n^{20}_D 1.4852). In other experiments, dimethylcarbamyl azide was isolated as a colorless liquid, b.p. 72–74° (30 mm.).[28]

Anal. Calcd. for $C_3H_6ON_4$: C, 31.59; H, 5.30; O, 14.02; N, 49.10; Cl, 0. Found: C, 31.83, 31.77; H, 5.27, 5.21; O, 14.2, 14.6; N, 45.3, 45.6; Cl, 0.4. No explanation for the low nitrogen analysis can be given. The infrared spectrum was completely consistent with the assigned structure, showing frequencies characteristic of dimethylamino, carbonyl and azide groups.

Acknowledgment.—We are deeply indebted to Mrs. Nancy G. Abbadini, Mrs. Janet W. Willoughby, and Mr. John Bair for excellent technical assistance.

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[30] R. Stollé, *J. prakt. Chem.*, (2) **117**, 201 (1927), gives b.p. 59° (15 mm.).

The Kinetics of the Acidic and Alkaline Hydrolysis of Ethyl Thionbenzoate

Stanley G. Smith and Marion O'Leary[1]

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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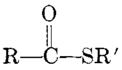
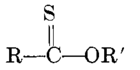
The hydrolysis of ethyl thionbenzoate in 40% aqueous acetone, in the presence of sodium hydroxide at 25.0° and in the presence of hydrochloric acid at 125°, has been shown to yield thiobenzoic acid and ethyl benzoate which is hydrolyzed to benzoic acid. The rate constants for the various steps in this reaction scheme are reported, and a possible mechanism for the reaction is discussed in the light of these data.

The hydrolysis of thiol esters I has been the subject of a number of studies because of interest in their reactivity compared to their oxygen analogs. In basic solution the rates of hydrolysis of analogous thiol and oxygen esters are generally within a factor of two, but in acid solution most oxygen esters hydrolyze more rapidly than the corresponding thiol esters by at least a factor of ten.[2] However, the isomeric thion esters II have received relatively little attention aside from their conversion to oxygen esters with aqueous silver nitrate[3,4] and their rearrangement to the isomeric thiol esters.[4-6]



$R-\overset{\overset{O}{\|}}{C}-SR'$

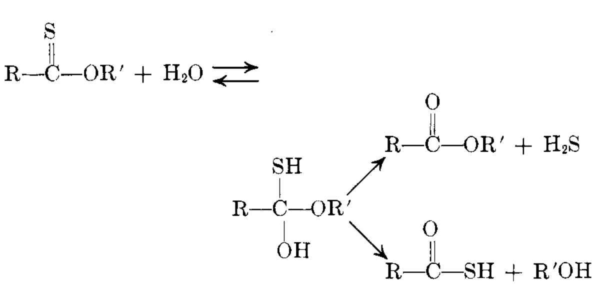
I



$R-\overset{\overset{S}{\|}}{C}-OR'$

II

A detailed study of the hydrolysis of thion esters II is of interest because it provides a particularly illuminating example of the carbonyl-addition mechanism[7] of hydrolysis. An intermediate III resulting from addition of water to the thiocarbonyl group of the thion ester could give rise to either an oxygen ester and hydrogen sulfide or a thio acid and an alcohol (equation 1).



(1)

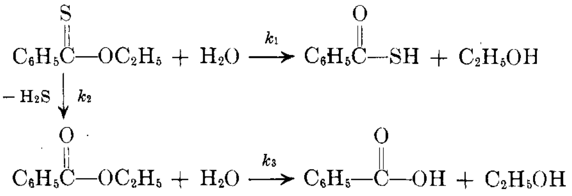
III

In addition, the rate level for this hydrolysis is important in connection with the recent application of thionbenzoate as an ambident leaving group in studies of ionization and ion-pair return.[6]

In the present work the kinetics of hydrolysis of ethyl thionbenzoate were studied under acid and alkaline conditions in 40% aqueous acetone.

Results

Alkaline Hydrolysis.—The hydrolysis of ethyl thionbenzoate in 40% aqueous acetone in the presence of sodium hydroxide at 25.0° was followed by analysis for ethyl thionbenzoate and ethyl benzoate by vapor phase chromatography. As illustrated in Fig. 1, ethyl benzoate is formed early in the reaction and subsequently disappears, the maximum concentration of ethyl benzoate being 9.3% of the initial thion ester concentration. This formation and disappearance of ethyl benzoate indicates that the rate constants k_1, k_2, and k_3 as defined in equation 2 are all of the same order of magnitude.



