benzene, 100-00-5; ammonia, 7664-41-7; formamide, 75-12-7; *p*-nitroaniline, 100-01-6; *p*-aminobenzoic acid, 150-13-0.

## References and Notes


(1) The classical synthesis involves nitration of toluene (36% para), separation of isomers, oxidation of *p*-nitrotoluene, and reduction of the nitro group. It is not a route adaptable to large-scale manufacture of pure *p*-aminobenzoic acid because of heavy losses to unwanted isomers.
(2) The potassium salt was much easier to handle than the sodium salt.
(3) The crude product contained up to 5% each of unchanged DMT and potassium terephthalate.
(4) M. Gordon, J. G. Miller, and A. R. Day, *J. Am. Chem. Soc.* **71**, 1245 (1949); R. Baltzly, I. M. Berger, and A. A. Rothstein, *ibid.*, **72**, 4149 (1950).
(5) H. Bredereck, R. Gompper, H. G. v. Schuh, and G. Theilig, in "Newer Methods of Preparative Organic Chemistry", Vol. III, W. Foerst, Ed., Academic Press, New York, N.Y., 1964, pp 241–303.
(6) P. K. Glasoe, J. Kleinberg, and L. F. Audrieth, *J. Am. Chem. Soc.*, **61**, 2387 (1939); F. H. Wetzel, J. G. Miller, and A. R. Day, *ibid.*, **75**, 1150 (1953), and previous papers by A. R. Day; T. C. Bruice et al., *ibid.*, **92**, 1370 (1970), and references cited therein.
(7) H. A. Staab and W. Rohr, in ref 5, Vol. V, 1967, pp 61–108.
(8) T. A. Koch, J. G. Miller, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 953 (1953).
(9) H. G. Zengel and M. J. Bergfeld, *Ind. Eng. Chem. Prod. Res. Dev.*, **15**, 186 (1976).
(10) Dielectric constant.
(11) Reference 5, pp 273–276.
(12) A. E. Pierce, "Silylation of Organic Compounds", Pierce Chemical Co., Rockford, Ill., 1968, Chapter 6.
(13) Reference 12, pp 63–71 and Chapter 9, shows that most amides are monosilylated on nitrogen.
(14) W. E. Dennis, *J. Org. Chem.*, **35**, 3253 (1970).
(15) Pierce Chemical Co., "Handbook of Silylation", GPA-3, offered a variety of reagents in kit form. These were tested according to the recommended procedures.
(16) W. G. Toland and C. D. Heaton, U.S. Patent 2 878 281.
(17) E. S. Wallis and J. F. Lane, *Org. React.*, **3**, 267 (1946).
(18) Mr. John Maciejczyk devised this application of sodium borohydride.
(19) J. S. Matthews and J. P. Cookson, *J. Org. Chem.*, **34**, 3204 (1969).
(20) This procedure is adapted from one originally devised by R. H. Sullivan.
(21) All pressure reactions must be conducted behind a suitable steel barricade with remotely actuated controls.


# β-Thioxo Ketones. 2.[1] Preparation and Structure of Some Five- and Six-Membered 2-Acylcycloalkanethiones and 2-Thioacylcycloalkanones


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2-Acetylcyclohexanethione, 2-thioacetylcyclopentanone, and 2-benzoylcyclopentanethione have been synthesized by acid-catalyzed reaction of the corresponding β-diketones with $H_2S$, while 2-thioacetylcyclohexanone was obtained by Claisen condensation of cyclohexanone with ethyl thionoacetate. $^1H$ NMR, IR, and UV spectroscopic investigations have shown that these β-thioxo ketones exist as equilibrium mixtures of the tautomeric (*Z*)-enethiol and (*Z*)-enol forms, which interconvert very rapidly by intramolecular chelate proton transfer. The direction of enolization/enethiolization is determined by the relative stabilities of the respective endo- and exocyclic C=C double bonds. A small equilibrium concentration of the (*E*)-enethiol form was recognized only for 2-thioacetylcyclopentanone. Methylation as well as acetylation of the β-thioxo ketones resulted in exclusive formation of the respective *S*-methyl and *S*-acetyl derivatives.


It has been demonstrated recently[1,3] that thioacetylacetone[1,3] and similar open-chain α-unsubstituted β-thioxo ketones[1] exist in solution as equilibrium mixtures of the tautomeric (*Z*)-enol and (*Z*)-enethiol forms, which interconvert very rapidly by intramolecular chelate proton transfer. The two tautomers are distinguishable as individuals in the electron[1,3] and vibrational[1] spectra, whereas the very fast interconversion gives rise to a $^1H$ NMR spectrum where the positions of the resonance signals are weighted averages of the chemical shifts of the separate tautomers.[1] This suggests a very low activation energy barrier to the tautomeric interconversion. Furthermore, for all compounds investigated,[1,3] the equilibrium was found to depend distinctly on the nature of the solvent. It was therefore anticipated that properties which may influence the stability of the alternative types of C=C double bonds also must determine the position of the tautomeric equilibrium. Six-membered homocyclic compounds possessing an exocyclic C=C double bond are generally considerably less stable than prototropic isomers having an endocyclic C=C double bond, whereas the opposite is true for five-membered ring compounds.[4,5] It might therefore be expected that 2-acetylcyclohexanethione (**1**) would exist predominantly as the enethiol tautomer (**1C**), whereas the enol tautomer (**2D**) should predominate for the isomeric 2-thioacetylcyclohexanone (**2**).[3] For monothio analogues of 2-acylcyclopentanones a considerable contribution of the tautomer possessing an exocyclic C=C double bond would be expected. The purpose of the present work was primarily to demonstrate the fulfillment of these expectations, but also to extend generally our present knowledge of the tautomeric and structural properties of β-thioxo ketones.

