Triphenylethenethiol. Structure, Equilibria with the Thioketone, Solvation, and Association with DMSO†

Tzvia Selzer and Zvi Rappoport*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

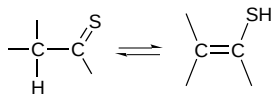
Received March 7, 1996⊗

The simple thioenols, triphenylethenethiol (**12**) and 2,2-diphenyl-1-anisylethenethiol (**13**) were prepared. Both are the only observed constituent of the thioenol ⇌ thioketone equilibria and comparison and estimation suggested that the thiocarbonyl ⇌ thioenol equilibrium constant K_{enol} for **12** and other simple thioenols is $\geq 10^6$ higher than for the corresponding carbonyl ⇌ enol equilibria. The X-ray diffraction of **12**, which is the first measured for a simple thioenol, shows a propeller arrangment of the three rings. The δ(SH) in the ^{1}H NMR spectrum increases with the increase in the hydrogen bonding accepting parameter β of the solvent. The association constant K_{assoc} of **12** with DMSO is 0.087, much lower than values of triarylethenols with DMSO. Reaction of diphenylacetaldehyde with Lawesson's reagent did not give the thioenol, but gave bis(2,2-diphenylvinyl) sulfide (**16**) and a substance (**17**) having a trithiaphosphorinane system.

Introduction

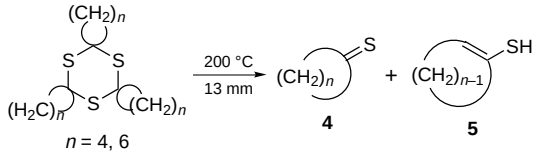
Simple enols, defined as enols substituted by hydrogen, alkyl, or aryl groups, but not by strongly electron-withdrawing hydrogen bond-accepting substituents[1] such as carbonyl, are usually much less stable than their carbonyl tautomers.[2] When the double bond substituents are bulky aromatic groups, such as mesityl, the enols are frequently stable,[3] and stability is also enhanced when two β-aryl groups can become coplanar or close to coplanar with the double bond. Appreciable keto ⇌ enol equilibrium constants were determined in these cases, and extensive structural and mechanistic investigations on poly(bulky)aryl-substituted enols were conducted in recent years.[4]

In contrast, the sulfur analogs, simple thioenols (**1**), are, in comparison with the thiocarbonyl tautomers (**2**), much more stable than are the enols vs the C=O derivatives. Indeed, even simple thiocarbonyl compounds **2** exist in equilbria (eq 1) with appreciable amount of the



2 **1** (1)

thioenol.[5] For example, the low-pressure pyrolysis of spirotrithienes **3** gives mixtures of cyclic thioketones (**4**) and their tautomeric cyclic thioenols **5**[6] (eq 2). For five- and seven-membered rings the percentage of **5** was ca. 3-fold higher than that of **4**.



3 **4** **5** (2)

With phenyl-substituted systems the thioenol is the only tautomer observed in several systems; e.g., only **6** was isolated from the reaction of benzhydryl benzyl ketone with H_2S/HCl, although the color of the thiocarbonyl compound was observed at an earlier reaction stage,[7] while **7** was the only product obtained from dibenzyl ketone and Lawesson's reagent.[8]

PhC(R)=C(SH)CH_2Ph
6: R = Ph
7: R = H

Simple thioaldehydes with α-hydrogens also prefer to be in the thioenol form, and no thioaldehyde was known up to 1991, when Ando and co-workers prepared both 2,2-di-*tert*-butylethanethial and its tautomer 2,2-di-*tert*-butylethenethiol.[9] In spite of the usual rapid thiocarbonyl to thioenol interconversion, the two species are nearly stable to mutual interconversion, presumably due to the high steric hindrance.

Although several preparative and quantitative studies on thioenol/thioketone systems activated by a β-carbonyl function had been conducted,[10] quantitative equilibration studies and physicochemical or structural information on simple systems are scarce. The only kinetic/equilibrium data known to us[11] are for the diisopropyl and diisobutyl systems **8/9** and **10/11** (eq 3). At 40 °C in CCl_4 **9** and **11**

† Dedicated to Prof. Michael Hanack on the occasion of his 65th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1996.

(1) Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1960; pp 663−702.

(2) Toullec, J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 6, pp 323−398.

(3) E.g.: (a) Fuson, R. C.; Foster, R. E.; Shenk, W. J., Jr.; Maynert, E. W. *J. Am. Chem. Soc.* **1945**, *67*, 1937. (b) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *J. Am. Chem. Soc.* **1946**, *68*, 389. (c) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J., Jr.; Sofer, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.

(4) For reviews see: (a) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442; (b) Hart, H.; Rappoport, Z.; Biali, S. E. in *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 8, pp 481−590.

(5) (a) Paquer, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1969**, 3327; (b) **1969**, 3595.

(6) Fraser, P. S.; Robbins, L. V.; Chilton, W. S. *J. Org. Chem.* **1974**, *39*, 2509.

(7) Campaigne, E.; Edwards, B. E. *J. Org. Chem.* **1962**, *27*, 3760.

(8) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

(9) Ando, W.; Ohtaki, J.; Suzuki, T.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7782.

(10) (a) Reyes, Z.; Silverstein, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 6367, 6373. (b) Bleisch, S.; Mayer, R. *Chem. Ber.* **1967**, *100*, 53. (c) Duus, F.; Pedersen, E. B.; Lawesson, S.-O. *Tetrahedron* **1969**, *25*, 5703. (d) Duus, F. *Tetrahedron* **1972**, *28*, 5923. (e) Fabian, J. *Tetrahedron*, **1973**, *29*, 2449. (f) Duus, F.; Anthonsen, J. W. *Acta. Chem. Scand. B* **1977**, *31*, 40. (g) Duus, F. *J. Org. Chem.* **1977**, *42*, 3123. (h) Duus, F. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon: New York, 1979; Vol. 3, pp 385−388.

