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Domino Reaction of 2,3-Dichloroprop-1-ene with Diphenyl Disulfide in the System Hydrazine Hydrate–Potassium Hydroxide

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Abstract—2,3-Dichloroprop-1-ene reacted with diphenyl disulfide in the system hydrazine hydrate–potassium hydroxide at 30–35°C to give three products: 2-chloro-3-phenylsulfanylprop-1-ene, 1-phenylsulfanylpropadiene, and 1-phenylsulfanylprop-1-yne. Variation of temperature ensures selective synthesis of one of the above products, which confirms their successive formation (domino reaction). The domino reaction at 60°C goes further to afford (*Z*)-1,2-bis(phenylsulfanyl)prop-1-ene.

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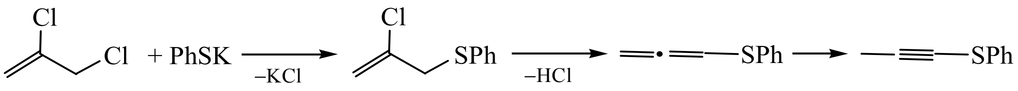
2,3-Dichloroprop-1-ene (**I**) molecule contains two chlorine atoms attached to carbons with different hybridization; therefore, these chlorine atoms exhibit different reactivities. We previously reported on the reactions of compound **I** with sulfur [1] and selenium [2] in the system hydrazine hydrate–KOH which preliminarily reduced these chalcogens to anions S_2^{2-} and Se_2^{2-}. The latter reacted with dichloride **I** in regioselective fashion with participation of only chlorine atom in the allylic position (i.e., at the sp^3-carbon atom). However, the reaction of **I** with ditelluride anion generated from elemental tellurium in the same basic reductive system involved elimination of both chlorine atoms as chloride ions with formation of allene and liberation of elemental tellurium [1, 3].

In continuation of our studies on reactions of 2,3-dichloroprop-1-ene (**I**) with chalcogen-containing nucleophiles, we examined its reaction with diphenyl disulfide in the system hydrazine hydrate–KOH. At 75–85°C this system promotes reductive cleavage of the S–S bond in disulfides to produce potassium thiolates [4].

$$2Ph_2S_2 + 4KOH + N_2H_4{\cdot}H_2O \rightarrow 4PhSK + N_2 + 5H_2O. \qquad (1)$$

To complete reaction (1), excess alkali with respect to its stroichiometric amount is necessary [5]; therefore, the ratio Ph_2S_2–KOH was 1 : 5.

In the reaction of potassium benzenethiolate (generated *in situ*) with 2,3-dichloroprop-1-ene (**I**) at 30–35°C three products were formed (according to the GLC, GC/MS, and ^{1}H NMR data): 2-chloro-3-phenylsulfantlprop-1-ene (**II**, yield 5%), 1-phenylsulfanylpropadiene (**III**, 23%), and 1-phenylsulfanylprop-1-yne (**IV**, 23%). The product structure allowed us to presume the following transformation sequence (domino reaction).

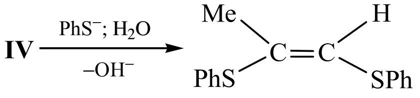


I **II** **III** **IV**

(2)

We succeeded in isolating from the product mixture only fractions enriched in each component **II**–**IV**. However, each compound **II**–**IV** can be obtained with high selectivity by proper choice of the reaction conditions (temperature and Ph_2S_2–KOH ratio). At –25 to –35°C, the major product of reaction (2) was chlorine-containing sulfide **II** (yield 70%). Acetylenic sulfide **IV** was not detected in the reaction mixture, while only traces of allene derivative **III** were formed. Raising the temperature to –5 to –10°C changed the product ratio: the yield of **II** was 56%, the yield of **III** was 15%, and only 5% of **IV** was formed. At slightly lower temperature but with stoichiometric ratio of Ph_2S_2 and KOH (1:2) in reaction (1), the only product was sulfide **II** (yield 66%), the conversion of **I** being 95%.

