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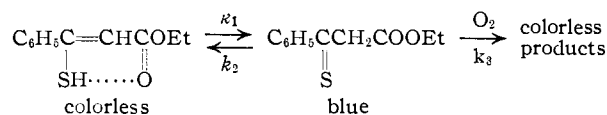
A Study of a Thio keto-Thioenol Tautomeric System. II. The Effects of Substituents on Ethyl Thiobenzoylacetate¹

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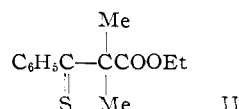
The effects of substitution of α,α -dimethyl, *p*-ethoxy and *p*-nitro groups on ethyl thiobenzoylacetate were assessed. It was shown how these substituents influenced the thio keto-thioenol tautomeric equilibrium, the chromophoric properties of the C=S group, and the effect of oxygen on the system.

In our previous paper¹ we discussed the thio keto-thioenol tautomeric equilibrium of ethyl thiobenzoylacetate (I) and the effect of oxygen upon this system. We showed that this sequence, where $k_3 \gg k_1$, adequately accounts for the experimental observations



The rate of oxidation in 95% ethanol was followed spectrophotometrically and k_3 was found to be $3.5 \times 10^{-3} \text{ sec.}^{-1}$. The rate of thio keto tautomerization was followed spectrophotometrically ($k_1 = 9.3 \times 10^{-3} \text{ sec.}^{-1}$), and by measuring the rate of oxygen uptake ($k_1 = 4.0 \times 10^{-5} \text{ sec.}^{-1}$). At equilibrium the thioenol concentration in 95% ethanol was 87%. Our current report deals with the effects of substituents upon this system.

α,α -Dimethyl Substitution.—Replacement of both α -hydrogens with methyl groups of course eliminated the possibility of thioenolization and gave us an unambiguous thione of similar structure, ethyl α,α -dimethylthiobenzoylacetate (II).



This compound was prepared by treating, with hydrogen sulfide and hydrogen chloride, ethyl α,α -dimethylbenzoylacetate which was synthesized in a single step from ethyl benzoylacetate, methyl iodide and sodium hydride. (The use of sodium metal requires a two-stage methylation.) The polarographic half-wave potential (double wave -0.85 and -0.89 v.) confirmed the assignment of the observed half-wave potential of -0.85 v. for I. Purification of II was difficult since there was no thioenol form from which a heavy metal salt could be prepared. A complex with mercuric chloride was formed, but the thione could not be regenerated with hydrogen sulfide or with potassium iodide.² The boiling points of II and its keto analog were too close for separation by distillation. Chromatography on Florisil was effective in providing a product which showed a strong peak in the infrared (Fig. 1) at 5.79μ (ester carbonyl) and a very small peak at 5.94μ (ketone carbonyl) which in the ketone analog was slightly stronger than the ester peak. A strong broad peak, absent in the

keto analog, at about 8.0μ was tentatively ascribed to the C=S bond.³ The absorption peak of II in the visible range was not shifted from that of I ($564 \text{ m}\mu$) but the molar extinction coefficient (ϵ) was increased from 2.0 for I to 100 for II. If the increase in ϵ were due only to the increase in thione form, an increase of about eightfold would be expected. The α -methyl groups thus exert a pronounced hyperchromic effect.

The rate of oxidation of II was measured by rapidly saturating a 95% ethanol solution of the compound with oxygen and measuring the rate at which the optical density (A) decreased at the absorption peak. (Beer's law applied in the pertinent concentration range.) In contrast with the behavior of I,¹ a plot of optical density against time gave a typical S-shaped autocatalytic curve. A straight line was obtained by plotting⁴ time against $\log A_{\text{time}}/(A_{\text{init.}} - A_{\text{time}})$ for the first 46 hours of the reaction. The rate constant (25°) was $3.1 \times 10^{-5} \text{ sec.}^{-1}$, much slower than the oxidation rate found¹ for the thione form of I. It was noted that when an impure sample of II (*i.e.*, not free of the keto analog) was used, there was no initial induction period. This suggests that a thione-keto complex may be an intermediate in the oxidation. The slower rate for II in contrast with I is probably a result of steric hindrance. The kinetic data are presented in Table I.

TABLE I
SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF OXIDATION FOR ETHYL α,α -DIMETHYLTHIOBENZYLACETATE

Time, hr.	A at $565 \text{ m}\mu$	$2.37 \times 10^{-5} M \log A_{\text{time}}/(A_{\text{init.}} - A_{\text{time}})$
0	0.242
1.0	.240	2.07918
2.0	.240	2.07918
4.0	.240	2.07918
7.0	.240	2.07918
15.0	.238	1.77452
20.5	.234	1.76613
22.5	.230	1.28255
38.5	.184	0.50139
42.0	.167	.34766
46.5	.143	.15970
51.5	.122	
62.5	.088	
70.0	.070	
86.5	.052	
93.5	.045	

The rate of oxygen uptake was followed directly in a Warburg apparatus. Again the S shaped auto-

(1) Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, California, April, 1958; Z. Reyes and R. M. Silverstein, *THIS JOURNAL*, **80**, 6367 (1958).

(2) F. Arndt and P. Nachtway, *Ber.*, **56**, 2406 (1923).

(3) Von Rolf Mecke, R. Mecke and A. Luttringhaus, *Z. Naturforschung*, **10b**, 367 (1955).

