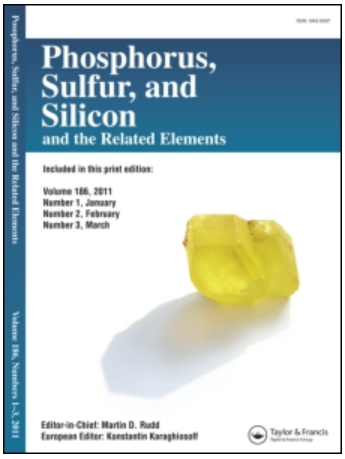


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# SOME REACTIONS OF CHOLESTERYL N-PHENYL-PHOSPHORAMIDIC CHLORIDE AND RELATED COMPOUNDS

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# SOME REACTIONS OF CHOLESTERYL N-PHENYL-PHOSPHORAMIDIC CHLORIDE AND RELATED COMPOUNDS

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Cholesteryl *N*-phenylphosphoramidic chloride has been converted to the corresponding phosphoramidic hydrazide and azide. The former compound was characterised by the preparation of a number of hydrazones, while the latter has been reacted with norbornene, dimethylsulphoxide, and triphenylphosphine. However, the azide did not react with decane, *o*-anisole, or butylamine. 17-Oxoandrost-5-ene-3β-yl *N*-phenylphosphoramidic chloride was prepared and was converted to the hydrazide, but a pure sample of the azide could not be isolated. Cholesteryl *N*-phenyl phosphoramidic triphenylphosphinimine has been reacted with eight carbonyl compounds and the structures of the products investigated. Cholesteryl *N*-cyclohexylphosphoramidic chloride was converted to the azide and the triphenylphosphinimine; the latter was reacted with acetone and *p*-nitrobenzaldehyde.

Cholesteryl phosphorodichloridate has been condensed with phenol, *p*-nitrophenol, and *p*-methoxyphenol to give the corresponding *O*-arylphosphorochloridates. The *O*-phenyl and *O*-*p*-methoxyphenyl phosphorochloridates have been converted to the corresponding azides, but the azide from the *p*-nitrophenyl derivative could not be isolated. The reactions of cholesteryl phosphorodichloridate with diethylamine, hydrazine, and sodium azide have also been examined; and cholesteryl phosphorodichloridothioate has been condensed with aniline and benzylamine.



## INTRODUCTION

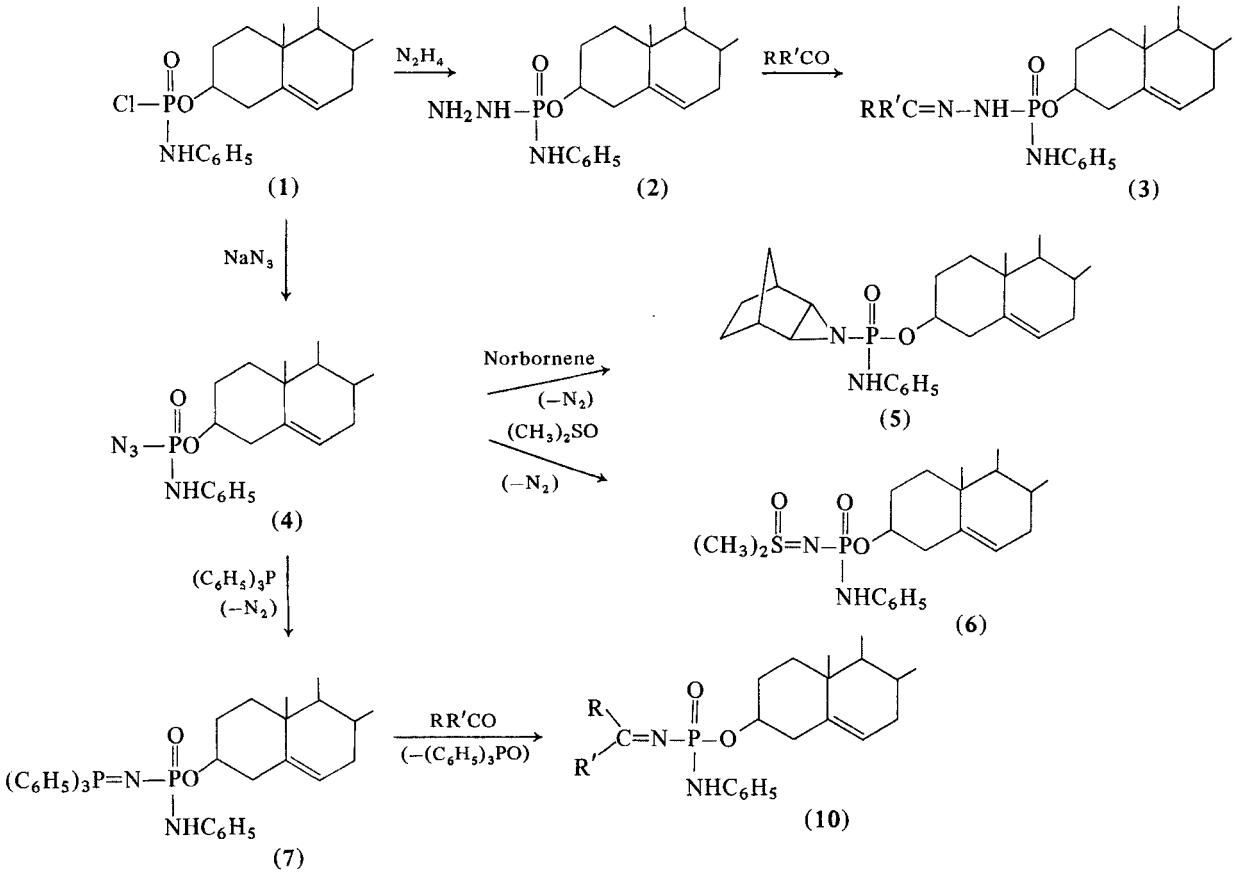
Previous studies[1-2] have investigated the phosphorylation of cholesterol to cholesteryl phosphorodichloridate. The dichloridate, by condensation with aniline (2 mol. equivs.), gave cholesteryl *N*-phenylphosphoramidic chloride.[3] The present work represents an extension to examine the reactions of the latter compound.

