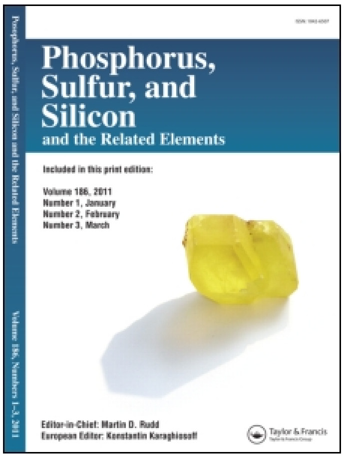

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SOME PHOSPHORYLATED DERIVATIVES OF BORNEOL

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Borneol (1 mol. equiv.) has been phosphorylated with phosphorus oxy(thio)chloride to the phosphorodichloridate; condensation with phenylphosphorodichloridate similarly afforded the phenylphosphorochloridate. The phosphorochloridates were characterized by preparation of various solid derivatives, such as diamidates, hydrazides, and phenylhydrazides.

With phosphorus trichloride, borneol gave the phosphorodichloridite which was characterized as the anilinium phosphite and by formation of the *N*,*N*^{1}-diphenyldiamidite.

Reaction of borneol (2 mol. equivs.) with phosphorus oxychloride gave bis(bornyl) phosphorochloridate, characterized as solid derivatives, e.g. the phosphate, hydrazide, phenylhydrazide, and cyclohexylamidate.

In contrast attempts to phosphorylate isoborneol (*exo*-OH) with, for instance, phosphorus oxychloride, thiophosphoryl chloride and phosphorus trichloride were unsuccessful as was the preparation of bis(isobornyl) phosphorochloridate.

Possible explanations for this failure are briefly discussed.

INTRODUCTION

Previous studies dealt with the phosphorylation of the alicyclic systems *cis*- and *trans*-4-*t*-butylcyclohexanol and menthol.[1–3] More recently[4] we described the phosphorylation of *exo*- and *endo*-norborneol. Both isomeric norborneols were successfully phosphorylated using such reagents as phosphorus oxychloride, thiophosphoryl chloride, and phenylphosphorodichloridate. The present paper describes the extension of these phosphorylation studies to the analogous bicyclic terpenes borneol and isoborneol.

The various phosphorylated derivatives are of interest as potential pesticides, especially in view of the recent development of organophosphorus compounds as herbicides and fungicides.[5]

