Heterocycles in Organic Synthesis. Part 6.[1] Nucleophilic Displacements of Primary Amino-groups *via* 2,4,6-Triphenylpyridinium Salts

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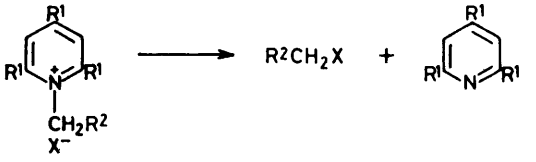
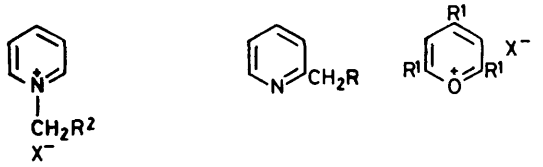
Benzylamine and 2-, 3-, and 4-pyridylmethylamine are readily converted into the corresponding 1-substituted 2,4,6-triphenylpyridinium cations, from which 2,4,6-triphenylpyridine is displaced in high yield by a variety of nucleophiles. This synthetic method avoids the use of unstable and obnoxious pyridylmethyl halides and shows steric selectivity of significance in the conversion of secondary into tertiary amines by alkylation.

ALTHOUGH in principle the pyridine ring in pyridinium salts (1) is potentially a good leaving group suitable for displacement by a wide variety of nucleophiles [*i.e.* (1) ⟶ (2) + (3)], this aspect of pyridinium salt chemistry has received little attention. Some examples of the unsubstituted pyridinium ring acting as a leaving group have been reported (see *e.g.* ref. 2). In particular, some reactions of 1-benzylpyridinium salts have been studied from the point of view of the influence of conditions on the course and yields of the reactions.[2] However, use of unsubstituted pyridine rings as leaving groups involves several disadvantages. First, the only practical method for the preparation of such substrates is by nucleophilic substitution reactions of pyridine with the corresponding halides, tosylates, *etc.* Secondly, various alternative reactions can occur: the pyridinium ring is susceptible to nucleophilic attack at the 2-, 4-, and 6-positions, particularly by small nucleophiles (*e.g.* I^-, OH^-), and this type of process often takes place more readily than pyridine displacement. Furthermore, alkyl- or benzyl-pyridinium halides (4) undergo the Ladenburg



(1) (2) (3)



(4) (5) (6)

rearrangement to isomeric pyridines [*e.g.* (5)] at temperatures in excess of 200 °C.[3] Thirdly, pyridine is a considerably *poorer* leaving group than halogen, necessitating more extreme reaction conditions.

These disadvantages can be largely overcome by employing 2,4,6-trisubstituted pyridinium salts (1; R^1 = alkyl or aryl) in which nucleophilic attack on the heterocycle is sterically hindered. Trisubstituted systems (1; $R^1 \neq H$) have the additional advantage that the bulk of the pyridinium group facilitates cleavage of the C–N bond during nucleophilic substitution (steric acceleration),[4] while simultaneously steric hindrance of the approach of the nucleophile to the electrophilic carbon attached to the quaternary nitrogen atom increases the selectivity of the reaction (see later).

Since 2,4,6-trisubstituted pyridinium salts are readily prepared by condensation between a 2,4,6-trisubstituted pyrylium salt (6) and a primary amine, the displacement of trisubstituted pyridines by nucleophiles [(1) ⟶ (2) + (3)] in effect provides a method of achieving nucleophilic displacement of primary amino-groups. This conversion of the amino-function (NH_2) into a good leaving group has obvious synthetic advantages.

Reviews published in 1966 [5a] and 1968 [5b] indicate the paucity of available methods for the nucleophilic replacement of aliphatic primary amino-groups: displacements on trimethylammonio-derivatives, nitrosoamide decomposition, and the triazene method all suffer from poor yields, lack of generality, or other difficulties. Since then work has appeared concerning displacements on sulphonimides. Good yields of n-hexyl acetate were obtained with $N(SO_2C_6H_4Me)_2$ or $N(SO_2C_6H_4NO_2)_2$ as leaving group, provided hexamethylphosphoric triamide was used as solvent [6] and also fair yields of n-hexyl iodide and bromide with $N(SO_2C_6H_4Me_2)_2$ whereas saccharine was poor as leaving group.[7] Similar replacements of NTs_2 by H have been reported,[8] and also limited success for displacement reactions of $N(SO_2CF_3)_2$.[9] However, in general such groups as benzene-1,2-disulphonimide do not appear to be promising for nucleophilic displacement.[10]

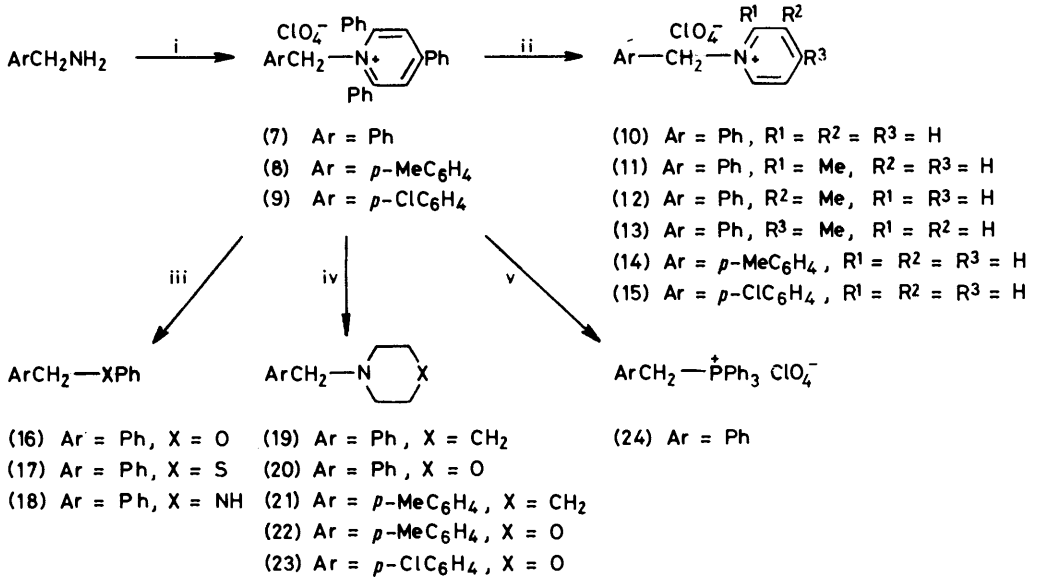
The use of 2,4,6-triphenylpyridine as a leaving group was, in fact, achieved as early as 1926 by Ziegler and Fries who showed that its *N*-methyl salts (1; R^1 = Ph, R^2 = H) underwent thermal decomposition giving the appropriate methyl derivative (MeX) and triphenylpyridine.[11] More recently Susan and Balaban [12] have also recognised the synthetic possibilities of this type of transformation for converting alkyl- or benzyl-amines into their halides (*e.g.* RCH_2NH_2 ⟶ RCH_2Br) but this procedure has not received detailed examination. We now report our studies on the use of 2,4,6-trimethyl- and 2,4,6-triphenyl-pyridinium salts (1; R^1 = Me or Ph) as intermediates for replacing amines by other functional groups. In particular, our interest in using trisubstituted pyridines as leaving groups has been directed towards their utility in synthetic transformations where

compounds containing the usual leaving groups (*e.g.* halide anions) are either inaccessible or unstable. In this connection we have been particularly interested in preparing furfuryl and 2-, 3-, and 4-pyridylmethyl derivatives where the amine is readily available but the halides are not. In addition we have also found *N*-substituted 2,4,6-triphenylpyridinium salts (1; R^1 = Ph) to be particularly useful for the conversion of secondary amines into tertiary amines without formation of the undesirable quaternary ammonium salt, a by-product which is often encountered in using other alkylating agents but which is avoided under these conditions owing to the high degree of steric hindrance in the transition state.

