Turk J Chem
36 (2012) , 93 – 100.

doi:10.3906/kim-1105-67

Synthesis of the novel benzothiazole compounds from 7-benzylidenebicyclo [3.2.0] hept-2-en-6-ones and 2-aminobenzenethiol

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Received: 01.06.2011

Synthesis of the 2-(2-styrylcyclopent-3-enyl)benzo-[*d*]thiazoles (**6a-i**) is reported for the first time. Reaction of 7-benzylidenebicyclo [3.2.0] hept-2-en-6-ones (**3a-i**) and 2-aminobenzenethiol (**4**) in the presence of *p*-TsOH as a catalyst, in ethanol under reflux, resulted in the formation of novel 2-(2-styrylcyclopent-3-enyl)benzo[*d*]thiazoles in high yields.

Key Words: Benzothiazole, 2-aminobenzenethiol, synthesis, 2-(2-styrylcyclopent-3-enyl)benzo-[*d*]thiazole

Introduction

Benzothiazoles are important heterocyclic compounds with multiple applications. They have long been known to be biologically active,[1–3] and their varied biological features are still of great scientific interest nowadays. Benzothiazoles are widely found in bioorganic and medicinal chemistry with applications in drug discovery and have a very intensive antitumor,[4–11] antiviral,[12] anti-HIV,[13] and microbiological activity.[14,15] Benzothiazoles are used for treatment of autoimmune and inflammatory diseases,[16] in the prevention of solid organ transplant rejection, epilepsy,[17–19] amyotrophic lateral sclerosis,[20] and analgesia.[21] Further industrial applications as antioxidants,[22,23] vulcanization accelerators,[24,25] and a dopant in light emitting organic electroluminescent devices[26] have also been reported.

Numerous methods have been reported in the literature for the synthesis of benzothiazoles. Traditionally used methods are (i) condensation of 2-aminothiophenols with aldehydes,[27–30] carboxylic acids,[31–34] acid chlorides,[35,36] or esters[37,38] and (ii) Jacobson's cyclization of thiobenzanilides.[39–42]

This paper reports the direct synthesis of the novel benzothiazole compounds, 2-(2-styrylcyclopent-3-enyl)benzo[*d*]thiazoles, from the acid-catalyzed reaction of 7-benzylidenebicyclo[3.2.0]hept-2-en-6-ones (**2a-i**) with 2-aminobenzenethiol (**4**).

Experimental

General: Solvents were dried over standard drying agents and freshly distilled prior to use. All commercially available chemicals were used without further purification. All reactions were performed under nitrogen. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were measured with a Bruker Avance 400 MHz with tetramethylsilane as internal standard for solutions in deuteriochloroform. J values are given in Hz. Chemical shifts were reported in ppm relative to the solvent signal. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), and quin (quintet). All column chromatographic separations were performed using silica gel (Merck 60-230 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C in vacuo. IR spectra were recorded on a Jasco FTIR-430 spectrophotometer with NaCl optics. Mass spectra were recorded on a Thermofinnigan Trace GC/Trace DSQ/A1300 (E.I. Quadrupole, 70 eV) equipped with a SGE-BPX5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm). Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer.

Synthesis of 7-(2-substitutedbenzylidene)bicyclo[3.2.0]hept-2-en-6-one (**3a-i**). The starting compounds (**3a-i**) were prepared by using the recently reported method.[43]

(1R,5S,E)-7-(2-Methoxybenzylidene)bicyclo[3.2.0]hept-2-en-6-one (**3a**) Yellow solid, 97%, mp 180-182 °C. IR (KBr): δ max cm^{-1} 3045, 2936, 1636, 1569; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, J = 7.6, 1.2 Hz, 1H, ArH), 7.40-7.36 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H, ArH), 6.93 (t, J = 8.4 Hz, 1H, ArH), 6.04-6.01 (m, 1H), 5.87-5.86 (m, 1H), 4.37-4.36 (m, 1H), 3.91-3.88 (m, 1H), 3.86 (s, 3H, -OCH_3), 2.83-2.78 (m, 1H), 2.63-2.55 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.1, 159.2, 148.8, 133.0, 131.5, 129.5, 128.7, 123.1, 120.6, 119.1, 111.2, 60.3, 55.5, 49.7, 34.6.