(11) Paquer, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1971**, 4407.

S0022-3263(96)00465-3 CCC: $12.00

$$(RR'CH)_2C{=}S \rightleftharpoons RR'C{=}C(SH)CHRR' \quad (3)$$

8: R = R′ = Me **9**: R = R′ = Me
10: R = *i*-Pr, R′ = H **11**: R = *i*-Pr, R′ = H

consist of 58% and 53% of the mixtures, respectively, and the equilibration is accelerated by pyridine. Calculations on the butane-2-thione and 2-methylbutane-3-thione systems[12] gave a 1 kcal mol^{-1} higher stability for the C=S tautomer and a very high kinetic barrier of 85 kcal mol^{-1} for the tautomerization.

In addition to the lack of equilibrium data we know of no crystal data or an association data with the solvent for a simple thioenol. Consequently, we tried to prepare a few aryl-substituted thioenols in order to obtain for them data comparable to those available for the oxygen analogs.[4]

Results

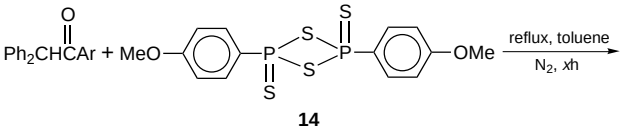
Synthesis. We attempted to prepare ethenethiols with 2,2-di(bulky)aryl, 1,2,2-triaryl, and 2,2-diphenyl substituents. The synthetic route to dimesityl and bis-(2,4,6-triisopropylphenyl) systems that involved an initial preparation of the thioketene led to polythio cyclic compounds, which will be discussed elsewhere.

Triphenylethenethiol (**12**) and 1-anisyl-2,2-diphenylethenethiol (**13**) were prepared in two ways. (i) Reaction of (2,2-diphenyl-1-aryl)magnesium bromides with sulfur (S_8) followed by hydrolysis with dilute H_2SO_4 solution gave **12** and **13** (eq 4).

$$Ph_2C{=}C(Br)Ar \xrightarrow[2.\ S_8\ \ 3.\ \text{dilute } H_2SO_4]{1.\ \text{Mg/solvent}} Ph_2C{=}C(SH)Ar \quad (4)$$

12: Ar = Ph, 44% (in ether)
13: Ar = An, 42% (in THF)

(ii) Reaction of 2,2-diphenyl-1-arylethanone with an equimolar amount of Lawesson's reagent [bis(p-methoxyphenyl)-1,3-dithiaphosphetane 2,4-disulfide (**14**)][8] in toluene under reflux followed by chromatographic separation of the product also gave **12** and **13** (eq 5).



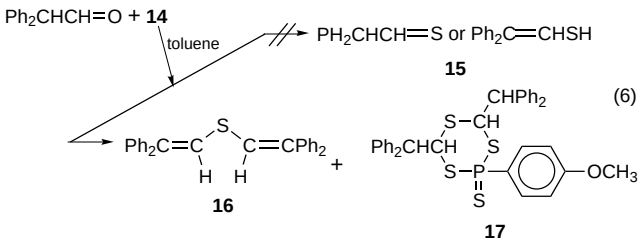
14

$Ph_2C{=}C(SH)Ar$ (5)

12: 15% (*x* = 50)
13: 34% (*x* = 48)

Thioenol **12** was previously prepared by method i by Koelsch[13] and was identified by microanalysis and its reactions with methyl sulfate or benzoyl chloride. We corroborated the thioenol structure by the mass spectra in which the base peaks are the molecular peaks at *m/z* 288 (**12**) and 318 (**13**), by the ν_{SH} stretching at 2562 (**12**) and 2578 cm^{-1} (**13**), by the SH signal in $CDCl_3$ at 3.28 (**12**) and 3.27 (**13**) ppm in the ^{1}H NMR spectra, by the signals at 126.13 (C_α) and 137.28 (C_β) for **12** in the ^{13}C NMR spectrum, and by X-ray diffraction of **12** (*vide infra*).

(iii) In an attempt to obtain the 2,2-diphenylethene-1-thiol (**15**) from diphenylacetaldehyde and Lawesson's reagent, two other compounds were isolated instead, bis-(2,2-diphenylvinyl) sulfide (**16**) and 1-(*p*-methoxyphenyl)-2,4,6-trithia-1-phospha-3,5-bis(diphenylmethyl)-1-thiocyclohexane (**17**) (eq 6). **16** was identified by its mass



(6)

spectral peaks at *m/z* 390 (M, B) and *m/z* 210 ($Ph_2C{=}C{=}S$) and its ^{1}H and ^{13}C NMR spectra. **17** was identified by its mass spectrum, *m/z* (B, Ph_2CHCHS), and its ^{1}H NMR spectrum, which showed signals at 3.85 (OMe), 6.98, 8.04 (Ar-H signals *meta* and *ortho*, respectively to the P, with the proper PH and HH coupling), a doublet at 4.52 ppm ascribed to the benzhydryl protons, and a doublet of doublets at δ 6.07 ppm ascribed to the aliphatic ring hydrogens, coupled by the phosphorous. The ^{13}C NMR spectrum displayed signals ascribed to the MeO group (56.91 ppm), the aliphatic ring carbons (56.91 ppm, J_{PH} = 28.8 Hz), the benzhydryl carbons (59.57 ppm), and the aromatic carbon signals.

