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β-Thioxoketones. I. Preparation and Structure of Thioacetylacetone

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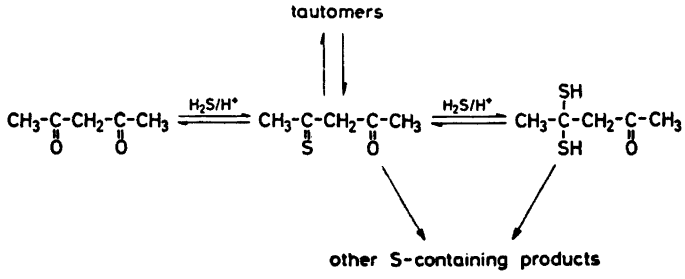
The acid catalysed reaction of acetylacetone with H_2S has been investigated, and conditions leading to complete conversion of the diketone into thioacetylacetone have been found. ^1H NMR, IR, Raman, and UV spectral investigations of the title compound and its *S*-methyl derivative have established that the former exists as an equilibrium mixture of two rapidly interconverting tautomers, (*Z*)-4-mercaptopent-3-en-2-one and (*Z*)-4-hydroxypent-3-ene-2-thione (predominant tautomer). Similar tautomeric features have been found for 1-phenylbutan-1-one-3-thione and 1,4-diphenyl-butan-1-one-3-thione, which were also obtained in good yields by acid catalysed reaction of the corresponding diketones with H_2S.

β-Thioxoketones have attracted considerable attention in the past as chelating agents with promising applications especially within analytical chemistry.[1–3] However, these compounds are also interesting for structural reasons, and because they may be of utility in the synthesis of a variety of heterocyclic compounds (exemplified recently [4]) just as are their oxygen analogues. Against this background thioacetylacetone, being related to the simplest β-diketone, is of particular interest.

Synthesis. Thioacetylacetone has been synthesized by basepromoted condensation of acetone with ethyl thionoacetate in 8 % yield,[5] by base catalysed reaction of acetylacetone with H_2S (yield: 24 %),[6–8] and by acid catalysed reaction of acetylacetone with H_2S (yield: 20 %).[9,10] Evidently, none of the reported methods can be satisfactory, if thioacetylacetone is required with a high degree of purity (*gem*-dithiol formation is a prevailing process under the reaction conditions stated in the two last mentioned cases) and in a quantity appropriate for further synthetic use. Referring to our experiences with the synthesis of β-thioxo esters [11,12] we decided to study the reaction of acetylacetone with H_2S under acidic conditions in order to find easily reproducible conditions leading to a complete conversion of the diketone into merely its monothio derivative (Scheme 1). The ambiguity of this type of reaction is well documented.[7,11,13] It should also be noticed that, in the hands of Fromm and Ziersch,[14] the reaction of acetylacetone with H_2S in acidic ethanol afforded a dimer of 2,4-pentanedithione with tetrathiaadamantane structure as the only isolated product. Our investigations led to the conclusion that the critical factors controlling the reaction course are the reaction temperature and the nature



Scheme 1.

of the solvent used, whereas a decisive dependence on the concentration of the catalyst (HCl), as stated by other authors,[9] could not be confirmed. Treatment of acetylacetone in acetonitrile solution (0.6 – 0.7 M) with excess of both H_2S gas and HCl gas at −40 °C leads to the complete and exclusive formation of thioacetylacetone within 6 h. The crude product (yield: 80 – 89 %) is sufficiently pure for further, immediate synthetic use. However, thioacetylacetone is thermally unstable, and distillation of the crude product (at reduced pressure) inevitably leads to partial decomposition, the degree of decomposition depending on the distillation conditions (Experimental). Decomposition also takes place slowly at room temperature, but freshly distilled thioacetylacetone can be kept for months in a closed ampoule at −20 °C.

The above-mentioned reaction conditions were found applicable also to the synthesis of 1-phenylbutan-1-one-3-thione (*2*), but the conversion of 1,4-diphenylbutane-1,3-dione into 1,4-diphenylbutan-1-one-3-thione (*3*) required a somewhat higher reaction temperature (−20 °C) as well as a prolonged reaction time.