Studies with Benzylamines.—Benzylamine is readily converted into *N*-benzyl-2,4,6-trisubstituted pyridinium salts (1; R^2 = Ph) by reaction with the appropriate trisubstituted pyrylium salt (6), and using this method we have prepared the 2,4,6-trimethyl and 2,4,6-triphenyl derivatives (1; R^1 = Me or Ph, R^2 = Ph, X = ClO_4). Attempts to bring about nucleophilic displacement of 2,4,6-trimethylpyridine (3; R^1 = Me) from the salt (1; R^1 = Me, R^2 = Ph) gave disappointing results. Thus, 1-benzyl-2,4,6-trimethylpyridinium perchlorate (1; R^1 = Me, R^2 = Ph, X = ClO_4) was unreactive towards several nitrogen and oxygen nucleophiles under various conditions. However, the results of reactions with the triphenylpyridinium perchlorate (7) were more encouraging. When compound (7) and pyridine were heated under reflux, 2,4,6-triphenylpyridine was displaced giving 1-benzylpyridinium perchlorate (10) (Scheme 1) in 88% yield; analogous, high yield, nucleophilic displacements were also achieved with 2-, 3-, and 4-methylpyridine. The structures of the pyridinium perchlorates (10)—(13) (Scheme 1) were established by their spectral properties and by elemental analysis.

The use of sodium phenoxide, sodium thiophenoxide, and aniline as nucleophiles was also investigated. When either sodium phenoxide or its sulphur analogue was fused with compound (7) under nitrogen, benzyl phenyl ether (16) (42%), or benzyl phenyl sulphide (17) (75%) was formed, respectively, and a similar experiment with an excess of aniline gave *N*-benzylaniline (18) (76%). These transformations (7) ⟶ (16)—(18) (Scheme 1) demonstrate convenient new routes for converting benzylamines into ethers, sulphides, and secondary amines. Attempts to achieve similar displacements using sodium ethoxide and potassium cyanide were unrewarding. The reaction of compound (7) with pyridine 1-oxide gave benzaldehyde (25%).*

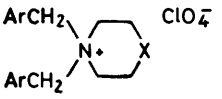
With secondary amines such as piperidine or morpholine, *N*-benzyl-2,4,6-triphenylpyridinium perchlorate (7) gave the tertiary amines (19) and (20) in high yield without complications arising from the formation of quaternary ammonium salts [*e.g.* (25)]. This absence of any quaternary ammonium perchlorate (25) is attributable to unfavourable steric interactions in the transition state. The procedure (7) ⟶ (19), therefore, has distinct advantages over the more conventional methods of preparing tertiary amines containing the benzyl group from secondary amines and a benzyl halide which inevitably lead to a mixture containing quaternary ammonium salts. An alternative method using benzoyl chloride to prepare an amide followed by reduction of the benzoyl group with lithium aluminium hydride requires two steps and also has the disadvantage that other functional groups in the molecule may also be sensitive to reduction. The use of *N*-benzyl-2,4,6-tri-



SCHEME 1 Reagents: i, 2,4,6-triphenylpyrylium perchlorate; ii, pyridine or substituted pyridine; iii, PhXH; iv, piperidine or morpholine; v, PPh_3

* Recent work (M. J. Cook, A. R. Katritzky, and G. H. Millet, *Heterocycles*, 1977, **7**, 227) has shown that with suitable oxidising nucleophiles the yield of benzaldehyde can be increased considerably. We have recently also succeeded in achieving displacement reactions with carbon nucleophiles.

phenylpyridinium perchlorate (7) can conveniently avoid these disadvantages.



(25)

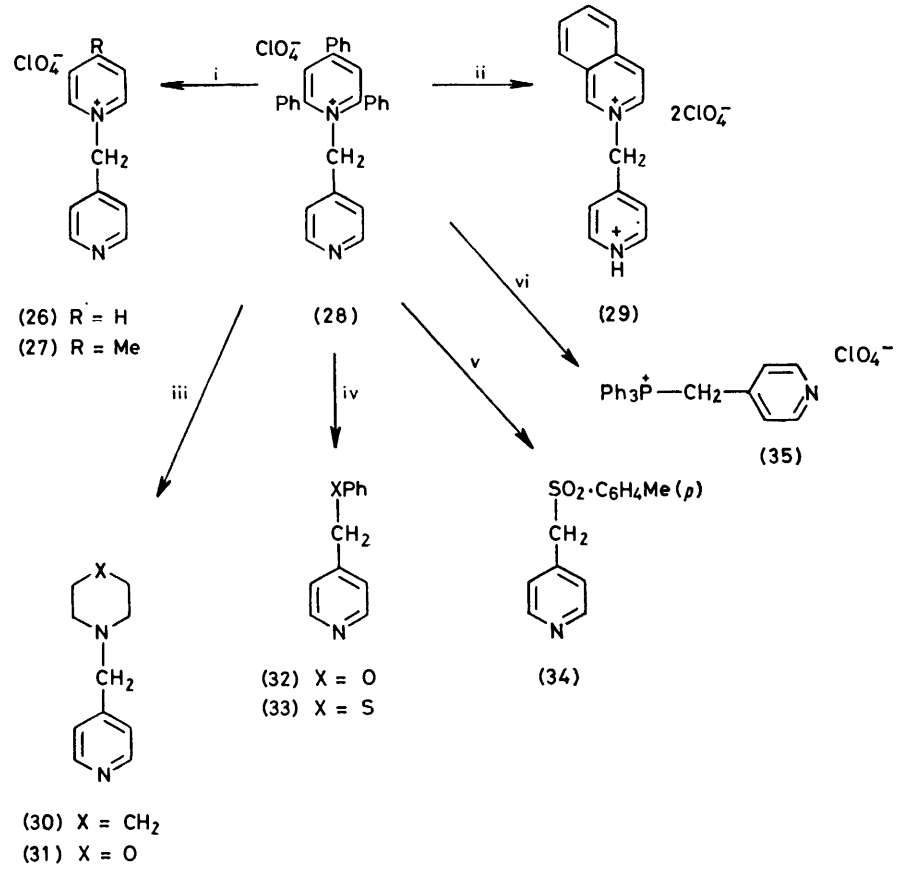
Triphenylphosphine reacts with compound (7) giving benzyltriphenylphosphonium perchlorate (24) in quantitative yield. The preparation of triphenylphosphonium salts [*e.g.* (24)] in this way provides, in principle, a method of achieving the Wittig reaction for systems where the bromide is not readily available or unstable.