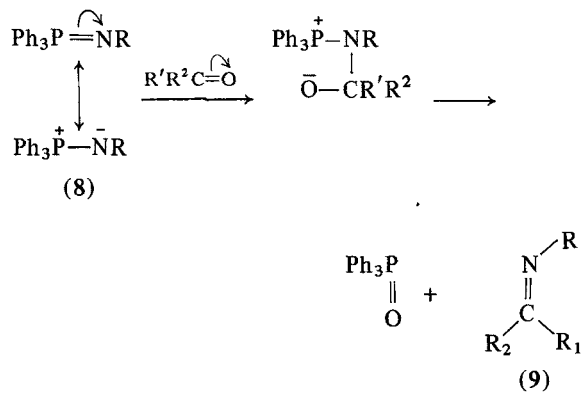
## DISCUSSION

Cholesteryl *N*-phenylphosphoramidic chloride (**1**) condenses with hydrazine hydrate to give the corresponding hydrazide (**2**), which has been characterized by formation of the acetone (**3**; R=R$^1$=Me) and *o*- and *p*-nitrobenzaldehyde (**3**; R=H, R$^1$=$NO_2C_6H_4$) hydrazones. The phosphoramidic chloride (**1**) also reacts with sodium azide to give the phosphoramidic azide (**4**). The azide (**4**) undergoes reactions with norbornene, dimethylsulphoxide, and triphenylphosphine to give the aziridine (**5**), sulphinimine (**6**), and triphenylphosphinimine (**7**) respectively as shown on page 2.

These reactions are well known[4] in the case of sulphonyl azides and have also been reported[5] with some phosphorus azides. Cholesteryl *N*-phenylphosphoramidic azide (**4**), however, did not undergo insertion reactions with such substrates as decane, *o*-xylene, and *o*-anisole, even on prolonged boiling (10 hr), although analogous insertions go readily[6] with sulphonyl azides. Similar resistance to insertion reactions has also been noted[7] with *N*,*N*$^1$-dibenzylphosphorodiamidic azide. The latter compound did, however, undergo pseudo-halogen displacement of the azide group by boiling benzylamine, but under similar conditions cholesteryl *N*-phenylphosphoramidic azide did not react with butylamine. Phosphinimines of general type (**8**), where R is an alkyl or aryl radical, are well-known[8-10] to react with carbonyl compounds to give substituted imines (**9**); the mechanism is believed to depend on the polarization of the phosphorus-nitrogen double bond as shown on page 326.

The reactivity of the triphenylphosphinimine (**8**) is especially influenced by the substituents on nitrogen; electron-withdrawing groups which delocalize the negative charge reduce the reactivity of the phosphinimine (**8**) and the reaction consequently needs more drastic conditions.[9]





It was therefore expected that cholesteryl *N*-phenylphosphoramidic triphenylphosphinimine (**7**) should react with aldehydes and ketones to form the phosphinimines (**10**). However the literature does not contain any examples of the reaction with phosphinimines (**8**) containing the phosphoryl group attached to the nitrogen atom and this feature would probably reduce the reactivity of the phosphinimines towards carbonyl compounds.

The results were rather confusing: the ir and nmr spectral data for the products isolated from the reactions of (**7**) with acetone, ethyl methyl ketone, *p*-nitrobenzaldehyde, and 3,4-dichlorobenzaldehyde were in agreement with the proposed structure (**10**), as also were the products from the analogous reaction of cholesteryl *N*-cyclohexylphosphoramidic triphenylphosphinimine with acetone and *p*-nitrobenzaldehyde.

However, the microanalytical results for nitrogen were generally only approximately half the required values, and repetition under different conditions did not significantly improve the figures.

Determination of the mass spectra of the products from acetone and *p*-nitrobenzaldehyde did not give the molecular ions (580 and 673) respectively. At 170° with both compounds, the highest fragment ion corresponded to cholesta-3,5-diene (386). On the other hand, at 125° the acetone derivative (**10**: R=R′=Me) in addition showed major fragment ions at 495, 481, 463, 400, and 398. The *p*-nitrobenzal-

dehyde derivative (**10**: R=H, R′=$NO_2C_6H_4$) showed ions at 471, 404, and 389.

Attempted reaction of the triphenylphosphinimine (**7**) with *p*-chloro- and *p*-fluorobenzaldehyde, *p*-anisaldehyde and cinnamaldehyde gave complex mixtures of products which could not be identified.

The ir spectra of some of the products (**10**) showed a band at 1510 $cm^{-1}$, which may be due to the stretching vibration of the N=C group; the normal frequency of 1660–1590 $cm^{-1}$ reported[11] having possibly been reduced by conjugation with the phosphoryl group.

The products also showed a broadish absorption band in the 960–980 $cm^{-1}$ region which may possibly be ascribed to the presence of the P–N=C group as Thomas has reported[12] that all compounds containing this group showed a strong band in the 900–1000 $cm^{-1}$ region.

However Bellamy[13] argues that the 1510 $cm^{-1}$ band cannot reasonably be assigned to N=C bond, since there will be little conjugation between the N=C and P=O bonds so the N=C stretching band is unlikely to appear lower than 1590 $cm^{-1}$. He also commented that the 980–960 $cm^{-1}$ range is wholly unreliable as a diagnostic region for phosphorus compounds. The ir spectra do indicate the presence in the products of the NH, P=O, and C=C groups.

The nmr spectra of the products were in general agreement with the proposed structure (**10**).

Thus the spectra clearly showed the presence of protons associated with the phenyl, imino, and steroid groups. It was also sometimes possible to locate the R, $R^1$ radicals but this proved very difficult when R and $R^1$ were methyl groups since they then merged with the signals due to the 5 methyl groups of the steroid nucleus. The 26 and 27 methyl protons were not generally resolved into separate signals, and this observation is in agreement with previous studies.[14,15]

The presence of the radicals R, $R^1$ in the structure of the products (**10**) was however, indicated, by the values obtained for the overall aliphatic-aromatic proton ratios.

Efforts to devise an alternative structure to (**10**) which would be in better agreement with the nitrogen analytical data clearly would involve loss of a nitrogen atom. The ir and nmr spectral data clearly show that the imino nitrogen atom, e.g. $NHC_6H_5$, is retained in the product, so that if a nitrogen atom is lost, it must be the doubly bonded nitrogen. It has, however, not been possible to devise a feasible reaction mechanism leading to such a product and, in view of the well known formation of substituted imines of type (**9**), we conclude that our products do in fact possess the structure as depicted in (**10**) but that there is some problem in analysing these compounds correctly for nitrogen.

17-Oxoandrost-5-ene-3β-yl phosphorodichloridate was prepared as previously described,[2] and condensation with aniline (2 mol. equivs.) afforded the corresponding 3β-yl *N*-phenylphosphoramidic chloride. The latter, by reaction with hydrazine hydrate, gave the *N*-phenylphosphoramidic hydrazide. However, attempted preparation of 17-oxoandrost-5-ene-3β-yl *N*-phenylphosphoramidic azide by condensation of the *N*-phenylphosphoramidic chloride with sodium azide in aqueous acetone or tetrahydrofuran failed to give a pure product.

