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Synthesis of chloromethyl(isopropoxy)diphenylsilane

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Chloromethyl(isopropoxy)diphenylsilane was synthesized by the reaction of chloro(isopropoxy)diphenylsilane with a binary mixture $P(NMe_2)_3$—CH_2BrCl.

Key words: chloromethyl(isopropoxy)diphenylsilane, chloro(isopropoxy)diphenylsilane, binary mixture $P(NMe_2)_3$—CH_2BrCl.

(Chloromethyl)silanes $ClCHRSiX_3$ are the starting compounds for the synthesis of a wide variety of α-carbofunctional organosilicon compounds $ZCHRSiX_3$ (Z = = Br, I, RO, R_2N, RS, $(R_3Si)_2N$, *etc.*). The development of mild and selective procedures to prepare these compounds from commercially available organochlorosilanes R_nSiCl_{4-n} is still highly desirable. Polyhaloalkanes are of interest as the reagents used in the synthesis of polyhalomethyl derivatives of organosilicon compounds. Thus, deprotonation of dibromo- and dichloromethane with lithium diisopropylamide in the presence of chlorosilane (−70 °C, THF) results in trialkylsilyl- and bis(trialkylsilyl)dihalomethanes in high yields.[1] In 1984, Ruppert and co-workers have described the original preparative method for trifluoromethylation of chlorotrimethylsilane with a binary mixture $(Alk_2N)_3P$—$CHal_nF_{3-n}$ (Hal = Cl, Br, I) (Scheme 1).[2] This system widely referred as the Ruppert's reagent is extensively used in the synthesis of trialkyl(perfluoro)organylsilanes.[3,4]

Scheme 1

$$\mathrm{Me_3SiCl + (Et_2N)_3P + BrCF_3 \xrightarrow[-(Et_2N)_3PClBr]{} Me_3SiCF_3}$$

The binary mixture $(Alk_2N)_3P$—$HCHal_3$ (Hal = Cl, Br, I) is regarded as a source of the trihalomethanide ion and is applicable for trihalomethylation of trimethylhalosilanes (Scheme 2).[5]

Scheme 2

$$\mathrm{Me_3SiHal + (R_2N)_3P + HCHal_3 \xrightarrow[-(R_2N)_3PHalHal']{} Me_3SiCHal_3}$$

In the present work, we aimed to elaborate the synthesis of chloromethyl(isopropoxy)diphenylsilane (**1**) *via* chloromethylation of chloro(isopropoxy)diphenylsilane (**2**) with the binary mixture $P(NMe_2)_3$—CH_2ClHal (Hal = Cl, Br) (Scheme 3).

Scheme 3

$$\underset{\mathbf{2}}{\mathrm{Ph_2SiCl(OPr^i)}} + \mathrm{P(NMe_2)_3 + CH_2ClHal} \xrightarrow[-(Me_2N)_3PClHal]{C_6H_6} \underset{\mathbf{1}}{\mathrm{ClCH_2SiPh_2(OPr^i)}}$$

The reaction of compound **2** with bromochloromethane in the benzene solution is very slow and is completed under reflux conditions within 10 h to give compound **1** in 63% isolated yield (distillation). It is of note that the moderate yield of compound **1** is caused by the side reaction, since under the selected conditions compound **1** alkylates tris(dimethylamino)phosphine producing phosphonium salt $[P(NMe_2)_3CH_2SiPh_2OPr^i]^+Cl^-$. When acetonitrile was used as a solvent, this side reaction predominates leading to a noticeable decrease in the yield of the target product **1** (up to 28%). Structure of compound **1** was confirmed by multinuclear NMR spectroscopy. Under the described conditions, dichloromethane reacts extremely slow (yield of compound **1** was only ~7%). Refluxing the reaction mixture for 15 h only slightly increases the yield of compound **1** (up to 11%).

Chloroisopropoxy(diphenyl)silane **2** was prepared by the reaction of chlorodiphenylsilane with propan-2-ol in hexane in the presence of urea as a hydrogen chloride scavenger.

In summary, we found that the binary mixture $P(NMe_2)_3$—CH_2BrCl can be used in preparative organoelement synthesis for chloromethylation of alkoxy(chloro)diorganylsilanes RR´Si(OAlk)Cl.

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Experimental

^1H, ^{13}C, and ^{29}Si NMR spectra of compounds **1** and **2** were recorded with a Bruker DPX 400 instrument (working frequencies of 400.13, 100.61, and 79.5 MHz, respectively) in $CDCl_3$. The chemical shifts are given in the δ scale relative to Me_4Si as an internal standard. Commercially available dichlorodiphenylsilane, tris(dimethylamino)phosphine, bromochloromethane, propan-2-ol, and urea were used. Dichlorodiphenylsilane and bromochloromethane were distilled prior to use. Propan-2-ol and other solvents were purified by the standard procedures.[6] All syntheses were carried out under dry argon.

Synthesis of chloromethyl(isopropoxy)diphenylsilane (1). To a solution of freshly distilled bromochloromethane (3.88 g, 0.03 mol) and chloro(isopropoxy)diphenylsilane **2** (2.77 g, 0.01 mol) in benzene (50 mL), tris(dimethylamino)phosphine (1.63 g, 0.01 mol) was added at room temperature. The reaction mixture was stirred at room temperature for 4 h and then refluxed for 10 h. After cooling, the solution was filtered and treated with pentane (50 mL) to remove the quaternary phosphonium salt. The precipitate was filtered off and the filtrate was concentrated. Vacuum distillation of the residue afforded 1.83 g (63%) of compound **1**, b.p. 168—170 (3 mm Hg), n_D^{20} 1.5332. ^1H NMR, δ: 1.24 (d, 6 H, Me_2CH, $^3J = 6.0$ Hz); 2.53 (s, 2 H, CH_2Cl); 4.31 (sept, 1 H, Me_2CH, $^3J = 6.0$ Hz); 7.37—7.63 (m, 10 H, Ph). ^{13}C NMR, δ: 25.27 (Me_2CH); 36.99 (CH_2Cl); 67.48 (Me_2CH); 128.06 (C_m); 130.92 (C_i); 134.44 (C_p); 135.02 (C_o). ^{29}Si NMR, δ: −16.40. Found (%): C, 65.67; H, 6.37. $C_{16}H_{19}ClOSi$. Calculated (%): C, 66.07; H, 6.58.

Synthesis of chloro(isopropoxy)diphenylsilane (2). To a solution of chloro(diphenyl)silane (5.6 g, 0.02 mol) in hexane (75 mL), excess urea (2 g, preliminary dried) was added following by slow dropwise addition of propan-2-ol (1.2 g, 0.02 mol) *via* a syringe under vigorous stirring at 5 °C. The reaction mixture was stirred for 10 h and kept for 16 h. The solution was decanted and concentrated *in vacuo*. Vacuum distillation of the residue afforded 4.19 g (74%) of compound **2**, b.p. 153—155 °C (3 mm Hg), n_D^{20} 1.5444. ^1H NMR, δ: 1.27 (d, 6 H, Me_2CH, $^3J = 5.9$ Hz); 4.43 (sept, 1 H, Me_2CH, $^3J = 5.9$ Hz); 7.41—7.69 (m, 10 H, Ph). ^{13}C NMR, δ: 25.19 (Me_2CH); 66.78 (Me_2CH); 128.00 (C_m); 130.87 (C_i); 134.39 (C_p); 154.93 (C_o). ^{29}Si NMR, δ: −10.94. Found (%): C, 64.71; H, 6.07. $C_{15}H_{17}ClOSi$. Calculated(%): C, 65.08; H, 6.19.

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