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Synthesis of perfluoroalkyl-containing multifunctional groups compounds for textile finishing

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Abstract

A new kind of perfluoroalkyl-containing multifunctional groups compound was designed. Treatment of 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane (**4**) with allylmagnesium bromide provided key intermediate 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriallylsilane (**2**). Hydroboration followed by oxidation, epoxidation and dihydroxylation of **2** gave perfluoroalkyl-containing multifunctional groups compound **1a**, **1b** and **1c**, respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Perfluoroalkyl-containing compound; Multifunctional groups compound; Textile finishing

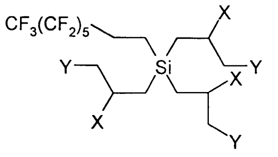
1. Introduction

Since the late 1980s, the market place has shown a steady increase in the demand for easy care, wrinkle-resistant 100% cotton (silk) apparel. The ability of durable press cotton (silk) fabrics to combine comfort with easy care provides a full spectrum of benefits that a consumer could possible expect. The overwhelming majority of the durable press finishing agents used today by the textile industries are formaldehyde-based reagents, which are cost effective and efficient [1]. However, the release of formaldehyde vapor during finishing processes as well as during the subsequent storage and consumer use of finished products has caused worldwide concern of its impact on human health and the environment. Highest priority has been given to non-formaldehyde durable press finishes in the textile finishing industry [2]. Recently, a number of non-formaldehyde di- or multi-functional cross-linking reagents appeared, which included aromatic acid anhydrides [3], dibasic anhydrides [4], epoxide [5], butanetetracarboxylic acid [6], glyoxal [7] and a mixture of citric acid and a terpolymer of maleic acid [8]. Fluorochemicals most abundantly used as repellent agents in textile finishing, not only satisfy the demand for high water repellency but also impart oil and soil repellency to finished textiles. Water and oil repellency are achieved by reducing the critical surface energy of fabrics [9].

In the light of the above facts, we envisaged that a molecule, which contains both perfluoroalkyl chain and multi-cross-linking groups, should be suitable finishing agents for fabrics with wrinkle resistance, water repellency, oil repellency and soil repellency. We describe herein the design and synthesis of a number of perfluoroalkyl-containing multifunctional groups compounds via a key intermediate **2**.

2. Results and discussion

The use of silane coupling agents bearing perfluoroalkyl chains to promote surface modification and/or adhesion are most familiar for $CF_3(CF_2)_nCH_2CH_2SiX_3$. The X functionality is a hydrolyzable group, often alkoxyl [10,11]. In order to introduce more functional groups into a molecule, we designed a new kind of perfluoroalkyl-containing multifunctional groups compound **1**, which can be easily prepared from a key intermediate **2**.



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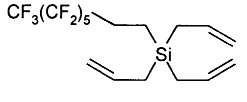

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The synthesis of **2** is outlined in Scheme 1. The addition of 1-iodoperfluorohexane to ethylene initiated by sodium

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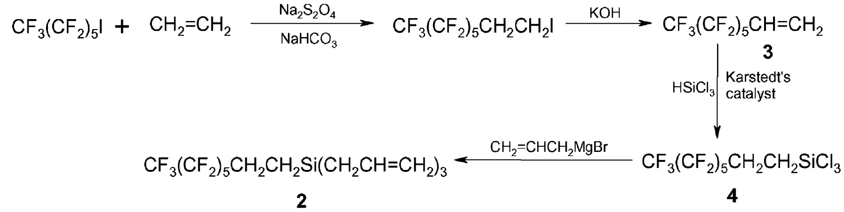
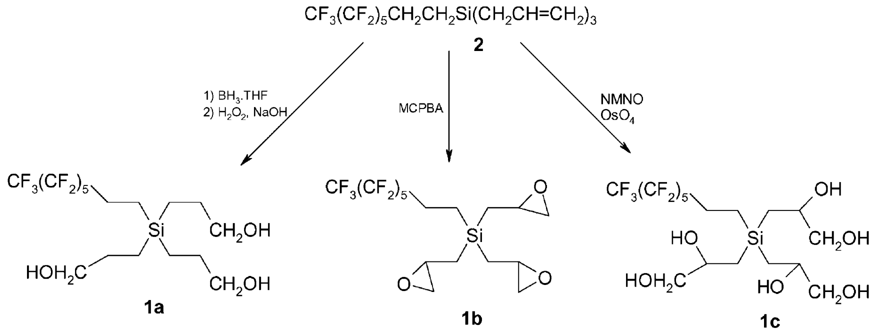


Scheme 1.



