



Facile methods of siloxanes derivatives modification by azodyes based on eugenol

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ABSTRACT

In this paper, two simple methods of introducing an azodye into a siloxane matrix using hydrosilylation and azo coupling reactions are presented by the example of the model heptamethyltrisiloxane. It has been shown that the introduction of the bisazoeugenol fragment into the heptamethyltrisiloxane molecule results in the crystallization of the siloxane derivative. The obtained compound was studied by nuclear magnetic resonance (NMR) spectroscopy methods, polarization optical microscopy (POM) and differential scanning calorimetry (DSC).

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1. Introduction

A number of works devoted to the functionalization of the siloxane matrix by azo-compounds have recently been published. The reason for this trend, on the one hand, is the large structural diversity of siloxane compounds, and on the other hand, the unique properties of azo compounds [1]. It is known, that *cis-trans* isomerization is observed for azo compounds under the irradiation of a specific wavelength [2,3]. This phenomenon allows to change the geometry of whole azo-containing macromolecules, and, in turn, reveals new opportunities in creating “smart materials”, i.e. materials that can change their physical characteristics under the influence of external factors. This effect was used for the development of siloxane photoactuators [4], materials with nonlinear optical properties based on polyorganosiloxanes [5–7], self-organizing photosensitive layers based on trialkoxysilyl derivatives of azolysiloxanes [8,9], amphiphilic photosensitive molecules [10]. Azobenzene fragments often exhibit the properties of a typical mesogenic group [11–15], leading to the formation of liquid crystal molecular structures with nonlinear optical properties, which makes it possible to use them in combination with siloxane polymers to develop optical storage devices, displays,

photo switches and other active optical devices [16–20]. Commonly, the azo moiety is introduced into the siloxane matrix through a sequence of steps: alkylation of 4-phenylazophenol with allyl bromide and further hydrosilylation [12] or hydrothiolation [21,22] of allyloxy derivatives with a suitable siloxane derivative.

However, this approach does not make it possible to obtain siloxane derivatives with azo moieties containing functional groups whose presence inhibits hydrosilylation or hydrothiolation reactions.

The aim of this work was to find a simple and universal method for the preparation of azosiloxane derivatives based on an available natural compound - eugenol. It is known that eugenol, on the one hand, readily reacts with hydrosiloxanes by hydrosilylation reactions [23,24], on the other hand, subject to the azo coupling reaction [25,26], leading to the formation of azodyes. Therefore, it was chosen as a convenient precursor for the synthesis of azodye and further functionalization of the siloxane matrix.

2. Material and methods

Solvents: toluene, ethanol, acetone were purified under standard conditions and freshly distilled prior to use. Eugenol, sodium nitrite, dimethylchlorosilane, 1,1,3,3-tetramethyldisiloxane were purchased from Sigma-Aldrich with purity not less than 95% and used as it is. The Karstedt's catalyst was purchased from ABCR GmbH. Gel Permeation Chromatography (GPC) analysis was

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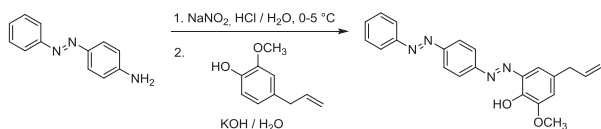
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performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation, Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 500 Å was used. ^1H , ^{13}C , ^{29}Si Nuclear Magnetic Resonance (NMR) spectra and their nucleus correlations were recorded using a Bruker Avance II 300 spectrometer at 300, 75 and 60 MHz, respectively. DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate 10 °C/min in argon. Polarization optical microscopy (POM) were performed with Axioscope 5 Series microscope (Carl Zeis).

2.1. Synthesis of 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMS)

This compound was synthesized according to the known procedure [2]. Yield of HMS was 78% as colorless dense liquid. B. p. 140–141 °C. ^1H NMR (300 MHz, Chloroform-*d*) δ : 4.65 (s, 1H, SiH), 0.12 (s, 21H, SiCH₃).

2.1.1. 6-(6-Phenylazo-3-phenylazo)-4-allyl-2-methoxyphenol (bis-azo-eug) (3)



To a stirred solution of 2.5 g (0.013 mol) of 4-aminoazobenzene in 50 ml of acetone, 28.2 ml of 11.3% HCl was added. Reaction mixture was then cooled to 0 °C. Then 10 ml 10% solution of NaNO₂ was added dropwise to the reaction mixture. Reaction mixture was stirred for 40 min at 0–5 °C. After that, 2.08 g (0.013 mol) of eugenol, dissolved in 50 ml acetone and 25 ml water with 25 ml of 10% aqueous NaOH were added to the reaction mixture. Reaction was stirred for 10 h at room temperature. After that, reaction mixture was acidified with 1 N HCl and precipitation was achieved via centrifugation. Pure product as dark red powder was obtained after recrystallization from concentrated AcOH. Yield of the product was 4.01 g (85%).