Unequivocal structural evidence was obtained from X-ray diffraction of **17**. The ORTEP drawing is shown in Figure 1, and selected crystallographic data are given in Table 1.[14]

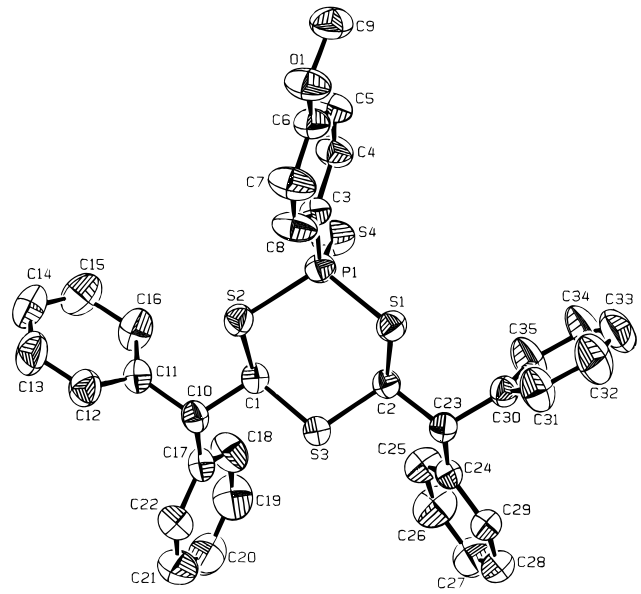


Figure 1. ORTEP drawing and numbering scheme for **17**.

The six-membered 2,4,6-trithia-1-phospha ring displays a chair conformation. If the ring plane is defined by atoms C(1), C(2), S(1), and S(2), the P and S(3) atoms are on opposite sides of this plane. The four rings display different torsional angles with the ring plane in the range of 48.42−88.48°.

Attempted Thioenol ⇌ Thioketone Equilibrations. In order to determine the position of the equilibrium of the thiols **12** and **13** with their keto tautomers

(12) Bruno, A. E.; Steer, R. P.; Mazey, P. G. *J. Comput. Chem.* **1983**, *4*, 104.
(13) Koelsch, C. F.; Ullyot, G. *J. Am. Chem. Soc.* **1933**, *55*, 3883.
(14) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EA, U.K.

Table 1. Bond Lengths and Angles for 17

bond	length, Å	angle	deg	dihedral angle[b]	deg
S(1)−P(1)	2.086(7)	2PCS	97.19 ± 0.21	A−An	75.28
S(2)−P(1)	2.094(8)	C(1)S(3)C(2)	103.8(1)	A−Ph[1]	88.48
S(4)−P(1)	1.932(8)	S(1)P(1)S(2)	104.9(3)	A−Ph[2]	67.21
S(1)−C(2)	1.836(2)	S(1)P(1)S(4)	113.7(4)	A−Ph[3]	48.42
S(2)−C(1)	1.834(2)	S(2)P(1)S(4)	114.1(4)	A−Ph[4]	68.60
S(3)−C(1)	1.809(2)	2SP(1)C(3)	102.8 ± 0.3	Ph[1]−Ph[2]	109.4
S(3)−C(2)	1.810(2)	S(4)P(1)C(3)	117.1(7)	Ph[3]−Ph[4]	90.54
C(1)−C(10)	1.546(3)	2SC(1)S	113.65 ± 0.05		
C(2)−C(23)	1.543(3)	SCC	107.95 ± 0.17		
4 C−C(Ph)	1.520(3)−1.523(3)	S(1)C(2)S(3)	113.7(1)		
		2PCC	120.8 ± 0.8		
Ar(C)−(C)	1.363(3)−1.401(4)[a]	6CS(sp^3)C	108.9(2)−113.9(1)		
		ring CCC	117.6(2)−121.4(3)		

[a] Except for C(32)−C(33) = 1.345(4) Å. [b] A = plane C(1)C(2)S(1)S(2); Ph[1] = C(11)−C(16); Ph[2] = C(17)−C(22); Ph[3] = C(24)−C(29); Ph[4] = C(30)−C(35).

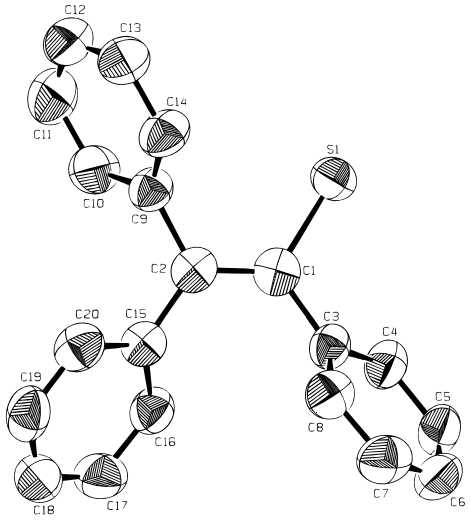


Figure 2. ORTEP drawing and numbering scheme for **12**.

18 and **19** from both sides, we tried to make the thioketones from the corresponding ethanones and **14**. As mentioned above, these reactions gave only the thioenols **12** and **13**, suggesting that if the equilibration is rapid, the thioenols are the exclusive equilibration products within our detection limits.

Equilibrations of 0.13−0.14 mol L^{-1} solutions of **12** and **13** were attempted in hexane at 60 °C for up to 2 weeks, and the mixtures were analyzed by ^{1}H NMR during this period for the presence of **18** and **19** (eq 7). No traces of

$$\underset{\mathbf{12}\ \ \mathbf{13}}{Ph_2C{=}C(SH)Ar} \xrightarrow[2\ \text{weeks}]{\text{hexane}} \underset{\mathbf{18}\ \ \mathbf{19}}{Ph_2CHC(Ph){=}S} \qquad (7)$$

$$Ar = Ph \qquad Ar = An$$

the thioketone (estimated detection limit 1−2%) were detected, and only **12** or **13** was observed. Likewise, no tautomerization to **18** or **19** was observed in the presence of 4% (v/v) of trifluoroacetic acid or up to 20% (v/v) pyridine in hexane.

Solid State Structure of 12. Since no solid state structure of a simple thioenol was determined so far, the structure of **12** was determined by X-ray crystallography. The ORTEP structure with atom numbering is given in Figure 2, and selected bond lengths, angles, and dihedral angles are given in Table 2.[14] The thioenol has a propeller conformation with different dihedral Ar−C=C angles in the range 44.5−62.3°. The torsional angle of the double bond is 7°. Except for the bond angles around the α-Ph ring, all bond angles and the bond lengths are close to those expected.

