DIELS–ALDER SELF-ADDITION AND RETROADDITION OF (CYCLOPENTADIENYLMETHYL)TRIETHOXYSILANE AND SYNTHESIS OF ITS PERMETHYLATED ANALOGUE

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Received June 10, 1993
Accepted June 24, 1993

Reversible Diels–Alder self-addition of (cyclopentadienylmethyl)triethoxysilane hampering its use as functionalizing agent and the synthesis of a new silica functionalizing agent, (tetramethylcyclopentadienylmethyl)triethoxysilane, are described.

Cyclopentadienyl and its alkyl substituted derivatives, e.g. pentamethylcyclopentadienyl, are among the most frequently used ligands in organometallic chemistry. Their trihalosilyl or trialkoxysilyl derivatives are usually utilized for the immobilization of transition metal complexes onto inorganic supports.

While some of the (cyclopentadienylalkyl)trialkoxysilanes were prepared[1,2], the synthesis of their permethylated analogues has not been reported. Alkyl substituted cyclopentadienyls are ligands with electronic and steric properties quite different from those of their parent compounds, which makes them valuable in catalyst design.

We report here on the synthesis of (tetramethylcyclopentadienylmethyl)triethoxysilane and on Diels–Alder self-addition and retroaddition of (cyclopentadienylmethyl)-triethoxysilane which takes place contrary to the stability[3] of a close homolog, (cyclopentadienylpropyl)triethoxysilane, towards dimerization and is crucial for its use as silica functionalizing agent.

EXPERIMENTAL

Chemicals

Preparation of functionalizing agents was carried out in dry argon, using the solvents dried by standard procedures. Sodium hydride (Katchem, Prague) was used as received, tetracyanoethylene (Fluka, Buchs) was recrystallized from chlorobenzene and then sublimed in vacuo at 120 °C. (Chloromethyl)triethoxysilane from the laboratory stock was distilled before use (boiling range 58 – 60 °C/1.1 kPa). Mixtures of tetramethylcyclopentadiene isomers[4] and (cyclopentadienylmethyl)-triethoxysilane[1] were prepared according to published procedures, the latter was kept at –78 °C.

NMR spectra were taken on Varian Unity 200 spectrometer at 220 MHz, 50.3 MHz, and 39.7 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively, in $CDCl_3$ solution.

(Cyclopentadienylmethyl)triethoxysilane[1] (*Ia*, *Ib*)

^{1}H NMR spectrum: δ 6.47 – 5.97 (m, 3 H), 3.80 (q, *J* = 6.9 Hz, 6 H); 2.95 (s, 2 H); 2.00 (d, *J* = 10.3 Hz, 2 H); 1.21 (t, *J* = 7.0 Hz, 9 H). ^{13}C NMR spectrum: δ 143.7, 140.8, 136.2, 133.3, 132.6, 129.8, 126.6, 125.9, 58.4, 45.1, 41.4, 18.2, 14.9, 13.8. ^{29}Si NMR spectrum: δ –50.0, –50.8. Mass spectrum (*m*/*z*): 242 ($M^{+\bullet}$, 20), 163 ($M^{+\bullet}$ – 79, 100).

(Tetramethylcyclopentadienylmethyl)triethoxysilane (*IIa*, *IIb*)

Sodium hydride (4.6 g, 0.19 mol) was suspended in DMF (100 ml) and tetramethylcyclopentadiene isomers (24.8 g, 0.20 mol) were added with stirring. The mixture was stirred for another 3 h at laboratory temperature, then cooled to –20 °C, and (chloromethyl)triethoxysilane (60.6 g, 0.29 mol) dissolved in DMF (35 ml) was slowly added. After standing overnight at room temperature, the solids were filtered off and the product was obtained by rectification in vacuo, boiling 104 – 106 °C/0.13 kPa (yield 30.0 g, 53%). ^{1}H NMR spectrum: δ 3.76 (q, *J* = 7.0 Hz, 6 H); 2.57 (dq, 1 H); 1.81 (s, 6 H); 1.77 (d, *J* = 1.4 Hz, 3 H); 1.19 (t, *J* = 7.0 H, 9 H); 1.00 (d, *J* = 7.7 Hz, 3 H) – signals at δ 3.76, 1.19, and 1.00 are doubled. ^{13}C NMR spectrum: δ 137.6, 137.3, 136.6, 136.0, 134.2, 133.9, 133.1, 133.0, 58.4, 51.3, 50.8, 18.2, 14.2, 14.1, 11.9, 11.7, 11.6, 11.3, 11.1, 11.1, 10.7, 10.5. ^{29}Si NMR spectrum: δ –50.7, –51.0. Mass spectrum (*m*/*z*): 298 ($M^{+\bullet}$, 100), 253 ($M^{+\bullet}$ – 45, 12).

