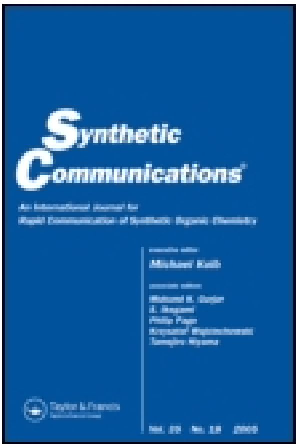

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Synthesis of 4-(*N*,*N*-Dialkylamino) benzyltriphenylphosphonium Iodides from Hydroxymethyltriphenylphosphonium Iodide and *N*,*N*-Dialkylaniline

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Abstract: Reinvestigation of the one-pot synthesis of 4-(*N*,*N*-dialkylamino) benzyltriphenylphosphonium iodides has shown that the product forms after the initial condensation of triphenylphosphine upon formaldehyde.

Keywords: Formaldehyde, *N*,*N*-dialkylaniline, triphenylphosphine, Wittig

Ongoing research efforts in nonlinear optical organic compounds made it necessary to prepare Wittig salts such as **1** and **2**, (Fig. 1). These compounds containing 4-*N*,*N*-dialkylaminobenzyl groups are convenient building blocks for the reaction with arylaldehydes to prepare stilbene derivatives.[1–4]

Porrès et al.[5] recently prepared 4-(*N*,*N*-dialkylamino)benzyltriphenylphosphonium iodides, including **1** and **2**, using conditions similar to Bredereck et al.[6] They found that refluxing a mixture of *N*,*N*-dialkylaniline, triphenylphosphine, paraformaldehyde, sodium iodide, water, and acetic acid in either chloroform or toluene gave the phosphonium iodides (**4**) in greatly reduced reaction times. It was implied that under these

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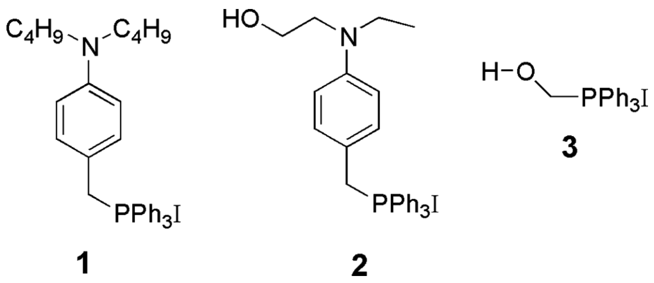
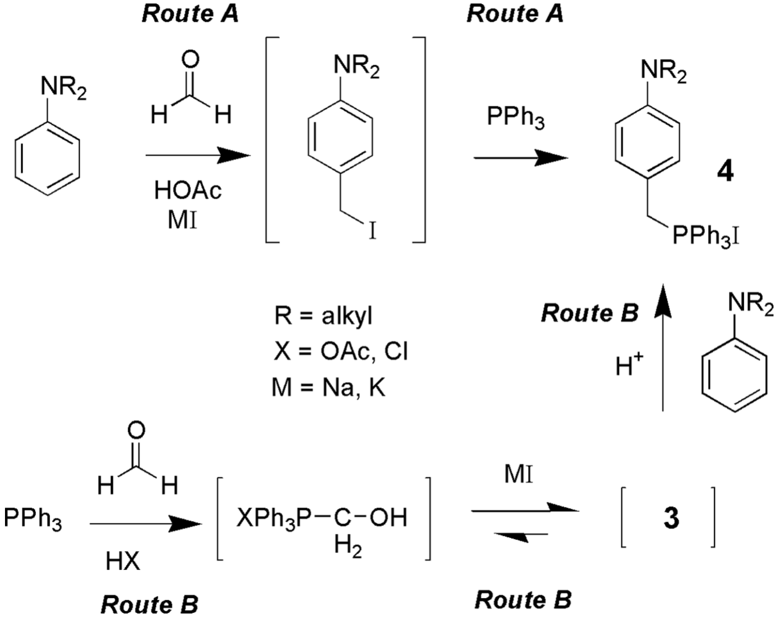


Figure 1. Phosphonium salts.

conditions the *N*,*N*-dialkylaniline first reacts to generate an in situ 4-(*N*,*N*-dialkylamino)benzyl iodide,[7] which then condenses with triphenylphosphine in the traditional method[8] of synthesizing benzyl salts of the latter (Route A, Scheme 1).

