[Contribution from the Department of Chemistry, University of Vermont]

TRIPHENYLMETHYL ARYL SULFIDES. II. OXIDATION WITH BROMINE IN AQUEOUS ACETIC ACID

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Earlier reports in the literature on the preparation of certain triphenylmethyl aryl sulfides (1–5) have indicated very few positive attempts to identify or characterize these compounds. A positive identification of these sulfides by hydrogenolysis using Raney nickel was reported in the first paper of this series (6). An attempt to characterize the sulfides by using mercuric chloride resulted in cleavage of the molecules (6).

Further studies to substantiate the identity of these sulfides have been made by using a method comparable to the procedure suggested by Siggia and Edsberg (7) for the determination of alkyl sulfides and disulfides. Briefly, the method consists of titration of the sulfide with a bromate-bromide solution. The sulfides used by Siggia and Edsberg were oxidized quantitatively to the corresponding sulfoxides. Disulfides were oxidized to the corresponding sulfonyl bromides. Alkyl thiols were oxidized through the disulfides to the alkylsulfonyl bromides. The present authors have oxidized thiophenol and the isomeric thiocresols by using the same titration procedure. These aryl thiols also consumed three moles of bromine per mole of thiol:

$$2\mathrm{ArSH} + \mathrm{Br_2} \rightarrow \mathrm{ArSSAr} \xrightarrow[\mathrm{HOH}]{5\mathrm{Br_2}} 2\,\mathrm{ArSO_2Br}$$

Similar oxidations of the triphenylmethyl aryl sulfides produced triphenylcarbinol and the corresponding arylsulfonyl bromides. The latter were characterized as the arylsulfonamides. The sulfides, in glacial acetic acid containing a small quantity of conc'd hydrochloric acid, were titrated with a 0.1 *N* bromate-bromide solution. The oxidations were rapid and nearly quantitative. Three moles of bromine were consumed per mole of sulfide oxidized.

$$\underset{\mathrm{I}}{(\mathrm{C_6H_5})_3\mathrm{CSC_6H_5}} + 3\mathrm{Br_2} \xrightarrow{\mathrm{HOH}} (\mathrm{C_6H_5})_3\mathrm{COH} + \mathrm{C_6H_5SO_2Br}$$

By investigating the behavior of phenyl triphenylmethyl sulfide (I) in the initial reaction mixture, it was found that I was cleaved before the addition of the bromate-bromide solution. After pouring the acidic solution into a relatively large volume of water, an appreciable quantity of triphenylcarbinol was isolated. Thiophenol was obtained and characterized as carboxymethyl phenyl sulfide. A typical run using one gram of I indicated that at least 50% of I had been cleaved.

Since a probable initial step in the oxidation of the sulfides appeared to be the oxidation of the aryl thiol that was present as the cleavage product of the sulfide, the corresponding disulfide was isolated as an intermediate. An incomplete oxidation of Compound I was carried out by using one-third of the theoretical amount of bromate-bromide solution required for complete oxidation. A significant quantity of diphenyl disulfide was obtained. The yield of triphenylcarbinol was 89%, based on complete cleavage of the sulfide and any sulfoxide. *p,p'*-Ditolyl disulfide was shown to be an intermediate in the oxidation of *p*-tolyl triphenylmethyl sulfide.

The experimental evidence indicated that the main initial step in the oxidation of the triphenylmethyl aryl sulfides was not the production of an unstable sulfoxide. A small amount of sulfoxide may have been produced; however, none of the probable cleavage products, the sulfenic acids, was detected.

