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A CONVENIENT SYNTHESIS OF 1,2-BIS(DICHLOROPHOSPHINO)ETHANE, 1,2-BIS(DIMETHYLPHOSPHINO)ETHANE AND 1,2-BIS(DIETHYLPHOSPHINO)ETHANE

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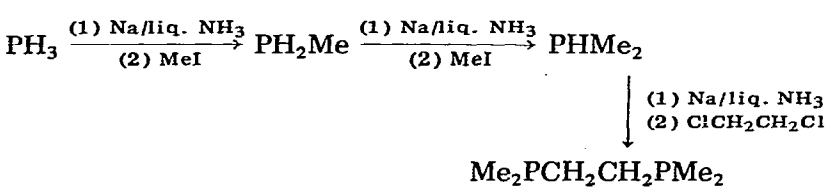
Summary

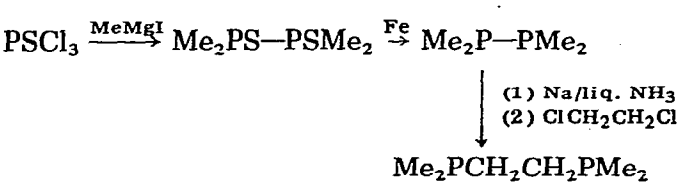
A simple synthesis of 1,2-bis(dimethylphosphino)ethane, 1,2-bis(diethylphosphino)ethane, and 1,2-bis(dicyclohexylphosphino)ethane is reported. The method involves the synthesis of 1,2-bis(dichlorophosphino)ethane using a procedure patented by Toy and Uhing; the halide is allowed to react with the appropriate Grignard reagent to give the required tetraalkyldiphosphine. The phosphines produced in this way are moderately sensitive to air but not spontaneously inflammable as previously reported.

The preparation of 1,2-bis(dimethylphosphino)ethane has previously been a lenghty and difficult process. The preparations of the diphosphine by the methods of Chatt and Hayter [1] (Scheme 1), Butter and Chatt [2] (Scheme 2), and Parshall [3] (Scheme 3) all involve multi-stage syntheses and toxic reagents.

SCHEME 1



SCHEME 2



SCHEME 3

$$Me_2PS—PSMe_2 \xrightarrow{I_2/CH_2=CH_2} Me_2PSCH_2CH_2PSMe_2 \xrightarrow[\text{or (b) Fe}]{\text{(a) } PBu_3} Me_2PCH_2CH_2PMe_3$$

The toxicity and hazards of PH_3 and Me_2PPMe_2 are well documented; in our laboratory two workers also developed rapid and severe reactions to the phosphorus—sulphur compounds; these involved a persistent rash on hands, arms and neck, and occurred despite the attention which was paid to containing the reagents and the good ventilation in the laboratory.

The new procedure involves the reaction of yellow phosphorus, phosphorus trichloride and ethylene in a stainless steel autoclave at 200°C for 16 h to give 1,2-bis(dichlorophosphino)ethane [4]. The tetrachlorodiphosphine is allowed to react with an excess of Grignard reagent to give the appropriate diphosphine. The preparation of 1,2-bis(dichlorophosphino)ethane is a modification of a previously reported procedure [4]. The syntheses of the diphosphines $Me_2PCH_2CH_2PMe_2$, $Et_2PCH_2CH_2PEt_2$ and $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$ are reported here.

Experimental

1. 1,2-Bis(dichlorophosphino)ethane

Phosphorus trichloride (300 g, 190 cm^3, 2.2 mol) was poured into an unlined 1 litre stainless steel autoclave in air. Yellow phosphorus (16.8 g, 0.54 mol) was removed from storage under water, dried with absorbent paper and the lumps added to the phosphorus trichloride. The autoclave was then assembled and charged with dinitrogen to a pressure of ca. 80 atmospheres; it was then vented to a suitable fume hood. This procedure was undertaken in order to reduce the levels of dioxygen, moisture and hydrogen chloride to acceptable levels. The autoclave was then charged to a pressure of 30 atmospheres with ethylene, and sealed. The ethylene supply was removed and the autoclave heated at 200°C for 16 h *. The autoclave was cooled to room temperature leaving a residual pressure of ca. 3 atm; the residual gas was vented to the fume hood and the autoclave flushed with dinitrogen as before.

The autoclave reaction vessel was removed from the surrounding heating jackets and transferred to an efficient fume hood before opening. The dark brown liquid product was poured into a dinitrogen-filled flask. A black solid remained in the reaction vessel. It was removed with a spatula and dropped into water to hydrolyse it.

Caution. The black solid also covered the surface of the steel. It was probably a mixture of iron phosphide and phosphorus halides. Rapid addition of water to the vessel gives copious fumes and a few flames. This is probably due to the generation of a small amount of phosphine and appropriate precautions to prevent the oxidation getting out of hand should be taken.

The crude liquid product, always under dinitrogen, was then heated at atmospheric pressure to remove the excess of phosphorus trichloride (b.p.

* The reaction time is not critical and times as short as 6 hours have been used without significant loss of yield. The pressure during this time drops from a maximum of 70 atm to 15 atm.

76°C) and a trace of P_2Cl_4. The 1,2-bis(dichlorophosphino)ethane was distilled at 68°C/1 mmHg. The yield was ca. 30 g (50%). The product is best stored under dinitrogen.