Association of 12 with the Solvent. We know of no data on the conformation of the C=C−S−H moiety that can be syn or anti, periplanar or clinal. Unfortunately, the thioenolic hydrogen was not located in the X-ray diffraction of **12**. Also, we know of no association data of the thioenolic SH with the solvent. We therefore tried to learn about the C=C−S−H conformation by comparing the δ(SH) values in the ^{1}H NMR spectrum of **12** with the δ(OH) values of stable simple enols. The δ-(SH) values in four solvents, together with the solvents' hydrogen bond accepting parameters β of the Kamlet−Taft solvatochromic equation,[15] are given in Table 3. The solvent dependence of the shift is relatively small, being <1 ppm between solvents at the extremes of the β scale.

When the values were plotted against δ(OH) of the stable enol 2,2-dimesitylethenol **20**,[15] a very approximate

$$\underset{\mathbf{20}}{Me_2C{=}CHOH} \qquad Mes = \text{mesityl}$$

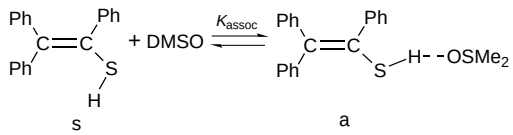
linear relationship (eq 8) was obtained. The small slope indicates a much lower sensitivity to the solvent change than for **20**. A plot of δ(SH) values vs β values also gave an approximate linear relationship (eq 9).

$$\delta(\text{SH})\ (\mathbf{12}) = 0.18\ \delta(\text{OH})\ (\mathbf{20}) + 2.41 \quad (R = 0.937) \qquad (8)$$

$$\delta(\text{SH})\ (\mathbf{12}) = 1.06\beta + 3.20 \quad (R = 0.953) \qquad (9)$$

In order to calculate an association constant (K_{assoc}) for the intermolecular RSH···DMSO hydrogen-bonded complex we measured the δ(SH) values of 0.02 M of **12** in binary CCl_4−DMSO-d_6 mixtures of varying compositions. The data are given in Table 4.

For calculating K_{assoc} it is assumed, on the basis of a similar study with **20**,[16] that only one DMSO-d_6 molecule is associated with **12** in the anti (a) C=C−S−H conformation (eq 10), which is in equilibrium with an unasso-



(10)

(15) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. Kamlet, M. J.; Doherty, R. M.; Abraham, M.; Carr, P. W.; Doherty, R. F.; Taft, R. W. *J. Phys. Chem.* **1987**, *91*, 1996. Kamlet, M. J., Taft, R. W. *Acta Chem. Scand.* **1986**, *B40*, 619.

(16) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

Table 2. Bond Lengths and Angles for 12

bond	length, Å	angle	deg	dihedral angle[a]	deg
S(1)−C(1)	1.803(3)	S(1)C(1)C(2)	120.4(3)	α-PhS(1)C(1)C(3)	55.74
C(1)−C(2)	1.356(5)	S(1)C(1)C(3)	113.9(2)		
C(1)−C(3)	1.503(5)	C(2)C(1)C(3)	125.7(3)	β-PhC(9)C(2)C(15)	44.54
C(2)−C(9)	1.490(5)	C(1)C(2)C(9)	119.5(3)		
C(9)−C(15)	1.473(4)	C(1)C(2)C(15)	122.7(3)	β′-PhC(9)C(2)C(15)	62.27
C−C(Ar)	1.368(5)−1.399(5)	C(9)C(2)C(15)	117.8(3)		
		CCC(Ar)	116.7 (3)−122.2(4)	S(1)C(1)C(3)−C(9)C(2)C(15)	173.00

[a] Key: α-Ph: C(3)−C(8); β-Ph: C(9)−C(14); β′-Ph: C(15)−C(20).

Table 3. δ(SH) Values (ppm) for 12 in Several Solvents at 295 K

solvent	β	δ(SH)
CCl_4	0	3.19
$CDCl_3$	0	3.28
CD_3COCD_3	0.48	3.54
DMSO-d_6	0.76	4.12

Table 4. δ(SH) (ppm) and *K* Values for 12 in CCl_4−DMSO-d_6 Mixtures at 295 K

DMSO-d_6:CCl_4 (v/v)	DMSO-d_6, M	δ(SH)	*K*
0:100	0	3.19	0
2:98	0.28	3.25	0.069
10:90	1.42	3.33	0.177
50:50	7.07	3.64	0.937
100:0	14.14	4.12	∞

ciated syn (s) conformation. The association constant K_{assoc} is then given by eq 11, where $[DMSO]_f$ is the free

$$K_{assoc} = [a]/[s][DMSO]_f = K/[DMSO]_f \qquad (11)$$

DMSO and $K = [a]/[s]$. When $[DMSO]_o$ is the free + associated [DMSO] in the mixture, $[DMSO]_f = [DMSO]_o - [a]$. When δ_{obs}, δ_a, and δ_s are the observed SH chemical shift and the unknown shifts for the anti and syn conformations, respectively, *K* is given by eq 12, which is based on the assumption of a rapid equilibrium between the a and s conformations.

$$K = (\delta_s - \delta_{obs})/(\delta_{obs} - \delta_a) \qquad (12)$$

A plot of *K* vs $[DMSO]_f$ should be linear with a slope = K_{assoc}. Using the same analysis applied before[16] we obtain eq 13, assuming as a first approximation that $\delta_a = \delta_{DMSO}$.

$$[DMSO]_o/(\delta_{obs} - \delta_{CCl_4}) = ([\mathbf{12}]_o + [DMSO]_o - [a])/(\delta_a - \delta_{CCl_4}) + 1/K_{assoc}(\delta_a - \delta_{CCl_4}) \qquad (13)$$

A plot of the $[DMSO]_o/(\delta_{obs} - \delta_{CCl_4})$ values vs $[\mathbf{12}]_o + [DMSO]_o - [a]$ should be linear with a slope of $1/(\delta_a - \delta_{CCl_4})$ and an intercept $1/K_{assoc}(\delta_a - \delta_{CCl_4})$. Since the [a] value is unknown, the $[DMSO]_o/(\delta_{obs} - \delta_{CCl_4})$ values were plotted vs $[\mathbf{12}]_o + [DMSO]_o$ values, and from the observed slope an approximate [a] value was calculated[16] and then used with eq 13. Since $[a] \ll [DMSO]_o$ for all the solutions, one iteration of eq 13 gave convergence to the δ_a and K_{assoc} values given in Table 5. K_{assoc} is low (0.087 L mol^{-1}), and since F_a is 0.62, we conclude that both the solvated anti conformer (62%) and the unsolvated cis conformer (38%) are present in DMSO solution.

