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Thio Derivatives of Cyclopentanone and Cyclohexanone

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Abstract—Mono- and bis(methylthiomethyl) substituted derivatives of cyclopentanone and cyclohexanone were obtained on the basis of natural methylmercaptan via the alkylthiomethylation of ketones, and these derivatives were converted into the corresponding γ-hydroxysulfides and ketosulfones via reduction with sodium borohydride and oxidation with hydrogen peroxide, respectively.

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The rational use of mercaptans, sulfides, and thiophenes present in hydrocarbon feedstock is one of the most important tasks of the gas-processing and oil-refining industries. Thus, the alkylthiomethylation (ATM) of ketones with sulfide–alkaline waste liquor (SAW) [1, 2], which contains reactive sodium sulfide and sodium mercaptides, makes it possible to obtain various γ-ketosulfides differing in structure and properties [3–6] as products promising for practical application and to simultaneously regenerate sodium hydroxide.

In this work, we studied the alkylthiomethylation of cyclopentanone and cyclohexanone with a mixture of formaldehyde and sodium methylmercaptide, which is present in SAW, and obtained mono- and bis(methylthiomethyl) substituted ketones and their derivatives.

EXPERIMENTAL

The IR spectra of the compounds were recorded on a Specord M-80 instrument (in film or vaseline oil), and the ^{1}H and ^{13}C NMR spectra were measured on a Brucker AM-300 spectrometer operating at frequencies of 75 and 300 MHz, respectively, in $CDCl_3$ using TMS as an internal standard. Gas-chromatographic analysis was carried out on a Chrom-5 chromatograph using a flame-ionization detector and a 1.2 m × 3 mm column packed with SE-30 (5%)-coated Chromaton N-AW-DMCS (0.16–0.20 mm) at a column temperature of 50–300°C; the carrier gas was helium. Gas chromatographic–mass spectrometric (GC–MS) determinations were performed with a Thermo Finnigan MAT 95 XP instrument. The chromatographic separation conditions were as follows: an HP-5MS column (5% dimethyl phenyl methyl silicone, 95% dimethyl silicone) and temperature programming from 50°C (5 min) to 280°C (10 min) at a rate of 7°C/min. The sulfide and mercaptan sulfur contents were determined by means of potentiometric titration with potassium iodate and diamminesilver nitrate, respectively [7].

To synthesize thio derivatives of cyclopentanone (**1**) and cyclohexanone (**2**), we used a sulfide–alkaline waste liquor (SAL) from the Orenburg gas-processing plant containing 0.038 wt % sulfide and 3.20 wt % mercaptide sulfur represented mainly by sodium methylmercaptide (95%).

Synthesis of 2-(methylthiomethyl)cyclopentan-1-one (3) and 2-(methylthiomethyl)cyclohexan-1-one (4). Equimolar amounts of formaldehyde (46 ml of a 30% solution) and cyclopentanone (45 ml) or cyclohexanone (52 ml) were successively added with stirring to 500 g of SAL containing 16 g (0.5 mol) of mercaptide sulfur. The resultant mixture was stirred at room temperature for 6 and 2 h, respectively, and, then, extracted with chloroform (3 × 50 ml). The extracts were washed with a 10% HCl solution, water (1 : 1 by volume), and dried with $MgSO_4$. Chloroform was evaporated, and the residue was distilled in vacuum. The yield of **3** was 54.7 g (76%), bp 80°C (4 mmHg), d_4^{20} 1.051, n_D^{20} 1.5085, MR_D 40.94 (calculated 40.41). IR, ν, cm^{-1}: 1738 (C=O). ^{1}H NMR, δ, ppm: 1.65–1.85 m (2H, C^3H^a, C^4H^a), 1.96–2.20 m (2H, C^3H^e, C^4H^e), 2.09 s (3H, SCH_3), 2.15–2.40 m (3H, C^2H, C^5H_2), 2.50 dd (1H, $C^{1'}H^aS$, J_{gem} 12.9 Hz, $J_{1'a,2}$ 8.4 Hz), 2.90 dd (1H, $C^{1'}H^eS$, J_{gem} 12.9 Hz, $J_{1'e,2}$ 3.7 Hz). ^{13}C NMR, δ, ppm: 16.26 (CH_3S), 20.42 (C^4H_2), 28.99 (C^3H_2), 34.16 (CH_2S), 38.10 (C^5H_2), 49.00 (C^2H), 219.28 (C=O). Found, %: C 58.30, H 8.35, S 23.66. Calculated for $C_7H_{12}OS$, %: C 58.29, H 8.38, S 23.23.

