Unusual intramolecular cyclization of adducts of diphenylacetylene with hetarenesulfenyl chlorides

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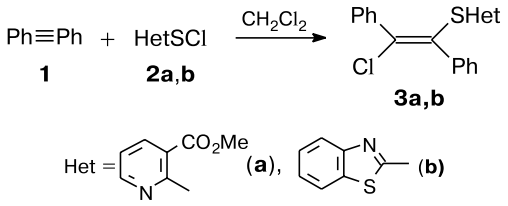
Earlier, it was shown[1—3] that products of 1,2-addition of alkane- and arenesulfenyl chlorides at the multiple bond of acetylenes, β-chlorovinyl sulfides, can undergo the intramolecular nucleophilic substitution with the sulfur atom in RS (R = Alk, Ar) fragment serving as the nucleophile. Depending on the structural features of the starting unsaturated compound, thiirenium salts or products of their isomerization, thietene derivatives, are formed.

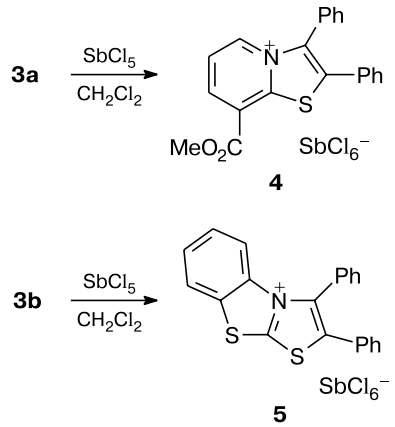
In the present work, a reaction of diphenylacetylene (**1**) with 3-methoxycarbonylpyridine-2- and 1,3-benzothiazole-2-sulfenyl chlorides (**2a**,**b**), containing potentially nucleophilic nitrogen atom in the hetaryl fragment, was studied. We found that the reactions under consideration proceed in dichloromethane at 20 °C to form β-chlorovinyl sulfides **3a** and **3b** in 95 and 92% yield, respectively (Scheme 1).

Scheme 1



Adducts **3a**,**b** were found to be stable compounds both under the reaction conditions and in the more polar media, for example, in nitromethane with or without lithium perchlorate, which were used earlier for the stimulation of the intramolecular cyclization of β-chloroalkyl sulfides.[4] The further transformations of compounds **3a**,**b** take place only upon treatment with such a strong Lewis acid as $SbCl_5$. The intramolecular cyclization of compounds **3a**,**b** proceeds in the presence of equimolar amount of $SbCl_5$ in dichloromethane at 20 °C with the ring closure by the nitrogen atom of the HetS fragment to form the condensed heterocycles **4** and **5** in 73 and 87% yield, respectively (Scheme 2). The complete conversion of adduct **3a** requires 120 h, of adduct **3b**, 96 h.

Scheme 2



^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer in DMSO-d_6.

β-Chlorovinyl sulfides 3a,b (general procedure). A solution of sulfenyl chloride **2a**,**b** (10 mmol) in dichloromethane (10 mL) was added to a solution of diphenylacetylene (**1**) (1.78 g, 10 mmol) in dichloromethane (20 mL) at 20 °C. After 12 h, the solvent was evaporated *in vacuo* to obtain compounds **3a**,**b**, which were recrystallized from hexane—dichloromethane.

Methyl 2-[(*E*)-2-chloro-1,2-diphenylethenylsulfanyl]nicotinate (3a). The yield was 95%, gray crystals with m.p. 118—120 °C. Found (%): C, 65.93; H, 4.17. $C_{21}H_{16}ClNO_2S$. Calculated (%): C, 66.05; H, 4.22. ^{1}H NMR, δ: 3.95 (s, 3 H, OMe); 7.21 (dd, 1 H, Het, ^3J = 4.7 Hz, ^3J = 7.5 Hz); 7.30—7.60 (m, 10 H, Ph); 8.18 (d, 1 H, Het, ^3J = 7.7 Hz); 8.38 (d, 1 H, Het, ^3J = 5.0 Hz).

(*E*)-1-(1,3-Benzothiazol-2-ylsulfanyl)-2-chloro-1,2-diphenylethene (3b). The yield was 92%, light yellow crystals with m.p. 145—146 °C. Found (%): C, 66.21; H, 3.63. $C_{21}H_{14}ClNS_2$. Calculated (%): C, 66.39; H, 3.71. ^{1}H NMR, δ: 7.30—7.55 (m, 10 H, 2 Ph); 7.40 (m, 2 H, Het); 8.10 (d, 1 H, Het, ^3J = 8.1 Hz); 8.21 (d, 1 H, Het, ^3J = 8.7 Hz).

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Intramolecular heterocyclization of β-chlorovinyl sulfides 3a,b (general procedure). A solution of $SbCl_5$ (2.99 g, 10 mmol) in dichloromethane (30 mL) was added to a solution of chlorosulfide **3a**,**b** (10 mmol) in dichloromethane (30 mL) at 20 °C and this solution was kept at room temperature with monitoring of its content every 12 h (^{1}H NMR spectra were registered for the residue after concentration of 0.5 mL of the solution). The solution, containing only product **4** or **5**, was concentrated, and salts **4** or **5** were isolated from the residue by crystallization from ether—dichloromethane.

8-Methoxycarbonyl-2,3-diphenyl[1,3]thiazolo[3,2-*a*]pyridinium hexachloroantimonate (4). The yield was 73%, yellow crystals with m.p. 96—98 °C. Found (%): C, 36.92; H, 2.31. $C_{21}H_{16}Cl_6NO_2SSb$. Calculated (%): C, 37.04; H, 2.37. ^{1}H NMR, δ: 4.10 (s, 3 H, OMe); 7.35—7.65 (m, 10 H, 2 Ph); 8.06 (dd, 1 H, Het, ^3J = 6.5 Hz, ^3J = 7.4 Hz); 8.92 (d, 1 H, Het, ^3J = 6.5 Hz); 8.95 (d, 1 H, Het, ^3J = 7.4 Hz).

2,3-Diphenylbenzo[*d*][1,3]thiazolo[2,3-*b*][1,3]thiazolium-4 hexachloroantimonate (5). The yield was 87%, yellow crystals with m.p. 218—220 °C. Found (%): C, 37.03; H, 2.11. $C_{21}H_{14}Cl_6NS_2Sb$. Calculated (%): C, 37.15; H, 2.08. ^{1}H NMR, δ: 6.78 (d, 1 H, Het, ^3J = 8.5 Hz); 7.30—7.65 (m, 12 H, Ph, Het); 8.43 (d, 1 H, Het, ^3J = 8.3 Hz).

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