**Synthesis.** 2-Acetylcyclohexanethione (**1**) was obtained as the only product by the acid-catalyzed reaction of 2-acetylcyclohexanone with $H_2S$ under conditions very close to those applied successfully in the synthesis of thioacetylacetone.[1] It is noteworthy that no 2-thioacetylcyclohexanone (**2**) was formed by this reaction. The latter compound was, however, easily synthesized by Claisen condensation of cyclohexanone with ethyl thionoacetate.[6] 2-Thioacetylcyclopentanone (**3**) was obtained in a low yield by reaction of the corresponding β-diketone with $H_2S$ in acidic acetonitrile solution. The product was isolated from the crude reaction mixture as its lead complex, which was decomposed to the free ligand by dilute sulfuric acid. The crude reaction mixture was not further investigated, but very probably a main component was 1,3-dimethyldicyclopentano[5,9,7,10]-2,4,6,8-tetrathiaadamantane (a formal dimer of 2-thioacetylcyclopentanethione), which in an earlier investigation[7] of this reaction was isolated as the only product. The reaction of 2-benzoylcyclopentanone with $H_2S$ in acidic acetonitrile solution afforded as the only product 2-benzoylcyclopentanethione (**4**), which was also purified via its lead complex.

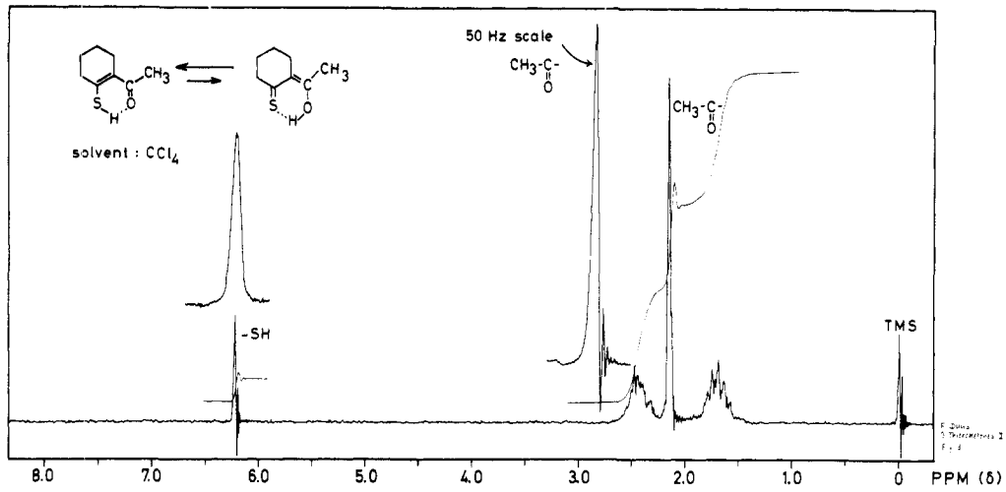
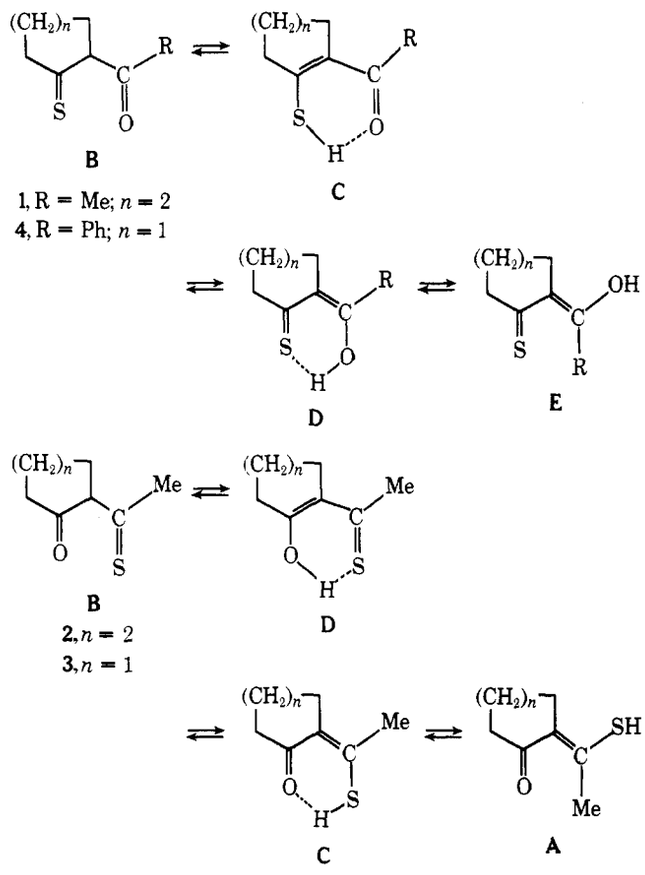