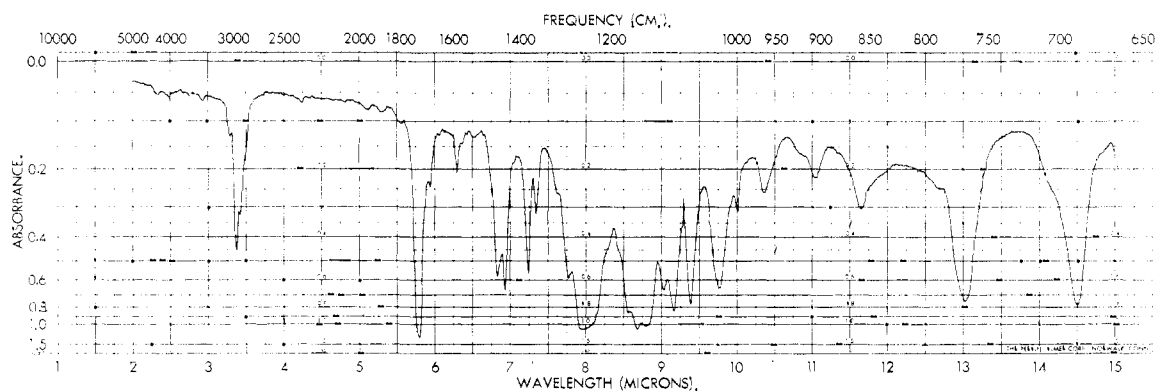


Fig. 1.—Infrared spectrum of ethyl α,α -dimethylthiobenzoylacetate.

catalytic curve was obtained (albeit with a somewhat less pronounced induction period) on a time *versus* uptake of oxygen plot. A straight line was obtained by plotting⁴ time against $\log x/(a - x)$ where a is the initial moles of compound and x is moles of oxygen absorbed. The rate constant (25°), $2.3 \times 10^{-5} \text{ sec.}^{-1}$, was in substantial agreement with that obtained spectrophotometrically. An over-all stoichiometry of one mole of oxygen consumed for each mole of II was obtained. The kinetics used assume the production of one mole of ketone for each mole of II. We can neither describe the course nor the mechanism of oxidation; the only isolable product was the keto analog. The kinetic data for the Warburg run are presented in Table II.

TABLE II
RATE OF OXIDATION OF ETHYL α,α -DIMETHYLTHIOBENZOYL-
ACETATE BY OXYGEN UPTAKE IN 95% ETHANOL

Time, hr.	$5.94 \times 10^{-3} M$	
	Moles O_2 $\times 10^{-3}$	$\log x/(a - x)$
0.85	0.0450	$\bar{2}.18932$
1.35	.0514	$\bar{2}.24835$
3.35	.05816	$\bar{2}.30040$
5.10	.07108	$\bar{2}.38949$
16.6	.1292	$\bar{2}.65791$
18.6	.1411	$\bar{2}.70114$
20.6	.1680	$\bar{2}.77785$
22.6	.2326	$\bar{2}.92938$
25.1	.3037	$\bar{1}.05659$
40.6	.8592	$\bar{1}.60971$
43.8	1.027	$\bar{1}.72328$
46.6	1.163	$\bar{1}.80866$
49.6	1.292	$\bar{1}.88659$
54.6	1.518	0.01945
64.6	1.848	.21673
71.3	2.067	.35981
88.6	2.474	.69807
96.1	2.630	.88846
115.1	2.913	1.70856

The steric influence of the α,α -dimethyl groups again was noted on treating both II and its keto analog in alcohol with a 2,4-DNPH reagent⁵ at room temperature. The other keto- and thioketo-

esters described in this work gave a heavy precipitate with this reagent in a matter of minutes under similar conditions. In contrast, II (and its keto analog) developed only a moderate amount of turbidity over a period of about two hours. After 24 hours, the yellow precipitate was filtered, and recrystallized from ethanol to give the yellow dinitrophenylhydrazone. Its identity is treated in a separate report.⁶

p-Ethoxy Substitution.—Substitution on I of a *p*-ethoxy group to give ethyl *p*-ethoxythiobenzoylacetate (III) decreased the equilibrium thioenol content, caused a hypsochromic shift, and increased the molecular extinction coefficient. The equilibrium thioenol content, determined by Mitra's method,⁷ in 95% ethanol was 82% (87% for I), $\lambda_{\text{max}}^{95\% \text{ ethanol}}$ was 550 m μ (564 m μ for I), and ϵ was 17 (2.0 for I). As in the case of replacement of α -hydrogens by methyl groups (II), the effect of the *p*-ethoxy groups on ϵ was more pronounced than the effect on the equilibrium would account for.

Purification of III was accomplished by precipitating, filtering, and washing the lead salt of the thioenol form, regenerating with H_2S , and chromatographing on Florisil. All steps were carried out under N_2 . Examination of the infrared spectrum (Fig. 2) both as a liquid film and in CCl_4 disclosed a broad, moderately strong band at 4.10 μ (intramolecularly hydrogen bonded SH) with a pronounced shoulder at 3.92 μ (normal SH).⁸ A strong band at 5.71 μ was ascribed to the ester carbonyl of the thione tautomer, a very strong band at 5.95 μ to the hydrogen bonded α,β -unsaturated ester carbonyl of the thioenol tautomer, and a pronounced shoulder at 5.88 μ to the ester carbonyl of the non-hydrogen bonded α,β -unsaturated thioenol tautomer (*i.e.*, correlating with the normal SH shoulder). It is of interest to note that the ketone-ester analog showed only two equally strong bands at 5.77 and 5.99 μ . Since this compound exists predominantly as the keto tautomer,⁹ the band at 5.77 μ can be assigned to the ester carbonyl of the keto form, and the band at 5.99 μ to the ketone carbonyl with a minor contribution from the ester carbonyl of the hydrogen bonded α,β -un-

(6) To be published.