Substituted benzyl derivatives also undergo substitution reactions. Thus, 1-(4-methylbenzyl)- and 1-(4-chlorobenzyl)-2,4,6-triphenylpyridinium perchlorates [(8) and (9)] with pyridine gave the corresponding pyridinium perchlorates (14) and (15) (Scheme 1) in high yield. By using morpholine and piperidine the derivatives (21)—(23) were also obtained in good yield and characterised as their picrates.

However, all the derivatives prepared by the methods described above (Scheme 1) can, in principle, be synthesised by alternative routes employing benzyl halides, and these novel synthetic transformations of primary amines are potentially of the greatest value in systems where the halides are not available or are difficult to prepare and use. We now demonstrate the application of these reactions to two examples of this type: the preparation of methylpyridine derivatives is described in the following section and the preparation of furfuryl derivatives is described in the following paper.

Studies with Pyridylmethylamines.—4-Pyridylmethylamine was readily converted into the 2,4,6-triphenylpyridinium perchlorate (28) which on heating at reflux temperature in pyridine solution gave the pyridinium perchlorate (26) (Scheme 2) in 75% yield. Under similar conditions, 4-methylpyridine gave the 4-methyl derivative (27), and isoquinoline in acetic acid solution gave the isoquinolinium salt (29). In reactions analogous to those of the benzyl derivatives (7)—(9), the 4-methylpyridyl derivative (28) also underwent the following useful transformations (Scheme 2): reaction with piperidine and morpholine gives the tertiary amines (30) and (31); sodium phenoxide and thiophenoxide give the ether (32) and the sulphide (33); sodium toluene-*p*-sulphinate gives the sulphone (34); triphenylphosphine gives the phosphonium perchlorate (35). All these transformations (Scheme 2) were achieved in high yield (70—90%).

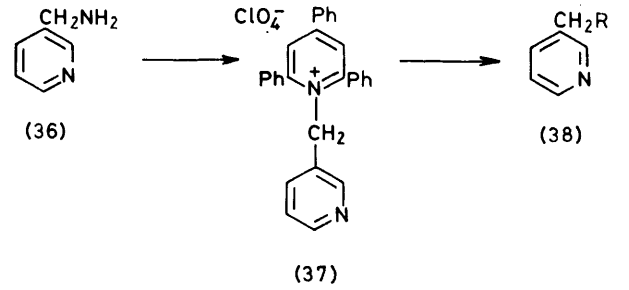
In a similar manner 3-pyridylmethylamine (36) and 2-pyridylmethylamine (39) were also converted into the



(26) R = H
(27) R = Me
(28)
(29)
(30) X = CH_2
(31) X = O
(32) X = O
(33) X = S
(34)
(35)

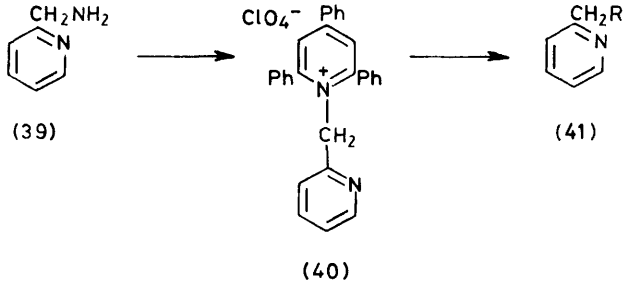
SCHEME 2 Reagents: i, pyridine or 4-methylpyridine; ii, isoquinoline; iii, piperidine or morpholine; iv, PhXH; v, *p*-$MeC_6H_4 \cdot SO_2^-Na^+$; vi, Ph_3P

corresponding triphenylpyridinium perchlorates (37) and (40). These salts underwent reactions analogous to



SCHEME 3

those of the 4-pyridylmethyl derivative (28) giving 3-pyridylmethyl derivatives (38) (Scheme 3) and 2-pyridylmethyl derivatives (41) (Scheme 4).



SCHEME 4

Chloromethylpyridines ($ClCH_2{\cdot}C_5H_4N$) are unstable, difficult to prepare, and not readily available. Although the corresponding hydrochlorides are available commercially, their stability at ambient temperatures is low and they readily undergo self quaternisation; moreover, they are stated by the suppliers to have dangerous physiological properties. In contrast, aminomethylpyridines ($H_2NCH_2{\cdot}C_6H_4N$) are stable, readily available compounds easily converted into 2,4,6-triphenylpyridinium perchlorates [(28), (37), and (40)]. Our results, described above, provide a method of preparing methylpyridine derivatives by nucleophilic substitution without the disadvantages of using chloromethyl derivatives, and thus represent a convenient new synthetic method.

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for samples in Nujol mull, and n.m.r. spectra (60 MHz) for solutions in deuteriochloroform (tetramethylsilane as internal reference). Evaporation refers to the removal of volatile materials under diminished pressure. When substances are stated to be identical, this refers to comparison by m.p., mixed m.p., and i.r. spectra.

2,4,6-Trimethylpyrylium perchlorate [13] (6; R^1 = Me, X = ClO_4) and 2,4,6-triphenylpyrylium perchlorate [14] (6; R^1 = Ph, X = ClO_4) were prepared by reported methods.

1-Benzyl-2,4,6-triphenylpyridinium Perchlorate (7).—2,4,6-Triphenylpyrylium perchlorate (6; R^1 = Ph, X = ClO_4) (28.5 g), benzylamine (9.8 g), and EtOH (100 ml) were stirred at room temperature (4 h). The red colouration faded leaving a colourless solid which was filtered off and recrystallised from EtOH giving the *pyridinium salt* (7) (30.2 g, 37%), as prisms, m.p. 196—198 °C (Found: C, 72.3; H, 4.5; N, 2.4. $C_{30}H_{24}ClNO_4$ requires C, 72.4; H, 4.8; N, 2.8%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ[$(CD_3)_2CO$] 1.8 (2 H, s, arom.), 1.9—2.7 (15 H, m, arom.), 2.8—3.6 (5 H, m, arom.), and 4.3 (2 H, s, CH_2).