The yield of **4** was 56.1 g (71%), bp 91–93°C (4 mmHg), d_4^{20} 1.056, n_D^{20} 1.5090, MR_D 44.75 (calculated, 45.03). IR, ν, cm^{-1}: 1708 (C=O). ^{1}H NMR, δ, ppm: 1.30 m (1H, C^3H^a), 1.60 m (2H, C^4H^a, C^5H^a), 1.80 m (1H, C^5H^e), 1.95–2.05 m (1H, C^4H^e), 2.12 s (3H, CH_3S), 2.15–2.40 m (4H, $C^{1'}H^eS$, C^3H^e, C^6H_2); 2.40–2.60 m (1H, C^2H^a), 2.95 dd (1H, $C^{1'}H^aS$, J_{gem} 13.2

Hz, $J_{1'a,2}$ 4.8 Hz). ^{13}C NMR, δ, ppm: 16.02 (CH_3S), 24.59 (C^4H_2), 27.56 (C^5H_2), 33.02 (C^3H_2), 33.68 (CH_2S), 41.61 (C^6H_2), 50.17 (C^2H), 211.09 (C=O). Found, %: C 60.90, H 8.85, S 19.76. Calculated for $C_8H_{14}OS$, %: C 60.72, H 8.91, S 20.26.

Synthesis of 2,5-bis(methylthiomethyl)cyclopentan-1-one (5) and 2,6-bis(methylthiomethyl)cyclohexan-1-one (6). Equimolar amounts of formaldehyde (46 ml of a 30% solution) and 0.25 mol of cyclopentanone (22.5 ml) or cyclohexanone (26 ml) were successively added with stirring to 500 g of SAL containing 16 g (0.5 g-at) of mercaptide sulfur. The resultant mixtures were stirred at 50°C for 1 and 0.5 h, respectively, cooled, and extracted with chloroform (3 × 50 ml). The extracts were washed with a 10% HCl solution, water (1 : 1 by volume), and dried with $MgSO_4$. Chloroform was evaporated, and the residue of 5(19) was chromatographed on a column packed with SiO_2 (a 1 : 4 ethyl acetate–petroleum ether solvent blend (40–70°C)). The yield of **5** was 0.49 g (49%). IR, ν, cm^{-1}: 1726 (C=O). ^1H NMR, δ, ppm: 2.10 s, 2.08 s (6H, $2CH_3S$), 2.20–2.34 m (4H, C^3H_2, C^4H_2), 2.60 m (4H, C^2H, C^5H, $C^{1'}H^eS$, $C^{1''}H^eS$), 2.73 dd (2H, $C^{1'}H^aS$, $C^{1''}H^aS$, J_{gem} 12.1, $J_{1'a,2} = J_{1''a,5}$ 4.2 Hz). ^{13}C NMR, δ, ppm: *cis*-isomer, 17.74 ($2CH_3S$), 27.08 (C^3H_2, C^4H_2), 37.88 ($2CH_2S$), 56.59 (C^2H, C^5H); 222.49 (C=O); *trans*-isomer, 17.63 ($2CH_3S$), 27.14 (C^3H_2, C^4H_2), 37.41 ($2CH_2S$), 56.68 (C^2H, C^5H), 222.50 (C=O). Found, %: C 52.77, H 7.75, S 31.66. Calculated for $C_9H_{16}OS_2$, %: C 52.90, H 7.89, S 31.38.