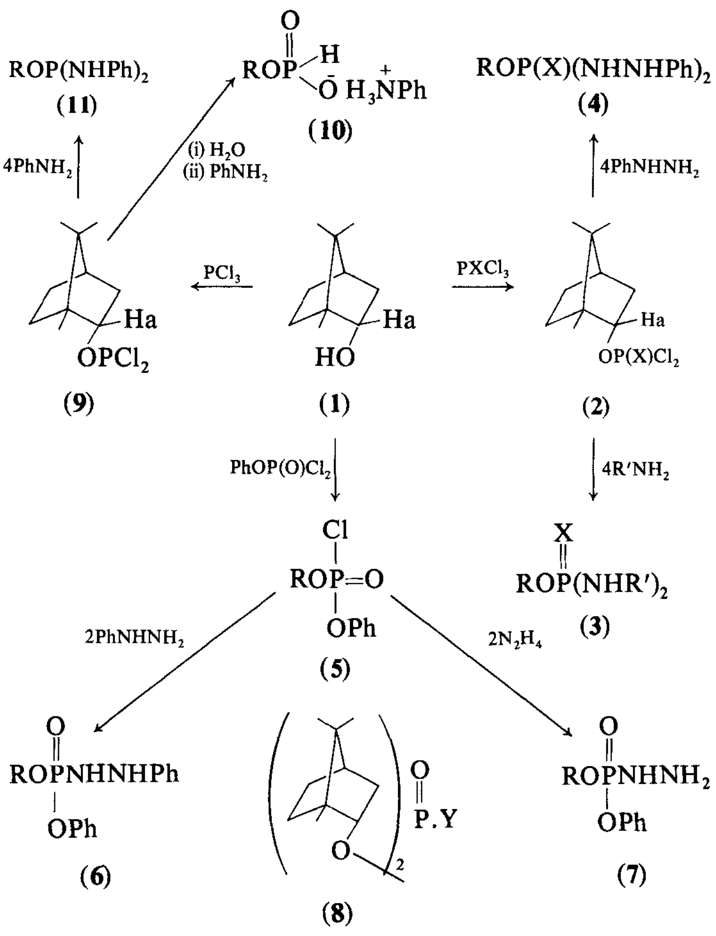
DISCUSSION

Borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol) (**1**, Scheme 1) by reaction with an equimolar amount of phosphorus oxychloride or thiochloride at room temperature gave the phosphorodichloridate (**2**; X = O or S). This was characterized by conversion to the solid derivatives (**3**, **4**) as shown in Scheme 1. Borneol (**1**) with phenylphosphorodichloridate at room temperature gave the phenylphosphorochloridate (**5**; X = O) which by reaction with phenylhydrazine or hydrazine (2 mol. equivs.) gave the corresponding *N*-phenylhydrazide (**6**) and hydrazide (**7**).

When borneol (2 mol. equivs.) was caused to react with phosphorus oxychloride (1 mol. equiv.) bis(bornyl) phosphorochloridate (**8**; Y = Cl) was obtained. The phosphorochloridate was hydrolysed to the phosphate (**8**; Y = OH), while condensation with hydrazine hydrate gave the hydrazide (**8**; Y = $NHNH_2$). The hydrazide was further converted to the acetone hydrazone (**8**: Y = $NH \cdot N = CMe_2$) and the *N*-phenylcarbamoyl derivative (**8**; Y = NHNHCONHPh).

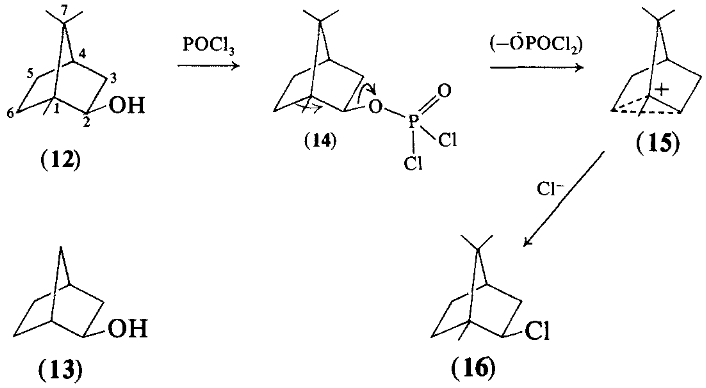
Reaction of borneol (**1**) with phosphorus trichloride gave the dichloridite (**9**). Hydrolysis and subsequent reaction with aniline gave the solid anilinium phosphite (**10**). The dichloridite (**9**) was also condensed with aniline to give the *N*,*N*'-diphenylphosphorodiamidite (**11**).

In contrast to the successful phosphorylation of borneol (**1**), attempts to phosphorylate isoborneol (**12**; *exo*-OH) failed to give identifiable phosphorylated products. The reagents investigated were: (a) phosphorus oxychloride; (b) *O*-phenyl *N*-phenylphosphoramidic chloride; (c) *N*-cyclohexyl *O*-phenylphosphoramidic chloride; (d) *N*-phenylphosphoramidic dichloride; (e) ethylphenylphosphorochloridate; (f) thiophosphoryl chloride, and (g) phosphorus trichloride. With (a) at room temperature, the unchanged alcohol (**12**) was isolated although in boiling toluene the product was isobornyl chloride.



R = bornyl

SCHEME 1



SCHEME 2

With (b) the unchanged reagent was recovered, but with the cyclohexyl analogue (c) an unknown compound resulted. Both reagents (d) and (e) gave isoborneol (**12**).

Reagents (f) and (g) gave unknown phosphorus-containing oils and efforts to characterize the oils respectively as the dimorpholidate and *N,N'*-diphenyldiamidate derivatives failed.

