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SHORT COMMUNICATIONS

4-(1-Adamantyl)-1,2,3-thiadiazole as a Source of Adamantylethynyl Sulfides

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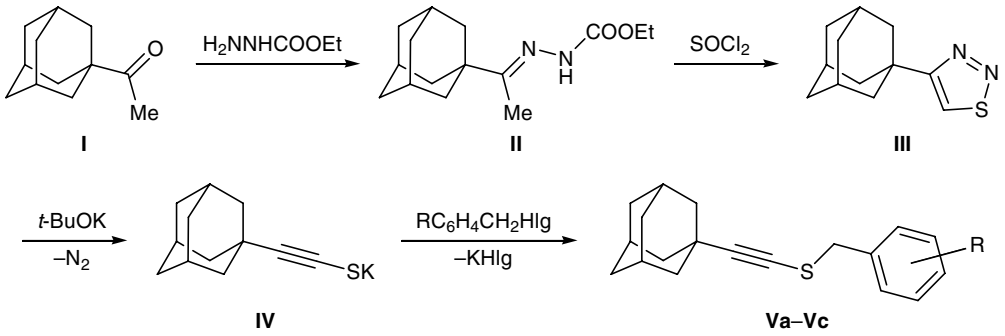
Prior to our studies, adamantyl-substituted 1,2,3-chalcogenadiazoles were almost unexplored. Only two representatives of such heterocyclic compounds were reported: 5-(1-adamantyl)-1,2,3-thiadiazole was synthesized from methyl adamantane-1-carbothioate and diazomethane [1], and a spiro derivative of 5-(2-adamantyl)-4,5-dihydro-1,2,3-thiadiazole was prepared from adamantane-2-thione [2]. We were the first to synthesize 4-(1-adamantyl)-1,2,3-thiadiazole according to Hurd and Mori [3]. The reaction of 1-adamantyl methyl ketone (**I**) with ethyl hydrazinecarboxylate gave 1-adamantyl methyl ketone ethoxycarbonylhydrazone (**II**) which was treated with thionyl chloride to obtain the target adamantyl-substituted 1,2,3-thiadiazole **III**. The structure of compound **III** was proved by the ^{1}H and ^{13}C NMR and mass spectra. 1,2,3-Thiadiazole **III** readily underwent decomposition by the action of such a strong base as potassium *tert*-butoxide in tetrahydrofuran; the process was accompanied by liberation of nitrogen, and weakly stable potassium 2-(1-adamantyl)ethynethiolate (**IV**) was formed. Despite instability of compound **IV**, we succeeded in recording its IR spectrum which contained a strong absorption band at 2115 cm^{-1} due to stretching vibrations of the C≡C bond. The corresponding band in the spectrum of potassium 2-phenylethynethiolate is located at 2089 cm^{-1} [4].

When the reaction with potassium *tert*-butoxide was performed in the presence of benzyl halides, we isolated the corresponding adamantylethynyl benzyl sulfides **Va**–**Vc** in good yields. The structure of acetylenic sulfides **Va**–**Vc** was confirmed by the ^{1}H and ^{13}C NMR, IR, and mass spectra. 1-(1-Adamantyl)-2-(3-nitrobenzylsulfanyl)ethyne (**Va**) showed in the IR spectrum a very weak absorption band at 2091 cm^{-1}, belonging to stretching vibrations of the C≡C bond. Analogous adamantyl-substituted acetylenic sulfides were not reported previously, though adamantylacetylenes were synthesized for the first time as early as 1962 [5], and they found fairly wide application in organic chemistry [6–9]. Thus we have developed a new method for the synthesis of adamantyl-substituted acetylenes from 4-(1-adamantyl)-1,2,3-thiadiazole.

Ethyl 2-[1-(1-adamantyl)ethylidene]hydrazine-1-carboxylate (II). A mixture of 50 g (0.28 mol) of



V, R = 3-O_2N, Hlg = Cl (**a**); R = 4-O_2N, Hlg = Br (**b**); R = 4-Br, Hlg = Br (**c**).

