Journal of Organometallic Chemistry, 288 (1985) 145–147
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SYNTHESIS OF 2-CHLOROPHENYL DERIVATIVES OF GROUP V

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(Received December 6th, 1984)

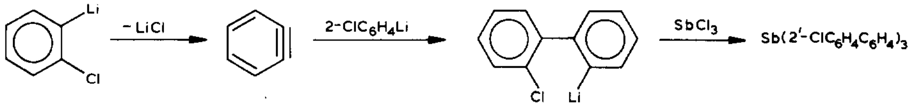
Summary

The thermal stability of 2-chlorophenyllithium can be markedly increased by the addition of tetramethylethylene diamine, thus allowing its use in the high yield sysnthesis of tris(2-chlorophenyl) derivatives of the Group V elements.

Introduction

The 2-halophenyllithium reagents are thermally unstable and have to be synthesised at very low temperatures [1]. For example, 2-chlorophenyllithium may be prepared in almost quantitative yield at −90°C by adding butyllithium to 2-chlorobromobenzene but the synthesis fails completely at −30°C. Carbonation has to be carried out at −100°C; when attempted by the usual method of pouring the lithium reagent onto a slurry of powdered carbon dioxide in ether, only a 6% yield of 2-chlorobenzoic acid is obtained, because of extensive thermal decomposition via benzyne formation [1].

Benzyne-derived products were obtained when we added antimony trichloride to 2-chlorophenyllithium at −90°C and allowed the mixture to warm up slowly to room temperature. The only isolable product from the reaction was tris(2′-chlorobiphenyl)antimony, which presumably arose from the reaction sequences:



occurring at temperatures well below that required for attack of antimony trichloride by 2-chlorophenyllithium. Obviously the thermal fragility of 2-chlorophenyllithium precludes its use in many potentially-useful synthetic reactions.

The corresponding Grignard reagents, 2-chlorophenylmagnesium bromide and iodide, are somewhat more thermally stable but the yields of tris(2-chlorophenyl)phosphorus [2] and tris(2-chlorophenyl)antimony [3] derived from them are still described as "always low" and "very low", respectively. We repeated these Grignard preparations and have confirmed the consistently low yields (ca. 1%).

We wondered if the addition of tetramethylethylene diamine (TMEDA) to 2-chlorophenyllithium would hinder the benzyne-formation reaction shown above by complexing with the lithium atom and making it sterically larger. To check this, we prepared 2-chlorophenyllithium at −90°C from a mixture of butyllithium, 2-chloroiodobenzene and TMEDA; after addition of antimony trichloride, the temperature was allowed to rise slowly to ambient when a yield of over 90% of tris(2-chlorophenyl)antimony resulted. Obviously the 2-chlorophenyllithium has been stabilised sufficiently for it to survive intact at the temperature required for reaction with the $SbCl_3$; the other Group V trichlorides react in similar fashion.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. Analytical data are given in Tab. 1.

Attempted preparation of tris(2-chlorophenyl)antimony from 2-chlorophenyllithium

A mixture of n-butyllithium (40 mmol) and 2-chlorobromobenzene (7.68 g, 40 mmol) in ether/hexane was stirred at −95°C for 30 min. A solution of antimony trichloride (3.0 g, 13.3 mmol) in 50 ml of dry ether was added and stirring continued for a further 1 h. The cooling bath was then removed and the reaction flask allowed to warm up slowly to room temperature; the resulting white solid was filtered off and washed with acetone. The ether filtrate and acetone washings were combined and the solvents stripped off under vacuum to leave a sticky, white solid, which on recrystallization from acetone, gave a 5% yield of tris(2′-chlorobiphenyl)antimony, m.p. 221–220°C (Found: C, 62.95; H, 3.5; Cl, 15.4; $C_{36}H_{24}Cl_3Sb$ calcd.: C, 63.15, H, 3.5; Cl, 15.15%)

Preparation of tris(2-chlorophenyl)phosphorus using 2-chlorophenylmagnesium iodide

