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).

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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).

TABLE I

ARYLDICHLOROSTIBINES

Dichlorostibine	Method of prepn.	Yield,[a] %	M. p.,[b] °C.	Formula	Sb analyses,[c] % Calcd.	Found	Cl analyses,[c,d] % Calcd.	Found
Phenyl-[e]	A	35	60	$C_6H_5Cl_2Sb$	45.14	45.09	26.29	26.43
	B	25						
p-Tolyl-[f,g]	A	34	94.5	$C_7H_7Cl_2Sb$	42.91	43.00	24.99	24.98
m-Tolyl	A	16.5	51[h]	$C_7H_7Cl_2Sb$	42.91	42.98	24.99	24.85
p-Chlorophenyl-[i]	A	28	74	$C_6H_4Cl_3Sb$	40.02	40.08	34.95	34.83
	B	45						
p-Bromophenyl-[j]	A	31	90	$C_6H_4BrCl_2Sb$	34.92	34.91	20.33	20.27
p-Ethylphenyl-	A	6	43	$C_8H_9Cl_2Sb$	40.88	40.51	23.81	23.35
p-Acetylphenyl-	A	24	141	$C_8H_7Cl_2OSb$	39.05	38.51	22.74	22.46
p-Nitrophenyl-	B	42	95	$C_6H_4Cl_2NO_2Sb$	38.68	38.83	22.53	22.58

[a] Yields are calculated for pure compounds (three recrystallizations) on the basis of aromatic amine. [b] Melting points were taken on a Fisher melting point block. The thermometer was calibrated against U.S.P. melting point reference standards, *cf.* Rosin, *J. Am. Pharm. Assoc., Sci. Ed.*, **35**, 56 (1946). [c] All analyses are the average of two or more determinations. [d] Chlorine was determined as ionizable chloride, or by the method of Willard and Thompson, THIS JOURNAL, **52**, 1893 (1930). [e] Previously reported by Schmidt ref. 1 and others. [f] Previously reported by Clark ref. 3 and others. [g] Mol. wt. Calcd.: 283.66. Found: 264. [h] The m. p. of this compound varied between 43 and 51° with different preparations and was unaffected by recrystallization. [i] Mol. wt. Calcd.: 304.24. Found: 295. [j] Previously prepared by Blicke and Oakdale ref. 4c.

factory are given in the experimental part and the compounds prepared are listed in Table I. The molecular weights of *p*-tolyl- and *p*-chlorophenyldichlorostibines in benzene were determined by cryoscopic measurements. The results obtained showed these two compounds to be monomolecular.

The arylstiboso compounds listed in Table II were obtained by hydrolysis of the dichlorostibines with aqueous sodium hydroxide at 0°. Other alkaline hydrolytic agents did not yield analytically pure products. The physical properties of the arylstiboso compounds preclude the use of the customary criteria of purity, such as melting point, refractive index, etc. Since analyses do not reveal the traces of impurities which catalyze the disproportionation, the reproducibility of the rate of this reaction was taken to indicate absence of these impurities. The *m*-tolyl and *p*-ethylphenyl derivatives failed to give reproducible rate constants. The remaining stiboso compounds were used for the kinetic study,

TABLE II

ARYLSTIBOSO COMPOUNDS

Compound R = Stiboso	Formula	Sb analyses,[a] % Calcd.	Found
R-Benzene[b]	C_6H_5OSb	56.67	56.50
p-R-Toluene[c]	C_7H_7OSb	53.20	53.31
m-R-Toluene	C_7H_7OSb	53.20	53.32
p-Ethyl-R-benzene	C_8H_9OSb	50.13	50.12
p-Chloro-R-benzene	C_6H_4ClOSb	48.84	48.80
m-Chloro-R-benzene[d]	C_6H_4ClOSb	48.84	48.85
p-Bromo-R-benzene[e]	C_6H_4BrOSb	41.45	41.46
p-Nitro-R-benzene	$C_6H_4NO_3Sb$	46.86	46.60
p-R-Acetophenone	$C_8H_7O_2Sb$	47.40	47.30