(2)

Determination of Rate Constant ($k_1 + k_2$).—In addition to the v.p.c. analysis, the disappearance of ethyl thionbenzoate in 40% aqueous acetone at 25.0° in the presence of 0.06 to 0.2 M sodium hydroxide was followed spectrophotometrically at 414 mμ. The absorption data for runs with *ca.* 0.01 M ester and 0.06 to 0.08 M base were treated with the aid of the usual integrated second-order rate equation, a good fit being obtained, as illustrated in Table I. The second-order rate equation is actually an approximation in this case because of loss of base due to the concurrent hydrolysis of ethyl benzoate, but with the concentrations employed the error thus introduced is less than 1% at 50% reaction. At the higher base concentrations pseudo-first-order kinetics were observed. The calculated second-order rate constants are summarized in Table II. In terms of the reaction scheme given in

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[1] Participant in the National Science Foundation Undergraduate Science Education Program.

[2] (a) L. H. Noda, S. A. Kuby, and H. A. Lardy, *J. Am. Chem. Soc.*, **75**, 913 (1953); (b) J. R. Schaefgen, *ibid.*, **70**, 1308 (1948); (c) B. K. Morse and D. S. Tarbell, *ibid.*, **74**, 416 (1952); (d) P. N. Rylander and D. S. Tarbell, *ibid.*, **72**, 3021 (1950); (e) J. G. Overbeek and V. V. Koningsberger, *Koninkl. Ned. Akad. Wetenschap Proc.*, **58B**, 266 (1955); (f) Y. Iskander, *Nature*, **155**, 141 (1945); (g) K. A. Connors and M. L. Bender, *J. Org. Chem.*, **26**, 2498 (1961).

[3] M. Matsui, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **3**, 247 (1909).

[4] S. A. Karjala and S. M. McElvain, *J. Am. Chem. Soc.*, **55**, 2966 (1933).

[5] S. G. Smith, *ibid.*, **83**, 4285 (1961).

[6] S. G. Smith, *Tetrahedron Letters*, **21**, 979 (1962).

[7] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

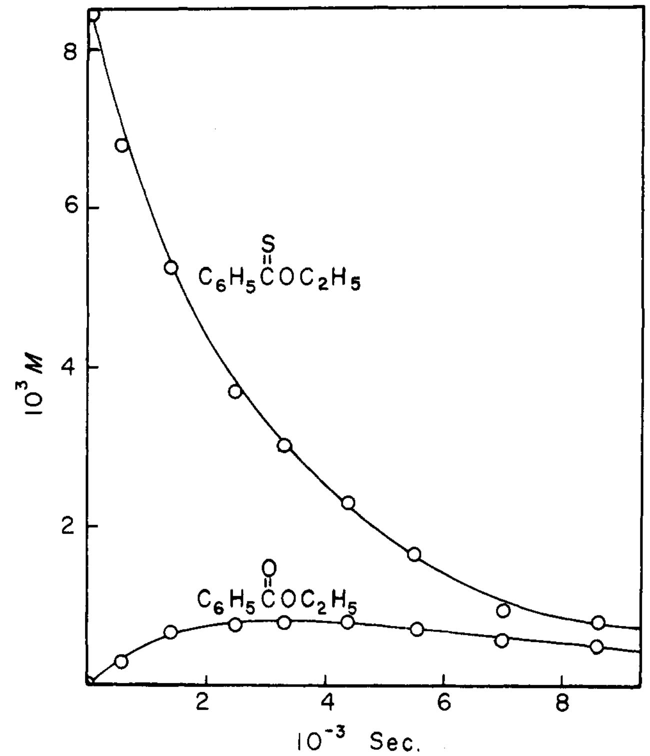


Fig. 1.—Plot of concentration *vs.* time for the reaction of 0.0085 *M* ethyl thionbenzoate with 0.0557 *M* sodium hydroxide in 40% acetone at 25.0°.

equation 2, these second-order rate constants are $(k_1 + k_2)$. The value of $(k_1 + k_2)$ used in further calculations was the average of the values from the four spectrophotometric runs at low base concentration.