A reaction to prepare **1** was set up using the same conditions as Porrès et al.[5] Reaction progress was monitored by NMR by simply dissolving an aliqout of the reaction mixture in deuteriochloroform.[9] But rather than ^{1}H, which would be complicated in the aromatic region, the disappearance of triphenylphosphine was monitored by ^{31}P NMR

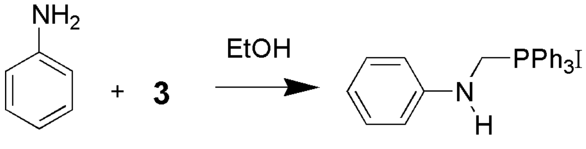


Scheme 1. Synthetic routes.

to determine reaction completetion. Shortly after starting the reaction, three peaks were seen in the ^{31}P NMR relative to external 85% phosphoric acid: ~5ppm for triphenylphosphine, ~21 ppm for product and an unknown peak at ~18 ppm. The reaction continued overnight, after which time the mixture only contained the product peak. The same ~18 ppm ^{31}P resonance was observed in the preparation of **2** as well. Clearly, an intermediate phosphorus-containing compound was generated during the reaction.

Bredereck et al.[6] noted their procedure for synthesizing 4-(*N*,*N*-dimethylamino)benzyltriphenylphosphonium iodide was based on a private communication of H. Hoffmann. A thorough literature search shed light on what may be the probable mechanism for this reaction. Hoffmann et al.[10] first described the preparation of hydroxymethyltriphenylphosphonium iodide **3** (Fig. 1) by heating a mixture of triphenylphosphine, formaldehyde, and hydrochloric acid then adding sodium iodide. Other salts were prepared later.[11–14] This reaction is analogous to that of phosphine (PH_3) with formaldehyde in aqueous hydrochloric acid, forming tetrakis(hydroxymethyl)phosphonium chloride (THPC) described earlier by A. Hoffman.[15,16] Later, in a short description of some chemistry of **3**, H. Hoffmann[17] mentions that *N*,*N*-dimethylaniline reacts to form the corresponding 4-(*N*,*N*-dimethylamino)benzyltriphenylphosphonium iodide, although no experimental details were given.

The salt **3** was prepared, and ^{31}P NMR showed the chemical shift of the phosphorus was 18.65 ppm, close to the chloride (17.7 ppm)[18] and nitrate (18.6 ppm)[12] analogs, explaining the mystery resonance observed during the one-pot synthesis of **4**. Reaction of **3** and *N*,*N*-dialkylaniline in chloroform in the presence of acetic acid also gave the triphenylphosphonium salts **4**. So, the more likely mechanism for the one-pot synthesis of **1**, **2**, and others by this method is shown in Route B (Scheme 1). In the first step, triphenylphosphine combines with formaldehyde to form the hydroxymethyltriphenylphosphonium acetate, which undergoes metathesis with sodium or potassium iodide to form **3**. The in situ formed **3** then reacts with the pi-electron-rich *N*,*N*-dialkylaniline in an electrophilic aromatic substitution.



5

Scheme 2. New phosphonium salt.

The chemistry of unsubstituted aniline with **3** is worth noting. Both Porrès et al.[5] and Hoffmann[17] indicate that the reactivity is similar to *N*,*N*-dialkylanilines, yielding 4-aminobenzyltriphenylphosphonium salts (**4**, R = H), although spectroscopic data were not provided. It was found that reaction of aniline with **3** in ethanol gave **5** in almost quantitative yield (Scheme 2), analogous to the reaction of aniline with THPC.[19,20] It appears that **5** is an unreported molecule and ^{1}H NMR clearly shows this structure, as all five aromatic protons of the aniline appear and there is a single NH resonance. It remains for further study whether **5** can undergo rearrangement to a structure such as **4** (R = H).

Crystal structures were obtained for **1**–**3** because it appeared they were not reported previously (Chart 1).

Recently, Hernández et al.[21] showed another method to prepare 4-(*N*,*N*-dialkylamino)benzyltriphenylphosphonium salts but requires transformation of the *N*,*N*-dialkylaniline into the corresponding benzyl alcohol by Vilsmeier formylation, followed by aldehyde reduction.