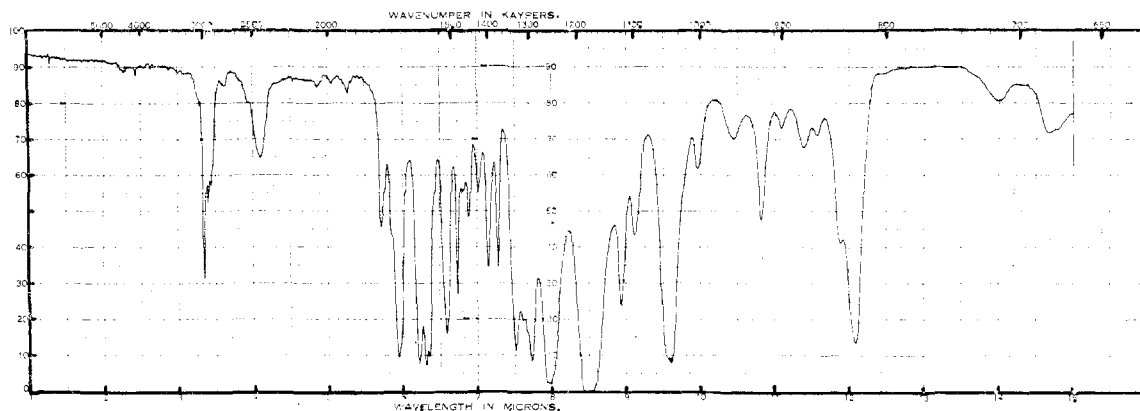
(7) S. K. Mitra, *J. Indian Chem. Soc.*, **15**, 205 (1938).

(8) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 288, 289.

(9) See discussion and references in Paper I (ref. 1).

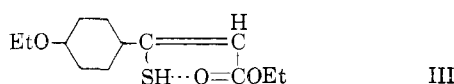
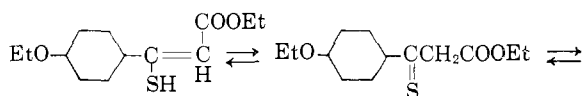
(4) F. Daniels, *et al.*, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 144.

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

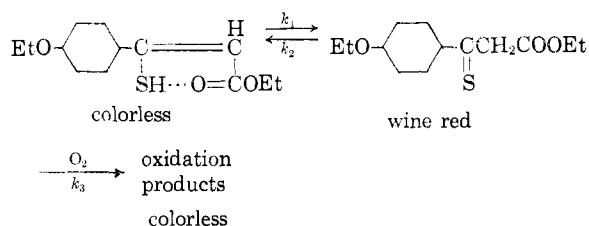
Fig. 2.—Infrared spectrum of ethyl *p*-ethoxythiobenzoylacetate.

saturated enol tautomer. This overlapping of bands makes it impossible to state definitely that III was completely free of ketone impurity. However, the combination of lead salt precipitation and washing followed by chromatography should afford reasonable assurance of purity.

The equilibrium picture deduced from the foregoing information is



As in the case of I, the decolorization of III by oxygen followed by return of the color on removal of oxygen can be rationalized by the next sequence where $k_3 \gg k_1$ (ignoring the small amount of unbonded thioenol form).



The rate constant of oxidation of the thione form (k_3) was measured spectrophotometrically (after determining that Beer's law applied over the pertinent concentration range) by rapidly saturating a 95% ethanol 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 plot of time against $\log(A_{\text{init.}}/A_{\text{time}})$ gave a straight line for a reasonable period of time; k_3 was found to be $7.3 \times 10^{-4} \text{ sec.}^{-1}$. The rate constant of thioketonization (k_1) was obtained by flushing the decolorized solution (immediately after the k_3 run) with nitrogen and following the increase in optical density at the same wave length. A pseudo-first-order rate constant ($k_1 = 5.1 \times 10^{-5} \text{ sec.}^{-1}$) was obtained by plotting time against $\log a/(a-x)$ where

$(a-x)$ where

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

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

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

Both k_3 and k_1 are slower for III than for I¹ but the effect of the *p*-OEt group on k_3 was greater than on k_1 . The ratio of $k_3:k_1$ for III was 14, whereas for I it was 38. Kinetic data are presented in Tables III and IV.

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF OXIDATION FOR THE THIONE FORM OF ETHYL *p*-ETHOXYTHIOBENZOYLACETATE IN 95% ETHANOL (k_3)

Time, min.	A at 550 $m\mu$	$0.0688 M \log(A_{\text{init.}}/A_{\text{time}})$
0	1.09
2	0.970	0.05066
3	.940	.06430
4	.900	.08320
5	.860	.1029
6	.838	.1142
7	.800	.1343
8	.760	.1566
10	.700	.1923
12	.635	.2347
14	.580	.2740
16	.540	.3050
18	.515	.3256
38	.400	.4354

The rate of oxygen uptake by III in 95% ethanol was followed directly in a Warburg apparatus. Again, as in the case of I, the initial rapid uptake was apparently more rapid than diffusion of oxygen into the solution, and k_3 could not be obtained. The slow rate of oxygen uptake following the initial fast oxidation was assumed to be a measure of k_1 . A pseudo first-order rate constant of $2.7 \times 10^{-5} \text{ sec.}^{-1}$ for k_1 was found by plotting time against $\log a/(a-2x)$ where a is the initial moles of compound and x is the moles of oxygen absorbed. The overall stoichiometry of $\text{C}=\text{S}:\text{O}_2 = 2$ was obtained from the total amount of oxygen absorbed. The agreement between spectrophotometric and Warburg values is reasonable considering that the reactions are not kinetically clean throughout, and that the over-all stoichiometry may be different from that of the direct oxidation of the thione form. We