The failure to isolate a phosphorylated product from isoborneol (**12**), which is in marked contrast to the successful phosphorylation of *exo*-norborneol (**13**),[4] is undoubtedly due mainly to the steric effect of the *syn*-7-methyl group and to a lesser extent to that of the adjacent 1-methyl group.[6] While direct *exo*-attack at the 2- or 3-carbon atoms (**12**) by reagents is very largely prevented by these steric effects,[7a] attack on the *exo*-hydroxyl group of isoborneol should be possible if the incoming group has a low steric requirement. Thus the bulky phosphorylating agents (b)–(e) failed to react with isoborneol. Phosphorus oxychloride, however, a less sterically demanding reagent, under forcing conditions (boiling toluene) appears to give isobornyl phosphorodichloridate (**14**). The combination of high steric strain in this molecule, the ability of the phosphorodichlorido group to act as a leaving group,[4] and the possibility of σ-bond participation[8] favours the formation of the intermediate carbonium ion species. The subsequent reaction of the carbonium ion (**15**) with chloride ion would explain the observed formation of isobornyl chloride (**16**) (Scheme 2); however, whether the driving force for the rearrangement is solely steric in nature or entirely due to σ-bond participation leading to the non-classical ion is currently a matter of controversy.[7b]

When the reaction was examined under milder conditions (room temperature), phosphorus oxychloride did not phosphorylate isoborneol, although the reaction was successful with exo-norborneol. In the reactions of isoborneol (**12**) with reagents (f) and (g) some phosphorylation appears to have occurred. This would be expected in view of their low steric requirements, and the lack of any rearrangement products are probably due to the fact that the $PSCl_2$ and PCl_2 groups are not as good leaving groups as the dichlorophosphoro group.

In the ir spectra of the bornyl phosphorus compounds, the P=O stretching bands appeared in the range 1205–1310 cm^{-1}; substitution of chlorine atoms by amino functions substantially reduced the phosphoryl frequency from 1310–1300 cm^{-1} to 1245–1205 cm^{-1}. This would be expected in view of the electron-releasing effect of the nitrogen atom (cf. Refs. 9 and 10). In agreement with our previous results[3,4] the P=S stretching band appeared in the range 830–845 cm^{-1} and the P—O—C band in the range 930–1050 cm^{-1}. As in the norbornyl phosphorus derivatives,[4] the nmr spectra showed the Ha protons as complex multiplets (δ 4.74–4.55) due to extensive coupling with the adjacent alicyclic protons and with the phosphorus atom through oxygen.

EXPERIMENTAL

Ir spectra were determined as liquid films or Nujol mulls using a Perkin Elmer 127 spectrometer. Nmr spectra were measured using a Varian A60A Spectrometer with tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS 9 spectrometer at 70 ev. Melting points were determined with Kofler hot-stage apparatus and are uncorrected. Tlc was carried out on Silica gel G plates developed with iodine vapour. Microanalyses were carried out by Butterworth Microanalytical Consultants Ltd., Teddington, England.

Bornyl Phosphorodichloridate (**2**; X = O)

A solution of borneol (*endo*-1,7,7-trimethylbicyclo[2.2.1] heptan-2-ol) (**1**) (15.4 g; 0.1 mole) and triethylamine (12.12 g; 0.12 mole) in toluene (125 ml) was added dropwise to a stirred solution of phosphorus oxychloride (18.42 g; 0.12 mole) in toluene (50 ml) at 0°. After 20 h at room temperature, triethylamine hydrochloride (14.0 g) was filtered off, and the filtrate evaporated to give the *phosphorodichloridate*, as an oil (20.2 g; 74.5%). ν_{max} 1310, 1295d (P=O), 1025, 1010, 998 (P—O—C) cm^{-1}. Tlc (EtOAc–petroleum ether 60–80° 1:1) gave one spot, R_F 0.75.