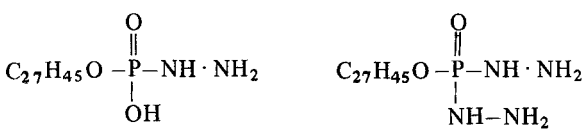
Cholesteryl phosphorodichloridate was condensed with phenol, *p*-nitrophenol and *p*-methoxyphenol in the presence of triethylamine to give the corresponding cholesteryl *O*-arylphosphorochloridates. These compounds were also obtained by reaction of cholesterol with the corresponding arylphosphorodichloridates.

Cholesteryl *O*-phenylphosphorochloridate on reaction with sodium azide in hot aqueous acetone did not give the azide, but instead hydrolysis occurred to the *O*-phenyl phosphate. On the other hand, when the reaction was carried out in aqueous tetrahydrofuran at 0° the *O*-phenyl azide was obtained.

Cholesteryl *O*-*p*-methoxyphenylphosphorochloridate was also successfully converted to the corresponing azide, but attempts to condense cholesteryl *O*-*p*-nitrophenyl phosphorochloridate with sodium azide did not yield the pure azide.

The failure is probably due to the greater electrophilicity of the phosphorus atom in the *p*-nitrophenyl derivative promoting hydrolytic decomposition of the initially formed azide.

Similarly, when cholesteryl phosphorodichloridate was reacted with a large excess of hydrazine hydrate in boiling tetrahydrofuran the product was cholesteryl monohydrogen phosphoric acid hydrazide (**11**); but when the reaction was carried out at 0° the expected phosphorodihydrazide (**12**) was obtained:



(**11**)



(**12**)

Attempted preparation of cholesteryl phosphorodiazide by condensation of cholesteryl phosphorodichloridate with sodium azide (4 mol. equivs.) gave a product (mp 191–192°) which did not show an azide

band in the ir spectrum and appeared to be cholesteryl dihydrogen phosphate (lit.[1] m.p. 186–188°). Reaction of cholesteryl phosphorodichloridate with diethylamine (2 mol. equivs.) gave the the *N,N*-diethylphosphoramidic chloride. Cholesteryl phosphorodichloridothioate[1] has been reacted with benzylamine (4 mol. equivs.) to give the $N,N^1$-dibenzylphosphorodiamidic thioate; and with aniline (2 mol. equivs.) the corresponding *N*-phenylphosphoramidochloridothioate was obtained.

Selected steroid phosphorus compounds were examined for antifertility and bronchodilator properties but no appreciable activity was shown.

## EXPERIMENTAL

Ir spectra were determined as liquid films or Nujol mulls using a Perkin Elmer 127 spectrometer. Nmr spectra were measured in $CDCl_3$ using a Varian A60A spectrometer with tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS9 spectrometer at 70 eV. Melting points were determined with a 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.



### *Cholesteryl Phosphorodichloridate*

This compound was prepared by treatment of cholesterol with phosphorus oxychloride and triethylamine as previously described.[2]

### *Cholesteryl N-Phenylphosphoramidic Chloride* (1)

This was obtained by reaction of cholesteryl phosphorodichloridate with aniline (2 mol. equivs.) in tetrahydrofuran as previously described.[3] It was obtained (80% yield) by boiling cholesteryl phosphorodichloridate (2 g) in pentane (100 ml) with aniline (2 mol. equivs.) for 12 hr.

### *Cholesteryl N-Cyclohexylphosphoramidic Chloride*

was obtained as previously described.[3]

### *Cholesteryl N,N-diethylphosphoramidic Chloride*

Cholesteryl phosphorodichloridate (2 g) was stirred with diethylamine (0.6 g, 2 mol. equivs.) in chloroform (40 ml) for 4 hr. The solvent was evaporated under reduced pressure to give a sticky residue. This was triturated with water and the solid recrystallized from ether-acetonitrile to give the *N,N-diethylphosphoramidic chloride* (1.2 g), m.p. 109–111° (Found: C, 68.8; H, 10.75; N, 2.6. $C_{31}H_{55}Cl\,NO_2P$ requires C, 68.9; H, 10.3; N, 2.6%).

Tlc (toluene-ethyl acetate 5 : 2) showed one spot, $R_F$ 0.51. $\nu_{max}$ 1280 (PO), 1210, 1170, 1015, 1000 (P–O–C). Nmr δ 0.67, 0.82, 0.88, 0.91, 1.06, 1.14, 1.24 ($7CH_3$), 2.50 ($4\text{-}CH_2$), 3.2, m (4H, $2CH_2CH_3$), 5.45, d (6β-*H*)

### *Cholesteryl N-Phenylphosphoramidic Azide* (4)

Cholesteryl *N*-phenylphosphoramidic chloride (5.0 g) in tetrahydrofuran (80 ml) was reacted with a solution of sodium azide (1.2 g) in water (10 ml) at room temperature for 6 hr. Tetrahydrofuran was distilled off under reduced pressure, and the residue was crystallized from aqueous tetrahydrofuran to give *the N-phenylphosphoramidic azide* (2.4 g), mp 180° (in sealed tube). (Found: C, 69.7; H, 9.1; N, 9.7. $C_{33}H_{51}N_4O_2P$ requires C, 69.9; H, 9.0; N, 9.9%). $\nu_{max}$ 3150 (NH), 2160 ($N_3$), 1600, 1500 (arom C=C), 1230 (PO), 1040, 1030 (P–O–C) $cm^{-1}$. Tlc [(petroleum ether) – ethyl acetate (2 : 1)], decomposition occurred, giving three spots; $R_F$ 0.50, 0.48, 0.38. This preparation can also be carried out in aqueous acetone.

### *Cholesteryl N-Phenylphosphoramidic Hydrazide* (2)

Cholesteryl *N*-phenylphosphoramidic chloride (2 g) in tetrahydrofuran (15 ml) was gradually added to a stirred solution of hydrazine hydrate (0.54 g of 99%; 3 mol. equivs.) in tetrahydrofuran (20 ml) at room temperature.