In a similar manner the following derivatives were prepared: *1-(4-methylbenzyl)-2,4,6-triphenylpyridinium perchlorate* (8) (59%), prisms from EtOH, m.p. 174—176 °C (Found: C, 72.2; H, 5.1; N, 2.6. $C_{31}H_{26}ClNO_4$ requires C, 72.9; H, 5.1; N, 2.7%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 2.1 (2 H, s, arom.), 2.7 (15 H, s, arom.), 3.25 (2 H, d, *J* 6.5—7 Hz, arom.), 3.8 (2 H, d, *J* 6.5—7 Hz, arom.), 4.5 (2 H, s, CH_2), and 7.95 (3 H, s, CH_3); *1-(4-chlorobenzyl)-2,4,6-triphenylpyridinium perchlorate* (9) (95%), plates from Me_2CO–Et_2O, m.p. 143 °C (Found: C, 67.4; H, 4.5; N, 2.4. $C_{30}H_{23}Cl_2NO_4$ requires C, 67.7; H, 4.4; N, 2.6%); $\nu_{max.}$ 1 050—1 140 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.90—2.50 (21 H, m, arom.), and 4.18 (2 H, s, CH_2); *1-(2-pyridylmethyl)-2,4,6-triphenylpyridinium perchlorate* (40) (77%), prisms from EtOH, m.p. 226—227 °C (Found: C, 69.2; H, 4.8; N, 5.6. $C_{29}H_{23}ClN_2O_4$ requires C, 69.8; H, 4.6; N, 5.6%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ 1.2 (1 H, d, *J* 6 Hz, arom.), 1.7 (2 H, s, arom.), 1.75—2.5 (17 H, m, arom.), 3.05 (1 H, d, *J* 10 Hz, arom.), and 3.8 (2 H, s, CH_2); *1-(3-pyridylmethyl)-2,4,6-triphenylpyridinium perchlorate* (37) (76%), needles from EtOH–H_2O, m.p. 188 °C (Found: C, 68.7; H, 4.7; N, 5.3. $C_{29}H_{23}ClN_2O_4{,}0.5H_2O$ requires C, 68.6; H, 4.7; N, 5.5%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ 1.75 (1 H, m), 2.5 (18 H, m), 2.85 (2 H, m), and 4.25 (2 H, s); *1-(4-pyridylmethyl)-2,4,6-triphenylpyridinium perchlorate* (28) (80%), prisms from EtOH, m.p. 178 °C (decomp.) (Found: C, 69.6; H, 4.6; N, 5.8. $C_{29}H_{23}ClN_2O_4$ requires C, 69.8; H, 4.6; N, 5.6%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.3—1.5 (2 H, d, *J* 7 Hz, arom.), 1.8 (2 H, s, arom.), 1.9—2.7 (17 H, m, arom.), and 3.8 (2 H, s, CH_2).

Reactions of 1-Benzyl-2,4,6-triphenylpyridinium Perchlorate (7).—(a) *With pyridine.* Compound (7) (3.0 g) in pyridine (10 ml) was refluxed for 4 h. Dilution with Et_2O (50 ml) and storage overnight at 0 °C gave a solid product which was recrystallised from EtOH giving 1-benzylpyridinium perchlorate (10) (1.43 g, 88%), needles, m.p. 88—89 °C (lit.,[15] 89—92 °C).

(b) *With 2-methylpyridine.* Compound (7) (2.0 g) and 2-methylpyridine (10 ml) were refluxed for 48 h. The mixture was worked up as for the reaction with pyridine, and recrystallisation of the solid product, from EtOH and then from Me_2CO–Et_2O, gave *1-benzyl-2-methylpyridinium perchlorate* (11) (1.0 g, 90%), brown prisms, m.p. 98 °C (Found: C, 55.0; H, 5.0; N, 5.0. $C_{13}H_{14}ClNO_4$ requires C, 55.0; H, 5.0; N, 5.0%); $\nu_{max.}$ 1 060—1 120 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 1.30—2.50 (4 H, m, pyridinium), 3.08 (5 H, s, Ph), 4.5 (2 H, s, CH_2), and 7.58 (3 H, s, Me).

(c) *With 3-methylpyridine.* Compound (7) (1.0 g) and 3-methylpyridine (5 ml) were refluxed for 48 h; work-up as above gave an oil which crystallised on storage at room temperature for several weeks. Recrystallisation from MeOH gave *1-benzyl-3-methylpyridinium perchlorate* (12) (0.8 g, 72%), buff prisms, m.p. 69 °C (Found: C, 55.1; H, 5.0; N, 4.8. $C_{13}H_{14}ClNO_4$ requires C, 55.0; H, 5.0; N, 5.0%); $\nu_{max.}$ 1 060—1 120 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 1.3—3.5 (9 H, m, arom.), 4.65 (2 H, s, CH_2), and 8.00 (3 H, s, Me).

(d) *With 4-methylpyridine.* Compound (7) (2.0 g) and 4-methylpyridine (10 ml) were treated as above (6 h). Recrystallisation of the solid product from EtOH gave *1-benzyl-4-methylpyridinium perchlorate* (13) (0.9 g, 81%), buff prisms, m.p. 128 °C (Found: C, 55.0; H, 5.0; N, 5.1. $C_{13}H_{14}ClNO_4$ requires C, 55.0; H, 5.0; N, 5.0%); $\nu_{max.}$ 1 075 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 0.85—2.7 (9 H, m, arom.), 4.58 (2 H, s, CH_2), and 7.32 (3 H, s, Me).

(e) *With piperidine.* Compound (7) (2.0 g) and piperidine (6 ml) were refluxed for 6 h and the excess of piperidine was then removed under diminished pressure. The residual yellow solid was treated with dilute aqueous NaOH and the aqueous solution was then extracted with Et_2O. The extract gave a yellow solid which was shown to contain triphenylpyridine (insoluble in dilute acid). This solid was extracted with dilute HCl and the extract was made alkaline (aq. NaOH) and extracted with Et_2O. The Et_2O extract upon drying and evaporation gave *N*-benzylpiperidine (19) (0.6 g, 85%) as an oil; $\nu_{max.}$ (film) 2 930 cm^{-1} (CH); τ(CCl_4) 2.5—3.1 (5 H, m, arom.), 6.69 (s, PhCH_2), 7.5—7.9 (4 H, m, piperidyl), and 8.3—8.8 (6 H, m, piperidyl), which was characterised as its picrate, m.p. 178.5—179 °C (lit.,[16] 178—179 °C), plates from MeOH (Found: C, 53.3; H, 5.1; N, 13.7. Calc. for $C_{18}H_{20}N_4O_7$: C, 53.5; H, 5.0; N, 13.9%).

(f) *With morpholine.* Compound (7) (4.0 g) and morpholine (10 ml) were treated and worked up as for the reaction with piperidine. *N*-Benzylmorpholine (20) (1.3 g, 92%) was obtained as an oil and was characterised as its picrate, m.p. 195 °C (lit.,[17] 193.5—195 °C), plates from EtOH (Found: C, 50.2; H, 4.6; N, 13.7. Calc. for $C_{17}H_{18}N_4O_8$: C, 50.2; H, 4.5; N, 13.8%).

