	7.85	—
22	O		108–110	$C_{33}H_{50}N_3O_3P$	68.7	9.2	7.6	—	68.8	8.8	7.4[b]	—
23	O		235–240	$C_{27}H_{49}N_2O_3P$	67.4	10.2	5.7	—	67.5	10.2	5.8	—
24	O	NH–N=Glucose	122–128	$C_{26}H_{51}N_2O_8P$	56.6	9.3	4.9	—	56.7	9.3	5.1	—
25	O		87–90	$C_{27}H_{48}NO_3P$	69.8	10.4	3.0	—	69.7	10.3	3.0	—
26	O	$N{=}PPh_3$	130–132	$C_{38}H_{53}NO_3P$	72.3	8.5	2.1	—	72.0	8.4	2.25	—
27	O	NHNHCONHPh	233–235	$C_{27}H_{46}N_3O_4P$	64.0	8.9	8.2	6.0	63.9	9.1	8.3[c]	6.1
28	O	NH_2	186–190	$C_{20}H_{40}NO_3P$	64.5	11.0	3.6	—	64.3	10.7	3.75	—
29	O	NHCONHPh	152–154	$C_{27}H_{45}N_2O_4P$	66.2	9.4	5.7	—	65.9	9.15	5.7	—

30	O		130	$C_{40}H_{78}N_2O_6P_2$	64.3	10.7	3.8	8.1	64.5	10.5	3.8	8.3[d]
31	O		186–189	$C_{27}H_{47}N_2O_5PS$	59.7	8.8	5.1	—	59.8	8.7	5.2[e]	—
32	O		119–120	$C_{26}H_{41}Cl_4N_2O_5PS$	47.2	6.0	4.2	—	46.85	6.2	4.2	—
33	O		146–149	$C_{26}H_{44}N_3O_7PS$	54.5	8.0	6.9	—	54.4	7.7	7.3	—
34	O		184–187	$C_{32}H_{49}N_2O_6PS$	62.0	8.2	4.25	—	61.9	7.9	4.5	—
35	O	NHNHPh	244–246	$C_{26}H_{45}N_2O_3P$	67.25	9.7	6.2	—	67.2	9.7	6.0[f]	—
36	O	NHNHCSNHPh	189–192	$C_{27}H_{46}N_3O_3PS$	61.9	8.8	8.2	5.7	61.95	8.8	8.3	5.9
37	O		236–239	$C_{28}H_{45}N_2O_5P$	64.9	8.9	5.3	—	64.62	8.65	5.4	—
38	S	NHNHPh	165–167	$C_{26}H_{45}N_2O_2PS$	65.3	9.2	5.8	—	65.0	9.4	5.8	—
39	S	NH_2	160–162	$C_{28}H_{40}NO_2PS$	61.2	10.8	3.5	—	61.4	10.7	3.6	—

[a] Nmr ($CDCl_3$) δ: 6.50; 6.26d (1N$\overset{*}{H}$ J_{P-NH} 12 Hz), 4.36m (2H, Ha), 2.32–1.04m (18 cyclohexyl protons), 0.85s (18H, 2 × (CH_3)$_3$C).

[b] $CDCl_3$, δ: 7.86–7.32m (9 ArH), 6.78, 6.7d (NH_2), 6.3, 6.08d (PON$\overset{*}{H}$ J_{P-NH} 13 Hz), 4.24m (2H, Ha), 2.20–0.98m (18 cyclohexyl protons), 0.85s (2 × (CH_3)C).

[c] $CDCl_3$(CD_3)$_2$SO δ: 8.43s (PhN$\overset{*}{H}$), 7.82d (PON$\overset{*}{H}$, J_{P-NH} 14 Hz), 6.9s (N–N$\overset{*}{H}$), 7.56–6.98m (5 ArH), 4.28m (2Ha), 2.54–1.0m (18 cyclohexyl H), 0.83s (2 × (CH_3)$_3$C).

[d] $CDCl_3$ δ: 5.48br (N$\overset{*}{H}$–N$\overset{*}{H}$), 4.26m (4H, Ha), 2.38–1.02m (36H, cyclohexyl H), 0.86s (36H, 4(CH_3)$_3$C).

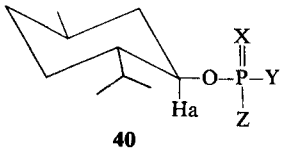
[e] (CD_3)$_2$SO δ: 7.84–7.76d (2 ArH next to SO_2), 7.45–7.37d (2 ArH next to Me) 4.18–4.1m (2Ha), 3.56br (2N$\overset{*}{H}$), 3.42s (Ar–CH_3), 2.32–0.98m (18 cyclohexyl H), 0.84s (2 × (CH_3)$_3$C).

[f] $CDCl_3$ 7.34–6.91m (5 ArH), 5.52s (N$\overset{*}{H}$–Ph), 4.95s (P–N$\overset{*}{H}$), 4.50m (2Ha), 2.45–1.00m (18 cyclohexyl H), 0.86s (18H, 2 × (CH_3)$_3$C).

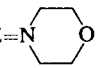
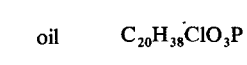
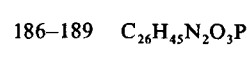
* Signals removed after treatment with D_2O.

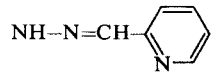
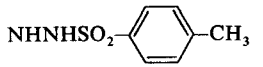
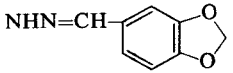
TABLE II

Derivatives of 2-Isopropyl-5-Methylcyclohexyl Phosphorodichloridate (**40**; X = O, Y = X = Cl)



40

No.	X	Y	Z	Mp°	Formula	Analysis					
						Found (%)			Required (%)		
						C	H	N	C	H	N
41	O			110–112	$C_{18}H_{35}N_2O_4P$	57.9	9.1	7.4	57.75	9.4	7.5[a]
42	O	Y=Z=NHNHPh		157–161	$C_{22}H_{33}N_4O_2P$	63.6	7.9	13.2	63.5	7.9	13.5[c]
43	O	OH	OH	129–133	$C_{10}H_{21}O_4P$	50.5	8.7	P, 12.7	50.85	8.9	P, 13.0
44	O	Cl	NHPh	oil	$C_{16}H_{25}ClNO_2P$	58.1	7.9	4.0	58.3	7.6	4.2
45	O	NHNHPh	NHPh	oil	$C_{22}H_{32}N_3O_2P$	65.6	7.8	10.7	65.8	8.0	10.5[b]
46	O	$NH(CH_2)_2OH$	NHPh	126–127	$C_{18}H_{31}N_2O_3P$	61.0	8.7	7.8	61.0	8.7	7.9
47	O	Y=Z=NHCHMe$_2$		117–121	$C_{16}H_{35}N_2O_2P$	60.2	11.0	9.0	60.4	11.0	8.8
48	O	N_3	NHPh	146–150	$C_{16}H_{25}N_4O_2P$	56.9	7.6	16.3	57.1	7.45	16.7[c]
49	O		NHPh	193–195	$C_{21}H_{30}N_3O_2P$	65.1	8.0	10.5	65.1	7.75	10.85
50	O	$NHNH_2$	NHPh	oil	$C_{16}H_{28}N_3O_2P$	59.2	8.7	13.0	59.1	8.6	12.9
51	O	NHNHCONHPh	NHPh	168	$C_{23}H_{33}N_4O_3P$	61.9	7.6	12.6	62.2	7.4	12.6
52	O	NHN=CMe$_2$	NHPh	112	$C_{19}H_{32}N_3O_2P$	62.2	9.0	11.5	62.5	8.8	11.5
53	O	Cl		oil	$C_{20}H_{38}ClO_3P$	61.4	10.0	P, 8.1	61.1	9.7	P,7.9
54	O	NHNHPh		186–189	$C_{26}H_{45}N_2O_3P$	67.5	9.4	6.0	67.2	9.7	6.0
55	O	OPh	NH–NHPh	91–92	$C_{22}H_{31}N_2O_3P$	65.8	7.7	6.8	65.7	7.7	7.0
56	O	OPh	NH·NH_2	123–126	$C_{16}H_{27}N_2O_3P$	58.7	8.5	8.7	58.9	8.3	8.6

57	O	OPh		112	$C_{22}H_{30}N_3O_3P$	63.4	7.1	10.0	63.6	7.2	10.1
58	O	OPh		168–170	$C_{23}H_{33}N_2O_5PS$	57.7	6.8	5.6	57.5	6.9	5.8
59	O	OPh		121–124	$C_{23}H_{31}N_2O_5P$	61.7	6.9	6.2	61.9	6.95	6.3
60	O	OPh	$\overset{-}{O}\overset{+}{N}H_3Ph$	130–131	$C_{22}H_{32}NO_4P$	65.6	7.8	3.6	65.2	7.9	3.5
61	O	OPh	NHPh	94–96	$C_{22}H_{30}NO_3P$	68.0	7.65	3.6	68.2	7.75	3.6
62	O	OPh	N_3	liquid	$C_{16}H_{24}N_3O_3P$	56.8	7.2	12.3	57.0	7.1	12.5
63	S	Y=Z=NHNHPh		152–154	$C_{22}H_{33}N_4OPS$	61.2	7.6	13.25	61.1	7.6	13.0
64	S	Y=Z=C_6H_{11}NH		114	$C_{22}H_{43}N_2OPS$	63.8	10.3	6.9	63.8	10.4	6.8
65	S	Y=Z= 		123–124	$C_{18}H_{35}N_2O_3PS$	55.6	9.05	7.0	55.4	9.0	7.2
66	S	Y=Z=NH_2		103	$C_{10}H_{23}N_2OPS$	47.7	9.15	11.4	48.0	9.2	11.2
67	S	Y=Z=NHCONHPh		246	$C_{24}H_{33}N_4O_3PS$	58.9	6.4	11.8	59.0	6.8	11.5
68	S	Y=Z=NHNHCONHPh		247–249	$C_{24}H_{35}N_6O_3PS$	56.3	6.5	16.2	55.6	6.75	16.2[d]
69	O	OEt	OH	230–234	$C_{12}H_{25}O_4P$	54.3	9.2	P, 11.5	54.5	9.5	P, 11.7
70	S	OEt		63–65	$C_{16}H_{32}NO_3PS$	54.7	9.6	4.2	55.0	9.2	4.0

