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LETTERS TO THE EDITOR

Synthesis of 1-Naphthylacetylene Sulfides from 4-(1-Naphthyl)-1,2,3-thiadiazole

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Abstract—4-(1-Naphthyl)-1,2,3-thiadiazole is readily decomposed under the action of potassium *tert*-butylate with the release of nitrogen and the formation of potassium 2-(1-naphthyl)ethynylthiolate. Upon further treatment of the reaction mixture with excess of alkyl halide, the corresponding alkyl 2-(1-naphthyl)-1-ethynylsulfides have been obtained. In the case of the reaction with allyl bromide, the resulting sulfide has undergone rearrangement. A mixture of *Z*- and *E*-isomers of 2-(1-naphthyl)-1-ethynyl-1-propenylsulfide has been obtained as the product of allylic rearrangement instead of the expected product of the thio-Claisen rearrangement.

Keywords: naphthalene, 1,2,3-thiadiazole, acetylene sulfides, alkylation, rearrangement

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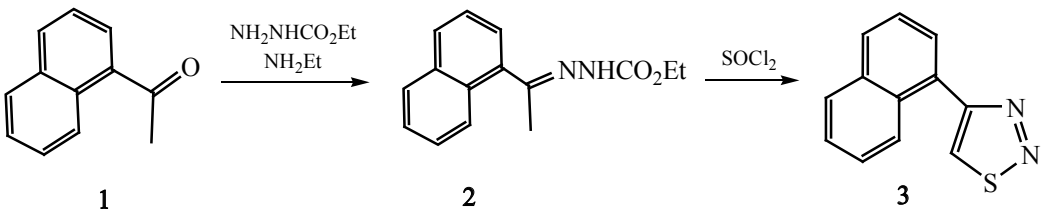
The first representative of 1-naphthylacetylene sulfides, phenyl-substituted 8-iodo-1-naphthylacetylene sulfide, was prepared for the first time during the synthesis of chiral dinaphthyl disulfides, the reagents for asymmetric synthesis [1]. *p*-Tolyl-substituted 1-naphthylacetylene sulfide has been recently synthesized via the reaction of C–S coupling of the corresponding thiophenol with 1,1-dibromo-1-alkene derivative of 1-naphthalene under the action of cesium carbonate [2]. Nickel-catalyzed cross-coupling of thioglycosides with bromoacetylene derivatives of 1-naphthalene leads to glycoside-substituted 1-naphthylacetylene sulfides, the inhibitors of b-glucosidase [3]. Synthesis of trifluoromethyl-substituted 1-naphthylacetylene sulfides has been reported [4, 5].

The review of reported data has shown significant interest to the synthesis of 1-naphthylacetylene sulfides. We have recently investigated the reactivity of 4-(1-naphthyl)-1,2,3-thiadiazole. It has been shown that this compound is readily decomposed under the action of strong bases to give 1-naphthylacetylene thiolate. it forms the corresponding amides of 1-naphthalenethioacetic acid in the presence of secondary amines; 1-naphthylacetylene thiolate gives 4-(1-naphthyl)-2-[1-(1-naphthyl)methylidene]-1,3-dithiol, the so-called dimer of acetylene thiolates, when treated with ethanol as the source of protons [6].

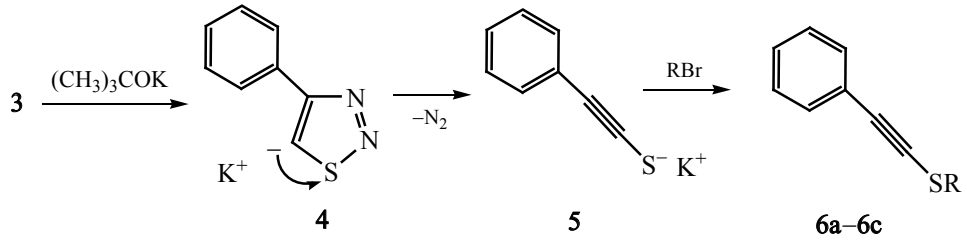
We suggested a new method for obtaining 1-naphthylacetylene sulfides from easily available 4-(1-naphthyl)-1,2,3-thiadiazole **3**. The latter compound was prepared from 1-naphthylmethylketone via the treatment of its ethoxycalbonylhydrazone **2** with thionyl chloride as described in [6] (Scheme 1).

Scheme 1.



1 **2** **3**

Scheme 2.



R = Bu (**a**), CH_2Ph (**b**), CH_2CO_2Et (**c**).

