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PREPARATION OF ALKYL-ARYL ETHERS AND THIOETHERS

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Abstract - A method, which involves no molecular rearrangement, and which is also stereospecific, for the preparation of alkyl-aryl ethers and thioethers is described. Stable alkoxyphosphonium salts, $R\text{-}O\text{-}\overset{+}{P}(NMe_2)_3\ PF_6^-$, have been prepared and treated with phenols and thiophenols, under basic conditions, to yield the corresponding alkyl-aryl ethers and thioethers respectively.

The three component system $ROH/CCl_4/Ph_3P$, used for the conversion of alcohols to the corresponding alkyl chloride, was originally thought to have the simple stoichiometry.[1-4]

$$ROH + CCl_4 + Ph_3P \longrightarrow RCl + CHCl_3 + Ph_3PO$$

Subsequently, however, it was shown that the above reaction represented only one mode of behaviour of the system, in that, though yields of alkyl chloride were generally good, less chloroform than indicated by the above scheme was formed, and in addition to triphenylphosphine oxide the non-volatile product of reaction contained (chloromethyl)triphenylphosphonium chloride.[5,6]

However, whatever the route of reaction, a drawback of the above system is the potential difficulty in separation of the alkyl chloride from the triphenylphosphine oxide by-product. A way of overcoming this problem is to substitute tris(dimethylamino)phosphine, $(Me_2N)_3P$, for triphenylphosphine, as the by-product arising here HMPT, $(Me_2N)_3PO$, is water soluble. Further the aminophosphine is more nucleophilic than triphenylphosphine and hence milder reaction conditions may be used.

In an investigation of the reaction route of the three component system $ROH/CCl_4/P(NMe_2)_3$ a stable intermediate $RO\text{-}\overset{+}{P}(NMe_2)_3\ \overset{-}{P}F_6$ was isolated,[2] and subsequently this and other such stable intermediates have been used in synthesis.[7-9] This mechanistic study was possible because of the rapid rate of formation of the alkyloxyphosphonium salt (due to the high nucleophilicity of the aminophosphine) according to the equation:

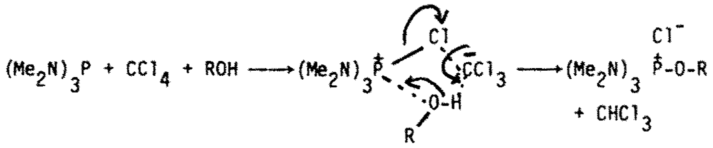
$$(Me_2N)_3P + CCl_4 + ROH \longrightarrow RO — \overset{+}{P}(NMe_2)_3\ Cl^- + CHCl_3$$

and its relatively slow rate of collapse:

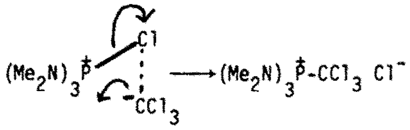
$$Cl^-\ \ R\text{-}O\text{-}\overset{+}{P}(NMe_2)_3 \longrightarrow Cl\text{-}R + O = P(NMe_2)_3.$$

This is in contrast to the $ROH/CCl_4/Ph_3P$ system where it has been reported, for R = primary alkyl, that the rate of collapse of the alkoxyphosphonium ion proceeds more rapidly than its formation, [10,11] thus precluding its ready isolation.

Suffice it to say the system ROH/CCl_4/$P(NMe_2)_3$, from which the required stable alkoxyphosphonium salts could be obtained, appeared appropriate to our needs and has been briefly, partially reported.[12] Indeed our results also indicate that the major reaction path for this system is the simple one:-



with the alternative reaction:



being observed in only one case, and then only as a minor competitor

In order to see whether or not the neopentyl-aryl ethers could potentially be made via the alkyloxyphosphonium salt it seemed reasonable to prepare neopentyl chloride in a two stage partial model. Thus the first step involved the addition of the aminophosphine to an ice-cold ethereal solution of carbon tetrachloride and neopentanol which gave the phosphonium salt as a yellow oil. The salt was dealkylated, by heating under reflux in DMF, to afford neopentyl chloride (61%) and HMPT.