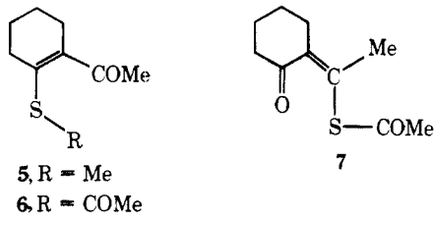

**Figure 1.** $^1$H NMR spectrum of 2-acetylcyclohexanethione (1) in $CCl_4$.

**Scheme I**




The β-thioxo ketones **1–4** are unstable compounds. At room temperature and in contact with air, decomposition to tarry substances is significant after a few days. However, they can be stored for months under $N_2$ in ampules at −20 °C.

Some β-thioxo ketone derivatives were synthesized in order to facilitate interpretation of the spectra of the parent compounds. 1-Acetyl-2-methylthiocyclohexene (**5**) was obtained by reaction of **1** with NaH and MeI, and in better yield by the ion-pair extraction reaction of **1** with tetrabutylammonium hydrogen sulfate and MeI. Upon treatment with acetic anhydride, the β-thioxo ketones **1** and **2** gave the respective S-acylated products **6** and **7** in high yields.




**Structure.** The $^1$H NMR spectrum of 2-acetylcyclohexanethione (**1**) (Figure 1) shows the pattern of a single component, just as in the case of thioacetylacetone.[1] If this spectrum is interpreted in terms of the existence of a very fast tautomeric interchange between merely the forms **1C** and **1D**, the observed weighted average chemical shift of the chelate proton (δ 6.63 ppm at infinite dilution[8]) clearly reflects a preponderant contribution of **1C**. For comparison, the mercapto proton signal of 2-ethoxycarbonyl-1-mercaptocyclohexene is found at δ 5.23 ppm,[9] whereas the hydroxyl proton signal of enolic 2-ethoxycarbonylcyclohexanone is found at δ 12.12 ppm,[10] and the chemical shift of the chelated hydroxyl proton of enolic nonaromatic β-diketones in general has a δ value between 13 and 18 ppm[11,12] ($\delta_{OH}$ 15.90 ppm for enolic 2-acetylcyclohexanone[12]). The chemical shift of the methyl protons (δ 2.16 ppm) is also in accordance with the predominance of **1C** (compare with the corresponding data for **5** and **6**, Table I), as otherwise a somewhat lower value should have been observed.[1]

The $^1$H NMR spectrum of **2** is very similar to that of **1** except for the positions of the chelate proton signal (δ 15.50 ppm at infinite dilution) and the methyl signal (δ 2.47 ppm). According to the above considerations, these shifts clearly indicate predominance of **2D** in the equilibrium system **2C** ⇄ **2D**. The methyl proton shift is considerably higher than that found for the corresponding methyl group of thioacetylacetone (δ 2.37 ppm[1]), although not as high as for a "true" thioacetyl group (δ 2.63–2.73 ppm[8,13]). A preponderant contribution of **2C** would have given rise to a considerably lower methyl proton shift and observable coupling of the methyl protons to the chelate proton[1,8] and probably also the ring protons in the 3 position[8] (compare the NMR data for the *S*-acetyl derivative **7**, Table I).

According to the introductory considerations, tautomeric structures with exocyclic C=C double bonds should be of importance for the five-membered ring compounds **3** and **4**. In the case of **3** the fulfillment of these expectations is very nicely illustrated by its $^1$H NMR spectrum (Figure 2). In $CCl_4$ solution **3** exhibits the chelate proton signal at δ 10.45 ppm, i.e., approximately halfway between the positions typical of chelated enethiolic mercapto protons ($\delta_{SH} \sim 6.0$ ppm for α-substituted β-mercaptocrotonates[8]) and chelated enolic hydroxyl protons ($\delta_{OH}$ 13.08 ppm for enolic 2-acetylcyclopentanone[11]), thus demonstrating the existence of a considerable

**Table I. $^1$H NMR Chemical Shifts ($\delta$ ppm) and Coupling Constants (Hz, in Parentheses) of 2-Acylcycloalkanethiones, 2-Thioacylcycloalkanones, and Derivatives[a]**

| Registry no. | | Solvent | $\delta_{chelat-H}$ | $\delta_{Me}$ | $\delta_{Ph}$ | $\delta_{SR}$ |
|---|---|---|---|---|---|---|
| | 1 | $CCl_4$ | 6.63[b] s | 2.16 s | | |
| | | $CD_3CN$ | 4.53 t (0.35) | 2.18 s | | |
| | 2 | $CCl_4$ | 15.50[b] s | 2.47 s | | |
| | | $CD_3CN$ | 13.48 s | 2.43 s | | |
| | 3[c] | $CCl_4$ | 10.45[b] q (0.95) | 2.13 q (0.95) | | |
| | 4 | $CCl_4$ | 14.33[b] s | | 7.2–7.8 m | |
| | | $CD_3CN$ | 11.82 s | | 7.3–7.8 m | |
| 62460-75-7 | 5 | $CCl_4$ | | 2.19 s | | 2.19[d] s |
| | | $C_6D_6$ | | 1.87[e] s | | 2.05[d,e] s |
| 62460-76-8 | 6 | $CCl_4$ | | 2.15 s | | 2.27[f] s |
| 62460-77-9 | 7 | $CS_2$ | | 2.09 t (1.5) | | 2.30[f] s |

