THE SMALL-SCALE SYNTHESIS OF ^{13}C-LABELLED DICHLOROMETHYLPHOSPHINE (METHYLPHOSPHONOUS DICHLORIDE)

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Dichloromethylphosphine (methylphosphonous dichloride) is a valuable starting material for many syntheses, but published methods[1-4] for its preparation are not well suited to labelling with ^{13}C. We have found that the route of equations (1) - (4) which starts from the readily available ^{13}C-labelled methyl iodide and relies upon the protecting effect of N,N-diethylamino groups to prevent di- or tri-methylation of phosphorus works satisfactorily on a small scale, although it is also suitable when larger amounts of product are wanted.

$$PCl_3+2Et_2NH+2Et_3N \xrightarrow{Et_2O} (Et_2N)_2PCl+2Et_3NH^+Cl^- \quad (1)$$

$$^{13}CH_3I+Mg \xrightarrow{Et_2O} {}^{13}CH_3MgI \quad (2)$$

$$^{13}CH_3MgI+(Et_2N)_2PCl \xrightarrow[-70^o]{Et_2O} (Et_2N)_2P^{13}CH_3+MgICl \quad (3)$$

$$(Et_2N)_2P^{13}CH_3+PhPCl_2 \longrightarrow {}^{13}CH_3PCl_2+(Et_2N)_2PPh \quad (4)$$

All preparations were carried out and products were handled under an atmosphere of dry nitrogen, and especial care should be exercised with $(Et_2N)_2PCl$ which reacts explosively with water.

BIS-(DIETHYLAMINO)CHLOROPHOSPHINE

Diethylamine (2.92 g.; 40 m mol) in ether (10 ml.) was added dropwise over 0.5 h to a stirred mixture of phosphorus trichloride (2.76 g.; 20 m mol) and triethylamine (4.04 g.; 40 m mol) in sodium-dried ether (25 ml.). When the reaction was complete the bulky precipitate of triethylamine hydrochloride was filtered off and washed with two 15 ml. portions of dry ether; the filtrate and washings were combined and most of the ether was removed under vacuum. When the bulk had been reduced to ca 8 ml. the residue was decanted into a small distillation pot fitted with a short Vigreux column and distillation gave 2.96 g. of $(Et_2N)_2PCl$ as a clear colourless liquid, b.p. 60-62°/0.1 mm Hg.

BIS-(DIETHYLAMINO)-P-METHYL (^{13}C) PHOSPHINE

A solution of the methyl Grignard reagent enriched in ^{13}C was prepared from methyl iodide (2.0 g.; 11 m mol, enriched to 90% in ^{13}C) and magnesium (0.34 g.; 14 m mol) in dry ether (10 ml.). The yield was assumed to be 85%. It was filtered through glass wool and added dropwise over 0.5 hour to a stirred and cooled (dry ice-acetone) solution of $(Et_2N)_2PCl$ (2.52 g.; 12 m mol) in dry ether (15 ml.). The reaction mixture was allowed to warm to room temperature and was then refluxed for 0.5 hour when solid matter was found to have become gummy and to have adhered to the walls of the flask. The solution was then cooled to room temperature and decanted, the ether was removed by distillation at atmospheric pressure and the residue was distilled through a short Vigreux column into a 10 ml. round-bottom flask to yield 1.72 g. (75%) of $(Et_2N)_2PCH_3$ as a clear colourless liquid, b.p. 85°/10 mm.Hg.

DICHLOROMETHYLPHOSPHINE

Dichlorophenylphosphine (4.0 g.; 22.4 m mol, an excess) was added to

the flask containing the product from the previous step. Heat was evolved, a small teflon-coated magnetic stirrer bar was added, and the flask was made the pot of an apparatus set up for distillation under nitrogen at atmospheric pressure. The contents of the flask were stirred gently and heated in a silicone-fluid bath; at a bath temperature of 200-220° $MePCl_2$ (0.8 g., 76% distilled as a clear colourless liquid, b.p. 81°/750 mm.Hg. Comparison of the proton nmr spectra of the initial enriched methyl iodide and the product showed that no isotopic dilution of the ^{13}C content had occurred.

References

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