As the chloride ion had dealkylated the phosphonium salt it seemed hopeful that aryloxide and arylsulphide ions would do likewise. Hence the aminophosphine was added to an ethereal solution at 0°C containing an equimolar amount of neopentanol and carbon tetrachloride (in slight excess). After completion of addition an ice-chilled aqueous solution of ammonium hexafluorophosphate was added affording a precipitate of neopentyl oxy(trisdimethylamino)phosphonium hexafluorophosphate in 70% yield. No other products were obtained.

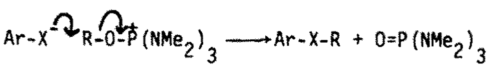
More generally the three component reaction was effected at -78° for primary alcohols, and at -20° for octan-2-ol, with subsequent addition of ice-cold aqueous ammonium hexafluorophosphate. The case of the secondary alcohol was the only one where evidence of the competing reaction was observed: trichloromethyl(trisdimethylamino)phosphonium chloride being isolated as a precipitate (before addition of the ammonium hexafluorophosphate solution) and characterized as its perchlorate salt (5%).

The phosphonium hexafluorophosphates were prepared throughout as they are readily isolable and they do not undergo decomposition as readily as the corresponding phosphonium chlorides; in fact the hexafluorophosphate derivatives, which are non-hygroscopic, may be recrystallized from protic organic solvents, and are stable at room temperature for some months.

$$(Me_2N)_3P + CCl_4 + ROH \xrightarrow[\text{temp.}]{\text{low}} (Me_2N)_3\overset{+}{P}\text{-O-R} \quad \overset{-}{Cl} + CHCl_3$$

$$(Me_2N)_3\overset{+}{P}\text{-O-R} \ \overset{-}{Cl} + NH_4PF_6 \longrightarrow (Me_2N)_3\overset{+}{P}\text{-O-R} \ \overset{-}{P}F_6 \ \downarrow$$

Having developed a satisfactory class of potential alkylating agents a series of alkyl-aryl ethers and thioethers were prepared by allowing the potassium salt of the phenol or thiophenol to react with the appropriate alkoxyphosphonium salt.



X = O or S

We were also able to show that when potassium phenate reacted with the phosphonium salt prepared from (-)-(R)-octan-2-ol it gave (+)-(S)-2-octyl phenyl ether in 93% yield.

EXPERIMENTAL

General

All solvents were distilled and dried by conventional methods prior to their use.

I.r. spectra were determined using potassium bromide discs in the case of solids, or as thin films in the case of liquids, on a Perkin-Elmer 257 spectrometer. U.V. spectra were determined on ethanolic solutions with a Pye-Unicam SP 8000 spectrophotometer. ^{1}H n.m.r. spectra were determined at 90 MHz, peaks being recorded as δ values from internal $SiMe_4$ as reference, using a Perkin-Elmer R32 spectrometer. Mass spectra were recorded on an A.E.I. M.S.12 spectrometer. High resolution mass spectrometry was carried out on an A.E.I. M.S.9. Melting points were determined on a Kofler block and are uncorrected.

Preparation of Neopentyl chloride

A solution of tris(dimethylamino)phosphine (16.3g, 0.1 mol) in ether (15 ml) was added dropwise to a stirred ice-cold solution of neopentanol (8.8g, 0.1 mol) and carbon tetrachloride (15.4g, 0.1 mol) in ether (50 ml). A yellow oil separated out which was dissolved in DMF (100 ml), and the resulting solution was heated under reflux for one hour and then poured into water (100 ml). The mixture was extracted with ether (2 x 75 ml) and each extract washed with water (2 x 50 ml). The combined ether layers were then dried over anhydrous magnesium sulphate, and then distilled to give, after the removal of solvent, neopentyl chloride (6.02g, 61%); b.p. 84-85°C (lit.,[13] b.p. 84.4°C).