TABLE I

TITRATION OF TRIPHENYLMETHYL ARYL SULFIDES, $(C_6H_5)_3CSAr$, WITH 0.1 *N* BROMATE-BROMIDE SOLUTION[a]

AR	SAMPLE WT., G.	ML. OF BROMATE-BROMIDE SOLUTION (CORRECTED)	% OF COMPOUND TITRATED
Phenyl	0.2028	33.1	95.7
Phenyl	.2068	34.1	96.4
o-Tolyl	.3754	60.1	97.6
o-Tolyl	.1875	29.9	97.1
m-Tolyl	.2212	34.8	95.8
p-Tolyl	.2277	36.0	96.4
TITRATION OF ARYL THIOLS (ArSH)[a]			
Thiophenol	.0663	34.4	95.0
m-Thiocresol	.0746	33.4	92.2
p-Thiocresol	.0845	38.9	95.0

[a] Each sample was in 80 ml. of glacial acetic acid and 6 ml. of conc'd hydrochloric acid at 80°.

EXPERIMENTAL

All organic reagents used, except common solvents, were Eastman Kodak best grade chemicals. Temperatures are uncorrected.

Preparation of the triphenylmethyl aryl sulfides. The sulfides were prepared by using the procedures reported previously (6).

Titrations of the triphenylmethyl aryl sulfides. The procedure employed was similar to the method described by Siggia and Edsberg (7). The 0.1 *N* bromate-bromide solution was prepared as indicated by them. A sample of 0.0005–0.0007 mole of the sulfide was dissolved in 80 ml. of glacial acetic acid by warming the solution to 80°. After addition of 6 ml. of conc'd hydrochloric acid, the solution was titrated immediately with 0.1 *N* bromate-bromide solution. The end point was the appearance of the first permanent coloration due to elemental bromine. Blank titrations were run and the appropriate corrections made. Addition of the conc'd hydrochloric acid to the sulfide in glacial acetic acid, before starting the titration, produced a distinct yellow coloration, due to the formation of triphenylmethyl cations. This yellow coloration disappeared before the end point of the titration was reached. At temperatures between 60° and 80° the titrations were rapid and the end points reasonably distinct and reproducible. The results of a few representative titrations are indicated in Table I. The determinations were comparable quantitatively to the titration of diphenyl disulfide (7).

Titrations of the aryl thiols. The procedure used in the titrations was the same as with the sulfides; however, no coloration was observed upon addition of conc'd hydrochloric acid to the thiols in glacial acetic acid. Three representative titrations are indicated in Table I.

Isolation of triphenylcarbinol. Samples weighing 1–3 g. (0.0027–0.008 mole) were dissolved in 100 ml. of glacial acetic acid at 80°, to which was added 10 ml. of conc'd hydrochloric acid. The theoretical amount of 0.5 *N* bromate-bromide solution was added slowly with agitation. The reaction mixture was poured into an equal volume of water and the solid material that precipitated was suspended in 20 ml. of 10% sodium hydroxide solution. The solid was digested for ten minutes at 70–80° in order to hydrolyze any arylsulfonyl bromide and triphenylmethyl bromide. After filtration, the solid was washed thoroughly with water and dried. Nearly quantitative yields of triphenylcarbinol were obtained. Mixture melting points with authentic carbinol showed no depressions. Results are indicated in Table II.

Characterization of the arylsulfonyl bromides as arylsulfonamides. The sulfide (3 g.) was dissolved in 150 ml. of glacial acetic acid and 5 ml. of conc'd hydrochloric acid at 80°. The theoretical volume of 1.0 *N* bromate-bromide solution was then added. After the reaction mixture was cooled rapidly to near room temperature, 40 ml. of benzene was added and the mixture poured into 300 ml. of water. After separation of the benzene layer, the aqueous layer was extracted again with 25 ml. of benzene. Conc'd aqueous ammonia (75 ml.) was added to the combined benzene solutions and the mixture heated until the aqueous phase was at 75°. The aqueous layer was separated and then evaporated to a small volume and acidified to obtain the amide. More sulfonamide was obtained by extracting the benzene solution with 5% sodium hydroxide solution. The crude sulfonamides were recrystallized from water. The *p*-toluenesulfonamide was dried at 115°. Mixture melting points were taken with authentic samples in the case of benzenesulfonamide and *p*-toluenesulfonamide. No depressions were noted. Yields and melting points were: benzenesulfonamide, 0.65 g. (50%) 147–149°; *o*-toluenesulfonamide, 0.5 g. (36%), 154–157°; *m*-toluenesulfonamide, 0.68 g. (49%) 106–109°; *p*-toluenesulfonamide, 0.6 g. (43%), 135–137°.