Table 5. K_{assoc} and δ_y Values for 12 in CCl_4−DMSO-d_6 Mixtures at 295 K

param	value	param	value
K_{assoc}[a]	0.13	R[c]	0.815
δ_{DMSO}	4.12	δ_a[b]	4.7
K_{assoc}[b]	0.087	F_a in DMSO[d]	0.62

[a] According to eq 11, assuming that $\delta_a = \delta_{DMSO}$. [b] After one iteration according to eq 13. [c] Correlation coefficient for eq 13. [d] According to $(\delta_{DMSO} - \delta_{CCl_4})/(\delta_a - \delta_{CCl_4})$.

Discussion

Thioenol/Thioketone Equilibria. From examples and references given above it is clear that thioenols are more stable in relation to their thiocarbonyl compound than their oxygen analogs and that simple thioenols may be the predominant or exclusive components of the equilibria. This should be mainly ascribed to the large difference in bond energies of C=O (177 kcal mol^{-1}) and C=S (115 kcal mol^{-1}), which apparently more than overcome the differences (in kcal mol^{-1}) for CO (88)/CS (61) and OH (110)/SH (82).[17]

Our results resemble the earlier ones. Only the thioenol was obtained from **12** and **13** with no trace of the thioketones **18** and **19**. Since the two synthetic methods that were designed to give the thioenols and the thioketones, respectively, gave only the thioenols the latter seem the thermodynamically more stable species at equilibria.

The only value available for comparison is for triphenylethanone/triphenylvinyl alcohol. In DMSO, the best solvent for stabilizing the enol species, at 295 K K_{enol} = ca. 0.06.[18] For **12** (and **13**) in hexane, the solvent that least stabilizes enols, K_{enol} is ≥100 judged by the detection limit of the NMR.

The higher the β value of the solvent,[15] the higher is K_{enol},[16,18,19] e.g., K_{enol} (DMSO)/K_{enol} (H_2O) for diphenylacetaldehyde is ca. 50.[18,19] The only comparison available between DMSO and hexane is for 2-(2,4,6-triisopropylphenyl)acenaphthen-1-ol and its keto isomer where K_{enol}(DMSO)/K_{enol}(hexane) ≥ 650-fold.[19a] From this value and the K_{enol} values for **12** in hexane and for Ph_2C=C(OH)Ph in DMSO,[18] K_{enol} [Ph_2C=C(SH)Ph]/K_{enol} [Ph_2C=C(OH)Ph] ≥ 650 × 100/0.06 = ≥10^6. This estimation involves the assumption that the Ph−C= dihedral angles that affect the stability of the enols and thioenols by Ph−C= conjugation[4b,20] are the same in both systems, but a ratio of 10^6 as a lower value seems reasonable.

If this is the case, the lack of observation of **15** in the attempt to generate it is due to further reactions of the formed **15** to give **16** and **17**, since K_{enol} (Ph_2C=CHOH) is 5.06 in DMSO[17] and ca. 0.1 in water.[21]

(17) For experimental values see: (a) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 24. (b) Price, C. C.; Oae, S. *Sulfur Bonding*: Ronald Press Co.: New York, 1962; pp 1−7. (c) See also: Schaumann, E. In *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1989; Chapter 17, pp 1269−1274. (d) For calculated C=S and C−S energies see: Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(18) Rochlin, E.; Rappoport, Z. *J. Am. Chem. Soc.* **1992**, *114*, 230.

(19) (a) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599. (b) Rappoport, Z.; Nugiel, D. A.; Biali, S. E. *J. Org. Chem.* **1988**, *53*, 5361. (c) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 213.

(20) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.

(21) Chiang, Y.; Kresge, A. J.; Krogh, E. T. *J. Am. Chem. Soc.* **1988**, *110*, 2600.

The exclusive observation of **6** and **7** in their (presumable) mixtures with the thiocarbonyl compounds[7,8] is consistent with these values. For PhCH=CHOH $pK_{enol}(H_2O)$ values are 3.35 (*E*) and 3.07 (*Z*).[22] Using a K_{enol} (EtOH)/K_{enol} (hexane) ratio of ≥ 6[19a] (assuming that K_{enol} (MeOH) $\sim$ K_{enol} (EtOH)), a pK_{enol} (**7**) ≥ 2 in MeOH,[8] and a $K_{\alpha-CH_2Ph}/K_{\alpha-H}$ ratio of ca. 30 (based on $K_{\alpha-Me}/K_{\alpha-H}$ ratio of 31 for the Mes_2C=C(OH)R system in hexane),[23] the PhC(R)=C(SH)CH_2Ph/PhC(R)=C(OH)CH_2Ph ratio will also be $\geq 10^6$.

Finally, for **9** and **11**, in CCl_4[11] K_{enol} values are ca. 1−1.5. Comparison with the reliable pK_{enol} value of 7.52 for diisopropyl ketone,[24] correcting for the solvent effect as done above and assuming that hexane resembles CCl_4, will give again a K_{enol} ratio of $\geq 10^6$ for simple aliphatic thioketone compared with the corresponding ketone.

pK_{enol} value for methyl fluorene-9-thionocarboxylate was recently determined in water as 5.80, and K_{enol} for the ester was estimated to be 4 orders of magnitude higher than that of the oxygen analog—methyl fluorene-9-carboxylate.[25] This estimation is lower than in our case, but the systems and solvents are sufficiently different so that further discussion is unwarranted.