Scheme 2.

dithionite [12], followed by dehydroiodination with KOH [13] provided 1*H*,1*H*,2*H*-perfluoro-1-octene (**3**) in 77% yield. The hydrosilylation reaction of trichlorosilane with **3** under the catalysis of Karstedt's catalyst [14,15] gave 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane (**4**) as a single compound in 80% yield. The Karstedt's catalyst was prepared by the reaction of chloroplatinic acid with divinyltetramethyldisiloxane. The Karstedt's catalyst was more active and regioselective than chloroplatinic acid in the hydrosilylation. Treatment of **4** with allyl magnesium bromide afforded **2** in 82% yield.

With 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriallylsilane (**2**) in hand, the transformation of **2** into perfluoroalkyl-containing multifunctional groups compounds was investigated (Scheme 2). The hydroboration of **2**, followed by treatment with hydrogen peroxide in the presence of sodium hydroxide gave **1a** 76% yield [16]. The epoxidation of **2** with *m*-chloroperbenzoic acid in chloroform led to **1b** in 62% yield [17]. Initial attempts to prepare **1c** by treatment of **2** with potassium permanganate failed. Fortunately, the dihydroxylation of **2** with *N*-methylmorpholine-*N*-oxide (NMNO) and catalytic osmium tetroxide provided **1c** in 67% yield.

In conclusion, new three perfluoroalkyl-containing multifunctional groups compounds were prepared from the key intermediate 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriallylsilane. The application of these compounds for textile finishing will be reported in due course.

3. Experimental

^{1}H NMR spectra were recorded on a Bruker AM 300 (300 MHz) spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were obtained on Bruker AM 300 (282 MHz) spectrometer using trifluoroacetic acid as external standard, downfield shifts being designated as negative. All chemical shifts (δ) are expressed in ppm, coupling constants (J) are given in Hz. Mass spectra were recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. IR spectra were recorded on a Shimadzu IR-440 spectrometer.

3.1. 1H,1H,2H-perfluoro-1-octene (3)

A 2 l stainless steel pressure cylinder was charged with a mixture of 1-iodoperfluorohexane (520 g, 1.16 mol), $Na_2S_2O_4$ (20.9 g, 0.12 mol), Na_2HPO_4 (21.5 g), CH_3CN (900 ml), water (300 ml) and ethylene (40 atm.). The mixture was heated at 40–45 °C for 3 h. Excess ethylene was released. The organic layer was washed with water, brine, dried over anhydrous Na_2SO_4 and distilled to give 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorooctane (525 g, 95%, bp 90–92 °C/45 mmHg). A solution of 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorooctane (47.4 g, 0.1 mol) in ethanol (100 ml) was added dropwise to a mixture of KOH (7.0 g, 0.1 mol) and ethanol (30 ml) at room temperature. After the addition, the reaction mixture was stirred at reflux for 3 h. The mixture was poured into water (250 ml). The organic layer was separated, washed with water, dried over anhydrous Na_2SO_4 and distilled to give 1*H*,1*H*,2*H*-perfluoro-1-octene (**3**) (28.0 g, 81% yield, bp 103–105 °C).

3.2. 1H,1H,2H,2H-perfluorooctyltrichlorosilane (4)

Under a nitrogen atmosphere, $HSiCl_3$ (20 ml) was added dropwise to a mixture of **3** (34.6 g, 0.1 mol) and Karstedt's catalyst (0.2 ml). After the addition, the reaction mixture was stirred at 60 °C for 4 h. Then the solution was distilled to give **4** as a colorless liquid (38.3 g, 80% yield, bp 105–110 °C/40 mmHg).

3.3. *1H,1H,2H,2H-perfluorooctyltriallylsilane* (**2**)

Under a nitrogen atmosphere and at 0–5 °C, the solution of allyl bromide (30 ml) in dry ether (30 ml) was added dropwise to a mixture of magnesium (10.0 g) and dry ether (150 ml). After the addition, the reaction mixture was stirred at 0–5 °C for 2 h. Under a nitrogen atmosphere, the allylmagnesium bromide solution was transferred to a dropping funnel and then was slowly added to a mixture of **4** (24.5 g, 0.05 mol) and dry ether (150 ml) at reflux. The reaction mixture was stirred at reflux for 24 h. The saturated aqueous ammonium chloride was slowly added to the reaction mixture. The organic layer was separated and the water layer was extracted with ether. The combined organic layer was washed with water, brine, dried over anhydrous $MgSO_4$ and distilled to yield **2** (20.4 g, 82% yield, 88–90 °C/0.7 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.83–0.89 (m, 2H), 1.64 (d, $J = 8.0$ Hz, 6H), 2.06–2.12 (m, 2H), 4.90–4.96 (m, 6H), 5.71–5.85 (m, 3H) ppm. IR (thin film) 2978, 1633, 1241, 1210, 1145, 901, 810 cm^{-1}; MS *m/z* 389 (2), 289 (6), 151 (11), 101 (100); Anal. Calcd. for $C_{17}H_{19}F_{13}Si$: C, 40.97; H, 3.84. Found: C, 40.90; H, 3.84%.