When reaction (2) was carried out with Ph_2S_2 and KOH taken at a ratio of 1:5, at 60°C the major product was (*Z*)-1,2-bis(phenylsulfanyl)prop-1-ene (**V**, 40% calculated on the initial diphenyl disulfide). Obviously, the transformations **I** → **II** → **III** → **IV** at that temperature proceed at a high rate, and the presence in the reaction mixture of benzenethiolate ions favors their regio- and stereoselective addition to the triple bond of acetylenic sulfide **IV**.



V

(3)

In keeping with the *trans*-addition rule [6], the *Z* isomer was formed with high stereoselectivity. In this case, no sulfide **II** was present among the products, traces of **III** were detected, and the yield of acetylenic sulfide **IV** was 22%. Compound **V** was obtained in 57% yield (calculated on the initial diphenyl disulfide) when reaction (2) was carried out at 60°C with equimolar amounts of diphenyl disulfide and 2,3-dichloroprop-1-ene (**I**); under these conditions, no sulfides **III** and **IV** were present in the reaction mixture. The conversion of **I** in reactions (2) and (3) was complete, but the yield of **V** increased to a lesser extent than expected (by only 17%). Therefore, after extraction of bis(phenylsulfanyl)propene **V**, the aqueous hydrazine layer was treated with methyl iodide, and 28% of thioanisole (**VI**) was isolated.

$$PhS^- \xrightarrow[-I^-]{MeI} \underset{\textbf{VI}}{PhSMe} \qquad (4)$$

The formation of thioanisole (**VI**) indicated that a part of potassium benzenethiolate was not involved in the reaction with 2,3-dichloroprop-1-ene (**I**). The conversion of diphenyl disulfide in reaction (2) was 73%, and the yield of **V** (calculated on the reacted diphenyl disulfide) was 78%. Dehydrochlorination of **II** and isomerization of **III** into **IV** are possible only under the conditions of reaction (2), i.e., in the presence of alkali and a fairly strong base, hydrazine. After separation of the products by extraction, the product ratio did not change on storage and on distillation. The effect of temperature on the results of reaction (2) shows that compounds **II** and **III** are kinetically controlled products and that sulfide **IV** is a thermodynamically controlled product.

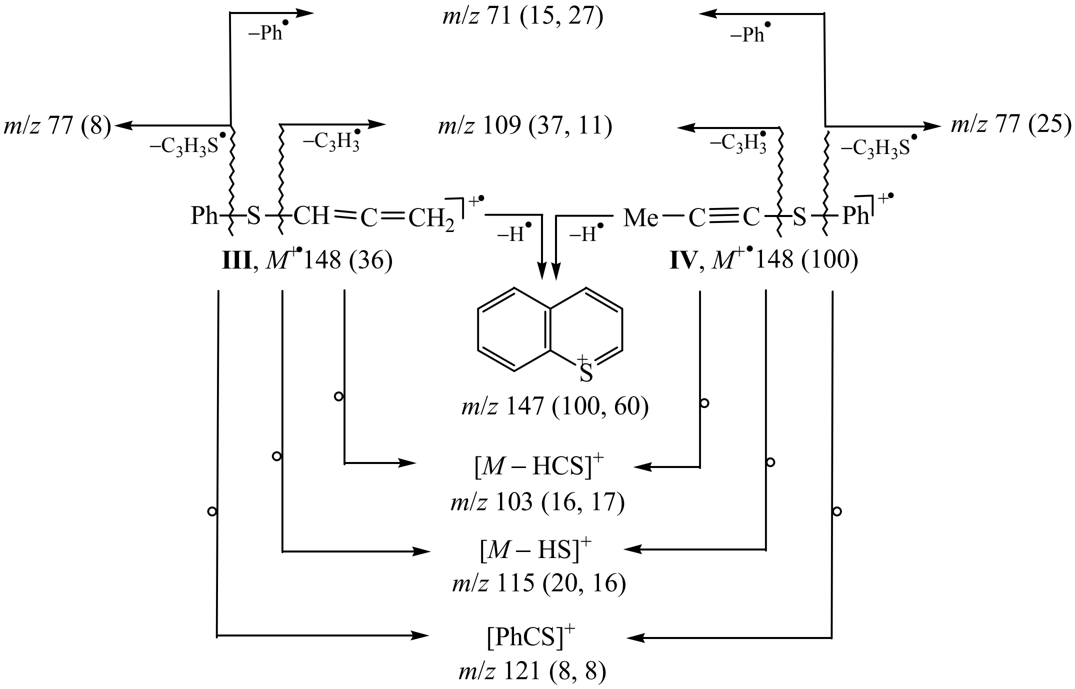
2-Chloro-3-phenylsulfanylprop-1-ene (**II**), 1-phenylsulfanylprop-1-yne (**IV**), and 1,2-bis(phenylsulfanyl)-prop-1-ene (**V**) were isolated as individual substances and were fully characterized. The maximum yield of allenyl sulfide **III** was 23%; this product was not isolated as individual substance and was characterized by IR, ^{1}H and ^{13}C NMR, and mass spectra. According to [7], isomer mixture **III**/**IV** cannot be separated even by column chromatography on silica gel. However, GC/MS analysis allowed us to obtain mass spectra of particular isomers.