The phosphorodichloridate (**2**; X = O) was characterized by formation of the following derivatives:

N,N'-Dicyclohexyldiamidate (**3**; X = O, R' = C_6H_{11}) (EtOH) (71%), mp 199–202°. (Found: C, 67.0; H, 10.2: N, 7.15. $C_{22}H_{41}N_2O_2P$ requires C, 66.7; H, 10.35; N, 7.1%.) ν_{max} 3260 (NH), 1205 (P=O), 1030, 1020 (P—O—C) cm^{-1}.

N,N'-Diphenyldiamidate (**3**; X = O, R' = Ph), a liquid (50%). ν_{max} 3210, 3090, 3050 (NH), 1605 (arom C=C), 1230 (P=O), 1032, 1020 (P—O—C) cm^{-1}. Ms gave the molecular ion (M^+, 384) other major ions were at 248 ($(PhNH)_2POOH$), 136, 122. Nmr ($CDCl_3$) δ: 8.10br (2H, 2NH), 7.28–6.91m (10 ArH) 6.10br (2NH), 4.74m (1H, *exo*-Ha), 3.70m (3H, CH_3), 2.40–1.80m (7 alicyclic H), 0.80 (6H, $C(CH_3)_2$). Signal at 6.10 removed by D_2O treatment.

N,N,N',N'-Tetramethyldiamidate, liquid (60%). ν_{max} 1230 (P=O), 1050, 1040 (P—O—C) cm^{-1}. Ms gave the molecular ion (M^+, 288) and other ions at 152 ($(Me_2N)_2POOH$), 136, 135, 121, 119.

N,N'-Diphenylhydrazide (**4**; X = O) (51%), mp 175–177°. (Found: C, 63.8; H, 7.7; N, 13.5. $C_{22}H_{31}N_4O_2P$ requires C, 63.8; H, 7.5; N, 13.5%.) ν_{max} 3340, 3250 (NH), 1605 (arom C=C), 1225 (P=O), 1035, 1025 (P—O—C) cm^{-1}.

Bornyl Phosphorodichloridothioate (**2**; X = S)

A solution of borneol (**1**) (15.4 g; 0.01 mole) and pyridine (7.9 g; 0.01 mole) in acetone (125 ml) was caused to react with a stirred solution of thiophosphoryl chloride (16.9 g; 0.01 mole) in acetone (100 ml) for 20 h to give the crude *dichloridothioate* as a purple oil (17 g; 49%). ν_{max} 1020–990br (P–O–C), 830 (P=S) cm^{-1}.

The dichloridothioate (**2**; X = S) was characterized as the derivatives:

N,N'-Dicyclohexyldiamidate (**3**; X = S, R' = C_6H_{11}) (petroleum ether 40–60°) (45%), mp 148–151°. (Found: C, 64.3; H, 10.0; N, 7.0. $C_{22}H_{42}N_2OPS$ requires C, 64.1; H, 9.95; N, 6.8%.) ν_{max} 3400, 3250 (NH), 1000 (P–O–C), 840 (P=S) cm^{-1}.

Dimorpholidate pale yellow needles (70%), mp 104–106°. (Found: C, 56.0; H, 8.6; N, 7.3. $C_{18}H_{33}N_2O_3PS$ requires C, 55.7; H, 8.5; N, 7.2%.) ν_{max} 1020, 960 (P–O–C), 845 (P=S) cm^{-1}.

N,N'-Diphenylhydrazide (**4**; X = S), yellow needles (petroleum ether) (52%), mp 137–139°. (Found: C, 61.4; H, 7.0; N, 13.2. $C_{22}H_{31}N_4OPS$ requires C, 61.4; H, 7.2; N, 13.0%.) ν_{max} 3320, 3290, 3260 (NH), 1610, 1500 (arom C=C), 1025 (P–O–C), 840 (P=S) cm^{-1}. Nmr δ ($CDCl_3$) 7.40–6.55 (10 ArH), 6.17, 5.10br (4NH), 4.55m (1H, *exo*-Ha), 3.77m (3H, CH_3), 1.87m (7 alicyclic H), 0.85s (6H, $C(CH_3)_2$). The signals at δ 6.17, 6.10 were removed by D_2O treatment.