The yield of **6** was 50.7 g (93%), d_4^{20} 1.095, n_D^{20} 1.5425, MR_D 62.81 (calculated, 62.33). IR, ν, cm^{-1}: 1714 (C=O). ^1H NMR, δ, ppm: *cis*-isomer, 1.39 dq (2H, C^3H^a, C^5H^a, $J_{gem} = J_{3a,4a} = J_{3a,2a}$ 13.2 Hz, $J_{3a,4e}$ 4.0 Hz), 1.78 dtt (1H, C^4H^a, J_{gem} 13.8 Hz, $J_{4a,3a} = J_{4a,5a}$ 13.2 Hz, $J_{4a,3e} = J_{4a,5e}$ 3.7 Hz), 1.94 dtt (1H, C^4H^e J_{gem} 13.8 Hz, $J_{4e,3a} = J_{4e,5a}$ 4.0 Hz, $J_{4e,3e} = J_{4e,5e}$ 3.0 Hz), 2.12 s (6H, $2CH_3S$), 2.37–2.45 m (2H, C^5H^e, C^3H^e), 2.37 dd (2H, $C^{1'}H^eS$, $C^{1''}H^eS$, J_{gem} 13.2 Hz, $J_{1'в,2a} = J_{1''в,6a}$ 7.8 Hz), 2.57 dddd (2H, C^2H^a, C^6H^a, $J_{2a,1'в} = J_{6a,1''в}$ 7.8 Hz, $J_{2a,1'a} = J_{6a,1''a}$ 5.0 Hz, $J_{2a,3a} = J_{6a,5a}$ 13.2 Hz, $J_{2a,3e} = J_{6a,5e}$ 3.5 Hz), 2.95 dd (2H, $C^{1'}H^aS$, $C^{1''}H^aS$, J_{gem} 13.2 Hz, $J_{1'a,2} = J_{1''a,6}$ 5.0 Hz); *trans*-isomer, 1.62 br.s (2H, C^4H_2), 1.70–1.80 m (2H, C^5H^a, C^3H^a), 2.09 s (6H, CH_3S), 2.50–2.60 m (4H, $C^{1'}H^eS$, $C^{1''}H^eS$, C^3H^e, C^5H^e); 2.70 dq (2H, C^2H, C^6H, $J_{2,3a} = J_{2,1'a} = J_{2,1'в}$ 6.0 Hz, $J_{2,3e}$ 1.5 Hz), 2.89 dd (2H, $C^{1'}H^aS$, $C^{1''}H^aS$, J_{gem} 12.8 Hz, $J_{1'a,2} = J_{1''a,6}$ 6.0 Hz). ^{13}C NMR, δ, ppm: *cis*-isomer, 16.22 ($2CH_3S$); 24.82 (C^4H_2); 33.57 (C^3H_2, C^5H_2); 34.37 ($2CH_2S$); 50.70 (C^2H, C^6H); 211.01 (C=O); *trans*-isomer, 15.58 ($2CH_3S$), 19.92 (C^4H_2), 31.70 ($2CH_2S$), 34.02 (C^3H_2, C^5H_2), 48.09 (C^2H, C^5H), 212.34 (C=O). Found, %: C 54.25, H 8.28, S 29.60. Calculated for $C_{10}H_{18}OS_2$, %: C 55.00, H 8.31, S 29.37.

Synthesis of γ-hydroxysulfides (7–9). A solution of 0.01 mol of ketosulfide **3**, **4,** or **6** in 15 ml of ethanol was added gradually to a mixture of 0.38 g (0.01 mol) of $NaBH_4$, 26.7 ml of ethanol, 13.3 ml of water, and 0.2 ml of 10% NaOH solution heated to 50°C. The resultant mixture was stirred at 50°C for 3 h, cooled, diluted with 100 ml of water, and extracted with chloroform (3 × 50 ml). The extract was dried with $MgSO_4$, and chloroform was evaporated.