A solution of 2-chloroiodobenzene (9.54 g, 40 mmol) in dry ether (20 ml) was added dropwise to 0.96 g (40 mmol) of magnesium in 20 ml of dry ether. The mixture was stirred at room temperature for 1 h and then cooled to 0°C as a solution of PCl_3 in ether (13.28 mmol) was added; stirring was continued at room temperature for a further 1 h. After hydrolysing the reaction mixture the ether layer was separated and dried over $MgSO_4$; filtration followed by evaporation of the ether gave an oil which yielded 50 mg (1.0%) of tris(2-chlorophenyl)phosphorus after

TABLE 1

ANALYTICAL DATA (Found (calcd.) (%)) AND YIELDS FOR $M(C_6H_4Cl)_3$ DERIVATIVES

Compound	M.p. (°C)	Yield (%)	C	H	Cl
$P(C_6H_4Cl)_3$	184–185	78	58.9 (59.1)	3.3 (3.3)	29.4 (29.1)
$As(C_6H_4Cl)_3$	156–157	87	52.7 (52.8)	2.8 (2.9)	25.6 (26.0)
$Sb(C_6H_4Cl)_3$	135–136	94	47.0 (47.3)	2.6 (2.6)	23.7 (23.3)
$Bi(C_6H_4Cl)_3$	140–141	63	39.8 (39.8)	2.1 (2.2)	17.7 (19.6)

extraction and crystallization using ethanol (m.p. 184–185°C; lit. [2] 185°C). The sample had an identical infrared spectrum to that prepared from 2-chlorophenyllithium in the presence of TMEDA.

Preparation of tris(2-chlorophenyl)antimony from 2-chlorophenyllithium in the presence of TMEDA

A mixture of n-butyllithium (21 mmol) and TMEDA (3 ml, 21 mmol) was cooled to −95°C before a solution of 2-chloroiodobenzene (5.0 g, 21 mmol) in dry ether was added, with stirring, over a period of 5 min. Stirring was continued for 20 min and then antimony trichloride (1.6 g, 7 mmol) in 20 ml dry ether added; after 1 h the cold bath was removed and the mixture allowed to warm to room temperature. The ether layer was separated and the solvent removed under reduced pressure to yield white, feathery crystals (3.0 g, 94%) of tris(2-chlorophenyl)antimony. Recrystallization from ethanol gave the analytical sample, m.p. 135–136°C (lit. [3] 136–137°C) The compounds $P(C_6H_4Cl)_3$ and $As(C_6H_4Cl)_3$ are only slightly soluble in ether and are deposited with the lithium chloride during their preparation; they were extracted with boiling ethanol.

Infrared spectra (cm^{-1}; Nujol mulls)

$P(C_6H_4Cl)_3$. 1570w, 1551w, 1426s, 1417sh, 1268w, 1249m, 1158w, 1122m, 1105m, 1034sh, 1030s, 944w, 759m, 749s, 746s, 728m, 721s, 657w, 647vw, 527w, 515m, 470m, 438m, 414m, 373w, 350w, 332w.

$As(C_6H_4Cl)_3$. 1556m, 1425s, 1416sh, 1269w, 1254m, 1157m, 1117m, 1096m, 1033m, 1025s, 1021s, 942m, 857w, 751sh, 746s, 742s, 712s, 639w, 502vw, 497w, 440s, 433m, 428sh, 371m, 286m, 273w.

$Sb(C_6H_4Cl)_3$. 1567w, 1555m, 1423s, 1419sh, 1269m, 1256m, 1159w, 1155vw, 1114m, 1090s, 1030m, 1020s, 1016s, 1007wsh, 945w, 753s, 748s, 709s, 437m, 434sh, 425sh, 357w.

$Bi(C_6H_4Cl)_3$. 1551m, 1417s, 1265m, 1250m, 1154w, 1106m, 1078s, 1023s, 1009s, 1006s, 940m, 749sh, 744s, 700s, 693sh, 481w, 428s, 414sh, 343w.

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