(1R,5S,E)-7-(2-Bromobenzylidene)bicyclo[3.2.0]hept-2-en-6-one (**3b**) Yellow solid, 97%, mp 176-178 °C. IR (KBr): δ max cm^{-1} 3081, 2834, 1622, 1563; ^{1}**H-NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 1H, ArH), 7.64 (d, J = 8.0 Hz, 1H, ArH), 7.38 (t, J = 7.4 Hz, 1H, ArH), 7.28-7.22 (m, 2H), 5.98-5.96 (m, 1H), 5.91-5.89 (m, 1H), 4.37-4.36 (m, 1H), 3.95-3.90 (m, 1H), 2.86-2.81 (m, 1H), 2.65-2.58 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.4, 151.2, 133.8, 133.7(2C), 130.9, 128.8(2C), 127.5, 127.1, 122.6, 60.7, 49.5, 34.9.

General procedure for the synthesis of 2-(2-styrylcyclopent-3-enyl)benzo[*d*]-thiazoles (**6a-i**). An equimolar mixture of 7-benzylidenebicyclo [3.2.0] hept-2-en-6-ones (**3a-i**) and 2-aminobenzenethiol in ethanol and catalytic amount of p-TsOH was refluxed for 5 h. After the reaction was completed, the mixture was extracted with 20 mL of ethyl acetate and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give the desired products. Further purification was carried out by short column chromatography on silica gel (hexane/ethyl acetate (19:1)).

2-((1S,2S)-2-(2-Methoxystyryl)cyclopent-3-enyl)benzo[*d*]thiazole (**6a**) Yellow viscous oil, 93%. IR (KBr): δ max cm^{-1} 3056, 2927, 2852, 1513, 1461, 1290, 1243, 1105, 1027, 971, 754, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H, ArH), 7.89 (d, J = 8.0 Hz, 1H, ArH), 7.54-7.49 (m, 2H), 7.40 (t, J = 7.6 Hz, 1H, ArH), 7.26 (t, J = 7.4 Hz, 1H, ArH), 6.98 (t, J = 7.2 Hz, 1H, ArH), 6.94-6.90 (m, 2H), 6.38 (dd, J = 16.8, 8.0 Hz, 1H), 5.99-5.97 (m, 1H), 5.89-5.87 (m, 1H), 4.03-4.01 (m, 1H), 3.88 (s, 3H, -OCH_3), 3.86-3.82 (m, 1H), 3.18-3.12 (m, 1H), 3.07-3.00 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.9, 156.6, 153.2, 135.1, 132.9, 131.9, 129.8, 129.5, 128.3, 127.6, 126.7, 125.8, 125.6, 124.6, 122.7, 121.4, 120.6, 57.2, 55.3, 50.4, 40.1. GC-MS calcd. = 333. Found: M+1 = 333. Anal. Calcd for: $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20; S,

9.62. Found: C, 75.45; H, 5.36; N, 4.42; S, 9.95.

2-((1S,2S)-2-(2-Bromostyryl)cyclopent-3-enyl)benzo[*d*]thiazole (**6b**) Yellow viscous oil, 98%. IR (KBr): δ max cm^{-1} 3056, 2925, 2850, 1643, 1513,1465, 1436, 1311, 1261, 1108, 1022, 964, 755, 727; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.55 (bd, J = 8.0 Hz, 2H, ArH), 7.49 (t, J = 7.6 Hz, 1H, ArH), 7.38 (t, J = 7.6 Hz, 1H, ArH), 7.27 (t, J = 7.6 Hz, 1H, ArH), 7.09 (t, J = 7.6 Hz, 1H, ArH), 6.89 (d, J = 15.6 Hz, 1H), 6.29 (dd, J = 15.6, 8.0 Hz, 1H), 5.98-5.97 (m, 1H), 5.84-5.83 (m, 1H), 4.02-4.01 (m, 1H), 3.81 (dd, J = 8.0 Hz, 1H), 3.15-3.09 (m, 1H), 3.03-2.96 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.5, 153.1, 137.1, 135.1, 134.5, 132.9, 132.2, 130.3, 129.7, 128.4, 127.4, 127.1, 125.9, 124.8, 123.5, 122.7, 121.5, 56.5, 50.6, 39.9. GC-MS calcd. = 381/383. Found: M+1 = 381/383. Anal. Calcd for: $C_{20}H_{16}BrNS$: C, 62.83; H, 4.22; N, 3.66; S, 8.39. Found: C, 62.64; H, 4.29; N, 3.87; S, 8.56.