4-(1-Naphthyl)-1,2,3-thiadiazole **3** was readily decomposed when treated with potassium *tert*-butylate in anhydrous THF with liberation of nitrogen and formation of potassium 2-(1-naphthyl)ethynthiolate **5** (Scheme 2). Further treatment of the reaction mixture with the excess of alkyl halide gave butyl, benzyl, and ethylacetyl 2-(1-naphthyl)-1-ethynyl sulfides **6a**–**6c**.

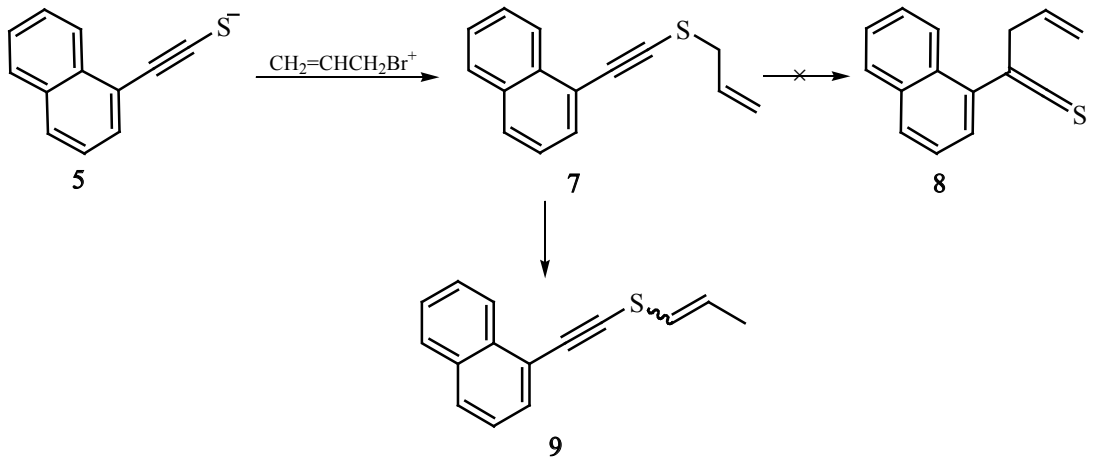
Structure of alkyl-2-(1-naphthyl)-1-ethynylsulfides **6a**–**6c** was elucidated by means of IR, ^{1}H NMR, and ^{13}C NMR spectroscopy as well as mass spectrometry. IR spectra of compounds **6a**, **6b** contained distinct signals of the triple bond stretching $\nu_{C\equiv C}$ at 2156 cm^{-1}. In the case of the ethylacetyl derivative **6c**, the bands of the triple bond stretching $\nu_{C\equiv C}$ (2119 cm^{-1}) and of the carbonyl group stretching $\nu_{C=O}$ (1720 cm^{-1}) were observed. The ^{13}C NMR spectra contained the signals of the triple bond carbon atoms at 82.07–84.66 ppm (C≡C–S) and 91.10–92.72 ppm (C≡C–S). Those data coincided with the experimental and calculated data for 2-phenylacetylene sulfides [7].

Alkyl- and phenyl-substituted ethynyl thiolates are known to form the product of thio-Claisen rearrangement **8** when alkylated with allyl bromide [8, 9]. In this study, alkylation of potassium 2-(1-naphthyl)ethynthiolate **5** with excess of allyl bromide initially gave 2-(1-naphthyl)ethynyl sulfide **7** which also underwent the rearrangement, but a mixture of *Z*- and *E*-isomers of 2-(1-naphthyl)-1-ethynyl-propenyl sulfide **9**, the products of allyl rearrangement, was isolated instead of the expected product of the thio-Claisen rearrangement (Scheme 3).

IR spectrum of compound **9** contained the stretching band of the triple bond ($\nu_{C\equiv C}$ 2151 cm^{-1}) and the stretching band of the double bond ($\nu_{C=C}$ 1621 cm^{-1}). ^{1}H NMR spectrum of that compound contained two signals of the methyl groups of *E*- and *Z*-isomers instead of a signal of the CH_2 group. The signals were assigned to *Z*- or *E*-isomers basing on the value of the CH=CH coupling constant: J =8.8 Hz for *Z*- and 14.4 Hz for *E*-isomer. The isomers ratio was determined from the integral intensities of the signals: *E*/*Z* = 54 : 46.

Butyl-2-(1-naphthyl)-1-ethynyl sulfide (6a). A solution of 0.4 g (9 mmol) of 4-(1-naphthyl)-1,2,3-thiadiazole

Scheme 3.



