Reduction of the Tetralone VIIb.—The ketone (2.93 g.) was added to a mixture of 2.2 g. of potassium hydroxide, 11.5 ml. of hydrazine hydrate and 40 ml. of ethylene glycol. The reaction was carried out and the product obtained in the same manner as described above. After three recrystallizations from low boiling (30–60°) petroleum ether (chilling), there was obtained 1.85 g. (68%) of the crystalline hydrocarbon, m.p. 50–55°. A sample was recrystallized from the same solvent to a constant m.p. of 58–60°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.82; H, 8.03.

Aromatization of *cis*-1-Methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene.—A small sample (0.30 g.) of the hydrocarbon and 0.20 g. of catalyst was heated at 230° for 2 hr., and then at 250° for an additional hr. The reaction mixture was treated as above to yield 0.21 g. (70%) of flaky plates, m.p. 82–84.5°. This was again recrystallized to afford a sample, m.p. 84–85°. The mixed m.p. of this with the substituted naphthalene obtained from the *trans*-hydrocarbon was 84–85°.

Cyclization of *erythro*-2,3-Diphenylglutaric Acid.—To 100 ml. of liquid hydrogen fluoride there was added 5.0 g. (0.018 mole) of the glutaric acid.[13] The clear gum which remained when the liquid had evaporated was washed with water and taken up in ether. The ethereal solution was then extracted with aqueous sodium bicarbonate. The gum which came out on acidification of this solution was crystallized from aqueous ethanol to give 1.27 g. of crystalline solid, m.p. 135–145° (melting and resolidification 79°). Material of adequate purity for further work, m.p. 144–153°, was obtained by one further crystallization from the same solvent. A sample was recrystallized from ethyl acetate–high boiling (60–90°) petroleum ether to give tiny glistening plates, m.p. 152–154°, λ_{max} 5.82, 5.95 μ. The mixed m.p. of this with a sample of the indanone XII,[10] m.p. 152.5–155°, was 125–135°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.91; H, 5.38.

Conversion of the Keto-acid XIII to the Acid XIV.—A solution of 0.97 g. (3.6 mmoles) of the keto-acid and 0.70 g. of potassium hydroxide in 14 ml. of ethylene glycol and 4 ml. of hydrazine hydrate was heated under reflux for 30 min. The temperature of the mixture was then raised to 192° by allowing water to distil over. The evolution of gas, which started at 150°, was complete after 45 min. The cooled solution then was diluted with water (100 ml.) and washed with ether. The solid which came out on acidification of the aqueous solution was collected by filtration and crystallized from aqueous ethanol to yield 0.70 g. (75%) of the acid, m.p. 142–145°. Repeated crystallization from the same solvent yielded a sample m.p. 144.5–146°, λ_{max} 5.83 μ.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.74; H, 6.61.

Aromatization and Decarboxylation of Acid XIV.—An intimate mixture of 0.18 g. of the acid and 0.075 g. of 10% palladium-on-charcoal was placed in a bath at 160°. Over 10 min. the temperature was brought to 265°. After an additional 10 min. the mixture was allowed to cool. The solid was taken up in ether and the catalyst removed by filtration. The solid, m.p. 94–99° (0.15 g.), which remained when the ethereal solution was taken to dryness was crystallized from aqueous ethanol. There were obtained glistening colorless flakes of 2-phenylnaphthalene, m.p. 101.5–102.5°, lit.[14] 103–104°. The ultraviolet absorption spectrum of this compound is identical to that in the literature.[15]

Preparation of *threo*-2,3-Diphenylglutaric Acid from the Anhydride XI.—To a solution of 5.68 g. (0.02 mole) of the anhydride[10] in 25 ml. of acetone was added cautiously with stirring 20 ml. of 2 *N* sodium hydroxide at such a rate as to keep the solution just basic. When the reaction was complete the solution was diluted with 300 ml. of water and washed with ether. Acidification with dilute hydrochloric acid afforded a white solid which was collected by filtration. One crystallization from ethanolic water afforded 4.72 g. of the acid m.p. 205–210°, lit.[9] 208–210°.

Attempted Cyclization of *threo*-2,3-Diphenylglutaric Acid.—A sample of the acid (1.80 g.) was dissolved in 50 ml. of liquid hydrogen fluoride. This was worked up in the same manner as the mixture obtained from the cyclization of the isomeric acid. In this case, however, no pure crystalline material could be obtained.

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[13] Obtained by fractional crystallization of a mixture containing *threo*- and *erythro*-acids prepared by the method of C. R. Hauser and M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1958).

[14] W. Smith and T. Takamatsu, *J. Chem. Soc.*, **39**, 546 (1881).

[15] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, structure 297.

DURHAM, N. C.