1-adamantyl methyl ketone (**I**), 32.5 g (0.31 mol) of ethyl hydrazinecarboxylate, 500 ml of ethanol, and two drops of hydrochloric acid was heated for 2 h under reflux. The solvent was partially distilled off (200 ml), and the residue was left for crystallization. The precipitate was filtered off, washed with 100 ml of ethanol, and dried. The product was chromatographically pure and was brought into further synthesis without additional purification (TLC: chloroform–methanol, 9:1; hexane–acetone–diethyl ether, 5:2:1). Yield 69 g (94%). Colorless fine needles, mp 153–155°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.27 t (CH_3CH_2), 1.68 m (CH_2, Ad), 1.70 s (CH_3C=N), 2.00 (CH, Ad), 4.12 q (OCH_2), 9.14 br.s (NH). Mass spectrum, *m*/*z* (I_{rel}, %): 264 (100) $[M]^+$, 176 (14) $[M - NHCO_2Et]^+$, 135 (16) $[Ad]^+$, 129 (19) $[M - Ad]^+$, 79 (10), 41 (5). Found, %: C 68.31, 68.43; H 9.42, 9.19. $C_{15}H_{24}N_2O_2$. Calculated, %: C 68.15; H 9.15. *M* 264.37.

4-(1-Adamantyl)-1,2,3-thiadiazole (III). A flask equipped with a magnetic stirrer, reflux condenser, and gas-outlet tube (connected with a system for absorption of gaseous hydrogen chloride) was charged with 69 g (0.26 mol) of hydrazone **II**, 400 ml of freshly distilled thionyl chloride was added, and the mixture was stirred for 1 h at 50°C. The mixture was then cooled to 20–25°C, excess thionyl chloride was distilled off under reduced pressure, and the residue was washed with water, dried, and recrystallized from 200 ml of methanol to isolate 42 g (72%) of thiadiazole **III**. The product was chromatographically pure (TLC: ethyl acetate–hexane, 1:10; chloroform–hexane, 1:2). Pale yellow plates, mp 95–97°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.82 m (6H) and 2.1 m (9H) (Ad), 8.57 s (5-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.92 (CH, Ad), 35.08 (C^1, Ad), 36.12 and 42.27 (CH_2, Ad), 129.98 (C^5), 172.37 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 192 (68) $[M - N_2]^+$, 149 (30), 135 (100) $[Ad]^+$, 111 (19), 97 (15), 91 (20), 79 (21), 41 (17). Found, %: C 65.23, 65.49; H 7.14, 7.41. $C_{12}H_{16}N_2S$. Calculated, %: C 65.42; H 7.32.

1-(1-Adamantyl)-2-(3-nitrobenzylsulfanyl)ethyne (Va). Thiadiazole **III**, 1 g (4.5 mmol), was dissolved in 25 ml of anhydrous tetrahydrofuran, 0.55 g (4.9 mmol) of potassium *tert*-butoxide was added under argon at room temperature, and the mixture was stirred for 5 min until nitrogen no longer evolved; during that time, potassium salt **IV** separated from the solution. A solution of 0.83 g (4.9 mmol) of *m*-nitrobenzyl chloride in 15 ml of anhydrous THF was then added, and the light violet mixture was stirred for 2 h, poured into 150 ml of water, and extracted with chloroform (3×15 ml). The combined extracts were dried over anhydrous sodium sulfate, the drying agent was filtered off, and the filtrate was treated with charcoal at the boiling point, filtered, and evaporated. The residue was recrystallized from ethanol to isolate 0.9 g (61%) of sulfide **Va**. The product was chromatographically pure (TLC: ethyl acetate–hexane, 1:10; hexane–acetone–diethyl ether, 5:2:1). Pale pink plates, mp 132–133°C. IR spectrum, ν, cm^{-1}: 2896, 2848, 2091 w (C≡C), 1532 (NO_2, asym.), 1350 (NO_2, sym.), 893, 870, 808, 692. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.66 m and 1.71 m (6H each, CH_2, Ad), 1.9 (CH, Ad), 3.98 s (CH_2), 7.62 t (5-H), 7.73 d (6-H), 8.15 d (4-H), 8.17 s (2-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 32.05 (CH, Ad), 35.17 (C^1, Ad), 40.66 (CH_2, Ad), 42.58 (CH_2), 47.17 (CH_2, Ad), 71.28 (SC≡), 109.27 (Ad**C**≡), 127.16 (C^2), 128.51 (C^4), 134.41 (C^5), 140.54 (C^6), 144.63 (C^1), 152.6 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 327 (87) $[M]^+$, 191 (75) $[M - Ad - H]^+$, 135 (100) $[Ad]^+$, 90 (78), 79 (52), 67 (31), 53 (22), 41 (34). Found, %: C 69.76, 69.83; H 6.29, 6.43. $C_{19}H_{21}NO_2S$. Calculated, %: C 69.69; H 6.46. *M* 327.44.