3 and 1 mL (9.32 mmol) of 1-bromobutane in 10 mL of THF was added to a suspension of 1.2 g (10.71 mmol) of potassium *tert*-butylate in 8 mL of freshly distilled THF. The reaction mixture was stirred for 5 min until nitrogen evolution was complete and then refluxed with stirring for 2 h. After removal of THF, the residue was suspended in water and extracted with chloroform. The extract was dried over sodium sulfate, and chloroform was distilled off. Yield 0.37 g (82%), brown oil, R_f 0.73. IR spectrum, ν, cm^{-1}: 2156 (C≡C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.02 t (3H, CH_3, J = 8.0 Hz), 1.59 sextet (2H, $CH_2CH_2\underline{CH_2}CH_3$, J = 7.2 Hz), 1.92 quintet (2H, $CH_2\underline{CH_2}CH_2CH_3$, J = 7.2 Hz), 2.94 t (2H, $\underline{CH_2}CH_2CH_2CH_3$, J = 7.2 Hz), 7.42–7.46 m (1H, Ar), 7.53–7.63 m (2H, Ar), 7.69–7.71 m (1H, Ar), 7.82–7.88 m (2H, Ar), 8.36–8.38 m (1H, Ar). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.69 (CH_3), 21.52 ($CH_2CH_2\underline{CH_2}CH_3$), 31.58 ($CH_2\underline{CH_2}CH_2CH_3$), 35.85 ($\underline{CH_2}CH_2CH_2CH_3$), 84.66 (=C−S), 91.10 (C=), 121.33, 125.27, 126.20, 126.41, 126.73, 128.32, 128.41, 130.18, 133.22, 133.39 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 240 (59) $[M]^+$, 184 (100) $[M - C_4H_8]^+$, 165 (24), 155 (83), 127 (46) $[C_{10}H_7]^+$, 71 (16), 57 (47) $[C_4H_9]^+$. Mass spectrum (HRMS), *m/z*: 263.0865 $[M + Na]^+$ (calculated for $C_{16}H_{16}S$: 263.0871).

Benzyl-2-(1-naphthyl)-1-ethynyl sulfide (6b) was obtained similarly from 2.82 g (25.18 mmol) of potassium *tert*-butylate in 10 mL of freshly distilled THF, 0.94 g (21.15 mmol) of 4-(1-naphthyl)-1,2,3-thiadiazole **3**, and 3 mL (27.05 mmol) of benzyl bromide in 6.0 mL of THF. After removal of chloroform, residual benzyl bromide was distilled off in vacuum. The residue was crystallized from ethanol. Yield 1.03 g (85%) yellow crystals, mp 63–64°C. R_f 0.46. IR spectrum, ν, cm^{-1}: 2156 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.12 s (2H, CH_2), 7.34–7.42 m (5H, Ar), 7.47–7.52 m (4H, Ar), 7.58–7.60 m (1H, Ar), 7.79–7.85 m (2H, Ar), 8.04–8.06 m (1H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.61 (CH_2), 83.78 (≡C−S), 92.72 (C≡), 121.03, 125.18, 126.27, 126.37, 126.68, 127.65, 127.84, 128.17, 128.42, 128.54, 128.71, 129.23, 130.22, 133.11, 133.27, 135.73 (Ar). Mass spectrum (HRMS), *m/z*: 297.0708 $[M + Na]^+$ (calculated for $C_{19}H_{14}S$: 297.0714).

Ethyl-2-[2-(1-naphthyl)-1-ethynylsulfanyl] acetate 6c was obtained similarly from 1.2 g (10.71 mmol) of potassium *tert*-butylate in 8 mL of freshly distilled THF, 0.4 g (9 mmol) of 4-(1-naphthyl)-1,2,3-thiadiazole **3**, and 1.53 mL (13.52 mmol) of ethyl bromoacetate in 10 mL of THF. Yield 0.44 g (86%), brown oil, R_f 0.65. IR spectrum, ν, cm^{-1}: 2119 (C≡C), 1720 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, CH_3, J = 7.2 Hz), 3.67 s (2H, CH_2C=O), 4.24 q (2H, $\underline{CH_2}CH_3$, J = 7.2 Hz), 7.40–7.42 m (1H, Ar), 7.51–7.60 m (2H, Ar), 7.65–7.67 m (1H, Ar), 7.82–7.86 m (2H, Ar), 8.29–8.31 m (1H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.10 (CH_3), 37.92 (CH_2C=O), 61.98 ($\underline{CH_2}CH_3$), 83.78 (=C−S), 92.72 (C=), 120.60, 125.18, 126.12, 126.47, 126.85, 128.28, 128.91, 130.497, 133.13, 133.33 (Ar), 168.39 (C=O). Mass spectrum, (HRMS), *m/z*: 271.0787 $[M + H]^+$ (calculated for $C_{16}H_{14}O_2S$: 271.0793).