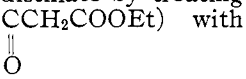
[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE]

A Study of a Thioketo–Thioenol Tautomeric System. I. Ethyl Thiobenzoylacetate[1]

BY ZOILA REYES AND ROBERT M. SILVERSTEIN

RECEIVED JUNE 2, 1958

It was shown that the decolorization of a solution of ethyl thiobenzoylacetate by oxygen can be attributed to a rapid oxidation of the colored thione tautomer, and the return of the color upon removal of oxygen to the slower reestablishment of the equilibrium thione concentration. The equilibrium picture was inferred from infrared and nuclear magnetic resonance spectra, and from iodimetric titration. The effect of oxygen upon the equilibrium was followed spectrophotometrically and manometrically.

Ethyl thiobenzoylacetate  $(C_6H_5\underset{\underset{S}{\|}}{C}CH_2COOEt)$ was obtained as a deep blue distillate by treating ethyl benzoylacetate  $(C_6H_5\underset{\underset{O}{\|}}{C}CH_2COOEt)$ with hydrogen sulfide and hydrogen chloride, precipitating the sulfur compound as the lead salt, regenerating with hydrogen sulfide and distilling. In contact with air, the blue color of ethyl thiobenzoylacetate gradually disappeared. When the dissolved air was removed by evacuation, by boiling in a solvent or by flushing with nitrogen, the blue color reappeared. This cycle could be repeated a number of times, but eventually the decolorization would be irreversible.

Polymerization and depolymerization as have been reported for a number of thiones[2] were not the explanation since there was no apparent change in viscosity on decolorization. Furthermore, the infrared and the n.m.r. spectra of the blue material and of the material just decolorized with air were

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[1] Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] For a general review of thione chemistry, see E. Campaigne, *Chem. Revs.*, **39**, 1 (1946); A. Schönberg and A. Wager, in "Methoden der Organischen Chemie," (Houben-Weyl), Georg Thieme Verlag, Stuttgart, 1955, p. 695. Thiobenzoylacetates have not been previously described.

identical; the ultraviolet spectra showed some differences but were complex and not informative. The n.m.r. spectrum (Fig. 1) was clear-cut and unequivocal. From right to left, the following assignments were made: CH_3 (triplet), CH_2 (quadruplet), $=CH$ (singlet), benzene protons (broad), and chelated SH (singlet). Confirmation of the latter assignment was obtained from the shift of the singlet upfield on warming.

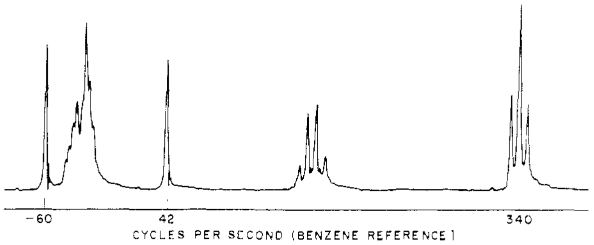


Fig. 1.—Proton nuclear magnetic resonance spectrum of ethyl thiobenzoylacetate.

Thus, so far as the n.m.r. spectrum is concerned, the compound exists only in the thioenol form, and wholly as an intramolecularly hydrogen-bonded structure, there being no evidence for the non-hydrogen-bonded conformation. If the blue color is ascribed to the thioketo form (thiobenzophenone, for example, is intensely blue),[2] then its equilibrium concentration in the neat liquid must be below the sensitivity of n.m.r., *i.e.*, *ca.* 1%, and its destruction by oxygen has no effect on the spectrum.

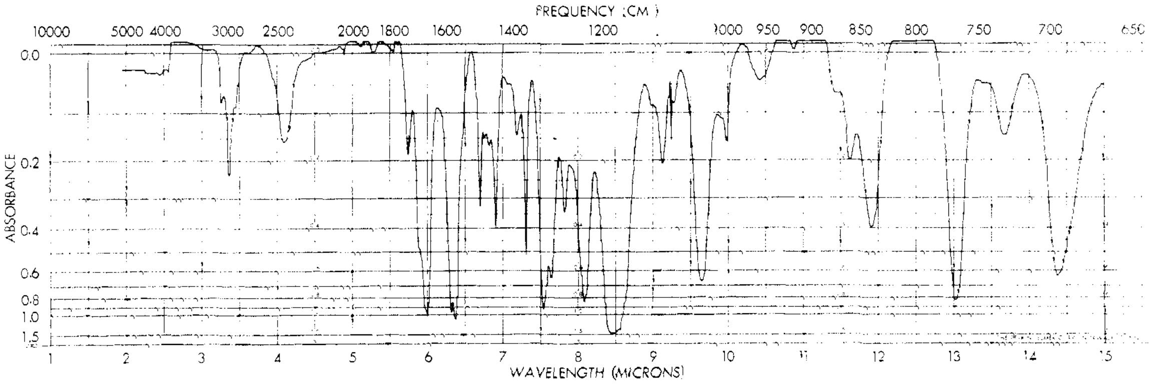
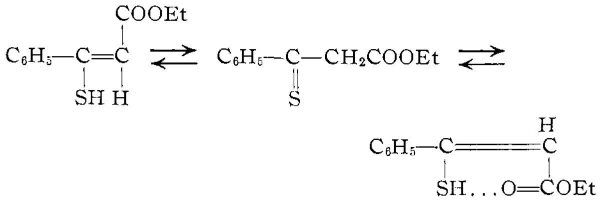


Fig. 2.—Infrared spectrum of ethyl thiobenzoylacetate.