The methylation of thioacetylacetone (*1*) with sodium hydride and iodomethane afforded as the only product the *S*-methyl derivative (*Z*)-4-(methylthio)pent-3-en-2-one (*4*).

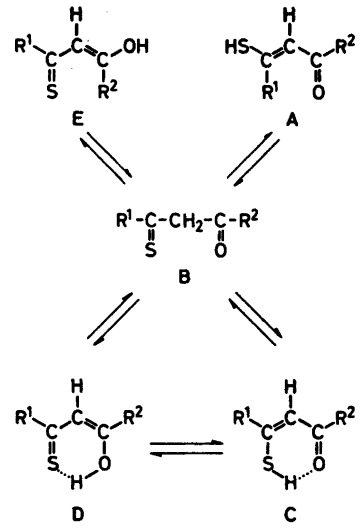
Structure. A survey over the potential tautomeric forms of thioacetylacetone and the likely pathways of their interconversion is given in Scheme 2 ($R^1 = R^2 = Me$). In general, tautomeric interconversion is sufficiently slow to allow for NMR spectroscopic distinction between the tautomers.[15] The ^1H NMR spectrum of thioacetylacetone shows only four sharp signals, at δ 2.09 (3 H), 2.37 (3 H), 6.20 (1 H), and 13.53 (1 H) (Table 1).* Immediately, this points to the existence of either of the tautomers *C* and *D*. The low-field signal at δ 13.53 occurs in the region characteristic for enolic protons engaged in intramolecular hydrogen bonding (δ 12 – 17).[17–20] Chelated enethiolic protons give rise to signals in the region δ 4.8 – 8.5.[11,12,21] On this background the enolic structure *D* seems preferable, as also suggested by Klose *et al.*[22] On the other hand, the existence of a weak coupling ($J = 0.4$ Hz) between the vinylic proton and the methyl group protons (R^1) lends support to the preference of the enethiol structure *C*, as chelated enethiols,[11,12,21]

* Possible minor peaks at δ 1.83, 2.13 (2.17[16]), 2.97 (3.03[16]), and 3.27 (3.23[16]) are indicative of the presence of the *gem*-dithiol 4,4-dimercaptopentan-2-one (MeC<, Ac, CH_2, and SH, resp.) and not, as stated previously,[7,16] of the presence of the thioxo ketone tautomer (*B*). For comparison, the ^1H NMR spectrum of ethyl 3,3-dimercaptobutyrate exhibits signals at δ 1.89 (MeC<), 2.94 (CH_2), and 3.25 (SH).[7]

Table 1. ^1H NMR chemical shifts and coupling constants (in brackets) of β-thioxoketones and derivatives. The solvent is CCl_4.

	R^1	R^2	$\delta(R^1)$	$\delta(R^2)$	$\delta(=CH-)$	$\delta(H^{chel})$	δ(SMe)
1	Me	Me	2.37 d (0.4)	2.09 s	6.20 q (0.4)	13.53[a] s[b]	
2	Me	Ph	2.54 m[c,d]	7.2 – 7.9 m	6.91 m[c]	15.09[a] m[c]	
3	$PhCH_2$	Ph	3.97 s[b](2H) 7.13 s(5H)	7.1 – 7.8 m	6.78 s[b]	14.86[a] s[b]	
4	Me	Me	2.30 d (1.1)	2.08 s	5.73 q (1.1)		2.26 s

[a] Value at infinite dilution.[11] [b] Any higher multiplicity could not be detected by signal expansion. [c] Multiplicity uncertain due to limitations in the resolution capacity of the apparatus. [d] Apparently dd (0.2/0.2).