(*Z*,*E*)-2-(1-Naphthyl)-1-ethynyl-1-propenylsulfide (9) was obtained similarly from 1.2 g (10.71 mmol) of potassium *tert*-butylate in 8 mL of freshly distilled THF, 0.4 g (9 mmol) of 4-(1-naphthyl)-1,2,3-thiadiazole **3**, and 1.0 mL (11.55 mmol) of allyl bromide in 10 mL of THF. Yield 0.28 g (66%), brown oil, R_f 0.73. IR spectrum, ν, cm^{-1}: 1621 (C=C), 2151 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85 d. d (3H, *E*-$\underline{CH_3}$CH=CH, J = 6.8, 1.6 Hz), 1.89 d. d (3H, *Z*-$\underline{CH_3}$CH=CH, J = 6.4, 1.6 Hz), 5.90 d. q (1H, *E*-$CH_3\underline{CH}$=, J =14.4, 6.8 Hz), 6.02 d. q (1H, *E*-CH_3CH=$\underline{CH}$, J = 14.4, 1.6 Hz), 6.12 d. q (1H, *Z*-$CH_3\underline{CH}$=, J = 8.8, 6.4 Hz), 6.27 d. q (1H, *Z*-CH_3CH=$\underline{CH}$, J = 8.8, 1.6 Hz), 7.42–7.47 m (1H, Ar), 7.55–7.63 m (2H, Ar), 7.68–7.73 m (1H, Ar), 7.83–7.89 m (2H, Ar), 8.29–8.31 m (1H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.22 (CH_3), 82.27 (≡C−S), 91.26 (C≡), 118.3 (*E*-SCH=), 120.74 (*E*-SC=CH), 120.81 (*Z*-SC=CH), 125.23 (*Z*-SCH=), 126.14, 126.17, 126.47, 126.50, 126.84, 126.90, 127.66, 128.21, 128.32, 128.75, 128.93, 130.39, 130.63, 133.18, 133.34 (Ar). Mass spectrum (HRMS), *m/z*: 225.1588 $[M + H]^+$ (for $C_{15}H_{12}S$ calculated: 225.0738).

Melting points were measured using a Boetius apparatus. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance III HD spectrometer (400.13 and 100.16 MHz, respectively). Mass spectra were obtained using a Finnigan INCOS 50 spectrometer (direct injection of specimen, ionization cell temperature 200°C, ionizing electron energy 70 eV). High-resolution mass spectra (HRMS-ESI) were registered using a Micromass 70-VSE device with electrospray ionization. IR spectra were obtained using a Shimadzu IRTracer 100 Fourier spectrometer with the Specas DCIR console equipped with a diamond window. Reactions progress was monitored by TLC on Silufol UV-254 plates (elution with 1 : 4 ethyl acetate–hexane), development with UV light and iodine vapor. The solvents were purified and dehydrated according to standard protocols.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Feldman, K.S., Ruckle, R.E., Ensel, S.N., and Weinreb, P.H., *Tetrahedron Lett*., 1992, vol. 33, no. 47, p. 7101. doi 10.1016/50040-4039(00)60846-8
2. Ni, Z., Wang, S., Mao, H., and Pan, Y., *Tetrahedron Lett*., 2012, vol. 53, no. 30, p. 3907. doi 10.1016/j.tetlet.2012.05.072
3. Brachet, E., Brion, J.-D., Alami, M., and Messaondi, S., *Chem. Eur. J*., 2013, vol. 19, no. 45, p. 15276. doi 10.1002/chem.201302999
4. Zhu, S.-Q., Xu, X.-H., and Qing, F.-L., Eur, J. Org. Chem., 2014, no. 21, p. 4453. doi 10.1002/ejoc.201402533
5. Chem, C., Chu, L., and Quing, F.-L., *J. Am. Chem. Soc*., 2012, vol. 134, no. 30, p. 12454. doi 10.1021/ja305801m
6. Yekhlef, M., Petrov, M.L., and Pevzner, L.M., *Russ. J. Gen. Chem*., 2016, vol. 86, no. 7, p. 1762. doi 10.1134/S1070363216070379
7. Petrov, M.L. and Belyakov, A.V., *Tetrahedron Lett*., 2003, vol. 44, no. 3, p. 599. doi 10.1016/S0040-4039(02)02576-5
8. Sukhai, R.S. and Brandsma, L., *Rec. Trav. Chim. Pays-Bas*., 1979, vol. 98, no. 2, p. 55. doi 10.1002/recl.19790980207
9. Schaumann, E. and Grabley, F.-F., *Lieb. Ann. Chem*., 1979, no. 11, p. 1746. doi 10.1002/jlac.197919791113