After ½ hr no more precipitation occurred the suspension was filtered to remove hydrazine hydrochloride. The filtrate was evaporated to give a white powder (1.9 g). Recrystallization from tetrahydrofuran gave the *N-phenylphosphoramidic hydrazide.* (1.2 g, 60%), mp 180–183° (Found: C, 71.4; H, 9.9; N, 7.5. $C_{33}H_{54}N_3O_2P$ requires C, 71.3; H, 9.8; N, 7.6%). $\nu_{max}$ 3340 3260 ($NH_2$), 3150 (NH), 1600, 1500 (arom C=C), 1220 (PO), 1070 (P–O–C) $cm^{-1}$. Nmr δ 0.59 (18-Me), 0.68 (26/27 Me),[14,15] 0.82 (21-Me), 1.0 (19-Me) 2.50, m (2H, $4CH_2$), 3.45–3.65, m (3H, $NH\text{–}NH_2$), 4.30 br (1H, ArN*H*), 5.40, m (1H, 6β-H), 6.85–7.62, m (5ArH). $D_2O$ treatment removed signal at δ4.30. Cholesteryl *N*-phenylphosphoramidic hydrazide was converted into the following hydrazones:

*p-Nitrobenzaldehyde.* (3; R = H, $R^1$ = *p*-$NO_2C_6H_4$) yellow needles (61%), mp 132–134° (Found: C, 69.8; H, 8.1; N, 8.0. $C_{40}H_{57}N_4O_4P$ requires C, 69.7; H, 8.3; N, 8.3%). $\nu_{max}$ 3342, 3265 (NH), 1605, 1500 (arom C=C), 1205 (PO), 1035, 1030, d (P–O–C) $cm^{-1}$. Nmr δ 0.59 (18-Me), 0.69 (26/27Me), 0.82 (21-Me), 0.95 (19-Me), 2.60, d (2H, $4CH_2$) 3.80, m (1H, NH), 4.30, br (1H, N*H*), 5.50 (1H, 6β-H), 6.90–7.40, m (5ArH) 8.37, q (4H, $NO_2C_6H_4$), 10.30, s, 1H, C*H* = N), Signal at δ 4.30 was removed by $D_2O$ treatment.

*o-Nitrobenzaldehyde.* (3; R = H, $R^1$ = *o*-$NO_2C_6H_4$ yellow needles (80%), mp 184°. (Found: C, 70.0; H, 8.0; N, 8.2. $C_{40}H_{57}N_4O_4P$ requires C, 69.7; H, 8.3; N, 8.3%). $\nu_{max}$ 3300 (NH), 1600 (C=C), 1210 (PO), 1030 (P–O–C) $cm^{-1}$.

*Acetone.* (3; R = $R^1$ = Me), plates (65%), mp 109–109° (Found: C, 72.6; H, 9.7; N, 619. $C_{36}H_{58}N_3O_2P$ requires C, 72.6; H, 9.8; N, 7.05%. $\nu_{max}$ 3340, 3160 (NH), 1670 (N=C), 1600, 1500 (arom C=C), 1222 (PO), 1045, 1030 (P–O–C) $cm^{-1}$.

### *Cholesteryl N-Phenylphosphoramidic $N^1$-Phenylhydrazide*

Cholesteryl *N*-phenylphosphoramidic chloride (2g) in tetrahydrofuran (12 ml) was added dropwise to a stirred solution of phenylhydrazine (1.16 g, 3 mol. equivs.) in tetrahydrofuran (12 ml) at room temperature. After 1 hr the precipitate of

phenylhydrazine hydrochloride was filtered off, and the filtrate, by evaporation, gave a yellow residue. Recrystallazition from ethanol-pentane gave the $N^1$-phenylhydrazide as white plates (1.01 g, 45%), mp 165–168°. (Found: C, 73.8; H, 9.35; N, 6.5, $C_{39}H_{58}N_3O_2P$ requires C, 74.1; H, 9.2; N, 6.6%). $\nu_{max}$ 3350, 3060 (NH), 1250 (PO), 1065 (P–O–C) $cm^{-1}$. Nmr δ 0.62 (18 Me), 0.75 (26/27-Me), 0.87 (21-Me), 1.08 (19-Me), 3.62 (2H, N*H*-N*H*), 7.0–7.50 (10 ArH).

*Reaction of Cholesteryl N-Phenylphosphoramidic Azide* (**4**) *with Norbornene*

Cholesteryl *N*-phenylphosphoramidic azide (0.5 g) was dissolved in tetrahydrofuran (40 ml), norbornene (0.083 g) was added and the solution boiled under reflux for 36 hr. (The reaction was followed by tlc by noting the disappearance of the spot due to norbornene). After this period, the ir spectrum showed absence of the azide, and the solution was evaporated to give a solid residue. Recrystallization from pentane gave the aziridine (**5**). (0.3 g), mp 143–146. (Found: C, 75.6; H, 9.6; N, 4.0. $C_{40}H_{61}N_2O_2P$ requires C, 75.2; H, 9.6; N, 4.3%). $\nu_{max}$ 3145 (NH), 1600, 1500 (C=C), 1240 (PO), 1045, 1030 (P–O–C) $cm^{-1}$.

Nmr δ 0.60 (18-Me), 0.82, 0.88 (26/27-Me), 0.90 (21-Me), 1.00 (19-Me), 2.56, d (4-C*H*$_2$), 5.48 (6β-H), 7.15–7.60, m (6H, NHC$_6$*H*$_5$).

*Reaction of Cholesteryl N-Phenylphosphoramidic Azide* (**4**) *with Dimethylsulphoxide*

Cholesteryl *N*-phenylphosphoramidic azide (0.5 g) was boiled under reflux with dimethylsulphoxide (0.62 g, 1 mol. equiv.) in tetrahydrofuran (50 ml).

The reaction was continued until the ir spectrum showed the absence of the azide group.

The solution was evaporated under reduced pressure. The residue, after repeated crystallization from hexane, gave the *sulphinimine* (**6**) (0.1 g), mp 175–178°. (Found: C, 67.9; H, 9.4; N, 4.2; S, 5.5 · $C_{35}H_{57}N_2O_3PS$ requires C, 68.2; H, 9.25; N, 4.5; S, 5.2%).

*17-Oxoandrost-5-ene-3β-yl Phosphorodichloridate*

This was prepared by reaction of 3β-hydroxy-17 oxoandrost-5-ene with phosphorus oxychloride-triethylamine as previously described.[2]

*17-Oxoandrost-5-ene-3β-yl N-Phenylphosphoramidic chloride*

17-Oxoandrost-5-ene-3β-yl phosphorodichloridate (4 g) was reacted with aniline (1.8 ml; 2 mol. equivs.) in ether (800 ml) for 3 hr. Aniline hydrochloride was filtered off, and the filtrate was concentrated to 50 ml, when cooling gave a solid (2.2 g).