[a] Aliphatic proton resonances at 2.0–3.0 (flanking methylene protons) and 1.5–2.1 ppm (other ring protons). [b] Chemical shift extrapolated to infinite dilution.[8,9] [c] Equilibrium percentage of trans enethiol form (**3A**) 15% (calculated from integrals). $\delta_{SH}$ (**3A**) 3.18 ppm (3.00 ppm at infinite dilution[8]), $\delta_{Me}$ (**3A**) 2.24 ppm. [d] R = Me. [e] Assignment tentative. [f] R = COMe.

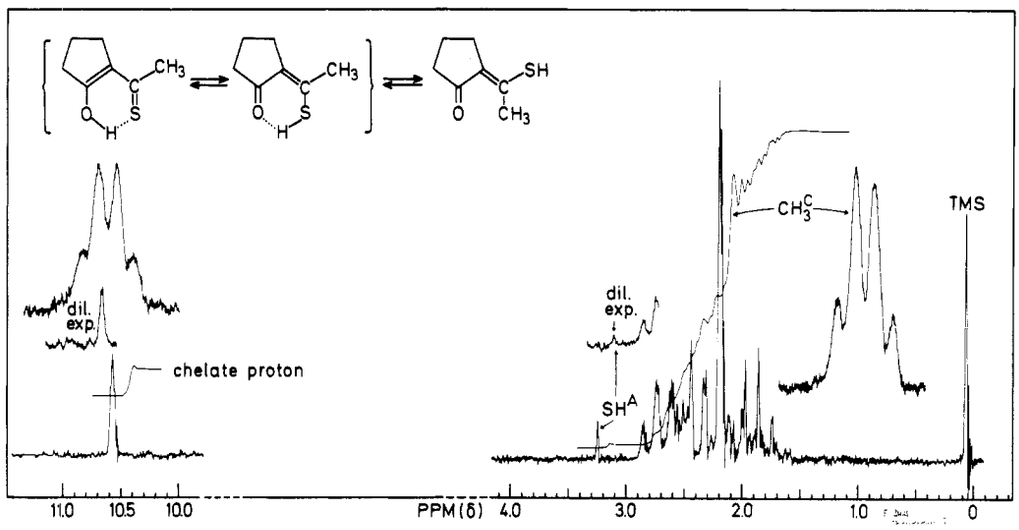



**Figure 2.** $^1$H NMR spectrum of 2-thioacetylcyclopentanone (3) in $CS_2$.

equilibrium concentration of **3C**. The importance of the contribution of **3C** is furthermore reflected by the occurrence of well-defined couplings between the chelate proton and the methyl protons and between the methyl protons and the ring protons in the 3 position, the two coupling constants being of approximately the same magnitude. Such couplings are also characteristic of $\alpha$-alkyl-substituted (*Z*)-$\beta$-mercaptocrotonates.[8]

Besides the resonance signals from the rapidly interconverting tautomers **3C** and **3D**, a small peak at $\delta$ 3.18 ppm (3.22 ppm in $CS_2$ solution, see Figure 2), which upon dilution moves to higher field (up to the limiting position of 3.00 ppm at infinite dilution[8]), is notable. This peak can be unambiguously designated as the mercapto proton resonance signal from the trans enethiol tautomer **3A**.[8] According to the integrals, the equilibrium percentages of **3A** are 15 ± 2%. The methyl resonance signal of **3A** is found at $\delta$ 2.24 ppm (2.25 ppm in $CS_2$ solution, see Figure 2).

In the $^1$H NMR spectrum of 4 (Table I), the chelate proton signal is found at $\delta$ 14.33 ppm in accord with a preponderant contribution of the enol tautomer **4D** (the chelate proton signal of enolic 2-benzoylcyclopentanone is found at $\delta$ 14.35 ppm in $CDCl_3$[14]). **4D** has the preferred exocyclic C=C double bond framework, which in this case may be further stabilized by the conjugative effect of the phenyl group.