TABLE I

RATE OF HYDROLYSIS OF 0.018 *M* ETHYL THIONBENZOATE IN THE PRESENCE OF 0.0592 *M* SODIUM HYDROXIDE IN 40% AQUEOUS ACETONE AT 25.0° BY ABSORBANCE AT 414 mμ

Time, 10^{-3} sec.	Absorbance	$10^3(k_1 + k_2)$, l./mole-sec.
0.36	0.880	
0.67	.834	6.58
1.11	.733	7.84
1.65	.638	8.10
2.24	.571	7.70
2.67	.522	7.81
3.08	.486	7.79
3.78	.431	7.93
86.4	.268	
	Average	7.7 ± 0.3

Rough values for $(k_1 + k_2)$ also may be calculated from the v.p.c. data. Although rate constants obtained this way are of lower precision, they are in good agreement with the values obtained spectrophotometrically (Table II).

Determination of Rate Constant k_3.—The second-order rate constant k_3 for the hydrolysis of ethyl benzoate was measured directly in a separate experiment using only this ester by titration of unchanged sodium hydroxide in aliquots withdrawn at appropriate times during the course of a run. The integrated second-order rate constants for this reaction are summarized in Table II.

Determination of Rate Constants k_1 and k_2.—The rate of formation of ethyl benzoate from ethyl thionbenzoate may be calculated from the total rate of disappearance of the thion ester, the rate of hydrolysis of ethyl benzoate, and the concentration of the two esters as a function of time, the ester concentration being determined by v.p.c.

TABLE II

SUMMARY OF RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ETHYL THIONBENZOATE AND ETHYL BENZOATE IN 40% AQUEOUS ACETONE AT 25.0°

Ester, 10^2 *M*	Sodium hydroxide, 10^2 *M*	$10^3(k_1 + k_2)$, l./mole-sec.
	Ethyl thionbenzoate[a]	
1.18	5.92	7.91
0.985	5.95	7.20
.383	8.29	7.33
.571	8.29	6.71
	20	6.9
	20	6.2
1.12	5.20	7.18[b]
0.85	5.57	6.77[b]
	Ethyl benzoate[c]	
		$10^3 k_3$, l./mole-sec.
1.40	5.25	5.65
1.97	4.97	5.57
1.85	4.97	5.66
2.52	8.02	5.21
1.69	2.66	5.36

[a] Determined spectrophotometrically. [b] Determined by v.p.c. [c] Determined by titration.

If *O* denotes the concentration of ethyl benzoate and *S* denotes the concentration of ethyl thionbenzoate, then for the reaction scheme that is given in equation 2

$$\frac{dS}{dt} = -(k_1 + k_2)(S)(\text{NaOH}) \tag{3}$$

$$\frac{dO}{dt} = k_2(S)(\text{NaOH}) - k_3(O)(\text{NaOH}) \tag{4}$$

Elimination of time by dividing equation 4 by equation 3 gives the following.

$$\frac{dO}{dS} = \frac{-k_2}{k_1 + k_2}\left[1 - \frac{k_3(O)}{k_2(S)}\right] \tag{5}$$

Integration of equation 5 and substitution of initial conditions, $S = S_0$ and $O =$ zero, gives equation 6, which relates k_2 to the known values of $(k_1 + k_2)$, k_3, and the concentrations of ethyl benzoate and ethyl thionbenzoate.

$$k_2 = \frac{\left[\frac{O}{S}\right](k_1 + k_2 - k_3(}{\left[\frac{S}{S_0}\right]^{\left[\frac{k_3 - k_1 - k_2}{(k_1 + k_2)}\right]} - 1} \tag{6}$$

Numerical evaluation of k_2 from equation 6 was done on an IBM 7090 computer, a value of k_2 being calculated for each pair of ester concentrations. The results obtained in a typical run are given in Table III.

The rate of hydrolysis of ethyl thionbenzoate to thiobenzoic acid and ethanol, k_1, was determined by difference from the rate constants $(k_1 + k_2)$ and k_2.

