Russian Journal of General Chemistry, Vol. 73, No. 5, 2003, pp. 782–785. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 5, 2003, pp. 827–830.
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Organylthiochloroacetylenes: VI.[1] Reaction of Alkylthiochloroacetylenes with Sodium Azide

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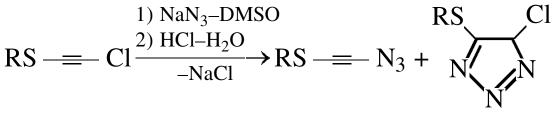
Received May 4, 2001

Abstract—Alkylthiochloroacetylenes react with sodium azide in mild conditions (20°C, DMSO) to give alkylthioethynyl azides and 4-chloro-5-alkylthio-4*H*-1,2,3-triazoles in a total yield of 72%.

Organyl azides are easily formed in reactions of alkali metal azides with various electrophiles [2]. At the same time, haloacetylenes have never been involved in such reactions. Unsuccessful nucleophilic substitution of chlorine in dialkyl (2-chloroethynyl)phosphonates with sodium azide has only been reported [3]. On the other hand, acetylenes with electron-acceptor substituents, such as C≡N, RC=O, O=CNH$_2$, O=COR, (EtO)$_2$P=O, and Ph$_3$P$^+$, react with metal azides by the 1,3-dipolar addition scheme, yielding (in protic solvents or on treatment of the reaction mixture with acids) 1,2,3-triazoles [4–6]. Substituted triazoles have also been prepared from perfluoroalkyl(aryl)bromoacetylenes and aromatic azides [7]. We recently showed for the first time that chloro(ethylthio)acetylene reacts with sodium azide in DMSO to give ethylthioethynyl azide in 28% yield [8].

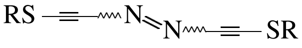
Aiming at extending the synthetic potential of organylthiochloroacetylenes and obtaining new data of the scarcely explored nucleophilic substitution at *sp*-carbon atom, we have studied reaction of alkylthiochloroacetylenes **Ia** and **Ib** with sodium azide to show that successive treatment of chloroacetylenes **Ia** and **Ib** with NaN$_3$–DMSO and aqueous HCl results in formation of not only alkylthioethynyl azides **IIa** and **IIb**, but also 4-chloro-5-alkylthio-4*H*-1,2,3-triazoles **IIIa** and **IIIb**. The reaction is exothermic (the reaction temperature was maintained at 25–28°C by external cooling), and the yields of products **IIa**, **IIb** and **IIIa**, **IIIb** are 28–34 and 34–38%, respectively.



Ia, Ib **IIa, IIb** **IIIa, IIIb**

R = Et (**Ia, IIa, IIIa**), *n*-Pr (**Ib, IIb, IIIb**).

The IR spectra of ethynyl azides **IIa** and **IIb** display strong absorption bands at 2114 [ν_{as}(N=N=N)] [9] and 2200 cm^{-1} [ν(C≡C)], whereas the ν(C≡C) band of the starting alkylthiochloroacetylenes is much weaker and shifted red (2150 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of compounds **IIa** and **IIb** are also consistent with the proposed structure. At the same time, we failed to obtain a high-quality ^{15}N NMR spectum of these azides, since they are unstable and easily decompose even in an inert atmosphere, evolving nitrogen and forming dark brown products. Thus, after a day, the nitrogen content of these products is ~60% lower that in starting azides **II**. The spectral data and elemental analyses allow these compounds to be assigned the structure of 1,2-bis[2-alkylthioethynyl]diazenes **IV** and their oligomers.



IV

As would be expected, the latter compounds are unstable and readily available for further transformations.

In the IR spectra of compounds **IV**, the C≡C band at 2200 cm^{-1} is preserved, but the N=N=N band is lacking. The ^{1}H NMR spectra show signals of two alkylthio groups, and the ^{13}C NMR spectrum contains, along with alkyl proton signals at 12–30 ppm, two more signals at 90 and 152 ppm from the ≡C–S and ≡C–N=N carbon atoms. The ^{15}N NMR spectra display a single signal at –112 ppm, assignable to the N=N nitrogen atoms [10–14]. The formation of these compounds is consistent with known transformation schemes of organyl azides [15] and involves elimination of a nitrogen molecule from azides **II**, followed by dimerization of the intermediate alkylthioethynylnitrenes.

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[1] For comminication V, see [1].