1-(1-Adamantyl)-2-(4-nitrobenzylsulfanyl)ethyne (Vb) was synthesized in a similar way using 1 g (4.5 mmol) of thiadiazole **III**, 0.55 g (4.9 mmol) of potassium *tert*-butoxide, and 1.05 g (4.9 mmol) of *p*-nitrobenzyl bromide. Yield 0.7 g (47%), pale yellow rhombic crystals, mp 97–98°C. IR spectrum, ν, cm^{-1}: 2894, 2848, 1515 (NO_2, asym.), 1349 (NO_2, sym.), 852, 796, 701. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.63 m and 1.69 m (6H each, CH_2, Ad), 1.91 (CH, Ad), 3.96 s (CH_2), 7.56 d (2-H, 6-H), 8.19 d (3-H, 5-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.01 (CH, Ad), 30.28 (C^1, Ad), 35.67 (CH_2, Ad), 37.94 (CH_2), 42.21 (CH_2, Ad), 66.34 (SC≡), 104.04 (Ad**C**≡), 123.05 (C^3, C^5), 130.01 (C^2, C^6), 145.00 (C^1), 146.65 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 327 (100) $[M]^+$, 191 (60) $[M - Ad - H]^+$, 135 (73) $[Ad]^+$, 91 (18), 79 (15), 67 (31), 53 (3), 40 (18). Found, %: C 69.41, 69.58; H 6.61, 6.72. $C_{19}H_{21}NO_2S$. Calculated, %: C 69.69; H 6.46. *M* 327.44.

1-(1-Adamantyl)-2-(4-bromobenzylsulfanyl)-ethyne (Vc) was synthesized in a similar way using 1 g (4.5 mmol) of thiadiazole **III**, 0.55 g (4.9 mmol) of potassium *tert*-butoxide, and 1.2 g (4.9 mmol) of *p*-bromobenzyl bromide. Yield 1 g (61%), colorless needles, mp 115–117°C. IR spectrum, ν, cm^{-1}: 2902, 2850, 1495, 1456, 832, 797. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.64 m and 1.70 m (6H each,

CH_2, Ad), 1.92 (CH, Ad), 3.81 s (CH_2), 7.22 d (3-H, 5-H), 7.46 d (2-H, 6-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.31 (CH, Ad), 30.27 (C^1, Ad), 35.74 (CH_2, Ad), 38.27 (CH_2), 42.26 (CH_2, Ad), 66.87 (SC≡), 103.49 (Ad**C**≡), 120.58 (C^4), 130.83 (C^2, C^3, C^5, C^6), 136.29 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 361 (2) $[M]^+$, 281 (2) $[M - Br]^+$, 191 (3) $[M - CH_2C_6H_4Br]^+$, 170 (71) $[CH_2C_6H_4Br]^+$, 135 (100) $[Ad]^+$, 90 (23), 79 (13), 67 (5), 53 (4), 41 (11). Found, %: C 62.89, 63.05; H 5.65, 5.77. $C_{19}H_{21}BrS$. Calculated, %: C 63.16; H 5.86. *M* 361.34.

The melting points were determined on a Boetius melting point apparatus. The IR spectra were recorded in KBr on an IKS-29 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AMX-400 instrument at 400 and 100 MHz, respectively, using residual proton signals and carbon signals of the deuterated solvent as reference. The mass spectra (electron impact, 70 eV) were obtained on a Kratos MS-890 mass spectrometer with direct sample admission into the ion source (ion source temperature 200°C). The progress of reactions was monitored by TLC on silica gel 60 F_{254}; spots were visualized under UV light or by treatment with iodine vapor. All solvents used in this work were purified and dehydrated according to standard procedures.

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