The average values of the rate constants k_1, k_2, and k_3 for the basic hydrolysis of ethyl thionbenzoate at 25.0 in 40% aqueous acetone are summarized in Table IV. The fit of the three rate constants to the data was independently checked by programming an

TABLE III

RATE OF HYDROLYSIS OF 0.00851 *M* ETHYL THIONBENZOATE TO ETHYL BENZOATE IN THE PRESENCE OF 0.0557 *M* SODIUM HYDROXIDE IN 40% AQUEOUS ACETONE AT 25.0° BY GAS CHROMATOGRAPHY

Time, 10^{-3} sec.	Ethyl thionbenzoate, 10^3 *M*	Ethyl benzoate, 10^4 *M*	10^3k_2, l./mole-sec.	10^3 $(k_1 + k_2)$, l./mole-sec.
0.59	6.78	2.75	1.27	
1.44	5.23	6.59	1.78	7.09
2.49	3.68	7.54	1.61	7.49
3.37	3.01	7.94	1.62	6.76
4.43	2.29	7.90	1.62	6.56
5.49	1.65	7.10	1.55	6.68
7.00	0.944	5.53	1.46	8.48
8.61	0.794	4.91	1.40	6.17
		Average	1.53 ± 0.14	7.1 ± 0.6

analog computer for the kinetic scheme given in equation 2 using the rate constants given in Table IV under the assumption that the reactions are pseudo-first order, a satisfactory fit to the data being obtained.

Acidic Hydrolysis.—The rate constants k_1, k_2, and k_3 were also evaluated for the acid-catalyzed hydrolysis in 40% aqueous acetone at 125.0°. However, because of rapid solvent decomposition under the reaction conditions, the constant $(k_1 + k_2)$ for the total rate of disappearance of ethyl thionbenzoate was evaluated only from the v.p.c. data. As a result, the data for the acid-catalyzed hydrolysis are of lower precision than those obtained under basic conditions. The constant k_3 for the hydrolysis of ethyl benzoate, however, was measured by the usual titration procedure. The rate constants are summarized in Table IV.

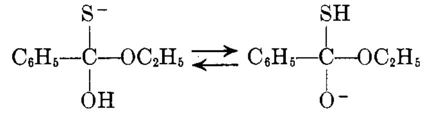
TABLE IV

SUMMARY OF RATE CONSTANTS FOR ESTER HYDROLYSIS IN 40% AQUEOUS ACETONE

Conditions	Temp., °C.	10^4k_1, l./mole-sec.	10^4k_2, l./mole-sec.	10^4k_3, l./mole-sec.
NaOH	25.0	57.2 ± 4.5	15.7 ± 1.2	54.9 ± 1.6
HCl	125.0	0.96 ± 0.56	5.3 ± 0.3	5.9 ± 0.9

Discussion

The present data indicate that under alkaline conditions in 40% aqueous acetone at 25.0° the initial hydrolysis product from ethyl thionbenzoate is 22% ethyl benzoate and 78% thiobenzoate and ethanol. Although compelling data are not yet available, it is convenient to discuss this product ratio in terms of the addition mechanism which has been demonstrated for hydrolysis of analogous oxygen esters.[7] On this basis reversible addition of hydroxide to the thiocarbonyl carbon would give rise to an intermediate which, after appropriate proton transfers, could lose bisulfide to form ethyl benzoate or lose ethoxide to form thiobenzoic acid. If this product ratio is determined by the partitioning of a neutral species then the present data indicates that ethoxide is a better leaving group than bisulfide by a factor of 3.6. However, to the extent that products may arise from species such as III and IV, the observed ratio k_1/k_2, is a measure of the relative loss of ethoxide and bisulfide only if anion III does not yield product. If product comes from a species like III, then the actual value for the ease of loss of ethoxide compared to bisulfide may be less than 3.6.



$$C_6H_5-\overset{S^-}{\underset{OH}{C}}-OC_2H_5 \rightleftarrows C_6H_5-\overset{SH}{\underset{O^-}{C}}-OC_2H_5$$

III IV

Under acidic conditions at 125.0° the fraction of the reaction proceeding by way of ethyl benzoate is significantly increased, 85% ethyl benzoate being produced. In acid the net rate of loss of sulfur is 5.5 times greater than the rate of loss of oxygen, the change from alkaline to acidic conditions producing an inversion of the relative rates of formation of ethyl benzoate and thiobenzoic acid. In contrast to the case of ethyl benzoate, where Bender[8] has suggested that a neutral adduct of water and the ester is involved under both acidic and alkaline conditions, this rate inversion suggests that the nature of the intermediate or intermediates involved in thion ester hydrolysis depends upon the acidity of the reaction medium. Just as in the case of alkaline hydrolysis, the interpretation of the values of k_1 and k_2 requires a knowledge of the nature and role of possible intermediates, a large number of which can be envisioned.

