Inhibition by *p*-Benzoquinone.—Without excluding air, 20 ml. of a solution containing 0.05 mole of hypophosphorous acid was cooled to 13.8° and 0.0275 g. (0.00025 mole) of *p*-benzoquinone was dissolved in it by vigorous shaking. The solution was placed in B and 1.08 g. (0.005 mole) of *p*-tolyldiazonium hydrogen sulfate was put in A. The apparatus was assembled and placed in the constant temperature bath held at 13.8°. After five minutes the reactants were mixed and the gas produced measured as described previously.

Time, minutes	N_2 evolved,[21] %	Time, minutes	N_2 evolved,[21] %
30	0.0	108	1.5
60	.3	114	2.5
90	.4	120	3.5
96	.5	180	9.5
102	.8		

Summary

The hypophosphorous acid reduction of diazonium salts is catalyzed by traces of oxidizing agents and inhibited by small amounts of quinones. This, in conjunction with other facts, leads to the conclusion that the reduction of diazonium salts by hypophosphorous acid is a free radical chain reaction. A detailed mechanism is presented.

WEST LAFAYETTE, INDIANA RECEIVED SEPTEMBER 6, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Cleavage of the Carbon–Sulfur Bond. Rates of Hydrolysis of Some Alkyl Acetates and the Corresponding Thiolacetates in Aqueous Acetone

BY PAUL N. RYLANDER AND D. STANLEY TARBELL

This paper describes the results of a kinetic study of the hydrolysis of a series of thiolacetates and the corresponding oxygen esters in aqueous acetone, and is a continuation of work on the cleavage of the carbon–sulfur bond being carried out in this Laboratory.[1]

The only previous quantitative work on the hydrolysis of thiolesters is the recent research of Schaefgen[2] on the hydrolysis of ethyl thiolacetate in aqueous acetone. This medium was also used in the present study, because its solvent properties were satisfactory over the range of composition studied, and the measurements were not complicated by back-reactions or exchange reactions. The compounds investigated were the methyl, ethyl, isopropyl, isobutyl and *t*-butyl acetates, and the corresponding thiolacetates. The rates of hydrolysis were measured under basic conditions with sodium hydroxide, and under acidic conditions with hydrochloric acid as catalyst.

Experimental

Preparation of Materials.—Methyl, ethyl, isopropyl and isobutyl thiolacetate were prepared by dropping the appropriate mercaptan slowly into excess acetyl chloride. The resulting solution was diluted with ice, the layers separated, and the ester layer was washed with saturated sodium bicarbonate solution and with water. The thiolester was dried over Drierite, and fractionally distilled twice from anhydrous potassium carbonate through an efficient column. The center fraction which was collected each time boiled over a range of less than 1°. The observed properties are tabulated below.

ALKYL THIOLACETATES, CH_3COSR

R	B. p., °C., 760 mm.	$n^{22.5}D$	d^{30}_4
CH_3[a]	95–96	1.4661	1.0111
$(CH_3)_2CH$[b]	126–127	1.4502	0.9322
$(CH_3)_2CHCH_2$[c]	151–152	1.4555	.9291
$(CH_3)_3C$[d]	38 (14 mm.)	1.4490	.9290

[a] Wenzel and Reid, THIS JOURNAL, **59**, 1089 (1937), report b. p. 98° (760 mm.); $n^{25}D$ 1.4600; d^{25}_4 1.0170. [b] Ralston and Wilkinson, *ibid.*, **50**, 2160 (1928), report the b. p. as 122–123°. [c] The same b. p. is given by Ipatieff and Friedman, *ibid.*, 61, 71 (1939). [d] Rheinboldt, Mott and Motzkus, *J. prakt. Chem.*, **134**, 274 (1932), report the b. p. as 31–32° (11 mm.).

***t*-Butyl Thiolacetate.**—This compound was prepared in about 20% yield by the method described for *t*-butyl acetate.[3] The low yield was probably due to mechanical difficulties. The thiolester prepared by this method was used in the kinetic study.