The infrared spectrum (Fig. 2, liquid film prepared under N_2) showed a broad moderately strong band at 4.14 µ (intramolecularly hydrogen bonded SH)[3] with a slight shoulder at 3.90 µ (normal SH).[3] A narrow band at 5.75 µ (of slightly greater peak height than the band at 4.14 µ) was ascribed to the ester carbonyl of the thione tautomer, a very strong band at 6.00 µ to the hydrogen bonded α,β-unsaturated ester carbonyl of the thioenol tautomer, and slight shoulder at 5.90 µ to the ester carbonyl of the non-hydrogen bonded α,β-unsaturated thioenol tautomer (*i.e.*, complementary to the normal SH shoulder). The foregoing is consonant with this picture of the equilibrium state



$$C_6H_5-\underset{SH}{C}=\underset{H}{\overset{COOEt}{C}} \rightleftarrows C_6H_5-\underset{S}{\overset{}{\underset{\|}{C}}}-CH_2COOEt \rightleftarrows \underset{SH\cdots O=COEt}{C_6H_5-C=\overset{H}{C}}$$

It appears then, that the infrared is more responsive than n.m.r. to small concentrations of the thione form and of the non-hydrogen-bonded thioenol form (presumably with the SH and COOEt groups *trans*). Destruction of the thione form would have no effect on the band at 5.75 µ since, as will be shown later, one product of oxidation is ethyl benzoylacetate, and its ester band is also at 5.75 µ. Nor would the shoulder at 5.90 µ be noticeably affected since the ketone carbonyl band of ethyl benzoylacetate occurs at 5.89 µ.

The literature offers no information on the equilibrium condition of this system. However, Mitra[4] determined the thioenol concentration of ethyl thioacetoacetate in ethanol to be 41% compared with an enol concentration of ethyl acetoacetate in ethanol of 11%.[5] Ethyl benzoylacetate has been reported[5] to be 29% in the enol form as a liquid. It would be reasonable to expect that a carbon 2 sp^3-orbital would overlap to a lesser extent with a sulfur 3 p-orbital than with an oxygen 2 p-orbital, that therefore a C=S would possess less double bond character than a C=O, and that the thioenol to thioketo ratio would be greater than that of enol to keto. Mitra carried out his determinations by addition of an excess of iodine solution at −7° followed by back-titration with thiosulfate. Under these conditions, only the thioenol form reacts and no appreciable equilibrium shift occurs. Following Mitra's procedure, we determined the thioenol concentration of ethyl thiobenzoylacetate in alcohol to be 87%. The disappearance of the yellow iodine color in the presence of the blue thione color could be detected with practice. By an indirect procedure described below, we estimated the thioenol concentration of ethyl thiobenzoylacetate in isooctane to be about 95%. The enol content of

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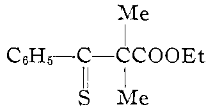
(3) This represents a considerable shift from the usual SH assignment of 3.8–3.9 µ in contrast with the small shifts reported for weak intermolecularly bonded SH. See L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 288–289.

(4) S. K. Mitra, *J. Indian Chem. Soc.*, **15**, 205 (1938).

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 535–536.

ethyl acetoacetate in hexane has been reported to be 46%[5] (compared with 11% in ethanol). Thus both the thioketo and the keto concentrations increase with increased solvent polarity, indicating that these are the more polar forms. Presumably then, the thioenol would be the more volatile and could, in theory at least, be distilled out of the thioketone in a quartz vessel along the lines of the classical Kurt Meyer separation of the enol and keto tautomers of ethyl acetoacetate.[6]

Examination of the visible spectrum confirmed the low equilibrium concentration of the blue tautomer. The broad absorption band had a maximum in isoöctane at 575 mμ and in alcohol at 564 mμ. The molar extinction coefficients were 1.6 and 2.0, respectively. In order to get a comparison with an unambiguous thione of similar structure, we prepared ethyl α,α-dimethylthiobenzoylacetate[7] and

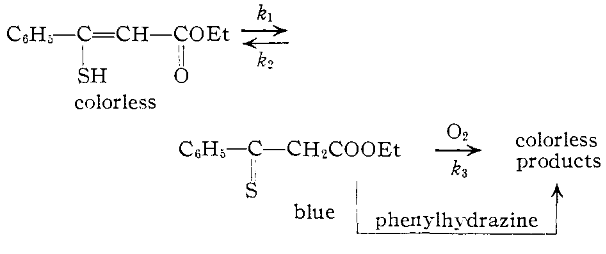


$$C_6H_5\text{—}\underset{\underset{S}{\|}}{C}\text{—}\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{C}}COOEt$$

found its molar extinction coefficient in alcohol to be 100 at λ_{max} 565 mμ.