The electron-impact mass spectrum of acetylenic sulfide **IV** completely matched that included into the Wiley Library Class-5000 database. The base peak in the mass spectrum of allene isomer **III** belongs to the $[M - H]^+$ ion with m/z 147 (100%). The molecular ions of both isomers undergo further decomposition to produce ions with identical m/z values, which are typical of fragmentation of phenyl vinyl ethers and sulfides [8]. Possible fragmentation pathways of the molecular ions of **III** and **IV** are shown below (relative intensities I_{rel}, %, are given in parentheses).

The presence in the mass spectra of ions with m/z 121 $[PhCS]^+$, 115 $[M - HS]^+$, and 103 $[M - HCS]^+$ indicates possible migration of the phenyl group to one carbon atom of the propadiene or propyne fragment. This process is typical of fragmentation of aryl vinyl sulfides having no phenyl substituent in the vinyl group [9]. In keeping with the assumed fragmentation scheme, essential differences in the mass spectra of isomers **III** and **IV** are observed mainly in the region corresponding to their molecular ions. The intensity ratio of the $[M - H]^+$ and $M^{+\cdot}$ ion peaks for allenyl sulfide **III** is 2.8 against 0.6 for acetylenic sulfide **IV**. Thus, analysis of the mass spectra allowed us to reliably distinguish between isomers **III** and **IV**.

The structure of **V** was proved by the IR, ^{1}H and ^{13}C NMR, and mass spectra. The *cis* orientation of the phenylsulfanyl groups in molecule **V** was confirmed by the presence of correlation between the CH_3 and =CH protons in the NOESY spectrum.

Thus the domino reaction of 2,3-dichloroprop-1-ene with diphenyl disulfide in the system hydrazine



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hydrate–KOH ensures selective synthesis of highly reactive unsaturated sulfides that are promising as intermediate products for the preparation of new organosulfur compounds.

EXPERIMENTAL

The IR spectra were recorded from thin films on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400.13 and 100.62 MHz, respectively, from solutions in $CDCl_3$ using tetramethylsilane as internal reference. The electron impact mass spectra (70 eV) were obtained on a Shimadzu GCMS–QP5050A instrument equipped with a quadrupole mass analyzer (SPB-5 column, 60000×0.25 mm, ion source temperature 190°C, a.m.u. range 34–650). The progress of reactions was monitored, and liquid products were analyzed, by GLC on an LKhM 80-MD-2 chromatograph (2000×3-mm column packed with 5% of DC-550 on Chromaton N-AW-HMDS; linear oven temperature programming at a rate of 12 deg/min; carrier gas helium).

