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SHORT COMMUNICATIONS

Synthesis of Bis(2-acyl-2-chlorovinyl) Sulfides

G. V. Bozhenkov, V. A. Savosik, A. N. Mirskova, and G. G. Levkovskaya

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: ggl@irioch.irk.ru

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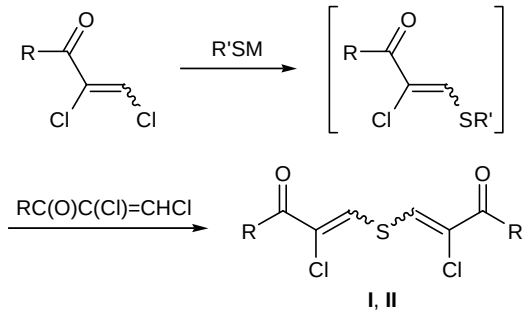
While studying the reactivity of alkyl 1,2-dichlorovinyl ketones [1] synthesized from carboxylic acid chlorides and 1,2-dichloroethylene (which is a large-scale product), we examined their reactions with sulfur-centered nucleophiles and ambident sulfur-containing reagents. It is known that 2,2-dichlorovinyl ketones (which are structural analogs of 1,2-dichlorovinyl ketones) react with sodium sulfides to give dithiols and dithietanes [2–4] and that their reactions with thiourea and thioacetamide lead to formation of the corresponding thiazinethiones [2, 5].

By contrast, 1,2-dichlorovinyl ketones reacted with thiourea, thioacetamide, and sodium sulfide to afford exclusively bis(2-acyl-2-chlorovinyl) sulfides **I** and **II** in up to 90% yield. The reaction did not change its direction upon variation of the solvent (both proton-donor and aprotic solvents were used), temperature, and even reactant ratio (in the presence of a large excess of the sulfur-containing reagent). The result was the same in the presence of both acids and bases. Presumably, initially formed products of replacement of the halogen atom in the β-position with respect to the carbonyl group by R'S group react with the second 1,2-dichlorovinyl ketone molecule with elimination of the R' group and formation of stable sulfide. Under the given conditions, we did not observe formation of acylthioketenes or acylethynethiols whose dimerization (according to [6]) could lead to heterocyclic compounds.



I, **II**

I, R = Me; **II**, R = Et; M = H, Na; R' = Na, $H_2NC(=NH)$, MeC(=NH).

The structure of sulfides **I** and **II** was confirmed by the IR and ^1H and ^{13}C NMR spectra and elemental analyses. The IR spectra of **I** and **II** contained strong absorption bands due to vibrations of the =C–H, C=O, and C=C bonds. The signal from the olefinic proton in the ^1H NMR spectra of chlorovinyl sulfides **I** and **II** was located in a weaker field ($\Delta\delta \approx 0.4$ ppm) relative to the corresponding signal of initial 1,2-dichlorovinyl ketones. In going from $CDCl_3$ to DMSO-d_6, the vinyl proton signal shifts strongly downfield (by 0.9 ppm), indicating a high polarity of the C–H bond in ketones **I** and **II**.

Thus we have found a procedure for the synthesis of polyfunctional halovinyl sulfides which are promising as ligands and synthons for the preparation of various heterocyclic compounds via reactions with N-, O-, and S-centered nucleophiles and polyfunctional nucleophiles, dienes, and heterodienes. Studies on further reactions of 1,2-dichlorovinyl ketones and bis-(2-acyl-2-chlorovinyl) sulfides **I** and **II** are now in progress.

Bis(2-chloro-3-oxo-1-butenyl) sulfide (I). *a*. A solution of 1.39 g (0.01 mol) of methyl 1,2-dichlorovinyl ketone in 5 ml of ethanol was added under stirring to a solution of 2.88 g (0.012 mol) of $Na_2S \cdot 9H_2O$ in 10 ml of ethanol. The mixture was stirred for 6 h at room temperature and poured into water. The precipitate was filtered off, washed with water, and dried. Yield 2.07 g (87%).

b. Methyl 1,2-dichlorovinyl ketone, 1.39 g (0.01 mol), was added dropwise under stirring to a solution of 1.52 g (0.02 mol) of thiourea in 20 ml of ethanol. The mixture was stirred for 8 h at room

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temperature and poured into water, and the precipitate was filtered off, washed with water, and dried. Yield 2.04 g (85%).

c. Methyl 1,2-dichlorovinyl ketone, 1.39 g (0.01 mol), was added dropwise under stirring to a solution of 0.75 g (0.01 mol) of thioacetamide in 15 ml of ethanol. The mixture was stirred for 3 h at room temperature and poured into water, and the precipitate was filtered off, washed with water, and dried. Yield 1.85 g (77%), mp 141°C. IR spectrum, ν, cm^{-1}: 3020, 3050 (=C–H); 1680 (C=O); 1575, 1540 (C=C); 700 (C–Cl). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.87 s (1H, =CH); 2.44 s (3H, CH_3). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.93 (1H, =CH), 2.46 (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 188.50 (C=O), 140.24 (CH), 130.12 (CCl), 26.11 (CH_3). Found, %: C 40.62; H 3.50; Cl 30.40; S 13.31. $C_8H_8Cl_2O_2S$. Calculated, %: C 40.18; H 3.37; Cl 29.65; S 13.41.

Bis(2-chloro-3-oxo-1-pentenyl) sulfide (II). *a*. Compound **II** was synthesized as described above for **I** (method *a*) from 2.88 g (0.012 mol) of $Na_2S\cdot 9H_2O$ and 1.52 g (0.01 mol) of ethyl 1,2-dichlorovinyl ketone. Yield 2.07 g (78%).

b. Compound **II** was synthesized as described above for **I** (method *b*) from 0.19 g (0.0025 mol) of thiourea and 0.76 g (0.005 mol) of ethyl 1,2-dichlorovinyl ketone. Yield 1.05 g (79%).

c. Compound **II** was synthesized as described above for **I** (method *c*) from 0.75 g (0.01 mol) of thioacetamide and 1.53 g (0.01 mol) of ethyl 1,2-dichlorovinyl ketone. Yield 1.00 g (75%), mp 90°C. IR spectrum, ν, cm^{-1}: 3090, 3045 (=C–H); 2880, 2935, 2900 (C_2H_5); 1680 (C=O); 1550 (C=C); 700 (C–Cl). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.91 s (1H, =CH); 2.02 q (2H, CH_2, J = 7.21 Hz); 1.16 t (3H, CH_3, J = 7.21 Hz). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.83 s (1H, =CH), 2.85 q (2H, CH_2, J = 7.21 Hz), 1.06 t (3H, CH_3, J = 7.21 Hz). ^{13}C NMR spectrum, δ_C, ppm: 191.38 (C=O), 139.30 (CH), 129.65 (CCl), 30.99 (CH_2), 8.75 (CH_3). Found, %: C 44.61; H 4.65; Cl 26.51; S 12.07. $C_{10}H_{12}Cl_2O_2S$. Calculated, %: C 44.96; H 4.53; Cl 26.54; S 12.00.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz, respectively, using HMDS as internal reference. The IR spectra were measured in KBr on a Specord IR75 spectrophotometer.

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