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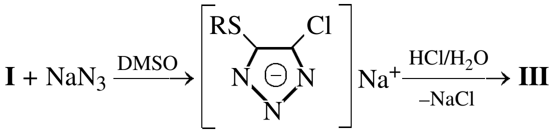
$$2\mathbf{II}\xrightarrow[-\mathrm{N}_2]{}2\mathrm{RS}{-}{\equiv}{-}\mathrm{N}{:}\longrightarrow\mathbf{IV}$$

The structure of 4-chloro-5-alkylthio-4*H*-1,2,3-triazoles **III** was proved by ^{1}H and ^{13}C NMR and IR spectroscopy, and their composition, by elemental analysis. According to [16–19], the IR absorption bands of triazoles **III** at 1291, 1100, 1014, and 942 cm^{-1} relate to triazole ring vibrations. The ^{13}C NMR spectra show, along with alkyl carbon signals, two more signals at 63 and 112 ppm, due to ring carbon atoms [20–22]. In the proton-coupled ^{13}C spectrum of compound **IIIb**, the upfield triazole ring carbon signal is a doublet with the coupling constant 158 Hz [20].

Triazoles **III** are expected [6] products of 1,3-dipolar cycloaddition of sodium azide to acetylenes **I**.



Chloroacetylenes **I** fail to react with sodium azide in dioxane or diethyl ether. From the reaction mixture we isolated the starting NaN_3 and polymerization products of chloroacetylenes **I**.

Knowing that palladium halides catalyze reactions of haloacetylenes, specifically, carbonylation with carbon monoxide [23], we checked utility of the $PdCl_2$ catalyst for enhancing the efficiency and selectivity of the reaction of compound **I** in study. Contrary to expectations, in this case alkylthiochloroacetylenes form with sodium azide a complex mixture of unidentified products.

Thus, the reaction of sodium azides with accessible alkylthiochloroacetylenes [24] provides a convenient synthetic route to previously unknown organylthioethynyl azides and 4-chloro-5-alkylthio-4*H*-1,2,3-triazoles.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in microlayer. The ^{1}H and ^{13}C NMR spectra were obtained on Jeol FX-90Q (90 MHz) and Bruker DPX-400 (400 MHz) spectrometers in $CDCl_3$; internal reference HMDS.

Thin-layer chromatography was performed on alumina plates in hexane, developer I_2.

Reaction of ethylthiochloroacetylene (Ia) with sodium azide. Acetylene **Ia**, 2.00 g, was added dropwise with stirring over the course of 25 min to a suspension of 1.08 g of sodium azide in 10 ml of DMSO. Heat release was observed. The reaction temperature was maintained within 25–28°C by external cooling. When addition of acetylene **Ia** was complete, the reaction mixture was allowed to stir for an additional 3 h at 20–22°C and then poured into 40 ml of cold water and extracted with ether (3 × 10 ml). The ether extract was washed with water (3 × 10 ml), dried with Na_2SO_4, the ether was removed in a vacuum, and the residue was subjected to a vacuum to isolate 0.59 g (28%) of ethylthioethynyl azide (**IIa**) as an oily substance soluble in most organic solvents and insoluble in water. IR spectrum, cm^{-1}: 2960, 2928, 2870 [ν(C–H)], 2198 [ν(C≡C)], 2114 [ν_{as}(N=N=N)], 1514, 1442, 1370, 1084, 1042, 956, 900, 865, 814 [δ(C–H)], 1242 [ν_s(N=N=N)], 760 [ν(C–S)]. ^{1}H NMR spectrum, δ, ppm: 1.35 t (3H, CH_3), 2.68 q (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.34 (CH_3), 28.13 (CH_2), 85.95 (≡CS), 116.21 (≡CH_3) [20, 22, 25, 26]. Found, %: C 37.05; H 4.49; N 32.03; S 25.85. $C_4H_5N_3S$. Calculated, %: C 37.78; H 3.96; N 33.04; S 25.22.

Azide **IIa** was allowed to stand for 48 h at room temperature in an inert atmosphere (argon) and analyzed once more. The spectral characteristics and elemental analyses are consistent with structure **IVa**. IR spectra, cm^{-1}: 2960, 2914, 2870 [ν(C–H)], 2198 [ν(C≡C)], 1514, 1442 [δ(C–H)], 1370, 1256, 1084, 1042, 956, 914, 865, 814 [δ(C–H)], 760 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.35 t (3H, CH_3), 2.87 q (2H, CH_2) 2.99 t (2H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.83, 14.60, 28.15, 28.18, 90.70 (≡C–S), 152.38 (≡C–N=N) [20, 22, 25, 26]. Found, %: C 47.93; H 5.19; N 13.00; S 31.89. $C_8H_{10}N_2S_2$. Calculated, %: C 48.45; H 5.08; N 14.13; S 32.34.

The aqueous layer after ether extraction was combined with washings, acidified with 10% HCl (~2 ml) to pH 4, and extracted with chloroform (5 × 5 ml). The chloroform extract was washed with water (3 × 10 ml), dried with Na_2SO_4, and the solvent was removed in a vacuum to obtain 0.93 g (34%) of 4-chloro-5-ethylthio-4*H*-1,2,3-triazole (**IIIa**), viscous light brown liquid. IR spectrum, cm^{-1}: 2980, 2932, 2850 [ν(C–H)], 1442, 1335, 1164, 824 [δ(C–H)], 1260 [ν(N–N=N)], 1080, 970, 890 (triazole ring), 782, 734, 656 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 t (3H, CH_3), 2.74 q (2H, CH_2), 2.89 s (1H, CHCl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.45, 28.62 (EtS), 64.28 (ring CHCl), 113.79 (ring S–C=N). Found, %: C 30.02; H 4.05; Cl 22.00; N 25.03; S 20.01. $C_4H_6Cl \cdot N_3S$. Calculated, %: C 29.36; H 3.70; Cl 21.67; N 25.68; S 19.60.