The ratio of 87% thioenol:13% thioketo in alcohol determined by titration was corroborated by polarography. The polarogram showed an SH wave with a half-wave potential at −0.29 v. and a C═S wave with a half-wave potential at −0.85 v.; their respective concentrations were about 10:1. Bubbling air through the solution caused the virtual disappearance of the C═S wave without appreciably affecting the SH wave. The α,α-dimethyl compound gave a double C═S wave with half-wave potentials at −0.85 and −0.89 v.

Having arrived at a picture of the equilibrium state, we proceeded to study the aforementioned effect of oxygen upon this system. We made the additional observation that the blue color of ethyl thiobenzoylacetate also could be discharged by dropwise addition under nitrogen of an ethanol solution of phenylhydrazine. When the addition was stopped immediately on discharge of the color, the color slowly returned—provided, of course, that air was excluded. The sequence shown, where $k_3 >> k_1$, was postulated to rationalize the foregoing observations (the non-bonded enol form is ignored)



In this sequence, k_3 is the rate of disappearance of the blue color in the presence of oxygen, and k_1 is the rate of color return on removal of oxygen. Taken in conjunction with the relatively small amount of the thioketo form present at equilibrium, this sequence accounts for the observation that the cycle of decolorizing and color return could be repeated a number of times before decolorization became irreversible. The rate of oxidation of the thione form (k_3) was measured spectrophotometrically by rapidly saturating a solution of the compound in a stoppered cell with oxygen and following the rate at which the optical density (A) decreased at the absorption peak. The stoppered cell was thermostated at 25° and shaken between readings. A pseudo-first order reaction rate (O_2 being in excess) was found in 95% ethanol and in isoöctane for an acceptable portion of the total reaction time by plotting t against log $(A_{\text{init.}}/A_{\text{time}})$. The rate of equilibrium shift k_1 was obtained by flushing the decolorized solution (end of k_3 readings) with nitrogen and following the increase in optical density at the same wave length. A pseudo-first-order reaction rate was obtained in 95% ethanol and in isoöctane for the first 15 minutes of the shift by plotting t against log $(a/a - x)$ where

$$a \equiv [\text{thioenol}]_{\text{initial}} = \text{molarity} \times \%\ \text{thioenol}$$

$$[\text{thione}]_{\text{initial}} = \text{molarity} \times \%\ \text{thione}$$

$$x \equiv [\text{thione}]_{\text{time}} = \frac{A_{\text{time}}}{A_{\text{final}}} \times [\text{thione}]_{\text{initial}}$$

A recycle value for k_1 was obtained by once again decolorizing the solution with oxygen and reflushing with nitrogen. Beer's law applied over the concentration range utilized in both 95% ethanol and in isoöctane. The spectrophotometric data are presented in Tables I–IV. It can be seen from the results summarized in Table VI that the ratio of k_3:k_1 in ethanol was 38, and the ratio in isoöctane was 820. Apparently, k_1 is much more dependent on solvent polarity than k_3 as would be expected on the basis of the usual assumption that a keto–enol shift involves ionic intermediates whereas oxidations with molecular oxygen involve radicals.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF OXIDATION FOR THE THIONE FORM OF ETHYL THIOBENZOYLACETATE IN 95% ETHANOL (k_3)

	Run 1, 0.435 M		Run 2, 0.486 M	
Time, min.	A at 564 mμ	log $(A_{\text{init.}}/A_{\text{time}})$	A at 564 mμ	log $(A_{\text{init.}}/A_{\text{time}})$
0	0.840	....	0.803	....
2	.560	0.1761	.680	0.0722
3	.370	0.3561	.540	.1723
4	...	....	.430	.2713
5	0.316	0.4246	.350	.3607
6	.249	.5381	.295	.4349
7	.201	.6211	.235	.5337
9	.155	.7340	...	....
10	.107	.8949	...	....
11	.078	1.0322	.150	.7286
12	.070	1.0792	...	....
13	.070	1.0792	.098	.9135

Direct manometric measurement of the absorption of oxygen should provide another method for determining k_3 and k_1. The rate of oxygen uptake was followed in a Warburg apparatus. As anticipated, there was an initial period of rapid absorption which lasted for a short time followed by a slow absorption period during which the greater part of total oxygen consumption occurred. The

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(6) K. H. Meyer and V. Schoeller, *Ber.*, **53**, 1410 (1920); K. H. Meyer and H. Hopff, *ibid.*, **54**, 579 (1921).