2-((1S,2S)-2-(4-Chlorostyryl)cyclopent-3-enyl)benzo[*d*]thiazole (**6c**) Yellow viscous oil, 96%. IR (KBr): δ max cm^{-1} 3056, 2962, 2850, 1646, 1509, 1436, 1261, 1091, 1012, 802, 727; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H, ArH), 7.85 (d, J = 8.0 Hz, 1H, ArH), 7.48 (t, J = 7.4 Hz, 1H, ArH), 7.36 (t, J = 7.4 Hz, 1H, ArH), 7.28 (m, 4H), 6.46 (d, J = 15.6 Hz, 1H), 6.30 (dd, J = 15.6, 8.0 Hz, 1H), 5.96-5.94 (m, 1H), 5.80-5.78 (m, 1H), 3.98-3.94 (m, 1H), 3.79 (dd, J = 16.0, 7.6 Hz, 1H), 3.13-3.09 (m, 1H), 3.01-2.96 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.6, 153.1, 135.7, 135.0, 132.9, 132.3, 132.2, 130.3, 129.5, 128.6, 127.5, 126.0, 124.8, 122.8, 121.5, 56.5, 50.3, 40.0. GC-MS calcd. = 337/338/339. Found: M+1 = 337/339. Anal. Calcd for: $C_{20}H_{16}ClNS$: C, 71.10; H, 4.77; N, 4.15; S, 9.49. Found: C, 70.92; H, 4.54; N, 4.36; S, 9.54.

2-((1S,2S)-2-(3-Bromostyryl)cyclopent-3-enyl)benzo[*d*]thiazole (**6d**) Yellow viscous oil, 95%. IR (KBr): δ max cm^{-1} 3056, 2929, 2850, 1590, 1436, 1311, 1241, 1108, 964, 759, 728, 682; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.85 (d, J = 8.0 Hz, 1H, ArH), 7.55 (bs, 1H), 7.47 (t, J = 7.6 Hz, 1H, ArH), 7.38-7.33 (m, 2H), 7.26 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 6.32 (dd, J = 15.6, 8.0 Hz, 1H), 5.95-5.94 (m, 1H), 5.78-5.76 (m, 1H), 3.97-3.93 (m, 1H), 3.77 (dd, J = 15.6, 8.0 Hz, 1H), 3.14-3.06 (m, 1H), 3.00-2.94 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.5, 153.1, 139.3, 134.9, 133.5, 133.1, 132.2, 130.4, 130.2, 130.0, 129.4, 129.1, 126.0, 125.0, 124.8, 122.8, 121.6, 56.5, 50.2, 40.0. GC-MS calcd. = 381/383. Found: M+1 = 381/383. Anal. Calcd for: $C_{20}H_{16}BrNS$: C, 62.83; H, 4.22; N, 3.66; S, 8.39. Found: C, 62.68; H, 4.08; N, 3.74; S, 8.48.

2-((1S,2S)-2-(3-Methylbromostyryl)cyclopent-3-enyl)benzo[*d*]-thiazole (**6e**). Yellow viscous oil, 97%. IR (KBr): δ max cm^{-1} 3056, 2923, 2854, 1513, 1436, 1311, 1108, 964, 759, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.49 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.23-7.21 (m, 3H), 7.07 (m, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.31 (dd, J = 16.0, 8.0 Hz, 1H), 5.97-5.94 (m, 1H), 5.81-5.79 (m, 1H), 3.96-3.92 (m, 1H), 3.79 (dd, J = 16.0, 7.2 Hz, 1H), 3.14-3.07 (m, 1H), 3.01-2.96 (m, 1H), 2.37 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.8, 153.1, 138.0, 137.0, 134.9, 132.6, 131.2, 130.8, 130.1, 128.4, 128.1, 127.0, 125.9, 124.7, 123.4, 122.7, 121.5, 56.7, 50.3, 39.9, 21.4. GC-MS calcd. = 317. Found: M+1 = 317. Anal. Calcd for: $C_{21}H_{19}NS$: C, 79.45; H, 6.03; N, 4.41; S, 10.10. Found: C, 79.23; H, 5.96; N, 4.21; S, 10.21.

