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Short Note

4-(2-Bromovinyl)benzocyclobutene

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Abstract: 4-(2-Bromovinyl)benzocyclobutene was prepared via a five stage synthesis starting from benzocyclobutene in an overall 30% yield. 4-(2-Bromovinyl)benzocyclobutene has a potential applications in synthesis of monomers for dielectric materials.

Keywords: BCB; benzocyclobutene; dielectric materials

1. Introduction

Benzocyclobutene containing polymers are of great interest in modern science because they have a variety of prominent characteristics, such as great thermal stability [1–4], low water uptake [1,5,6], high alkaline and acid stability [7,8], to complete with good dielectric properties [1,9–11]. These features make such materials prospective to use as dielectric coatings and this, in turn, stimulates the searching of benzocyclobutene containing monomers and their precursors.

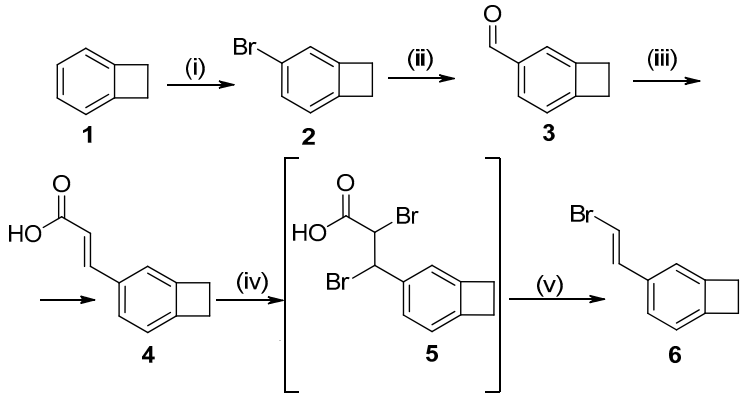
In this short communication, we describe synthesis of previously unknown 4-(2-bromovinyl) benzocyclobutene, a potential precursor for dielectric materials.

2. Results and Discussion

The target compound was synthesized in five steps. On the first stage 4-bromobenzocyclobutene (**2**) was prepared by biphasic bromination of benzocyclobutene (BCB) (**1**) using bromine [12]. Water was used as a medium which helps to remove hydrobromic acid produced. That is important as yields of bromination reactions are described to be strongly dependent on side processes of BCB aliphatic cycle cleavage in acidic media. 4-Bromobenzocyclobutene (**2**) reacted with magnesium in dry THF to produce Grignard reagent which with subsequent dry DMF addition into the reaction mixture gave 4-benzocyclobutenecarbaldehyde (**3**). Compound **3** reacted with malonic acid in pyridine using piperidine as a catalyst to give benzocyclobutenylacrylic acid (**4**) [13]. Bromination of **4** in carbon tetrachloride allowed to prepare compound **5** which was not isolated and used in the subsequent reaction with sodium carbonate and water to obtain the title compound. 4-(2-Bromovinyl)benzocyclobutene (**6**) was purified by vacuum distillation. In accordance with [14] dibromide **5** apparently reacted with base in aqueous media through E1 mechanism to give *trans*- and *cis*- isomers of **6** at a ratio of 95% to 5%.

The synthesis route is shown in Scheme 1.

Thus 4-(2-bromovinyl)benzocyclobutene was prepared from benzocyclobutene in 5 steps for the first time in overall yield of 30%.



Scheme 1. Synthesis route to the 4-(2-bromovinyl)benzocyclobutene. (i) Br_2, H_2O; (ii) a) Mg, THF (dry); b) DMF (dry); (iii) $CH_2(COOH)_2$, Py, Pip (cat.); (iv) Br_2, CH_2Cl_2; (v) Na_2CO_3, heating.

