# Synthetic Uses of Iminophosphoranes. Monoalkylation of Primary Aromatic Amines

Elizabeth M. Briggs, Geoffrey W. Brown*, Josef Jiricny, Mohamed F. Meidine

Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY, U.K.

There are few convenient high-yield general methods available for the monoalkylation of primary aromatic amines[1]. We wish to report an apparently widely applicable route to *N*-alkylbenzenamines **4** through conversion of anilines **1** into the iminophosphorane derivatives[2] **2** followed by quaternisation with an alkyl iodide[3] and subsequent alkaline hydrolysis.

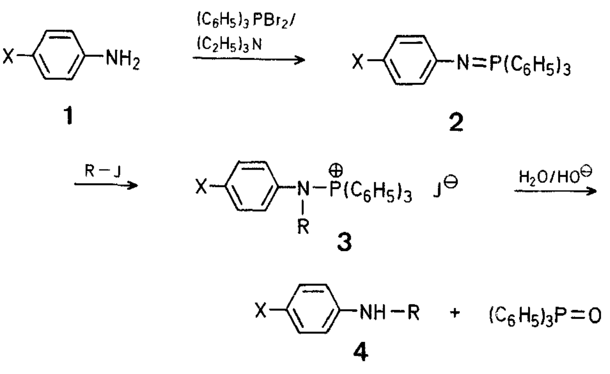
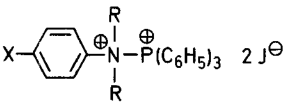


**Table 1.** *P*-(Alkylphenylamino)-triphenylphosphonium Iodides **3** from Phenyliminotriphenylphosphoranes **2** and Alkyl Iodides

| 3 | X | R | Yield [%] | m.p. [°C] | m.p. [°C] reported or Molecular formula[a] |
|---|---|---|---|---|---|
| **a** | H | CH$_3$ | 80 | 241 | 239.5–241°[11] |
| **b** | CH$_3$ | CH$_3$ | 70 | 231 | $C_{26}H_{25}JNP$ (509.1) |
| **c** | —CO—CH$_3$ | CH$_3$ | 78 | 197 | $C_{27}H_{25}JNOP$ (537.1) |
| **d** | —COOC$_2$H$_5$ | CH$_3$ | 87 | 176 | $C_{28}H_{27}JNO_2P$ (567.1) |
| **e** | —CN | CH$_3$ | 89 | 236 | $C_{26}H_{22}JN_2P$ (520.1) |
| **f** | Cl | CH$_3$ | 69 | 118 | $C_{25}H_{22}ClJNP$ (529.5) |
| **g** | Br | CH$_3$ | 58 | 219 | $C_{25}H_{22}BrJNP$ (574.0) |
| **h** | J | CH$_3$ | 51 | 229 | $C_{25}H_{22}J_2NP$ (621.2) |
| **i** | —OCH$_3$ | CH$_3$ | 83 | 120 | $C_{26}H_{25}JNOP$ (525.4) |
| **j** | —NO$_2$ | CH$_3$ | 65 | 208 | $C_{25}H_{22}JN_2O_2P$ (540.3) |
| **k** | H | *n*-C$_4$H$_9$ | 86 | 260 | $C_{28}H_{29}JNP$ (537.4) |

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.26; H, ±0.32; N, ±0.37; P, ±0.26.

The *N*-alkyl derivatives **4** which result from this sequence are easily isolated and are uncontaminated by bis-alkylated products because alkylation of the iminophosphorane **2** is unlikely to lead to formation of the doubly-charged salt:



Yields are high for the overall conversion both when the aromatic ring is substituted by electron-donating and electron-withdrawing groups.

From the results listed in Table 1 it is seen that the quaternisation of iminophosphoranes **2** affords similar yields of aminophosphonium salts **3** when carried out with methyl iodide or with 1-iodobutane. This is in contrast to earlier work[4] describing the synthesis of *N*-alkylated aliphatic amines from alkyliminophosphoranes by a route similar to that described here, where it was found that alkyl iodides higher than ethyl iodide were dehydrohalogenated by the strongly basic phosphoranes and gave no alkylated product. *N*-Aryliminophosphoranes **2** are much less basic, and this side-reaction does not affect the yield of *N*-alkylated phosphonium salt. The earlier work[4] also suffered from the need to use sodium in liquid ammonia in generating the iminophosphorane: *N*-aryliminophosphoranes can be prepared much more conveniently, using only triethylamine as base on the mixture of amine and triphenylphosphine dibromide[2].

**Phenyliminotriphenylphosphoranes 2:**
These compounds are prepared according to the procedure of Horner and Oediger[2].