The IR spectra of **1–4** (Table II) are fully consistent with the above interpretation of the $^1$H NMR spectra. The IR spectra of 1 and 3 show unmistakable S–H, C=O, and C=C stretching vibration bands at wavenumbers expectable[1] for the predominant enethiol tautomers **1C** and **3C**. In addition, the IR spectrum of 3 displays C=O and C=C stretching vibration bands arising from the minor tautomer **3A** (assignments are made by comparison with the IR data for (*E*)-$\beta$-mercaptocrotonates[8]). The IR spectra of 2 and 4 show, in accord with the prevalence of the enol tautomer **D** for these compounds, no distinct C=O or S–H stretching vibration bands, whereas in both cases the C=C stretching vibration band is very intense. Furthermore, a band assignable to the stretching vibration of a chelating, conjugated C=S group is found in both spectra (in the IR spectrum of thioacetylacetone[1] the C=S stretching vibration band of the **C** tautomer is at 1125 $cm^{-1}$). For comparison, IR data for the *S*-methyl and *S*-acetyl derivatives **5–7** are also given in Table II.

Previous investigations of thioacetylacetone and related open-chain $\alpha$-unsubstituted $\beta$-thioxo ketones have shown that the existence of the **C** $\rightleftarrows$ **D** equilibrium can be confirmed nicely by UV spectroscopy and that the position of the equilibrium can be determined, at least semiquantitatively, by UV absorbance measurements.[1,3] The UV spectra of thioacetylacetone in different solvents were found to be characterized by two bands within the regions 291–296 and 354–357 nm, the exact positions depending on the solvent. These bands were assigned to $\pi \rightarrow \pi^*$ transitions in the SC=CC=O chromophore (the enethiol tautomer **C**) and in the OC=CC=S

**Table II. Some Characteristic IR Absorption Bands ($cm^{-1}$) of 2-Acylcycloalkanethiones, 2-Thioacylcycloalkanones, and Derivatives[a]**

| | ν(S–H) | ν(C=O) | ν(C=C) | ν(C=S) |
|---|---|---|---|---|
| 1 | ~2540 w | 1670 s | 1555 s | |
| 2 | | | 1545 s | 1121[b] m |
| 3 | 2410 m, br | 1670 s | 1555 s | |
| | | 1702[c] m | 1598[c] m | |
| 4 | | | 1545 s | 1119[d] w |
| 5 | | 1665 s | 1536 s | |
| 6 | | 1710 vs | ~1625 w, br | |
| 7 | | 1710 vs | 1610 m, br | |

[a] Measured on $CCl_4$ solutions. [b] Tentative assignment, made by comparison with the IR spectrum of thioacetylacetone.[1] This band was absent in the IR spectra of 1 and 2-acetylcyclohexanone. [c] Attributed to the trans etheniol form (**3A**). [d] Tentative assignment.[1] A band at 1104 $cm^{-1}$ (m) is an alternative.

chromophore (the enol tautomer **D**), respectively.[1,3] The assignment of the band at lower wavelength is in agreement with UV spectral data for other compounds also containing the SC=CC=O chromophore (α,β-unsaturated β-mercaptoesters,[8] α,β-unsaturated β-mercapto thiolesters,[15] *S*-alkyl derivatives of these,[8,15] the enethiol tautomer of thiodimedone[16]). Unfortunately, comparable UV data for compounds possessing the OC=CC=S moiety are lacking in the literature. Both of the above assignments, however, are consistent with CNDO/2 calculations.[3] From these assignments, the intensities of the two bands in question must reflect directly the equilibrium concentrations of the two tautomers **C** and **D**, if other tautomers (see Scheme I) are nonexistent or present only in negligible concentrations. Assuming approximately equal molar absorption coefficients for the two bands, guiding equilibrium percentages of **C** and **D** may be easily calculated from the equations % **D** = $100A_D/(A_C + A_D)$ and % **C** = $100A_C/(A_C + A_D)$, where $A_C$ and $A_D$ are the measured absorbances. However, a comparison of the UV data of **5** (representative of the pure **C** structure) and **2** (existing in inert solvents to the extent of ~90% in the enol form **D**) reveals that the molar absorption of **D** may be possibly up to twice that of **C**. If so, the equilibrium percentages of **C** and **D** should be calculated according to the equations % **D** = $100A_D/(2A_C + A_D)$ and % **C** = $200A_C/(2A_C + A_D)$.

The UV spectra of the compounds **1–5** are tabulated in Table III, which also contains calculated absorbance ratios ($A_D/A_C$) and equilibrium percentages of the **C** and **D** tautomers. The percentages listed are averages of those calculated from the above pairs of equations, which are considered to represent cases of extremity. Whereas the *S*-methyl derivative **5** shows only one intense UV absorption, consistent with the existence of only the SC=CC=O chromophore, each of the β-thioxo ketones **1–4** exhibits both of the expected UV absorption bands. It is seen that the absorbance ratios as well as the calculated equilibrium percentages of the **C** and **D** tautomers (in the cases where the less polar solvents $C_6H_{12}$ and $CCl_4$ were used) go nicely with the estimates made from the $^1H$ NMR data. The more polar solvents EtOH and MeCN give rise to a general displacement of the **C** ⇄ **D** equilibrium in favor of the enethiol tautomer **C** (Table III). This effect was also observed for thioacetylacetone[1,3] and 1,4-diphenyl-3-thioxo-1-butanone.[1] In order to establish the interpretation of the observed solvent-induced change in the absorbance ratio $A_D/A_C$ as a solvent-promoted equilibrium displacement, $^1H$ NMR spectra of **1**, **2**, and **4** were also recorded in $CD_3CN$ solution. In accordance with the principle of weighted average signals, a general displacement of the chelate proton signal to higher field (about 2 ppm) was observed (Table I).