Thioenol−DMSO Association. Whereas hydrogen bond association of alcohols ROH with hydrogen bond acceptors were extensively investigated,[26] the corresponding associations of thiols were much less investigated. The lower boiling points of thiols as compared to those of the analogous alcohols indicate that the association is much weaker in RSH compared with ROH.[27]

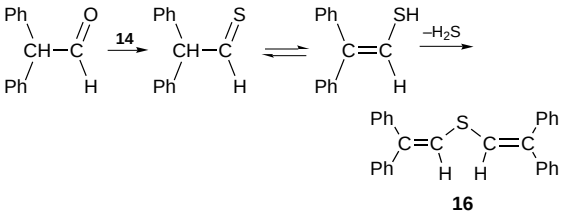
The weak hydrogen bonds of thiols may be studied by IR and NMR techniques. K_{assoc} values for association of PhSH with various solvents in CCl_4 at 26 °C range from 0.039 (with C_6H_6) to 0.43 (with (n-Bu)$_3$P=O) L mol^{-1}.[28a] Miller et al. determined thermodynamic parameters for the association of aliphatic thiols with various solvents.[28b] However, no analogous study on thioenols is available.

The main conclusion from Tables 3 and 4 is that the solvent-dependent shift of δ(SH) is due to hydrogen bonding association of the S−H bond with the solvent. From the approximate linear correlation between δ(SH) for **12** and δ(OH) for **20** (the latter being linear with δ-(OH) values of other polyarylethenols)[15] the two association processes seem similar. Since the conformation of the C=C−O−H moiety of **20** was deduced from the $^3J_{HCOH}$ values to be anti-clinal in hydrogen-bonding solvents, syn-planar in non-hydrogen-bonding solvents, and mixture of the two conformers in solvents of intermediate β[16] we assume without further evidence an exclusive syn conformation of **12** in CCl_4 and an equilibrium between the anti (clinal) conformation and the syn conformation in the other solvents.

The K_{assoc} value for **12** with DMSO (0.087 L mol^{-1}) is of the same order of magnitude as the very few K_{assoc} values available for the aliphatic and aromatic thiols. For *n*-BuSH and *t*-BuSH, K_{assoc} values with DMSO are 0.17 (at 307 K) and 0.30 (at 305 K) L mol^{-1}, respectively,[28b] an order opposite to the order of the pK_a's of the thiols.[27] However, the order of the K_{assoc} values in DMF [PhSH (0.24 at 298 K), Me_2CHSH (0.12 at 298 K), and Me_3CSH (0.084 at 309 K)] is the same as for the pK_a's (6.5, 10.86, and 11.2, respectively).[28b] The acidity of **12** is probably higher than that of the aliphatic thiols and closer to that of thiophenol.

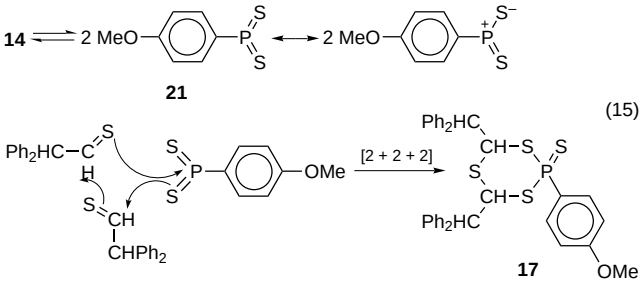
Whereas there is no K_{assoc} value for triphenylethenol, K_{assoc} values with DMSO for Mes_2C=C(OH)Ar are 1.82 for Ar = Mes and 1.93 for Ar = Ph and K_{assoc} = 2.75 for (*Z*)-MesC(Ph)=C(OH)Mes.[19c] Hence, the change from α- or β-Mes to Ph increases K_{assoc} only slightly, suggesting that the value for Ph_2C=C(OH)Ph is close to 3 L mol^{-1}. Consequently, the K_{assoc} of the thiol **12** is ca. 35 times lower than that for the oxygen analog. The fraction of associated thioenol (0.62) is much lower than those of the triarylethenols (0.99).[19c]

Side Products from Diphenylacetaldehyde. Neither diphenylethanethial nor its thioenol **15** were obtained from Ph_2CHCHO and **14**. However, formation of sulfide **16** and the heterocyclic compound **17** (eq 6) can be accounted for by an initial reaction of diphenylacetaldehyde with **14** to give the corresponding thioaldehyde, which immediately tautomerizes to **15**. Reaction of **15** with the thioaldehyde, loss of H_2S, and ketonization can account for formation of **16**, but the details of the process are unknown. Likewise, Lawesson and co-workers[29] had observed that 2-R-cyclohexanones (R = Me, Ph) gave with **14** the thioketones/thioenols, which after a few days gave the bis(2-R-cyclohexen-1-yl) sulfides. The suggested mechanism of nucleophilic attack of the thioenol on the thioketone followed by a loss of H_2S (eq 14) was proposed earlier[30] as a route for addition of thioenols to ketones.



(14)

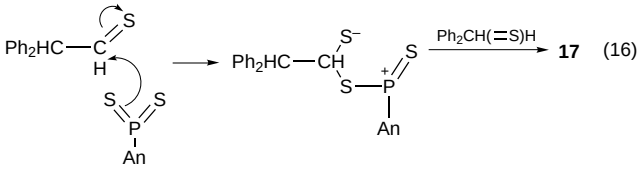
Trithiophosphorinane analogs of **17** from reaction of **14** and cycloalkanones were previously formed. Lawesson has suggested that **14** decomposes in solution to two thionophosphine sulfide molecules **21**.[31] In our reaction **21** could react either with two molecules of **15** in a concerted [2 + 2 + 2] cycloaddition (eq 15) or with one



(15)

thioaldehyde molecule followed by reaction of the formed zwitterion with a second thioaldehyde molecule (eq 16).