3.4. **1a**

Under a nitrogen atmosphere and at 10 °C, a solution of **2** (7.5 g, 15 mmol) in anhydrous THF (90 ml) was slowly added dropwise to a solution of BH_3. THF (27 ml, 1 M in THF) in THF (45 ml). After the mixture was stirred at room temperature for 3 h, 3 M NaOH (30 ml) and then 30% H_2O_2 (4.5 ml) were added to the mixture at 20 °C. After stirring for 2 h, water (100 ml) was added to the mixture. The mixture was extracted with dichloromethane. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. Purification of the residue by column chromatography on silica gel and elution with 15:1 dichloromethane:methanol gave compounds **1a** (6.3 g, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.55–0.62 (m, 6H), 0.72–0.80 (m, 2H), 1.52–1.61 (m, 6H), 1.98–2.05 (m, 5H), 3.62 (t, $J = 7.0$ Hz, 6H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 3.9 (s, 3F), 38.2 (m, 2F), 45.1 (s, 2F), 46.2 (s, 4F), 49.2 (s, 2F) ppm. IR (thin film) 3338, 2930, 2875, 1239, 1210, 1145, 1065, 894, 745 cm^{-1}; MS *m/z* 493 (98), 477 (98), 289 (42); 239 (93), 107 (100); Anal. Calcd. for $C_{17}H_{25}F_{13}SiO_3$: C, 36.96; H, 4.53. Found: C, 37.13; H, 4.57%.

3.5. **1b**

To a solution of 3-chloroperbenzoic acid (0.86 g, 5.0 mmol) in chloroform (20 ml), 2 (0.47 g, 0.94 mmol) was added at 5 °C. After the mixture was stirred at 5 °C for 2 days, 3-chlorobenzoic acid and excess 3-chloroperbenzoic acid were extracted with 1 M NaOH. The chloroform solution was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. Purification of the residue by column chromatography on silica gel and elution with 8:1 hexane:ethyl acetate gave compounds **1b** (0.32 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.97–1.00 (m, 2H), 1.15–1.19 (m, 6H), 2.10–2.25 (m, 2H), 2.42–2.46 (m, 3H), 2.83–2.90 (m, 3H), 3.05–3.10 (m, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -1.6 (s, 3F), 33.2 (m, 2F), 39.6 (s, 2F), 41.2 (s, 4F), 44.2 (s, 2F) ppm. IR (thin film) 2992, 2923, 1240, 1207, 1145, 1070, 932, 845 cm^{-1}; MS *m/z* 546 (M^+, 2), 489 (74), 161 (35), 81 (100); Anal. Calcd. for $C_{17}H_{19}F_{13}SiO_3$: C, 37.37; H, 3.48. Found: C, 37.34; H, 3.41%.

3.6. **1c**

A 25 ml three-necked round-bottomed flask with a magnetic stirrer and a nitrogen inlet was charged with NMNO· H_2O (0.7 g, 5.2 mmol), water (1 ml) and acetone (6 ml). To this solution was added osmium tetraoxide (0.06 ml) and **2** (0.5 g, 1 mmol).The reaction mixture was stirred at room temperature overnight. The saturated aqueous ammonium chloride was slowly added to the reaction mixture. The mixture was extracted with dichloromethane. The organic layer was washed with aqueous $Na_2S_2O_4$ and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. Purification of the residue by column chromatography on silica gel and elution with 4:1 dichloromethane:methanol gave compounds **1c** (0.4 g, 67% yield). ^{1}H NMR (300 MHz, CD_3SOCD_3) δ: 0.67–0.70 (m, 2H), 0.87–0.90 (m, 6H), 2.35–2.45 (m, 2H), 3.20–3.30 (m, 6H), 3.60 (br, 3H), 4.45–4.52 (m, 6H) ppm. ^{19}F NMR (282 MHz, CD_3SOCD_3) δ: -1.6 (s, 3F), 33.2 (m, 2F), 39.6 (s, 2F), 41.2 (s, 4F), 44.2 (s, 2F) ppm. IR (thin film) 3385, 2978, 1261, 1211, 1145, 1022, 869, 803 cm^{-1}; MS *m/z* 531 (1), 431 (2), 121 (28), 41 (100); Anal. Calcd. for $C_{17}H_{25}F_{13}SiO_6$: C, 34.00; H, 4.19. Found: C, 34.27; H, 4.08%.

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