Preparation of Neopentyloxy-tris(dimethylamino)phosphonium hexafluorophosphate

A solution of tris(dimethylamino)phosphine (32.6g, 0.2 mol) in ether (100 ml) at 0°C, was added to a stirred solution of neopentanol (18g, 0.2 mol) and carbon tetrachloride (38.5g, 0.25 mol) in ether (100 ml), also at 0°C.

When the addition was complete the cold mixture was poured into an ice-chilled saturated aqueous solution of ammonium hexafluorophosphate (34g, 0.2 mol) with the immediate formation of a while solid. This precipitate was collected, washed with ice-cold water (75 ml) and ether (75 ml), and then dried over calcium chloride. Recrystallization from ethanol gave neopentyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (58g, 70%) as colourless plates; m.p. 202-204°C (lit.,[14] m.p. 202-204°C); ν_{max} (KBr) 2960, 1460, 1310, 1170, 1065, 995, 825, 765, and 750 cm^{-1}; δ_H (90 MHz., $CDCl_3$) 3.82 (2H, d, J_{PH} 4 Hz), 2.82 (18H, d, J_{PH} 11 Hz), and 1.05 (9 H, s). [Found: C, 32.70; H, 7.05; N, 10.70%. Calc. for $C_{11}H_{29}F_6N_3OP_2$: C, 33.42; H, 7.34; N, 10.63%]

Preparation of Phenoxy-tris(dimethylamino)phosphonium hexafluorophosphate

Using the procedure described in the previous experiment, tris(dimethylamino)phosphine (8.15g, 0.05 mol), phenol (4.7g, 0.05 mol), carbon tetrachloride (10.0g, 0.065 mol) were allowed to react with subsequent addition of the resulting reaction mixture to ammonium hexafluorophosphate (8.5g, 0.05 mol) to give phenoxy-tris(dimethylamino)phosphonium hexafluorophosphate (13.4g, 67%) as white plates; m.p. 93-94°C (from ethanol) (lit.,[15] m.p. 92°C); ν_{max} (KBr) 2970, 1600, 1495, 1465, 1320, 1210, 1180, 1170, 1010, 955, 840 (broad), 785, 775, 760, and 690 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.65-7.1 (5H, m) and 2.80 (18H, d, J_{PH} 10Hz).

Preparation of n-Propoxy-tris(dimethylamino)phosphonium hexafluorophosphate

Tris(dimethylamino)phosphine (16.3g, 0.1 mol), in ether (50 ml) at -78°C, was added dropwise to a stirred solution of n-propanol (6.0g, 0.1 mol) and carbon tetrachloride (23g, 0.15 mol) in ether (100 ml), also at -78°C.

When the addition was complete the cold mixture was poured into an ice-chilled saturated aqueous solution of ammonium hexafluorophosphate (16.3g, 0.1 mol) with the immediate formation of a white solid. The precipitate was filtered off, washed with ice-chilled water (30 ml) and ether (30 ml), and then dried over calcium chloride. Recrystallization from ethanol gave n-propoxy-tris(dimethylamino)phosphonium hexafluorophosphate (19.1g, 52%) as a crystalline white solid; m.p. 226-228°C; ν_{max} (KBr) 2950, 1500, 1470, 1320, 1180, 1075, 1060, 1010, 880, 850, 780, 770, 740, and 665 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 4.18 (2H, t, J 6 Hz), 2.82 (18H, d, J_{PH} 11 Hz), 1.85 (2H, sextet, J 6 Hz), and 1.04 (3H, t, J 6 Hz). [Found: C, 29.70; H, 6.55; N, 11.50% $C_9H_{25}F_6N_3OP_2$ requires C, 29.43; H, 6.81; N, 11.44%].