The following modification of the above method gave quite satisfactory yields. Eighty-seven grams (1.10 moles) of dry pyridine was dissolved in 400 cc. of dry chloroform and the solution cooled in an ice-bath. To this was added 86 g. (1.10 moles) of acetyl chloride drop by drop with cooling and constant stirring. When done in this manner the resulting solution was nearly colorless. *t*-Butyl mercaptan (90.2 g., 1.00 mole) was added dropwise over several hours, and the solution allowed to warm spontaneously by standing overnight. Water was added, the layers separated and the chloroform layer washed with water, 10% sulfuric acid, saturated sodium bicarbonate, and again with water. It was dried over Drierite and anhydrous potassium carbonate, and fractionally distilled. The yield was 81% of material with a b. p. of 38° (14 mm.).[4]

The oxygen esters were dried over calcium chloride, then over Drierite, and were twice fractionally distilled through an efficient column from potassium carbonate, the center fraction being collected each time. The physical properties agreed well with those in the literature.

The acetone–water mixtures were made up by mixing the correct quantity of boiled distilled water and purified acetone. The acetone was purified by distillation from potassium permanganate, followed by drying the distillate over anhydrous potassium carbonate, and fractionation through an efficient column from potassium carbonate.

(1) Harnish and Tarbell, THIS JOURNAL, **70**, 4123 (1948).

(2) Schaefgen, *ibid.*, **70**, 1308 (1948).

(3) Hauser, *et al.*, "Organic Syntheses," Vol. 24, p. 19.

(4) The preparation of this compound, in unspecified yield, by the action of acetyl chloride on mercury *t*-butyl mercaptide, has been reported by Rheinboldt, Mott and Motzkus, *J. prakt. Chem.*, **134**, 274 (1932).

Alkaline Hydrolysis.—The basic solutions were made by weighing out appropriate quantities of distilled water, acetone and aqueous carbonate-free sodium hydroxide, and the strength of the mixture was determined by titration with 0.1 *N* hydrochloric acid. The thiolester (or ester) was weighed in a small wide-mouth container, and the reaction was begun by dropping this container into 100.00 ml. of the basic solution which had been brought to the desired temperature in a thermostat. The reaction was followed by withdrawing samples, stopping the reaction with excess standard acid and back-titrating with sodium hydroxide.[2]

Acid Hydrolysis.—The thiolester solutions were prepared and the reaction started by adding standard acidic aqueous acetone to a weighed quantity of the ester in a volumetric flask. The reaction was followed by direct titration of aliquots with 0.05–0.10 *N* sodium hydroxide.

With oxygen esters, the ester was weighed in a small wide-mouth stoppered container, and the reaction was begun by dropping this container into 100.00 ml. of standard acidic solution which had been brought to the desired temperature in a thermostat.

In all cases, appropriate corrections were made for the dilution of the acid (or base) by the ester.

Calculations.—The alkaline hydrolysis followed second-order kinetics, and proceeded according to the equation[2]

$$\underset{(a-x)}{CH_3COSR} + \underset{(b-2x)}{2OH^-} \longrightarrow \underset{(x)}{CH_3COO^-} + \underset{(x)}{RS^-} + H_2O$$

This equation assumes that the mercaptide ion is not appreciably hydrolyzed by water, which is true if the mercaptan is as strongly acidic as ethyl mercaptan.[5] The rate constants for alkaline hydrolysis were obtained therefore from the slope of the straight line resulting from a plot of log $((a - x)/(b - 2x))$ against time (see ref. 2, eq. 3).[6]

All rate constants were checked in several independent runs, and the published constants for ethyl thiolacetate[2] were checked.