TABLE IV
SPECTROPHOTOMETRIC DETERMINATION OF THE RATE OF
THIOKETONIZATION FOR ETHYL *p*-ETHOXYTHIOBENZOYLACETATE IN 95% ETHANOL (k_1)

Time, min.	0.0688 M	
	A at 550 m μ	$\log a/(a-x) \times 10^2$
0	0.430	4.992
1	.440	5.115
2	.460	5.362
3	.475	5.548
5	.500	5.861
6	.508	5.961
7	.520	6.112
8	.530	6.239
9	.543	6.403
10	.555	6.556
12	.593	7.043
16	.610	7.263
18	.630	7.522
22	.660	7.915

can describe neither the course nor the mechanism of oxidation. The only isolable product was ethyl *p*-ethoxybenzoylacetate. The kinetic data are presented in Table V.

TABLE V
RATE OF OXYGEN UPTAKE FOR ETHYL *p*-ETHOXYTHIOBENZOYLACETATE IN 95% ETHANOL AS A MEASURE OF k_1

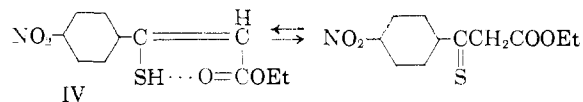
Time, min.	0.107 M	
	Moles O ₂ absorbed $\times 10^3$	$\log a/(a-2x)$
48	1.025	0.04391
100	1.90	.08481
160	2.77	.12997
220	3.51	.17246
290	4.23	.21821
375	4.67	.24875
7 days	11.05

Treatment of III with a stoichiometric amount of I₂ in ethanol produced the disulfide which even after repeated low temperature recrystallizations remained a viscous liquid at room temperature. It is quite probable that the product obtained represents a mixture of isomers. The analytical values and infrared spectrum are in accordance with those expected of a disulfide.

Addition to an ethanol solution of III at room temperature of excess 2,4-DNPH reagent⁵ gave a heavy deep red precipitate in a matter of minutes as did addition of this reagent to the keto analog; the same derivative was obtained from both compounds. Its identity is discussed in a subsequent publication.⁶

***p*-Nitro Substitution.**—The consequences of *p*-nitro substitution were quite striking. Ethyl *p*-nitrothiobenzoylacetate (IV) was a pale greenish-yellow solid. Our immediate impression was that we were dealing with either a trimer (trimerization is a common occurrence in thione chemistry) or with a completely thioenolized system such as we had encountered in the case of thiobenzoylacetate.¹ However, a molecular weight determination was in agreement with that expected for the monomer. Furthermore, no color appeared either on heating in a solvent or on melting the *p*-nitro compound in contrast with the behavior of thiobenzoylacetate. The spectral, polarographic and titri-

metric evidence all pointed to an equilibrium picture quite similar to that constructed for ethylthiobenzoylacetate (I)¹ except for the absence in the case of the *p*-nitro compound of a detectable amount of non-hydrogen bonded thioenol form.



The equilibrium thioenol content in 95% ethanol, determined by Mitra's iodimetric titration,⁷ was 97%. The infrared spectrum (Fig. 3) showed the moderately strong band at 4.12 μ of the intramolecularly hydrogen bonded SH group with no indication of a shoulder at the usual position (*ca.* 3.8–3.9 μ) for the non-bonded configuration. The strong band at 5.95 μ was assigned to the intramolecularly hydrogen bonded α,β -unsaturated carbethoxy carbonyl group. The presence of the normal carbethoxy carbonyl of the thione tautomer was shown by a pronounced "hook" at 5.75 μ . There was only the slightest indication of an inflection in the 5.8–5.9 μ region as evidence for the possible existence of a very small amount of the unbonded thioenol structure. A polarogram showed an SH wave with a half-wave potential of -0.32 v. and a NO₂ wave with a half-wave potential of -0.455 v.; their respective heights were in the proper ratio of 1:6. In addition there was a small wave with a half-wave potential of -0.93 v. The assignment of the latter wave to a C=S group seems reasonable in view of its proximity to the unequivocal C=S wave of II (-0.85 , -0.89 v.). The effect of the *p*-NO₂ group on the C=S wave cannot be assessed since the *p*-NO₂ reduction occurs first.

Having established the existence of the thione tautomer at equilibrium in ethanol, we must now rationalize the lack of color. It is generally accepted that the low intensity long wave length absorption band of thiones is caused by an $n \rightarrow \pi^*$ electronic transition. Substituent groups that make electrons available to the system characteristically cause a "blue shift" and a hyperchromic effect. Electron withdrawing groups have a bathochromic and hypochromic effect. For example, a *p*-methoxy group on thiobenzophenone shifts the absorption band from 595 to 585 m μ and increases the extinction coefficient from 167 to 252. A *p*-nitro group shifts the band to 610 m μ and decreases the extinction coefficient to 130.¹⁰ Since the hyperchromic influence of a *p*-ethoxy group on our system is considerably greater than the effect of a *p*-methoxy group on thiobenzophenone, we assume that the hypochromic effect of a nitro group would also be more pronounced in our system. Apparently this effect, together with the marked shift toward the thioenol tautomer, is sufficient to reduce the $n \rightarrow \pi^*$ absorption of our *p*-nitro compound below detectable limits.