[a] All analyses are the average of two or more determinations. [b] Previously reported by Schmidt, ref. 1, and by Hasenbäumer, *Ber.*, **31**, 2910 (1898). [c] Previously reported by Hasenbäumer, *loc. cit.* [d] Previously reported by Pfeiffer and Schmidt, *J. prakt. Chem.*, **152**, 27 (1939). [e] Previously reported by Blicke and Oakdale (ref. 4c) without analyses.

the results of which are reported in the following paper.[5]

Experimental

Preparation of Aryldichlorostibines: Method A.—The following procedure is similar to Campbell's method[4b] for the preparation of *p*-cyanophenyldichlorostibine, but differs in several important details. A diazo solution, prepared from 0.6 mole of the aromatic amine in 150 ml. of concentrated hydrochloric acid and 300 g. of ice, was added dropwise to a stirred solution of 0.6 mole of antimony trichloride in 450 ml. of concentrated hydrochloric acid maintained between −15 and −20°. The heavy precipitate of diazonium chloroantimonate(III) was removed by filtration and washed with 500 ml. of alcohol previously cooled in a deep-freeze. The moist salt was decomposed by suspending it in 1 liter of absolute alcohol which contained 10 g. of cuprous bromide; the mixture was stirred mechanically to facilitate the evolution of nitrogen. The application of heat was necessary only when *p*-anisidine was used. When the reaction was complete the solution was added, with stirring, to 6 liters of water to precipitate the crude stibonic acid. This was collected on a large Buechner funnel, thoroughly washed with water, and air dried.[6]

The crude acid was treated with 100 to 200 ml. of concentrated hydrochloric acid.[7] In each case a minimum amount of hydrochloric acid was used since the dichlorostibines were usually quite soluble in this solvent. The reaction mixture, cooled to −20° and stirred, was treated dropwise with a 5 molar solution of stannous chloride in hydrochloric acid until precipitation of the dichlorostibine was complete. The crystalline product was collected on a sintered glass filter which was surrounded with Dry Ice–alcohol and equipped with a drying tube to exclude atmospheric moisture. The product was washed with small quantities of cold concentrated hydrochloric acid and then dissolved in a minimum amount of chloroform. The residual hydrochloric acid was quickly separated in a separatory funnel and the chloroform layer was filtered through paper into a flask surrounded by a cooling bath. A maxi-

(5) Jaffé and Doak, THIS JOURNAL, **72**, 3027 (1950).

(6) Miss Campbell has stated that complete drying of *p*-cyanobenzenestibonic acid reduced its solubility in hydrochloric acid. With the compounds reported in the present paper, we have not observed this effect.

(7) Depending on the solubility of the arylantimony tetrachloride formed, the reaction mixture at this stage was either a suspension or a solution. Where solutions were obtained (*e. g.*, benzene-, *m*- and *p*-toluenestibonic acid), a small amount of dark gummy material was removed by filtration.

mum yield of crystalline dichlorostibine was obtained by further cooling, first in a deep-freeze and finally in a Dry Ice–alcohol-bath. The compound was recrystallized repeatedly from chloroform by dissolving it at room temperature and cooling the solution in a Dry Ice-bath.

The compounds prepared by the above procedure are so indicated in Table I. On reduction, the *p*-methoxybenzenestibonic acid yielded a crystalline product which was probably the dichlorostibine. Attempts at recrystallization invariably resulted in decomposition. No crystalline product was obtained using *m*-bromo-, *m*-chloro-, *m*-carboxy- and *m*-ethoxybenzenestibonic acids.

We have also used the same procedure to reduce stibonic acids previously purified through the pyridinium arylchloroantimonates(V).[8] No advantage over the simpler procedure was found.

Method B.—Schmidt prepared phenyldichlorostibine in small yield by treating an acetic acid solution of stibosobenzene with 5 *N* hydrochloric acid.[1] The following modification has resulted in a substantial increase in yield. Either the crude stibonic acid obtained as an intermediate in method A or a purified stibonic acid[8] was reduced with sulfur dioxide and hydriodic acid as described previously.[2]

The resulting impure stiboso compound was suspended in a minimum amount of chloroform, cooled in a Dry Ice-bath, and treated with a slow stream of dry hydrogen chloride. The amorphous solid was rapidly converted to crystalline dichlorostibine, which was collected on a sintered glass filter cooled with Dry Ice. Recrystallization was achieved as described under method A.

