Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

TRIS- AND TETRAKIS(DIMETHYLPHENYLSILYL)METHANE

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(Received March 16th, 1970)

SUMMARY

Tris- and tetrakis(dimethylphenylsilyl)methane have been synthesized by coupling carbon tetrachloride with chlorodimethylphenylsilane. Temperature control is found to be of first importance for selective formation of these compounds. The infrared absorption at 10 μ is found to be of diagnostic value for distinguishing tris- and tetrakis-silylated methanes; the dimethylphenylsilyl group is the largest group that is attached to a single carbon atom in the known stable compounds of tetrakis-silylmethane type.

Synthesis of compounds of the type $(R_3Si)_4C$ is possible when the R_3Si groups are small[1,2]. Thus Et_3Si, i-Pr_3Si and $MePh_2Si$ groups cannot be introduced into such compounds. Compounds containing the Me_2PhSi group can be obtained, however, though only in very poor yield.

When carbon tetrachloride was coupled with dimethylphenylchlorosilane in the presence of magnesium in tetrahydrofuran, bis(dimethylphenylsilyl)methane[3], tris(dimethylphenylsilyl)methane, and tetrakis(dimethylphenylsilyl)methane were obtained, the last two being new compounds. The main product is bis(dimethylphenylsilyl)methane, and this is usually accompanied by small amounts of a byproduct, which is tris(dimethylphenylsilyl)methane when the reaction temperature is $>35°$ and tetrakis(dimethylphenylsilyl)methane when the reaction temperature is $<20°$. The temperature mainly determines which byproduct is formed, but the molar ratio of reagents is of secondary importance.

The ^1H NMR spectra of $(Me_2PhSi)_4C$ and $(Me_2PhSi)_3CH$ differ in that the phenyl protons in the latter show a single peak whereas those in the former show two peaks because of restriction to the rotation of phenyl group.

EXPERIMENTAL

Tris(dimethylphenylsilyl)methane

A mixture of carbon tetrachloride (3.9 g, 0.025 mole), dimethylphenylchlorosilane (18 g, 0.106 mole), magnesium (2.5 g, 0.103 g-atom), and tetrahydrofuran (70 ml) was stirred for 48 h at a temperature above 35°. Hydrochloric acid (30 ml of 5% acid) was added to destroy the unreacted magnesium and dissolve the magnesium salt, the tetrahydrofuran layer was separated, and the solvent was evaporated off to leave an oil from which crystals separated after one week at room temperature. Filtration removed crystals (1.6 g) from the oil (13.7 g), which proved to be bis(dimethylphenylsilyl)methane[3]. The crystalline compound was recrystallized from alcohol to give material of m.p. 105–106°, which was shown to be tris(dimethylphenylsilyl)methane (15%). (Found: C, 71.91; H, 8.58; Si, 19.75%; mol.wt., 415. $C_{25}H_{34}Si_3$ calcd.: C, 71.77; H, 8.13; Si, 20.09%; mol.wt., 418.) This compound is soluble in alcohol, benzene, carbon tetrachloride. The IR showed the characteristic bands of CH_3–Si at 7.9 μ, of C_6H_5–Si at 7 μ and 9 μ. A very strong absorption band occurs at 10 μ, and is a combination of weak band of C_6H_5–Si and the strong characteristic band of trissilylmethanes. The ^1H NMR spectrum showed peaks at τ 9.58 (Me) and 2.6 (Ph).

Tetrakis(dimethylphenylsilyl)methane

A mixture of carbon tetrachloride (4.8 g, 0.03 mole), dimethylphenylchlorosilane (20.6 g, 0.12 mole), magnesium (2.8 g, 0.12 g-atom) and tetrahydrofuran (140 ml) was stirred at 20°–15°. The consumption of magnesium was slow, and 70 h were needed for completion of the reaction. Treatment with 5% hydrochloric acid and separation of the organic components were carried out as before, to give a mixture of crystals and oil. Filtration removed 2.0 g, of solid crystals from 11.7 g of liquid, which after vacuum distillation was shown to be bis(dimethylphenylsilyl)methane. Recrystallisation of the solid from carbon tetrachloride gave 1.3 g of tetrakis(dimethylphenylsilyl)methane (11%), as white needles, m.p. 205–206°. (Found: C, 71.50; H, 7.86; Si, 20.43; mol.wt., 556. $C_{33}H_{44}Si_4$ calcd.: C, 71.74; H, 7.79; Si, 20.11%; mol.wt., 552.) This compound is slightly soluble in alcohol, benzene, ether and readily soluble in carbon tetrachloride. The IR spectrum shows CH_3–Si bands at 7.9 μ, of C_6H_5–Si bands at 7 μ, 9 μ, and 10 μ vw. A large difference in the intensity of 10 μ band is observed between trisilylmethane and this compound and is of diagnostic value[2]. The ^1H NMR spectrum showed peaks at τ 9.76 (Me), 2.64 and 2.37 (both Ph). As expected, the phenyl group in this compound was a doublet.

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