Bornyl O-Phenylphosphorochloridate (**5**)

A solution of borneol (**1**) (5.18 g; 0.34 mole) and triethylamine (3.4 g; 0.34 mole) in petroleum ether (60–80°) (75 ml) was caused to react with phenylphosphorodichloridate[11a] (7.1 g; 0.34 mole) in petroleum ether (75 ml) for 36 h to give the *O-phenylphosphorochloridate* as a liquid (8.5 g, 76%). ν_{max} 1590, 1490 (arom C=C) 1300 (P=O), 1010, 995 (P–O–C) cm^{-1}. R_F (EtOAc–petroleum ether 60–80° 1:1) showed two spots, R_F 0.75, 0.64. The *O-phenylphosphorochloridate* (**5**) was characterized as the solid derivatives:

N-Phenylhydrazide (**6**) (58%), mp 141–143°. (Found: C, 66.3; H, 7.4; N, 7.2. $C_{22}H_{29}N_2O_3P$ requires C, 66.0; H, 7.25; N, 7.0%) ν_{max} 3320, 3260 (NH), 1600, 1500, 1490 (arom C=C), 1220, 1200 (P=O), 930 (P–O–C) cm^{-1}. Tlc (EtOAc–petroleum ether 60–80° 1:1) showed one spot, R_F 0.54.

Hydrazide (**7**) liquid (75%), n_D^{25} 1.5121. (Found: C, 59.0; H, 8.0; N, 8.4. $C_{16}H_{25}N_2O_3P$ requires C, 58.9; H, 7.7; N, 8.6%.) ν_{max} 3350, 3270–3220 (NH), 1590, 1495 (arom C=C), 1205 (P=O), 1030, 1015 (P–O–C) cm^{-1}.

The hydrazide (**7**) was converted to the *p-nitroacetophenone hydrazone* (petroleum ether) light yellow needles (54%), mp 151–152.5°. (Found: C, 62.3; H, 6.5; N, 8.8. $C_{24}H_{30}N_3O_5P$ requires C, 61.15; H, 6.4; N, 8.9%.) ν_{max} 3160 (NH) 1610, 1590, 1490 (arom C=C), 1515 (NO_2), 1250 (P=O), 1020 (P–O–C) cm^{-1}. Tlc (Pr^{i}OH–toluene–EtOAc–H_2O 5:1:2.5:1.25) showed a single spot, R_F 0.89.

bis(Bornyl)Phosphorochloridate (**8**; Y = Cl)

Borneol (15.4 g; 0.1 mole) and triethylamine (10.1 g; 0.1 mole) in toluene (150 ml) was slowly added to a stirred solution of phosphorus oxychloride (7.68 g; 0.05 mole) in toluene (75 ml). After 2 h the mixture was boiled under reflux for 10 h to give the *phosphorochloridate* as a liquid (9.4 g; 48%). ν_{max} 1308 (P=O), 1025 (P–O–C) cm^{-1}. Tlc (EtOAc–petroleum ether 60–80° 1:1) showed one spot, R_F 0.81.

The phosphorochloridate (**8**; Y = Cl) was converted into the derivatives:

Phosphate (**8**; Y = OH). The phosphorochloridate (1 g) by boiling with water (25 ml) gave the *phosphate*, recrystallized from acetone (0.51 g) (54%), mp 217–219° (lit.[12] 221°). (Found: C, 64.9; H, 9.3; P, 8.15. $C_{20}H_{35}O_4P$ requires C, 64.85; H, 9.5; P, 8.4%.) ν_{max} 2580–2540, 2305–2275 (P–OH), 1240 (P=O), 1035 (P–O–C) cm^{-1}. Tlc (Pr^{i}OH–toluene–EtOAc–H_2O 5:1:2.5:1.25) gave one spot, R_F 0.73. EtOH, R_F 0.68.