This procedure is technically more difficult than method A, but it probably has a wider range of application. It is of particular value with stibonic acids containing groups which are themselves reduced by stannous chloride, *e. g.*, *p*-nitrobenzenestibonic acid.

***m*-Chlorophenyldichlorostibine.**—A number of attempts have been made to obtain this compound. The difficulties encountered were apparently associated with a low melting point and extreme solubility. Both crude and purified *m*-chlorobenzenstibonic acid, as well as a sample recrystallized from benzene, were reduced by method A, but no dichlorostibine was isolated in any case. Similar results were obtained in the reduction of a crude stibonic acid with sulfur dioxide, following the procedure of Blicke and Oakdale.[4c] Method B yielded a crystalline solid which rapidly changed to an oil when removed from the cold filter. All attempts to recrystallize this oil have been unsuccessful. Analysis of the product without recrystallization gave values which approached the theoretical (Calcd. for $C_6H_4Cl_3Sb$: Sb, 40.02. Found: Sb, 39.46). Hydrolysis of this product also yielded analytically pure *m*-chlorostibosobenzene.

***m*-Chlorophenyldiiodostibine.**—Crude *m*-chlorostibosobenzene (45 g.) was dissolved in 100 ml. of concentrated hydrochloric acid; the solution was cooled to 0°, and a saturated aqueous solution of potassium iodide was added. The yellow diiodostibine which precipitated was washed with cold water to remove sodium chloride, dried *in vacuo* for three hours, and finally recrystallized several times from chloroform; m. p. 67–68°.

Anal. Calcd. for $C_6H_4ClI_2Sb$: Sb, 25.00; I, 52.10. Found: Sb, 25.02; I, 52.07.

Stiboso Compounds.—A solution of the dichlorostibine in cold absolute alcohol (0.2 mole in 200 ml.) was added dropwise with stirring to a solution of 18 g. of sodium hydroxide in 4 liters of ice and water. The stiboso compound which precipitated was washed with water on a large Buechner funnel until free from chlorides. It was then washed successively with cold alcohol and cold ether and finally dried *in vacuo*. With the exception of *m*-stibosotoluene the yields in each case exceeded 90%. The stiboso compounds prepared are listed in Table II.

Acknowledgments.—*p*-Aminoethylbenzene was obtained through the courtesy of Dr. Arthur Roe and Dr. R. L. McKee, Department of Chemistry, University of North Carolina. The authors also wish to acknowledge the assistance of Miss Marjorie L. Chapman in performing the analyses.

Summary

Improved methods for the synthesis of aryldichlorostibines have been developed. Eight aryldichlorostibines and one diiodostibine have been prepared. The corresponding stiboso compounds were prepared by hydrolysis with aqueous sodium hydroxide.

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(8) Doak and Steinmann, THIS JOURNAL, **68**, 1987 (1946).

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The Disproportionation of Aromatic Stiboso Compounds. III. Effect of Structure[1]

BY H. H. JAFFÉ AND G. O. DOAK

It has long been known that a variation in structure produces a marked effect on the stability of metallo-organic compounds. This received formal recognition by Kharasch and coworkers,[2] who, in studying the effect of structure on the acid cleavage of unsymmetrical organic mercury compounds, established an "electronegativity scale" for a large number of aliphatic and aromatic radicals. The stability of various metallo-organic compounds was predicted on the basis of this scale.[3] Unfortunately this work was based on competitive reactions, a technique which is open to considerable criticism,[4] and which necessarily yields only qualitative comparisons. Further, a scale of this type will have general application only to series of reactions having a constant entropy of activation. Such constancy has never been demonstrated for series containing aliphatic and ortho-substituted aromatic radicals.[5]

(1) Paper presented in part before the Division of Physical and Inorganic Chemistry at the 113th meeting of the American Chemical Society, Chicago, April, 1948.

(2) Kharasch, *et al.*, *J. Org. Chem.*, **3**, 347, 405, 409 (1939); THIS JOURNAL, **54**, 674 (1932), and earlier papers.

(3) Kharasch and Isbell, *ibid.*, **53**, 2701 (1931); Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

(4) Adkins, in Gilman, "Organic Chemistry," John Wiley & Sons, New York, N. Y., 1943, p. 1074.

(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 194.