EXPERIMENTAL

Melting points were collected on an electrothermal capillary melting-point apparatus and are not corrected. All NMR data were collected on a Bruker Avance II 300-MHz spectrometer (^{1}H at 300 MHz, ^{13}C at 75 MHz, ^{31}P at 121 MHz). NMR data free induction decays (FIDs) were processed using NUTS software from Acorn NMR (Livermore, CA). All ^{1}H and ^{31}C spectra are referenced to tetramethylsilane (TMS). For ^{31}P NMR, spectra were referenced to 85% H_3PO_4 (from a new bottle) contained in a capillary tube suspended in the middle of the 5-mm NMR tube. All reagents were purchase from Sigma-Aldrich (Milwaukee) and

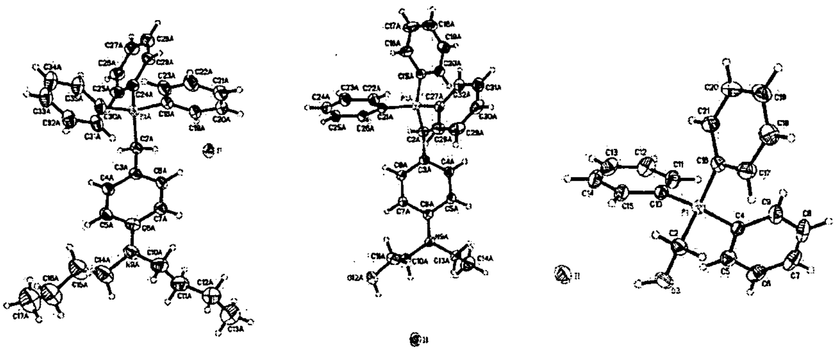


Chart 1. Crystal structures **1**, **2**, and **3** (from left to right, respectively).

used as received. Inverse Dean-Stark distillation receiver (catalog no. CG-1266) was purchased from ChemGlass Scientific Apparatus (Vineland, NJ). Elemental analyses were made by Atlantic Microlab, Inc. (Norcross, GA).

4-(*N*,*N*-Dibutylamino)benzyltriphenylphosphonium Iodide (1)

A 250-mL, round-bottomed flask equipped with magnetic stirbar was charged with 4.2 g of **3** (0.01 mol), 2.05 g of *N*,*N*-di-*n*-butylaniline (0.01 mol), 100 mL of $CHCl_3$, and 600 mg of glacial HOAc (0.01 mol, 1 equiv). An inverse Dean–Stark trap was equipped, and the mixture was refluxed for 12 h with removal of the generated by-product H_2O. The mixture was rotary evaporated, leaving a crude oil. Trituration of the oil with acetone gave a crystalline solid. The solid was collected on a coarse-porosity glass frit (4.7 g, 78%). Recrystallization from EtOH gave the title compound as colorless rhombohedrons. Mp 211–215 °C (lit.[5] 206–209 °C). δ_H ($CDCl_3$): 7.73–7.63 (m, 3H), 7.59–7.46 (m, 12H), 6.68 (dd, $J = 9.0$ and 2.3 Hz, 2H), 6.25 (d, $J = 8.9$ Hz, 2H), 4.72 (d, $J = 12.7$ Hz, 2H), 3.06 (t, $J = 7.8$ Hz, 4H), 1.37 (pent, $J = 6.8$ Hz, 4H), 1.18 (hext, $J = 7.7$ Hz, 4H), 0.81 (t, $J = 7.3$ Hz, 6H); δ_C ($CDCl_3$): 148.23, 135.12 (d, $J = 3.4$ Hz), 134.38 (d, $J = 9.8$ Hz), 132.18 (d, $J = 5.3$ Hz), 130.26 (d, $J = 12.4$ Hz), 117.93 (d, $J = 84.9$ Hz), 111.77, 110.78, 50.62, 30.78 (d, $J = 46.6$ Hz), 29.23, 20.26, 14.01; δ_P ($CDCl_3$): 20.95. Elemental analysis calculated for $C_{33}H_{39}INP$: C, 65.23; H, 6.43; N, 2.30. Found: C, 65.28; H, 6.42; N, 2.43.