Preparation of Allyloxy-tris(dimethylamino)phosphonium hexafluorophosphate

Using the procedure described in the previous experiment, tris(dimethylamino)phosphine (16.3g, 0.1 mol), allyl alcohol (5.8g, 0.1 mol) and carbon tetrachloride (23g, 0.15 mol) were allowed to react, and subsequent addition of the resulting reaction mixture to ammonium hexafluorophosphate (16.3g, 0.1 mol) gave allyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (32g 86%); m.p. 208-209°C (from ethanol); ν_{max} (KBr) 2940, 1500, 1470, 1430, 1320, 1180, 1040, 950, 830, 775, 760, and 670 cm^{-1}; δ_H (90, MHz, $CDCl_3$) 6.0 (1H, m), 5.45 (2H, m), 4.75 (2H, m) and 2.85 (18H, d, J_{PH} 10 Hz).

Preparation of Benzyloxy-tris(dimethylamino)phosphonium hexafluorophosphate

Tris(dimethylamino)phosphine (16.3g, 0.1 mol), in ether (30 ml) at -78°C, was added dropwise to a stirred solution of benzyl alcohol (10.8g, 0.1 mol) and carbon tetrachloride (23.0g, 0.15

mol) dissolved in ether (100 ml) at -78°C. When the addition was complete the reaction mixture was poured into an ice-chilled saturated solution of ammonium hexafluorophosphate (16.3g, 0.1 mol) in water, which resulted in the immediate formation of a white solid. This solid was filtered off, washed with ice-cold water (50 ml) and ether (50 ml), and then dried over calcium chloride.

The solid was then washed with chloroform (3 x 50 ml) to isolate the insoluble chloro-tris-(dimethylamino)phosphonium hexafluorophosphate (3.27g, 9%), m.p. 198-200°C, from the crude product. Removal of the solvent from the filtrate gave a white solid which recrystallized from ethanol to afford benzyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (28.1g, 68%) as colourless plates; m.p. 130-132°C; ν_{max} 2940, 1495, 1470, 1460, 1320, 1180, 1170, 1075, 1010, 840, 780, 770, 750, 705, and 670 cm $^{-1}$; δ_H (90 MHz, $CDCl_3$) 7.45 (5H, s), 5.22 (2H, d, J_{PH} 8 Hz), and 2.8 (18H, d, J_{PH} 10 Hz). [Found: C, 38.00; H, 5.85; N, 9.85%. $C_{13}H_{25}F_6N_3OP_2$ requires C, 37.69; H, 6.02; N, 10.12%].

Preparation of 2-Octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate

A solution of tris(dimethylamino)phosphine (32.6g, 0.2 mol) in ether (100 ml) at -20°C was added dropwise over a period of two hours to a stirred solution of octan-2-ol (26g, 0.2 mol) and carbon tetrachloride (38.5g, 0.25 mol) in ether (150 ml), also at -20°C.

A white precipitate of trichloromethyl-tris(dimethylamino)phosphonium chloride was formed, which was filtered off and subsequently characterized as its stable perchlorate (3.8g, 5%) m.p. 280-285°C (dec.) (from water), (lit.,[16] m.p. >290°C).

The addition of an ice-chilled saturated aqueous solution of ammonium hexafluorophosphate (32.6g, 0.2 mol) to the filtrate afforded a white solid which was filtered off and washed with ether (75 ml), and then dried over calcium chloride. Recrystallization from ethanol gave 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (40g, 46%) as a white crystalline solid; m.p. 113-114°C; ν_{max} (KBr) 2970, 2940, 1490, 1470, 1390, 1315, 1190, 1075, 1020, 1000, 840 (broad), 770, and 665 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 4.6 (1H, m), 2.82 (18H, d, J_{PH} 11 Hz), and 1.8-0.7 (16H, m). [Found: C, 38.00; H, 7.60; N, 9.80%. $C_{14}H_{35}F_6N_3OP_2$ requires C, 38.44; H, 8.00; N, 9.61%].