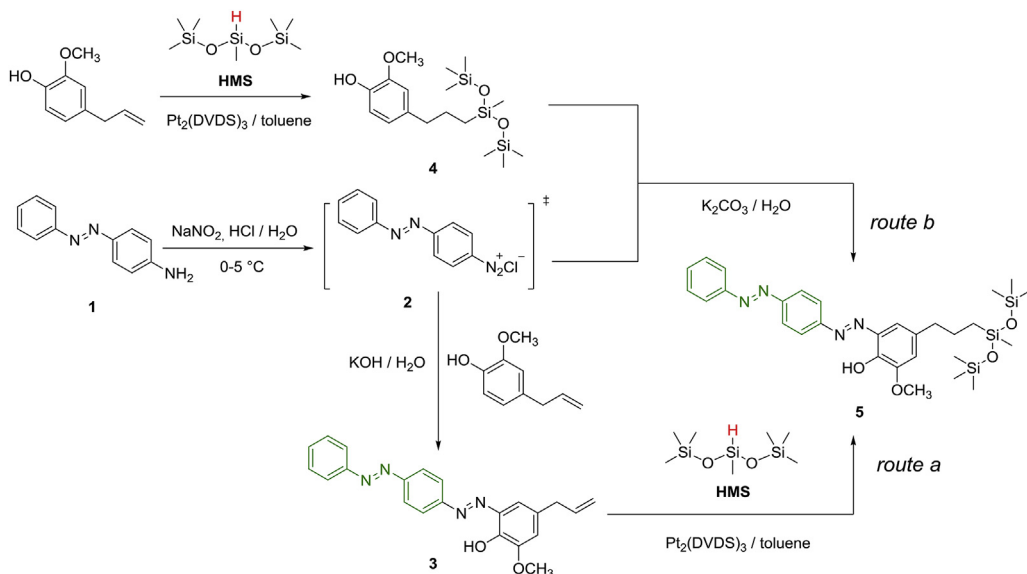
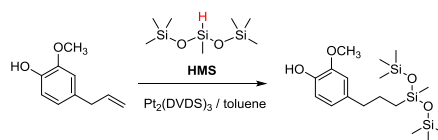


Fig. 1. Two approaches to the synthesis of the trisiloxane derivative of bisazoeugenol.

^1H NMR (300 MHz, DMSO-*d*₆) δ : 8.10 (dd, 4H, $J_1 = 8.5$ Hz; $J_2 \approx 21.1$ Hz; Ar-H), 7.51 (m, 5H, Ar-H), 6.98 (s, 2H, Ar-H), 5.99 (m, 1H, Vin), 5.15 (m, 2H, Vin), 3.96 (s, 3H, OCH₃), 3.47 (t, 2H, $J = 6.4$ Hz, CH₂). Calculated for C₂₂H₂₀N₄O₂: C 70.95%; H 5.41%; N 15.04%; O 8.59%. Found: C 71.11%; H 5.36%; N 15.67%.

2.2. Synthesis of 4-heptomethylsilylpropyl-2-methoxyphenol (4)



To a stirred mixture of 4.47 g (0.021 mol) of 1,1,1,3,5,5,5-heptomethyltrisiloxane (HMS) and 3.0 g (0.018 mol) of eugenol, purged with argon, were added 30 ml dry toluene and 30 μL of Karstedt's catalyst. Reaction mixture was stirred for 3 h. After reaction completed, reaction mixture was passed through silica and solvent was removed by evaporation under reduced pressure. Pure product was obtained as yellow oil. Yield of the product was 7.5 g (96%).

^1H NMR (300 MHz, Chloroform-*d*) δ : 6.85 (m, 3H, Ar-H), 6.68 (m, 2H, Ar-H), 3.89 (s, 3H, OCH₃), 2.55 (m, 2H, CH₂), 1.61 (m, 2H, CH₂), 0.50 (m, 2H, CH₂), 0.09 (s, 21H, Si-CH₃).

2.3. Synthesis of 4-heptomethylsilylpropyl-2-methoxy-6-(phenylazo)phenol (HMS-bis-azo-eug) (5)

2.3.1. Procedure 1

To the mixture of 2.0 g (0.01 mol) 4-aminoazobenzene in 20 ml H₂O, 5 ml of conc. HCl was added. After dissolving, reaction mixture was cooled to –5 °C and 0.86 g (0.01 mol) of aqueous solution of KNO₂ was added. After stirring for 60 min, the water emulsion of 3.93 g (0.01 mol) of 4-heptomethylsilylpropyl-2-methoxyphenol and 8.42 g (0.061 mol) of K₂CO₃ were added dropwise to the reaction mixture at vigorous stirring. After 3 h of stirring, toluene (50 ml) was added to the reaction mixture. Organic layer was washed with water and dried over Na₂SO₄. Solvent was

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