Although the thione group of IV has greatly diminished chromophoric properties, it was nonetheless oxidized by oxygen, and, as was the case

(10) R. H. Abeles, R. F. Hutton and F. H. Westheimer, *THIS JOURNAL*, **79**, 712 (1957); G. Sartori and C. Furloni, *Ann. Chim. (Rome)*, **44**, 113 (1954). For a recent review of electronic transitions of non-bonding electrons, see J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

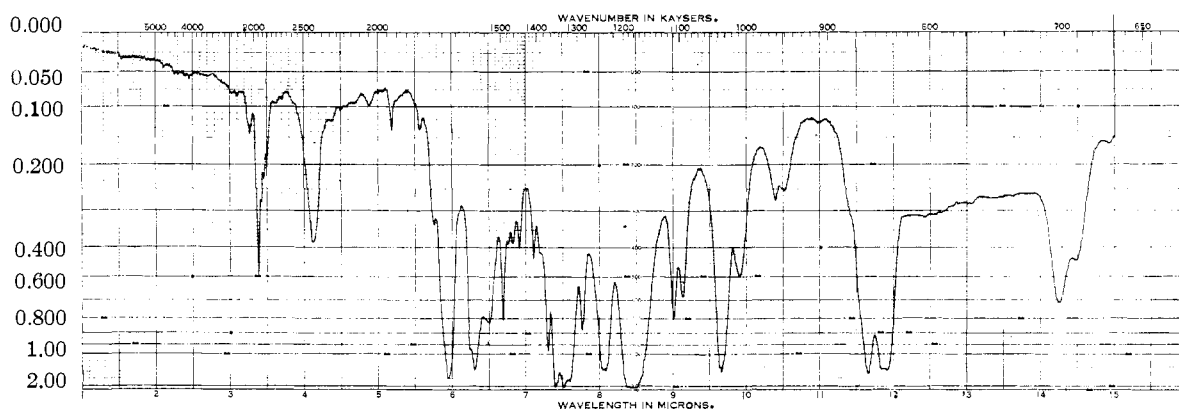


Fig. 3.—Infrared spectrum of ethyl *p*-nitrothiobenzoylacetate.

for the other thioketothioenol systems studied, thioketone formation proceeded as the thione form was removed by oxidation. It was, of course, impossible to study the kinetics of oxidation of IV spectrophotometrically as had been done for the colored thiobenzoylacetates. The rate constant of oxidation of the thioketo form (k_3) could not be determined by following the oxygen uptake since the small amount of the thioketo form present at equilibrium required the use of more compound than could be dissolved in the limited volume of ethanol. Modification of the apparatus to accommodate this situation was not considered worthwhile since oxygen absorption measurements were not satisfactory for k_3 determinations in the other compounds. The rate constant of thioketone formation (k_1) in 95% ethanol was measured as a function of the slow rate of oxygen uptake as described for the other compounds of this series. An over-all stoichiometry of five moles of IV to one mole of oxygen was established. A pseudo-first-order rate constant of $9.1 \times 10^{-5} \text{ sec.}^{-1}$ was obtained for k_1 by plotting $\log a/(a - 5x)$ against time for the first 65 minutes of the reaction. The effect of the *p*-nitro substituent then is not very pronounced (compared with $4.0 \times 10^{-5} \text{ sec.}^{-1}$ for I), but is in the opposite direction from the effect of the *p*-OEt group (k_1 for III was $2.7 \times 10^{-5} \text{ sec.}^{-1}$). The kinetic data for IV are presented in Table VI.

TABLE VI

RATE OF OXYGEN UPTAKE FOR ETHYL *p*-NITROTHIOBENZOYLACETATE IN 95% ETHANOL AS A MEASURE OF k_1

Time, min.	$3.74 \times 10^{-2} M$	
	Moles O ₂ absorbed $\times 10^6$	$\log a/(a - 5x)$
1	1.15	0.01344
2	1.43	.01681
6	2.09	.02488
15	4.18	.05147
30	6.50	.08291
65	11.0	.15127
90 hr.	36.8

A cream-colored crystalline precipitate was noted at the end of the Warburg run. Oxidation in ethanol was carried out on a larger scale in order to isolate and identify this precipitate which, by analogy with Staudinger's oxidation products,¹¹

(11) H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1576, 1936 (1928).

we expected would be the trisulfide. However, a sulfur analysis, a molecular weight determination and congruence of the infrared spectrum with that of an authentic disulfide showed that the oxidation product in fact was the disulfide. This finding raises the possibility that in the case of IV, it is the thioenol rather than the thioketo form which is oxidized. However the similarity of the rate constant k_1 with those of the other compounds in the series argues for a similar mechanism. In fact, it is quite possible that a disulfide is an intermediate in all the oxidations, and was isolated in the one instance only because its insolubility prevented further reaction.

A solution of IV in isoöctane did not absorb any measurable amount of oxygen over a period of three days. Since the amount of the thioketo form at equilibrium in isoöctane was undoubtedly very small (see Paper I¹ for effect of solvent on equilibrium), the oxygen consumed by the thioketo form would not have been detectable at the concentrations used. Thus, in isoöctane there was no observable rate of thioketone formation. The influence of solvent on the rate of thioketone formation has been noted previously.¹

In common with the other thiobenzoylacetates (except for the α, α -dimethyl substituted compound), IV reacted with iodine to give the disulfide and with the "ketonic" reagent, 2,4-DNPH, to give a dinitrophenylhydrazone.⁶

The influence of the substituents studied in this paper on the equilibrium, on the color and on the effects on oxygen are summarized in Table VII.

Acknowledgment.—The authors are indebted to the Analytical Section of Stanford Research Institute under Dr. D. M. Coulson for analytical values, the polarographic studies and the spectral data; to Dr. R. J. Marcus of the Physical Chemistry Section for advice on kinetic problems; and to Dr. A. Weissberger of Eastman Kodak Co. for a sample of ethyl *p*-nitrobenzoylacetate. This work was supported by the Division Research Committee of Stanford Research Institute.