Preparation of a Series of Alkyl Aryl Ethers and Thioethers

A number of alkyl aryl ethers and thioethers were prepared by a procedure identical to that employed for the preparation of neopentyl phenyl ether which is described in detail.

Preparation of Neopentyl phenyl ether

DMF (50 ml) was added, with stirring, to powdered potassium hydroxide (1.12g, 0.02 mol). Phenol (0.94g, 0.01 mol) was then added and the mixture was stirred for thirty minutes. Neopentyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (8.2g, 0.02 mol) was added, and the mixture heated under reflux for 15 hours. After cooling to room temperature the reaction mixture was poured into water (100 ml), and extracted with ether (3 x 50 ml) and each extract washed with water (3 x 30 ml). The combined ether layers were twice washed with an aqueous solution of sodium hydroxide, to remove unreacted phenol, and then dried over anhydrous magnesium sulphate. The solvent was removed and the residue was placed on a column of alumina; elution with 10% ether-light petroleum gave neopentyl phenyl ether (1.24g, 75%); b.p. 55-58°C (1.5 mm Hg) [lit.,[17] b.p. 82-83°C (12 mm Hg)]; ν_{max} (film) 2960, 2910, 2880, 1610, 1595, 1500, 1480, 1370, 1300, 1245, 1055, 1020, 755 and 690 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.4-6.8 (5H, m), 3.6 (2H, s), and 1.0 (9H, s).

Preparation of 2-Neopentyloxy-2'-nitrobiphenyl

The reaction of 2-hydroxy-2'-nitrobiphenyl (0.7g) with potassium hydroxide (0.8g) and neopentyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (2.76g) in DMF (35 ml) gave 2-neopentyloxy-2'-nitrobiphenyl (0.68g, 70%); m.p. 90-91°C (from light petroleum, b.p. 60-80°C). [Found: C, 72.0; H, 6.6; N, 5.2; M (mass spectrum 285). $C_{17}H_{19}NO_3$ requires C, 71.55; H, 6.7; N, 4.9%; M.285] ν_{max} (film) 2960, 2940, 2880, 1615, 1530, 1505, 1470, 1370, 1360, 1250, 1125, 1020, 750 and 740 cm^{-1}; λ_{max} 215, 240, and 274 nm (log ϵ 4.32, 3.93, and 3.73 dm^3 mol^{-1} cm^{-1}); δ_H (90 MHz, $CDCl_3$) 8.1-6.8 (8H, m), 3.55 (2H, s), and 0.78 (9H, s).

Preparation of p-Methoxyphenyl neopentyl ether

The reaction of p-methoxyphenol (0.62g, 0.005 mol) with potassium hydroxide (0.56g, 0.01 mol), and neopentyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (3.95g, 0.01 mol) in DMF (25 ml) gave p-methoxyphenyl neopentyl ether [0.22g, 66% (based on reacted p-methoxyphenol)] as a white solid; m.p. 59-60°C (from light petroleum, b.p. 60-80°C) (lit.[17] m.p. 60°C); δ_H (90 MHz, $CDCl_3$) 6.70 (4H, s), 3.68 (3H, s), 3.5 (2H, s), and 1.0 (9H, s).

Preparation of 2-(2-octyloxy)-2'-nitrobiphenyl

The reaction of 2-hydroxy-2'-nitrobiphenyl (0.1g) with potassium hydroxide (0.13g) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (0.36g) in DMF (25 ml) gave 2-(2-octyloxy)-2'-nitrobiphenyl (0.14g, 81%) as a yellow oil; b.p. 186-196°C (1 mm Hg). ν_{max} (film) 2940, 2860, 1620, 1530, 1500, 1455, 1360, 1250, 1130, 855, 755, and 740 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 8.0-6.8 (8H, m), 4.28 (1H, sextet, J 6 Hz), and 1.7-0.8 (16H, m).