(g) *With pyridine N-oxide.* Compound (7) (2.0 g) and pyridine *N*-oxide (2.0 g) were melted together under nitrogen and the temperature was maintained at 150 °C (5 min). Distillation gave benzaldehyde (0.11 g, 25%), identical with an authentic sample.

(h) *With sodium phenoxide.* Compound (7) (2.0 g) and sodium phenoxide (2.0 g) were melted together (170 °C) under nitrogen (2 min). Extraction with Et_2O and chromatography [alumina; light petroleum (b.p. 60—80 °C) as eluant] gave benzyl phenyl ether (16) (0.3 g, 42%) as an oil which solidified, m.p. 40 °C (lit.,[18] 40 °C); $\nu_{max.}$ 2 920, 1 600, 1 590, 1 500, 1 240, 750, and 690 cm^{-1}; τ(CCl_4) 2.2—3.5 (10 H, m, arom.) and 5.10 (2 H, s, CH_2).

(i) *With sodium thiophenoxide.* In the manner described for sodium phenoxide, compound (7) (3.0 g) and sodium thiophenoxide (3.0 g) gave benzyl phenyl sulphide (17) (0.9 g, 75%), plates from light petroleum (b.p. 60—80 °C), m.p. 45 °C (lit.,[19] 42 °C); $\nu_{max.}$ 2 920, 1 070, and 730 cm^{-1}; τ(CCl_4) 2.84 (10 H, s, arom.) and 6.01 (2 H, s, CH_2).

(j) *With aniline.* Compound (7) (2.0 g) was heated at reflux temperature (5 min) with aniline (5 ml). Treatment with aqueous NaOH (2M) (15 ml), extraction with Et_2O, and evaporation of the extract gave a semi-solid. Triphenylpyridine was separated by addition of cold EtOH and the ethanolic mother liquor gave a dark oil. Fractional distillation gave *N*-benzylaniline (18) (0.6 g, 76%) as a yellow oil, b.p. 180 °C at 12 mmHg (lit.,[20] 178—180 °C at 12 mmHg); $\nu_{max.}$ 1 605 and 1 505 cm^{-1}; τ(CCl_4) 2.2—3.8 (10 H, m, arom.), 5.84 (2 H, s, CH_2), and 6.49 (1 H, s, NH).

(k) *With triphenylphosphine.* Compound (7) (1.5 g) and triphenylphosphine (1.0 g) were melted together under nitrogen. After cooling, Et_2O was added and the residual solid collected and washed with Et_2O. Recrystallisation from EtOH gave *benzyltriphenylphosphonium perchlorate* (24) (1.35 g, 100%), long needles, m.p. 225 °C (Found: C, 66.1; H, 5.0. $C_{25}H_{22}ClO_4P$ requires C, 66.3; H, 4.9%); $\nu_{max.}$ 1 085 cm^{-1} (ClO_4); τ[$(CD_3)_2CO$] 2.1—3.7 (20 H, m, arom.), 5.67 (d, CH_2, J_{P-C-H} 8 Hz).

Reactions of 1-(4-*Methylbenzyl*)-2,4,6-*triphenylpyridinium Perchlorate* (8).—(a) *With pyridine.* Compound (8) (2.5 g) and pyridine (10 ml) were refluxed for 16 h. The mixture was then poured into Et_2O. The brown oil which separated was dissolved in EtOH, and Et_2O was added giving a solid precipitate. Repetition of this procedure (× 2) gave a colourless solid which was recrystallised from EtOH and identified as N-(*4-methylbenzyl*)*pyridinium perchlorate* (14) (1.31 g, 94%), prisms, m.p. 63 °C (Found: C, 54.9; H, 4.8. $C_{13}H_{14}ClNO_4$ requires C, 55.0; H, 5.0%); $\nu_{max.}$ 1 000—1 160 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.0—2.0 (5 H, m, pyridinium), 2.62 (4 H, s, C_6H_4), 4.2 (2 H, s, CH_2), and 7.6 (3 H, s, Me).

(b) *With piperidine.* Compound (8) (2.0 g) and piperidine (10 ml) were refluxed for 6 h. Excess of piperidine was removed under diminished pressure. Work-up of the residue as for the benzyl derivative (19) gave N-(*4-methylbenzyl*)*piperidine* (21) (1.29 g, 79%) as an oil; τ(CCl_4) 2.88 (4 H, s, C_6H_4), 6.67 (2 H, s, CH_2), 7.6—7.9 (7 H, m, Me + 2 × CH_2), and 8.3—8.7 (6 H, br, s, 3 × CH_2), which was fully characterised as its *picrate* (small rods), m.p, 146 °C (EtOH) (Found: C, 54.7; H, 5.5; N, 13.3. $C_{19}H_{22}N_4O_7$ requires C, 54.5; H, 5.3; N, 13.4%).

(c) *With morpholine.* In the manner described for piperidine, compound (8) (2.0 g) and morpholine (10 ml) gave *N*-(4-methylbenzyl)morpholine (22) (1.57 g, 96%) as an oil which was fully characterised as its *picrate*, needles (EtOH), m.p. 199—200 °C (Found: C, 51.3; H, 5.2; N, 13.5. $C_{18}H_{20}N_4O_8$ requires C, 51.4; H, 4.8; N, 13.3%); τ($CF_3{\cdot}CO_2H$) 1.3 (s, picrate), 3.12 (4 H, s, C_6H_4), 5.9—7.0 (8 H, m, 4 × CH_2), and 8.05 (3 H, s, Me).

Reactions of 1-(4-*Chlorobenzyl*)-2,4,6-*triphenylpyridinium Perchlorate* (9).—(a) *With pyridine.* In the manner described for compound (7), compound (9) (2.5 g) and pyridine (10 ml) gave N-(*4-chlorobenzyl*)*pyridinium perchlorate* (15) (1.32 g, 92%), needles from EtOH, m.p. 99 °C (Found: C, 47.2; H, 3.8; N, 5.0. $C_{12}H_{11}Cl_2NO_4$ requires C, 47.4; H, 3.7; N, 4.6%); $\nu_{max.}$ 900—1 160 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.0—3.0 (5 H, m, pyridinium), 2.5 (4 H, s, C_6H_4), and 4.18 (2 H, s, CH_2).

(b) *With morpholine.* In the manner described for the preparation of compound (7), compound (9) and morpholine gave *N*-(4-chlorobenzyl)morpholine (23), which was fully characterised as its *picrate* (thin plates) (EtOH) (1.89 g 88%), m.p. 227 °C (Found: C, 46.1; H, 4.0; Cl, 8.0; N, 12.8. $C_{17}H_{17}ClN_4O_8$ requires C, 46.3; H, 3.9; Cl, 8.0; N, 12.7%); τ($CF_3{\cdot}CO_2H$) 2.97 (4 H, s, C_6H_4), 5.9 (2 H, s, CH_2), and 6.0—7.2 (8 H, m, 4 × CH_2).