## Experimental Section

$^1H$ NMR spectra were recorded on a Varian A-60 and/or on a JOEL C-60 HL spectrometer with 20–0.5% solutions. The chemical shifts are expressed as δ values in parts per million downfield from $Me_4Si$, and are correct to ±0.02 ppm. The chelate proton chemical shifts were found to be constant, unaffected by further dilution, at solute concentrations below 2%. Coupling constants were measured on expanded signals, and are expressed numerically in hertz with an accuracy of ±0.1 Hz. Attainment of tautomeric equilibrium was checked by repetitive NMR measurements during several days on solutions kept in closed tubes at constant temperature (25 °C). All signals were integrated at least five times.

Infrared spectra were recorded for 20–1% $CCl_4$ solutions on a Perkin-Elmer 457 grating spectrophotometer.

UV spectra were recorded on a Beckman Acta III spectrophotometer. Attainment of equilibrium was checked by repeated measurements on standard solutions.

Boiling and melting points are uncorrected. The yields refer to pure products. The purity was checked by NMR and elemental analyses (carried out by the microanalytical laboratory of the Department of General and Organic Chemistry, H.C. Ørsted Institute, University of Copenhagen).

Known methods were employed for preparation of the starting 2-acylcycloalkanones[17–19] and of ethyl thionoacetate.[20] Cyclohexanone was commercially available. The purity of the starting materials was checked by NMR.

**2-Acetylcyclohexanethione (1).** A solution of 14.0 g (0.1 mol) of 2-acetylcyclohexanone in 200 mL of MeCN was cooled to −50 °C. A stream of $H_2S$ was passed through the solution for 1.5 h, followed by another stream of dry HCl for 1.5 h (during which the temperature was allowed to rise to −40 °C). Finally, a moderate stream of $H_2S$ was passed through the solution during 3 h while the temperature was kept strictly constant at −40 °C. The reaction mixture was cautiously poured with stirring into a mixture of 300 mL of ice water and 200 mL of light petroleum (or pentane). The aqueous layer was extracted with a further 200 mL of light petroleum (or pentane), and the combined organic layers were washed twice with water until neutral and dried ($CaSO_4$). The solvent was evaporated at reduced pressure at room temperature to leave 10.0–11.4 g of yellow oil,[21] which was immediately distilled[22] twice through a short Vigreux column to give 4.6–6.1 g (30–39%) of pure product as a yellow oil that partly solidified on standing in the refrigerator, bp 76–77 °C (0.1 mm), $n^{25}D$ 1.5750. Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75; S, 20.48. Found: C, 61.85; H, 7.80; S, 19.96.

**2-Thioacetylcyclohexanone (2).** A solution of 39.2 g (0.4 mol) of cyclohexanone in 50 mL of dry ether was added dropwise during 10 min to a stirred suspension of 15.6 g (0.4 mol) of $NaNH_2$ in 300 mL of dry ether at 0 °C. After stirring for 50 min at 0 °C, a solution of 20.8 g (0.2 mol) of ethyl thionoacetate in 50 mL of dry ether was added dropwise during 1 h with stirring at 0 °C. The stirring was continued overnight, during which period the temperature in the reaction flask was allowed to reach room temperature. Ice water (400 mL) was stirred in, and the aqueous layer was isolated and washed with 200 mL of ether. Then 200 mL of ether was added, and 2 N aqueous HCl was added in small portions with vigorous stirring until the aqueous layer had pH about 2. The ethereal layer was separated, the aqueous layer was extracted with a further 200 mL of ether, and the combined ethereal extracts were washed once with water and dried ($CaSO_4$). The solvent was evaporated to leave 24.9 g of practically pure **2**. Distillation[22] through a short Vigreux column gave 15.4 g (49%) of pure **2** as a yellow oil that solidified in the refrigerator, bp 69–70 °C (0.1 mm) [lit.[6] 90–92 °C (0.2 mm)], $n^{25}D$ 1.6172. Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75; S, 20.48. Found: C, 61.68; H, 7.88; S, 20.28.

**2-Thioacetylcyclopentanone (3).** Through a solution of 12.6 g (0.1 mmol) of 2-acetylcyclopentanone in 150 mL of MeCN there was passed successively $H_2S$ (1.5 h at −50 °C), dry HCl (1.5 h at −50 to −40 °C), and $H_2S$ (5 h at −40 °C). The reaction mixture was worked up as described for **1**. The crude product was purified via its lead salt according to a previously described procedure[8] (method D). The final distillation[22] gave 0.65 g (4.5%) of pure **3** as a yellow oil, bp 47 °C (0.1 mm) [lit.[23] bp 80–83 °C (0.5 mm)], $n^{25}D$ 1.5784. Anal. Calcd for $C_7H_{10}OS$: C, 59.14; H, 7.09; S, 22.51. Found: C, 59.41; H, 6.95; S, 22.64.

