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Short Note

Bicyclo[4.2.0]octa-1,3,5-trien-3-yl-dimethyl((*E*)-styryl)-silane

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Abstract: Bicyclo[4.2.0]octa-1,3,5-trien-3-yl-dimethyl-((*E*)-styryl)-silane was synthesized via three stage synthesis starting from benzocyclobutene and (2-bromo-vinyl)-benzene. The structure of the product was determined using ^{1}H- and ^{13}C-NMR and HRMS.

Keywords: benzocyclobutene; Grignard reaction; bicyclo[4.2.0]octa-1,3,5-trien-3-yl-dimethyl-((*E*)-styryl)-silane; (2-bromo-vinyl)-benzene

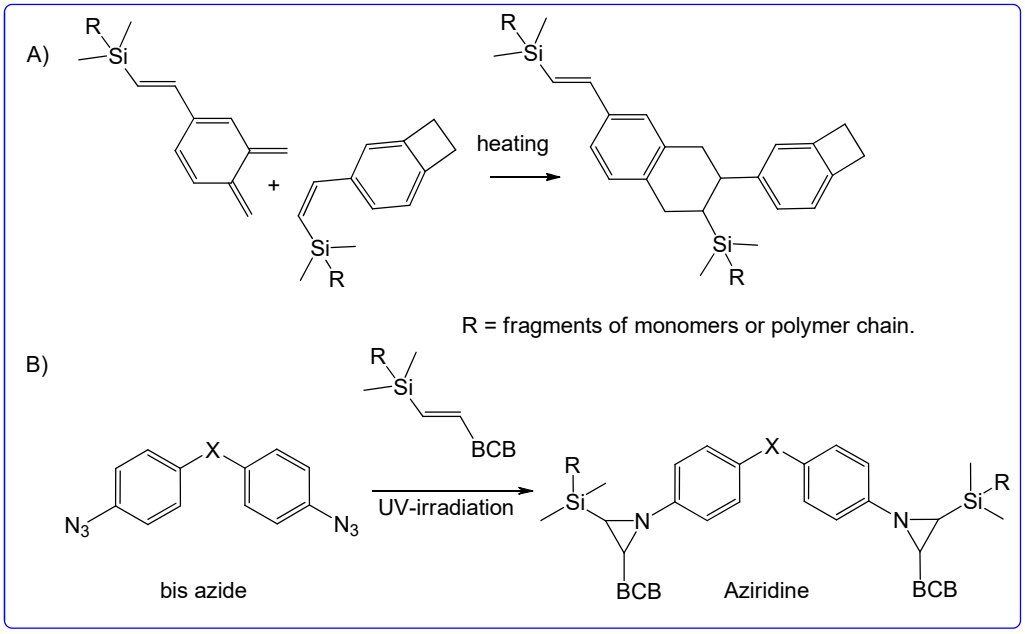
1. Introduction

Silicon organic compounds are widely used as intermediates in various syntheses and as target substances in industrial chemistry. Polysiloxanes and polysilanes are known as coupling agents for enhanced adhesion [1,2]. They increase mechanical and dielectric properties of composites [3], improve dispersion of pigments and industrial minerals, provide crosslinking, immobilize catalysts, and bind biomaterials [4].

Many companies are developing silane- and siloxane-based photo or thermo curable materials for electronics. For example, Polyset company (https://www.polyset.com) created a family of novel siloxane-based monomers and oligomers that are especially attractive for such applications as microelectronics, photonics, composites, coatings, and adhesives. These novel materials bear reactive functional groups consisting of cyclohexyl epoxy, glycidyl ether, vinyl ether, and acrylate moieties as well as combinations of these group. Dow chemicals (www.dow.com) presents a line of composite materials (CYCLOTENE™) with divinylsiloxane (**DVS**) and benzocyclobutene (**BCB**) based component as photoresists and thermosets (Divinyl siloxane bis-benzocyclobutene, **DVS-BCB**). In recent years, many new articles have appeared devoted to the development of hybrid silanes or siloxanes and BCB containing monomers [5–10]. The polymerization of these compounds occurs due to the presence of acrylate, silocyclobutene groups, alkenes (including vinyl, styryl, and allyl groups), etc. Crosslinking of the polymers provides a benzocyclobutene fragment capable of thermal opening (t > 200 °C) with the formation of active o-xylylenes. Several polymerization mechanisms are known: Interactions of o-xylylenes with active alkenes ([4+2] cycloaddition, (Scheme 1, A)) or by itself with the formation of a polydiphenylethylene or cyclooctane structures [11]. Photocurable DVS-BCB composites include [12] photoactive bisazide compounds that are capable of forming aziridines (Scheme 1B) under UV-irradiation. BCB crosslinked polymers have high values of glass transition temperatures and thermal stability [5,6,13].