Reactions of 2,4,6-*Triphenyl*-1-(4-*pyridylmethyl*)*pyridinium Perchlorate* (28).—(a) *With pyridine.* Compound (28) (2.2 g) and pyridine (10 ml) were refluxed for 14 h. After cooling, Et_2O (50 ml) was added and the resultant brown precipitate collected. Recrystallisation from EtOH–Et_2O gave 1-(*4-pyridylmethyl*)*pyridinium perchlorate* (26) (0.8 g, 75%), prisms, m.p. 104—105 °C (Found: C, 48.4; H, 4.2; N, 10.6. $C_{11}H_{11}ClN_2O_4$ requires C, 48.9; H, 4.1; N, 10.4%); $\nu_{max.}$ 1 080 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 0.3—2.4 (9 H, m, arom.) and 3.75 (2 H, s, CH_2).

(b) *With 4-methylpyridine.* Under the conditions des-

cribed above, compound (28) (0.25 g) and 4-methylpyridine (5 ml) gave 4-methyl-1-(4-*pyridylmethyl*)*pyridinium perchlorate* (27) (0.1 g, 70%), prisms from EtOH–Et_2O, m.p. 150—152 °C (Found: C, 50.5; H, 4.4; N, 9.7. $C_{12}H_{13}ClN_2O_4$ requires C, 50.7; H, 4.6; N, 9.9%); $\nu_{max.}$ 1 080 cm^{-1} (ClO_4^-); τ(CF_3·CO_2H) 1.0—1.4 (4 H, m, arom.), 1.9—2.1 (4 H, m, arom.), 3.80 (2 H, s, CH_2), and 7.26 (3 H, s, Me).

(c) *With isoquinoline*. Compound (28) (1.65 g) and isoquinoline (5.4 g) in HOAc (10 ml) were refluxed for 12 h. After cooling, Et_2O was added and the red oil which separated was collected and dissolved in $HClO_4$ (70%; 10 ml). Addition of Et_2O gave a precipitate which was collected. Recrystallisation from EtOH–Et_2O (1 : 1) gave N-(4-*pyridiniomethyl*)*isoquinolinium diperchlorate* (29) (1.15 g, 83%), pale pink needles, m.p. 180 °C (Found: C, 42.5; H, 3.6; N, 6.8. $C_{15}H_{14}Cl_2N_2O_8$ requires C, 42.8; H, 3.3; N, 6.7%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 2.1 (11 H, m, arom.), 3.75 (2 H, s), and 4.18 (1 H, s).

(d) *With piperidine*. Compound (28) (5.0 g) and piperidine (10 ml) were refluxed for 14 h. Excess of amine was removed by distillation under diminished pressure and the residue treated with aqueous NaOH (100 ml). Extraction of the alkaline solution with Et_2O (3 × 50 ml) and evaporation of the extract gave a residue which was washed with dilute HCl (50 ml). This acid solution after filtering was made alkaline and extracted with Et_2O (3 × 30 ml). The Et_2O solution, after drying ($MgSO_4$), was evaporated giving *N*-(4-pyridylmethyl)piperidine (30) (1.45 g, 82%); τ (neat) 1.55 (2 H, d, *J* 6 Hz), 2.85 (2 H, d, *J* 6 Hz), 6.67 (2 H, s), 7.75 (4 H, m), and 8.55 (6 H, m), which was identified as its dipicrate, needles, m.p. 190 °C (lit.,[21] 193—194 °C).

(e) *With morpholine*. Compound (28) (5.0 g) and morpholine (20 ml) were refluxed for 1 h. Fractional distillation gave 1-(4-*pyridylmethyl*)*morpholine* (31) (1.3 g, 70%), oil, b.p. 40—50 °C at 5 mmHg; $\nu_{max.}$ (film) 1 600, 1 550, 1 400, 1 100, and 850 cm^{-1}; τ 1.0—1.3 (2 H, m, pyridyl H-1 and H-6), 2.2—2.5 (2 H, m, pyridyl H-2 and H-5), 5.7—6.1 (4 H, m, 2 × NCH_2CH_2O), 6.14 (2 H, s, CH_2), and 7.0—7.4 (4 H, m, 2 × NCH_2CH_2O), characterised as its *picrate*, yellow prisms from EtOH, m.p. 192—194 °C (Found: C, 41.8; H, 3.5; N, 17.6. $C_{12}H_6N_6O_{14}$ requires C, 41.5; H, 3.1; N, 17.6%).

(f) *With triphenylphosphine*. Compound (28) (0.25 g) and triphenylphosphine (1.0 g) were heated with a microburner until the mixture became black (5 min). Et_2O was added to the cooled residue and the resulting precipitate was collected. Recrystallisation from EtOH gave *triphenyl*-4-*pyridylmethylphosphonium perchlorate* (35) (0.16 g, 71%), needles, m.p. 219—222 °C (Found: C, 63.3; H, 4.9; N, 2.9. $C_{24}H_{21}ClNO_4P$ requires C, 63.6; H, 4.6; N, 3.1%); $\nu_{max.}$ 1 100 cm^{-1} (ClO_4^-); τ[$(CD_3)_2CO$–CF_3·CO_2H (20 : 1)] 1.1—1.4 (2 H, m, arom.), 2.0—2.8 (17 H, m, arom.), and 4.60 (2 H, d, J_{PH} 14 Hz, CH_2).

(g) *With sodium phenoxide*. NaOH (0.8 g) was added to phenol (8.0 g) and the mixture gently heated until the alkali had dissolved. Compound (28) (5.0 g) was then added and the mixture heated at 200 °C (2 h). After cooling, water was added and the resultant precipitate collected. Distillation of this solid under diminished pressure gave phenyl 4-pyridylmethyl ether (32) (1.4 g, 75%), b.p. 175—180 °C at 1 mmHg; $\nu_{max.}$ (film) 3 300—3 100, 2 900—1 600, 1 500, 1 250, 1 100, 800, and 750 cm^{-1}; τ 0.9—1.2 (2 H, m, arom.), 2.0—2.9 (7 H, m, arom.), and 4.55 (2 H, s, CH_2), characterised as the *picrate*, m.p. 166—167 °C, needles from EtOH (Found: C, 52.0; H, 3.5; N, 13.1. $C_{18}H_{14}N_4O_8$ requires C, 52.1; H, 3.3; N, 13.5%).

(h) *With sodium thiophenoxide*. Sodium metal (0.28 g) was added to dry EtOH (15 ml) and when the reaction was complete thiophenol (1.4 g) was added. After 5 min compound (28) (5.0 g) was added and the solution refluxed for 1 h. Evaporation gave a residue which was extracted into Et_2O (100 ml); the extract was dried ($MgSO_4$) and evaporated. Vacuum distillation of the residue gave a liquid which solidified at room temperature. Recrystallisation from light petroleum (b.p. 60—80 °C) gave *phenyl 4-pyridylmethyl sulphide* (33) (1.6 g, 76%), needles, b.p. 182—192 °C at 20 mmHg, m.p. 37 °C (lit.,[22] b.p. 126—128 °C at 1 mmHg, m.p. 48—51 °C) (Found: C, 71.7; H, 5.5; N, 6.8; S, 16.1. $C_{12}H_{11}NS$ requires C, 71.6; H, 5.5; N, 7.0; S, 15.9%); $\nu_{max.}$ 1 600, 1 550, 1 400, 1 060, 1 010, 800, and 750 cm^{-1}; τ 0.9—1.2 (2 H, m, arom.), 2.1—2.5 (7 H, m, arom.), and 5.58 (2 H, s, CH_2).