Determination of Monomer Content by Reaction with Tetracyanoethylene (TCNE)

The sample was treated with an excess of benzene solution of TCNE. The unreacted TCNE was determined by spectrophotometry at 387 nm (Lambert–Beer law checked in the range 10^{-4} – 10^{-3} mol/l) on Varian DMS 300 UV/VIS spectrophotometer.

RESULTS AND DISCUSSION

Both (cyclopentadienylmethyl)triethoxysilane and its permethylated analogue were synthesized by the reaction of (chloromethyl)triethoxysilane with corresponding sodium cyclopentadienides (Scheme 1). While cyclopentadiene reacts smoothly with sodium hydride in THF, tetramethylcyclopentadienes formed an anion only in DMF. Both compounds are formed as an approximately 1 : 1 mixture of isomers (*Ia*, *Ib* and *IIa*, *IIb*), the third possible isomer was not found.

As expected, (tetramethylcyclopentadienylmethyl)triethoxysilane is stable in respect to dimerization. However, (cyclopentadienylmethyl)triethoxysilane dimerizes slowly by Diels–Alder self-addition on standing at laboratory temperature.

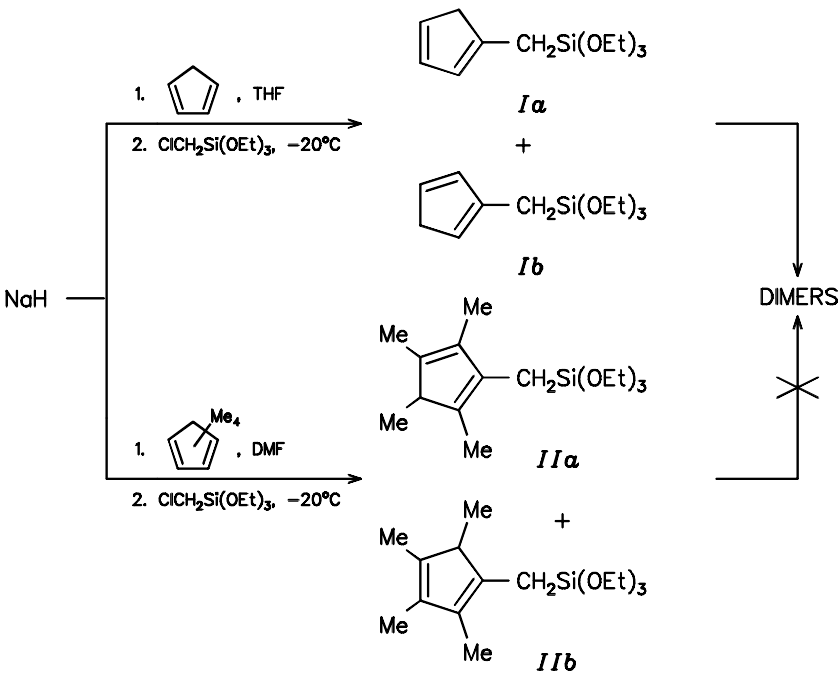
Two independent methods that gave comparable results were used to determine monomer content of freshly prepared functionalizing agent and of the samples stored at various conditions. In the first method, the monomer content was calculated from ^{1}H NMR spectra from the ratio of the integrals of methylene protons in the ethoxy groups to the integrals of methylene protons on the ring, the ratio for pure monomers being 3 : 1. It is worth noting that ^{13}C NMR spectrum of the mixture, almost half of

which consists of dimers, is identical with the spectrum of pure monomers under low signal/noise conditions. Many different dimers are produced by Diels–Alder self-addition, and this results in a great number of low carbon signals.

In the second method, Diels–Alder reaction with tetracyanoethylene was applied to determine the monomer content and the results with both methods are summarized in Table I.

TABLE I
Monomer content of (cyclopentadienylmethyl)triethoxysilane samples

Sample	Monomer content (%) determined by	
	^{1}H NMR	TCNE reaction
Stored for several months at room temperature	0	0
Distilled and stored 5 days at room temperature	54	55
Freshly distilled	100	100
Freshly distilled and stored 15 days at −78 °C	100	100



SCHEME 1

It was further observed that the rate of dimerization increases substantially at temperatures around 100 °C, which is a serious obstacle in silica functionalization, since the standard procedure[5,6] uses reflux in toluene. At temperatures around 170 °C, the dimerization equilibrium is sufficiently shifted towards monomer so that it can be removed by distillation in vacuo. In one experiment, 94% of the monomer were recovered from the mixture containing 36% of the monomer and 64% of the dimers.

In summary, there is a danger of binding dicyclopentadienyl instead cyclopentadienyl groups to the surface when using (cyclopentadienylmethyl)triethoxysilane in functionalization procedure. This can be excluded when the newly synthesized (tetramethylcyclopentadienylmethyl)triethoxysilane is used for this purpose.

The authors thank Dr V. Blechta for measuring NMR spectra and Dr R. Rericha for GC/MS analysis.

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Translated by the author (J. C).