Rate constants for the alkaline hydrolysis of oxygen esters were determined by plotting log $((a - x)/(b - x))$ against time. The acid-catalyzed hydrolysis of both oxygen and thiolesters followed pseudo first-order kinetics, and the rate constants were determined from a plot of log $(a - x)$ against time. Activation energies for all reactions were obtained from plots of log k *vs.* $1/T$, using three different temperatures. The $\log_{10} PZ$ factors were obtained using the collision theory equation for reaction rates, and E values from Arrhenius plots.

The activation energies (Table II) for alkaline hydrolysis of methyl, ethyl,[7] isopropyl and iso-

TABLE I

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ALKALINE HYDROLYSIS OF ALKYL ACETATES AND ALKYL THIOLACETATES IN AQUEOUS ACETONE SOLUTIONS

Wt. % acetone	Temp., °C.	Initial NaOH	Concn. (m./l.) ester	k, l./mole/min.	E, cal./mole	$\log_{10} PZ$
			Methyl thiolacetate			
43	0.0	0.0943	0.0348	0.605	12,200	9.50
43	10.0	.0580	.0227	1.32		
43	20.0	.0655	.0180	2.75		
62	0.0	.0603	.0250	0.466		
62	10.0	.0636	.0170	1.06	13,100	10.2
62	20.0	.0584	.0185	2.41		
			Isopropyl thiolacetate			
43	0.0	0.0588	0.0171	0.109	16,800	12.5
43	20.0	.0629	.0119	0.874		
43	30.0	.0391	.0126	2.42		
62	0.0	.0674	.1038	0.0868	17,600	13.0
62	20.0	.0664	.0176	0.818		
62	30.0	.0437	.01520	2.11		
			Isobutyl thiolacetate			
43	0.0	0.0681	0.0178	0.0825		
43	10.0	.0711	.0134	0.275	18,100	13.40
43	20.0	.0511	.0106	0.792		
43	30.0	.0603	.0137	2.24		
62	10.0	.0729	.0103	0.248	18,500	14.0
62	20.0	.0705	.0114	0.717		
62	30.0	.0632	.0180	2.12		
			t-Butyl thiolacetate			
43	0.0	0.0845	0.0204	0.0416	16,700	11.9
43	10.0	.0848	0.0187	.117		
43	30.0	.0391	.0109	.858	17,000	12.0
62	0.0	.0792	.0171	.0259		
62	10.0	.0809	.0205	.0753		
62	20.0	.0631	.0186	.222		
			Methyl acetate			
62	0.40	0.0446	0.0146	0.910		
62	10.8	.0244	.0083	2.08	12,200	9.7
62	19.9	.0191	.0107	3.96		
			Ethyl acetate			
62	0.6	0.0544	0.0161	0.405	12,000	9.2
62	10.9	.0481	.0148	0.908		
62	20.3	.0357	.0126	1.75		
			Isopropyl acetate			
62	0.30	0.0679	0.0133	0.0628		
62	10.40	.0761	.0136	0.1395	12,200	8.5
62	20.2	.0424	.0158	0.289		
			Isobutyl acetate			
62	0.30	0.0595	0.0149	0.147	12,400	9.1
62	9.70	.0605	.0110	.314		
62	20.0	.0568	.0108	.676		
			t-Butyl acetate			
62	30.0	0.0630	0.0219	0.0280	14,300	8.70
62	40.0	.0546	.0133	.0606		

(5) The acid dissociation constant for C_2H_5SH is reported to be 3×10^{-11} (Gordy and Stanford, THIS JOURNAL, **62**, 498 (1940)).

(6) The validity of this equation might be questioned for *t*-butyl mercaptan, because this might be such a weak acid that its salt would be largely hydrolyzed; the acid dissociation constant for *t*-butyl alcohol is estimated to be smaller than that of methanol by a factor of 10^3. However, calculations of the rate constants for *t*-butyl thiolacetate using the $(b - 2x)$ equation as above, and the usual $(b - x)$ equation, show that the ΔE values differ by a maximum of 2.7%, the latter being higher. The rate constants by the $(b - 2x)$ equation are higher by a maximum of 8%. Since the maximum possible difference in E by the two methods is small, and the necessity for the correction is not certain, the tabulated values have been obtained from the $(b - 2x)$ equation.