(i) *With sodium toluene-*p*-sulphinate*. Compound (28) (0.25 g) and sodium toluene-*p*-sulphinate (0.09 g) in EtOH (20 ml) were refluxed for 2 days. After cooling the mixture was concentrated under reduced pressure, the triphenylpyridine which precipitated was collected, and the mother liquor was evaporated. The residue was extracted with Et_2O (100 ml) and the remaining solid crystallised from EtOH–Et_2O to give (4-*pyridylmethyl*) p-*tolyl sulphone* (34) (0.16 g, 82%), prisms, m.p. 181—183 °C (Found: C, 63.5; H, 5.4; N, 5.7. $C_{13}H_{13}NO_2S$ requires C, 63.2; H, 5.3; N, 5.7%); $\nu_{max.}$ 1 600, 1 300, 1 150, 820, 770, and 680 cm^{-1}; τ 0.9—1.2 (2 H, m, arom.), 1.9—2.7 (6 H, m, arom.), 5.32 (2 H, s, CH_2), and 7.14 (3 H, s, Me).

Reactions of 2,4,6-*Triphenyl*-1-(3-*pyridylmethyl*)*pyridinium Perchlorate* (37).—(a) *With pyridine*. Compound (37) (2.2 g) and pyridine (10 ml) were refluxed for 20 h. After cooling, the mixture was washed with Et_2O (6 × 20 ml) and the residual red oil treated with $HClO_4$ (70%, 5 ml) giving a viscous solution which was poured into Et_2O (150 ml). The precipitate was collected and identified as 1-(3-*pyridiniomethyl*)*pyridinium diperchlorate* (1.6 g, 97%), microcrystals, m.p. 155 °C (Found: C, 35.1; H, 3.1; N, 7.2. $C_{11}H_{12}Cl_2N_2O_8$,0.5H_2O requires C, 34.7; H, 3.4; N, 7.4%); $\nu_{max.}$ 1 080 cm^{-1} (ClO_4^-); τ(CF_3·CO_2H) 1.75 (9 H, m, arom.) and 4.17 (2 H, s, CH_2).

(b) *With 4-methylpyridine*. A solution of compound (37) (2.2 g) in 4-methylpyridine (10 ml) was refluxed for 12 h. After cooling and washing with Et_2O (3 × 25 ml) the residual brown oil was dissolved in hot EtOH (10 ml) and saturated ethanolic picric acid (5.0 ml) was added. The product was recrystallised from HOAc giving 4-*methyl*-1-(3-*pyridiniomethyl*)*pyridinium dipicrate* (0.9 g, 32%), yellow prisms, m.p. 182 °C (Found: C, 44.7; H, 2.8; N, 17.4. $C_{24}H_{18}N_8O_{14}$ requires C, 44.9; H, 2.8; N, 17.4%); τ[$(CD_3)_2SO$] 0.85 (2 H, d, arom., *J* 6 Hz), 1.40 (8 H, m, arom.), 1.95 (2 H, d, arom., *J* 6 Hz), 3.85 (2 H, s, CH_2), and 7.43 (3 H, s, Me).

(c) *With isoquinoline*. A solution of compound (37) (2.2 g) in isoquinoline (10 ml) was heated at 110 °C (18 h). The cold mixture was washed with Et_2O (4 × 20 ml) and the residual red oil dissolved in $HClO_4$ (70%; 10 ml). This acid solution was poured into Et_2O (150 ml) and the resulting precipitate recrystallised from HOAc giving 1-(3-*pyridiniomethyl*)*isoquinolinium diperchlorate* (1.6 g, 86%), brownish plates, m.p. 198 °C (Found: C, 42.4; H, 3.5; N, 6.5. $C_{15}H_{14}Cl_2N_2O_8$ requires C, 42.7; H, 3.3; N,

6.7%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 1.05 (1 H, s, arom.), 1.90 (11 H, m, arom.), and 3.98 (2 H, s, CH_2).

(d) *With piperidine.* Compound (37) (5.0 g) and piperidine (10 ml) were refluxed for 14 h. The mixture was distilled under reduced pressure and the fraction of b.p. 62 °C at 1.0 mmHg (0.35 g) was collected and identified as crude *N*-(3-pyridylmethyl)piperidine (38; R = piperidino), b.p. 62 °C at 1 mmHg (lit.,[23] 123—123.5 °C at 8 mmHg); τ 1.50 (2 H, m, arom.), 2.55 (2 H, m, arom.), 6.55 (2 H, s, CH_2), 7.67 (4 H, m, 2 × CH_2), and 8.55 (6 H, m, 3 × CH_2). This product gave a picrate, m.p. 173 °C (lit.,[23] 172—173 °C).

(e) *With morpholine.* Compound (37) (5.0 g) and morpholine (10 ml) were refluxed for 14 h. Excess of morpholine was removed by distillation under diminished pressure and the residue was worked up as for the benzyl derivative (20) giving *N*-(3-pyridylmethyl)morpholine (38: R = morpholino) (0.5 g, 28%) as a brown oil; τ(CCl_4) 1.38 (1 H, s, arom.), 2.35 (3 H, m, arom.), 6.08 (4 H, m, 2 × CH_2), 6.22 (2 H, s, CH_2), and 7.30 (4 H, m, 2 × CH_2), which was converted into its picrate, m.p. 220 °C (lit.,[23] 217 °C), yellow prisms from EtOH.

(f) *With sodium phenoxide.* A mixture of NaOH (0.28 g) and phenol (2.8 g) was melted until the alkali had dissolved. Compound (37) (1.75 g) was added and the mixture heated to form a melt (15 min). After cooling the mixture was washed with water (100 ml) and the residue distilled under vacuum giving *phenyl (3-methylpyridyl) ether* (38; R = PhO) (0.37 g, 57%), yellow oil (b.p. 180 °C at 6 mmHg), which crystallised; τ (neat) 2.35 (9 H, m, arom.) and 5.05 (2 H, s, CH_2). The product was fully characterised as its *picrate*, yellow prisms from EtOH, m.p. 117 °C (Found: C, 52.0; H, 3.6; N, 13.5. $C_{18}H_{14}N_4O_8$ requires C, 52.2; H, 3.4; N, 13.5%).