Recrystallization from benzene gave the *N-phenylphosphoramidic chloride* (1.5 g), mp 146–148°. (Found: C, 65.1; H, 7.1; N, 2.9). $C_{25}H_{33}ClNO_3P$ requires C, 65.0; H, 7.15; N, 3.0%). $\nu_{max}$ 3175 (NH), 1745 (CO), 1610, 1500 (C=C), 1270 (PO), 1060 (P–O–C), 525, 460 (P–Cl). Nmr δ 0.86 (18-Me), 1.04 (19-Me), 3.40, m (1H, 3α-H), 4.35, br (1H, ArN*H*), 5.50 (6β-H), 6.80–7.65, m (5ArH). The signal at δ 4.35 was removed by $D_2O$ treatment.

A similar experiment using tetrahydrofuran gave an impure product, mp 143–146°.

*17-Oxoandrost-5-ene-3β-yl N-Phenylphosphoramidic Hydrazide*

17-Oxoandrost-5-ene-3β-yl *N*-phenylphosphoramidic chloride (0.5 g) was dissolved in tetrahydrofuran (15 ml) and the solution added to hydrazine hydrate (0.15 ml of 99%) in tetrahydrofuran (5 ml).

After ½ hr, the product was precipitated by addition of 20% aqueous sodium chloride (20 ml). The solid was extracted with ethyl acetate and the solution concentrated to give the *N-phenylphosphoramidic hydrazide* (0.18 g, 37%), mp 154–157°. (Found: C, 65.3; H, 7.8; N, 8.9. $C_{25}H_{36}N_3O_3P$ requires C, 65.6; H, 7.9; N, 9.2%). $\nu_{max}$ 3200 (NH), 1035, 1010 (P–O–C) $cm^{-1}$. Nmr δ 0.84 (18-Me), 0.97 (19-Me), 3.35, s (2H, N*H*$_2$), 3.44, m (1H, 3α-H), 4.50, br (1H, ArN*H*), 5.40, br (1H, 6β-H), 6.60–7.60 (5ArH).

*Cholesteryl Phosphorodichloridothioate*

This was obtained (88% yield) by reaction of cholesterol with thiophosphoryl chloride in acetone-pyridine as previously described.[1]

Attempts to prepare this compound using triethylamine as base (cf. Ref. 2) were unsuccessful.

*Cholesteryl N,N'-Dibenzylaminothioate*

Cholesterylphosphorodichloridothioate (0.41 g) was treated with benzylamine (0.32 g; 4 mol. equivs.) in tetrahydrofuran (20 ml) overnight. Evaporation under reduced pressure gave a solid which was triturated with water. Recrystallization from methanol gave the *N,N'-dibenzylaminothioate* (0.46 g, 85%), mp 94–96°. (Found: C, 74.6; H, 9.3; N, 4.0; P, 4.8. $C_{41}H_{61}N_2OPS$ requires C, 74.5; H, 9.3; N, 4.2; P, 4.7%). $\nu_{max}$ 3220 (NH), 1500 (arom C=C), 1030, 1020 (P–O–C), 740, 700 (PS). Nmr δ 0.41 q (4H, 2 x CH$_2$), 0.63, 0.76, 0.88, 0.94, 1.02 (5 x C*H*$_3$), 2.9, d, (4-CH$_2$), 3.3 (3α-H, d, $J_{P\text{-}H}$ 8.0H$_2$), 5.33 (6-H, 1H), 7.23, s (10ArH).

*Cholesterylphosphorochlorido-N-Phenylaminothioate*

Cholesterylphosphorodichloridothioate (2 g) was treated with aniline (0.7 ml; 2 mol. equivs.) in tetrahydrofuran (80 ml). After 10 min, the precipitate of aniline hydrochloride was filtered off. The filtrate was evaporated under reduced pressure to give a pinkish solid, which was purified by dissolution in petroleum ether (40–60°), and boiling with activated charcoal. Recrystallization from acetonitrile-tetrahydrofuran gave the *N-phenylaminothioate* (1.6 g, 72%, mp 145–146°. (Found: C, 68.5; H, 8.5; N, 2.3. $C_{33}H_{51}ClNOPS$ requires C, 68.9; H, 8.9; N, 2.3%).

$\nu_{max}$ 3390 (NH), 1600 (arom C=C), 1020, 1000 (P–O–C), 740, 710 (PS), 730 (P–NH) $cm^{-1}$.

Nmr δ: 0.68, 0.82, 0.88, 0.94, 1.02 (5 x C*H*$_3$), 2.50, d (4-CH$_2$), 3.70† (3α-H), 4.70 (N*H*) 5.4, d(6β-H), 7.1, m (5ArH).

The signal at δ 4.70 was removed by $D_2O$ treatment.

*Reaction of Cholesteryl N-Phenylphosphoramidic Azide* (4) *with Triphenylphosphine*

Cholesteryl *N*-phenylphosphoramidic azide (1 g) in ether (25 ml) was boiled under reflux with a solution of triphenylphosphine (0.47 g, 1 mol. equiv.) in ether (8 ml) for 3 hr. After this period, the ir spectrum indicated absence of the azido group. The solution was evaporated to give a crystalline residue* which was recrystallized from tetrahydrofuran-

hexane to give the *N-phenylphosphoramidic triphenylphosphinimine* (7) (1.02 g, 85%), mp 103–105°. (Found: C, 76.1; H, 8.2; N, 3.6. $C_{51}H_{66}N_2O_2P_2$ requires C, 76.3; H, 8.3; N, 3.95%).

$\nu_{max}$ 3170, 3080 (NH), 1605, 1503 (C=C), 1240 (PO) 1085 (P-Ph), 1020 (P–O–C), 700 (P-Ph)[12] $cm^{-1}$.

Nmr δ: 0.60, 0.67, 0.82, 0.90, 0.95 (5 x $CH_3$), 2.46 m (4-$CH_2$), 3.80, t (3α-H), 4.30 (NH), 4.35, m (6β-H), 6.8–7.8, m (15ArH).

Treatment with $D_2O$ removes the signal at δ 4.30.

The preparation of the triphenylphosphinimine (7) could also be carried out using excess of triphenylphosphine (1.5 mol. equivs.). The excess of triphenylphosphine was removed by chromatography of the crude product* on silica gel when the required compound (7) was eluted with petroleum ether (40–60°) while the triphenylphosphine required either for elution.