Condensation with hydrazine hydrate (2 mol. equivs.) in ethanol (6 h) gave the *hydrazide* (**8**; Y = $NHNH_2$) (petroleum ether 60–80°) (52%), mp 155–157°. (Found: C, 62.7; H, 9.8; N, 7.6. $C_{20}H_{37}N_2O_3P$ requires C, 62.5; H, 9.65; N, 7.3:.) ν_{max} 3350, 3220 (NH), 1235 (P=O), 1030 (P–O–C) cm^{-1}. Tlc (Pr^{i}OH–toluene–EtOAc–H_2O 5:1:2.5:1.25) showed one spot, R_F 0.83; EtOAc–petroleum ether (60–80°) 1:1, one spot R_F 0.24.

Acetone hydrazone (EtOAc–MeCN) (**8**; Y = NHN = CMe_2) (85%), mp 120–121°. (Found: C, 64.9; H, 9.8; N, 6.4. $C_{23}H_{41}N_2O_3P$ requires C, 65.1; H, 9.7; N, 6.6%.) ν_{max} 3180 (NH), 1245 (P=O), 1015, 1000 (P–O–C) cm^{-1}.

The hydrazide (**8**; Y = $NHNH_2$) by boiling with phenylisocyanate (1 mol. equiv.) in petroleum ether (60–80°) for 6 h gave the *N-phenylcarbamoyl hydrazide* (**8**; Y = NHNHCO-NHPh) (petroleum ether 40–60°) (62%), mp 232–234°. (Found: C, 64.6; H, 8.6; N, 8.6. $C_{27}H_{42}N_3O_4P$ requires C, 64.4; H, 8.35; N, 8.35%.) ν_{max} 3290, 3220 (NH), 1672 (CO), 1600, 1500 (arom C=C), 1240 (P=O), 1030 (P–O–C) cm^{-1}.

Phenylhydrazide (**8**; Y = NHNHPh) (EtOH) (43%), mp 206–208°. (Found: C, 67.8; H, 8.8; N, 6.3. $C_{26}H_{41}N_2O_3P$ requires C, 67.8; H, 8.9; N, 6.1%.) ν_{max} 3220, 3120 (NH), 1605, 1590, 1500 (arom C=C), 1215 (P=O), 1055 (P–O–C) cm^{-1}.

Cyclohexylamidate (**8**; Y = NHC_6H_{11}) (C_6H_6–petroleum ether 2:1) (62%), mp 217–218°. (Found: C, 69.4; H, 10.2; N, 3.3. $C_{26}H_{46}NO_3P$ requires C, 69.2; H, 10.2; N, 3.1%.) ν_{max} 3175 (NH), 1245, 1230 (P=O), 1025 (P–O–C) cm^{-1}. Tlc (Pr^{i}OH–toluene–EtoAC–H_2O 5:1:2.5:1.25) showed one spot, R_F 0.33.

Bornyl Phosphorodichloridite (**9**)

Borneol (**1**) (10 g) was added gradually to a solution of phosphorus trichloride (10 ml) at 0°, and the mixture was stirred at room temperature for 15 min. Evaporation *in vacuo* gave the *phosphorodichloridite* as a clear oil (13.2 g, 80%). ν_{max} 1010–975 (P–O–C) cm^{-1}.

This was characterized as the solid derivatives:

The Anilinium Phosphite (**10**)

Bornyl phosphorodichloridite (2 g) was stirred with water (50 ml) for 5 h; and the product extracted with ether (100 ml). Treatment with aniline (2 ml) and recrystallization from acetone gave the *anilinium phosphite* (1.6 g), mp 124–128°. (Found: C, 61.5; H, 8.2; N, 4.7. $C_{16}H_{26}NO_3P$ requires C, 61.7; H, 8.4; N, 4.5%.) ν_{max} 2600–2560, 2365, 2140, 1640, 1620, 1560 ($PhNH_3$), 1605, 1500 (arom C=C), 1195 (P=O), 1050, 1030, (P–O–C) cm^{-1}.