Scheme 2.

but not chelated enols,[17–20] exhibit such a coupling. Structure *C* is plausible also because of the fact that the degree of enethiolization of thioketones in general is considerably higher than the degree of enolization of the corresponding ketones.[23] However, the coupling constant in question is remarkably smaller than that usually found for structurally related enethiols (as an example, $J = 1.2$ Hz in the (*Z*)-enethiol tautomer of ethyl thioacetoacetate)[11] as well as that found for the *S*-methyl derivative (*4*) (Table 1). The occurrence of a very rapid intramolecular proton exchange in (*Z*)-enolized β-diketones has been established,[24–26] and it is attractive to assume the occurrence of a similar proton exchange also among β-thioxo ketones, *i.e.* the occurrence of a very rapid interconversion between the equilibrated tautomers *C* and *D* by simple chelate proton transfer. If the interconversion $C \rightleftharpoons D$ takes place at a rate much higher than the difference in resonance frequencies between the NMR signals from the two tautomers, a single spectrum will be observed, where the positions of the resonance signals are weighted averages of the chemical shifts of the separate tautomers.[27] Weighted averages of couplings may also be expected. In fact, any apparent discrepancy is removed, if the NMR spectrum of thioacetylacetone is interpreted in terms of an equilibrium mixture of the two rapidly interconverting tautomers *1C* and *1D*. The small coupling ($J = 0.4$ Hz) between the vinylic proton and the methyl protons (R^1) suggests the contribution of about 33 % of the enethiol tautomer (*1C*) (*J* estimated to ~1.2 Hz[11]) and about 67 % of the enol tautomer (*1D*) (*J* estimated to ~0 Hz) according to the principle of weighted averages. Similarly, the chelate proton chemical shift is between those normally observed for chelated enethiols[11] and that found for enolic acetylacetone (δ 15.57)[17,20] Assuming the δ-values 15.57 and 7.30 (the chemical shift of the mercapto-proton of the (*Z*)-enethiol tautomer of ethyl thioacetoacetate[11]) as the representative chelate proton chemical shifts of *1D* and *1C*, respectively, the observed average shift at δ 13.53 would reflect the existence of about 25 % of *1C*. However, according to predictions based on a theoretical study of hydrogen bondings by means of the Schroeder-Lippincott potential function model,[28] intramolecular O–H···S hydrogen bondings are stronger than the corresponding O–H···O hydrogen bondings, *i.e.* presumably the chemical shift of the enolic proton of *1D* is even higher than δ 15.57. Consequently, the equilibrium percentages of *1C* should be estimated to be somewhat higher than 25 %. The ^{1}H NMR spectra of *2* and *3* (Table 1) are also consistent with the existence of solely the $C \rightleftharpoons D$ equilibrium system. In both cases increased chelate proton chemical shifts and reduced allylic couplings are observed, thus indicating relatively smaller equilibrium percentages of the enethiol tautomer (*C*).

The conclusion that thioacetylacetone must exist as an equilibrium mixture of the tautomers *1C* and *1D* has been drawn very recently also by Fabian[29] on the basis of UV spectroscopic investigations combined with LCAO-MO calculations. Our UV spectral data (Table 2) are in good agreement with those of Fabian,[29] although smaller deviations with respect to band intensities are notable. The UV spectra of *1–3* are all characterized by two significant bands of which the band at shorter wavelength (with absorbance A_s) is attributed to a $\pi \rightarrow \pi^*$ transition in the S–C=C–C=O chromophore (*C*), and that at longer wavelength (with absorbance A_l) to a $\pi \rightarrow \pi^*$ transition in the O–C=C–C=S chromophore (*D*). The solvent

Table 2. UV spectral data of β-thioxoketones and derivatives. Calculated percentages of enethiol tautomer (*C*) in different solvents.

	Solvent	Concentration 10^{-5} mol/l	λ_{max}(nm)[a] A_1	A_2	A_3	A_4	%*C*[b]
1	C_6H_{12}	6.63	455	354	296	237	27
			0.0026	0.600	0.226	0.110	(30)
	CCl_4	6.65	455	356	296		32
			0.0028	0.524	0.243		(34)
	EtOH	7.61	448	354	293	236	39)
			0.0024	0.579	0.374	0.120	(50)
	MeCN	8.92	445	357	291		44
			0.0026	0.562	0.440		(48)
4	C_6H_{12}	3.23			286		
					0.610		
2	C_6H_{12}	8.31		389	322		19
				1.205	0.280		
3	C_6H_{12}	4.44		392	307		20
				0.766	0.190		
	EtOH	5.30		394	314		30
				0.792	0.344		
	MeCN	3.89		394	311		40
				0.452	0.308		

