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Preliminary communication

Silatranes from reactions of chloromethylsilatrane with chlorosilanes and magnesium in tetrahydrofuran

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Abstract

Some silatranylmethylsilanes have been obtained by reaction of chloromethylsilatrane with chlorosilanes and magnesium in THF (i.e. under Barbier conditions).

Syntheses of new silatranes are of much interest in the light of the specific biological [1], physico-chemical [2], and structural [3] properties of this type of compound. Chemical investigations of these hypervalent silicon species are being intensively studied [4]. Recently Corriu and coworkers showed that the silatranyl ring is unstable towards Grignard reagents [4d], and cleavage of three Si–O bonds by C-nucleophile was usually observed when an excess of the organomagnesium reagent was used.

We have now found that chloromethylsilatrane readily reacts (65 °C, THF, 1–3 h) with chlorosilanes in the presence of magnesium in THF (Barbier reaction conditions [5]) to give cross-coupling products (**1–5**) in good yields (54–78%):

$$R_3SiCl + ClCH_2Si(OCH_2CH_2)_3N \xrightarrow[\text{THF, 65°C}]{\text{Mg}} R_3SiCH_2Si(OCH_2CH_2)_3N$$

(**1–5**)

$R_3 = Me_3$ (**1**); $R_3 = Me_2Ph$ (**2**); $R_3 = MePh_2$ (**3**); $R_3 = HMe_2$ (**4**); $R_3 = HMePh$ (**5**)

It should be noted that in absence of added trapping chlorosilane the starting silatrane is recovered unchanged even after prolonged boiling, indicating the Grignard reagent is not formed. The reaction observed is probably radical in character, taking place on the magnesium surface [6]. No products of self-coupling of the reagents were detected.

Several new α-silyl substituted silatranes have been obtained in good yields by the new route.

Experimental

General procedure for synthesis of silatranes 1–5. The mixture of chlorosilane, chloromethylsilatrane, magnesium (activated by iodine) and THF (dried with sodium

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benzophenone ketyl) was heated in argon until the mixture became clear as the initially almost insoluble silatrane went into solution. The mixture was then treated cautiously with water and the product extracted into ether, recovered and purified by column chromatography on silica gel with 1/1 hexane–ethyl acetate as eluant. Except for **4** (80% yield by GC, and 31% isolated yield) all the products are stable in air and water.

Trimethyl(silatranylmethyl)silane (1). This compound (424 mg, 65%) was obtained from chloromethylsilatrane (500 mg, 2.5 mmol), trimethylchlorosilane (543 mg, 5 mmol), and magnesium (120 mg, 5 mmol) in 10 ml of THF. ^{1}H NMR ($CDCl_3$, δ, ppm): −0.28 (s, 2H, $SiCH_2$), 0.02 (s, 9H, $SiCH_3$), 2.76 (distorted t, 6H, NCH_2), 3.71 (distorted t, 6H, OCH_2); MS *m/e* (rel. intensity, %): 261 (M^+, 1.1), 246 ($(M-CH_3)^+$, 75), 174 ($Si(OCH_2CH_2)_3N^+$, 100).

Dimethylphenyl(silatranylmethyl)silane (2). This compound (0.462 g, 72%) was obtained from chloromethylsilatrane (447 mg, 2 mmol), dimethylphenylchlorosilane (409 mg, 2.4 mmol) and magnesium (96 mg, 4 mmol) in 10 ml of THF. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.00 (s, 2H, $SiCH_2$), 0.32 (s, 6H, $SiCH_3$), 2.75 (t, 6H, NCH_2), 3.70 (t, 6H, OCH_2), 7.22–7.64 (m, 5H, C_6H_5); MS *m/e* (rel. intensity, %): 323 (M^+, 0.1), 308 ($(M-CH_3)^+$, 69), 246 ($(M-C_6H_5)^+$, 36), 174 ($Si(OCH_2CH_2)_3N^+$, 100).

Methyldiphenyl(silatranylmethyl)silane (3). This compound (600 mg, 78%) was obtained from chloromethylsilatrane (447 mg, 2 mmol), methyldiphenylchlorosilane (558 mg, 2.4 mmol), and magnesium (96 mg, 4 mmol) in 10 ml of THF. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.26 (s, 2H, $SiCH_2$), 0.59 (s, 3H, $SiCH_3$), 2.70 (t, 6H, NCH_2), 3.61 (t, 6H, OCH_2), 7.18–7.64 (m, 10H, C_6H_5); MS *m/e* (rel. intensity, %): 370 ($(M-CH_3)^+$, 22), 308 ($(M-C_6H_5)^+$, 100), 174 ($Si(OCH_2CH_2)_3N^+$, 96).

Dimethyl(silatranylmethyl)silane (4). This compound (3.9 g, 31%; by GLC 80%) was obtained from chloromethylsilatrane (11.5 g, 0.05 mol), dimethylchlorosilane (5.67 g, 0.06 mol) and magnesium (2.4 g, 0.1 mol) in 120 ml of THF. ^{1}H NMR ($CDCl_3$, δ, ppm): −0.23 (distorted d, 2H, $SiCH_2$), 0.12 (distorted d, 6H, $SiCH_3$), 2.77 (t, 6H, NCH_2), 3.73 (t, 6H, OCH_2) 3.93 (m, 1H, SiH); MS *m/e* (rel. intensity, %): 247 (M^+, 5), 232 ($(M-CH_3)^+$, 24), 174 ($Si(OCH_2CH_2)_3N^+$, 100).

Methylphenyl(silatranylmethyl)silane (5) This compound (10.1 g, 54%) was obtained from chloromethylsilatrane (14.1 g, 0.061 mol), methylphenylchlorosilane (11.65 g, 0.074 mol) and magnesium (2.95 g, 0.123 mol) in 122 ml of THF. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.14 (m, 2H, $SiCH_2$), 0.38 (d, 3H, $SiCH_3$, J 3.5 Hz), 2.76 (t, 6H, NCH_2), 3.72 (t, 6H, OCH_2), 4.44 (q, 1H, SiH, J 3.5 Hz), 7.22–7.67 (m, 5H, C_6H_5); MS *m/e* (rel. intensity, %): 309 (M^+, 1.5), 294 ($(M-CH_3)^+$, 10), 232 ($(M-C_6H_5)^+$, 21), 174 ($Si(OCH_2CH_2)_3N^+$, 100).

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