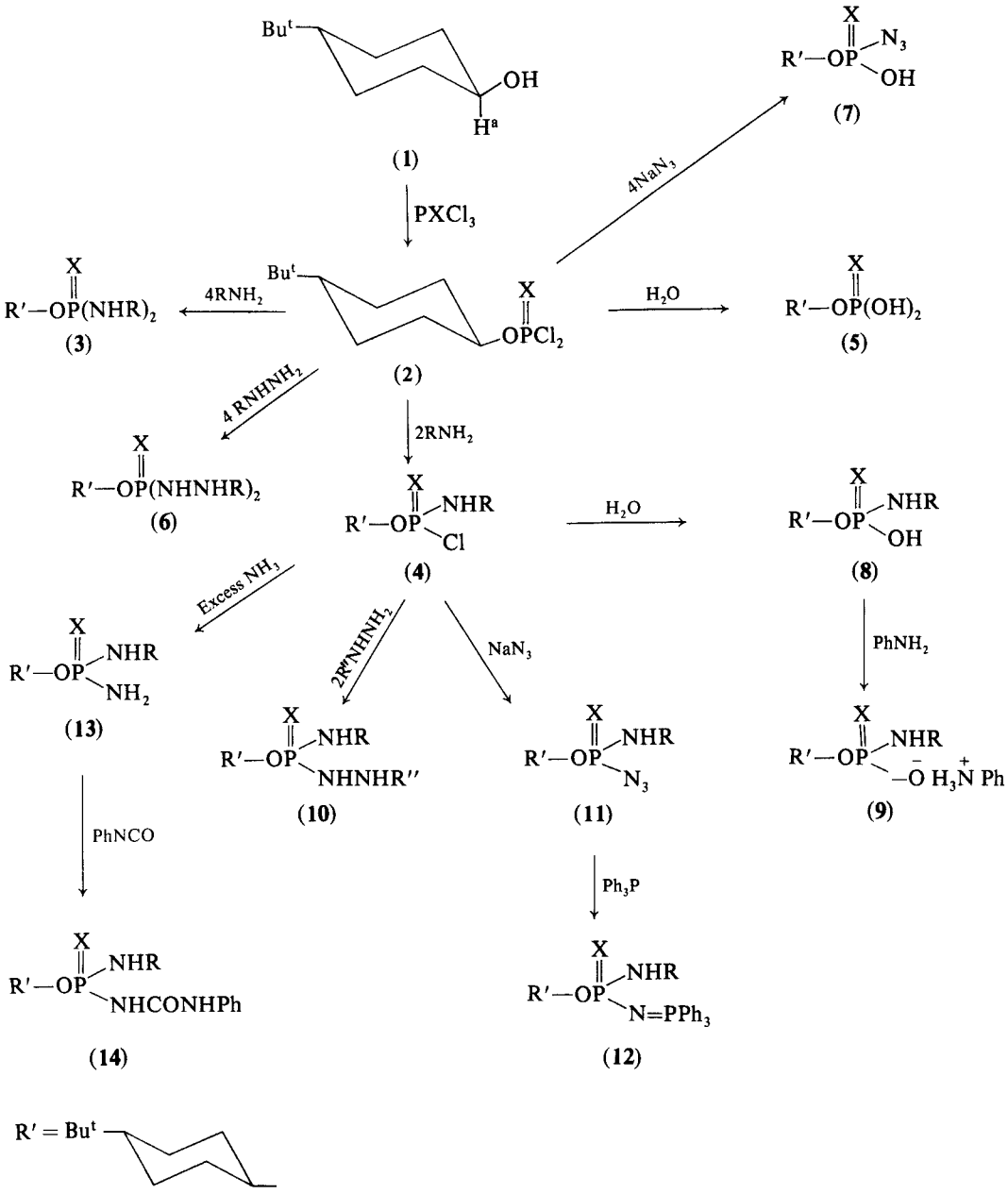
[a] Nmr ($CDCl_3$) δ: 4.4–4.1m (Ha), 3.83t (8H, heterocyclic hydrogens next to 0), 3.18t (18H, heterocyclic protons next to N), 2.36–0.80 (9 cyclohexyl protons), 1.0, 0.92, 0.80 (3 × CH_3).

[b] $CDCl_3$ δ: 7.63–6.3 (10 ArH), 5.7 (2 × P*–N*H*), 4.3br (1H, N*H*–Ph), 3.1s (7H, $(CH_3)_2CH$), 4.2m (Ha), 1.53–0.9m (18H, alicyclic and methyl protons).

[c] $CDCl_3$ δ: 7.4–6.76m (10 ArH), 5.46 (4 N*H*), 4.33–4.2m (Ha), 2.38–0.72m (18H, cyclohexyl protons and $3CH_3$).

[d] $CDCl_3$ δ: 7.5–6.84m (10 ArH), 8.17–8.08 br (2H, CON*H* Ph × 2), 5.7brd (4H, 2 × NH–NH), J_{NH-NH} 3 Hz), 4.5m (Ha), 2.46–0.98m (18 cyclohexyl and methyl protons). * Denotes signals removed by D_2O treatment.

[e] MS 336 (M^+) and major fragment ions at 197 ($M-C_{19}H_{19}$), 173, 156 ($C_{10}H_{19}OH$), 155, 138, 123, 107, 93 ($PhNH_2$), 85, 43 (HN_3).



SCHEME 1

to the phenylhydrazide, hydrazide etc. (see Experimental).

trans-4-*t*-Butylcyclohexanol (**1**) with thiophosphoryl chloride gave the phosphorodichloridothioate (**2**; X = S, 52%), characterized by formation of derivatives such as the dimorpholidate (**3**; R = morpholino, X = S); dihydrazide (**6**; X = S, R = H); and dihydrazones. The alcohol was similarly phosphorylated with ethyl phosphorodichloridothioate.[6]

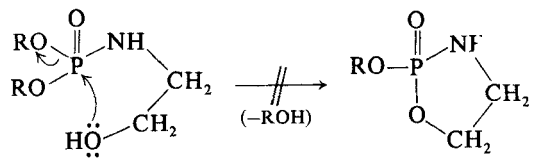
cis-4-*t*-Butylcyclohexanol (**1b**; OH axial) was phosphorylated with phosphorus oxychloride at −78° to give the dichloridate (**2b**; X = O, 69%); at −10° the yield decreased to 50%. The dichloridate was characterized as the diphenylhydrazide (**6b**; X = O, R = Ph) and the phosphate (**5b**; X = O).

The *cis*-phosphorodichloridate decomposed in warm petroleum ether (55°) to give 4-*t*-butylcyclohexene, although the *trans*-isomer was stable under these conditions and even in boiling toluene. The greater ease of elimination of the axial dichlorophosphoro group would be expected since it is known[7] that eliminations involving phosphorus oxychloride generally proceed by the bimolecular (E_2) mechanism which requires *trans*-diaxial geometry of the groups to be eliminated.

cis-4-*t*-Butylcyclohexanol was condensed with *trans*-4-*t*-butylcyclohexyl phosphorodichloridate in the presence of triethylamine to give the *cis*, *trans* -bis (4-*t*-butylcyclohexyl) phosphorochloridate *trans*-4-*t*-Butylcyclohexanol condensed with *cis*-4-*t*-butylcyclohexylphosphorodichloridate under the same conditions to give the identical phosphorochloridate showing there is no difference in the reactivities of the *cis* and *trans* alcohols towards the phosphorodichloridate.

This is not surprising since the reaction does not occur at the C(1)-carbon atom but at the phosphorus atom and therefore should not be sensitive to the conformation of the dichlorophosphoro group.

bis (*trans*-4-*t*-Butylcyclohexyl) phosphorochloridate (**15**; X = O, Y = Cl) has been prepared by phosphorylation of *trans*-4-*t*-butylcyclohexanol (**1**; 2 mol equivs.) with phosphorus oxychloride as previously described.[1,2] The phosphorochloridate was converted into the derivatives shown in Table I (nos. 16–37) (see Experimental). Reaction with ethanolamine afforded the amidoethanol derivative (**15**; X = O, Y = $NHCH_2CH_2OH$) illustrating the greater nucleophilicity of the NH_2 as cf. OH group. There was, however, no evidence of the formation of the possible cyclic product:



Similar reaction of *trans*-4-*t*-butylcyclohexanol (2 mol equivs.) with thiophosphoryl chloride gave the chloridothioate (**15**; X = S, Y = Cl) which was characterized by formation of the phenylhydrazide (**38**) and the amidate (**39**). Reaction of the amidate (**39**) with phenylisocyanate (2 mol equivs.) was expected to give the *N*-phenylcarbamoyl derivative, but analysis and spectral data indicated that the product was the *N,N*-diphenylurea (**15**; X = S, Y = NH · $CONPh_2$).

cis-4-*t*-Butylcyclohexanol (**1**; OH axial) by reaction with thiophosphoryl chloride at room temperature gave *cis*-4-*t*-butylcyclohexyl phosphorodichloridothioate (55%). This was characterized by formation of the diphenylhydrazide (**6**; X = S, R = Ph) and dimorpholidate (**3**, X = S, R = morpholino).