TABLE II

ISOLATION OF TRIPHENYLCARBINOL AFTER OXIDATION OF TRIPHENYLMETHYL ARYL SULFIDES WITH BROMATE-BROMIDE SOLUTION[a]

OXIDATION OF TRITYL ARYL SULFIDE		TRIPHENYLCARBINOL ISOLATED	
Compound	Wt. of Sulfide, G.	M.P., °C.	Yield, %
Phenyl	1.4767	161–162	96.5
o-Tolyl	1.3585	160–162	94.2
m-Tolyl	2.7552	160–162	98.0
p-Tolyl	1.1405	160–161	96.0

[a] The sulfides were dissolved in 100 ml. of glacial acetic acid and 10 ml. of conc'd hydrochloric acid at 80°. The theoretical amount of bromate-bromide solution for complete oxidation was added.

Cleavage of compound I. One gram (0.0028 mole) of I was dissolved in 100 ml. of glacial acetic acid at 80°; then 6 ml. of conc'd hydrochloric acid was added, and within 20 seconds the mixture was poured slowly with stirring into 400 ml. of water. The aqueous suspension was extracted twice with benzene, and then the benzene solution was extracted with 30 ml. of 30% sodium hydroxide. To the alkaline extract was added 8 g. of chloroacetic acid, and the solution heated on the steam-bath for 30 minutes. From the reaction mixture there was isolated 0.25 g. of carboxymethyl phenylsulfide, m.p. 59–61°. The benzene solution was evaporated to dryness, and the residue dissolved in ethanol. Upon fractional crystallization, 0.38 g. of triphenylcarbinol and 0.3 g. of I were isolated. Mixture melting points, using each with the respective authentic compound, showed no depressions. The yield of triphenylcarbinol was 52%, based on complete cleavage of I.

Isolation of the disulfide as an intermediate. Compound I (3 g., 0.0085 mole) was dissolved in 200 ml. of glacial acetic acid and 6 ml. of conc'd hydrochloric acid at 60°. Then 17.7 ml. of 1.0 *N* bromate-bromide solution was added slowly with agitation. The reaction mixture was poured into 400 ml. of water, and the solid product was digested with 30 ml. of 8% potassium hydroxide at 60–70° for ten minutes. After filtration, the solid was dissolved in a small volume of warm cyclohexene. The triphenylcarbinol was only slightly soluble in cold cyclohexene, while the diphenyl disulfide was very soluble. The yield of triphenylcarbinol was 1.95 g. (89%). A mixture melting point with an authentic sample showed no depression. The yield of diphenyl disulfide was 0.7 g. (75% based on the theoretical amount of thiophenol expected from complete cleavage of the sulfide). *p*-Tolyl triphenylmethyl sulfide (3 g.) was oxidized in an identical manner. The yields obtained from this oxidation were: *p,p'*-ditolyl disulfide, 0.4 g., (40%), m.p. 43–45°; triphenylcarbinol, 1.7 g., (80%), m.p. 158–161°.

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SUMMARY

The triphenylmethyl aryl sulfides were titrated rapidly and nearly quantitatively in an acidic medium with 0.1 *N* bromate-bromide solution. The complete oxidation required three moles of bromine per mole of sulfide. The products of the oxidations were triphenylcarbinol and the corresponding arylsulfonyl bromides. The latter were characterized as the arylsulfonamides. Because the triphenylmethyl aryl sulfides were cleaved in the acidic medium, the main initial step in the reactions was the oxidation of one of the cleavage products, the aryl thiol, to the disulfide.

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