*Reaction of Cholesteryl N-Phenylphosphoramidic Triphenylphosphinimine* (7) *with various Carbonyl Compounds*

*(a) With Acetone.* Cholesteryl *N*-phenylphosphoramidic triphenylphosphinimine (7) (1.3 g) was boiled under reflux with excess dry acetone (50 ml) for 20 hr. Concentration of the solution and cooling to 0° gave needles (0.30 g), mp 149–152°. Recrystallization from acetone gave the *dimethyl phosphinimine monohydrate* (**10**; R = R′ = Me) (0.15 g), mp 150–153°. Found: C, 72.35; H, 9.8; N, 2.3; P, 4.9. $C_{36}H_{59}N_2O_3P$ requires C, 72.2; H, 9.9; N, 4.7; P, 5.2%). $\nu_{max}$ 3160 (NH), 1600 (arom C=C), 1510 (N=C?), 1240 (PO), 1040 (P–O–C), 970 (P–N=C?) $cm^{-1}$.

Nmr δ 0.60 (18-Me), 0.85 (26/27-Me), 0.92 (21-Me), 0.96 (19-Me), 2.40 (4$CH_2$), 3.82 (3α-*H*), 4.40 (N*H*), 5.40 (6β-*H*), 6.90–7.40 (5Ar*H*).

The signal at δ 4.40 was removed after $D_2O$ treatment.

The weak signals at δ 1.18 and 1.19 may be due to the $=C(CH_3)_2$ group.[16] (The aliphatic: aromatic proton ratio was 11 : 1).

The mother liquor, by evaporation and crystallization of the residue from acetone-hexane, gave triphenyl phosphine oxide (0.65 g), mp 156–157° (lit.[17] 156–157°).

*(b) With ethyl methyl ketone.* Cholesteryl *N*-phenylphosphoramidic triphenylphosphinimine (7) (1 g) was boiled under reflux with excess of ethyl methyl ketone (25 ml) for 20 hr. Cooling at 0° gave the *ethyl methylphosphinimine monohydrate* (**10** = R; Me, R′ = Et) (0.2 g), mp 105–107° (after recrystallization from methanol). (Found: C, 73.0; H, 9.7; N, 2.6; P, 5.0. $C_{37}H_{61}N_2O_3P$ requires C, 72.5; H, 9.9; N, 4.6; P, 5.1%). $\nu_{max}$ 3200 (NH), 1600 (arom C=C), 1510 (N=C?), 1260 (PO), 1060, 1025 (P–O–C), 980 (P–N=C?) $cm^{-1}$.

Nmr δ: 0.70 (18-Me), 0.83 (26/26-Me), 0.89 (21-Me), 1.30 (19-Me), 1.45 (=C-$CH_3$), 2.70 (4-$CH_2$), 4.42 (N*H*), 5.40 (6β-H), 6.90–7.30 (5Ar*H*).

The signal at δ 4.40 was removed by $D_2O$ treatment. (The aliphatic-aromatic proton ratio was 12.1).

The filtrate, after removal of the phosphinimine (**10**) and recrystallization from acetone-hexane, gave triphenylphosphine oxide (0.25 g), mp 156° (lit.[17] 156–157°).

*(c) With p-nitrobenzaldehyde.* Cholesteryl *N*-phenylphosphoramidic triphenylphosphinimine (7) (1 g) was boiled under reflux with *p*-nitrobenzaldehyde (0.19 g; 1 mol. equiv.) in benzene (15 ml) for 72 hr. The yellow solution was evaporated to give a solid which was recrystallized from pentane to give the *p-nitrophenylphosphinimine monohydrate* (**10**; R = H, R′ = $NO_2C_6H_4$) (0.38 g, 45%), mp 163–165°. (Found: C, 69.0; H, 8.5; N, 3.5; P, 4.3. $C_{40}H_{58}N_3O_5P$ requires C, 69.4; H, 8.4; N, 6.1; P, 4.5%). $\nu_{max}$ 3145 (NH), 1600, (arom C=C), 1510 (N=C?), 1315 ($NO_2$), 1255 (PO), 1040, 1025 (P–O–C), 980 (P–N=C?) $cm^{-1}$.

Nmr δ: 0.52, 0.71, 0.86, 0.92, 0.98 (5$CH_3$), 2.66; d (4-$CH_2$), 3.84,† (3α-*H*), 5.48, m (6β-H), 6.50 (N*H*), 7.20–7.65 (5ArH), 8.42, q (4H, $NO_2C_6H_4$), 10.26 (*CH*=N). (The aliphatic-aromatic proton ratio was 6 : 1).

When the reaction was attempted in boiling nitrobenzene (20 min), the ir spectrum of the crude product indicated absence of the carbonyl group and tlc (toluene) showed four components: $R_F$ 0.79, 0.60, 0.45 and 0.10. The only isolable compound was cholesta-3,5-diene (0.35 mg) (from methanol), mp 78–79°, (lit.[18] mp 80°).

Other experiments in boiling xylene and dimethylformamide, again indicated formation of a complex mixture of products.

*(d) With 3,4-dichlorobenzaldehyde.* Cholesteryl *N*-phenylphosphoramidic triphenylphosphinimine (7) (3.3 g) was boiled under reflux with 3,4-dichlorobenzaldehyde (0.71 g) in benzene (50 ml). After 5 days, the ir spectrum indicated absence of the carbonyl group, benzene was evaporated to give a sticky residue. Extraction with petroleum ether (40–60°) gave the *3,4-dichlorophenylphosphinimine hydrate* (**10**; R = H, R′ = 3, 4$Cl_2C_6H_3$) (0.5 g), mp 181–184°. (Found: C, 66.6; H, 8.4; N, 2.5; P. 4.1. $C_{40}H_{57}Cl_2N_2O_3P$ requires C, 67.1; H, 8.0; N, 3.9; P, 4.3%). $\nu_{max}$ 3200 (NH), 1600 (arom C=C), 1508 (N=C), 1240 (PO), 1030 (P–O–C), 980 (P–N=C?), 630 (C–Cl) $cm^{-1}$.

A similar experiment in boiling xylene (12 hr) afforded cholesta-3,5-diene (mp 78–80°) as the major product.

*Cholesteryl O-phenylphosphorochloridate*

Cholesterol (2 g) was boiled under reflux with phenylphosphorodichloridate[19] (1.2 g, 1 mol. equiv.) and triethylamine (0.6 g) in tetrahydrofuran (40 ml) for 3 hr.

After standing overnight, the solution was filtered to remove triethylamine hydrochloride (0.7 g) and the solvent evaporated.