**2-Benzoylcyclopentanethione (4).** A solution of 12.2 g (65 mmol) of 2-benzoylcyclopentanone in 200 mL of MeCN was cooled to −50 °C and treated successively with $H_2S$ (1.5 h at −50 °C), dry HCl (1.5 h at −50 °C), and $H_2S$ (8 h, during which the temperature rose to −37 °C). The reaction mixture was poured (caution!) with stirring into a mixture of 400 mL of ice water and 200 mL of chloroform, and the organic layer was washed with water and dried ($CaSO_4$). The solvent

**Table III. UV Spectra of 2-Acylcycloalkanethiones, 2-Thioacylcycloalkanones, and S-Methyl Derivatives[a]**

| | Solvent | Concn, $10^{-5}$ mol/L | $\lambda_{max}$ (A) | $\lambda_{max}$ (C) ($A_C$) | $\lambda_{max}$ (D) ($A_D$) | $\lambda_{max}$ (A) | $A_D/A_C$ | % D | % C | Registry no. D | Registry no. C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_6H_{12}$ | 6.27 | | 293 (0.341) | 372 (0.139) | | 0.41 | 23 ± 6 | 77 ± 6 | 62460-78-0 | 62460-82-6 |
| | $CCl_4$ | 7.15 | | 296 (0.420) | 372 (0.157) | | 0.37 | 21.5 ± 5.5 | 78.5 ± 5.5 | | |
| | EtOH | 7.08 | | 295 (0.475) | 370 (0.085) | | 0.18 | 11.5 ± 3.5 | 88.5 ± 3.5 | | |
| | $CH_3CN$ | 6.40 | | 293 (0.384) | 370 (0.057) | | 0.15 | 10 ± 3 | 90 ± 3 | | |
| 5 | EtOH | 13.68 | | 316 (0.873) | | | | | | | |
| 2 | $C_6H_{12}$ | 6.13 | 242 (0.103) | 290 (0.052) | 369 (0.790) | ~460 (0.0038) | 15.20 | 91 ± 3 | 9 ± 3 | 62460-79-1 | 62460-83-7 |
| | $CCl_4$ | 5.56 | | 290 (0.040) | 371 (0.707) | ~460 (0.0066) | 17.67 | 92.5 ± 2.5 | 7.5 ± 2.5 | | |
| | EtOH | 4.73 | 242 (0.067) | 302 (0.136) | 370 (0.504) | ~460 (0.0022) | 3.71 | 72 ± 7 | 28 ± 7 | | |
| | $CH_3CN$ | 5.69 | 242 (0.093) | 294 (0.164) | 370 (0.599) | ~460 (0.0030) | 3.65 | 71.5 ± 6.5 | 28.5 ± 6.5 | | |
| 3 | $C_6H_{12}$ | 11.82 | | 302 (0.655) | 373 (0.330) | | 0.65[b] 31.5 ± 7.5[d] | 26.5 ± 6.5[c] 68.5 ± 7.5[d] | 58.5 ± 6.5[c] | 62460-80-4 | 62460-84-8 |
| | EtOH | 11.32 | | 302 (0.788) | 368 (0.205) | | e | 16.54 ± 4.5 | e | | |
| 4 | $C_6H_{12}$ | 9.12 | | ~320 (~0.20) | 394 (1.393) | | ~7.0 | 83 ± 5 | 17 ± 5 | 62460-81-5 | 62460-85-9 |
| | EtOH | 7.84 | | 325 (0.283) | 395 (0.684) | | 2.42 | 63 ± 8 | 37 ± 8 | | |

[a] λ is expressed in nm. Absorbances (A) are given in parentheses. [b] $A_c$ was corrected for a contribution by 15% of **3A**. [c] Calculated as coexisting with 15% of **3A**. [d] Relative percentages, referring to the system **3C** ⇄ **3D** only. [e] Not calculable because the equilibrium percentage of **3A** in EtOH is not known.

was evaporated to leave 11.2 g of a red-brown syrup, which was distilled. The fraction collected at 125–130 °C (0.25 mm), a red oil (6.5 g), was further purified via its lead salt according to a previously described procedure[8] (method C). The final distillation[22] gave 1.6 g (12%) of pure **4** as a red oil, bp 122 °C (0.15 mm). Anal. Calcd for $C_{12}H_{12}OS$: C, 70.57; H, 5.92; S, 15.67. Found: C, 70.74; H, 5.96; S, 15.73.

**2-Acetyl-1-methylthiocyclohexene (5). A.** To a suspension of 0.60 g (25 mmol) of NaH in 75 mL of dry benzene was added dropwise during 30 min, with stirring, a solution of 3.12 g (20 mmol) of **1** in 15 mL of dry benzene. After stirring for a further 2 h a solution of 3.12 g (22 mmol) of MeI in 15 mL of dry benzene was added dropwise during 15 min. The reaction mixture was refluxed for 4 h, allowed to stand overnight, and filtered. Evaporation of the filtrate left an orange oil that solidified in the refrigerator. Recrystallization from a 1:5 mixture of benzene and light petroleum (60–80 °C) gave 0.81 g (24%) of **5** as pale orange crystals, mp 65 °C. Anal. Calcd for $C_9H_{14}OS$: C, 63.51; H, 8.29; S, 18.80. Found: C, 63.86; H, 7.92; S, 18.91.

