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

TRIPHENYLMETHYL ARYL SULFIDES. III. CERTAIN OXIDATIONS IN ACIDIC MEDIA

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The first two papers in this series (1, 2) described two unsuccessful attempts to characterize the triphenylmethyl (trityl) aryl sulfides by preparation of two common sulfide derivatives, the sulfoxides and the mercuric chloride addition compounds. In both cases the sulfides were cleaved during reaction.

Further attempts have been made to prepare derivatives by using well-known procedures. In each attempt an acidic medium was used and in no case was a sulfoxide or a sulfone obtained. The experimental evidence gathered from previous studies (2) and the present work seems to indicate that the aryl trityl sulfides were cleaved in the acidic medium and that the oxidation products were primarily those of the aryl thiol fragment. The cleavage of these sulfides in acidic media has been reported by Lecher (3) and Tarbell and Harnish (4, 5).

TABLE I

Oxidation of Aryl Trityl Sulfides, $(C_6H_5)_3CSAr$, with Chromic Acid in Aqueous Acetic Acid[a]

Ar	$\frac{\text{moles } CrO_3}{\text{moles sulfide}}$	Products isolated; yield, %		
		Triphenylcarbinol	Diaryldisulfide	Arylsulfonic acid
Phenyl	1	54	27	25
Phenyl	2	90	21	48
o-Tolyl	2	88	—	—
m-Tolyl	2	91	—	—
p-Tolyl	1	48	33	24
p-Tolyl	2	92	18	51

[a] The sulfide (3 g.) was in 100 ml. of glacial acetic acid at 80°. The chromic acid was added in 25 ml. of water. Reaction was complete within ten minutes.

Knoll (6) reported the preparation of phenyl trityl sulfoxide (m.p. 163°) by the oxidation of phenyl trityl sulfide with one mole of chromic acid in 80% acetic acid. Repeated attempts have been made to duplicate Knoll's preparation. In every case triphenylcarbinol, diphenyl disulfide, and benzenesulfonic acid were identified as products. (See Table I.) A significant quantity, usually 12–14%, of phenyl trityl sulfide was recovered. Knoll implied that phenyl trityl sulfoxide could be produced when two moles of chromic acid were used per mole of sulfide. By using this mole ratio, oxidations have produced excellent yields of triphenylcarbinol. Since at least five different methods of oxidation of the sulfide have failed to produce the sulfoxide, it appears doubtful that Knoll prepared this compound by using the method he described.

Knoll (6) also reported an unsuccessful attempt to prepare phenyl trityl sulfone by oxidation of the sulfide with 30% hydrogen peroxide in acetic acid at room temperature. He stated that there was no reaction. Recent studies have shown that at least partial oxidation does occur, but no sulfone was produced. The results of these studies are to be reported soon.

Oxidations of the aryl trityl sulfides have been run by using dilute (4 *N*) nitric acid at reflux temperature. Excellent yields of triphenylcarbinol and good yields of the sodium arylsulfonates were obtained. The sulfonic acids were converted to sodium sulfonates for convenience, and the S-benzylthiuronium salts prepared by using the customary procedure.

Good yields of triphenylcarbinol and of the respective arylsulfonic acids (as sulfonates) were obtained by oxidation of the aryl trityl sulfides with potassium permanganate in acetic acid at 80°.

The oxidation of phenyl trityl sulfide with an excess of ferric chloride in glacial acetic acid at 80° for five minutes produced high yields of triphenylcarbinol and diphenyl disulfide. *p*-Tolyl trityl sulfide was oxidized in a similar manner.

EXPERIMENTAL

All organic reagents used, except common solvents, were Distillation Products best grade chemicals. The chromic acid (chromium trioxide) was Merck reagent grade. Temperatures are uncorrected. All yields are based on complete cleavage of the aryl trityl sulfides during oxidation.

Preparation of the aryl trityl sulfides. The sulfides were prepared by using the procedures reported previously (1).

Oxidation of phenyl trityl sulfide with one mole of chromic acid (Knoll's experiment). To 3 g. (0.0085 mole) of phenyl trityl sulfide in 100 ml. of glacial acetic acid at 80°, was added 0.86 g. (0.0086 mole) of chromic acid in 25 ml. of water. The reaction mixture was kept at 70–80° for 15 minutes and then poured into 400 ml. of cold water. The aqueous suspension was extracted with ether and the ethereal extract was washed several times with water and dilute potassium carbonate solution. After evaporation of the ether, the residue was dissolved in 15 ml. of warm cyclohexane. Triphenylcarbinol crystallized from the solvent at room temperature and 1.2 g. (54%) of the purified carbinol was obtained. A mixture melting point with an authentic sample showed no depression. The filtrate, after separation of the carbinol, was evaporated to dryness and the residue was dissolved in warm ethanol. Upon cooling, 0.4 g. (13% recovery) of phenyl trityl sulfide was obtained. After concentration of the ethanolic filtrate, 0.25 g. (27%) of diphenyl disulfide was obtained. Mixture melting points substantiated the identity of these products. The aqueous solution, which remained after extraction of the reaction mixture with ether, was evaporated to dryness. The residue was dissolved in water and aqueous ammonia was added to precipitate chromic hydroxide. After digestion and removal of the precipitate, the filtrate was evaporated to dryness and aqueous sodium hydroxide was added to remove ammonia. After evaporation of this solution to dryness, conc'd hydrochloric acid was added and this solution was evaporated to dryness to remove acetate ions as acetic acid. This acidic treatment was repeated at least once. The residue was dissolved in water and the sodium benzenesulfonate was characterized by conversion to the S-benzylthiuronium benzenesulfonate. The yield was 0.7 g., (25%), m.p. 146–148°. A mixture melting point with an authentic sample showed no depression. The oxidation of the phenyl trityl sulfide was run at 55–60° and the yields of products isolated were comparable to those listed above.