2-((1S,2S)-2-(4-Methylbromostyryl)cyclopent-3-enyl)benzo[*d*]-thiazole (**6f**) Yellow viscous oil, 97%. IR (KBr): δ max cm^{-1} 3054, 3021, 2919, 2852, 1513, 1436, 1311, 1241, 1108, 966, 759, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 7.50 (t, J = 7.2 Hz, 1H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 6.50 (d, J

= 15.6 Hz, 1H), 6.29 (dd, J = 15.6, 8.0 Hz, 1H), 5.97-5.95 (m, 1H), 5.83-5.81 (m, 1H), 3.97-3.93 (m, 1H), 3.80 (dd, J = 16.0, 7.2 Hz, 1H), 3.15-3.08 (m, 1H), 3.02-2.97 (m, 1H), 2.37 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ74.9, 153.1, 137.1, 135.0, 134.3, 132.7, 130.7, 130.4, 130.0, 129.2, 126.2, 125.9, 124.7, 122.7, 121.5, 56.7, 50.4, 39.9, 21.2. GC-MS calcd. = 317/318/319. Found: M+1 = 316/317/318. Anal. Calcd for: $C_{21}H_{19}NS$: C, 79.45; H, 6.03; N, 4.41; S, 10.10. Found: C, 79.54; H, 6.11; N, 4.37; S, 10.25.

2-((1S,2S)-2-((4-Methoxystyryl)cyclopent-3-enyl)benzo[*d*]thiazole (**6g**) Yellow viscous oil, 97%. IR (KBr): δ max cm^{-1} 3056, 2931, 2834, 1606, 1509, 1436, 1249, 1174, 1033, 759, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.48 (t, J = 7.6 Hz, 1H, ArH), 7.37 (t, J = 7.6 Hz, 1H, ArH), 7.34 (d, J = 8.6 Hz, 2H, ArH), 6.87 (d, J = 8.6 Hz, 2H, ArH), 6.47 (d, J = 15.6 Hz, 1H), 6.19 (dd, J = 15.6, 8.0 Hz, 1H), 5.95-5.93 (m, 1H), 5.81-5.80 (m, 1H), 3.93-3.88 (m, 1H), 3.81 (s, 3H, -OCH_3), 3.81-3.75 (m, 1H), 3.13-3.07 (m, 1H), 3.01-2.94 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.9, 159.1, 153.1, 135.0, 132.8, 130.2, 129.9, 129.3, 127.5, 125.9, 124.8, 122.1, 121.5, 113.9, 56.7, 55.3, 50.5, 39.9. GC-MS calcd. = 333/334. Found: M+1 = 333/334. Anal. Calcd for: $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20; S, 9.62. Found: C, 75.72; H, 5.57; N, 4.28; S, 9.77.

2-(1S,2S)-2-((E)-2-(Thiophen-2-yl)vinyl)cyclopent-3-enyl)benzo-[*d*]thiazole (**6h**) Yellow viscous oil, 97%. IR (KBr): δ max cm^{-1} 3060, 2927, 2850, 1610, 1513, 1455, 1311, 1241, 1108, 954, 757, 694; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.49 (t, J = 7.2 Hz, 1H, ArH), 7.38 (t, J = 7.2 Hz, 1H, ArH), 7.14 (d, J = 4.8 Hz, 1H, **-**thienyl), 6.98-6.94 (m, 2H, **-**thienyl), 6.65 (d, J = 15.6 Hz, 1H), 6.18 (dd, J = 15.6, 8.0 Hz, 1H), 5.96-5.94 (m, 1H), 5.79-5.77 (m, 1H), 3.95-3.91 (m, 1H), 3.78 (dd, J = 16.0, 7.2 Hz, 1H), 3.13-3.06 (m, 1H), 3.00-2.93 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.7, 153.1, 142.3, 135.0, 132.3, 131.2, 130.3, 127.3, 125.9, 125.3, 124.8, 124.0, 123.9, 122.7, 121.5, 56.5, 50.2, 40.0. GC-MS calcd. = 309/310. Found: M+1 = 309/310. Anal. Calcd for: $C_{24}H_{19}NS2$: C, 74.77; H, 4.97; N, 3.63; S, 16.63. Found: C, 74.58; H, 4.69; N, 3.74; S, 16.81.