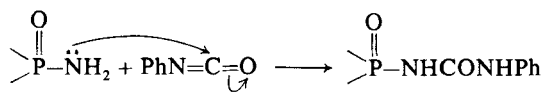
1-Menthol was converted to the phosphorodichloridate (**40**, X = O, Y = Z = Cl, Table II) (74%) and this gave a wide range of derivatives (Table II, nos. 41–54. 1-Menthol was also phosphorylated with phenyl phosphorodichloridate, and the product characterized by formation of derivatives (55–61).

Reaction of 1-menthol with thiophosphoryl chloride in the presence of pyridine gave the dichloridothioate (**40**; X = S, Y = Z = Cl, 66%) which was converted into the derivatives (62–67). Treatment of 1-menthol with ethyl phosphorodichloridothioate gave the corresponding ethyl chloridothioate which was characterized as the morpholidate (69); on hydrolysis desulphuration occurred to give the corresponding phosphate (68).

Attempts to obtain dimenthylphosphorochloridate by reaction of 1-menthol (2 mol equivs.) with phosphorus oxychloride-triethylamine (50 hr at room temperature) only gave a mixture of 1-menthol and the phosphorodichloridate (**40**; X = O, Y = Z = Cl). The failure is almost certainly due to steric hindrance of the hydroxyl group by the bulky 2-isopropyl group.

P^1:P^2-Di(4-*t*-butylcyclohexyl)-P^1:P^2-Dianilinopyrophosphate was obtained by partial hydrolysis of the *N*-phenyl phosphoramidic chloride (**4**; X = O, R = Ph). Similar preparative procedure (Toy's method)[8] afforded the analogous P^1:P^2-dicyclohexylaminopyrophosphate and the P^1:P^2-dimenthyl P^1:P^2-dianilinopyrophosphate. The pyrophosphates showed a characteristic ir band in the 945–950 cm^{-1} region which according to Thomas [9a] is a good indication of the presence of the P–O–P group.

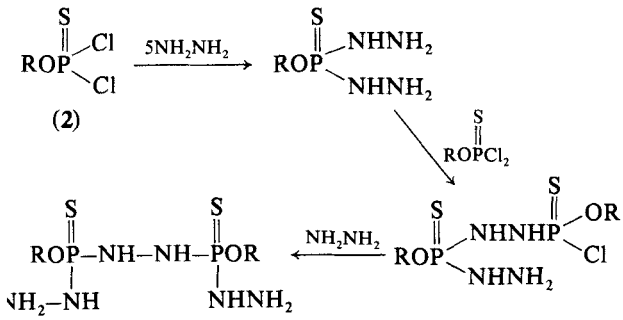
The phosphorohydrazides and amidates were characterized by reaction with phenylisocyanate to give the corresponding *N*-phenylcarbamoyl derivatives:



The thionodihydrazide (**6**; X = S, R = H) reacted with phenylisocyanate (2 mol equivs.) to give the *N,N'*-diphenylcarbamoyl derivative; while the dihydrazide (**6**; X = O, R = H) reacted with a

mixture of equimolar amounts of phenylisocyanate and phenylisothiocyanate to give the *N*-phenylcarbamoyl *N'*-phenylthiocarbamoyl derivative.

Although *trans*-4-*t*-butylcyclohexyl phosphorodichloridate (**2**; X = O) reacted normally with excess of hydrazine to give the dihydrazide (**6**; X = O, R = H), when the analogous dichloridothioate (**2**; X = S) was reacted with hydrazine (5 mol equivs.) the product was the $P^1:P^2$-dihydrazide (**71**). The structural assignment is supported by analytical and spectral data and by formation of the acetone bishydrazone. A possible mechanistic route to the dihydrazide (**71**) is shown below:



(**71**) (R = 4-*t*-butylcyclohexyl)

On the other hand, condensation of the dichloridothioate (**2**; X = S) with a smaller quantity of hydrazine (4 mol equivs.) afforded the expected dihydrazide (**6**; X = S, R = H).

The ir spectra of the phosphoramidic compounds, including the hydrazides and hydrazones, were in general agreement with the values previously reported[10] for the P=O and NH stretching vibrations. The P–O–C aliphatic stretching vibration appeared in the region 965–1060 cm^{-1} and the P–O–C aromatic band at 910–960 cm^{-1} (cf. Ref. 9b). The detection of the P=S band is more difficult since it can vary considerably in position (600–840 cm^{-1}) and in some cases two absorption bands appear.[9c] In a series of tetrathiophosphates the P=S frequency was in the region 688–715 cm^{-1},[11] although in the thiono compounds described here the characteristic frequency associated with the P=S group appeared to be in the range 820–860 cm^{-1}.

EXPERIMENTAL

Ir spectra were determined as liquid films or Nujol mulls using a Perkin Elmer 237 spectrometer. Nmr spectra were measured with a Varian A60A spectrometer using tetramethylsilane as internal standard. Mass spectra were determined with an A.E.I. MS 9 Spectrometer at 70 eV. Glc was carried out using a Philips PV4000 chromatograph, a 6 m PEG column at a temperature of 150°. Melting points were determined with Kofler hot-stage apparatus and are uncorrected. Tlc was carried out using Silica gel G plates developed with iodine vapour. Microanalyses were carried out by Butterworth Microanalytical Consultants Ltd., Teddington, England.

trans-4-t-Butylcyclohexyl Phosphorodichloridate (**2**; X = O)

Commercial-4-*t*-butylcyclohexanol (shown by glc to be 75% *trans* 25% *cis*) was converted to the phosphorodichloridate (50%) by phosphorus oxychloride-triethylamine in ether as previously described.[1,2] 4-*t*-Butylcyclohexanol (**1**) (18.2 g) (99% *trans* obtained by sodium-propanol or lithium aluminium hydride reduction of the ketone[3]) was reacted with phosphorus oxychloride (21.5 g, 1.2 mol equiv.) and triethylamine (14.1 g, 1.2 mol equiv.) in dry toluene (160 ml) for 3 hr. The precipitated triethylamine hydrochloride was filtered off, and the filtrate evaporated under reduced pressure (75°/0.5 mm) to give the phosphorodichloridate (**2**; X = O) as an oil (32.6 g, 87%). ν_{max} 1310, 1295 (P=O), 1020, 990 (P–O–C) cm^{-1}. The phosphorodichloridate was characterized as the following diamidates (**3**; X = O).

N,N'-Dimorpholidate (**3**; R = morpholino, X = O), oil. (Found: C, 57.5; H, 9.5; N, 7.7; P, 8.4. $C_{18}H_{35}N_2O_4P$ requires C, 57.75; H, 9.4; N, 7.5; P, 8.3%.) ν_{max} 1260, 1240 (P=O), 1015, 970 (P–O–C) cm^{-1}. Nmr ($CDCl_3$) δ: 3.57m (cyclohexyl H next to O), 3.10t (8 heterocyclic protons next to O), 2.7t (8 cyclohexyl protons next to N), 1.8–0.9m (9 cyclohexyl protons), 0.71 s ($CH_3)_3C$).

N,N'-Diphenyl (**3**; X = O, R = Ph), mp 171–174° (EtOH). (Found: C, 68.2; H, 8.2; N, 8.4. $C_{22}H_{31}N_2O_2P$ requires C, 68.4; H, 8.0; N, 7.25%.) ν_{max} 3180 (NH), 1600, 1495 (C=C), 1195 (P=O), 1020 (P–O–C) cm^{-1}. Nmr ($CDCl_3$) δ: 7.29–6.83m (10 ArH), 5.53br (2H, 2 × PhN*H*), 5.03br (2H, 2 × P–NH*), 4.45brm (1H, cyclohexyl H_a), 2.20–0.91m (9H, cyclohexyl H), 0.77s (2 × $(CH_3)_3C$).

The diamidates (**3**; X = O) were obtained by reaction of the phosphorodichloridate (**2**; X = O) with the amine (4 mol equivs.) in petroleum ether overnight; however, when only 2 mol equivs. of the amine was used the amidic chlorides (**4**; X = O) were formed.

N-Phenyl (**4**; X = O, R = Ph), mp 121–125°. (Found: C, 58.1; H, 7.6; N, 4.6. $C_{16}H_{25}ClNO_2P$ requires C, 58.3; H, 7.6; N, 4.3%.) ν_{max} 3180 (NH), 1260, 1240 (P=O), 1050, 1040 (P–O–C) cm^{-1}. Tlc (C_6H_6) showed one spot, R_F 0.81.

N-Cyclohexyl (**4**; X = O; R = C_6H_{11}), mp 123–127°. Tlc (EtOH) one spot, R_F 0.80. (Found: C, 57.5; H, 8.6; N, 4.4. $C_{16}H_{29}ClNO_2P$ requires C, 57.6; H, 8.7; N, 4.2%.)

The Phosphate (**5**; X = O). The phosphorodichloridate (**2**; X = O) was boiled with water for 24 hr to give the phosphate (**5**; X = O), (Me_2CO), mp 196–200° (lit.[4] 194–197°). Nmr ($CDCl_3$) δ: 9.94 (2H, OH†), 4.20m (1H, Ha), 2.26–1.04m (9 cyclohexyl protons), 0.85s (9H, $(CH_3)_3C$).