(7) Z. Reyes and R. M. Silverstein, THIS JOURNAL, **80**, 6373 (1958).

rapid reaction obviously corresponds to oxidation of the equilibrium amount of thioketo tautomer (k_3). The slow reaction then is a measure of thioketonization (k_1); that is, the rate of oxygen absorption is controlled by the rate at which the thioketo form is made available.

As it turned out, the initial uptake of oxygen by ethyl thiobenzoylacetate in 95% ethanol and in isoöctane was too rapid to be followed. Apparently, the limiting factor was the relatively slow rate of diffusion of oxygen into the solution. Although k_3 could not be determined in this way, the abrupt change in rate of oxygen uptake (Fig. 3) permitted an evaluation of the equilibrium ratio of thioenol to thioketo in isoöctane. Using the determined stoichiometry (from the total consumption of oxygen) of four moles of compound to one mole of oxygen, this ratio is 95:5. In ethanol, the change in rate was not as abrupt since the ratio of k_3 to k_1 is smaller than the ratio in isoöctane.

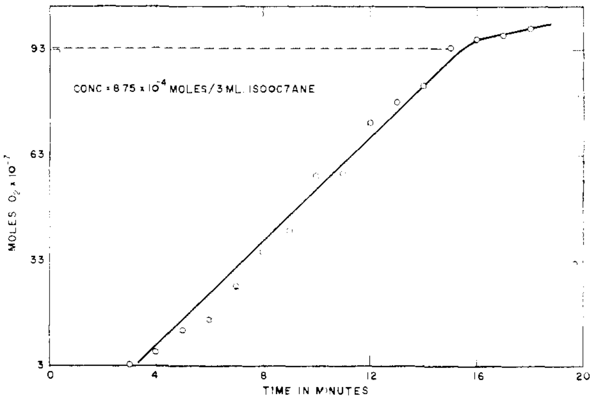

Fig. 3.—Initial oxygen uptake for ethyl thiobenzoylacetate in isoöctane.

TABLE II

SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF OXIDATION FOR THE THIONE FORM OF ETHYL THIOBENZOYLACETATE IN ISOÖCTANE (k_3)

Time, min.	0.674 *M*	
	A at 575 mμ	log ($A_{\text{init.}}/A_{\text{time}}$)
0	0.600	....
0.75	.590	0.0073
1	.570	.0223
1.5	.564	.0269
2	.545	.0418
2.5	.527	.0563
3	.510	.0706
4	.480	.0969
5	.455	.1201
6	.435	.1397
8	.382	.1961
10	.340	.2467
12	.303	.2967
16	.238	.4016
80	.015	....

The rate of thioketonization (k_1) of ethyl thiobenzoylacetate in 95% ethanol was obtained by plotting *t versus* log $a/(a - 2x)$ for the first 225 minutes of the reaction ($a \equiv$ original concentration of the compound, $x \equiv$ moles of oxygen absorbed, and the stoichiometry was two moles of compound to one of oxygen). The pseudo-first order rate constant of 4.0×10^{-5} sec.$^{-1}$ obtained was in fair agreement with that derived spectrophotometrically for k_1. Oxygen consumption data are presented in Table V. A similar treatment of the raw data for oxygen uptake in isoöctane did not give a first-order plot.

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF THIOKETONIZATION FOR ETHYL THIOBENZOYLACETATE IN 95% ETHANOL (k_1)

Time, min.	Run 1, 0.435 *M*		Run 2, 0.435 *M* (recycle)		Run 3, 0.486 *M*	
	A at 564 mμ	log ($a/a - x$)	*A* at 564 mμ	log ($a/a - x$)	*A* at 564 mμ	log ($a/a - x$)
0	0.270	0.02153	0.220	0.02034	0.250	0.02122
1	.305	.02428	.270	.02509	.285	.02427
2	.345	.02756	.305	.02844	.311	.02655
3	.370	.02962	.347	.03251	.340	.02910
4	.407	.03269	.375	.03523	.370	.03176
5	.435	.03503	.420	.03965	.394	.03390
6	.470	.03805	...	.....	.412	.03550
7	.489	.03957	.470	.04462	.438	.03785
8	.500	.04051	.491	.04662	.460	.03984
9	.534	.04340	.500	.04763	.480	.04166
10	...	.....	...	.....	.495	.04303
11	.560	.04562	...	.....	...	.....
12	.580	.04734	.560	.....	.525	.....
60	.840	.....	.720	.....	.785	.....

TABLE IV

SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF THIOKETONIZATION FOR ETHYL THIOBENZOYLACETATE IN ISOÖCTANE (k_1)

Time, min.	0.674 *M*	
	A at 575 mμ	log $a/(a - x)$
0	0.037	0.00121
3	.042	.00137
8	.052	.00170
16	.060	.00215
52	.108	
10 hr.	.240	.....