(7) In our work, E for the alkaline hydrolysis of ethyl acetate was found to be much higher than the value reported by Davies and Evans (*J. Chem. Soc.*, 339 (1940)). The values of these investigators have also been criticized by Smith and Steel, THIS JOURNAL, **63**, 3466 (1941). Some of the discussion by Schaefgen[2] was based on Davies' and Evans' data for ethyl acetate.

butyl acetates are very nearly the same, but the value for *t*-butyl acetate is considerably higher. This behavior closely parallels that for the hydrolysis of the corresponding benzoates.[8] The very slow rate for *t*-butyl acetate is obviously due to a combination of a high activation energy and a low log *PZ* factor.

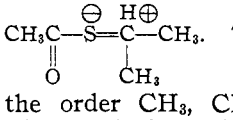
Table II shows that the activation energies for alkaline hydrolysis of the alkyl thiolacetates increase markedly as the series is ascended, having a spread of over 5,000 cal. This indicates that sulfur is able to transmit to the carbonyl carbon the electron-releasing inductive effects of the alkyl group more strongly than oxygen, a property of sulfur which is expected in view of the greater polarizability of the sulfur atom compared to

TABLE II

ACTIVATION ENERGIES FOR ALKALINE HYDROLYSIS IN 62% ACETONE

R	*E*, cal./mole	log₁₀ *PZ*
A. Of Thiolesters, CH_3COSR		
CH_3	13,100	10.2
C_2H_5[2]	14,400	10.9
$(CH_3)_2CH$	17,600	13.0
$(CH_3)_2CHCH_2$	18,500	14.0
$(CH_3)_3C$	17,000	12.0
B. Of Esters, CH_3COOR		
CH_3	12,200	9.7
C_2H_5	12,000	9.2
$(CH_3)_2CH$	12,200	8.5
$(CH_3)_2CHCH_2$	12,400	9.1
$(CH_3)_3C$	14,300	8.7

oxygen. It is possible that sulfur can also increase the electron density at the carbonyl carbon by a hyperconjugative mechanism[9] through contributions from resonance forms such as

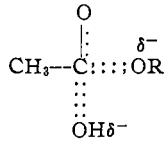


This effect would *decrease* in the order CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, whereas the inductive effect would *increase* in the same order. The observed values of *E* for R = $CH(CH_3)_2$ and $C(CH_3)_3$ might be due to the fact that, in the former, the result of the inductive plus the hyperconjugative effect is greater in raising *E* than the inductive effect alone in the *t*-butyl compound. The high value of *E* for the isobutyl compound on this basis would be ascribed to a large contribution from the hyperconjugative effect in addition to the inductive effect.[10]

Methyl and ethyl acetates hydrolyze faster than the corresponding thiolesters, due to lower activation energies for the former compounds. However, isopropyl and *t*-butyl acetates hydrolyze more slowly than the corresponding thiolesters in spite of a favorable activation energy. The rapid rate of hydrolysis of the thiolesters is due to a high log *PZ* factor compared to the oxygen esters; since the entropy of activation (in the transition state theory of reaction rates) is proportional to log *PZ* the fact that the log *PZ* term for the thiolesters is larger than for the oxygen esters means that the oxygen esters have a less positive entropy of activation than the thiolesters. This means that in entering the transition state the oxygen esters lose more degrees of freedom, *i.e.*, form a more rigid, exactly oriented structure, relative to the original compound, than the thiolesters do.

This effect may be due to several factors. Since sulfur is a larger atom than oxygen, the groups around it would not need to be as exactly oriented in the transition state, and hence its entropy change would be more positive than that of the oxygen esters. If, as suggested,[2] the oxygen esters are hydrated in the transition state and the thiolesters are not, this factor would reinforce the one mentioned above.