In this short note we present a synthesis of a new bicyclo[4.2.0]octa-1,3,5-trien-3-yl-dimethyl-((*E*)-styryl)-silane (**BCB-KS**) that include

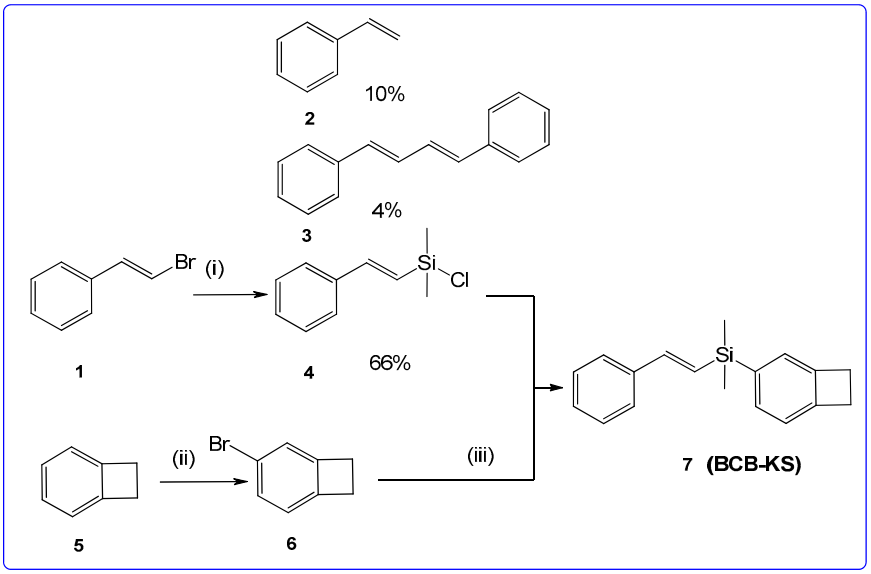
benzocyclobuten-3-yl and vinylbenzene moieties. It may be of interest in the creation of photo and thermopolymerizable composites and used in synthetic processes as an intermediate compound.



Scheme 1. Scheme of photo and thermo polymerization of **DVS-BCB** and analogs in absence (**A**) or presence (**B**) of bisazide photocoupling agent.

2. Results and Discussion

Synthesis of the title compound is presented on Scheme 2 and include a three stage process from (2-bromovinyl)benzene and benzocyclobutene. In the first step, (2-bromovinyl)benzene was added to mixture of dichlorodimethylsilane and magnesium in tetrahydrofuran (THF) at 25–30 °C. The resulting dimethylchloro((*E*)-styryl)silane was purified by vacuum distillation. The byproducts in this reaction are 1,4-diphenylbutadiene and styrene.



Scheme 2. Synthesis of bicyclo[4.2.0]octa-1,3,5-trien-3-yl-dimethyl-((E)-styryl)-silane (BCB-KS). (i) Mg, Me_2SiCl_2 THF, 25–30 °C; (ii) Br_2, H_2O, −10–20 °C, 20 h; and (iii) Mg, THF, 4, 25–30 °C, after r.t., overnight.

Dimethylchloro((*E*)-styryl)silane can also be obtained from phenylacetylene and dimethylchlorosilane [14,15]. Upon receipt in this way, the target product is contaminated with dimethylchloro(1-phenylvinyl)silane.

Dimethylchloro((*E*)-styryl)silane reacts with benzocyclobuten-3-yl magnesium bromide to produce the desired benzocyclobuten-3-yl-dimethyl((E)-styryl)silane (**BCB-KS**) as colorless fusible solid with 65.6% yield.

All compounds were characterized by ^{1}H, ^{13}C NMR, and HRMS analysis. NMR data of known compounds were compared with previously published data [16–18]. These NMR, HRMS and FTIR data of compounds can be found in the Supplementary Materials.

Signals of the carbon atoms of the $–CH_2–CH_2–$ of the compound **7** (**BCB-KS**) cyclobutene ring were found in the ^{13}C NMR spectra at 29.83 and 29.95 ppm, hydrogen atoms were detected as slightly broadened singlet at 3.21 ppm. Double bond of **7** gives two signals in ^{1}H NMR spectra at 7.07 and 6.71 ppm with high value of *J*-constants (19.1 Hz), which confirms its *trans* orientation. Two CH_3 groups of $–Si(CH_3)_2$ are detected in ^{1}H NMR and ^{13}C NMR spectra at 0.52 (s) and −2.26, respectively. Aromatic hydrogens were indicated at 7.11–7.50 ppm. In ^{13}C NMR spectrum there were found high-intensity signals at 126.50 and 128.52 ppm related to pairs of symmetric carbons of the phenyl group. Six signals (145.06, 132.25, 128.10, 127.72, 127.59, and 122.01) of tertiary carbon atoms and four signals of quaternary carbon atoms (147.22, 145.63, 138.25, and 136.59) were found.