Diphenylhydrazide (**6**; X = O, R = Ph). The phosphorodichloridate (2.73 g) was reacted with phenylhydrazine (4.32 g, 4

† Signals removed after treatment with D_2O.

mol equivs.) in acetonitrile (15 ml) for 24 hr at 4°. The precipitate was filtered off and well washed with water. Recrystallization from ethanol gave the *dihydrazide* (1.2 g), mp 173–177°. (Found: C, 63.2; H, 8.1; N, 13.8. $C_{22}H_{33}N_4O_2P$ requires C, 63.5; H, 7.9; N, 13.5%.) ν_{max} 3280, 3240 (NH), 1500 (C=C), 1228 (P=O), 1030, 1015 (P–O–C) cm^{-1}. Nmr ($CDCl_3$) δ: 7.22–6.60 (10 ArH), 5.26br (2H, 2 × Ph–N*H**), 4.77br (2H, PON*H*)*, 4.52–3.92m (1H, cyclohexyl Ha), 2.20–0.90m (9H, cyclohexyl protons), 0.82 ($CH_3)_3C$).

Hydroxy-azide (**7**). The phosphorodichloridate (**2**; X = O) (1.0 g) was stirred with a solution of sodium azide (0.92 g, 4 mol equiv.) in aqueous acetone (20 ml) overnight. Addition of ice-water (100 ml) gave a precipitate which was filtered to give the hydroxy-azide (**7**; X = O). (100 mg), mp 221–225° (decomp.). (Found: C, 46.3; H, 8.0; N, 16.5. $C_{10}H_{20}N_3O_3P$ requires C, 46.0; H, 7.8; N, 16.1%.) ν_{max} 2400–2300 (P–OH), 2150s (N_3), 1660–1620 (P–OH), 1240 (P=O), 1060, 1030 (P–O–C) cm^{-1}.

Derivatives of the Phenyl Amidic Chloride (**4**; X = O, R = Ph)

The phosphate (**8**; X = O, R = Ph). The amidic chloride (**4**) (200 mg) was boiled under reflux with water (20 ml) for 4 hr. Decantation of water gave an oil which by trituration with acetone gave a solid, which on recrystallization from EtOH gave the *N-anilino phosphate* (**8**; X = O, R = Ph) (120 mg), mp 169–172°. (Found: C, 48.7; H, 11.3; N, 6.4; P, 13.2. $C_{16}H_{26}NO_3P$ requires C, 48.5; H, 11.25; N, 6.1; P, 13.4%.) Reaction with aniline (1 mol equiv.) in acetone gave the *anilinium phosphate* (**9**; X = O, R = Ph). Tlc (EtOH) gave a single spot, R_F 0.69. (Found: C, 65.45; H, 8.3; N, 6.8. $C_{22}H_{33}N_2O_3P$ requires C, 65.35; H, 8.2; N, 6.9%.) ν_{max} 3190 (NH), 2180–2140 (NH_3), 1610, 1500 (C=C), 1150, 1055 (P–O–C) cm^{-1}.

The hydrazide (**10**; X = O, R = Ph, R″ = H). The amidic chloride (**4**; X = O, R = Ph) was stirred with hydrazine hydrate (3 mol equivs.) in ethanol for 4 hr. Treatment with ice-water and recrystallization of the solid from ethanol gave the *hydrazide* (85%), mp 205–209°. ν_{max} 3320, 3210, 3130, 3080 (NH), 1605, 1505 (C=C), 1210 (P=O), 1060, 1030 (P–O–C) cm^{-1}. Tlc (EtOH) showed a single spot, R_F 0.77. The *hydrazide* was characterized by formation of hydrazones:

Acetone 78% (petroleum ether), mp 166–169°. (Found: C, 62.5; H, 9.1; N, 11.6. $C_{19}H_{32}N_3O_2P$ requires C, 62.5; H, 8.8; N, 11.5%.) ν_{max} 3190, 3100, 3060 (NH), 1605, 1505 (C=C), 1210 (P=O), 1050, 1030 (P–O–C) cm^{-1}.

Glucose 50% (pentane), mp 238–241°. (Found: C, 54.0; H, 7.65; N, 8.9. $C_{22}H_{38}N_3O_7P$ requires C, 54.2; H, 7.8; N, 8.6%.) ν_{max} 3400–3200 (OH, NH), 1610, 1500 (C=C), 1210 (P=O), 1050, 1020 (P–O–C) cm^{-1}.

Furfuraldehyde 83% (petroleum ether), mp 148–150°. (Found: C, 62.4; H, 7.5; N, 10.4. $C_{21}H_{30}N_3O_3P$ requires C, 62.5; H, 7.4; N, 10.4%.) ν_{max} 3170, 3070, 3050 (NH), 1605, 1500 (C=C), 1205 (P=O), 1015 (P–O–C) cm^{-1}.

The phenylhydrazide (**10**; X = O, R = R″ = Ph). The amidic chloride (**4**; X = O, R = Ph) was stirred with phenylhydrazine (2 mol equivs.) in acetonitrile at 4° for 48 hr. Recrystalization from ethanol gave the *phenylhydrazide* (46%), mp 98–101°. (Found: C, 65.5; H, 7.9; N, 10.7. $C_{22}H_{32}N_3O_2P$ requires C, 65.8; H, 8.0; N, 10.5.) ν_{max} 3280, 3200, 3100 (NH), 1500 (C=C), 1200, 1185 (P=O), 1030, 1020 (P–O–C) cm^{-1}.

The amino derivative (**13**; X = O, R = Ph). The amidic chloride (**4**; X = O, R = Ph) (2 g) was stirred with a solution of ammonia (5 ml of 0.88) in acetone (50 ml) for 6 hr. Treatment with ice-water (250 ml) and recrystallization of the solid product from acetone gave the *phosphorodiamidate* (**13**; X = O, R = Ph), (1.4 g), mp 159–161°. (Found: C, 61.6; H, 8.8; N, 9.1. $C_{16}H_{28}N_2O_2P$ requires C, 61.7; H, 9.0; N, 9.0%.) ν_{max} 3425, 3260, 3110 (NH), 1605, 1505 (C=C), 1200 (P=O), 1055, 1030 (P–O–C) cm^{-1}.

Reaction of the Diamidate (**13**; X = O, R = Ph) *with Phenylisocyanate*

The diamidate (0.7 g) was boiled under reflux with phenylisocyanate (0.27 g, 1 mol equiv.) in benzene (40 ml) for 60 hr. Evaporation and recrystallization of the residue from ethanol–petroleum ether gave the *N-phenylcarbamoyl derivative* (**14**; X = O, R = Ph) (0.28 g), mp 232–235°. Tlc (EtOH) showed a single spot, R_F 0.78. (Found: C, 64.5; H, 7.3; N, 9.9. $C_{23}H_{32}N_3O_3P$ requires C, 64.3; H, 7.5; N, 9.8%.) ν_{max} 3330, 3280, 3190 (NH), 1650 (CONH), 1600, 1500 (C=C), 1230 (P=O), 1050, 1030 (P–O–C) cm^{-1}.

P^1:P^2(Di-4-t-Butylcyclohexyl)-P^1:P^2-Dianilino Pyrophosphate

The amidic chloride (**4**; X = O, R = Ph) (1.65 g) in pyridine (15 ml) was stirred with 1 N-aqueous pyridine (2.5 ml) for 6 hr. Addition of ice-water (1 l) and recrystallization from acetonitrile gave the *pyrophosphate* (0.57 g), mp 178–181°. Tlc (EtOH) showed one spot, R_F 0.80. (Found: C, 63.2; H, 8.2; N, 5.0. $C_{32}H_{50}N_2O_5P_2$ requires C, 63.6; H, 8.3; N, 4.6%.) ν_{max} 3160, 3090 (NH), 1610, 1505 (C=C), 1240 (P=O), 1040 (P–O–C), 950 (P–O–P) cm^{-1}.

The azide (**11**; X = O, R = Ph). The amidic chloride (**4**; X = O, R = Ph) was reacted with sodium azide (2 mol equivs.) in aqueous acetone for 4 hr to give the *azide* (49%), mp 93–95°. ν_{max} 3170, 3100, 3060 (NH), 2155 (N_3), 1605, 1505 (C=C), 1255, 1230 (P=O), 1040, 1025 (P–O–C) cm^{-1}. Tlc (EtOH) gave a single spot, R_F 0.78. This was characterized by reaction with triphenyl phosphine (1 mol equiv.) in boiling 60–80° petroleum ether for 4½ hr to give the *triphenyl iminophosphorane* (**12**; X = O, R = Ph), mp 237–239°. (Found: C, 71.7; H, 7.1; N, 5.0. $C_{34}H_{40}N_2O_2P_2$ requires C, 71.6; H, 7.0; N, 4.9%.)

Derivatives of the Cyclohexyl Amidic Chloride (**4**; X = O, R = C_6H_{11})

P^1:P^2-(Di-4-t-Butylcyclohexyl)-P^1:P^2-Dicyclohexylamido Pyrophosphate

The amidic chloride (**4**; X = O, R = C_6H_{11}) (1 g) in pyridine (5 ml) was stirred with 1 N-aqueous pyridine (2 ml) for 5 hr. Addition of ice-water (800 ml) gave a solid which by recrystallization (CH_3CN) gave the *pyrophosphate* (0.3 g), mp 172–175°. Tlc (EtOH) showed a single spot, R_F 0.79. (Found: C, 62.6; H, 9.8; N, 4.7. $C_{32}H_{62}N_2O_5P_2$ requires C, 62.3; H, 10.0; N, 4.55%.) ν_{max} 3200 (NH), 1245, 1225 (P=O), 1045, 1030 (P–O–C), 945 (P–O–P) cm^{-1}.

The hydrazide (**10**; X = O, R = C_6H_{11}) (51%), mp 107–110°. ν_{max} 3330, 3220 (NH), 1235 (P=O), 1040, 1010 (P–O–C) cm^{-1}. This was characterized as the *acetone hydrazone* (71%) from petroleum ether, mp 92–94°. (Found: C, 61.45; H, 10.5; N, 11.1. $C_{19}H_{38}N_3O_2P$ requires C, 61.5; H, 10.2; N, 11.3%.)