Reaction of 2,3-dichloroprop-1-ene (I) with diphenyl disulfide. Diphenyl disulfide, 5.46 g (0.03 mol), was added in portions to a solution of 7.0 g (0.12 mol) of potassium hydroxide in 30 ml of hydrazine hydrate heated to 40–50°C. The mixture was heated for 3 h at 85–90°C and cooled to room temperature (25°C), and 5.55 g (0.05 mol) of 2,3-dichloroprop-1-ene (**I**) was added dropwise. The mixture was stirred for 2.5 h at 25°C and for 2 h at 30–35°C, cooled to room temperature, and extracted with methylene chloride (3×50 ml). The extracts were combined, dried over $MgSO_4$, and evaporated. The residue, 3.92 g, contained compounds **II**, **III**, and **IV** at a ratio of 1.0:3.3:3.3 (according to the GC, GC/MS, and ^{1}H NMR data; the yields are given in text).

2-Chloro-3-phenylsulfanylprop-1-ene (II). Diphenyl disulfide, 7.0 g (0.03 mol), was added to a solution of 9.0 g (0.16 mol) of potassium hydroxide in 40 ml of hydrazine hydrate, and the reduction of Ph_2S_2 was carried out as described above. The mixture was cooled to –30°C, 7.13 g (0.06 mol) of 2,3-dichloroprop-1-ene (**I**) was added dropwise, and the mixture was stirred for 7.5 h at –28 to –35°C. Extraction with methylene chloride, followed by removal of the solvent, gave 8.35 g of almost pure sulfide **II**, bp 83–84°C (2 mm). IR spectrum, ν, cm^{-1}: 3075, 3060, 3020, 2922, 1641, 1628, 1584, 1480, 1439, 1408, 1234, 1207, 1114, 1088, 1068, 1025, 1000, 890, 739, 690, 629, 526, 484. ^{1}H NMR spectrum, δ, ppm: 3.67 d (2H, CH_2S, ^4J = 1.1 Hz), 5.19 d (1H, *cis*-HC=, ^2J = 1.3 Hz), 5.27 d.t (1H, *trans*-CH=, ^2J = 1.3, ^4J = 1.1 Hz), 7.20 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 42.65 (CH_2S), 114.66 (CH_2=), 127.00 (C^p), 128.91 (C^m), 130.75 (C^o), 134.76 (C^i), 137.79 (=CCl). Mass spectrum, *m/z* (I_{otn}, %): 184 (29) $[M]^+$ ((^{35}Cl), 149 (45) $[M - Cl]^+$, 147 (18), 135 (19), 134 (15), 116 (16), 115

(26), 109 (100) (PhS^+), 91 (8), 77 (18), 75 (19), 65 (19). Found, %: C 58.33; H 4.73; S 17.11; Cl 19.13. C_9H_9SCl. Calculated, %: C 58.53; H 4.91; S 17.36; Cl 19.20.

1-Phenylsulfanylpropadiene (III). IR spectrum: ν 1941 cm^{-1} (C=C=C). ^{1}H NMR spectrum, δ, ppm: 5.00 d (2H, CH_2=), 5.96 t (1H, =CHS, ^4J = 6.2 Hz), 7.32 m (5H, C_6H_5) (cf. [7]). ^{13}C NMR spectrum, δ_C, ppm: 78.65 (CH_2=), 85.94 (=CHS), 209.32 (=C=). The mass spectrum of **III** is given in text.