2-(Methylthiomethyl)cyclopentan-1-ol (7). The yield 1.37 g (94%), d_4^{20} 1.044, n_D^{20} 1.5170, MR_D 42.38 (calc. 41.92). IR, ν, cm^{-1}: 3392 (OH). ^1H NMR, δ, ppm: *trans*-isomer, 1.15–1.35 m (1H, C^3H^a), 2.15 s (3H, CH_3S), 2.20–2.70 br.s (2H, OH, C^2H), 2.53 dd (1H, $C^{1'}H^aS$, J_{gem} 12.9 Hz, $J_{1'a,2}$ 7.9 Hz), 2.62 dd (1H, $C^{1'}H^eS$, J_{gem} 12.9 Hz, $J_{1'в,2}$ 5.7 Hz), 3.95 q (1H, C^1H, J 6.2 Hz), *cis*-isomer, 2.15 s (3H, CH_3S), 2.20–2.70 br.s (2H, OH, C^2H), 2.55–2.72 m (2H, $C^{1'}H^aS$, $C^{1'}H^eS$); 4.30 dd (1H, C^1H, J 6.2 Hz, J 4.8 Hz); *trans*- and *cis*-isomers, 1.50–2.00 m (5H + 6H, $C^3H^e + C^3H_2$, C^4H_2, C^5H_2). The ^{13}C NMR spectrum, δ, ppm: *trans*-isomer, 15.70 (CH_3S), 21.49 (C^4H_2), 30.12 (C^3H_2), 34.14 (C^5H_2), 38.41 (CH_2S), 46.35 (C^2H), 79.08 (C^1H); *cis*-isomer, 15.95 (CH_3S), 22.21 (C^4H_2), 29.31 (C^3H_2), 34.31 (C^5H_2), 34.51 (CH_2S), 44.53 (C^2H), 73.74 (C^1H). Found, %: C 57.45, H 9.48, S 21.01. Calculated for $C_7H_{14}OS$, %: C 57.49, H 9.65, S 21.92.

2-(Methylthiomethyl)cyclohexan-1-ol (8). The yield of **8** was 1.57 g (98%), d_4^{20} 1.040, n_D^{20} 1.5171, MR_D 46.63 (calc. 46.54). IR, ν, cm^{-1}: 3384 (OH). ^1H NMR, δ, ppm: *trans*-isomer, 1.05 dq (1H, C^3H^a, J_{gem} 12.5 Hz, $J_{3a,4e}$ 3.3 Hz), 2.15 s (3H, CH_3S), 2.52 dd (1H, $C^{1'}H^aS$, J_{gem} 13.0 Hz, $J_{1'a,2}$ 6.7 Hz), 2.78 dd (1H, $C^{1'}H^eS$, J_{gem} 13.0 Hz, $J_{1'в,2}$ 5.6 Hz), 3.40 dt (1H, C^1H^a, $J_{1,6a} = J_{1,2}$ = 9.8 Hz, $J_{1,6e}$ 4,4 Hz); *cis*-isomer, 2.08 s (3H, CH_3S), 2.48 dd (1H, $C^{1'}H^aS$, J_{gem} 12.8 Hz, $J_{1'a,2}$ 6.5 Hz), 2.62.dd (1H, $C^{1'}H^eS$, J_{gem} 12.8 Hz, $J_{1'в,2}$ 8.0 Hz), 4.08 br.s (1H, C^1H); *trans*- and *cis*-isomers, 1.20–1.35 m, 1.40–.60 m, 1.60–1.75 m, 1.75–2.00 m (9H + 10H, C^2H, $C^3H^e + C^3H_2$, C^4H_2, C^5H_2, C^6H_2, OH). ^{13}C NMR, δ, ppm: *trans*-isomer, 16.45 (CH_3S), 24.76 (C^5H_2), 25.58 (C^4H_2), 35.54 (C^3H_2), 37.27 (C^6H_2), 38.63 (CH_2S), 44.15 (C^2H), 74.85 (C^1H); *cis*-isomer, 16.18 (CH_3S), 25.20 (C^5H_2), 26.62 (C^4H_2), 30.81 (C^3H_2), 33.08 (CH_2S), 38.63 (C^6H_2), 40.71 (C^2H), 68.19 (C^1H). Found, %: C 59.20, H 10.10, S 19.91. Calculated for $C_8H_{16}OS$, %: C 59.95, H 10.06, S 20.01.

2,6-Bis(methylthiomethyl)cyclohexan-1-ol (9). The yield of **9** was 2.14 g (97%), d_4^{20} 1.105, n_D^{20}