(*n*-Propylthio)ethynyl azide (IIb) and 4-chloro-5-alkylthio-4*H*-1,2,3-triazole (IIIb) were prepared with the above procedure from 0.97 g of sodium azide and 2.00 g of acetylene **Ib** in 8 ml of DMSO. Yields of compounds **IIb** and **IIIb** 0.72 (34%) and 1.00 g (38%), respectively. *n*-Propylthioethynyl azide (**IIb**). IR spectrum, cm^{-1}: 2950, 2928, 2860 [ν(C–H)], 2200 [ν(C≡C)], 2114 [ν_{as}(N=N=N)], 1514, 1460, 1380, 1292, 1092, 938, 898, 782 [δ(C–H)], 1230 [ν_s(N=N=N)], 728 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 m (CH_3), 1.70 m (CH_2), 2.67 m (CH_2S). Found, %: C 41.90; H 5.20; N 28.25; S 22.98. $C_5H_7N_3S$. Calculated, %: C 42.53; H 5.00; N 29.76; S 22.71. 4-Chloro-5-(*n*-propylthio)-4*H*-1,2,3-triazole (**IIIb**). IR spectrum, cm^{-1}: 2970, 2928, 2870 [ν(C–H)], 1470, 1414, 1384, 1300, 830 [δ(C–H)], 1242 [ν(N–N=N)], 1120, 1099, 1056, 900 (triazole ring) 728, 700 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 t (3H, CH_3), 1.73 m (2H, CH_2), 2.87 s (1H, CHCl), 3.04 t (2H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.75, 23.62, 36.39 (PrS), 63.69 (ring CHCl), 112.57 (ring S–C=N). ^{13}C–{^{1}H} NMR spectrum ($CDCl_3$), δ, ppm: 13.62 q, 23.86 t, 36.10 t (PrS), 64.02 d (*J* 158 Hz), 113.12 s. Found, %: C 34.02; H 5.28; Cl 20.30; N 24.03; S 18.95. $C_5H_8 \cdot ClN_3S$. Calculated, %: C 33.80; H 4.54; Cl 19.96; N 23.66; S 18.05.

Reaction of chloro(*n*-propylthio)acetylene with sodium azide in DMSO in the presence of $PdCl_2$. Acetylene **Ib**, 2.00 g, and 0.026 g of $PdCl_2$ were added dropwise with stirring to 0.97 g of sodium azide in 8 ml of DMSO. Heat release was observed. The reaction temperature could be maintained within 65–70°C by external heating. After addition of acetylene was complete, the mixture was allowed to stir for an additional 3 h at 20–25°C, poured into 30 ml of cold water and extracted with ether (3 × 10 ml). The ether extract was washed with water (3 × 10 ml), dried with Na_2SO_4, the ether was removed in a vacuum, and the residue was subjected to a vacuum to isolate 0.85 g of a mixture of compounds (TLC). IR spectrum, cm^{-1}: 2970, 2935, 2870 [ν(C–H)], 2200 [ν(C≡C)], 2156 [ν(C≡C)], 2121, 1642, 1512, 1463, 1412, 1374, 1298, 1235, 1200, 1091, 1021, 949, 877, 784, 735, 535. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99–1.25 m (CH_3), 1.70–1.82 m (CH_2), 2.63–2.70 m (CH_2S), 3.44 s. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.56, 13.85, 13.97, 23.23, 23.27, 23.52, 33.23, 37.83, 39.22, 60.86, 69.58, 86.44, 91.46. Found, %: C 46.03; H 6.75; Cl 12.48; N 6.07; S 28.54.

The aqueous layer after ether extraction was combined with washings, acidified with 10% HCl (~2 ml) to pH 4, and extracted with chloroform (5 × 5 ml). The chloroform extract was washed with water (3 × 10 ml), dried with Na_2SO_4, and the solvent was removed in a vacuum to isolate 0.33 g of a dark brown liquid (according to TLC, a mixture of compounds). IR spectrum, cm^{-1}: 2970, 2928, 2810, 2242, 2211, 2128, 1648–1642, 1521, 1470, 1442, 1391, 1330, 1242, 1144, 1028, 984, 900, 798, 742. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99–1.03 m, 1.24 m, 1.63–1.76 m, 2.91 m, 3.06 m. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.85, 19.44, 23.72, 36.49, 36.54, 92.56, 112.27, 122.32. Found, %: C 42.39; H 5.26; Cl 5.08; N 20.05; S 19.29.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32939).

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