(22) Chiang, Y.; Kresge, A. J.; Walsh, P. A.; Yin, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 869.
(23) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669.
(24) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000.
(25) Chiang, Y.; Jones, J., Jr.; Kresge, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 8358.
(26) Rochester, C. H. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Wiley: Chichester, 1971; Chapter 7, pp 327−392.
(27) Crampton, M. R. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: Chichester, 1974; Chapter 8, pp 379−415.
(28) (a) Mathur, R.; Becker, E. D.; Bradley, R. B.; Li, W. C. *J. Phys. Chem.* **1963**, *67*, 2190. (b) Hu, S. J.; Goldberg, E.; Miller, S. I. *Org. Magn. Reson.* **1972**, *4*, 683.
(29) Scheibye, S.; Shabana, R.; Lawesson, S.-O.; Roemming, C. *Tetrahedron* **1982**, *38*, 993.
(30) Campaigne, E.; Moss, R. D. *J. Am. Chem. Soc.* **1954**, *76*, 1269.
(31) Campaigne, E. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Wiley: Chichester, 1966; Chapter 17, pp 917−959.



(16)

The Cambridge Structural Database contains only one trithiaphosphorinane structure that was determined by X-ray diffraction, i.e., 2-(*p*-methoxyphenyl)-4,6-bis(pentafluorophenyl)-1,3,5,2-trithia 2-thiophosphorinane.[32] It has a chair conformation with P−S bond lengths of 2.102−2.117 Å, C−S bond lengths of 1.816−1.851 Å, P=S bond length of 1.937 Å, and S−P−S and P−S−C bond angles of 103.9° and 96.4−98.2°, respectively. The structure of **17** resembles this structure.

Experimental Section

General Methods. Melting points are uncorrected. For X-ray diffraction Mo Kα (λ = 0.170 69 Å) radiation with a graphite crystal monochromator in the incident beam was used. All crystallographic computing was done on a VAX 9000 computer using the TEXSAN structure analysis software.

Solvents and Materials. Ether, THF, hexane, benzene, and toluene were kept over metallic sodium, distilled, and used immediately. Pyridine was kept over KOH and distilled before use. Commercial DMSO-d_6 (Aldrich) was used without further purification. Lawesson's reagent and diphenylacetaldehyde were purchased from Aldrich. Triphenylvinyl bromide, mp 114−5 °C, was prepared according to Koelsch.[33] Triphenylethanone, mp 37 °C,[34] was prepared by a Grignard reaction of diphenylketene with PhMgBr. 2,2-Diphenyl-1-anisylethanone (mp 130 °C) was prepared by a modification of the reaction for the preparation of the mesityl analog.[35] 1-Anisyl-2,2-diphenylvinyl bromide, mp 137−139 °C, was prepared according to Gal.[36]

Triphenylethenethiol (12). (a) To a solution of triphenylvinyl bromide (4 g, 12 mmol) in dry ether (70 mL) were added magnesium turnings (0.4 g, 16 mmol) and a crystal of iodine. The mixture was refluxed for 6 h, during which time most of the magnesium had disappeared. Sulfur (0.4 g, 1.5 mmol) was then added, and the mixture was refluxed for an additional 2 h. A dilute H_2SO_4 solution (50 mL) was then added, the mixture was cooled to 0 °C, the aqueous and the organic phases were separated, the organic phase was dried ($MgSO_4$) and filtered, and the ether was removed, leaving a yellow solid. Crystallization from benzene gave triphenylethenethiol (2.3 g, 48%), mp 110−112 °C (lit.[13] mp 110−111 °C).

MS *m/z* (relative abundance, assignment): 288 (100, M^+), 253 (7, $C_{20}H_{13}$), 165 (10, $C_{13}H_9$), 121 (41, PhC=S^+).

IR ν_{max}(Nujol): 2562 (SH), 1607 (C=C), 1589 (C=C) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 3.28 (1H, s, SH), 6.89−7.42 (15H, m, PhH).

^{13}C NMR ($CDCl_3$) δ: 126.13 (C=C), 127.36, 127.46, 127.59, 128.20, 128.67, 129.56, 129.83, 130.37, 130.53 (Ph−C), 137.28 (C=C), 141.69, 142.24, 142.98 (CPh).

Microanalysis: C, 82.80; H, 5.17; S, 9.53. Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.17; S, 11.11.

Crystallographic data: space group *Pna*2, a = 9.305(2) Å, b = 19.351(3) Å, c = 8.592(1) Å, V(Å^3) = 1563.1(5), Z = 4, ρ_{calcd} = 1.23 g cm^{-3}, μ (Cu Kα) = 16.94 cm^{-1}, R = 0.033, R_w = 0.051.

(b) Triphenylethanone (0.35 g, 3 mmol) and Lawesson's reagent (0.55 g, 1.4 mmol) were dissolved in toluene (15 mL), the solution was refluxed under nitrogen, and the progress of the reaction was followed by TLC. After 50 h, when no more changes were observed, the mixture was cooled, absorbed on a dry silica column, and then chromatographed using 95:5 petroleum ether:ether as eluent. The triphenylethenethiol obtained (130 mg, 46%) was identical with the product obtained by method a.

2,2-Diphenyl-1-anisylethenethiol (13). A mixture of 2,2-diphenyl-1-anisylvinyl bromide (0.95 g, 2.6 mmol) and Mg (0.07 g, 2.7 mmol) in dry THF (20 mL) was refluxed for 5 h. Sulfur (65 mg, 0.25 mmol) was added, and the mixture was refluxed for an additional 2 h. After addition of 10% H_2SO_4 solution (20 mL) at 0 °C, the phases were separated, the organic phase was dried ($MgSO_4$), and the ether was removed, leaving 2,2-diphenyl-1-anisylethenethiol (**13**) (0.35 g, 55%). Crystallization from $CHCl_3$ gave **13**, mp 109 °C.