Another feature of the rate constants summarized in Table IV is that under alkaline conditions the rates of loss of ethoxide from ethyl thionbenzoate and from ethyl benzoate are the same, within experimental error. In acid, ethyl benzoate is hydrolyzed six times faster than ethyl thionbenzoate is converted to thiobenzoic acid. It is very likely that the similar reactivity of oxygen esters, thiol esters, and thion esters is the result of a balance between significant changes in the rates of formation of an intermediate and its partitioning between products and starting material. Experiments in progress should provide information on these points.

Experimental

Ethyl Thionbenzoate.—This compound was prepared in 21% yield from the corresponding imino ester by the method of Renson and Bidaine,[9] b.p. 101° (4.0 mm.); λ_{max} 414 mμ (ϵ 137 ± 1). Commercial **ethyl benzoate** was distilled at reduced pressure before use.

Solvent.—Deionized water was distilled before use. Acetone was dried as previously described.[10] To make the solvent, 400 ml. of acetone and 600 ml. of water were combined by use of a 200-ml. volumetric pipet at 25°.

Sodium Hydroxide.—For the kinetic runs in base, solid sodium hydroxide added to the solvent and the solution was standardized immediately with standard hydrochloric acid in 75% ethanol–water. Titrations were done in 90% acetone with bromphenol blue as indicator. The basic solution turns slightly yellow within a few hours at room temperature, but no change of titer is observed after 3 days.

Hydrochloric Acid.—For the kinetic runs in acid, a small amount of concentrated hydrochloric acid was added to the distilled water before the water and acetone were combined. The solvent was standardized with sodium methoxide which had been standardized against standard samples of potassium acid phthalate using phenolphthalein as the indicator. Other titrations were done in 90% acetone with bromphenol blue. The solvent is quite stable at room temperature but forms a noticeable yellow color in a few hours at 125°. However, no change in titer was observed after 24 hr. at 125°.

Kinetic Measurements.—All runs in basic solution were done in a 50-ml. volumetric flask in a thermostated water bath at

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[8] M. L. Bender, R. D. Ginger, and J. P. Unik, *J. Am. Chem. Soc.*, **80**, 1044 (1958).

[9] M. Renson and J. Bidaine, *Bull. soc. chim. Belges*, **70**, 519 (1961).

[10] S. G. Smith, A. H. Fainberg, and S. W. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

25.00 ± 0.02°. After the solvent had been equilibrated for at least 30 min., a weighed sample of ester was introduced.

Kinetic runs in acid were done in a sealed ampoule at 125.0– ± 0.1°.

Absorbance Measurements.—The hydrolysis of ethyl thionbenzoate in base was followed by measuring the absorbance of the reaction mixture at 414 mμ on a Beckman DU spectrophotometer equipped with a photomultiplier. An aliquot of the reaction mixture was withdrawn and its absorbance measured within 1 min. The time noted was the time at which the actual reading was made.

The absorbance of a solution of thiobenzoic acid under the reaction conditions was found to increase gradually over a period of several days. The absorbance of the reaction mixture showed a similar increase after the completion of the reaction. The amount of this increase was observed to be about 8% in the first 24 hr. The infinity readings for the kinetic runs were taken after 24 hr. Therefore, an 8% correction was made on all of the infinity readings.

Two determinations of the rate constant were made in 0.20 *M* sodium hydroxide using a Cary Model 14 spectrophotometer with a thermostated jacket held at 25.0°. At this base concentration the solvent begins to turn noticeably yellow after about 5 min.

Titrations.—The rate of hydrolysis of ethyl benzoate in base was determined by titrating unchanged base in aliquots withdrawn during the course of a run. The aliquot was added to a beaker containing about 25 ml. of pentane and 25 ml. of water containing almost enough acid to neutralize the remaining base. It was shown that use of this procedure stops the reaction completely. Cresol red was used as indicator

The runs in acid were done by a similar procedure, except that the formation of benzoic acid was followed by noting the increase in titer with time. Two of the runs in acid were done by plotting the titration curve for each aliquot on a Polared automatic titrimeter, Model AT-2A. The results of these determinations did not differ significantly from the determinations by direct titration.