TABLE V

RATE OF OXYGEN UPTAKE FOR ETHYL THIOBENZOYLACETATE IN 95% ETHANOL AS A MEASURE OF k_1

Time, min.	0.105 *M*	
	Moles O_2 absorbed $\times 10^5$	log $a/(a - 2x)$
45	2.40	0.04156
65	3.75	.06681
87	5.13	.09424
105	6.24	.11763
130	7.50	.14580
155	8.60	.17199
225	11.10	.23812
3 days	22.45	.....

It is obvious that neither the thione oxidation nor the reattainment of equilibrium is kinetically clean throughout. The kinetic results do not allow us to specify the course and the mechanism of the oxidation step from the observed over-all stoichiometry which was influenced by the solvent ($2C{=}S{:}O_2$ in ethanol and $4C{=}S{:}O_2$ in isoöctane). Staudinger and Freudenberger[8a] studied the oxida-

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[8] (a) H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1576, 1936 (1928); for proof of structure of trisulfide, see E. Campaigne and W. B. Reid, Jr., *J. Org. Chem.*, **12**, 807 (1947). (b) We did not obtain a straight line when we plotted *t* against log $a/(a - 6x)$.

tion of thiobenzophenone and found that the amount of oxygen absorbed and the ratio of products varied with solvent and temperature. Room temperature oxidation in benzene gave them the following stoichiometry (approximately) and major products

$$6(C_6H_5)_2C{=}S + O_2 \longrightarrow 2(C_6H_5)_2C{=}O + 2[(C_6H_5)_2C]_2S_3{}^{8b}$$

Small amounts of SO_2 and of sulfur also were formed. They pictured the trisulfide as formed from two moles of thiobenzophenone and one atom of sulfur. Our reaction was apparently more complex. Acetophenone and ethyl benzoylacetate were the major products isolated. Isolable amounts of sulfur crystallized out of the oxidized alcoholic solutions, and all attempts to manipulate the gummy residue after separation of the ketones and sulfur resulted only in the formation of more sulfur. Only trace amounts of either SO_2 or SO_3 were detected. A purple distillate, whose odor was that of ethyl thiobenzoylacetate and which was decolorized on exposure to air, was obtained on heating the sulfur-containing residue to 180–195° (bath temperature) at 1 mm. Among the side reactions possible in our system might be slow oxidation of the thioenol tautomer, addition of SH across a double bond, condensation of the thioenol tautomer with the thione form or with either of the ketone oxidation products, splitting out of H_2S, hydrolysis, decarboxylation and polymerization. Certainly the spectrophotometric method is more satisfactory for the determination of k_1 than the Warburg procedure. Calculations of k_1 from the rate of oxygen uptake are based on the unproved assumption that the over-all stoichiometry is the same as that for the oxidation of the thione form. Actually, the agreement in rates obtained is probably better than might reasonably have been expected.[9] The reaction rate constants are assembled in Table VI.

TABLE VI

REACTION RATE CONSTANTS FOR ETHYL THIOBENZOYLACETATE

	k_3, sec.$^{-1}$	k_1, sec.$^{-1}$	k_3/k_1
Spectrophotometric		9.2×10^{-5}	
In 95% ethanol	3.5×10^{-3}	9.7×10^{-5} recycle	
	3.5×10^{-3}	9.3×10^{-6}	38
In isoöctane	9.9×10^{-3}	1.2×10^{-6}	820
Warburg			
In 95% ethanol		4.0×10^{-5}	

In order to provide further verification for the structure of the parent compound, and to confirm some of the spectral assignments, several derivatives were prepared. Their preparation and properties are described briefly in the next few paragraphs.

Treatment of ethyl thiobenzoylacetate with a stoichiometric amount of I_2 in ethanol gave the disulfide. Attempted oxidation with hydrogen peroxide in acetic acid and with benzoyl peroxide in benzene[10] failed to give an isolable disulfide. The disulfide was a light yellow solid, m.p. 94–96°, whose infrared spectrum showed an α,β-unsaturated ester carbonyl band at 5.88, 5.93 μ (notched peak), and whose ultraviolet spectrum showed a single broad band, $\lambda_{\max}^{\text{isooctane}}$ 263 μ (ϵ 17,200).

Ethyl β-ethylthiocinnamate was prepared by treating ethyl thiobenzoylacetate with sodium hydride and ethyl iodide. The completely colorless liquid showed only a band at 5.80 μ assignable to an α,β-unsaturated ester carbonyl; the other ester carbonyl bands of the parent compound were absent.