3. Materials and Methods

All reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and AlfaAesar (Lancaster, UK) and used without further purification unless otherwise stated. DMF was dried under calcium hydride and distilled under reduced pressure. NMR spectra were acquired using a Bruker AM-300 or a Bruker Avance 600 spectrometer (Bruker Corporation, Billerica, MA, USA) in $CDCl_3$. The chemical shifts are given in the δ scale relative to the residual proton signals and carbon atom signal of the solvent. High resolution electrospray ionization mass spectra were obtained with a Bruker micrOTOF II mass spectrometer (Bruker Corporation, Billerica, MA, USA) operating in either a positive ion mode (capillary voltage was 4500 V) or a negative ion mode (capillary voltage was 3200 V). The mass-to-charge (*m/z*) ratio ranges from 50 to 3000 Da. Both internal and external calibrations were accomplished with Electrospray Calibrant Solution (Fluka). A solution of the sample in MeCN, methanol, or water was injected via syringe, injection rate was 3 μL min^{-1}, nebulizing gas was nitrogen (3 L min^{-1}), inlet temperature was 180 °C. The reaction mixtures were analyzed, and the purity of all products was checked by TLC on Merck Silica gel 60 F254 UV-254 plates. All the spectra can be found at the Supplementary Materials.

*3.1. 4-Bromobenzocyclobutene (**2**)*

Benzocyclobutene (**1**) (23.7 g, 228 mmol, 1 equiv) was dispersed in water (240 mL) at room temperature. After cooling with ice water (−10–5 °C), bromine (11.7 mL, 228 mmol, 1 equiv) was added dropwise. After the completion of the 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 benzocyclobutene disappeared. The mixture was diluted with *n*-hexane (50 mL). Sodium sulfite (~3 g) was added. Upon the completion of the addition, the mixture was stirred at room temperature for 30 min until solution became colorless. Then, the organic layer separated and dried over anhydrous sodium sulfate was filtered to remove a drying agent, and concentrated under reduced pressure. The residue was distilled under reduced pressure (15 mm Hg) at 110–114 °C to give the title compound (**2**) (28–30 g, 67%–72%) as colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.26 (s, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.31–3.10 (m, 4H). NMR is in accordance with [15].

*3.2. Benzocyclobutene-4-carbaldehyde (**3**)*

To magnesium turnings (6.6 g, 274 mmol, 2 equiv), previously activated with an iodine crystal in anhydrous THF, 4-bromobenzocyclobutene (25 g, 137 mmol, 1 equiv) was added dropwise with stirring and cooling in an ice bath. After the completion of the addition, the reaction mixture was allowed to warm up to room temperature, stirred for 30 min, cooled again in an ice bath, and anhydrous DMF (20 g, 274 mmol, 2 equiv) was added dropwise, after which the reaction mixture was stirred overnight. A saturated solution of ammonium chloride was added, mixture was extracted with ethyl acetate,

the organic phase was washed with water, dried over sodium sulfate, and the solvent was evaporated on a rotary evaporator to obtain the title compound **3** as colorless liquid (17.2 g, 95%). It was used in the next step without purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.58 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 3.25 (s, 4H). NMR is in accordance with [16]. UV-vis (in hexane), λmax, nm: 207 (A = 0.66 a.u., log ε = 1.16), 251 (br) (A = 0.40 a.u., log ε = 0.94).