Gas Chromatography.—The concentrations of ethyl benzoate and ethyl thionbenzoate were followed during the course of a reaction by gas chromatography. In the runs in base, an aliquot of the reaction mixtures was added to a mixture of about 25 ml. of pentane and 25 ml. of water, to which an aliquot of a standard solution of 2,4-dimethylacetophenone had been added as an internal standard. The pentane layer, containing the two esters and the internal standard, was concentrated to about 0.1 ml. and chromatographed on an Aerograph Hy-Fi gas chromatograph equipped with a hydrogen-flame detector. The column used was 20% Carbowax on Chromosorb W, 3 ft. long and 1/8 in. in diameter.

The same chromatographic procedure was followed for the determinations in acid solution, except that carbon disulfide was used instead of pentane, sodium bicarbonate was added to the water in order that the benzoic and thiobenzoic acids would not be extracted into the organic layer, and *m*-nitrotoluene was used as the internal standard.

Ion-Radicals. III.[1] The Isolation of a Hydroxythianthrene Oxide from Thianthrene Monoxide in Concentrated Sulfuric Acid

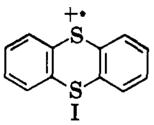
H. J. SHINE AND T. A. ROBINSON[2]

Department of Chemistry, Texas Technological College, Lubbock, Texas

Received May 20, 1963

A hydroxythianthrene oxide II has been isolated from the cyclohexane-insoluble, tan solid obtained by pouring solutions of thianthrene monoxide in 96% sulfuric acid onto ice. Reduction of this oxide by tin in acetic acid gave 2-hydroxythianthrene. The oxide II in 96% sulfuric acid undergoes reactions which are analogous to those of thianthrene oxide. That is, II is converted to an ion-radical whose electron spin resonance, ultraviolet, and visible spectra are similar to those obtained from 2-hydroxythianthrone in 96% sulfuric acid.

When thianthrene monoxide dissolves in concentrated sulfuric acid it undergoes, in part, a transformation to thianthrene.[3] This transformation is accompanied by a change in the color of the solution, from amber to purple. Similar color changes are observed with solutions of thianthrene *cis*-5,10-dioxide.[3] Further, somewhat related transformations occur when these two oxides are suspended in concentrated hydrochloric acid.[3,4] Recent investigations[5–7] have shown that these transformations are associated with the formation of a radical. It has been shown that this radical is the same as that obtained from solutions of thianthrene in sulfuric acid,[5,6,8] and from solutions of thianthrene containing aluminum chloride.[6] Solutions of the radical give rise to a symmetrical five-line e.s.r. spectrum, not only in sulfuric acid but also in hydrochloric acid.[9] This spectrum and other data have led to the proposal[6,8] that the solutions contain the ion-radical I.



I

It was shown in our earlier work[6] that, whereas the pouring of solutions of thianthrene in sulfuric acid onto ice gave only thianthrene and its monoxide as products, similar treatment with the monoxide gave thianthrene, the monoxide, and a tan solid. It was noted that the composition of the tan solid, although unknown, appeared to vary with the length of time the sulfuric acid solution was kept before pouring onto ice. The formation of both thianthrene and the tan solid and the shape of the e.s.r. spectrum obtained from a solution of the tan solid in sulfuric acid, led to the proposal[6] that the tan solid was a hydroxythianthrene oxide. The transfer-hydroxylation of one molecule of thianthrene oxide was proposed as a mode by which the reduction of a second, protonated, molecule of monoxide could occur.

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[1] (a) Part IV, H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, in press; (b) We are grateful for the generous support of parts of this work by the Robert A. Welch Foundation and the Directorate of Chemical Sciences, Air Force Office of Scientific Research (grant no. AF-AFOSR-23-63).

[2] Post-doctoral Fellow, 1961–1962.

[3] K. Fries and W. Vogt, *Ann.*, **381**, 312 (1911).

[4] K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

[5] A. Fava, P. B. Sogo, and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

[6] H. J. Shine and L. Piette, *ibid.*, **84**, 4798 (1962).

[7] H. J. Shine, C. F. Dais, and R. J. Small, *J. Chem. Phys.*, **38**, 569 (1963).

[8] W. C. Needler, Ph.D. thesis, University of Minnesota, August, 1961.

[9] C. F. Dais, unpublished experiments to be used as part of a Ph.D. thesis at Texas Technological College. In a subsequent contribution we shall deal in detail with the reactions of, and trapping of intermediates from, thianthrene monoxide in concentrated hydrochloric acid.