It proved to be possible to carry out a controlled alkaline hydrolysis of ethyl thiobenzoylacetate to the free acid without extensive decarboxylation or hydrolysis of the thio group. This acid has been prepared[11] previously by treating phenylpropiolic acid with thiourea and hydrolyzing the adduct. The acid was a colorless solid, evidently almost completely in the thioenol form, which melted at 110–111° to a blue liquid; cooling again produced the colorless solid. The blue color of the melt can probably be ascribed to the appearance of the thione form.[12] Further heating caused decarboxylation to thioacetophenone which also has a blue tautomer. The blue thione form also appears on heating a carbon tetrachloride solution of the acid, and disappears on cooling. The infrared spectrum of a carbon tetrachloride solution was in accord with the observed properties. The intramolecularly hydrogen bonded SH band was at 4.04 μ, and the complementary hydrogen bonded COOH carbonyl band was at 6.04 μ. The spectrum was clean in the carbonyl region below 6 μ.

It was noted earlier in this paper that phenylhydrazine temporarily decolorized a solution of ethyl thiobenzoylacetate. It is now clear that rapid reaction with the thione form followed by slow reestablishment of equilibrium was involved. Addition at room temperature of excess 2,4-dinitrophenylhydrazine reagent (prepared according to Shriner and Fuson)[13] to an alcoholic solution of ethyl thiobenzoylacetate produced a heavy orange precipitate in a matter of minutes, as did addition of this reagent to an alcoholic solution of ethyl benzoylacetate. Each precipitate was recrystallized from acetic acid; each melted at 162–164°, and there was no depression on admixture. Each analyzed correctly for a hydrazone derivative plus a mole of acetic acid of crystallization. Recrystallization from ethanol–ethyl acetate followed by drying at 78° (1 mm.) gave a compound whose melting point was unchanged and which analyzed correctly for a hydrazone.[14]

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[9] It has been reported (A. Schönberg and A. Mustapha, *J. Chem. Soc.*, 275 (1943)) that some thioflavones oxidize only in the presence of light. We noted that ethyl thiobenzoylacetate in 95% ethanol was decolorized with oxygen in the complete absence of light.

[10] E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 32 (1956).

[11] E. Fischer and W. Brieger, *Ber.*, **47**, 2469 (1914).

[12] An analogous effect has been described for benzoylacetone by K. von Auwers and H. Jacobsen, *Ann.*, **426**, 161 (1922).

[13] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[14] The literature on 2,4-DNPH derivatives of β-keto esters is in a confused state. We have attempted to resolve the issue in a separate paper.

ternak and Dr. R. J. Marcus for advice on kinetic problems; to Dr. P. Lim for assistance with infrared interpretations; and to Dr. J. N. Shoolery and Mr. R. C. Jones of Varian Associates for the n.m.r. spectra. This work was supported by a grant from the Division Research Committee of Stanford Research Institute.

Experimental

Visible and ultraviolet spectra were determined on a Cary recording spectrophotometer model 14M. The kinetic runs were made on a Beckman model B spectrophotometer.

Infrared spectra were determined on a Beckman spectrophotometer, model IR4, and on a Perkin-Elmer spectrophotometer, model 21.

Polarographic determinations were made with a Sargent model XXI recording polarograph. An H type cell was used with provisions for flushing out the portion of the salt bridge adjacent to the dropping mercury electrode compartment with saturated potassium chloride solution between determinations. The reference cell was a saturated calomel electrode. The value of $M^{2/3}t^{1/6}$ was 1.6. Samples were prepared in 75% ethanol and to 0.4 ml. of the sample solution was added 3.6 ml. of a buffer solution, 0.2 *M* in both sodium acetate and acetic acid in 47.5% ethanol.

The proton nuclear magnetic resonance spectra were obtained on a Varian Associates high resolution spectrometer at 60 mc. Calibration was carried out with reference to benzene in an external annular cell.

Spectrophotometric determinations of k_3 and k_1 were carried out in a 1-cm. stoppered cell. The colored solutions (equilibrated for 4 hours under nitrogen) were saturated with oxygen by bubbling with a fine stream of oxygen for one minute. Zero time was taken at the start of bubbling. The stoppered cell was replaced in a thermostated (25°) bath and shaken between readings. When the optical density remained constant (end of k_3 run), the solution was purged for two minutes with a fine stream of nitrogen. Zero time was taken at the end of the purging period.

The rate of oxygen pickup was measured in a 15-ml. Warburg flask (thermostated at 25°). Two ml. of the solvent was equilibrated in the oxygen filled flask, and to this was added 3 ml. of a nitrogen-flushed solution of the test compound equilibrated for four hours at the same temperature. In order to measure the initial rapid absorption, the solution was injected into the flask through a rubber serum cap with a hypodermic syringe. Atmospheric pressure changes and minor temperature fluctuations were compensated by simultaneous readings on a control flask containing the same solvent under oxygen.

