Organosilicon compounds

XXXI*. By-products in Wurtz-Fittig syntheses in toluene

Toluene is frequently used as a solvent for the Wurtz-Fittig coupling of organic halides, RX, with silicon halides in presence of sodium[1]. The possibility has been pointed out that the initially-formed organosodium compounds, RNa, might undergo metal–hydrogen exchange with the solvent, and thus that some benzylsilicon compounds might be formed[2]. By vapour-phase chromatographic analysis of the products, we have now confirmed that this does indeed happen in couplings involving aryl chlorides, as shown in Table 1.

TABLE 1

PRODUCTS FROM XC_6H_4Cl AND R_3SiCl IN TOLUENE

X	*R_3*	*Products*
o-Me	Me_3	o-$MeC_6H_4SiMe_3$ + $C_6H_5CH_2SiMe_3$
o-Me	Me_2Et	o-$MeC_6H_4SiMe_2Et$ + $C_6H_5CH_2SiMe_2Et$
H	Me_2Et	$C_6H_5SiMe_2Et$ + $C_6H_5CH_2SiMe_2Et$
p-Me	Me_2Et	*p*-$MeC_6H_4SiMe_2Et$ + $C_6H_5CH_2SiMe_2Et$
p-OMe	Me_3	*p*-$MeOC_6H_4SiMe_3$ + C_6H_5OMe + $C_6H_5CH_2SiMe_3$

Benzyltrimethylsilane formed up to 7% of the products from *o*-chlorotoluene and chlorotrimethylsilane. The possibility that the benzylsodium was formed in this case by intramolecular rearrangement of *o*-tolylsodium was virtually ruled out by the observation that the by-product was (*o*-methylbenzyl)trimethylsilane when *o*-xylene was used as solvent. No trace of benzyltrimethylsilane was found in the products from coupling of *o*-tolyl-lithium and chlorotrimethylsilane in ether.

The suggested mode of production of the benzylsilicon compounds in toluene requires that the products XC_6H_5 and $C_6H_5CH_2SiR_3$ should be formed in equimolar amounts from the halide XC_6H_4Cl (see eqn. 1).

$$XC_6H_4Na + C_6H_5CH_3 \longrightarrow XC_6H_5 + C_6H_5CH_2Na \qquad (1)$$

In agreement with this, 8% of anisole and 7% of benzyltrimethylsilane were isolated along with 77.5% of (*p*-methoxyphenyl)trimethylsilane from a preparative scale reaction between *p*-chloroanisole and chlorotrimethylsilane in toluene.

Clearly, inert solvents, such as saturated paraffins, are preferable to toluene for Wurtz-Fittig syntheses when benzylsilicon products would be undesirable.

Experimental

Coupling of p-chloroanisole and chlorotrimethylsilane. A mixture of *p*-chloroanisole (0.50 mole) and chlorotrimethylsilane (0.55 mole) in an equal volume of sulphur-free toluene was added with vigorous stirring to molten sodium (0.50 g-atom) in boiling toluene (200 ml) at such a rate as to maintain gentle reflux. The mixture

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* For Part XXX, see ref. 3.

was subsequently refluxed for 30 min, and then allowed to cool. Insoluble products were removed by filtration and then extracted (by the Soxhlet procedure) with hot toluene (100 ml). The combined filtrates were fractionated to give anisole (4.3 g, 8 %), b.p. 152°, n_D^{20} 1.5163, benzyltrimethylsilane (5.5 g, 6.7 %), b.p. 191°, n_D^{20} 1.4906, unchanged *p*-chloroanisole (1.4 g, 2 %), b.p. 198°, n_D^{20} 1.5350, and (*p*-methoxyphenyl)-trimethylsilane (69.9 g, 77.5 %), b.p. 222.5–223°, n_D^{20} 1.5020.

Analysis of products by vapour-phase chromatography. The couplings were carried out, on a 0.3 molar scale, as described above, and the filtrates were analysed on a 60 × 0.4 cm column of dinonyl phthalate (5 wt-%) on kieselguhr (60–80 mesh) at 115°. An argon ionisation detector was used. In some cases ethyldimethylsilyl chloride was used in place of chlorotrimethylsilane (see Table 1) to facilitate the chromatographic separations.

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Aromatic reactivity

XXX*. Acid cleavage of (5-halo-2-methoxyphenyl)trimethylsilanes

Interest attaches to the reactivity of polysubstituted benzene derivatives in electrophilic aromatic substitutions, and Stock and Brown[1] have recently observed that "the scope and limitations of the application of the additivity principle deserve further attention". The principle seems to apply reasonably well to the reactivity of polymethylbenzenes[1–5] and gives at least a semi-quantitative interpretation of the isomer distributions in substitutions in many di-substituted benzenes[6]. However, deviations have been noted, and de la Mare and Ridd[6] have shown that the principle tends to underestimate the ease of substitution at a position which is activated, or slightly deactivated, by one substituent but strongly deactivated by another, as for example in nitration at the 2-position of 4-chlorotoluene[6] or 4-nitrotoluene[7]. More

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* For Part XXIX, see ref. 16.