Preparation of p-Methoxyphenyl 2-octyl ether

The reaction of p-methoxyphenol (0.5g) with potassium hydroxide (0.5g) and 2-octyloxy-tris-(dimethylamino)phosphonium hexafluorophosphate (3.5g) in DMF (25 ml) gave p-methoxyphenyl 2-octyl ether (0.55g, 68%); b.p. 119°C (1.5 mm Hg); M (mass spectrum 236.1772; $C_{15}H_{24}O_2$ requires M

236.1776; ν_{max} (film) 2940, 2860, 1510, 1470, 1445, 1380, 1290, 1235, 1180, 1135, 1125, 1105, 1045, and 825 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 6.8 (4H, s), 4.22 (1H, sextet, J 6 Hz), 3.75 (3H, s), and 1.75-0.75 (16H, m).

Preparation of p-Nitrophenyl 2-octyl ether

The reaction of p-nitrophenol (0.7g, 0.005 mol) with potassium hydroxide (0.56g, 0.01 mol) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (4.37g, 0.01 mol) in DMF (30 ml) gave p-nitrophenyl 2-octyl ether (1.20g, 80%); b.p. 154°C (1.5 mm Hg); [Found C, 66.8; H, 8.3; N, 5.2; M (mass spectrum 251); $C_{14}H_{21}NO_3$ requires C, 66.9; H, 8.4; N, 5.6; M, 251]; ν_{max} (film) 2960, 2940, 2860, 1615, 1600, 1520, 1500, 1470, 1385, 1345, 1300, 1266, 1175, 1115, 940, 845, 755, and 690 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 8.2 (2H, AB d, J_{AB} 9 Hz), 6.90 (2H, AB d, J_{AB} 9 Hz), 4.48 (1H, sextet, J 6Hz), and 1.8-0.7 (16H, m).

Preparation of 2-Octyl phenyl ether

The reaction of phenol (0.94g, 0.01 mol) with potassium hydroxide (1.12g, 0.02 mol) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (8.74g, 0.02 mol) in DMF (60 ml) gave 2-octyl phenyl ether (2.02g, 90%); b.p. 104°C (1.5 mm Hg) [lit.,[18] b.p. 144° 20 mm Hg)]; ν_{max} (film) 2960, 2940, 2870, 1605, 1595, 1500, 1380, 1300, 1245, 1175, 1120, 755, and 690 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.4-6.8 (5H, m), 4.4 (1H, sextet, J 6 Hz), and 1.8-0.7 (16H, m).

Preparation of (+)(S)-2-Octyl phenyl ether

The reaction of phenol (0.94g, 0.01 mol) with potassium hydroxide (1.12g, 0.02 mol) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (8.74g, 0.02 mol), derived from (-)(R)-2-octanol, in DMF gave (+)(S)-2-octyl phenyl ether (1.94g, 93%); b.p. 99°C (1 mm Hg); $[\alpha]_D^{26}$ +15.5° (c. 5.0 in ethanol). (-)(R)-2-octyl phenyl ether has the value $[\alpha]_D^{26}$ -15.0° (c. 5.0 in ethanol).[18]

Preparation of Allyl phenyl ether

The reaction of phenol (0.47g, 0.005 mol) with potassium hydroxide (0.56g, 0.01 mol) and allyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (3.65g, 0.01 mol) in DMF (30 ml) gave allyl phenyl ether (0.47g, 79%); b.p. 40°C (2 mm Hg) [lit.,[19] b.p. 191-192°C (760 mm Hg)]; δ_H ($CDCl_3$) 7.55-6.8 (5H, m), 6.3-5.85 (1H, m), 5.6-5.2 (2H, m), and 4.6-4.4 (2H, m).

Preparation of Phenyl n-propyl ether

The reaction of phenol (0.47g, 0.005 mol) with potassium hydroxide (0.56g, 0.01 mol) and n-propoxy-tris(dimethylamino)phosphonium hexafluorophosphate (3.67g, 0.01 mol) in DMF (50 ml) gave phenyl n-propyl ether (0.58g, 86%); b.p. 56° (4.5 mm Hg) [lit.,[20] b.p. 69° (14 mm Hg)]; δ_H ($CDCl_3$) 7.5-6.8 (5H, m), 3.9 (2H, t, J 8 Hz), 1.8 (2H, sextet, J 8 Hz), and 1.05 (3H, t, J 8 Hz).