The residue was crystallized from ether-petroleum ether to give the *O-phenylphosphorochloridate* (1.3 g), mp 143–146°. (Mmp with cholesterol 126–132°). (Found: C, 70.7; H, 8.7; P, 5.5. $C_{33}H_{50}ClO_3P$ requires C, 70.65; H, 8.9; P, 5.6%). Tlc (toluene) gave one spot $R_F$ 0.08. $\nu_{max}$ 1600, 1500 (arom C=C), 1220 (PO), 1015, 1000 (P–O–C), 540, 490 (P–Cl) $cm^{-1}$. Nmr δ: 0.65 (18-Me), 0.82 (26/27-Me), 0.87 (21-Me), 1.00 (19-Me), 2.40 (4-$CH_2$), 5.35 (6β-H), 7.20 (5ArH).

This compound (mp 144–146°) was also obtained by reaction of cholesteryl phosphorodichloridate with phenol-triethylamine.

*Reaction of Cholesteryl O-phenylphosphorochloridate with Sodium Azide*

*(a) With heating.* The *O*-phenylphosphorochloridate (0.5 g) was heated with sodium azide (0.12 g; 2 mol. equivs.) in aqueous acetone (50 ml) for 24 hr.

Concentration of the solution and addition of water (30 ml), gave *cholesteryl O-phenylphosphate monohydrate* (0.5 g), mp 292–294°. (Found: C, 70.5; H, 9.2; P, 5.3.

$C_{33}H_{53}O_5P$ requires C, 70.7; H, 9.5; P, 5.5%). There was no nitrogen present. $\nu_{max}$ 2720, br (P–OH), 1600, 1495 (arom C=C), 1220 (PO), 1040 (P–O–C) $cm^{-1}$. Tlc (toluene) showed a single spot, $R_F$ 0.08.

The product was unchanged after prolonged boiling with water.

*(b) At room temperature.* A similar experiment at room temperature for 30 min gave a complex mixture of products. Tlc (toluene-ether 6 : 1) showed 2 main spots ($R_F$ 0.56 and 0.24) and 4 minor spots ($R_F$ 0.73; 0.59; 0.42; 0.30).

*(c) At 0°.* The reaction was carried out in aqueous tetrahydrofuran for 30 min to give cholesteryl *O-phenyl phosphorazide* (0.2 g), mp 135–140°. (Found: C, 69.6; H, 8.8; N, 7.1. $C_{33}H_{50}N_3O_3P$ requires C, 69.8; H, 8.9; N, 7.4%). $\nu_{max}$ 2160 ($N_3$), 1600, 1500 (arom C=C), 1200 (PO), 1045, 1022 (P–O–C) $cm^{-1}$.

*Cholesteryl N-cyclohexylphosphoramidic Azide*

Cholesteryl *N*-cyclohexylphosphoramidic chloride (1.5 g) was stirred with sodium azide (0.23 g; 2 mol. equivs.) in aqueous tetrahydrofuran (25 ml) for 4 hr. Evaporation under reduced pressure gave a crystalline residue; this was triturated with water, and recrystallized from tetrahydrofuran-petroleum ether (60–80°) to give the *N-cyclohexylphosphoramidic azide* (1.1 g), mp 130–132°. (Found: C, 68.9; H, 10.3; N, 9.7; $C_{33}H_{57}N_4O_2P$ requires C, 69.2; H, 10.0; N, 9.8%). $\nu_{max}$ 3190 (NH), 2140 ($N_3$), 1249 (PO), 1035 (P–O–C) $cm^{-1}$. Nmr: 0.68 (18-Me), 0.89 (26/27-Me), 0.94 (21-Me), 1.02 (19-Me), 3.30, br (3α-H), 4.40, br (1H, $C_6H_{11}NH$), 5.40, d (6β-H).

*Cholesteryl N-cyclohexylphosphoramidic Triphenylphosphinimine*

Cholesteryl *N*-cyclohexylphosphoramidic azide (2.15 g) and triphenylphosphine (1.0 g) was boiled under reflux in benzene (60 ml) for 12 hr. After this period, the ir spectrum indicated the absence of the azide band. Evaporation of the solvent gave a solid which was recrystallized from acetonitrile-ether to give the *triphenylphosphinimine* (1.6 g), mp 188–191°. (Found: C, 75.6; H, 9.2; N, 3.3; P, 7.4; $C_{51}H_{72}N_2O_2P_2$ requires C, 75.9; H, 9.0; N, 3.5; P. 7.7%). $\nu_{max}$ 3250; 3100 (NH), 1603, 1500 (arom C=C), 1250 (PO), 1040, 1018 (P–O–C), 720 (P–Ph) $cm^{-1}$.

Nmr δ: 0.64 (18-Me), 0.89 (26/27-Me), 0.91 (21-Me), 0.96 (19-Me), 3.05 (3α-H), 3.72 (NH), 5.25 (6β-H), 7.20–8.30 (15ArH).

When the reaction was attempted in boiling ether (16 hr) unchanged azide still remained.

*Reactions of Cholesteryl N-Cyclohexylphosphoramidic Triphenylphosphinimine with Acetone*

The triphenylphosphinimine (0.2 g) was boiled under reflux with acetone (70 ml) for 48 hrs. Cooling gave triphenylphosphine oxide (50 mg). Evaporation of the filtrate gave *cholesteryl N-cyclohexyldimethylphosphinimine hydrate*, which was crystallized from methanol (0.05 g), mp 130–134°. (Found: C, 71.8; H, 10.5; N, 2.95; P, 4.8. $C_{36}H_{65}N_2O_3P$ requires C, 71.5; H, 10.8; N, 4.6; P, 5.1%). $\nu_{max}$ 3230 (NH), 1250 (PO), 1040, 1020 (P–O–C), 970 $cm^{-1}$ (P–N=C?).

Nmr δ: 0.62 (18-Me), 0.86 (26/27-Me), 0.92 (21-Me), 1.0 (19-Me), 1.10, 1.12 (N=C$Me_2$), 3.15 (3-H), 4.30 (N*H*), 5.50 (6 H).

The signal at δ 4.30 is removed after $D_2O$ treatment.

*Reaction of Cholesteryl N-Cyclohexylphosphoramidic Triphenylphosphinimine with p-Nitrobenzaldehyde*

The triphenylphosphinimine (1 g) and *p*-nitrobenzaldehyde (0.19 g; 1 mol. equiv.) were boiled under reflux in benzene for 24 hr. After this period, the ir spectrum indicated absence of the carbonyl band. The solvent was concentrated under reduced pressure and triphenylphosphine oxide (0.4 g) removed. The filtrate was evaporated and the residue recrystallized from acetone-hexane to give the *p-nitrophenylphosphinimine hydrate* (0.3 g), mp 218–220°. (Found: C, 68.5; H, 9.55; N, 5.7; P, 5.0. $C_{40}H_{64}N_3O_5P$ requires C, 68.8; H, 9.2; N, 6.0; P, 4.55%). $\nu$max 1240, 1220 (PO), 1045 (P–O–C), 980 (P–N=C?) $cm^{-1}$.