[a] A_n = Absorbance of band No. *n*. [b] The percentages have been calculated under the assumption of approximately similar molar absorption coefficients of the bands 2 and 3 (% $C = 100A_3/(A_2+A_3)$ %).[29] The values in brackets are those determined by Fabian.[29]

interdependence of the two bands is interpreted in terms of a solvent promoted displacement in the $C \rightleftharpoons D$ equilibrium system. The assumption of approximately similar molar absorption coefficients for the two bands may lead to calculations of equilibrium percentages of the tautomers (Table 2), which are in good agreement with those estimated on the basis of the NMR data. However, for a more comprehensive discussion of the UV spectral properties of thioacetylacetone, the paper of Fabian [29] is recommended.

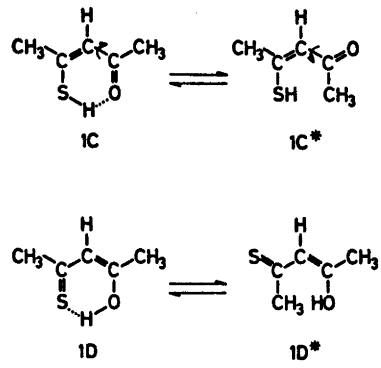
In contrast to the findings above, Siiman and his coworkers,[30] on the basis of IR and Raman

Table 3. Characteristic IR and Raman absorption bands (cm^{-1}) of thioacetylacetone (*1*) and its *S*-methyl derivative (*4*).

1			*4*		
IR	Raman	ΔI[a]	IR	Raman	ΔI[a]
2500(w,br.)	[b]				
1672(w,sh)	1671(w)	(−)	1683(s)	1682(s)	(−)
1652(m)	[b]				
1571(vs)	1573(vs)	(+)	1570(s)	1572(vs)	(+)
1422(m)	1422(w,sh)	(−)	1431(m)	1433(w)	(−)
1376(w,sh)	1378(w,sh)	(=)	1382(s)	1382(w)	(−)
1363(m)	1365(m)	(=)	1362(s)	1365(w)	(−)
1264(m)	1266(m)	(=)			
1218(w,sh)	1220(m)	(+)			
1202(s)	1202(w,sh)	(−)	1200(s)	1200(w)	(−)
1125(m)	1120(s)	(+)	1124(m)	1125(w)	(−)
1027(m)	1028(m)	(+)	1010(m)	1010(s)	(+)

[a] Intensity of Raman band compared with the corresponding IR band, increased: (+); decreased: (−); approximately unchanged: (=). [b] Absorption not detectable.

spectroscopic investigations combined with normal-coordinate analyses, reached the conclusion that thioacetylacetone should exist predominantly in the enethiol form (*1C*). The existence of a few percentages of the thioxo ketone form (*1B*) was also recognized, but the enol structure (*1D*) was not taken into consideration.[30] We have recorded the IR and Raman spectra of thioacetylacetone (*1*) and, for comparison, also of its *S*-methyl derivative (*4*), and we wish to proclaim that the vibrational spectra of thioacetylacetone clearly indicates the co-existence of the two tautomeric forms *1C* and *1D*. Some characteristic IR and Raman spectral data of *1* and *4* are found in Table 3.



Scheme 3.