Properties. 1,2-Bis(dichlorophosphino)ethane is a colourless liquid which oxidises slowly in air but is not pyrophoric. The product was characterised by gas chromatography (purity ca. 90%) and mass spectrometry (M^+ 232). The ^{31}P NMR spectrum gives a singlet δ −50.11 ppm relative to a trimethylphosphite (external standard).

2. 1,2-Bis(dimethylphosphino)ethane

Methylmagnesium iodide [5] was prepared in a 2 l flask containing 19 g (0.78 mol) of magnesium turnings in 500 cm^3 of sodium-dried ether. The flask was fitted with a dinitrogen inlet, reflux condenser, thermometer, stirrer and a 250 cm^3 pressure-equalised dropping funnel. Methyl iodide (111 g, 49 cm^3, 0.78 mol) in ether (200 cm^3) was added dropwise at a rate sufficient to maintain reflux (ca. 2 h addition period). The reaction mixture was then stirred overnight at room temperature before cooling to −30°C.

A solution of 1,2-bis(dichlorophosphino)ethane (30 g, 0.13 mol) in ether (200 cm^3) was added slowly (over 2 h) maintaining the reaction mixture at −30°C. When the addition was complete, the flask was allowed to warm to 10°C and the excess Grignard reagent hydrolysed with saturated ammonium chloride solution (125 g in 500 cm^3 of water). The ether layer was siphoned from the flask under dinitrogen and dried over anhydrous sodium sulphate for 16 h. It was then filtered and transferred under dinitrogen to a distillation apparatus. The ether was removed at atmospheric pressure (b.p. 35°C) leaving a pale yellow oil. The 1,2-bis(dimethylphosphino)ethane was distilled at 26°C/1.0 mmHg. The yield was 12 g (62%).

Properties. 1,2-Bis(dimethylphosphino)ethane is a colourless liquid which is moderately sensitive to air but is not spontaneously inflammable as reported previously [1,2,3]. The product was characterised by gas chromatography (purity ca. 98%) and mass spectroscopy (M^+ 150). The ^{31}P NMR spectrum shows a single peak at δ +188.7 ppm from trimethylphosphite (external standard) and the ^1H NMR spectrum is of 2nd order, consistent with the formulation.

Reaction of the diphosphine with sulphur in toluene gave a white precipitate of the *P,P,P',P'*-tetramethylethylenediphosphine disulphide which was recrystallised from dichloromethane, m.p. 257—258°C (lit. [3] 257—263°C) (Found C, 33.8; H, 7.8; $C_6H_{16}P_2S_2$ calcd.: C, 33.6; H, 7.5%). The *P—S* stretching frequency in the infrared spectrum was at 568 cm^{-1} (Nujol).

3. 1,2-Bis(diethylphosphino)ethane

The procedure adopted is identical to that described in section 2 except that ethylmagnesium bromide was prepared from magnesium (21 g, 0.86 mol) and ethyl bromide (93.7 g, 64.1 cm^3, 0.86 mol), and allowed to react with 1,2-bis-(dichlorophosphino)ethane (35.5 g, 0.15 mol).

The 1,2-bis(diethylphosphino)ethane was distilled at 116—118°C/10 mmHg. The yield was 21.3 g (69%).

Properties. 1,2-Bis(diethylphosphino)ethane is a pale yellow liquid which is moderately sensitive to air. The product was characterised by gas chromatography

(purity ca. 98%) and mass spectroscopy (M^+ 206). The ^{31}P NMR spectrum shows a single peak at δ +159.7 ppm, and the ^1H NMR spectrum is of 2nd order consistent with the formulation. (Found C, 56.1; H, 11.0. $C_{10}H_{24}P_2$ calcd.: C, 58.2; H, 11.7%).

4. 1,2-Bis(dicyclohexylphosphino)ethane

The procedure adopted is identical to that described in section 2 except that cyclohexylmagnesium chloride was prepared from magnesium (9.5 g, 0.39 mol) and cyclohexyl chloride (46 g, 0.39 mol) in ether (350 cm^3), and allowed to react with 1,2-bis(dichlorophosphino)ethane (15 g, 0.065 mol) in ether (100 cm^3). The crude product was recrystallised from tetrahydrofuran/ether to give white crystals, yield 12 g (45%), m.p. 82—85°C (lit. [6] m.p. 96- 97°C). (Found, C; 73.9; H, 11.3. $C_{26}H_{48}P_2$ calcd.: C, 73.9; H, 11.4%).

Properties. 1,2-Bis(dicyclohexylphosphino)ethane is a white crystalline solid soluble in tetrahydrofuran, ether and benzene. The mass spectrum shows (M^+ 422). The ^{31}P NMR spectrum shows a single peak at δ + 139.53 ppm from trimethylphosphite (external standard) and the ^1H NMR spectrum is complex as expected.

Reaction of the diphosphine in ether with excess carbon disulphide gave the bis(carbon disulphide) derivative as a red solid, m.p. 97—99°C (Lit. [6] m.p. 99—100°C) (Found C, 58.5; H, 8.4. $C_{28}H_{48}P_2S_4$ calcd.: C, 58.5; H, 8.4%).

Acknowledgements

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