N,N′-Diphenylphosphorodiamidite (**11**)

Bornyl phosphorodichloridite (2.55 g) was caused to react with aniline (3.72 g; 4 mol. equivs.) in ether (50 ml) at 4° for 12 h, to give the *N,N′-diphenylphosphorodiamidite* (2.1 g, 57%) (from acetone), mp 120–121°. (Found: C, 71.55; H, 7.9; N, 7.7. $C_{22}H_{29}N_2OP$ requires C, 71.7; H, 7.9; N, 7.6%.) ν_{max} 3130, 3095 (NH), 1605, 1500 (arom C=C), 975 (P–O–C) cm^{-1}.

Attempted Phosphorylation of Isoborneol

Isoborneol (12) (15.4 g; 1 mol. equiv.) and triethylamine (10.1 g; 1 mol. equiv.) in ether (75 ml) was added dropwise to phosphorus oxychloride (15.3 g; 1 mol. equiv.) in ether (75 ml). After 15 h the reaction gave isoborneol (13 g) (from acetonitrile), mp 208–210° (sealed tube) (lit.[13] 212°) mixed mp with isoborneol = 207–210°. ν_{max} 3430–3340 (OH) cm^{-1}. Ir spectrum was generally similar to that of isoborneol. A similar reaction in toluene at room temperature (12 h) also gave isoborneol; but when the reaction was carried out in boiling toluene a volatile solid was obtained. ν_{max} 1295, 1285, 1080, 1030, 930, 900, 800, 700, 670 cm^{-1} (absence of OH, P=O, and P–O–C stretching bands). The Beilstein test gave $(+)^{ve}$ result for Cl. (Calc. for isobornyl chloride: $C_{10}H_{17}Cl$, C, 69.55; H, 9.8. Found: C, 69.3; H, 9.16%.)

Attempts were also made to phosphorylate isoborneol (**12**) with the following reagents:

(*a*) *O-Phenyl N-Phenylphosphoramidic Chloride*

A solution of isoborneol (1.54 g) in pyridine (6 ml) was treated with *O*-phenyl *N*-phenylphosphoramidic chloride (2.67 g; 1 mol. equiv.) at 0° and 12 h at 4° to give the unchanged phenylphosphoramidic chloride (2.1 g, 54%), mp 132–135° (lit.[14] 129–133°).

(*b*) *With N-Cyclohexyl O-Phenylphosphoramidic Chloride*

Isoborneol (1.54 g) was caused to react with the phosphoramidic chloride (2.74 g; 1 mol. equiv.) in pyridine (12 ml) for 24 h. Recrystallization (ether–acetone) gave an unknown compound (1.3 g), mp 111–113°. (Found: C, 59.7; H, 7.0; N, 6.1. Isobornyl *N*-cyclohexyl *O*-phenylphosphoramidate, $C_{22}H_{34}NO_3P$ requires C, 67.5; H, 8.7; N, 3.6%.) ν_{max} 3190 (NH), 1590, 1490 (arom C=C), 1270, 1255d, 1210 (P=O), 1020, 990 (P–O–C alip), 950 (P–O–C arom) cm^{-1}. Tlc (petroleum ether–EtOAc 1:1) showed one spot, R_F 0.32; and $\mathrm{Pr^iOH}$–toluene–EtOAc–H_2O 5:1:2.5:1.25, one spot R_F 0.78.

(*c*) *With N-Phenylphosphoramidic Dichloride*

Isoborneol (4.62 g) with phenylphosphoramidic dichloride[11b] (6.3 g; 1 mol. equiv.) in pyridine (15 ml) at 4° for 12 h gave isoborneol (3.5 g), mp 209–213° (acetonitrile). (Confirmed by ir and mixed mp with an authentic sample.)

Attempted phosphorylation with ethyl phenylphosphorochloridate[15] under similar conditions again gave isoborneol.