1.5492, MR_D 63.46 (calc. 63.85). IR, ν, cm^{-1}: 3424 (OH). ^1H NMR, δ, ppm: *trans*, *trans*-isomer, 1.10 dq (2H, C^3H^a, C^5H^a, $J_{3a,4e}$ 3.4 Hz, $J_{gem} = J_{3a,4a} = J_{3a,2a}$ 13.0 Hz), 2.10 s (6H, $2CH_3S$), 2.48 dd (2H, $C^{1'}H^aS$, $C^{1''}H^aS$, J_{gem} 13.0 Hz, $J_{1'a,2} = J_{1''a,6}$ 7.1 Hz), 2.62 dd (2H, $C^{1'}H^eS$, $C^{1''}H^eS$, J_{gem} 13.0 Hz, $J_{1'e,2} = J_{1''e,6}$ 7.9 Hz), 3.24 t (1H, C^1H, J 9.6 Hz), 4.12 br.s (1H, OH); *trans*,*cis*-isomer, 2.18 s (6H, $2CH_3S$), 2.50 dd (2H, $C^{1'}H^aS$, $C^{1''}H^aS$, J_{gem} 13.0 Hz, $J_{1'a,2} = J_{1''e,6}$ 6.8 Hz), 2.80 dd (2H, $C^{1'}H^eS$, $C^{1''}H^eS$, J_{gem} 13.0 Hz, $J_{1'e,2} = J_{1''e,6}$ 5.1 Hz), 3.80 dd (1H, C^1H, $J_{1,6e}$ 3.4 Hz, $J_{1,2a}$ 6.4 Hz), 4.12 br.s (1H, OH); *trans,trans*- and *trans*,*cis*-isomers, 1.25–1.40 m, 1.40–1.50 m, 1.50–1.65 m, 1.65–2.00 m (6H + 8H, C^3H^e + C^3H_2, C^5H^e + C^5H_2, C^4H_2, C^2H, C^6H). ^{13}C NMR, δ, ppm: *trans*,*trans*-isomer, 16.10 ($2CH_3S$), 25.95 (C^3H_2, C^5H_2), 30.71 (C^4H_2), 37.84 ($2CH_2S$), 41.60 (C^2H, C^6H), 68.99 (C^1H); *trans*,*cis*-isomer, 16.43 ($2CH_3S$), 25.04 (C^4H_2), 25.47 (C^3H_2, C^5H_2), 38.45 ($2CH_2S$), 43.99 (C^2H, C^6H), 77.96 (C^1H); *cis*,*cis*-isomer, 15.97 ($2CH_3S$), 19.94 (C^3H_2, C^5H_2), 34.40 (C^4H_2), 37.06 ($2CH_2S$), 39.19 (C^2H, C^6H), 73.57 (C^1H). Found, %: C 55.80, H 9.15, S 29.47. Calculated for $C_{10}H_{20}OS_2$, %: C 54.50, H 9.15, S 29.10.

Synthesis of γ-ketosulfones (10–12). A mixture of 4.7 and 9.4 ml (0.046 and 0.092 mol, respectively) of 33% hydrogen peroxide and five drops of concentrated sulfuric acid were successively added with stirring to a cooled (ice bath) solution of 0.02 mol of ketosulfide **3**, **4**, or **6** in 10 ml of acetic acid. The resultant mixture was stirred at room temperature for 9 h and allowed to stand overnight, then diluted with water (50 ml), and extracted with chloroform (2 × 45 ml). The extract was successively washed with $NaHCO_3$ and NaCl solutions and water (1 : 1 by volume) and dried with $MgSO_4$. Chloroform was evaporated, and the residue was recrystallized from ethanol.

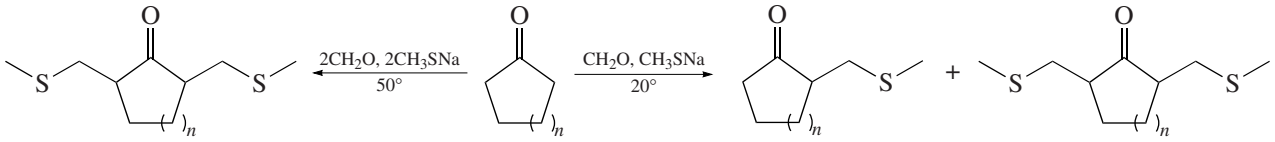
2-(Methylsulfonylmethyl)cyclopentan-1-one (10). The yield of **10** was 2.93 g (83%), mp 60–62°C. IR, ν, cm^{-1}: 1740 (C=O), 1292, 1136 (SO_2). ^1H NMR, δ, ppm: 1.70 dq (1H, C^3H^a, $J_{gem} = J_{3a,2a} = J_{3a,4a}$ 11.4 Hz, $J_{3a,4e}$ 6.1 Hz), 1.83–1.92 m (1H, C^4H^a), 2.08–2.20 m (2H, C^3H^e, C^4H^e), 2.33–2.50 m (1H, C^2H^a), 2.50–2.75 m (2H, C^5H_2), 2.90 dd (1H, $C^{1'}H^e$, J_{gem} 14.0 Hz, $J_{1'e,2}$ 9.0 Hz), 2.97 s (CH_3SO_2), 3.57 dd (1H, $C^{1'}H^a$, J_{gem} 14.0 Hz, $J_{1'a,2}$ 3.0 Hz). ^{13}C NMR, δ, ppm: 20.46 (C^4H_2), 29.94 (C^3H_2), 36.56 (C^5H_2), 41.87 (CH_3SO_2), 43.73 (C^2H), 54.63 (CH_2SO_2), 216.89 (C=O). Found, %: C 47.80, H 6.40, S 18.21. Calculated for $C_7H_{12}O_3S$, %: C 47.71, H 6.86, S 18.19.

