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AN IMPROVED SYNTHESIS OF (IODOETHYNYL)TRIALKYLSILANES

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SUMMARY

Iodine chloride reacts at room temperature with $R_3SiC{\equiv}CSiR_3$ compounds ($R = Me$, Et) in the absence of catalyst to give (iodoethynyl)trialkylsilanes, $IC{\equiv}CSiR_3$, in excellent yield.

INTRODUCTION AND DISCUSSION

(Iodoethynyl)trimethylsilane has hitherto been prepared by reaction of iodine with [(trimethylsilyl)ethynyl]magnesium bromide[1] or -mercuric acetate[2]. Both methods suffer from the disadvantage that synthesis of the volatile starting material, $Me_3SiC{\equiv}CH$, involves a somewhat lengthy fractionation[3]. Furthermore the final product must be worked up by a wet or filtration procedure in order to remove inorganic salts and free iodine. We wish to report that (iodoethynyl)trimethylsilane can easily be prepared in a simple one-step reaction from the accessible precursor $Me_3SiC{\equiv}CSiMe_3$ and iodine chloride in methylene chloride solution at room temperature:

$$Me_3SiC{\equiv}CSiMe_3 + ICl \rightarrow Me_3SiC{\equiv}CI + Me_3SiCl \quad 95\%$$

The yield is virtually quantitative, no catalyst is required and the product, obtained simply by removing solvent and chlorotrimethylsilane under reduced pressure, is sufficiently pure for most purposes. Bis(triethylsilyl)acetylene reacts likewise to give (iodoethynyl)triethylsilane in excellent yield; an attractive feature of this synthesis is that the liberated chlorotriethylsilane, can be isolated during the final distillation, for reuse.

Aluminium iodide is required to catalyse the reaction of iodine with bis(trimethylsilyl)acetylene, however, whilst the yield of $Me_3SiC{\equiv}CI$ is comparable to that of the iodine chloride method, this route suffers from most of the disadvantages inherent in the earlier syntheses.

The electron-withdrawing iodine substituent, once introduced, presumably deactivates the product towards further electrophilic attack by iodine chloride. A similar principle has been employed previously by others[4] and by us[5,6] to synthesise silylethynyl ketones[4,5] and sulphones[6] by aluminium chloride catalysed reactions between bis(trimethylsilyl)acetylene and aroyl or arenesulphonyl chlorides.

EXPERIMENTAL

Starting materials

Methylene chloride was redistilled from phosphorus pentoxide. A commercial sample of iodine chloride was frozen in an ice-salt bath, the supernatant liquid (ca. 20%) was discarded and the pure material was stored in the dark until required. Bis(trimethylsilyl)acetylene was prepared from dilithium acetylide and chlorotrimethylsilane in ether/THF[5].

Bis(triethylsilyl)acetylene. Ethylmagnesium bromide (0.1 mole) in THF (100 ml) was added during 2 h to ethynyl(triethyl)silane (14.1 g, 0.1 mole) in THF (120 ml). The mixture was boiled under reflux for 10 min to complete the metallation, then bromotriethylsilane (15.7 g, 0.08 mole) was added. Refluxing was continued for a further 2 h, then the reaction mixture was added to a slurry of ice and dilute hydrochloric acid. Organic products were extracted with ether and the ether extracts were dried ($MgSO_4$) and distilled to give bis(triethylsilyl)acetylene (92%), b.p. 133°/25 mm, n_D^{20} 1.4266 (lit.[7] b.p. 132–134°/25 mm, n_D^{20} 1.4268).

(Iodoethynyl)trimethylsilane

A solution of freshly purified iodine chloride (9.75 g, 0.06 mole) in methylene chloride (100 ml) was added during 4 h to a magnetically stirred solution of bis(trimethylsilyl)acetylene (10.3 g, 0.06 mole) in methylene chloride (100 ml), the reaction vessel and dropping funnel being wrapped in aluminium foil to exclude light. Disappearance of bis(trimethylsilyl)acetylene and appearance of (iodoethynyl)trimethyl silane was monitored at intervals by GLC and by the development of a strong infrared acetylene absorption at 2105 cm^{-1}. At the equivalence point, some 12% of the starting silane remained unreacted, and this was reduced to a minimum (5%) by the addition of a further quantity of iodine chloride (0.5 g, 0.003 mole). Solvent and chlorotrimethylsilane were then removed by rotary evaporation and the residue (13.5 g) was distilled to give pure (iodoethynyl)trimethylsilane (95%), b.p. 55°/20 mm, n_D^{20} 1.5110 (lit.[1] b.p. 53°/15 mm, n_D^{20} 1.5109). The NMR spectrum (5% solution in $CHCl_3$ with TMS as internal standard) exhibited a sharp singlet at τ 9.87 ppm.

(Iodoethynyl)triethylsilane

Bis(triethylsilyl)acetylene (14.85 g, 0.059 mole) in methylene chloride (100 ml) was treated in the same way during 4 h with a solution of iodine chloride (9.75 g, 0.06 mole) in methylene chloride. Solvent was removed by rotary evaporation and the residue was distilled to give chlorotriethylsilane (90%), b.p. 78–80°/0.5 mm followed by (iodoethynyl)triethylsilane (nc) (88%), b.p. 117–120°/0.4 mm, n_D^{20} 1.5270. (Found: C, 36.0; H, 5.8. $C_8H_{15}ISi$ calcd.: C, 36.1; H, 5.7%.)

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