The presence of the enethiol tautomer *1C* should be reflected by at least 3 characteristic absorptions bands, arising from the S–H stretching vibration, the C=O stretching vibration, and the C=C stretching vibration. A weak, broad band at ~2500 cm^{-1} indicates the intramolecularly chelated mercapto-group,[7,11,12,21] and the very intense band at 1571 cm^{-1} (1573 cm^{-1} in the Raman spectrum) reflects unambiguously a carbonyl-conjugated C=C double bond (compare with the vibrational spectral data of the *S*-methyl derivative *4* in Table 3). The two less intensive bands at 1652 cm^{-1} and 1672 cm^{-1} are ascribed to conjugated C=O stretchings in the intramolecularly H-bonded structure *1C*, and its rotamer *1C**, respectively (Scheme 3). It has been demonstrated[11,12] that α,β-unsaturated β-mercapto-esters ((*Z*)-enethiol form of β-thioxo esters) do exhibit such a rotameric effect, thus giving rise to two distinct ester carbonyl stretching absorption bands. With respect to the more abundant tautomer *1D*, bands arising from the O–H, the C=C, and the C=S stretchings should be immediately expected. However, the O–H stretching vibration bands of hydroxy-groups engaged in strong intramolecular H-bondings (as in enolized β-diketones) are known to be extremely broad and weak, and may very often escape detection.[31] The absence of a well-defined O–H stretching vibration band may therefore very probably simply reflect a strong intramolecular chelation. The C=C stretching absorption band of *1D* may be expected to coalesce with that of *1C*. It has been shown very recently that the C=S stretching vibration band of simple aliphatic thioketones occurs in the region 1244–1270 cm^{-1} with an intensity considerably lower than that of the C=O stretching band of the corresponding ketone.[32] In the actual case, the C=S band(s) should appear at a somewhat lower frequency due to conjugation and chelation. Using the values 1670 cm^{-1} (frequency of the conjugated, non-chelated carbonyl group, as in *1C**) and 1600 cm^{-1} (frequency of the conjugated, chelated carbonyl group in enolized β-diketones[33]) as references, the equation[32] $\nu(C=O)/\nu(C=S) = 1.38$ predicts C=S stretching vibration bands at 1212 cm^{-1} (structure *1D**) and 1160 cm^{-1} (structure *1D*), respectively. Furthermore, these bands should be of a strongly enhanced intensity in the Raman spectrum.[32–34] On this background, we ascribe the weak IR band at 1218 cm^{-1} (1220 cm^{-1} in the Raman spectrum) to ν(C=S) of *1D**, and the medium intensity band at 1125 cm^{-1} (1120 cm^{-1} in the Raman spectrum) to ν(C=S) of *1D*.

EXPERIMENTAL

^{1}H NMR spectra were recorded on 10–20 % solutions on a Jeol C-60 HL spectrometer. TMS was used as internal reference. The chemical shifts are correct within ±0.02 ppm. The coupling constants were measured on expanded signals and are expressed numerically with an accuracy within ±0.1 Hz. UV spectra were measured on a Beckman Acta III spectrophotometer. IR spectra were recorded on 5–20 % CCl_4 solutions on a Perkin-Elmer 457 grating spectrophotometer. Raman spectra were recorded on 20 % CCl_4 solutions on a

spectrometer equipped with a Jarrell-Ash model 25–101 double grating monochromator, and the exciting line was 514.5 nm from Spectra-physics model 165–00 argon ion laser.

Boiling and melting points are uncorrected. Unless stated otherwise the yields refer to the isolated quantities of the pure products. The purity was checked by NMR and elemental analysis. Elemental analyses were carried out in the micro-analytical laboratory of the Department of General and Organic Chemistry, the H. C. Ørsted Institute, University of Copenhagen.

Thioacetylacetone (1). A solution of 20.0 g (0.2 mol) of acetylacetone in 300 ml of MeCN was cooled to −50 °C, and a stream of H_2S gas was passed through it for 1.5–2 h, during which the temperature was allowed to rise to −40 °C. Then a stream of HCl gas was passed through the solution for 1.5 h, whilst the reaction temperature was kept carefully at −40 °C. After a further supply of H_2S gas for 2.5–3 h at −40 °C, the reaction solution was poured into a mixture of 500 ml of ice-water, 300 ml of pentane, and 100 ml of ether under manual stirring. The layers were separated, the aqueous layer was extracted with 200 ml of a 3:1 mixture of pentane and ether, and the combined organic extracts were washed twice with water (until neutral), and dried ($CaSO_4$). The solvents were removed by evaporation at reduced pressure at room temperature, leaving 18.5–20.5 g of a yellow oil, which by NMR analysis was found to consist of the desired product together with minor quantities of non-evaporated solvents (5–10 %). Subsequent distillation *in vacuo* afforded pure thioacetylacetone, but the yield was drastically reduced by this purification due to partial thermal decomposition. In four experiments (carried out under identical reaction conditions) the yields of pure, distilled *1* were found ranging from 11.9 g (51 %) (b.p. 58–59 °C/11 mmHg) to 7.8 g (33 %) (b.p. 73–75 °C/22 mmHg). Yellow oil, b.p. (see above), 59–60 °C/13 mmHg, 66–67 °C/18 mmHg (lit. 50–55 °C/10 mmHg,[9] 68 °C/14 mmHg,[35] 62 °C/15 mmHg [5]), n_D^{25} 1.5681 (lit. n_D^{19} 1.556,[9] n_D^{25} 1.559 [35]). Anal. C_5H_8OS: C, H, S.