(*d*) *With Thiophosphoryl Chloride*

Thiophosphoryl chloride (8.5 g; 1 mol. equiv.) in toluene (30 ml) was added dropwise to a stirred solution of isoborneol (**12**) (7.7 g; 1 mol. equiv.) and pyridine (4 g; 1 mol. equiv.) in toluene (70 ml). The mixture was stirred for 30 h to give a pale yellow oil (3.7 g)*. ν_{max} 1000, 990, 075 (P–O–C), 825 (P=S) cm^{-1} (no OH band). Sodium fusion indicated presence of phosphorus. A similar product was obtained in pyridine as solvent (35 h), but in acetone–pyridine (1 mol. equiv.) (35 h) isoborneol (85%) was isolated.

Attempted condensation of the oil* with morpholine (4 mol. equivs.) in acetonitrile gave an unknown solid (31%) (pentane) mp 201–203°. (Found: C, 59.2; H, 8.4; N, 3.0. The expected isobornyl dimorpholinophosphorodithioate, $C_{18}H_{33}N_2O_3PS$ requires C, 55.7; H, 8.5; N, 7.2%.) ν_{max} 1000, 970 (P–O–C), 1110 (P–N), 805 (P=S) cm^{-1}. Tlc. ($\mathrm{Pr^iOH}$–toluene–EtoAc–H_2O 5:1:2.5:1.25) showed one spot, R_F 0.67.

(*e*) *With Phosphorus Trichloride*

Isoborneol (10 g) was caused to react with phosphorus trichloride (10 ml) at 0° and for 15 min at room temperature, to give an oil (8 g). ν_{max} 985, 975 (P–O–C) cm^{-1}. Attempted condensation with aniline (4 mol. equivs.) in ether gave an unknown solid (40%), mp 133–136° (from pentane). (Found: C, 58.8; H, 5.4; N, 10.5. The expected isobornyl *N,N′*-diphenylphosphorodiamidite, $C_{22}H_{29}N_2OP$ requires C, 71.7; H, 7.9; N, 7.6%.) ν_{max} 3210, 3090 (NH), 1605, 1500 (arom C=C), 1160d (P=O), 940 (P–O–C) cm^{-1}. Sodium fusion indicated presence of P.

Attempted Preparation of bis(Isobornyl) Phosphorochloridate

Treatment of isoborneol (**12**) (15.4 g; 2 mol. equivs.) with phosphorus oxychloride (7.6 g; 1 mol. equiv.) in pyridine (7.9 g, 2 mol. equivs.) and ether (100 ml) (35 h) or boiling acetone (8 h) gave isoborneol (13 g).

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 I*, 1171 (1972).
3. R. J. W. Cremlyn, R. M. Ellam and N. Akhtar, *Phosphorus and Sulfur* **5**, 1 (1978).
4. R. J. W. Cremlyn, R. M. Ellam and N. Akhtar, *Phosphorus and Sulfur* (in press).
5. R. J. W. Cremlyn, *Internat. Pest Control* **20** (1), 12 (1978).
6. D. C. Kleinfelter and J. M. Miller, *J. Org. Chem.* **38**, 4142 (1973).
7. H. C. Brown, *The Nonclassical Ion Problem* (Plenum Press, New York, 1977), (a) p. 126 (b) p. 2.
8. T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.* 1188 (1939).
9. R. J. W. Cremlyn, B. B. Dewhurst and D. H. Wakeford, *J. Chem. Soc.* (*C*) 301 (1971).
10. L. C. Thomas, *Interpretation of Infra Red Spectra of Phosphorus Compounds* (Heydon, London, 1974).
11. G. M. Kosolapoff and L. Maier (Eds.) *Organic Phosphorus Compounds* (Wiley, New York, 1973), Vol. 6 (a) p. 496, (b) p. 647.
12. H. J. Jacobson and M. Jacobson, *Comp. Rend. Soc. Biol.* **105**, 154 (1930).
13. J. R. A. Pollock and R. Stevens (Eds.) *Dictionary of Organic Compounds* (Eyre and Spottiswoode, London, 1965), 4th ed., Vol. 3, p. 1894.
14. W. S. Zielinsky and Z. Lesnikowski, *Synthesis* 133 (1976).
15. A. Morel, *Bull. Soc. Chim.* **21** (3), 402 (1899).