Preparation of 2-Octyl phenyl sulphide

The reaction of thiophenol (0.6g) with potassium hydroxide (0.6g) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (4.4g) in DMF (25 ml) gave 2-octyl phenyl sulphide (0.73g, 61%); b.p. 107°C (0.7 mm Hg) [lit.,[21] b.p. 197°C (13 mm Hg)]; δ_H (90 MHz, $CDCl_3$) 7.6-7.15 (5H, m), 3.2 (1H, sextet, J 6 Hz), and 1.70-0.75 (16H, m).

Preparation of 2-Octyl p-tolyl sulphide

The reaction of p-toluenethiol (0.6g) with potassium hydroxide (0.6g) and 2-octyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (4.37g) in DMF (25 ml) gave 2-octyl p-tolyl sulphide (0.78g, 68%); b.p. 124°C(0.7 mm Hg); M (mass spectrum) 236.1595; $C_{15}H_{24}S$ requires M 236.1599; ν_{max} (film) 2940, 2860, 1495, 1460, 1380, 1265, 1095, 1020, and 810 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.22 (4H, m, AA'BB'), 3.2 (1H, sextet, J 6 Hz), 2.35 (3H, s), and 1.8-0.7 (16H, m).

Preparation of Benzyl phenyl sulphide

The reaction of thiophenol (0.6g) with potassium hydroxide (0.6g) and benzyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (4.75g) in DMF (30 ml) gave benzyl phenyl sulphide (0.84g, 83%); m.p. 40-41°C (from light petroleum b.p. 60-80°C), (lit.,[22] m.p. 39-40°C); δ_H ($CDCl_3$) 7.55-7.15 (10H, m) and 4.10 (2H, s).

Preparation of Benzyl p-tolyl sulphide

The reaction of p-toluenethiol (0.62g, 0.005 mol) with potassium hydroxide (0.56g, 0.01 mol) and benzyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (4.15g, 0.01 mol) in DMF (30 ml) gave benzyl p-tolyl sulphide (1.01g, 98%); m.p. 45-46°C (from light petroleum b.p. 60-80°C), (lit.,[23] m.p. 40-41°C); δ_H ($CDCl_3$) 7.55-6.95 (9H, m), 4.07 (2H, s), and 2.3 (3H, s).

Preparation of Allyl-p-tolyl sulphide

The reaction of p-toluenethiol (1.24g, 0.01 mol) with potassium hydroxide (1.12g, 0.02 mol) and allyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (7.30g, 0.02 mol) in DMF (50 ml) gave allyl p-tolyl sulphide (1.53g, 97%); b.p. 70°C (0.2 mm Hg), [lit.,[24] 99-100.5° (7.5 mm Hg)]; δ_H ($CDCl_3$) 7.2 (4H, q, J 9 Hz), 6.2-5.6 (1H, m), 5.25-4.95 (2H, m), 3.6-3.4 (2H, m) and 2.32 (3H, s).

Preparation of Allyl phenyl sulphide

The reaction of thiophenol (1.10g, 0.01 mol) with potassium hydroxide (1.12g, 0.02 mol) and allyloxy-tris(dimethylamino)phosphonium hexafluorophosphate (7.3g, 0.02 mol) in DMF (50 ml) gave allyl phenyl sulphide (1.36g, 90%); b.p. 75°C (2 mm Hg), lit.,[25] b.p. 84-86°C (5 mm Hg); δ_H ($CDCl_3$) 7.5-7.1 (5H, m), 6.15-5.6 (1H, m), 5.3-4.95 (2H, m), and 3.6-3.4 (2H, m).

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