Another possible explanation is based on the suggestion of Dewar[11] that the transition state during the hydrolysis of an ester may be planar, the alkoxyl and hydroxyl groups being linked by partial double bonds to the central carbon atom and not by partial single bonds as in a normal replacement.



Such a structure must be very rigid and its formation would involve a considerable decrease in entropy. With thiolesters, on the other hand, the contribution of the resonance hybrid with sulfur double bonded to the carbon would be expected to be small[12]; sulfur would then be linked to carbon by a single bond in the transition state and the structure would be less rigid. This idea, incidentally, might account for the higher activation energies of thiolesters, since the transition state would have less resonance energy relative to the normal state than the transition state for esters.

Acid Hydrolysis.—In both the thiolesters and oxygen esters the activation energies for acid hydrolysis are greater than those for alkaline hydrolysis, as is generally the case. Here, as in the alkaline hydrolysis, the activation energies for the esters (*t*-butyl acetate is exceptional and

(8) Tommila, *Ann. Acad. Sci. Fennicae*, Ser. A, 57, No. 13, 3-24 (1941); *C. A.*, **38**, 6172 (1944).

(9) For an excellent review of hyperconjugation, see Crawford, *Quarterly Rev.*, **3**, 226 (1949).

(10) This discussion is based on the assumption that the change in activation energy is determined chiefly by electronic displacements.

(11) Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, 1949, p. 118.

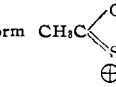
(12) Electron diffraction measurements show that in thiolacetic acid there is little shortening of the C–S bond distance, and hence little contribution from the resonance form  (Gordy, *J. Chem. Phys.*, **14**, 560 (1946)).

TABLE III

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ACID-CATALYZED HYDROLYSIS OF ALKYL ACETATES AND ALKYL THIOLACETATES IN AQUEOUS ACETONE SOLUTIONS

Wt. % acetone	Temp., °C.	Initial HCl	Concn. (m./l.) ester	$k \times 10^4$, min.$^{-1}$	E, cal./mole	log$_{10}$ PZ
			Methyl thiolacetate			
43	30.0	0.1938	0.1059	3.49	16,600	8.60
43	40.0	.1200	.0985	8.95		
62	30.0	.1938	.1026	1.94	17,100	8.60
62	40.0	.1334	.1113	4.82		
			Isopropyl thiolacetate			
43	30.0	0.1132	0.0824	1.84	19,000	10.1
43	40.6	.1250	.0768	5.40		
62	30.0	.1938	.0701	1.096	19,700	10.2
62	40.0	.1272	.0807	3.13		
			Isobutyl thiolacetate			
43	30.0	0.1136	0.0573	1.42	19,900	10.4
43	40.6	.1250	.0738	4.30		
62	30.0	.1938	.0713	0.996	20,500	10.7
62	40.6	.1137	.0706	3.19		
			t-Butyl thiolacetate			
43	30.0	0.1664	0.0640	1.29	20,200	10.6
43	40.0	.1341	.0827	3.76		
62	30.0	.1791	.0688	0.823	20,700	10.8
62	40.6	.1587	.0845	2.64		
			Methyl acetate			
62	30.1	0.1057	0.1136	52.0	15,700	9.00
62	40.1	.0834	.1012	120.0		
			Ethyl acetate			
62	30.1	0.1056	0.1057	42.6	16,000	9.10
62	40.0	.0871	.1042	98.5		
			Isopropyl acetate			
62	30.1	0.1011	0.0677	20.0	16,300	9.00
62	40.0	.0883	.0845	47.1		
			Isobutyl acetate			
62	30.1	0.1057	0.0707	30.9	16,050	9.00
62	40.0	.0894	.0999	71.6		
			t-Butyl acetate			
62	30.1	0.1011	0.0488	8.00	23,200	13.6
62	40.0	.0895	.0967	27.0		

will be considered later) are essentially constant over the series, while the activation energies for the thiolesters increase markedly as the series is ascended. The lower activation energies for the oxygen esters may be attributed to the importance of the resonance form $CH_3C(O^{\ominus})=O^{\oplus}-R'$ compared to the thiolesters: this makes the carbonyl oxygen more basic and favors attack by a proton.