4-(*N*-Ethyl-*N*-(2-hydroxyethyl)amino)benzyltriphenylphosphonium Iodide (2)

A 500-mL, round-bottomed flask equipped with magnetic stirbar was charged with 57.7 g of PPh_3 (0.22 mol), 8.25 g of paraformaldehyde (molecular weight = 90, 0.092 mol, 0.42 equiv), 45.4 g of *N*-ethyl-*N*-(2-hydroxyethyl)aniline (0.275 mol, 1.25 equiv), and 300 mL of $CHCl_3$. The mixture was stirred while 41.25 g of NaI (0.275 mol, 1.25 equiv) and a mixture of 19.5 mL of H_2O (1.08 mol, 4.9 equiv) and 55.5 mL of HOAc (0.97 mol, 4.4 equiv) were added. A condenser was attached, and the mixture was heated to reflux. After 1 h, all the solids had dissolved. After refluxing for 8 h, an inverse Dean–Stark trap was equipped, and the $H_2O/CHCl_3$ azeotrope was collected until completion (~8 h). The mixture was cooled to rt whereby solids precipitated. Chloroform (250 mL) and 200 mL of H_2O were added to dissolve all the solids. The organic phase was separated and washed again with 200 mL of H_2O, followed by 200 mL of brine, and then dried over anhydrous $MgSO_4$. The solvent was stripped at the rotovap, leaving a thick oil that foams under vacuum. The oil was dissolved in 250 mL of acetone and cooled in an ice bath. The product crystallizes out after a short time. The pale green microcrystalline powder was collected on a medium-porosity glass frit and dried under vacuum (107.4 g, 86%). The title compound was obtained as colorless rhomobedrons by recrystallization from EtOH. Mp 174–177 °C (lit.[5] 165–170 °C). δ_H ($CDCl_3$): 7.85 (m, 3H), 7.71–7.54 (m, 12H), 6.75 (dd, $J = 9.0$ and 2.3 Hz, 2H), 6.46 (d, $J = 8.7$ Hz, 2H), 4.75 (d, $J = 12.7$ Hz, Hz, 2H), 3.68 (t, $J = 6.6$ Hz, 2H), 3.39 (t, $J = 6.1$ Hz, 2H), 3.31 (q, $J = 7.1$ Hz, 2H), 2.96 (bs, OH), 1.04 (t, $J = 7.1$ Hz, 3H); δ_C ($CDCl_3$): 148.24 (d, $J = 2.8$ Hz), 135.11 (d, $J = 2.7$ Hz), 134.22 (d, $J = 9.4$ Hz), 132.06 (d, $J = 5.3$ Hz), 130.24 (d, $J = 12.0$ Hz), 117.20 (d, $J = 85$ Hz), 112.09, 111.13 (d, $J = 8.5$ Hz), 59.05, 52.19, 45.16, 30.68 (d, $J = 45.5$), 11.87; δ_P ($CDCl_3$): 20.89 (s). Elemental analysis calculated for $C_{29}H_{31}INOP$: C, 61.39; H, 5.51; N, 2.47. Found: C, 61.15; H, 5.58; N, 2.46.

Hydroxymethyltriphenylphosphonium Iodide (3)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 5.2 g of PPh_3 (0.02 mol), 3.6 g of paraformaldehyde (0.04 mol, 2 equiv), and 20 mL of H_2O. The mixture was stirred at rt, and 4 mL of conc. HCl (0.048 mol) was added in one portion. The mixture was heated to ~70 °C until all the solids dissolved (~15 min). In one portion, 6 g of NaI (0.04 mol, 2 equiv) were added, and heating was continued for 5 min. The mixture was cooled to rt, and a syrup precipitated. After about 10 min, the syrup solidified into a white solid. The solid was filtered and air dried on the frit. The solid was recrystallized from EtOH to give the title compound as colorless microcrystals (5.1 g, 60%). Mp 168–170 °C (lit.[10] 170–177 °C). δ_H (DMSO-d_6): 7.96–7.88 (m, 3H), 7.86–7.73 (m, 12H), 6.88 (bs, OH), 5.68 (s, 2H); δ_C (DMSO-d_6): 134.91 (d, $J = 2.6$ Hz), 133.88 (d, $J = 9.9$ Hz), 130.05 (d, $J = 12.0$ Hz), 117.17 (d, $J = 82.7$ Hz), 56.19 (d, $J = 60.9$ Hz); δ_P (DMSO-d_6): 18.65 (s); δ_P ($CDCl_3$): 17.81 (s). Elemental analysis calculated for $C_{19}H_{18}IOP$: C, 54.28; H, 4.28. Found: C, 54.46; H, 4.33.