Nmr δ: 0.62 (18-Me), 0.80 (26/27-Me), 0.89 (21-Me), 1.0 (19-Me), 2.50, d (4-C$H_2$), 3.80 (N*H*), 5.50 (6β-H), 8.38, q (4H, $NO_2C_6H_4$), 10.1 (N=C*H*). (The aliphatic-aromatic proton ratio was 14 : 1).

*Cholesteryl O-p-nitrophenylphosphorochloridate*

Cholesteryl phosphorodichloridate (10 g) was boiled under reflux with *p*-nitrophenol (2.77 g) and triethylamine (2.8 ml) in tetrahydrofuran (90 ml) for 24 hr. After cooling, the triethylamine hydrochloride was filtered off. The filtrate was evaporated and the residue was crystallized twice from acetone to give the *O-p-nitrophenylphosphorochloridate* (6.5 g) mp 154–156°. (Found: C, 65.7; H, 8.4; N, 2.1; P, 5.4. $C_{33}H_{49}ClNO_5P$ requires C, 65.4; H, 8.1; N, 2.3; P, 5.1%). $\nu_{max}$ 1605, 1590 (arom C=C), 1365 ($NO_2$), 1270 (PO), 1030, 1020 (P–O–C) $cm^{-1}$.

Nmr δ: 0.65 (18-Me), 0.82 (26/27-Me), 0.90 (21-Me), 1.0 (19-Me), 2.40 (2H, 4-C$H_2$), 5.40 (6β-*H*), 7.40, d (4H, $NO_2 \cdot C_6H_4O$).

This compound was also obtained (mp 153–156°) by condensation of cholesterol with *p*-nitrophenylphosphorodichloridate[19] by boiling in tetrahydrofuran in presence of triethylamine (1 mol. equiv.) for 4 hr.

*Reaction of Cholesteryl Phosphorodichloridate with Hydrazine Hydrate*

Cholesteryl phosphorodichloridate (1 g) was gradually added to a stirred solution of hydrazine hydrate (1.2 g of 99%, 10 mol. equiv.) in tetrahydrofuran (50 ml). The solution was boiled under reflux for 20 min, concentrated to small volume and treated with 10% sodium chloride solution. The precipitated solid was filtered off and crystallized from ether-methanol to give *cholesteryl monohydrogen phosphoric acid hydrazide monohydrate* (11) (0.8 g), mp 196–198°. (Found: C, 64.8; H, 10.0; N, 5.3; P, 6.0. $C_{27}H_{51}N_2O_4P$ requires C, 65.1; H, 10.3; N, 5.6; P, 6.2%). $\nu_{max}$ 3260 br (NH), 2720 (P–OH), 2145 (PO), 1040, 1015 (P–O–C) $cm^{-1}$.

The experiment was repeated at 0° for 1 hr. Dilution with water (250 ml) gave a precipitate which was filtered off. Recrystallization from acetonitrile-ether gave *cholesteryl phosphorodihydrazide* (12) (0.6 g), mp 151–153°. (Found: C, 65.7; H, 10.5; N, 11.1. $C_{27}H_{51}N_4O_2P$ requires C, 65.55;

H, 10.4; N, 11.3%). $\nu_{max}$ 3280, 3155 (NH), 1225 (PO), 1040, 1020 (P–O–C) $cm^{-1}$.

Nmr δ: 0.60 (18-Me), 0.69 (26/27-Me), 0.82 (21-Me), 1.0 (19-Me), 2.45, m (2H, 4-$CH_2$), 3.40–3.61, m (6H, 2 × NH · $NH_2$), 5.40 (6β-H).

*Reaction of p-Methoxyphenylphosphorodichloridate with Cholesterol*

Cholesterol (16.0 g) was reacted with *p-methoxyphenylphosphorodichloridate*[19] (10 g) and triethylamine (4.2 g) in ether (200 ml) for 48 hr. Triethylamine hydrochloride (5.7 g) was filtered off, and the filtrate was evaporated. The residue was crystallized twice from ether-pentane to give *cholesteryl O-p-methoxyphenylphosphorochloridate* (10 g), mp 115–117°. (Found: C, 69.0; H, 8.7; P, 5.3. $C_{34}H_{52}ClO_4P$ requires C, 69.1; H, 8.8; P, 5.2%). $\nu_{max}$ 1600, 1500 (arom C=C), 1270, 1260 (PO), 1050 (P–O–C) $cm^{-1}$.

Nmr δ: 0.60 (18-Me), 0.81 (26/27-Me), 0.90 (21-Me), 0.99 (19-Me), 1.17 ($OCH_3$), 3.03 (3α-H), 5.40 (6β-H), 7.40, d (4H, $MeOC_6H_4$). Tlc (toluene: ethyl acetate 10 : 1) gave one spot, $R_F$ 0.72.

This product (mp 116–118°) was also obtained by condensation of cholesteryl phosphorodichloridate with *p*-methoxyphenol-triethylamine in boiling tetrahydrofuran (3 hr).

*Cholesteryl O-p-methoxyphenyl Phosphoryl Azide*

Cholesteryl *O-p*-methoxyphenylphosphorochloridate (3.02 g) was stirred with sodium azide (0.66 g) in aqueous acetone (100 ml) at room temperature for 3 hr and kept at 0° for 24 hr. Dilution with ice-water (250 ml) gave a solid (1.2 g) which by recrystallization from ether-acetonitrile afforded the *O-p-methoxyphenyl phosphoryl azide* (0.7 g), mp 120–122°. (Found: C, 68.4; H, 8.9; N, 6.7. $C_{34}H_{52}N_3O_4P$ requires C, 68.3; H, 8.8; N, 7.0%). $\nu_{max}$ 2160 ($N_3$), 1500 (arom C=C), 1205 (PO), 1045, 1025 (P–O–C) $cm^{-1}$.

14 of these steroid phosphorus compounds were tested for biological activity in the antifertility and bronchodilator screens using female mice and guinea pigs respectively at doses of 100 mg/Kg oral and 400 μg/Kg intravenously. All the compounds were inactive in both tests, except that 17-oxo-androst-5-ene-3β-yl *N*-phenylphosphoramidic azide was toxic to mice at 50 and 10 mg/Kg whereas the corresponding cholesteryl *N*-phenylphosphoramidic azide was inactive and non-toxic at 100 mg/Kg.

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