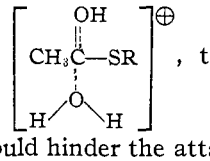
The increase in E for the thiolesters as the alkyl group becomes more branched is probably due to increased electron density at the carbonyl carbon from the inductive and/or hyperconjugative effect. If the transition state is that suggested by Schaefgen,[2]  , this higher electron density would hinder the attack of the water molecule at the carbonyl carbon, and hence raise E. As in the alkaline hydrolysis, the oxygen esters do not appear to transmit the inductive effect of the alkyl groups.

TABLE IV

ACTIVATION ENERGIES FOR ACID HYDROLYSIS IN 62% ACETONE

R	E, cal./mole	log$_{10}$ PZ
A. Of Thiolesters, CH_3COSR		
CH_3	17,100	8.6
C_2H_5[2]	18,000	9.0
$(CH_3)_2CH$	19,700	10.2
$(CH_3)_2CHCH_2$	20,500	10.7
$(CH_3)_3C$	20,700	10.8
B. Of Esters, CH_3COOR		
CH_3	15,700	9.0
C_2H_5	16,000	9.1
$(CH_3)_2CH$	16,300	9.0
$(CH_3)_2CHCH_2$	16,050	9.0
$(CH_3)_3C$	23,200	13.6

In all cases the ester hydrolyzes more rapidly than the corresponding thiolester. This is due almost entirely to the lower activation energy of the former, as the log PZ factors parallel each other rather closely in the two series.

The data for the acid hydrolysis of t-butyl acetate are interesting. It was shown by Skrabal and Hugetz[13] that in dilute alcohol t-butyl acetate hydrolyzes faster than methyl acetate. This was interpreted by Cohen and Schneider,[14] as an indication that t-butyl acetate hydrolyzed by cleavage of the oxygen–alkyl bond. The mechanism they suggested is

$$CH_3-\overset{OH^+}{\overset{\|}{C}}-O-C(CH_3)_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + \overset{+}{C}(CH_3)_3$$

$$^{+}C(CH_3)_3 + H_2O \longrightarrow HOC(CH_3)_3 + H^+$$

When the hydrolysis is carried out in dilute acetone, t-butyl acetate reacts more slowly than any of the other esters. Hence, a comparison of the rate constants alone provides no suggestion that t-butyl acetate might be hydrolyzing by a mechanism different from the rest of the series. However, inspection of Table II shows that t-butyl acetate has both an abnormally high activation energy and an abnormally high log PZ factor. One would expect, by analogy to the trend observed during alkaline hydrolysis, that the activation energy should be the order of 18,000–19,000 cal.; the measured value is 23,200 cal. This value and the high log PZ factor are in

(13) Skrabal and Hugetz, *Monatsh.*, **47**, 17 (1926).

(14) Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

accord with the mechanism written above. The catalyzing hydrogen atom coördinates with the unhindered carbonyl oxygen, and water does not attack the *t*-butylcarbonium ion until it is free from the steric effects of the adjacent carboxyl group.

In sharp contrast to the behavior of *t*-butyl acetate, acid catalyzed hydrolysis of *t*-butyl thiolacetate proceeds entirely by cleavage between the sulfur atom and the carbonyl group. If cleavage occurred between the alkyl group and the sulfur atom, the products would be *t*-butyl alcohol and thiolacetic acid, which would subsequently hydrolyze to acetic acid and hydrogen sulfide. An acid-catalyzed hydrolysis was carried out in an apparatus designed to detect any trace of hydrogen sulfide, but no evidence for its formation was obtained.