Oxidation of phenyl trityl sulfide with two moles of chromic acid. To 3 g. (0.0085 mole) of phenyl trityl sulfide in 100 ml. of glacial acetic acid at 80°, was added 1.72 g. (0.0172 mole) of chromic acid in 25 ml. of water. The reaction mixture was kept at 70–80° for ten minutes and then poured into 400 ml. of cold water. The insoluble solid was separated and dissolved in 20 ml. of warm cyclohexane. Triphenylcarbinol separated at room temperature and 2.0 g. (90%) of the purified carbinol was obtained. The residue obtained after evaporation of the cyclohexane filtrate was dissolved in the minimum of ethanol. From this solvent was isolated 0.2 g. (21%) of diphenyl disulfide. The isolation of sodium benzenesulfonate was carried out as described under the discussion of the oxidation of the sulfide with one mole of chromic acid. The S-benzylthiuronium benzenesulfonate was prepared and 1.3 g. (48%) of this salt was obtained. The oxidation of the sulfide was run at 55–60° and comparable yields of the products were obtained.

Oxidation of o-tolyl trityl sulfide with aqueous nitric acid. To 20 g. (0.055 mole) of *o*-tolyl trityl sulfide was added 200 ml. of 4 *N* nitric acid. The reaction mixture was refluxed for four hours. Then it was cooled, filtered, and the solid was washed with dilute sodium hydroxide, followed by water. The solid, triphenylcarbinol, was recrystallized from cyclohexane and 13.2 g. (92%) of the carbinol was obtained. A mixture melting point with authentic carbinol showed no depression. The filtrate from the reaction mixture was neutralized with dilute sodium hydroxide and concentrated by evaporation until precipitation of sodium *o*-toluenesulfonate commenced. The sulfonate precipitated upon cooling the solution and it was recrystallized once from water. The yield of sulfonate was 7.9 g. (74%). The purity of the salt was verified by a sodium analysis: (11.81%, Obs.; 11.85%, Calc'd). The sulfonate was characterized by preparation of the S-benzylthiuronium salt and the *o*-toluenesulfonamide. The oxidation was repeated by using *p*-tolyl trityl sulfide. The yields in this case were, 13.3 g. (94%) of triphenylcarbinol and 8.0 g. (75%) of sodium *p*-toluenesulfonate.

Oxidation of p-tolyl trityl sulfide with potassium permanganate in glacial acetic acid. To 200 ml. of glacial acetic acid was added 10 g. (0.0273 mole) of *p*-tolyl trityl sulfide and 8.64 g. (0.055 mole) of potassium permanganate. The reaction mixture was kept at 80° for one hour. The mixture was then cooled and poured into an equal volume of water. The precipitate was extracted with 100 ml. of boiling ethanol and was decolorized; 5.5 g. (77%) of triphenylcarbinol was obtained from this ethanolic extract. The aqueous filtrate was evaporated almost to dryness and the residue was acidified with dilute hydrochloric acid. This solution was evaporated to dryness and the residue was dissolved in dilute sodium hydroxide. After concentration and cooling of the solution, 3.1 g. (58%) of sodium (potassium) *p*-toluenesulfonate was obtained. This was characterized as the S-benzylthiuronium salt. Phenyl trityl sulfide was oxidized in an identical manner. The yields obtained were: triphenylcarbinol, 5.3 g. (72%); sodium (potassium) benzenesulfonate, 2.9 g. (57%).

Oxidation of phenyl trityl sulfide with ferric chloride in acetic acid. To 300 ml. of glacial acetic acid was added 10 g. (0.028 mole) of phenyl trityl sulfide and 73 g. (0.27 mole) of ferric chloride hexahydrate. The reaction mixture was heated to 80–85° and kept at that temperature for not more than five minutes. The solution was poured into 400 ml. of water which contained 10 ml. of conc'd hydrochloric acid. The precipitate was dissolved in a small volume of warm cyclohexane and 6 g. (84%) of triphenylcarbinol was obtained from the cool solution. The filtrate obtained after separation of the carbinol was evaporated to dryness and the residue was dissolved in warm methanol. Diphenyl disulfide crystallized upon cooling the solution. The yield was 2.8 g. (90%). *p*-Tolyl trityl sulfide was oxidized in an identical manner. The yields obtained were: triphenylcarbinol, 6.2 g. (87%); *p,p'*-ditolyl disulfide, 3.2 g. (95%).

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SUMMARY

1. The validity of Knoll's preparation of phenyl trityl sulfoxide has been questioned.

2. The aryl trityl sulfides, in acetic acid, were treated with three different

oxidizing agents, chromic acid, ferric chloride, and potassium permanganate. Each reaction produced good yields of triphenylcarbinol. The yields of arylsulfonic acids and diaryl disulfides varied with respect to the reaction conditions. When milder conditions were used significant yields of the diaryl disulfide were obtained.

3. Hot dilute nitric acid oxidized the sulfides to produce triphenylcarbinol and the respective arylsulfonic acids.

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