Microanalysis: C, 78.98; H, 5.62. Anal. Calcd for $C_{21}H_{18}OS$: C, 79.24; H, 5.65.

MS *m/z* (relative abundance, assignment): 318 (100, M^+), 285 (7, M − SH), 254 (5, $C_{20}H_{14}$), 239 (9, $C_{15}H_{11}OS$), 165 (12, $C_{13}H_9$), 151 (97, AnC=S^+), 108 (5, AnH), 77 (5, C_6H_5).

IR ν_{max}(Nujol): 2578 (SH), 1604 (C=C) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 3.27 (1H, s, SH), 3.77 (3H, s, OCH_3), 6.87−6.91 (10H, m, PhH), 6.73 (2H, d, AnH), 7.02 (2H, d, AnH).

^{13}C NMR ($CDCl_3$) δ: 55.17 (OCH_3), 113.53 (CAn), 125.95, 127.57, 128.66, 130.29, 130.46, 130.86 (CAr), 130.41 (C=C), 134.36 (C=C), 136.62, 141.97, 143.30 (CAr), 158.80 (COMe).

(b) A solution containing 2,2-diphenyl-1-anisylethanone (0.38 g, 1.3 mmol) and Lawesson's reagent (0.55 g, 1.35 mmol) in toluene (15 mL) was refluxed for 48 h under nitrogen. After being cooled to rt and absorbed on silica, the mixture was chromatographed on a dry silica column using 95:5 petroleum ether: ether as eluent. The 2,2-diphenyl-1-anisylethenethiol obtained (0.14 g, 34%) has spectral properties identical with those of the sample obtained above.

Reaction of Diphenylacetaldehyde with Lawesson's Reagent. A solution containing diphenylacetaldehyde (5 mL, 28 mmol) and Lawesson's reagent (8.5 g, 21 mmol) in toluene (40 mL) was refluxed for 21 h under nitrogen. The green oil obtained after evaporation of the solvent was chromatographed on a silica column using 80:20 ether:CH_2Cl_2 eluent. Two products were separated.

(a) Bis(2,2-diphenylvinyl) Sulfide (16). Crystallization from petroleum ether (60−80 °C) gave 0.93 g (17%) of the yellow sulfide, mp 116−117 °C.

MS *m/z* (relative abundance, assignment): 390 (100, M^+), 313 (3, M − Ph), 210 (14, Ph_2C=C=S), 178 (56, $C_{14}H_{10}$), 165 (41, $C_{13}H_9$), 134 (6, C_8H_6S), 102 (8, C_8H_6), 77 (23, C_6H_5).

IR ν_{max}(Nujol): 1598 (C=C) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 6.81 (2H, s, C=*C*H), 7.18−7.40 (20H, m, PhH).

^{13}C NMR ($CDCl_3$) δ: 124.53 (C=*C*S), 127.18, 127.23, 127.66, 128.27, 128.38, 129.67, 138.94, 139.88 (CPh), 141.67 (Ph*C*=).

Microanalysis: C, 85.98; H, 5.80; S, 7.81. Anal. Calcd for $C_{28}H_{22}S$: C, 86.11; H, 5.68; S, 8.21.

(b) 1-(*p*-Methoxyphenyl)-2,4,6-trithia-1-phospha-3,5-bis(diphenylmethyl)-1-thiocyclohexane (17). Crystallization from a 4:6 CH_2Cl_2:petroleum ether mixture gave white crystals of **17**, mp 200−202 °C (0.17 g, 2%).

MS *m/z* (relative abundance, assignment): 212 (100, Ph_2-CHCHS), 197 (10), 178 (42, $C_{14}H_{10}$), 165 (26, $C_{13}H_9$), 152 (13, $C_{12}H_8$), 134 (16, C_8H_6S), 121 (16), 89 (15, C_7H_5), 77 (14, C_6H_5).

IR ν_{max}(Nujol): 1595 (C=C) cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 3.85 (3H, s, OCH_3), 4.52 (2H, d, Ph_2-CH), 6.07 (2H, dd, CHS_2), 6.89 (2H, dd, AnH). 7.23−7.31 (10H, m, PhH), 8.04 (2H, dd, AnH).

^{13}C NMR ($CDCl_3$) δ: 55.58 (OCH_3), 56.91 (CHS_2, d, J = 7.2 Hz), 59.57 (Ph_2CH), 114.37 (*m*-AnH, d, J = 13 Hz), 122.5 (*p*-*C*An, d, J = 100 Hz), [127.19, 127.35, 128.40, 128.52, 128.95] (CPh), 133.73 (*o*-AnH, d, J = 14 Hz), 139.50, 139.99 (CPh), 164.08 (COMe).

Microanalysis: C, 67.12; H, 5.15. Anal. Calcd for $C_{35}H_{31}OPS_4$: C, 67.02; H, 4.98.

Crystallographic data: space group $P2_{1/n}$, a = 13.492(1) Å, b = 19.837(2) Å, c = 11.897(1) Å, β = 92.95(1)°, V(Å^3) = 3179.9(7), Z = 4, ρ_{calcd} = 1.31 g cm^{-3}, μ(Cu Kα) = 33.88 cm^{-1}, R = 0.032, R_w = 0.050.

Acknowledgment. We are indebted to Professor S. E. Biali for helpful discussions.

JO9604651

(32) Hasserodt, J.; Pritzkow, H.; Sundermeyer, W. *Chem. Ber.* **1993**, *126*, 1701.
(33) Koelsch, C. F. *J. Am. Chem. Soc.* **1952**, *74*, 2047.
(34) Ley, H.; Manecke, W. *Ber.* **1923**, *56B*, 777.
(35) Fuson, R. C.; Rachlin, A. I. *J. Am. Chem. Soc.* **1946**, *68*, 343.
(36) Rappoport, Z.; Gal, A. *J. Am. Chem. Soc.* **1969**, *91*, 5246.