N-Phenylaminomethyltriphenylphosphonium Iodide (5)

A 100-mL, round-bottomed flask equipped with magnetic stirbar was charged with 2.1 g of **3** (5 mmol) and 20 mL of anhydrous EtOH.

The mixture was heated briefly to dissolve all the solids. In one portion, 465 mg of aniline (5 mmol, 1 equiv) were added, and the mixture was stirred at rt. After 20 min, copious white solids precipitated. The precipitate was collected on a coarse-porosity glass frit and air-dried several hours (2.31 g, 93%). The white crystalline solid was found to be a 1:1 complex of **5** and EtOH. Mp 115–120 °C. δ_H ($CDCl_3$): 7.81–7.65 (m, 9H), 7.63–7.50 (m, 6H), 6.85 (t, $J = 7.9$ Hz, 2H), 6.57–6.45 (m, 3H), 5.94 (bs, NH), 5.36 (d, $J = 5.2$ Hz, 2H); δ_C (CD_3 CN): 147.26, 136.24, 135.35 (d, $J = 9.6$ Hz), 131.15 (d, $J = 12.4$ Hz), 129.92, 120.11, 118.24 (d, $J = 83.2$ Hz), 114.76, 42.26 (d, $J = 60.7$ Hz); δ_P (CD_3CN): 16.61 (s). Elemental analysis calculated for $C_{25}H_{23}INP \cdot EtOH$: C, 59.86; H, 5.36; N, 2.59. Found: C, 60.13; H, 5.36; N, 2.56.

X-Ray Structure Determination of 1–3

All three crystals were mounted on a MiteGen Micromount using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a Smart Apex II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation ($\lambda = 0.71073$). A Bruker Kryo-Flex low-temperature device was used to keep the crystals at a constant temperature during data collection, (Table 1).

For all three compounds, data collection was performed and the unit cell was initially refined using *APEX2* [v2.1].[22] Data reduction was performed using *SAINT* [v7.34A][23] and *XPREP* [v6.12].[24] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2.03].[25] The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v6.10] system of programs.[26] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. The butyl groups and phenyl rings of compound **1** have some small directional freedom, requiring constraints to be placed on the model to keep the refinement stable. One of the hydroxyethyl groups of compound **2** is disordered over two positions, with the relative population ratio of 73:27.

CCDC 678122, CCDC 678123, and CCDC 678124 contain the supplementary crystallographic data for this article (compounds **1**, **2**, and **3**, respectively). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Single-crystal X-ray diffraction analysis of compounds 1–3

Compound	**1**	**2**	**3**
Empirical formula	$C_{33}H_{39}INP$	$C_{29}H_{31}INOP$	$C_{19}H_{18}IOP$
Formula weight	607.52	567.42	420.20
Temperature (K)	223(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	$P2_1/c$
Unit cell dimensions (Å, °)	a = 27.616(3)	a = 11.302(3)	a = 9.2389(7)
	b = 37.221(3)	b = 12.208(3)	b = 17.4224(13)
	c = 23.909(3)	c = 20.762(6)	c = 11.4574(9
	$\alpha = 90$	$\alpha = 76.024(4)$	$\alpha = 90$
	$\beta = 90.356(2)$	$\beta = 82.317(4)$	$\beta = 103.3130(10)$
	$\gamma = 90$	$\gamma = 71.979(3)$	$\gamma = 90$
Volume (Å^3)	24575(5)	2638.0(12)	1794.7(2)
Z	32	4	4
Density (Mg/m^3)	1.314	1.429	1.555
Crystal size (mm)	0.23 × 0.14 × 0.06	0.23 × 0.22 × 0.03	0.52 × 0.50 × 0.08
Reflections collected	112720	27741	18638
Independent reflections	25156 [$R_{int} = 0.0265$]	13110 [$R_{int} = 0.0376$]	4480 [$R_{int} = 0.0201$]
Completeness (%)	99.7	97.8	99.6
Data/restraints/parameters	25156/600/1112	13110/0/609	4480/0/201
Goodness of fit on F^2	1.040	1.053	1.026
Final R [I > 2sigma(I)]	$R_1 = 0.0702$	$R_1 = 0.0291$	$R_1 = 0.0188$

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