3. Materials and Methods

NMR spectra were registered using a Bruker AM-300 or a Bruker Avance 600 spectrometer (Bruker Corporation, Billerica, MA, USA) in $CDCl_3$. Mass spectra were obtained on a Varian MAT CH-6 instrument (Varian, Inc, Palo Alto, CA, USA) using a direct inlet system; the ionization energy was 70 eV; the acceleration voltage was 1.75 kV. The reaction mixtures were analyzed and the purity of all products was checked by TLC on Merck Silica gel 60 F254 UV-254 plates. Dimethyldichlorosilane was purchased from abcr GmbH, Karlsruhe , Germany. Magnesium powder was purchased from Sigma-Aldrich, Co., USA. Bromine, solvents were purchase from «Base No. 1 «Chimreactivov», Staraya Kupavna, Russia. Other of the reagents were produced from JSC «Technomash, Russia.

3.1. 4-Bromobenzocyclobutene (**6**)

Benzocyclobutene (23.7 g, 22.8 mmol) was dispersed in 240 mL of water at room temperature. After cooling with ice water, 11.7 mL of bromine (−10–5 °C) was added dropwise. After complete of addition, the ice water bath was removed and the reaction mixture was warmed to room temperature and stirred overnight. The reaction was monitored by TLC until the starting benzocyclobutene disappeared. The mixture was diluted with 50 mL of *n*-hexane and sodium sulfite (3 g, 23.8 mmol) was added. Upon completion of the addition, the mixture was stirred at room temperature for 30 min. The mixture discolored. Then, the separated organic layer was dried over anhydrous sodium sulfate, filtered to remove the drying agent, and concentrated under reduced pressure to obtain 4-bromobicyclo [4.2.0] octa-1 (**6**), 2,4-triene. After distillation at 110–114 °C (15 mm of Hg), 28–30 g was obtained as a colorless liquid.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), and 3.31–3.10 (m, 4H).

3.2. Dimethylchloro((E)-styryl)silane (**4**)

(2-Bromovinyl)benzene (18.3 g, 100 mmol) was added to a mixture of Mg (2.4g, 100 mmol) and 12.9 g (100 mmol) of dimethyldichlorosilane in 50 mL of dry THF under Ar atmosphere and cooling (t = 20–35 °C). The next day, THF was evaporated. The residue was extracted with dry hexane several times. The extracts were combined and evaporated. Distillation under vacuum (2.25 mm of Hg) gives three fractions. The first fraction contains styrene, the second was collected at 90–130 °C and contains the main product. Higher boiling fractions contain 1,4-diphenylbutadiene. After

repeated distillation, dimethylchloro((*E*)-styryl)silane was obtained. Yield 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.29 (m, 5H), 7.15 (d, *J* = 19.1 Hz, 1H), 6.57 (d, *J* = 3.1 Hz, 1H), 0.66 (s, 6H).

3.3. Benzocyclobuten-3-yldimethyl((E)-styryl)silane (**7**) (**BCB-KS**)

4-Bromobenzocyclobutene (5.49g, 0.03 mol) was added over 1 h to a mixture of dimethylchloro (*E*)-styrylsilane (5.88 g, 0.03 mol) and Mg (760 mg, 0.032 mol) in 25 mL of THF at 25–32 °C. After addition, the mixture was left to stand overnight. The next day, water was added to the mixture. The resulting solution was extracted with methylene chloride. After evaporation, the oil is dissolved in hexane and passed through 1 cm^3 of silica gel and evaporated again. The residue was distilled in vacuum at a temperature of 167–169 °C (1.5 mm of Hg). A clear, viscous liquid (5.2 g, 65.6%) was obtained, which solidifies in the refrigerator. Mp 32 °C. 1H NMR (300 MHz, $CDCl_3$) 7.60–7.52 (m, 3H), 7.48–7.32 (m, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 19.1 Hz, 1H), 6.71 (d, *J* = 19.1 Hz, 1H), 3.31 (s, 4H), and 0.52 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.22, 145.63, 145.06, 138.25, 136.59, 132.25, 128.52, 128.10, 127.72, 127.59, 126.50, 122.01, 29.95, 29.83, and –2.26. HRMS, found: 265.1404, calculated [M + H]: 265.1407.

4. Conclusions

New benzocyclobuten-3-yldimethyl((E)-styryl)silane (**BCB-KS**) was obtained via three stage synthesis starting from benzocyclobutene and (2-bromovinyl)benzene with good yields. Obtained product can be useful for development of new polymerizable composite materials with good thermal stability and dielectric properties or used in synthetic processes as an intermediate.

Supplementary Materials: Supplementary data to this article can be found online. These data include MOL file, ^{1}H, ^{13}C NMR, HRMS, FTIR data of the title compound.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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