Reaction of the Phosphorodichloridate (**2**; X = O) *with Hydrazine*

The phosphorodichloridate (**2**; X = O) (2.73 g) was reacted with hydrazine hydrate (5 g; 10 mol equivs.) in ethanol at 0°. After mixing, the solution was kept at 4° for 24 h; addition of ice-water gave a sticky solid, which on trituration with acetonitrile gave the *dihydrazide* (**6**; X = O, R = H) (0.5 g), mp 198–203°. (Found: C, 45.1; H, 9.6; N, 21.4. $C_{10}H_{25}N_4O_2P$ requires C, 45.4; H, 9.5; N, 21.2%.) ν_{max} 3300 (NH_2), 3260 (NH), 1220, 1195 (P=O), 1055, 1035 (P–O–C) cm^{-1}.

Reaction of the Dihydrazide (**6**; X = O, R = H) *with Phenylisocyanate and thiocyanate*

The dihydrazide (0.4 g) was boiled with phenylisocyanate (0.18 g, 1 mol equiv.) and phenylisothiocyanate (0.21 g, 1 mol equiv.) in 60–80 petroleum ether (20 ml) for 4 hr. Cooling gave a solid which was recrystallized from ethanol to give the *N-phenylcarbamoyl. N'-phenylthiocarbamoyl derivative* (0.65 g, 83%), mp 248° (decomp.). Found: C, 55.75; H, 7.0; N, 15.9; P, 5.7. $C_{24}H_{35}N_6O_3PS$ requires C, 56.1; H, 6.75; N, 16.2; P, 6.0%.) ν_{max} 3270, 3220, 3160, 3100 (NH), 1675 (CONH), 1550, 1500 (C=C), 1340 (C=S), 1240, 1220 (P=O), 1055, 1035 (P–O–C) cm^{-1}. Nmr ($(CD_3)_2SO$) δ: 8.85 (1H, Ph–N*H*–CO), 7.98 (1 H, PhN*H*CS), 7.60–6.92m (10 ArH), 4.25m (1H, Ha), 4.0br (4H, PO(N*H*·N*H*–)$_2$), 2.24–0.96m (9 cyclohexyl protons), 0.82 (9H, $(CH_3)_3C$).

O-Phenyl 4-t-Butylcyclohexyl Phosphorochloridate

A solution of *trans*-4-*t*-butylcyclohexanol (**1**) (12.42 g) in ether (100 ml) was added dropwise to a stirred solution of phenyl phosphorodichloridate (16.8 g; 1 mol equiv.) and triethylamine (8.04 g, 1 mol equiv.) in ether (150 ml). The mixture was stirred for 3 hr then boiled under reflux for 2 hr and triethylamine hydrochloride (10.2 g) filtered off. The filtrate was washed with water (3 × 100 ml), $NaHCO_3$ (2 × 50 ml), dried ($MgSO_4$) and evaporated to give a yellow oil (15 g). The chloridate was converted to the following derivatives.

Phenylhydrazide. The phosphorochloridate by condensation with phenylhydrazine (2 mol equivs.) in acetonitrile for 4 hr gave the *phenylhydrazide* (EtOH), mp 176–179°. (Found: C, 65.8; H, 7.6; N, 7.0. $C_{22}H_{31}N_2O_3P$ requires C, 65.7; H, 7.7; N, 7.0%.) ν_{max} 3300, 3200 (NH), 1600, 1585, 1485 (C=C), 1215, 1195 (P=O), 1040, 1025 (P–O–C alk), 955 (P–O–C arom) cm^{-1}.

Hydrazide. The phosphorochloridate with hydrazine hydrate (2 mol equivs.) in acetonitrile (40 ml) for 4 hr gave the *hydrazide* (petroleum ether) (61%), mp 90–93°. ν_{max} 3365 (NH_2), 3232 (NH), 1585, 1485 (C=C), 1225, 1210 (P=O), 1040, 1022 (P–O–C alk), 910, 900 (P–O–C arom) cm^{-1}. The hydrazide was characterized as the *2-pyridine aldehyde hydrazone* (50%) EtOH mp 166–167°. (Found: C, 63.8; H, 7.3; N, 10.2. $C_{22}H_{30}N_3O_3P$ requires C, 63.6; H, 7.2; N, 10.1%.) ν_{max} 3235 (NH), 1580, 1485 (C=C), 1235 (P=O), 1025, 1015 (P–O–C alip), 950 (P–O–C arom).

Reaction of O-Phenyl 4-t-Butylcyclohexyl Phosphorohydrazide with Phenylisocyanate

The hydrazide (0.6 g) was boiled with phenylisocyanate (0.22 g, 1 mol equiv.) in 60–80° petroleum ether (30 ml) for 1 hr to give the *phenylcarbamoyl derivative* (0.6 g), mp 162–165°. (Found: C, 62.3; H, 7.3; N, 9.4. $C_{22}H_{31}N_2O_3P$ requires C, 62.0; H, 7.2; N, 9.4%.) ν_{max} 3370, 3350, 3200 (NH), 1685 (CONH), 1590, 1500 (C=C), 1215, 1195 (P=O), 1020 (P–O–C alip), 960 (P–O–C arom) cm^{-1}.

trans-4-t-Butylcyclohexyl Phosphorodichloridothioate (**2**; X = S)

A solution of 4-*t*-butylcyclohexanol (**1**) (15.6 g) and pyridine (7.9 g, 1 mol equiv.) in toluene (10 ml) was added dropwise to a solution of thiophosphoryl chloride (16.9 g, 1 mol equiv.) in toluene (50 ml). The mixture was stirred for 2 hr and boiled for ½ hr, after cooling filtration removed pyridine hydrochloride (12.5 g). The filtrate was evaporated under reduced pressure, the residue extracted with petroleum ether and washed with H_2O (3 × 100 ml), dried ($MgSO_4$) and evaporated to give an oil (15 g, 52%). ν_{max} 1025, 990 (P–O–C), 840 (P=S) cm^{-1}. Ms: major fragment ions at 150 ($HOP(:S)Cl_2$), 138 (*t*-butylcyclohexene), 123, 81 and 55. The following derivatives of the phosphorodichloridothioate (**2**; X = S) were obtained.

The dihydrazide (**6**; X = S, R = H). The phosphorodichloridothioate (5.78 g) in ethanol (20 ml) was added to hydrazine hydrate (4 g, 4 mol equivs.) in ethanol (10 ml). After 4 hr, the precipitate was collected, washed with water (500 ml), and petroleum ether to give the *dihydrazide* (3.51 g), mp 122–124°. (Found: C, 43.0; H, 8.8; N, 19.7. $C_{10}H_{25}N_4OPS$ requires C, 42.85; H, 8.9; N, 20.0%.) ν_{max} 3280 (NH_2), 3180 (NH), 1050, 1030 (P–O–C), 855 (P=S) cm^{-1}. This was characterized as the *di-p-nitroacetophenone hydrazone* 80% (EtOH) (yellow needles), mp 157–160°. (Found: C, 54.14; H, 6.1; N, 14.8. $C_{26}H_{35}N_6O_5PS$ requires C, 54.35; H, 6.1; N, 14.6%.) ν_{max} 3310 (NH), 1580 (NO_2), 1020 (P–O–C), 860 (P=S) cm^{-1}. Tlc (EtOAc–petroleum ether 1 : 1) gave one spot, R_F 0.74. Nmr ($(CD_3)_2SO$) δ: 8.25–7.75m (8 ArH), 7.25, 6.75d (2H, 2 × N*H**, J_{P-NH} 27 Hz), 4.22 (1H, Ha), 2.25s (6H, 2 × CH_3), 2.19–1.0m (9 cyclohexyl protons), 0.87s (9H, C(CH_3)$_3$).

p-Methoxyacetophenone (EtOH), (77%) needles, mp 133–135°. (Found: C, 62.4; H, 7.55, N, 10.33. $C_{28}H_{41}N_4O_3PS$ requires C, 62.6; H, 7.5; N, 10.3%.) ν_{max} 3330, 3210 (NH), 1610 (C=C), 1030, 1020 (P–O–C), 848, 830 (P=S) cm^{-1}. Tlc (EtOAc–petroleum ether 1 : 1) showed one spot, R_F 0.75. Nmr ($CDCl_3$) δ: 7.88–6.78 (8 ArH), 6.5 br (2H, NH*, J_{P-NH} 22 Hz), 4.65–4.47m (1Ha), 3.83s, (2 × CH_3O), 2.30s (2CH_3), 2.2–0.92 (9 cyclohexyl H), 0.84s ((CH_3)$_3$C).

Reaction of the Dihydrazide (**6**; X = S, R = H) *with Phenylisocyanate*

Phenylisocyanate (1.2 g, 2 mol equivs.) was added to the dihydrazide (1.4 g; 1 mol equiv.) in 60–80° petroleum ether (20 ml) and the solution was boiled under reflux for 3 hr. Concentration and recrystallization (40–60° petroleum ether) gave the *N,N'-diphenylcarbamoyl derivative* (2.2 g, 85%), mp 246–248°. (Found: C, 55.5; H, 6.9; N, 15.9. $C_{24}H_{35}N_6O_3PS$ requires C, 55.6; H, 6.75; N, 16.2%.) Tlc (EtOAc–petroleum ether 1 : 1) showed one spot, R_F 0.58. ν_{max} 3290, 3210 (NH), 1675 (CONH), 1020 (P–O–C), 860 (P=S) cm^{-1}. Nmr ($CDCl_3$) δ: 8.13 br (2H, 2 × N*H*Ph)*, 7.55–6.95 (10 ArH), 6.75 br (2H, 2 × N*H*–CO, J_{NH-NH} 18 Hz)*, 5.5 br (2H, 2 × P–N*H*)*, 4.45m (1H, Ha), 2.53–1.00 (9H, cyclohexyl H), 0.85s (9H, (CH_3)$_3$C).