**B.** A solution of 2.50 g (16 mmol) of **1** and 2.27 g (16 mmol) of MeI in 40 mL of chloroform was added to 40 mL of an aqueous solution of 1.82 g (32 mmol) of KOH and 5.42 g (16 mmol) of tetrabutylammonium hydrogen sulfate, and the mixture was stirred vigorously for 1.5 h. The organic layer was dried ($CaSO_4$), the solvent was evaporated, and the residue was shaken carefully with 50 mL of ether to separate crystalline tetrabutylammonium iodide. After filtration and evaporation of the ether, the remaining oil solidified in the refrigerator. Recrystallization (*n*-heptane) gave 1.59 g (72%) of **5**, mp 60–61 °C. The $^1H$ NMR and IR spectra of the two products were identical.

**2-Acetyl-1-acetylthiocyclohexene (6).** To a solution of 2.03 g (13 mmol) of **1** in 25 mL of $Ac_2O$ was added a few crystals of anhydrous sodium acetate. The mixture was allowed to stand for 2 days. Ether (50 mL) was added, and the ethereal solution was washed with aqueous potassium carbonate and water and dried ($CaSO_4$). The ether was evaporated and the remaining dark oil distilled to give 2.05 g (80%) of pure **6** as a colorless oil, bp 99–100 °C (0.35 mm), $n^{25}D$ 1.5278. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.59; H, 7.12; S, 16.15. Found: C, 60.50; H, 7.15; S, 15.99.

**2-(1-Acetylthioethylidene)cyclohexanone (7)** was prepared analogously to **6** from 3.28 g (21 mmol) of **2** and 40 mL of $Ac_2O$: yield 3.40 g (82%); colorless oil; bp 83 °C (0.15 mm); $n^{25}D$ 1.5396. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.59; H, 7.12; S, 16.15. Found: C, 60.62; H, 7.22; S, 15.98.

**Registry No.**—**3A**, 62460-86-0; 2-acetylcyclohexanone, 874-23-7; cyclohexanone, 108-94-1; ethyl thionoacetate, 926-67-0; 2-acetylcyclopentanone, 1670-46-8; 2-benzoylcyclopentanone, 36150-58-0.

## References and Notes


(1) Part 1: F. Duus and J. W. Anthonsen, *Acta Chem. Scand., Ser. B*, **31**, 40 (1977).
(2) Address correspondence to Department of Chemistry, Institute III, Roskilde University Center, P.O. Box 260, 4000 Roskilde, Denmark.
(3) J. Fabian, *Tetrahedron*, **29**, 2449 (1973).
(4) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).
(5) M. Gorodetsky, Z. Luz, and Y. Mazur, *J. Am. Chem. Soc.*, **89**, 1183 (1967).
(6) E. Uhlemann and P. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966).
(7) W. Uhde and K. Hartke, *Arch. Pharm. (Weinheim, Ger.)*, **304**, 42 (1971).
(8) F. Duus, *Tetrahedron*, **28**, 5923 (1972).
(9) F. Duus, *Tetrahedron*, **30**, 3753 (1974).
(10) S. J. Rhoads, *J. Org. Chem.*, **31**, 171 (1966).
(11) S. Forsén, F. Merényi, and M. Nilsson, *Acta Chem. Scand.*, **18**, 1208 (1964).
(12) S. Hünig and H. Hoch, *Justus Liebigs Ann. Chem.*, **716**, 68 (1968).
(13) D. Paquer and J. Vialle, *Bull. Soc. Chim. Fr.*, 3595 (1969).
(14) F. Duus, unpublished.
(15) F. Duus, P. Jakobsen, and S.-O. Lawesson, *Tetrahedron*, **24**, 5323 (1968).
(16) L. Dalgaard and S.-O. Lawesson, *Acta Chem. Scand., Ser. B*, **28**, 1077 (1974).
(17) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).
(18) R. M. Manyik, F. C. Frostick, J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 5030 (1953).
(19) R. D. Campbell and H. M. Gilow, *J. Am. Chem. Soc.*, **84**, 1440 (1962).
(20) U. Schmidt, E. Heymann, and K. Kabitzke, *Chem. Ber.*, **96** 1478 (1963).
(21) According to $^1H$ NMR analyses, this oil contained 85–90% of **1**, the remaining 10–15% being mainly residual solvent. Traces of unreacted 2-acetylcyclohexanone and the *gem*-dithiol 2-acetyl-1,1-dimercaptocyclohexane [$^1H$ NMR ($CS_2$) δ ($SH^{free}$) 2.79 (s), δ ($SH^{chel}$) 3.22 (m); cf. $^1H$ NMR data for 2-ethoxycarbonyl-1,1-dimercaptocyclohexane[9]] were detected in some experiments, but **2** was never observed as a product.
(22) The distillation inevitably led to partial thermal decomposition of the product.
(23) E. Uhlmann and P. Thomas, *Z. Chem.*, **7**, 430 (1967).