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Letters to the Editor

Reaction of alkylthiochloroacetylenes with sodium azide

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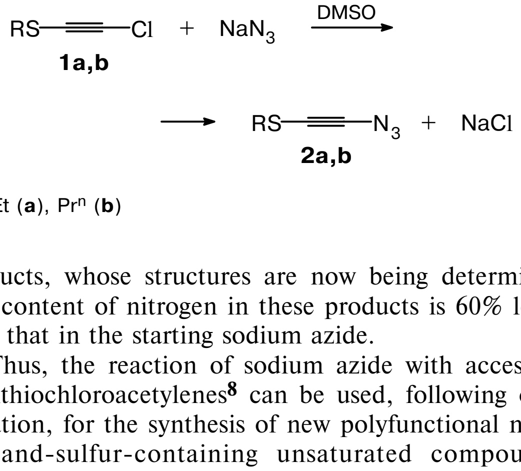
Organyl azides can be easily prepared by reactions of alkali metal azides with various electrophiles.[1] However, the possibility of involving haloacetylenes in this reaction has not been reported in the literature. An attempt to carry out the nucleophilic substitution of the Cl atom in dialkyl 2-chloroethynylphosphonates by the action of sodium azide failed.[2] On the other hand, the reactions of acetylenes possessing electron-acceptor substituents such as $C\equiv N$, $RC=O$, $CONH_2$, $COOR$, $(EtO)_2P=O$, and Ph_3P^+ with metal azides follow the mechanism of 1,3-dipolar addition to form 1,2,3-triazoles (in protic solvents or upon treatment of the reaction mixtures with acids).[3—5] Substituted triazoles were also synthesized from perfluoroalkyl(aryl)bromoacetylenes and aryl azides.[6]

We showed for the first time that haloacetylenes (*e.g.*, alkylthiochloroacetylenes (**1a,b**)) react with sodium azide under mild conditions (20—22 °C, 3 h, DMSO) according to the mechanism of nucleophilic substitution (Scheme 1) to give alkylthioethynyl azides (**2a,b**) in ~30% yield (non-optimized).

Scheme 1



R = Et (**a**), Pr^n (**b**)

The IR spectra of ethynyl azides **2** contain intense absorption bands at 2114 ($\nu_{as}(N=N=N)$)[7] and 2200 cm^{-1} ($\nu(C\equiv C)$); the latter is much less intense and shifted to longer wavelengths (2150 cm^{-1}) in the IR spectra of the starting alkylthiochloroacetylenes.

Compounds **2** are unstable and easily decompose even in an inert atmosphere to give viscous dark brown products, whose structures are now being determined. The content of nitrogen in these products is 60% lower than that in the starting sodium azide.

Thus, the reaction of sodium azide with accessible alkylthiochloroacetylenes[8] can be used, following optimization, for the synthesis of new polyfunctional nitrogen-and-sulfur-containing unsaturated compounds, which are highly reactive building blocks and intermediate products.

IR spectra were recorded on a Specord IR-75 spectrometer (thin film). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) in $CDCl_3$ with HMDS as the internal standard.

Ethylthioethynyl azide (2a). Acetylene derivative **1a** (2.00 g, 16.6 mmol) was added dropwise with stirring and cooling (25—28 °C) over 25 min to a suspension of NaN_3 (1.08 g, 16.6 mmol) in 10 mL of DMSO. The reaction is exothermic. The reaction mixture was stirred at 20—22 °C for 3 h and

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poured into 40 mL of cold water. The products were extracted with ether (3×10 mL), and the ethereal extract was washed with water (3×10 mL) and dried with Na_2SO_4. The solvent was removed *in vacuo*, and the residue was evacuated to give compound **2a** (0.59 g, 28%) as an oily substance that is soluble in most organic solvents, but insoluble in water. 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. ^1H NMR, δ: 1.35 (t, 3 H, CH_3); 2.68 (q, 2 H, CH_2). ^{13}C NMR, δ: 14.34 (CH_3); 28.13 (CH_2); 85.95 (C≡); 116.21 (C≡). IR, ν/cm^{-1}: 2960, 2928, 2870 (ν(C—H)); 2198 (ν(C≡C)); 2114 (ν_{as}(N=N=N))[7]; 1514, 1442, 1370, 1084, 1042, 956, 900, 865, 814 (δ(C—H)); 1242 (ν_s(N=N=N))[7]; 760 (ν(C—S)).

***n*-Propylthioethynyl azide (2b)** was obtained analogously from NaN_3 (0.97 g, 14.9 mmol) and compound **1b** (2.00 g, 14.9 mmol), yield 0.72 g (34%). Found (%): C, 41.90; H, 5.20; N, 28.05; S, 22.98. $C_5H_7N_3S$. Calculated (%): C, 42.53; H, 5.00; N, 29.76, S, 22.71. ^1H NMR, δ: 0.99 (t, 3 H, CH_3); 1.70 (m, 2 H, CH_2); 2.67 (t, 2 H, CH_2S). ^{13}C NMR, δ: 13.24 (CH_3); 20.89 (CH_2); 34.22 (CH_2S); 87.15 (C≡); 117.10 (C≡). IR, ν/cm^{-1}: 2950, 2928, 2860 (ν(C—H)); 2200 (ν(C≡C)); 2116 (ν_{as}(N=N=N)); 1514, 1460, 1380, 1292, 1092, 938, 898 (δ(C—H)); 1230 (ν_s(N=N=N)); 728 (ν(C—S)).

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