2-(Methylsulfonylmethyl)cyclohexan-1-one (11). The yield of **11** was 3.69 g (97%), mp 50–51°C. IR, ν, cm^{-1}: 1712 (C=O), 1304, 1132 (SO_2). ^1H NMR, δ, ppm: 1.51 dq (1H, C^3H^a, $J_{3a,4e}$ 3.8 Hz, J_{gem} 12.8 Hz), 1.60–1.90 m (3H, C^4H^a, C^5H_2), 1.95–2.00 m (1H, C^4H^e), 2.10–2.20 m (1H, C^3H^e), 2.35–2.55 m (2H, C^6H_2), 2.75 dd (1H, $C^{1'}H^e$, J_{gem} 14.4 Hz, $J_{1'e,2}$ 5.6 Hz), 2.95 s (3H, CH_3SO_2), 3.10 dddd (1H, C^2H^a, $J_{2,1'a}$ 5.2 Hz, $J_{2,1'a}$ 5.6 Hz, $J_{2,3a}$ 12.8 Hz, $J_{2,3e}$ 5.9 Hz), 3.85 dd (1H, $C^{1'}H^a$, J_{gem} 14.4 Hz, $J_{1'a,2}$ 5.6 Hz). ^{13}C NMR, δ, ppm: 25.16 (C^4H_2), 27.81 (C^5H_2), 35.05 (C^3H_2), 41.94 (C^6H_2), 42.49 (C^2H), 45.51 (CH_3SO_2), 54.34 (CH_2SO_2), 209.15 (C=O). Found, %: C 50.70, H 7.39, S 16.21. Calculated for $C_8H_{14}O_3S$, %: C 50.51 H 7.41, S 16.85.

2,6-bis(Methylsulfonylmethyl)cyclohexan-1-one (12). The yield of **12** was 4.86 g (86%), mp 146–148°C. IR, ν, cm^{-1}: 1712 (C=O), 1300, 1136 (SO_2). ^1H NMR, δ, ppm: *cis*-isomer, 1.50 m (2H, C^3H^a, C^5H^a), 1.95 m (2H, C^4H_2, J_{gem} 10.5 Hz), 2.50 m (2H, C^3H^e, C^5H^e), 2.80 dd (2H, $C^{1'}H^e$, $C^{1''}H^e$, J_{gem} 14.4 Hz, $J_{1'e,2}$ 5.1 Hz), 2.98 s (6H, $2CH_3SO_2$), 3.30 dddd (2H, C^2H^a, C^6H^a, $J_{2,1'a}$ 6.4 Hz, $J_{2,1'e}$ 5.1 Hz, $J_{2,3a}$ 12.0 Hz, $J_{2,3e}$ 6.0 Hz), 3.85 dd (2H,$C^{1'}H^a$, $C^{1''}H^a$, J_{gem} 14.4 Hz, $J_{1'a,2}$ 6.4 Hz). ^{13}C NMR, δ, ppm: *cis*-isomer, 24.82 (C^4H_2), 35.64 (C^3H_2, C^5H_2), 42.36 (C^2H, C^6H), 45.64 (CH_3SO_2), 53.99 (CH_2SO_2), 207.30 (C=O). Found, %: C 42.80, H 6.67, S 22.80. Calculated for $C_{10}H_{18}O_5S_2$, %: C 42.54, H 6.42, S 22.71.