Experimental

Instrumentation and kinetic techniques were described in the previous paper.¹

Ethyl α, α -Dimethylbenzoylacetate.—A solution of 38.4 g. (0.2 mole) of ethyl benzoylacetate in 50 ml. of dry benzene was added dropwise over a period of 15 minutes to a

TABLE VII

SUMMARY OF EFFECTS OF SUBSTITUENTS (IN ETHANOL)					
Substituent	Thioenol, %	k_1 (method)	k_2 (method)	$\lambda_{\text{max}}^{\text{ethanol}}$	ϵ
Unsubstituted	87	9.3×10^{-6} (spectro)	3.5×10^{-3} (spectro)	564	2.0
		4.0×10^{-8} (Warburg)		
α, α' -Dimethyl	0	3.1×10^{-6} (spectro)	565	100
		2.3×10^{-8} (Warburg)		
<i>p</i> -Ethoxy	82	5.1×10^{-6} (spectro)	7.3×10^{-4} (spectro)	550	17
		2.7×10^{-8} (Warburg)		
<i>p</i> -Nitro	97	9.1×10^{-8} (Warburg)	None	None

stirred suspension of 10.5 g. (0.438 mole) of sodium hydride in 150 ml. of dry benzene. After the vigorous gas evolution subsided, 60 ml. (0.961 mole) of methyl iodide was added over a period of about 15 minutes. The mixture was stirred, refluxed for 5 hours, allowed to remain at room temperature overnight, and filtered. The solvent was removed from the filtrate. The residual oil was distilled through a 1×60 cm. Nichrome spiral column at 1 mm.; a forerun (4.9 g., n_{D}^{20} 1.5037) was collected at a head temperature of 95–100°, and the main cut (26.7 g., n_{D}^{20} 1.5040) at 100–102°. The total yield (assuming adequate purity of the forerun) was 72%. Only the main cut was used.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C, 70.9; H, 7.27. Found: C, 70.6; H, 7.43.

Ethyl α, α' -Dimethylthiobenzoylacetate.—A mixture of hydrogen chloride and hydrogen sulfide was bubbled for one hour through a solution of 6.45 g. (0.0336 mole) of ethyl α, α' -dimethylbenzoylacetate in 40 ml. of 95% ethanol in an ice-bath. The hydrogen chloride stream was discontinued, and bubbling with a slow stream of hydrogen sulfide was continued for four hours (ice-bath cooling maintained throughout). The blue solution was evaporated under water-pump vacuum. Addition of carbon tetrachloride and removal thereof under vacuum served to purge the gases from the residue. A white complex was obtained on treating a portion of the residue in ethanol with an ethanolic solution of mercuric chloride, but attempted regeneration with hydrogen sulfide or with potassium iodide² was unsuccessful. A 1-g. portion of the residue was chromatographed on a Florisil column ($1'' \times 8''$, 500°F. activation, 200/300 mesh) under nitrogen with carbon tetrachloride. The blue band was eluted and rechromatographed twice under the same conditions. The final product (0.1 g.) was an intense blue liquid of not unpleasant odor (in contrast with the vile odor of the enolizable compounds); spectral data (under N_2), $\lambda_{\text{max}}^{95\% \text{ ethanol}}$ in μ : 565 (ϵ 100); $\lambda_{\text{max}}^{\text{liquid}}$ in μ : 5.79 (strong, COOEt), 5.94 (very weak, C=O impurity), 8.0 (strong, C=S?); polarographic data: double C=S wave with half-wave potentials at -0.85 and -0.89 v.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$: S, 13.6. Found: S, 13.5.

Ethyl *p*-Ethoxybenzoylacetate.¹²—A stirred mixture of 35.4 g. (0.30 mole) of diethyl carbonate, 7.2 g. (0.30 mole) of sodium hydride and 90 ml. of dry benzene was warmed to 40–50° and a solution of 24.6 g. (0.15 mole) of *p*-ethoxyacetophenone in 75 ml. of dry benzene was added dropwise over a period of one hour and 45 minutes. The reaction mixture was stirred at 50–60° until gas evolution ceased and for one hour thereafter. When the reaction was completed, the mixture was cooled in an ice-bath to about 10°, and 30 ml. of ethanol was added with stirring to destroy the unreacted sodium hydride. Then the mixture was cooled to 4° and a solution of 225 ml. of ice-water and 26 ml. of concentrated hydrochloric acid (slight excess) was added with stirring, keeping the temperature below 20°; stirring was continued until all the solid had dissolved. The benzene layer was separated and the aqueous phase was extracted with 100 ml. of ether. The combined ether and benzene extracts were washed with sodium bicarbonate, then with water, and dried over anhydrous sodium sulfate. The solvent was removed, and the β -keto ester was isolated by precipitation with cupric acetate¹³ and regeneration with acetic acid. The product was crystallized twice from a mixture of ether and petroleum ether (30–65°); yield (14.3 g.) 40%, m.p. 53–54°.

(12) F. W. Swamer and C. R. Hauser, *THIS JOURNAL*, **72**, 1356 (1950).

(13) H. R. McCleary and L. P. Hammett, *ibid.*, **63**, 2251 (1941).