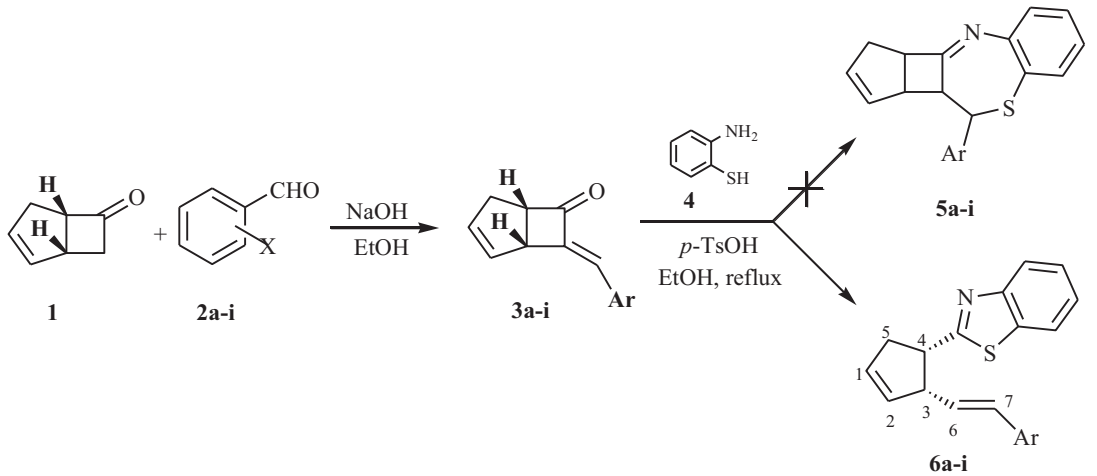
2-((1S,2S)-2-((E)-2-(Furan-2-yl)vinyl)cyclopent-3-enyl)benzo[*d*]-thiazole (**6i**) Yellow viscous oil, 93%. IR (KBr): δ max cm^{-1} 3056, 2925, 2852, 1513, 1436, 1311, 1241, 1014, 960, 759, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.49 (t, J = 7.2 Hz, 1H, ArH), 7.39-7.35 (m, 2H, ArH and -furyl), 6.37-6.36 (m, 1H, -furyl), 6.3-6.2 (m, 2H), 6.20 (d, J = 3.2 Hz, 1H, -furyl), 5.94-5.92 (m, 1H), 5.77-5.75 (m, 1H), 3.92-3.88 (m, 1H), 3.76 (dd, J = 16.0, 7.2 Hz, 1H), 3.11-3.0 (m, 1H), 2.97-2.93 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.8, 153.1, 152.6, 141.7, 134.9, 132.3, 130.2, 130.2, 125.9, 124.7, 122.7, 121.5, 119.2, 111.2, 107.3, 56.4, 50.3, 40.0; GC-MS calcd. = 293/294. Found: M+1 = 293/294; Anal. Calcd for: $C_{24}H_{19}NOS$: C, 78.02; H, 5.18; N, 3.79; S, 8.68. Found: C, 77.82; H, 5.02; N, 3.91; S, 8.84.

Results and discussion

The starting materials, 7-benzylidenebicyclo-[3.2.0]hept-2-en-6-ones (**3a,b** and **3c-i**[43]), were firstly synthesized from the condensation of *cis*-(1R,5S)-bicyclo[3.2.0]hept-2-en-6-one (**1**) with substituted benzaldehydes (**2a-g**), thiophene-2-carbaldehyde (**2g**), and furan-2-carbaldehyde (**2h**) according to our recently published procedure.[43]

Then the acid-catalyzed reaction of 7-benzylidenebicyclo[3.2.0]hept-2-en-6-ones (**3a-i**) with 2-aminobenzenethiol (**4**) was examined.[44] The reaction of 7-benzylidenebicyclo[3.2.0]hept-2-en-6-ones (**1a-i**) with 2-aminoben-

zenethiol (**4**) in the presence of 10% mol *p*-TsOH in ethanol under reflux resulted in the formation of the rearrangement products **6a-i**, 2-(2-styrylcyclopent-3-enyl)benzo[*d*]thiazoles (**6a-i**), instead of the expected 1,5-benzothiazepines (**5a-i**). The products **6a-i** were isolated in high yields (in the range of 93%-98%) after the usual work-up (Scheme 1, Table).