N,N'-Dimorpholino derivative (**3**; X = S, R = morpholino), mp 145–148° (petroleum ether). Found: C, 55.5; H, 8.9; N, 6.85. $C_{18}H_{35}N_2O_3PS$ requires C, 55.4; H, 9.0; N, 7.2%.) ν_{max} 1260 (P=O), 1025, 1015 (P–O–C), 700 (P=S) cm^{-1}.

Phosphorylation of trans-4-t-Butylcyclohexanol with Ethyl Phosphorodichloridothioate

A solution of *trans-4-t*-butylcyclohexanol (20.0 g) and triethylamine (12.98 g; 1 mol equiv.) in toluene (200 ml) was gradually added to a stirred solution of ethyl phosphorodichloridothioate (23 g; 1 mol equiv.) in toluene (100 ml) at 0°. After addition, the mixture was boiled under reflux for 5 hr, cooled and triethylamine hydrochloride (16 g) filtered off. Evaporation under reduced pressure gave an oil, which was extracted with ether (100 ml), washed with H_2O, dried ($MgSO_4$) and evaporated. Distillation of the residual oil under vacuum gave the *chloridothioate* as a colourless liquid (19 g), bp 49–50°/0.8 mm. Tlc (EtOAc–petroleum ether 1:1) gave one spot, R_F 0.76. (Found: C, 48.3; H, 8.3; P, 10.5. $C_{12}H_{24}ClO_2PS$ requires C, 48.2; H, 8.0; P, 10.4%.) ν_{max} 1025, 970 (P–O–C), 825 (P=S) cm^{-1}. MS 298 (M^+) and major ions at 235 ($M-C_2H_5Cl$), 179, 82 (cyclohexane), 64, 56 (C_4H_8). Condensation with phenylhydrazine (2 mol equiv.) in ether for 24 hr gave the *phenylhydrazide derivative*, mp 162–165°. (Found: C, 58.2; H, 8.1; N, 7.4. $C_{18}H_{31}N_2O_2PS$ requires C, 58.4; H, 8.4; N, 7.6%.) ν_{max} 3290 (NH), 1600, 1500 (C=C), 1025, 1010, 995 (P–O–C), 850 (P=S) cm^{-1}. Tlc (EtOAc–petroleum ether 1:1) gave a single spot, R_F 0.88. Nmr ($CDCl_3$) δ: 7.28–6.78m (5 ArH), 5.17br (2H, N*H*.N*H*)*, 4.82–4.33 br m (1H, Ha), 2.30–0.90m (12H, cyclohexyl and ethyl protons), 0.82s (9H, $CH_3)_3C$). Reaction with morpholine (2 mol equivs.) in acetonitrile at 50° for 2 hr gave the *morpholidate derivative* as an oil (51%). (Found: C, 54.9; H, 9.4; N, 3.8. $C_{16}H_{32}NO_3PS$ requires C, 55.0; H, 9.2; N, 4.0%.) ν_{max} (thin film), 1035, 1110 (P–O–C), 830 (P=S) cm^{-1}.

cis-4-t-Butylcyclohexanol (**1**) was obtained by reduction of 4-*t*-butylcyclohexanone using lithium tri-sec-butylborohydride ("L-Selectride") in tetrahydrofuran as previously described.[3]

cis-4-t-Butylcyclohexyl phosphorodichloridate (**2**; X = O). A solution of *cis*-4-*t*-butylcyclohexanol (1.5 g; 1 mol equiv.) and triethylamine (0.97; 1 mol equiv.) in ether (30 ml) was added to a stirred solution of phosphorus oxychloride (1.47 g, 1 mol equiv.) in ether (20 ml) at −78°. The mixture was stirred for 4 hr at room temperature and the triethylamine hydrochloride (1.1 g) filtered off. The filtrate was evaporated under reduced pressure, the residue shaken with 40–60° petroleum ether (20 ml) at 0°, and filtration removed more triethylamine hydrochloride. The filtrate was evaporated and the residue, by trituration with pentane at −5°, afforded the *cis-dichloridate* (1.8 g, 69%), mp 61–64°. Tlc (EtOAc–petroleum ether 1:1) gave one spot, R_F 0.72. ν_{max} 1290 (P=O), 1020, 990 (P–O–C) cm^{-1}. The solid on standing overnight at room temperature in a stoppered tube decomposed to a brown oil. The *cis*-dichloridate (**2**; X = O) was characterized as the following solid derivatives (structures are shown in Scheme 1 except that in all cases the C–O–P bond is axial to the cyclohexane ring).

The N,N'-diphenylhydrazide (**6**; X = O, R = Ph) The *cis*-phosphorodichloridate was reacted with phenylhydrazine (4 mol equivs.) in acetonitrile for 24 hr at 4° and 2 hr at room temperature to give *the diphenylhydrazide* (61%) (EtOH), mp 179–180°. (Found: C, 63.55; H, 7.9; N, 13.5. $C_{22}H_{33}N_4O_2P$ requires C, 63.5; H, 7.9; N, 13.5%.) ν_{max} 3365, 3330, 3290 (NH), 1610, 1500 (C=C), 1210 (P=O), 1010 (P–O–C) cm^{-1}. Tlc (propan-2-ol, toluene, EtOAc, H_2O) 5:1:2.5:1.25 showed one spot, R_F 0.79 (cf. *trans* isomer, R_F 0.77).

The *phosphate* (**5**; X = O). The *cis*-phosphorodichloridate was treated with water at room temperature for 6 hr; the precipitate was collected and recrystallized from acetone to give the *phosphate* (70%) mp 161–164°. (Found: C, 50.75; H, 8.7. $C_{10}H_{21}O_4P$ requires C, 50.85; H, 8.9%.) ν_{max} 2300, 1635–1595 (P–OH), 1205 (P=O), 1015 (P–O–C) cm^{-1}.

cis, trans-bis(4-t-Butylcyclohexyl) Phosphorochloridate

A solution of *cis*-4-*t*-butylcyclohexanol (3.4 g; 1 mol equiv.) and triethylamine (2.20 g; 1 mol equiv.) in ether (50 ml) was added to a stirred solution of *trans*-4-*t*-butylcyclohexylphosphorodichloridate (**2**; X = O) (5.95 g; 1 mol equiv.) in ether (50 ml). The mixture was stirred for 30 hr at room temperature, cooled, and triethylamine hydrochloride (1.8 g) (calculated weight 3 g) filtered off. This showed the reaction was not complete so the solvent was evaporated and the residual oil dissolved in toluene and more triethylamine (1 g) added. The solution was boiled under reflux for 24 hr. Evaporation gave a pale yellow liquid (2.39 g 33%). ν_{max} 1250 (P=O), 1025, 1000 (P–O–C) cm^{-1}. Condensation of the phosphorochloridate with phenylhydrazine (2 mol equivs.) in petroleum ether for 24 hr at 4° gave the *phenylhydrazide derivative* (34%) EtOH, mp 228–230.5°. Found: C, 67.05; H, 9.4; N, 6.0. $C_{26}H_{45}N_2O_3P$ requires C, 67.2; H, 9.7; N, 6.0%.) ν_{max} 3315, 3220, (NH), 1605, 1495 (C=C), 1225 (P=O), 1055, 1045, 1030 (P–O–C) cm^{-1}. Tlc (EtOH–petroleum ether) showed one spot, R_F 0.62. Condensation of *trans*-4-*t*-butylcyclohexanol with *cis*-4-*t*-butylcyclohexylphosphorodichloridate required identical conditions and the product with phenylhydrazine gave the same phenylhydrazide (mp 228–230.5; R_F 0.62).

Acetone cis,trans-bis(4-t-Butylcyclohexyl) Phosphorohydrazone

cis, trans-bis(4-*t*-Butylcyclohexyl) phosphorochloridate (1 g; 1 mol equiv.) was added to a stirred solution of hydrazine hydrate (3 mol equivs.) in acetonitrile (20 ml). The solution was stirred at room temperature for 6 hr, and poured onto ice-water to give the *hydrazide* (0.6 g, 61%), mp 228–231°. ν_{max} 3360, 3230 (NH), 1210 (P=O), 1055 (P–O–C) cm^{-1}. Boiling this material with acetone for 4 hr gave the *acetone hydrazone* (57%) mp 247–249° (from CH_3CN). (Found: C, 64.2; H, 10.5; N, 6.9. $C_{23}H_{45}N_2O_3P$ requires C, 64.5; H, 10.5; N, 6.5%.) ν_{max} 3240 (NH), 1215 (P=O), 1020, 1000 (P–O–C) cm^{-1}.