This difference in the mechanisms is undoubtedly due to the higher electronegativity of the oxygen, which would favor the formation of the *t*-butylcarbonium ion. Cleavage can, however, occur between the alkyl group and the sulfur atom of thiolesters if the carbonium ion formed is sufficiently stable; Iskander[15] has shown that acid catalyzed hydrolysis of triphenylmethyl thiolbenzoate results in the formation of thiolbenzoic acid and triphenylcarbinol.

In all cases, an increase in the water content of the medium decreases the activation energy of the reaction, which is to be expected, because a higher dielectric constant of the medium favors the addition to the carbonyl carbon of the ester.

Acknowledgment.—We are indebted to Dr. Seymour L. Friess for an interesting discussion.

Summary

The rates of acid and alkaline hydrolysis of methyl, isopropyl, isobutyl and *t*-butyl thiolacetates have been measured in aqueous acetone. Rates for the corresponding oxygen esters have been determined under comparable conditions, and the activation energies and *PZ* terms have been obtained. The results for the two series have been compared and discussed.

(15) Iskander, *Nature*, **155**, 141 (1945).

ROCHESTER, N. Y. RECEIVED AUGUST 12, 1949

[CONTRIBUTION FROM THE SYPHILIS EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, AND THE SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Disproportionation of Aromatic Stiboso Compounds. II. Methods of Synthesis

BY G. O. DOAK AND H. H. JAFFÉ

Stibosobenzene has been prepared previously from benzenestibonic acid by reduction with sulfur dioxide and hydriodic acid, followed by alkaline hydrolysis, without isolation of the intermediate phenyldichlorostibine.[1] We have shown that the product obtained by this procedure contains traces of impurities which affect markedly the rate of disproportionation to bis-(diarylantimony) oxide and antimony trioxide.[2] Similar results have also been obtained with several substituted arylstiboso compounds.

Unfortunately, no suitable method for the purification of these compounds has been found. Since they are insoluble in solvents other than acids and are thermally unstable, recrystallization and sublimation have not been accomplished. Purification by reprecipitation from acid solution has been used previously,[1] but in this Laboratory this method was found to effect only a crude separation of impurities. In the hope that hydrolysis of an aryldichlorostibine, after isolation and recrystallization, might yield a pure stiboso compound, we prepared *p*-tolyldichlorostibine using a known procedure.[3] This compound was recrystallized repeatedly from carbon tetrachloride and finally hydrolyzed to *p*-stibosotoluene. When disproportionation at elevated temperatures of duplicate preparations of this compound gave a reproducible rate constant, the study was extended to other aryldichlorostibines.

Previous methods for the preparation of these compounds, which include reduction of the corresponding arylstibonic acids[1,3,4] and the action of hydrochloric acid on the corresponding stiboso compounds,[1] have been reinvestigated and improved. The experimental difficulties encountered were found to vary widely with the substituent involved. *p*-Bromophenyl-, *p*-acetylphenyl- and *p*-tolyldichlorostibines, the least soluble of the compounds obtained, were synthesized and recrystallized without difficulty. In contrast to the para compound, *m*-tolyldichlorostibine possessed physical properties which rendered its isolation and purification extremely difficult. Different preparations of this compound showed variable melting points which were unaffected by recrystallization. Similar difficulties were encountered with the *p*-phenetyl derivative. The remaining compounds decomposed in the crude state at room temperature so that it was necessary to recrystallize rapidly from cold solvents in order to obtain pure compounds. The procedures finally adopted as most satis-

(1) Schmidt, *Ann.*, **421**, 174 (1920).

(2) Jaffé and Doak, THIS JOURNAL, **71**, 602 (1949).

(3) Clark, *J. Chem. Soc.*, 1826 (1932).

(4) (a) German Patent 268,451; (b) Campbell, *J. Chem. Soc.*, **4**, (1947); (c) Blicke and Oakdale, THIS JOURNAL, **55**, 1198 (1933).