

A NOVEL REACTION OF CARBON TETRACHLORIDE WITH [(DIPHENYLPHOSPHINO)METHYL]TRIMETHYLSILANE

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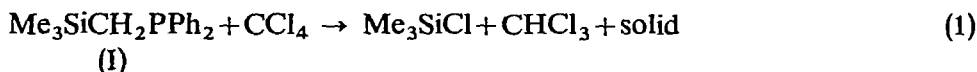
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SUMMARY

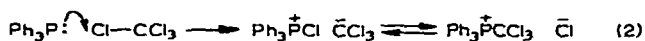
[(Diphenylphosphino)methyl]trimethylsilane reacts with carbon tetrachloride, in an ionic reaction, to yield chloroform, trimethylchlorosilane, and a polymer which does not contain silicon.

INTRODUCTION

We wish to report a new reaction between [(diphenylphosphino)methyl]-trimethylsilane (I) and excess carbon tetrachloride to give quantitative yields of chloroform and trimethylchlorosilane [eqn. (1)]:



Reactions between phosphines and perhalogen compounds, reported in the literature, generally involve a nucleophilic attack on halogen¹⁻³, e.g. for triphenylphosphine [eqn. (2)]:



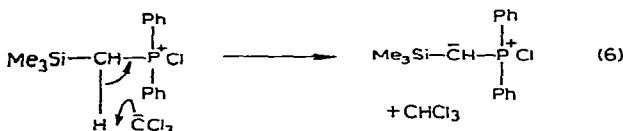
Hudson *et al.*⁴ have described the reaction between *N*-phenyldiphenylphosphinous amide and carbon tetrachloride to give chloroform and a resinous product that appears to be the phosphinimine [Ph₂P(Cl):NPh]. The mechanism suggested is as follows:



DISCUSSION

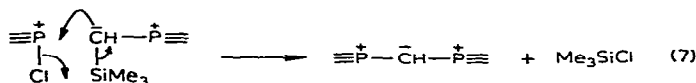
The reaction of (I) with carbon tetrachloride was independent of light, oxygen or radical initiators, thus suggesting an ionic rather than a radical mechanism. It is also probable that hydrogen was abstracted from carbon α to phosphorus, because methyldiphenylphosphine (II) also reacted with carbon tetrachloride to yield a small amount of chloroform (*ca.* 5%).

We suggest therefore that the mechanism of the first step in this reaction is a nucleophilic attack at chlorine [eqn. (5)] followed by abstraction of the α -H by $\bar{\text{C}}\text{Cl}_3$ [eqn. (6)]

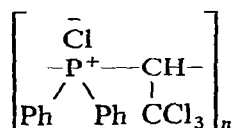


The large electron releasing effect of the Me_3SiCH_2 -group would assist the nucleophilic attack and the trimethylsilyl group could stabilise the ylid system by d orbital interaction⁵ and steric shielding⁶.

No evidence for the existence of this ylid was obtained, *i.e.*, no Wittig reaction was observed with aldehydes and ketones. The ylid presumably polymerises and eliminates trimethylchlorosilane [eqn. (7)].



We were unable to determine the structure of the polymer because of its poor solubility, but it contained hydrolysable chlorine and no silicon. Element analysis suggested the structure,



An alternative explanation is an elimination of the chlorosilane from the salt $\left[\text{Me}_3\text{SiCH}_2\text{P}^+\text{Ph}_2 \right] \bar{\text{C}}\text{Cl}$ to give the ylid $\text{Ph}_2\text{P}^+-\bar{\text{C}}\text{H}_2$, similar to the elimination observed by Schmidbaur and Tronich⁷ from $[\text{Me}_3\text{SiCH}_2\text{P}^+\text{Ph}_3] \bar{\text{C}}\text{Cl}$ at 200°, to give $\bar{\text{C}}\text{H}_2-\text{P}^+\text{Ph}_3$. This is unlikely, however, because 100% yields of both trimethylchlorosilane and

chloroform were obtained. An intramolecular elimination is also considered unlikely, because this would involve $\text{P}\equiv\text{CH}$ intermediates.