Reaction of cis,trans-bis(4-t-Butylcyclohexyl) Phosphorohydrazide with Phenylisocyanate

Phenylisocyanate (0.12 g; 1 mol equiv.) was added to a suspension of the hydrazide (0.04 g, 1 mol equiv.) in 60–80° petroleum ether (15 ml). The mixture was boiled under reflux for 3 hr. Cooling gave the *N-phenylcarbamoyl derivative* (0.04 g; 76%), mp 255–259°. (Found: C, 63.8; H, 8.9; N, 8.4. $C_{27}H_{46}N_3O_4P$ requires C, 63.9; H, 9.1; N, 8.3%.) ν_{max} 3320 br (NH), 1680 (C=O), 1600, 1500 (C=C), 1230 (P=O), 1060, 1030 (P–O–C) cm^{-1}. Tlc (EtOH) showed one spot, R_F 0.79.

bis(trans-4-t-Butylcyclohexyl) Phosphorochloridate (**15**; X = O, Y = Cl)

trans-4-*t*-Butylcyclohexanol was reacted with phosphoryl chloride and triethylamine in ether as previously described[1,2] to give the phosphorochloridate (54%), mp 115–119° (lit.[1,2] 127–128°). (Found: C, 61.0, h, 9.7; P, 8.0. Calc. for $C_{20}H_{38}ClO_3P$: C, 61.1; H, 9.7; P, 7.9%.) Nmr ($CDCl_3$(δ: 4.34m (2H, Ha), 2.38–0.98 (18 cyclohexyl protons), 0.99s (2 × $(CH_3)_3C$). This was converted into the derivatives (listed in Table I, Nos. 16–37). The hydrazide (18) was characterized by formation of the hydrazones (19–24, 37) and by reaction with phenylisocyanate and isothiocyanate to give the phenylcarbamoyl and phenylthiocarbamoyl derivatives (27, 36). The hydrazide was also converted to the arylsulphonamides (31–34). The phosphoramide (28) was also reacted with phenylisocyanate to give the phenylcarbamoyl derivative (29). The azide (17) by reaction with norbornene and triphenyl phosphine (cf. Refs. 12, 13) gave the aziridine (25) and the triphenylphosphinimine (26). Nmr of (26) ($CDCl_3$) δ: 7.96–7.30m (15 ArH), 4.20–3.81m (2H, Ha), 2.20–0.84m (18 cyclohexyl protons), 0.80 (18H, 2 × $(CH_3)_3C$).

Reaction of bis(trans-4-t-Butylcyclohexyl) Phosphorochloridate with Ethanolamine

Bis(*trans*-4-*t*-butylcyclohexyl) phosphorochloridate (**15**; X = O, Y = Cl) (3.92 g, 1 mol equiv.) in 60–80° petroleum ether (20 ml) was added dropwise to a stirred solution of ethanolamine (0.31 g of 99%; 2 mol equivs.) in 60–80° petrolum ether (5 ml). Stirring was continued for 1 hr at room temperature and the mixture left at 4° for 72 hr. The precipitate was washed with water, acetone, and pentane (5 ml) to give the *phosphoramidoethanol* (**15**; X = O, Y = $NHCH_2CH_2OH$) (0.98 g), mp 143–145°. (Found: C, 63.4; H, 10.58; N, 3.4. $C_{22}H_{44}NO_4P$ requires C, 63.3: H, 10.55; N, 3.35%.) The possible cyclic product (p. 5), $C_{12}H_{24}NO_3P$ requires C, 55.2; H, 9.2; N, 5.4%.) ν_{max} 3450 (OH) 3395 (NH), 1225 (P=O), 1000, 960 (P–O–C) cm^{-1}. Tlc (propan-2-ol : toluene : EtOAc : H_2O 5 : 1 : 2.5 : 1.25) one spot, R_F 0.79. Nmr ($CDCl_3$) δ: 4.6–4.35 (3H, Ha × 2), 4.02br (NH), 3.51–3.38t (2H, CH_2OH), 3.39s (1H, OH), 2.9–2.72 (NH–CH_2, *J* 6.5 H_2), 2.7–0.94m (18 cyclohexyl protons), 0.83s (18H, 2 × $(CH_3)_3C$). Signals at 4.02, 3.39 were removed by D_2O.

Bis(trans-4-t-Butylcyclohexyl) Phosphorochloridothioate (**15**; X = S, Y = Cl)

trans-4-*t*-Butylcyclohexanol (15.6 g; 2 mol equivs.) and triethylamine (10.1 g; 2 mol equivs.) in dry toluene (100 ml) was added to a stirred solution of thiophosphoryl chloride (8.45 g; 1 mol equiv.) in toluene (100 ml) at 0°. Stirring was continued for 1½ hr at room temperature and the mixture was boiled under reflux for 6 hr. After cooling, triethylamine hydrochloride (12.9 g) was filtered off. Evaporation and treatment with petroleum ether gave more hydrochloride (1.3 g). Evaporation of petroleum ether gave the crude *chloridothionate* as a brown semi-solid (10.1 g). ν_{max} 3420–3340 (OH), 2720–2660 ($Et_3\overset{+}{N}H\overset{-}{Cl}$), 990 (P–O–C), 840 or 775 (P=S) cm^{-1}. Experiments in ether or acetone using pyridine or triethylamine for up to 100 hr gave largely unreacted 4-*t*-butylcyclohexanol. The crude product was converted into the solid derivatives listed in Table I (Nos. 38–39).

Reaction of trans bis(trans-4-t-Butylcyclohexyl) Phosphoroamidothioate (**39**) *with Phenylisocyanate*

The amidothioate (39) (1.2 g; 1 mol equiv.) was boiled under reflux with phenylisocyanate (0.73 g; 2 mol equivs.) in 60–80° petroleum ether (25 ml) for 16 hr. Cooling and recrystallization from chloroform afforded the *N,N-diphenylurea derivative* (**15**; X = S, Y = NH–$CONPh_2$) (1.1 g), mp 149–150°. (Found: C, 67.6; H, 8.1; N, 4.7. $C_{33}H_{44}N_2O_3PS$ requires C, 67.8; H, 8.4; N, 4.8%.) ν_{max} 3340 (NH), 1705 (CONH), 1060, 1030 (P–O–C), 760, 745 (P=S) cm^{-1}. Nmr ($CDCl_3$) δ: 7.60–7.00m (10 ArH), 6.72 br (1NH), 4.76–4.53m (2H, 2 × Ha), 2.22–1.04m (18 cyclohexyl protons), 0.86s (18H, 2 × $(CH_3)_3C$).

cis-4-t-Butylcyclohexylphosphorodichloridothioate (**2**; X = S)

A solution of *cis*-4-*t*-butylcyclohexanol (4.8 g; 1 mol equiv.) and pyridine (2.43 g; 1 mol equiv.) in dry toluene (75 ml) was added to a stirred solution of thiophosphoryl chloride (5.2 g; 1 mol equiv.) in toluene (50 ml) at room temperature. After 2 hr, pyridine hydrochloride (2.6 g, calc. yield 3.6 g) was filtered off; the filtrate was boiled under reflux for 1½ hr, cooled and further pyridine hydrochloride (0.55 g removed). The filtrate was washed with water (3 × 100 ml), dried ($MgSO_4$), and evaporated to give a pale yellow oil (4.9 g, 55%). Tlc (EtOAc–petroleum ether 1 : 1) showed one spot, R_F 0.88. ν_{max} 970 (P–O–C), 870 (P=S) cm^{-1}. *cis*-4-*t*-Butylcyclohexylphosphorodichloridothioate was converted into the following derivatives.

Diphenylhydrazide (**6**; X = S, R = Ph). Condensation of the dichloridothioate with phenylhydrazine (4 mol equivs.) in acetonitrile for 2 hr at room temperature and 12 hr at 4° gave the *diphenylhydrazide* (37%), mp 163–165°. (Found: C, 61.0; H, 7.8; N, 12.8. $C_{22}H_{33}N_4OPS$ requires C, 61.1; H, 7.6; N, 12.95%.) ν_{max} 3305, 3260 (NH), 1600, 1490 (C=C), 1005, 980 (P–O–C), 800 (P=S) cm^{-1}. Tlc (EtOAc–petroleum ether 1 : 1) showed one spot, R_F 0.84.

The dimorpholidate. Treatment of the dichloridothioate with morpholine (4 mol equivs.) in acetonitrile at 4° for 24 hr gave the *dimorpholidate* (**3**; X = S, R = morpholino) (26%), mp 132–136°. (Found: C, 55.5; H, 16.2; N, 12.9. $C_{18}H_{35}N_2O_3PS$ requires C, 55.4; H, 16.20; N, 13.0%.) ν_{max} 1020, 1005 (P–O–C), 950 (P–N), 850 (P=S) cm^{-1}.

2-Isopropyl-5-methylcyclohexyl phosphorodichloridate (**40**; X = O, Y = Z = Cl). 2-Isopropyl-5-methylcyclohexanol (1-menthol) (7.8 g; 1 mol equiv.) and triethylamine (5.1 g; 1 mol equiv.) in ether (60 ml) was dropped into a stirred solution of phosphorus oxychloride (6.7 g; 1 mol equiv.) at 0°. The mixture was stirred at room temperature for 4 hr, and boiled under reflux for 15 min. After cooling (0°), triethylamine hydrochloride (6 g) was filtered off and the filtrate evaporated. The residue was triturated with petroleum ether and filtered to remove further amine hydrochloride. Evaporation gave the *phosphorodichloridate* as a pale yellow oil (10.1 g, 74%). ν_{max} 1295 (P=O), 1000, 980 (P–O–C) cm^{-1}. The phosphorodichloridate (**40**; X = O, Y = Z = Cl) was characterized by the preparation of derivatives (Table II, Nos. 41–54).

Phenyl 2-isopropyl-5-methylcyclohexyl phosphorochloridate (**40**; X = O, Y = OPh, Z = Cl). A solution of 1-menthol (15.6 g; 1 mol equiv.) and triethylamine (10.1 g; 1 mol equiv.) in ether (100 ml) was added dropwise to a stirred solution of phenyl phosphorodichloridate (21.1 g; 1 mol equiv.) in ether

(150 ml). After 36 hr at room temperature, triethylamine hydrochloride (11.2 g) was filtered off. The filtrate was washed with H_2O (3 × 100 ml), $NaHSO_3$ (100 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the *phenyl phosphorochloridate* as an oil (26.5 g, 80%). Tlc (EtOAc–petroleum ether 1 : 1) showed a single spot, R_F 0.64. (Found: C, 43.7; H, 6.8; P, 11.4. $C_{10}H_{19}Cl_2O_2P$ requires C, 43.95; H, 7.0; P, 11.35%.) ν_{max} 3060 (arom C–H), 1600, 1495 (C=C), 1300 (P=O), 1015, 1005 (P–O–C) cm^{-1}. This was converted into the derivatives listed in Table II (55–62).