Ethyl Thiobenzoylacetate (Adaptation of Mitra's General Method).[15]—Absolute ethanol (40 ml.) was saturated with dry hydrogen chloride at −6 to −10°. Hydrogen sulfide was passed through the solution for 30 minutes and then 10 g. (0.052 mole) of ethyl benzoylacetate was dropped in slowly. The stream of hydrogen sulfide was continued during this addition and for six hours thereafter. The temperature was kept at −6 to −10° throughout the entire period. A red solution was obtained. The alcohol was distilled off under reduced pressure at room temperature, the viscous red-blue residual oil was dissolved in 20 ml. of ethanol, and treated with lead acetate. The orange precipitate was filtered, washed with ethanol, suspended in ether, and treated with hydrogen sulfide. The precipitate of lead sulfide was filtered, the solvent removed, and the residue distilled under vacuum in a nitrogen atmosphere. A blue fraction which distilled at 102° (0.7 mm.) was collected; yield 6.2 g. (55%); spectral data (under nitrogen), $\lambda_{\max}^{\text{isooctane}}$ in mμ (ϵ): 233 (37,100), 250 (42,500), 297 (39,700), 575 (1.6); $\lambda_{\max}^{95\%\ \text{ethanol}}$ in mμ 564 (2.0); $\lambda_{\max}^{\text{liquid}}$ in μ 3.90 (shoulder, normal SH), 4.14 (moderately strong, intramolecularly bonded SH), 5.75 (moderately strong, thione tautomer COOEt), 5.90 (shoulder, α,β-unsaturated COOEt), 6.00 (very strong, hydrogen bonded α,β-unsaturated, COOEt); n.m.r. in cycles/sec.: +340 (middle peak of triplet; CH_3), +168 (highest peak of quadruplet, CH_2), +42 (singlet, =CH), −26 (singlet, C_6H_5), −60 (singlet, hydrogen bonded SH).

Anal. Calcd. for $C_{11}H_{12}O_2S$: C, 63.4; H, 5.80; S, 15.4. Found: C, 63.3; H, 5.89; S, 15.3.

Diethyl β,β'-Dithiobis-cinnamate.—A solution of 0.17 g. (0.00067 mole) of iodine in 3 ml. of absolute ethanol was added dropwise at room temperature to a swirled solution of 0.27 g. of ethyl thiobenzoylacetate in 2 ml. of absolute alcohol. The solution was allowed to stand overnight at room temperature to permit complete thioenolization, water was added and the mixture extracted with ether. The ether solution was shaken with a sodium bisulfite solution, washed, dried, and evaporated. The residue was recrystallized twice from petroleum ether (30–65°). A yield of 0.2 g. (37%) of colorless needles was obtained, m.p. 94–96°; spectral data, $\lambda_{\max}^{\text{isooctane}}$ in mμ: 263 (ϵ 17,200); $\lambda_{\max}^{\text{KBr}}$ in μ 5.88, 5.93 (notched peak, α,β-unsaturated COOEt).

Anal. Calcd. for $C_{22}H_{22}O_4S_2$: S, 15.5. Found: S, 15.8.

Ethyl β-Ethylthiocinnamate.—A solution of 1.3 g. (0.00625 mole) of ethyl thiobenzoylacetate in 5 ml. of dry benzene was added slowly to a stirred suspension of 0.20 g. (0.00834 mole) of sodium hydride in 5 ml. of dry benzene. After the vigorous evolution subsided, 1.0 g. (0.00635 mole) of ethyl iodide was added, the mixture was refluxed for three hours, cooled, and filtered. The solvent was removed from the filtrate and the residual liquid was distilled at 1 mm. at a head temperature of 120°. The colorless distillate weighed 0.93 g. (63%); spectral data, $\lambda_{\max}^{\text{isooctane}}$ in mμ (ϵ): 238 (7,500), 295 (7,800); $\lambda_{\max}^{\text{liquid}}$ in μ 5.80 (α,β-unsaturated COOEt).

Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.1; H, 6.82; S, 13.57. Found: C, 66.3; H, 6.90; S, 13.3.

Thiobenzoylacetic Acid.—Ethyl thiobenzoylacetate (0.323 g., 0.0015 mole) was dissolved in 2 ml. of ethanol and 2 ml. of alcoholic sodium hydroxide (33%) was added. The mixture was heated on a steam-bath for 20 minutes, cooled in an ice-bath, and acidified with ice-cold dilute hydrochloric acid. The colorless precipitate was filtered and recrystallized from a mixture of carbon tetrachloride and petroleum ether (30–65°); yield 0.205 g. (73%) glistening flakes, m.p. 110–111° (placed on m.p. block at 100°); spectral data, $\lambda_{\max}^{CCl_4}$ in μ: 3.3 (broad, OH of COOH), 3.45, 3.71, 3.86 (submaxima of OH), 4.04 (intramolecularly hydrogen bonded SH), 6.04 (intramolecularly hydrogen bonded COOH).

Anal. Calcd. for $C_9H_8O_2S$: S, 17.8. Found: S, 17.6.

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[15] S. K. Mitra, *J. Indian Chem. Soc.*, **15**, 31 (1938).