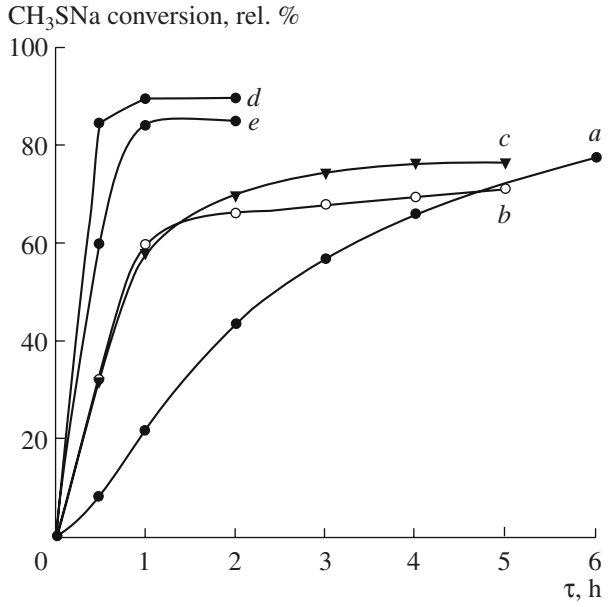
RESULTS AND DISCUSSION

The mono methylthiomethylated cyclic ketones 2-(methylthiomethyl)cyclopentan-1-one (**3**) and 2-(methylthiomethyl)cyclohexan-1-one (**4**) or the bis methylthiomethylated substituted ketones 2,5-bis(methylthiomethyl)cyclopentan-1-one (**5**) and 2,6-bis(methylthiomethyl)cyclohexan-1-one (**6**) were obtained with 76, 71, 49, and 93% yields, respectively, via the alkylthiomethylation of cyclopentanone **1** and cyclohexanone **2** with equimolar amounts or two molar equivalents of formaldehyde and SAL sodium methylmercaptide.



5, 6 **1, 2** **3, 4** **6**

where $n = 1$ for **1**, **3**, and **5** and $n = 2$ for **2**, **4**, and **6**.



Dependence of the sodium methanethiolate conversion on the time of alkylthiomethylation of (*a, b, d*) cyclopentanone and (*c, e*) cyclohexanone at (*a, b, c*) the equimolar reactant ratio, 20°C; (b) in the presence of sodium hydroxide (1 mol per mole of S_{mer}); and (*d, e*) at a ketone : CH_2O : S_{mer} molar ratio of 1 : 2 : 2, 50°C.

The ATM reactivity of cyclohexanone is higher than that of cyclopentanone (figure); however, the yield of 2-(methylthiomethyl)cyclohexan-1-one **4** (71%) is below that of 2-(methylthiomethyl)cyclopentan-1-one **3** (76%), a difference that is due to the subsequent transformation of **4** to 2,6-bis(methylthiomethyl)cyclohexan-1-one **6**. The introduction of the CH_3SCH_2 group into the molecule of **4** occurs at room temperature and the equimolar ratio of the reactants, whereas the reaction with **3** proceeds at 50°C and a twofold excess of the methylthiomethylated mixture. The reactivity of **4** is higher than that of **3**: the yield of 2,6-bis(methylthiomethyl)cyclohexan-1-one **6** is 1.9 times that of 2,5-bis(methylthiomethyl)cyclopentan-1-one **5**.

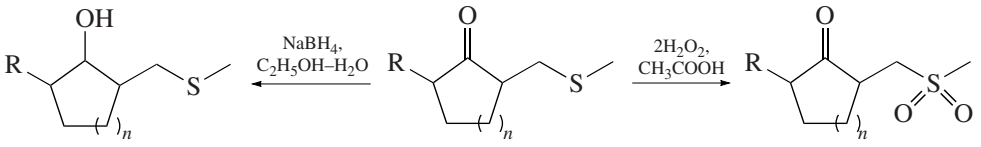
The yield of mono(methylthiomethyl) substituted cyclohexanone **4** decreases (from 71 to 65%) with an increase in the reaction time of more than 2 h owing to its transformation to 2,6-bis(methylthiomethyl)cyclohexan-1-one **6**.