The treatment of acetylacetone with H_2S and HCl at −50 °C, but otherwise under the same conditions as described above, resulted in incomplete conversion of the diketone into thioacetylacetone. At −30 °C the same reaction led to a mixture of thioacetylacetone and 4,4-dimercaptopentan-2-one (~10 %, identified by NMR and IR). A series of experiments, in which ethanolic solutions of acetylacetone were treated with H_2S and HCl at temperatures from −50 to 0 °C, resulted in less well-defined product mixtures of thioacetylacetone, unreacted starting material, 4,4-dimercaptopentan-2-one, and at temperatures above −20 °C, also other sulfur-containing products (not identified).

1-Phenylbutan-1-one-3-thione (2). A solution of 8.1 g (50 mmol) of benzoylacetone in 200 ml of MeCN was treated with H_2S and HCl according to the procedure given above. Following also the same working-up procedure, the crude product (8.4–8.9 g, containing ~10 % of non-evaporated solvents) was obtained as a yellow oil that solidified rapidly on cooling (refrigerator). Recrystallization (light petroleum) afforded 4.1–4.3 g (46–48 %) of the pure product. M.p. 26 °C (lit. m.p. 25–26 °C,[5] 28 °C[9]). Anal. $C_{10}H_{10}OS$: C, H, S. IR (CCl_4): 1580 (w, sh), 1548 (s), 1230 (s) cm^{-1}.

1,4-Diphenylbutan-1-one-3-thione (3): A solution of 5.95 g (25 mmol) of 1,4-diphenylbutane-1,3-dione in 250 ml of MeCN was cooled to −50 °C. H_2S gas was supplied for 1.5 h, during which the temperature was allowed to rise to −40 °C. Then dry HCl gas was supplied for 1.5 h (at −40 °C), followed by H_2S gas for further 3 h, during which the temperature was raised gradually to −20 °C. The reaction solution was kept at −20 °C for 16 h before working-up according to the usual procedure. The crude product (6.3 g) appeared as a reddish oil that rapidly solidified on cooling (refrigerator). Recrystallization (hexane) gave 3.44 g (54 %) of the pure product. Yellow crystals, m.p. 50–50.5 °C. Anal. $C_{16}H_{14}OS$: C, H, S. IR (CCl_4): 1608 (w, sh), 1593(m), 1558 (s), 1250 (s) cm^{-1}.

(Z)-4-(Methylthio)pent-3-en-2-one (4). A solution of 4.64 g (40 mmol) of thioacetylacetone in 20 ml of dry benzene was added dropwise at room temperature during 0.5 h to a stirred suspension of 1.00 g of NaH in 50 ml of dry benzene. Stirring was continued until the evolution of H_2 had ceased (1 h). Then a solution of 8.52 g (>40 mmol) of MeI in 20 ml of dry benzene was added dropwise under stirring during 0.5 h. The stirring was continued at room temperature overnight (16 h). 50 ml of ether and, successively, 200 ml of water (caution!) were added, and the reaction mixture was stirred until the two layers were completely clear. The layers were separated, and the organic layer was washed twice with 200 ml of water, and then dried ($CaSO_4$). The solvents were evaporated, and the residual oil (3.5 g) subjected to PLC (2 plates, silica gel $PF_{254+366}$ (Merck) support (450 × 250 × 3 mm), one elution with a 1:1 mixture of ether and light petroleum). The material absorbed in the R_F-region 0.64–0.84 was isolated to give 2.02 g (39 %) of the pure product. Colourless oil, b.p. 84–85 °C/12 mmHg (lit.[39] 60 °C/0.8 mmHg). Anal. $C_6H_{10}OS$: C, H, S.

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