EXPERIMENTAL

General comments

Gas liquid chromatography (GLC) was carried out on an F and M 720 unit, using 6 ft \times 0.25 inch silicone gum columns. The instrument was programmed at $20^\circ/\text{min}$ from 70° . NMR spectra were recorded on a Varian T60 spectrometer, without solvent, and using tetramethylsilane as standard. All reactions were carried out under an atmosphere of pre-purified nitrogen.

[(Diphenylphosphino)methyl]trimethylsilane, (I)

[(Diphenylphosphino)methyl]trimethylsilane (I) was prepared by the method of Hewertson and Watson⁸.

Sodium diphenylphosphine was prepared in liquid ammonia from sodium (5.65 g, 0.245 g-atom) and diphenylphosphine (45.5 g, 0.245 mole), and treated with (chloromethyl)trimethylsilane (30 g, 0.245 mole). The ammonia was allowed to evaporate overnight, before extracting the residue with dry ether. The ether extract was fractionated to give (I) (35 g, 75%) b.p. 110° (0.3 mm). (Found: C, 70.6; H, 7.94. $\text{C}_{16}\text{H}_{21}\text{PSi}$ calcd.: C, 70.6; H, 7.72%) NMR: τ 10.09 ppm (9H, Me_3Si) s; τ 8.61 ppm (2H, CH_2P) d, $J(\text{CH}_2\text{P}) \sim 1$ Hz; τ 2.7 ppm (10H, Ph_2P).

Methyldiphenylphosphine, (II)

Methyldiphenylphosphine (II) was similarly prepared: b.p. 87° (0.2 mm)(lit.⁹ 284°). (Found: C, 77.7; H, 6.98. $\text{C}_{13}\text{H}_{13}\text{P}$ calcd.: C, 78.0; H, 6.5%) NMR: τ 8.4 ppm (3H, CH_3P) d, $J(\text{CH}_2\text{P}) \sim 1$ Hz; τ 2.7 ppm (10H, Ph_2P) m.

Reactions with carbon tetrachloride

1. Reaction of (I) with CCl_4

A mixture of (I) (5 g, 0.0185 mole) and carbon tetrachloride (10 ml, 0.097 mole), was fractionated under nitrogen to give:

(a). A fraction b.p. $58\text{--}64^\circ$ (4.0 g, 95.5%). GLC analysis showed this to be a 1/1 mixture of chloroform and trimethylchlorosilane. The NMR spectrum consisted of 2 singlets at τ 9.65 ppm [$(\text{CH}_3)_3\text{SiCl}$] and τ 2.65 ppm (CHCl_3).

(b). A solid residue (4.2 g) insoluble in non-polar solvents. (Found: C, 48.0; H, 3.57; P, 8.70; Si, 0.00. $\text{C}_{14}\text{H}_{11}\text{Cl}_4\text{P}$ calcd.: C, 47.7; H, 3.13; P, 8.81%) Consistent chlorine analyses could not be obtained, but the values were of the order expected.

2. Reaction of (II) with CCl_4

Methyldiphenylphosphine (19 g, 0.1 mole) was mixed with carbon tetrachloride (50 ml) and the mixture fractionated. Chloroform (0.6 g, 5.0%) was produced, although a preliminary GLC analysis indicated higher yields than this.

3. Reaction of (I) and (II) with CCl_4 under various conditions

A 1/3 mixture of (I) and carbon tetrachloride was analysed on the GLC at intervals of 15 sec, 30 sec, 6 min, 8 min, and 15 min, after mixing. The change in height of the chloroform peak with time was found to be independent of light, oxygen, azobisisobutyronitrile or cyclohexene. Similar results were obtained with (II).

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