Ethyl *p*-Ethoxythiobenzoylacetate.—A solution of 3.54 g. (0.015 mole) of ethyl *p*-ethoxybenzoylacetate in 50 ml. of ethanol and 10 ml. of benzene was cooled to -5° , and slow streams of dry hydrogen chloride and hydrogen sulfide were passed through it for 3.5 hours, keeping the reaction mixture in an ice-salt-bath. The hydrogen chloride stream was stopped, and hydrogen sulfide was continued for 20 hours longer. The solution turned dark red. When the solvent was evaporated (reduced pressure at room temperature), a viscous red oil was obtained. This oil was dissolved in 20 ml. of carbon tetrachloride and treated with lead acetate in ethanol. The lead mercaptide precipitated slowly while the mixture was stirred in a nitrogen atmosphere. The precipitate was collected, washed with carbon tetrachloride and with low boiling petroleum ether. The thioketo ester was regenerated by passing hydrogen sulfide through a suspension of the lead salt in carbon tetrachloride. The precipitate of lead sulfide was removed, and the solvent evaporated under reduced pressure in a nitrogen atmosphere. A wine-red oil was obtained which was further purified by chromatography on a Florisil column ($1'' \times 8''$, 500°F. activation, 200/300 mesh) under nitrogen with carbon tetrachloride (yield 1.0 g., 26%); spectral data (under N_2), $\lambda_{\text{max}}^{95\% \text{ ethanol}}$ 550 μ : (ϵ 17.0); $\lambda_{\text{max}}^{\text{liquid}}$ in μ 3.92 (shoulder, normal SH), 4.10 (moderately strong, intramolecularly hydrogen bonded SH), 5.71 (strong, COOEt of thione tautomer), 5.95 (very strong, hydrogen bonded α, β -unsaturated COOEt), 5.88 (shoulder, α, β -unsaturated COOEt).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$: S, 12.7. Found: S, 12.6.

Diethyl β, β' -Dithiobis-*p*-ethoxycinnamate.—A solution of 0.344 g. (0.00136 mole) of ethyl *p*-ethoxythiobenzoylacetate in 10 ml. of 95% ethanol was treated at room temperature with a solution of 0.18 g. (0.0007 mole) of I_2 in 10 ml. of 95% ethanol. The mixture was stirred at room temperature for 15 minutes, then it was diluted with 20 ml. of carbon tetrachloride and the slight excess of iodine was destroyed by addition of a few drops of 0.1 *N* sodium thiosulfate. Cold water (80 ml.) was added; the organic layer was separated and the aqueous one was extracted with 20 ml. of carbon tetrachloride. This extract was combined with the organic layer, washed with dilute sodium carbonate and with water, and dried over anhydrous sodium sulfate. Upon evaporation of the carbon tetrachloride, a light-yellow viscous oil was obtained, which was crystallized once from a mixture of carbon tetrachloride and petroleum ether (35–60°) and once from an ether-petroleum ether (35–60°) mixture. (In both crystallizations, the solution was treated with Norit, cooled in Dry Ice and the product was separated from the mother liquor by decantation.) The nearly colorless viscous oil obtained was dried under vacuum at 50°; yield 0.21 g. (61%); spectral data, $\lambda_{\text{max}}^{\text{carbon tetrachloride}}$ in μ : 5.80 with shoulder at 5.88 (strong, α, β -unsaturated COOEt).

Anal. Calcd. for $\text{C}_{26}\text{H}_{30}\text{O}_6\text{S}_2$: S, 12.76. Found: S, 13.00.

Ethyl *p*-Nitrothiobenzoylacetate.—Absolute ethanol (40 ml.) was saturated with dry hydrogen chloride at -5 to 0° . Hydrogen sulfide was passed in for 15 minutes and a solution of 2.37 g. (0.01 mole) of ethyl *p*-nitrobenzoylacetate in a mixture of 15 ml. of benzene and 5 ml. of ether was dropped in slowly. The stream of hydrogen sulfide was maintained during this addition and for 6 hours thereafter. The mixture turned bluish-green. After standing overnight at room temperature, the solution was cooled in an ice-bath. The light-yellow crystals that separated were collected and recrystallized from a mixture of carbon tetrachloride and petroleum ether (30–65°); yield 0.94 g., 37%, greenish-yellow crystals, m.p. 80–81°, possessing the characteristic vile odor of this class of compounds; spectral data: $\lambda_{\text{max}}^{\text{acetone}}$

in μ : 258 (ϵ 17,200), 310 (ϵ 9,150); $\lambda_{\text{max}}^{\text{CCl}_4}$ in μ 4.12 (moderately strong, intramolecularly hydrogen bonded SH), 5.75 (hook, COOEt of thione tautomer), 5.95 (strong, intramolecularly hydrogen bonded α,β -unsaturated COOEt).

Another sample was purified by precipitation with lead acetate and regeneration with hydrogen sulfide as described for the *p*-ethoxy compound. The same m.p. and infrared spectrum were obtained.

Anal.: Calcd. for $\text{C}_{11}\text{H}_{11}\text{NO}_4\text{S}$: C, 52.2; H, 4.38; S, 12.65; mol. wt., 253. Found: C, 52.3; H, 4.48; S, 12.44; mol. wt., 246 (cryoscopic).

Diethyl β,β' -Dithiobis-(*p*-nitrocinnamate).—A solution of 0.0236 g. (0.00093 mole) of iodine in 2 ml. of 95% ethanol was added dropwise at room temperature to a swirled solution of 0.047 g. (0.00186 mole) of ethyl *p*-nitrothiobenzoylacetate in 3 ml. of 95% ethanol. The iodine color was discharged almost immediately following the addition of each drop, and a white precipitate settled out during the course of the addition. The mixture was allowed to stand for two hours at room temperature, cooled and filtered. The precipitate was washed with and twice recrystallized from, 95% ethanol, and twice recrystallized from a mixture of

benzene and petroleum ether (30–65°). The cream-colored product (0.033 g., 35% yield) melted at 153–154°; spectral data $\lambda_{\text{max}}^{\text{chloroform}}$ in μ : 5.84 with shoulder at 5.90 (strong, α,β -unsaturated COOEt).

