Nucleophilic reaction of propane-1,3-dithiol with tetrachloroethylene: formation of cyclic structures

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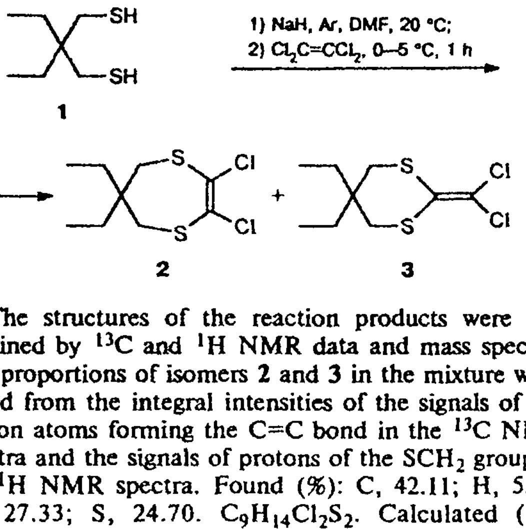
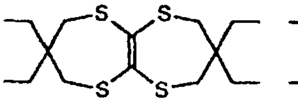
The reaction of aliphatic and aromatic thiolates with tetrachloroethylene (TCE) involves, depending on the ratio of the reactants, replacement of two, three, or four Cl atoms by RS groups.[1] The replacement of two Cl atoms affords only vicinal dichlorides, *trans*-1,2-dichloro-1,2-bis(organothio)ethylenes.[1,2]

We found that in the reaction of equimolar amounts of tetrachloroethylene and 2,2-diethylpropane-1,3-dithiol (**1**) under conditions of generation of thiolate anions, these anions substitute both vicinal and geminal Cl atoms. The vicinal substitution occurs with *cis*-orientation. The reaction of dithiol **1** and TCE taken in a molar ratio of 1:4 gives a mixture of heterocycles, 2,3-dichloro-6,6-diethyl-6,7-dihydro-5*H*-1,4-dithiepine (**2**) and 2-dichloromethylene-5,5-diethyl-1,3-dithiane (**3**) in 3:1 ratio (overall yield 52%).



The structures of the reaction products were determined by ^{13}C and ^{1}H NMR data and mass spectra. The proportions of isomers **2** and **3** in the mixture were found from the integral intensities of the signals of the carbon atoms forming the C=C bond in the ^{13}C NMR spectra and the signals of protons of the SCH_2 group in the ^{1}H NMR spectra. Found (%): C, 42.11; H, 5.28; Cl, 27.33; S, 24.70. $C_9H_{14}Cl_2S_2$. Calculated (%): C, 42.02; H, 5.49; Cl, 27.56; S, 24.93. ^{1}H NMR (250 MHz, $CDCl_3$), δ, **2**, **3**: 0.80, 0.85 (t, 6 H, CH_3, J = 7.5 Hz); 1.52, 1.52 (q, 4 H, $CH_3C\underline{H}_2$, J = 7.5 Hz); 3.05, 2.67 (s, 4 H, SCH_2). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ, **2**, **3**: 7.6, 7.7 (CH_3); 26.7, 27.5 ($CH_3\underline{C}H_2$); 38.1, 36.8 ($\underline{C}(CH_2)_4$); 123.8 (C=C); 105.5 (C=$\underline{C}$S); 133.1 ($C{=}CCl_2$). MS, m/z: 256 $[M]^+$.

Along with monocyclic isomers **2** and **3**, the reaction under these conditions gives, despite the excess of TCE, isomeric bicyclic products resulting from the replacement of the four Cl atoms in TCE by thiolate anions, namely, 3,3,8,8-tetraethyl-3,4,8,9-tetrahydro-2*H*,7*H*-1,4-dithiepino[2,3-*b*][1,4]dithiepine (**4**) and 5,5,5′,5′-tetraethyl-2,2′-bis(1,3-dithianylidene) (**5**) in a ratio close to 3:1 and in 16% total yield. The fractions containing compounds **2** + **3** and **4** + **5** were separated on a column with silica gel (L 40/100 μm).



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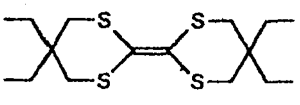

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The reaction of TCE with a threefold molar excess of dithiol **1** (the second step, *i.e.*, the reaction of thiolate with TCE, was carried out at 20—25 °C) affords only bicyclic products in 68% total yield (**4** : **5** ≈ 3 : 1). As in the case of isomers **2** and **3**, the ratio of **4** to **5** in the mixture was determined using the NMR spectra. Chromatographic separation on silica gel and recrystallization from hexane gave bicyclic compounds **4** and **5**. **Compound 4**, yield 48%, m.p. 78—80 °C. Found (%): C, 55.48; H, 8.20; S, 35.84. $C_{16}H_{28}S_4$. Calculated (%): C, 55.12; H, 8.09; S, 36.79. ^{1}H NMR ($CDCl_3$), δ: 0.77 (t, 12 H, CH_3, J = 7.5 Hz); 1.84 (q, 8 H, $CH_3C\underline{H}_2$, J = 7.5 Hz); 2.83 (s, 8 H, SCH_2). ^{13}C NMR ($CDCl_3$), δ: 7.5 (CH_3); 27.0 ($CH_3\underline{C}H_2$); 37.5 ($\underline{C}(CH_2)_4$); 42.3 (SCH_2); 127.8 (C=C). MS, m/z: 348 $[M]^+$. **Compound 5**, yield 12%, m.p. 131.0—132.5 °C. Found (%): C, 54.88; H, 8.16; S, 35.82. $C_{16}H_{28}S_4$. Calculated (%): C, 55.12; H, 8.09; S, 36.79. ^{1}H NMR ($CDCl_3$), δ: 0.83 (t, 12 H, CH_3, J = 7.5 Hz); 1.57 (q, 8 H, $CH_3C\underline{H}_2$, J = 7.5 Hz); 2.66 (s, 8 H, SCH_2). ^{13}C NMR ($CDCl_3$), δ: 7.8 (CH_3); 27.2 ($CH_3\underline{C}H_2$); 37.0 ($\underline{C}(CH_2)_4$); 40.4 (SCH_2); 122.6 (C=C). MS, m/z: 348 $[M]^+$.

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References

1. E. N. Prilezhaeva, N. E. Donzova, N. P. Petukhova, and V. S. Bogdanov, *Gazz. Chim. Ital.*, 1990, **120**, 235.
2. W. E. Truce, M. G. Rossmann, F. M. Perry, R. M. Burnett, and D. J. Abraham, *Tetrahedron*, 1965, **21**, 2899.

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