(g) *With sodium thiophenoxide.* Thiophenol (1.4 g) was added to a solution of sodium ethoxide [from sodium (0.3 g)] in EtOH (15 ml). After 5 min compound (37) (5.0 g) was added and the mixture refluxed for 2 h, then filtered. The filtrate was washed with EtOH (20 ml), and the combined EtOH solutions were evaporated. The residual oil was distilled under vacuum giving *phenyl (3-pyridylmethyl) sulphide* (38; R = PhS) (0.80 g, 40%), a pale straw-coloured liquid (b.p. >100 °C at 20 mmHg); τ (neat) 1.95 (2 H, m, arom.), 3.25 (7 H, m, arom.), and 6.51 (2 H, s, CH_2). The product was fully characterised as its *picrate*, yellow needles from EtOH, m.p. 147 °C (Found: C, 50.3; H, 3.4; N, 12.9; S, 7.5. $C_{18}H_{14}N_4O_7S$ requires C, 50.2; H, 3.3; N, 13.0; S, 7.4%).

Reactions of 2,4,6-Triphenyl-1-(2-pyridylmethyl)pyridinium Perchlorate (40).—(a) *With pyridine.* Compound (40) (2.2 g) was boiled in pyridine (10 ml) (24 h). After cooling, addition of Et_2O gave a brown oil which was dissolved in EtOH (50 ml) and heated under reflux with animal charcoal for 0.5 h. Evaporation gave an oil which was scratched with $HClO_4$ (70%; 10 ml). Addition of Et_2O (100 ml) to this mixture gave *1-(2-pyridiniomethyl)pyridinium diperchlorate* (0.8 g, 49%), prisms, m.p. 207 °C (Found: C, 35.6; H, 3.6. $C_{11}H_{12}Cl_2N_2O_8$ requires C, 35.6; H, 3.2%); $\nu_{max.}$ 1 080 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.85—2.85 (9 H, m, arom.) and 3.90 (2 H, s, CH_2).

(b) *With 4-methylpyridine.* Compound (40) (2.2 g) and 4-methylpyridine (10 ml) were refluxed (22 h). Work-up as for the reaction with pyridine (above) gave *4-methyl-1-(2-pyridiniomethyl)pyridinium diperchlorate* (0.85 g, 55%), buff needles, m.p. 255 °C (Found: C, 37.3; H, 3.9. $C_{12}H_{14}Cl_2N_2O_8$ requires C, 37.4; H, 3.6%); $\nu_{max.}$ 1 080 cm^{-1} (ClO_4^-); τ($CF_3{\cdot}CO_2H$) 1.55 (5 H, m, arom.), 2.35 (2 H, d, arom., *J* 6.6 Hz), 4.05 (2 H, s, CH_2), and 1.65 (3 H, s, Me) (some aromatic H signals masked by solvent).

(c) *With isoquinoline.* Compound (40) (2.2 g) and isoquinoline (10 ml) were heated at 140 °C (12 h). Work-up as described for the reaction with pyridine (above) and recrystallisation of the product from EtOH–Et_2O (1 : 1) gave *1-(2-pyridylmethyl)isoquinolinium perchlorate* (1.3 g, 92%), pink needles, m.p. 127 °C (Found: C, 55.8; H, 4.1; N, 8.8. $C_{15}H_{13}ClN_2O_4$ requires C, 56.2; H, 4.1; N, 8.7%); $\nu_{max.}$($CHCl_3$) 1 090 cm^{-1} (ClO_4^-); τ[$(CD_3)_2SO$] 1.9 (11 H, m, arom.) and 3.88 (2 H, s, CH_2).

(d) *With piperidine.* A mixture of compound (40) (2.2 g) and piperidine (10 ml) was refluxed (14 h). Excess of piperidine was removed by distillation under diminished pressure and the residue was worked up as for the benzyl derivative (19) giving *N*-(2-pyridylmethyl)piperidine (41; R = piperidino) (0.7 g, 90%); τ 1.50 (1 H, m, arom), 2.55 (3 H, m, arom.), 6.40 (2 H, s, CH_2), 7.65 (4 H, m, 2 × CH_2), and 8.50 (6 H, m, 3 × CH_2), which was fully characterised as its *picrate*, yellow needles from EtOH–Et_2O (1 : 1), m.p. 121 °C (Found: C, 50.2; H, 4.7; N, 17.2. $C_{23}H_{22}N_8O_{14}$ requires C, 50.4; H, 4.7; N, 17.3%).

(e) *With morpholine.* Compound (40) (2.2 g) and morpholine (10 ml) were heated at reflux temperature (14 h). The reaction was worked up as for that of the benzyl derivative (20) giving *N-(2-pyridylmethyl)morpholine* (41; R = morpholino) (0.18 g, 23%) as a brown oil; τ 1.45 (1 H, m, arom.), 2.60 (3 H, m, arom.), 6.28 (6 H, m, 3 × CH_2), and 7.48 (4 H, m, 2 × CH_2), which was fully characterised as its *picrate*, yellow prisms from EtOH, m.p. 187 °C (Found: C, 41.4; H, 3.4; N, 17.7. $C_{22}H_{20}N_8O_{15}$ requires C, 41.5; H, 3.1; N, 17.6%).

(f) *With triphenylphosphine.* Compound (40) (0.45 g) and triphenylphosphine (0.27 g) were heated with a microburner until the melt began to darken. The mixture was then washed with Et_2O (3 × 20 ml) and the residue recrystallised from EtOH–Et_2O (2 : 1) giving *triphenyl-(2-pyridylmethyl)phosphonium perchlorate* (0.15 g, 33%), needles, m.p. 222 °C (Found: C, 62.5; H, 5.0; N, 3.3. $C_{24}H_{21}ClNO_4P,0.5H_2O$ requires C, 62.3; H, 4.8; N, 3.0%); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); τ 2.85 (19 H, m, arom.) and 4.93 (2 H, d, CH_2P, J_{PH} 14.6 Hz).

(g) *With sodium thiophenoxide.* Thiophenol (1.4 g) was added to a solution of sodium (0.5 g) in EtOH (15 ml). After 5 min, compound (40) (5.0 g) was added and the mixture heated at reflux temperature (24 h). Evaporation gave a residue which was extracted with EtOH (100 ml). Evaporation of the ethanolic solution gave a product which was then extracted with Et_2O, and the Et_2O extract was then extracted with light petroleum (b.p. 40—60 °C) (4 × 20 ml). Evaporation of the petroleum solution gave phenyl (2-pyridylmethyl) sulphide (41; R = PhS) (1.4 g, 70%) as a pale straw coloured oil (lit.,[22] b.p. 123—127 °C at 0.4 mmHg) which crystallised and was fully characterised as its *picrate*, yellow needles from EtOH, m.p. 115 °C (Found: C, 50.4; H, 3.4; N, 13.1; S, 7.4. $C_{18}H_{14}N_4O_7S$ requires C, 50.2; H, 3.3; N, 13.0; S, 7.4%); τ(CCl_4) 1.75 (1 H, m, arom.), 2.8 (8 H, m, arom.), and 5.90 (2 H, s, CH_2).

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