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2$: S, 12.6. Found: S, 12.3.

Oxidation of Ethyl *p*-Nitrothiobenzoylacetate.—A solution of 0.20 g. (0.00079 mole) of ethyl *p*-nitrothiobenzoylacetate in 25 ml. of 95% ethanol was saturated with dried oxygen, stoppered and allowed to stand at room temperature. Cream-colored crystals gradually separated from the solution over a period of three days. The crystalline product was filtered, washed with alcohol, and with carbon tetrachloride, and crystallized from benzene; yield 0.029 g. (46%), m.p. 154–155°. The infrared spectrum in chloroform was identical with that of diethyl β,β' -dithiobis-(*p*-nitrocinnamate).

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2$: S, 12.6; mol. wt., 504.5. Found: S, 12.4; mol. wt. (isothermal distillation in benzene), 518.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Elimination Reactions. IX. Mechanisms for the Pyrolysis of Methyl Cyclohexyl Sulfites

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The pyrolyses of *cis*- and *trans*-2-*p*- $\text{C}_7\text{H}_7\text{SO}_2$ -, *cis*- and *trans*-2-*p*- $\text{C}_7\text{H}_7\text{S}$ - and *cis*-2-*t*-butyl-cyclohexyl methyl sulfites were found, for the most part, to parallel those of the corresponding S-methyl xanthates (*i.e.*, *cis* elimination). Evidence is presented to show that the formation of considerable quantities of 1-substituted-cyclohexene (the *trans* elimination product) from *cis*-2- $\text{C}_7\text{H}_7\text{S}$ - and *cis*-2- C_6H_5 -cyclohexyl methyl sulfites is caused largely by rearrangement of the 3-substituted-cyclohexene first formed, rather than by a *trans* elimination. It is concluded that methyl cyclohexyl sulfite pyrolyses probably occur by the concerted type mechanism generally accepted for xanthate and other ester pyrolyses. An ion pair mechanism *without participation* is an acceptable variation. Decomposition of *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite occurs by a *trans* elimination following first-order kinetics. This is represented by a stepwise reaction involving a dipolar intermediate.

Recently it was observed that pyrolysis of *cis*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate gave 1-*p*-tolylsulfonylcyclohexene.² This is apparently the first example in which a Chugaev elimination proceeds by abstraction of a *trans* β -hydrogen *in preference* to a *cis* β -hydrogen. Our attention was attracted in this respect to the conclusion by Berti³ that the pyrolysis of *cis*-2-phenylcyclohexyl methyl sulfite to give 1-phenylcyclohexene (78%) in preference to 3-phenylcyclohexene (22%) was an example of a *trans* pyrolytic elimination. Since this result was opposite to that obtained on pyrolysis of the S-methyl xanthate,^{3,4} Berti concluded that sulfite and xanthate pyrolyses proceed by different mechanisms, and Berti and Price⁵ suggested an ion pair mechanism with group participation for sulfite pyrolyses. Our study of xanthate pyrolyses² now has been extended to methyl sulfites.

Pyrolysis of the methyl sulfite of *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite gave 1-*p*-tolylsulfonylcyclohexene, the *trans* elimination product, and no detectable quantity of 3-*p*-tolylsulfonylcyclohexene. This parallels the result with the corresponding xanthate.² Pyrolysis of *cis*-2-*p*-tolyl-

thiocyclohexyl methyl sulfite gave about 40% of the *trans* elimination product (1-*p*-tolylthiocyclohexene) and 60% of the *cis* elimination product (3-*p*-tolylthiocyclohexene). Before concluding that 1-substituted-cyclohexenes, are formed from *cis*-esters by *trans* eliminations it is necessary to show that rearrangement of the 3-substituted-cyclohexene to 1-substituted-cyclohexene does not occur during the pyrolysis. The fact that 3-*p*-tolylsulfonylcyclohexene fails to rearrange in the presence of strong acid² ensures that a *trans* elimination is indeed occurring with the sulfite (and xanthate) pyrolysis when the *cis* 2-substituent is *p*- $\text{C}_7\text{H}_7\text{SO}_2$. In contrast, 3-*p*-tolylthiocyclohexene rearranges to 1-*p*-tolylthiocyclohexene to the extent of 40% in 20 min. at 195° in the presence of *p*-toluenesulfonic acid. When added to a sulfite pyrolysis 3-*p*-tolylthiocyclohexene rearranges to 1-*p*-tolylthiocyclohexene to the extent of about 20%. This suggests that in the pyrolysis of *cis*-2-*p*-tolylthiocyclohexyl methyl sulfite a maximum of 20% (40–20) of *trans* elimination occurred. Berti³ found that 3-phenylcyclohexene rearranged to 1-phenylcyclohexene to the extent of about 35% under pyrolysis conditions. Actually, these are probably minimum figures for rearrangement, since in the test cases the added olefin is present in high concentration relative to the acidic products causing rearrangement, whereas the olefin formed *in*

(1) Socony-Mobil Predoctoral Fellow, 1955–1958.

(2) F. G. Bordwell and P. S. Landis, *THIS JOURNAL*, **80**, 2450 (1958).

(3) G. Berti, *ibid.*, **76**, 1213 (1954).

(4) E. R. Alexander and A. Mudrak, *ibid.*, **73**, 59 (1951).

(5) See footnote 25 of reference 3.