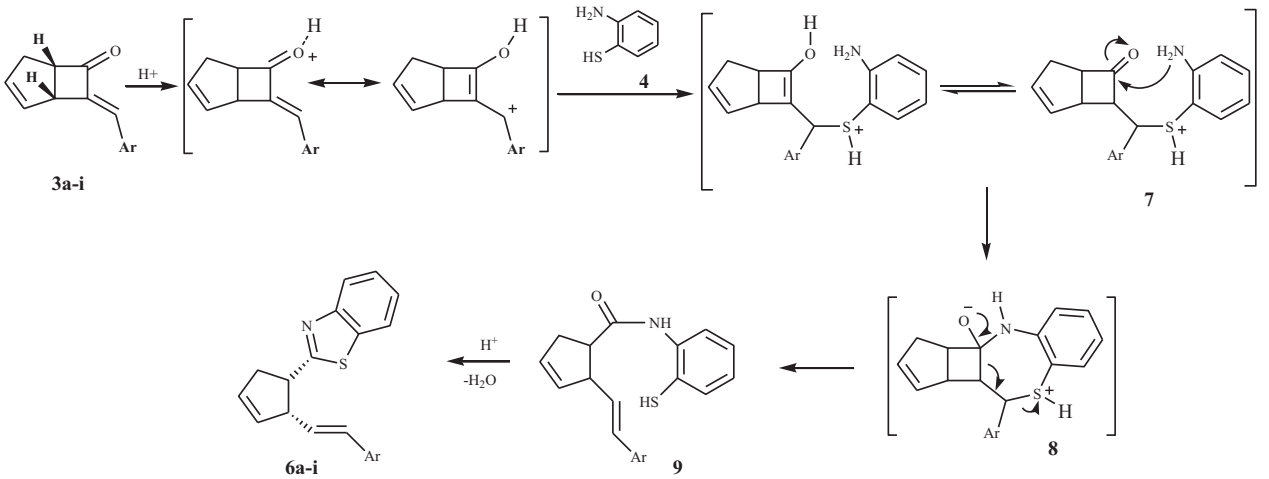
Scheme 1. Synthesis of the 2-(2-styrylcyclopent-3-enyl)benzo[*d*]thiazoles (**6a-i**).

Table. Synthesis of the 2-(2-styrylcyclopent-3-enyl)benzo[*d*]thiazoles (**4a-i**).

Entry	**3**	Ar	**6**	(% yield)
1	**3a**	2-$CH_3OC_6H_4$	**6a**	(93)
2	**3b**	2-BrC_6H_4	**6b**	(98)
3	**3c**	4-ClC_6H_4	**6c**	(96)
4	**3d**	3-BrC_6H_4	**6d**	(95)
5	**3e**	3-$CH_3C_6H_4$	**6e**	(97)
6	**3f**	4-$CH_3C_6H_4$	**6f**	(97)
7	**3g**	4-$CH_3OC_6H_4$	**6g**	(97)
8	**3h**	2-thiophenyl	**6h**	(97)
9	**3i**	2-furyl	**6i**	(93)

The structures of **6a-i** were established by IR, ^{1}H-NMR, ^{13}C-NMR, mass, and elemental analyses. The IR spectra of compounds **6** showed characteristic absorptions in the range of 759-728 cm^{-1} (C-S bond) and 1612-1590 cm^{-1} (C=N bond), respectively, which confirm the presence of a thiazole ring. In the ^{1}H-NMR spectra of **6a-i**, the styryl protons (H6 and H7) are represented as an AB system (A part of AB system, doublet of doublet, J = 16.8-15.6 and 8.0 Hz and B part of AB system, doublet J = 16.8-15.6 Hz) at the range of 6.89-6.47 and 6.38-6.19 ppm, respectively. The coupling constant JH6, H7 (16.8-15.6 Hz) confirms the *trans* configuration in compounds **6.** The ^{13}C-NMR spectra of **6a-i** showed the characteristic imine carbon atom (C=N) with chemical shift at 174.5-174.9 ppm. The mass spectra of compounds (**6a-i**) gave molecular ions peaks corresponding to their molecular masses.

We suggest the following mechanism to explain the rearrangement products (**6a-i**) (Scheme 2). The reaction proceeds first by Michael addition via the thiol pair of electrons followed by a reaction of the *o*-amino group with the carbonyl of the cyclobutanone moiety to give a hydroxyaminal intermediate **8** and this hydroxyaminal reverses by cleaving the cyclobutane system followed by elimination of the thiol functionality. At this stage, the reactants produce an *o*-mercaptoanilide **9**, which undergoes condensation, under acid catalysis, to give benzothiazole **6** as the final product.



Scheme 2. Proposed formation mechanism of rearrangement products 2-(2-styrylcyclopent-3-enyl) benzo[*d*]thiazoles (**6a-i**).

Conclusion

For the first time, the novel heterocycles 2-(2-styrylcyclopent-3-enyl)benzo[*d*]-thiazoles (**6a-i**) were prepared by the acid-catalyzed rearrangement reaction of 7-benzylidenebicyclo[3.2.0]hept-2-en-6-ones with 2-aminobenzenethiol in high yields.

Acknowledgment

We wish to thank the Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpaşa University.

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