*3.3. 4-(Bicyclo[4.2.0]octa-1,3,5-triene-3-yl)propene-2-oic acid (**4**)*

A mixture of benzocyclobutene-4-carbaldehyde (19.6 g, 0.15 mol), malonic acid (18.53 g, 0.18 mol, 1.2 equiv), pyridine (50 mL) and piperidine (2.5 mL, 25.4 mmol, 0.17 equiv) was refluxed under inert atmosphere for 4 h. After cooling down water (100 mL) was added, and the precipitate formed was filtered and dried at rt to give compound **4** [17] as colorless crystals (21.7 g, 84%). M.p. = 150–152 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.9 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.30 (s, *J* = 5.1 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 3.23 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d6) δ 172.8, 149.5, 148.4, 146.6, 132.9, 128.4, 123.1, 121.1, 115.8, 29.80 29.35. HRMS: calculated for $C_{11}H_{10}O_2$ $[M + H]^+$: 175.0754; found *m/z*: 175.0758; calculated for $C_{11}H_{10}O_2$ $[M+Na]^+$: 197.0573; found *m/z*: 197.0577. FTIR, wavenumber of maxima, cm^{-1}: 710(w), 829(m), 865(m), 948(m), 985(m), 1172(w), 1201(w), 1225(s), 1294(m), 1313(s), 1338(s), 1414(w), 1428(m), 1472(w), 1586(m), 1624(s), 1681(s). UV-vis (in hexane), λmax, nm: 288 (br) (A = 0.15 a.u., log ε = 0.64).

*3.4. 4-(2-Bromovinyl)benzocyclobutene (**6**)*

To 4-(bicyclo [4.2.0]octa-1,3,5-trien-3-yl)propen-2-oic acid (21.7 g, 0.125 mol, 1 equiv) in 150 mL of CCl_4 bromine (6.5 mL, 0.125 mol, 1 equiv) was added with stirring, left to stir overnight and then evaporated on a rotary evaporator. To the resulting precipitate Na_2CO_3 (13 g, 0.123 mol, 2 equiv) and water (60 mL) were added, boiled with stirring for 1.5 h, cooled. The resulting oil was extracted with methylene chloride. The organic phase was washed with water, dried and evaporated. The product was purified by vacuum distillation (2 mm Hg, 131–138 °C) and obtained as slightly yellow oil. According to HPLC amount of *trans*- isomer is 95.7% and 3.9% of *cis*-isomer. Yield 14.2 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19–7.02 (m, 4H), 6.71 (d, *J* = 13.9 Hz, 1H, *trans*-), 6.40 (d, *J* = 8.0 Hz, 0.047H *cis*-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.35, 146.33, 138.2, 134.9, 125.6, 122.9, 119.9, 105.1, 29.68, 29.45. HRMS: calculated for $C_{10}H_9Br$ $[M + H]^+$: 210.9940; found *m/z*: 210.9934. FTIR, wavenumber of maxima, cm^{-1}: 690(w), 742(s), 778(s), 831(m), 880(w), 933(s), 1168(w), 1202(w), 1224(w), 1418(w), 1432(w), 1471(w), 1578(w), 1609(w). UV-vis (in hexane), λmax, nm: 210(A = 0.37 a.u., log ε = 1.11), 261 (br) (A = 0.25 a.u., log ε = 0.94).

Supplementary Materials: The following are available online. Figure S1: ^{1}H NMR spectrum of 4-benzocyclobut enecarbaldehyde, Figure S2: IR spectrum of 4-benzocyclobutenecarbaldehyde, Figure S3: UV-vis spectrum of 4-benzocyclobutenecarbaldehyde in hexane, Figure S4: ^{1}H NMR spectrum of benzocyclobutene- 4-acrylic acid, Figure S5: ^{13}C NMR spectrum of benzocyclobutene-4-acrylic acid, Figure S6: HRMS spectrum of benzocyclobutene- 4-acrylic acid, Figure S7: FTIR spectrum of benzocyclobutene-4-acrylic acid, Figure S8: UV-vis spectrum of benzocyclobutene-4-acrylic acid in hexane, Figure S9: IR spectrum of benzocyclobutene-4-acrylic acid, Figure S10: ^{1}H NMR of 3-(2-bromovinyl)benzocyclobutene, Figure S11: ^{13}C NMR spectrum of 3-(2-bromovinyl)benzocyclobutene, Figure S12: HRMS of 3-(2-Bromovinyl)benzocyclobutene, Figure S13: FTIR spectrum of 3-(2-bromovinyl) benzocyclobutene. Figure S14: UV-vis spectrum of 4-(2-bromovinyl) benzocyclobutene in hexane, Figure S15: HPLC data on 4-(2-bromovinyl)benzocyclobutene.

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