1-Phenylsulfanylprop-1-yne (IV) was isolated in 22% yield in the reaction of 2,3-dichloroprop-1-ene (**I**) (7.13 g, 0.06 mol) with Ph_2S_2 (7.0 g, 0.03 mol) at 60°C. After extraction and removal of the solvent, the residue (5.45 g) contained ~2.1 g of sulfide **IV**, traces of **III**, and 3.35 g of bis(phenylsulfanyl)propene **V**. Pure sulfide **IV** was isolated by distillation; yield 1.2 g, bp 75–76°C (1.5 mm); published data: bp 83°C (2 mm) [10], 78–81°C (0.75 mm) [11]. IR spectrum: ν 2203 cm^{-1}, w (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.07 s (3H, CH_3), 7.29 m (5H, C_6H_5), (cf. [7, 10]). ^{13}C NMR spectrum, δ_C, ppm: 5.18 (CH_3), 63.85 (≡C–S), 95.33 ($CH_3\underline{C}\equiv$), 125.81 (C^m), 126.08 (C^p), 129.00 (C^o), 133.54 (C^i). Signals from the triple-bonded carbon atoms were assigned on the basis of the ^{13}C NMR spectrum recorded without decoupling from protons but with NOE: the signal at δ_C 63.85 ppm was a quartet with $^3J_{CH}$ = 5.2 Hz, and the signal at δ_C 95.33 ppm was a quartet with $^2J_{CH}$ = 10.6 Hz. The mass spectrum of **IV** is given in text.

(*Z*)-1,2-Bis(phenylsulfanyl)prop-1-ene (V) was isolated by distillation of the still residue after distillation of sulfide **IV**, bp 184–185°C (2 mm). IR spectrum, ν, cm^{-1}: 3073, 3058, 3019, 2970, 2950, 2912, 2868, 2849, 1583, 1478, 1439, 1374, 1321, 1306, 1257, 1178, 1157, 1105, 1090, 1069, 1024, 1008, 906, 740, 690, 629, 590, 564, 532, 487, 470. ^{1}H NMR spectrum, δ, ppm: 1.89 d (3H, CH_3, ^4J = 1.3 Hz), 6.36 q (1H, HC=, ^4J = 1.3 Hz), 7.22 m (10H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 24.00 (CH_3), 126.20 (HC=), 131.63 ($CH_3\underline{C}$=); 126.71 and 127.30 (C^p), 128.97 and 131.75 (C^m), 129.46 and 129.07 (C^o), 133.17 and 135.92 (C^i) (the first value refers to the PhS group located near the CH_3 group). Mass spectrum, *m*/*z* (I_{rel}, %): 258 (100) $[M]^+$, 199 (8), 186 (7), 167 (43), 149 (60), 148 (23), 147 (33), 134 (55), 121 (9), 115 (23), 109 (29), 105 (16), 91 (7), 77 (16), 65 (19). Found, %: C 69.46; H 5.68; S 24.56. $C_{15}H_{14}S_2$. Calculated, %: C 69.72; H 5.46; S 24.81.

Methylsulfanylbenzene (VI). Diphenyl disulfide, 7.0 g (0.03 mol), was added to a solution of 9.0 g (0.16 mol) of potassium hydroxide in 40 ml of hydrazine hydrate. After the reduction of Ph_2S_2 was complete (see above), the mixture was cooled to 25°C, 3.56 g (0.03 mol) of 2,3-dichloroprop-1-ene (**I**) was added, and the mixture was stirred for 19 h at 60°C, cooled, and extracted with methylene chloride. Evaporation of the extract gave 4.7 g of bis(phenylsulfanyl)propene **V**. The aqueous hydrazine layer was treated with 4.4 g (0.03 mol) of methyl iodide, the mixture was stirred for 4 h at 25–30°C and extracted with diethyl ether (3 × 50 ml), and the extract was dried over $MgSO_4$ and evaporated to obtain 2.2 g (28%) of thioanisole (**VI**). bp 76–78°C (15 mm); published data [12]: bp 78–79°C (15 mm). ^{1}H NMR spectrum, δ, ppm: 2.42 s (CH_3), 7.22 s (H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.83 (CH_3), 125.02 (C^p), 126.73 and 128.79 (C^o, C^m), 138.50 (C^i). Mass spectrum: *m*/*z* 124 $[M]^+$.

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