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**Table 2.** *N*-Alkylanilines[a] (**4**) from *P*-(Alkylphenylamino)-triphenylphosphonium Iodides (**3**)

| 4 | X | R | Yield [%] | Physical Data | |
|---|---|---|---|---|---|
| | | | | found | reported |
| **a** | H | $CH_3$ | 86 | $n_D^{22}$: 1.5702 | $n_D^{20}$: 1.5684[5] |
| **b** | $CH_3$ | $CH_3$ | 73 | $n_D^{22}$: 1.5565 | $n_D^{20}$: 1.5560[6] |
| **c** | $-CO-CH_3$ | $CH_3$ | 81 | m.p. 102–103 °C | m.p. 101–102 °C[7];<br>m.p. 102–103 °C[8] |
| **d** | $-COOC_2H_5$ | $CH_3$ | 52 | m.p. 62 °C | m.p. 59–62 °C[9] |
| **f** | Cl | $CH_3$ | 73 | $n_D^{22}$: 1.5853 | $n_D^{20}$: 1.5835[6] |
| **i** | $-OCH_3$ | $CH_3$ | 71 | m.p. 36–37 °C | m.p. 37 °C[6] |
| **k** | H | *n*-$C_4H_9$ | 72 | $n_D^{22}$: 1.5381 | $n_D^{22}$: 1.5361[10] |

[a] Identified by comparison of their physical data and spectral characteristics with the corresponding data from the literature.

*Phenyliminotriphenylphosphorane* (**2**, X=H); yield: 79%; m.p. 132 °C (Ref. [2], m.p. 128–130 °C).

*4-Methylphenyliminotriphenylphosphorane* (**2**, X=$CH_3$); yield: 83%; m.p. 135 °C (Ref. [2], m.p. 132–134 °C).

*4-Acetylphenyliminotriphenylphosphorane* (**2**, X=$-CO-CH_3$); yield: 72%; m.p. 124 °C (Ref. [12], m.p. 125 °C).

*4-Ethoxycarbonylphenyliminotriphenylphosphorane* (**2**, X=$-COOC_2H_5$); yield: 83%; m.p. 136 °C (Ref. [2], m.p. 135–136 °C).

*4-Cyanophenyliminotriphenylphosphorane* (**2**, X=$-CN$); yield: 73%; m.p. 192–193 °C (Ref. [2], m.p. 191–192 °C).

*4-Chlorophenyliminotriphenylphosphorane* (**2**, X=Cl); yield: 69%; m.p. 118 °C (Ref. [2], m.p. 118–120 °C).

*4-Bromophenyliminotriphenylphosphorane* (**2**, X=Br); yield: 71%; m.p. 124–126 °C.

*4-Iodophenyliminotriphenylphosphorane* (**2**, X=J); yield: 69%; m.p. 144–145 °C.

*4-Methoxyphenyliminotriphenylphosphorane* (**2**, X=$-OCH_3$); yield: 71%; m.p. 111 °C (Ref. [2], m.p. 117–118 °C).

*4-Nitrophenyliminotriphenylphosphorane* (**2**, X=$-NO_2$); yield: 68%; m.p. 159–160 °C (Ref. [2], m.p. 156–158 °C).

### *P*-(Alkylphenylamino)-triphenylphosphonium Iodides 3; General Procedure:

A solution of a phenyliminotriphenylphosphorane **2** (0.01 mol) and an alkyl iodide [methyl iodide: 1.6 g (0.011 mol); 1-iodobutane: 2.03 g (0.011 mol)] in benzene (sodium-dried; 15 ml) is refluxed for 6–8 h under an atmosphere of nitrogen. The mixture is then allowed to cool, the crystalline salt **3** is isolated by filtration, washed with dry benzene, and recrystallised from ethanol. The salts **3** are stable in air at room temperature.

### *N*-Alkylanilines 4 from *P*-(Alkylphenylamino)-triphenylphosphonium Iodides 3; General Procedure:

The phosphonium salt **3** (5 mmol) is heated under reflux for 1 h with 2 molar aqueous sodium hydroxide (50 ml). The mixture is then cooled, acidified with dilute hydrochloric acid, filtered to remove some of the triphenylphosphine oxide, and extracted with chloroform (3 × 20 ml). The aqueous phase is made strongly basic with 2 molar sodium hydroxide solution and the required amine is extracted from it using diethyl ether (3 × 50 ml). The combined ether extracts are dried with magnesium sulphate, filtered to remove the desiccant, and evaporated on a rotary evaporator to yield product **4** which may be further purified by distillation in vacuo or recrystallisation from aqueous alcohol.

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* Address for correspondence.

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