The yield of mono- and bis(methylthiomethyl) substituted cyclohexanones **4** and **6** significantly depends on the reagents ratio. For example, the use of a 1.7-fold excess of ketone and formaldehyde (over the stoichiometric amounts) decreases the yields of compounds **4** and **6** to 51 and 35%, respectively.

The alkylthiomethylation of cyclopentanone is accelerated by a sodium hydroxide admixture (1 mole per mole of S_{mer}) (figure); however, the yield of desired product **3** decreases from 71 to 61% because of the side process of the formation of 2-(cyclopentylidene)cyclopentan-1-one identified by GC–MS analysis. The mass spectrum of the compound was identical to that published in [8].

The structure of γ-ketosulfides **3**–**6** was established on the basis of spectral data. The IR spectra of **3**–**6** exhibit carbonyl absorption bands at 1708–1738 cm^{-1}. The ^{13}C NMR spectra of **3**–**6** contain methyl (δ 15.58–17.74 ppm) and methylene (δ 31.70–37.88 ppm) signals of methylthiomethyl carbon atoms along with the signals from the carbon atoms of the cycle. The ^1H NMR spectra contain a singlet of thiomethyl protons (δ 2.09–2.17 ppm). Bis(methylthiomethyl) substituted ketones **5** and **6** are represented by a mixture of the *cis*- and *trans*-isomers in ratios of 2 : 1 and 4 : 1, respectively.

The reduction of the carbonyl group of γ-ketosulfides **3**, **4**, and **6** with sodium borohydride (50°C, 3 h) results in the formation of γ-hydroxysulfides **7**–**9** with yields of 94, 98, and 97%, respectively.



7–9 **3, 4, 6** **10–12**

3, **7**, **10** – *n* = 1, R = H; **4**, **8**, **11** – *n* = 2, R = H;
6, **9** – *n* = 2, R = CH_2SCH_3; **12** – *n* = 2, R = $CH_2SO_2CH_3$.

The IR spectra of γ-hydroxysulfides **7**–**9** exhibit hydroxyl absorption bands at 3384–3424 cm^{-1}. The ^1H and ^{13}C NMR spectra contain proton (δ 3.24–4.30 ppm) and carbon (δ 68.19–79.08 ppm) signals, respectively, of the methine group with an attached hydroxyl group. γ-Hydroxysulfides **7** and **8** are represented by mixtures of their *trans*- and *cis*-isomers (1.3 : 1 and 1.5 : 1, respectively); **9** is a mixture of the *trans,trans*-, *trans,cis*-, and *cis,cis*-isomers (7 : 4 : 1).

The oxidation of γ-ketosulfides **3**, **4**, and **6** with two and four equivalents of hydrogen peroxide (20°C, 9 h), respectively, results in the formation of γ-ketosulfones **10**–**12** with yields of 83, 97, and 86%, respectively.

The IR spectra of γ-ketosulfones **10**–**12** exhibit intense absorption bands due to the carbonyl (1712–1740 cm^{-1}) and sulfonyl (1132–1136, 1292–1304 cm^{-1}) groups. In the ^{13}C NMR spectra, the signals of methyl (δ 41.87–45.51 ppm) and methylene (δ 53.99–

54.63 ppm) carbon atoms bearing the sulfonyl group are downfield shifted relative to those of the same carbon atoms in ketosulfides.

2-(Methylthiomethyl)cyclohexan-1-one **4** thus prepared was tested as a corrosion inhibitor for Steel 20 (a grade of structural steel) using model hydrogen sulfide-containing mineralized media. It was shown that the addition of 100 mg/l of γ-ketosulfide **4** to the corrosive medium increases the degree of protection against general corrosion to 90.8%.

In summary, the use of the sulfide–alkaline liquor from the Orenburg gas-processing plant as a source of sodium methylmercaptide in the ATM of cyclopentanone and cyclohexanone makes it possible to prepare the mono- and bis(methylthiomethyl) substituted ketones and to reduce them to γ-hydroxysulfides or to oxidize to γ-ketosulfones. The results of this work extend the range of practically useful compounds synthesized from natural mercaptans. The obtained ketosulfides can be used as corrosion inhibitors, extracting agents for noble metals [9], and intermediaries in organic synthesis [10, 11].

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