2-Isopropyl-5-methylcyclohexyl phosphorodichloridothioate (**40**; X = S, Y = Z = Cl). A solution of l-Menthol (15.6 g; 1 mol equiv.) and pyridine (7.9 g; 1 mol equiv.) in acetone (150 ml) was gradually added to a stirred solution of thiophosphoryl chloride (16.9 g; 1 mol equiv.) in acetone (100 ml) at 0°. After 24 h at room temperature, the solvent was removed under reduced pressure. The residue was triturated with 40–60° petroleum ether at 0°, filtration removed pyridine hydrochloride and evaporation of the filtrate gave the crude phosphorodichloridothioate as a pale yellow liquid (19 g, 66%). ν_{max} 995, 970 (P–O–C), 845 (P=S) cm^{-1}. The compound was characterized by formation of the derivatives (63–68, Table II).

2-Isopropyl-3-methylcyclohexyl thiophosphorodihydrazide (**40**; X = S, Y = Z = NH–NH_2). 1-Menthyl phosphorodichloridothioate (**40**; X = S, Y = Z = Cl) (1.45 g; 1 mol equiv.) was gradually added to a stirred solution of hydrazine hydrate (1.25 g, 5 mol equivs.) in ethanol (25 ml). The solution was boiled for 15 min and left 24 hr at room temperature. Addition of water and extraction with petroleum ether gave an oil (1.2 g, 85%). ν_{max} 3320br (NH_2, NH), 1025, 995 (P–O–C), 820 cm^{-1} (P=S). This was characterized by reaction with phenylisocyanate (2 mol equivs.) in boiling 60–80° petroleum ether to give the *N,N'-diphenylcarbamoyl derivative* (67) (0.7 g). ν_{max} 3290, 3220, 3100 (NH), 1670 (CONH), 1500 (C=C), 1015, 1000 (P–O–C), 825 (P=S) cm^{-1}.

Ethyl 2-isopropyl-5-methylcyclohexyl phosphorodichloridothioate (**40**; X = S, Y = Cl, Z = OEt). A solution of 1-menthol (15.6 g; 1 mol equiv.) and triethylamine (10.1 g; 1 mol equiv.) in toluene (100 ml) was gradually added to a stirred solution of ethyl dichloridophosphorothioate (17.9 g; 1 mol equiv.) in toluene (75 ml). The mixture was boiled under reflux for 5 hr and left at 4° overnight. Filtration removed triethylamine hydrochloride (14 g) and evaporation of the filtrate gave the chloridothioate as a yellow oil (21.6 g, 72%). ν_{max} 990, 980 (P–O–C), 835 (P=S) cm^{-1}. Characterized by formation of the *morpholidate* (Table II, 70). Hydrolysis (boiling 10% aqueous NaOH) caused desulphuration to give the corresponding *ethyl phosphate* (69).

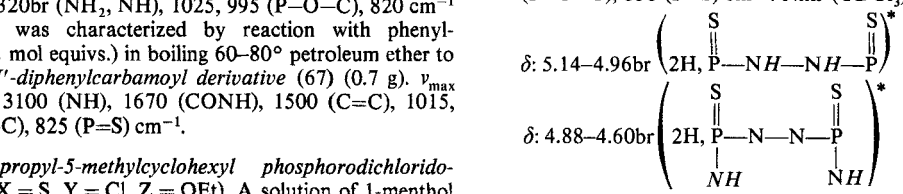
P^1:P^2-Di(2-Isopropyl-3-Methylcyclohexyl) P^1:P^2-Dianilino Pyrophosphate

2-Isopropyl-5-methylcyclohexyl *N*-phenylphosphoramidic chloride (**44**) (1.5 g) in pyridine (7 ml) was stirred with 1 N-aqueous pyridine (2.5 ml) for 3 hr. Dilution with ice-water (1 l) gave a solid, which by recrystallization (CH_3CN) afforded the *P^1:P^2-dianilino pyrophosphate* (0.5 g), mp 134–137°. (Found: C, 63.2; H, 8.5; N, 4.6. $C_{32}H_{50}N_2O_5P_2$ requires C, 63.6; H, 8.3; N, 4.6%.) ν_{max} 3170, 3100 (NH), 1610, 1505 (C=C), 1240 (P=O), 1020 (P–O–C), 950 (P–O–P) cm^{-1}.

Effect of heat on cis and trans 4-t-butylcyclohexyl phosphorodichloridates (**2**; X = O). *trans*-4-*t*-Butylcyclohexyl phosphorodichloridate (1 g) was boiled under reflux with 60–80° petroleum ether (20 ml) for 15 min. Tlc (EtOAc–petroleum ether 1 : 1) indicated unchanged dichloridate, R_F 0.64. Evaporation and boiling in toluene (15 ml) also gave unchanged dichloridate (0.8 g). There was no indication of any 4-*t*-butylcyclohexene (R_F 0.83). (The dichloridate was characterized as the diphenylhydrazide (**6**; R = Ph).) *Cis*-4-*t*-Butylcyclohexyl phosphorodichloridate (1 g) was dissolved in 60–80° petroleum ether (20 ml) and left at room temperature for 24 hr. Tlc (EtOAc–petroleum ether 1 : 1) indicated unchanged phosphorodichloridate, R_F 0.68. When the solution was heated at 55° for 15 min, Tlc showed one spot, R_F 0.83. The solution was washed with water (2 × 20 ml), dried ($MgSO_4$), and evaporated to give a clear oil (0.6 g), R_F 0.82. Authentic 4-*t*-butylcyclohexene showed R_F 0.82. ν_{max} 3030 (C=H), 1660 (C=C). Tests for P, Cl were negative. (Found: C, 87.1; H, 12.7. Calc. for $C_{10}H_{18}$: C, 87.0; H, 13.0%.)

Reaction of trans-4-t-Butylcyclohexyl Phosphorodichloridothioate with Hydrazine

The phosphorodichloridothioate (**2**; X = S) (1.44 g; 1 mol equiv.) in ethanol (15 ml) was added dropwise to hydrazine hydrate (1.25 g; 1 mol equiv.) in ethanol (10 ml). After stirring for 24 hr, the mixture was filtered and the solid washed with ice-water (500 ml). Recrystallization from ethanol gave *P^1:P^2-di(4-t-butylcyclohexyl) P^1:P^2-dihydrazide phosphorohydrazinodithioate* (**71**) (0.5 g), mp 166–168°. (Found: C, 45.35; H, 8.9; N, 16.2; P, 11.5. $C_{20}H_{46}N_6O_2P_2S_2$ requires C, 45.45; H, 8.7; N, 15.9; P, 11.7%.) ν_{max} 3340 (NH_2), 3280 (NH), 1030, 1010 (P–O–C), 850 (P=S) cm^{-1}. Nmr ($CDCl_3$)



4.55–4.22 (2H of cyclohexyl ring next to O), 3.72–3.20br (4H, $2NH_2$), 2.22–1.00m (18 cyclohexyl protons), 0.86s (18H, 2 × $(CH_3)_3C$). The same product (**71**) was obtained when the order of addition of the reactants was reversed. Treatment of the P^1:P^2-dihydrazine (**71**) with boiling acetone (4 hr) gave the *acetone bis hydrazone*, mp 110°. (Found: C, 51.8; H, 8.9; N, 14.1. $C_{26}H_{54}N_6O_2P_2S_2$ requires C, 51.5; H, 8.6; N, 13.9%.) Nmr ($CDCl_3$) δ: 5.83br (2H, 2 × C=N–NH), 4.46br (2H, 2 × P–NH), 3.80m (2H, cyclohexyl protons next to O), 2.30–0.93m (18 cyclohexyl protons), 1.91d (12H, 2 × $C(CH_3)_2$), 0.87s (18H, 2 × $(CH_3)_3C$).

REFERENCES

1. R. J. W. Cremlyn, B. B. Dewhurst and D. H. Wakeford, *Synthesis* 648 (1971).
2. R. J. W. Cremlyn, B. B. Dewhurst, D. H. Wakeford and R. A. Raja, *J. Chem. Soc. Perkin* **1**, 1171 (1972).
3. H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.* **94**, 7159 (1972).
4. J. M. Fortunato and B. Ganem, *J. Org. Chem.* **41**, 2194 (1976).
5. E. L. Eliel and M. N. Rerick, *J. Amer. Chem. Soc.* **82**, 1371 (1960).

6. H. S. Booth, D. R. Martin and F. E. Kendall, *J. Amer. Chem. Soc.* **70**, 2523 (1948).
7. E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* (Interscience, New York, 1965), p. 291.
8. A. D. F. Toy, *J. Amer. Chem. Soc.* **73**, 4670 (1951).
9. L. C. Thomas, *Interpretation of the Infrared Spectra of Phosphorus Compounds* (Heyden, London, 1974), (a) p. 46; (b), p. 51; (c) p. 129.
10. R. J. W. Cremlyn, B. B. Dewhurst and D. H. Wakeford, *J. Chem. Soc.* (*C*) 3011 (1971).
11. R. A. Shaw and M. Woods, *Phosphorus* **1**, 41 (1971).
12. R. J. W. Cremlyn and D. H. Wakeford, *Topics in Phosphorus Chemistry*. E. J. Griffith and M. Grayson, Eds. (Wiley, New York, 1976), Vol. 8, p. 1.
13. G. E. Chivers, R. J. W. Cremlyn, T. N. Cronje and R. A. Martin, *Aust. J. Chem.* **29**, 1573 (1976).