[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF VERMONT, AND UNIVERSITY OF NEW HAMPSHIRE]

TRIPHENYLMETHYL ARYL SULFIDES. I. HYDROGENOLYSIS WITH RANEY NICKEL. REACTIONS WITH MERCURIC CHLORIDE

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Triphenylmethyl phenyl sulfide (I) has been investigated by several workers (1–5). The oxygen analog of I, triphenylmethyl phenyl ether, undergoes spontaneous rearrangement in acidic media to produce 4-hydroxyphenyltriphenylmethane (6, 7, 9). No such rearrangement has been observed for I, and so it may be prepared in both acidic and basic media.

Finzi and Bellavita (5) also prepared triphenylmethyl *o*-tolyl sulfide (II) in both acidic and basic media. The spontaneous rearrangement of the oxygen analog of II in acidic media to form 3-methyl-4-hydroxyphenyltriphenylmethane (III) has been investigated extensively (7–13). Finzi and Bellavita reported that II melted at 145°, perhaps a misprint. The present authors report m.p. 97–99° for II.

Since little positive evidence has been reported to substantiate the suggested structures of the triphenylmethyl aryl sulfides, we have investigated these compounds by using two general procedures for the identification and characterization of organic sulfides: namely, hydrogenolysis (14) and the reactions with mercuric chloride (15–23). Attempts to characterize these sulfides by oxidation to the sulfoxides or sulfones have failed because cleavage of the sulfides or of the oxidation products occurred. Knoll (4) reported the preparation of the sulfoxide of Compound I. However, efforts to repeat Knoll's experiment have been without success. The results obtained by using several methods of oxidation are to be reported later.

The hydrogenolysis technique of Mozingo, *et al.* (14) was employed to identify the triphenylmethyl aryl sulfides. Hydrogenolysis of Compound II yielded the expected toluene and triphenylmethane. The isomeric *p*-tolyl and *m*-tolyl sulfides also yielded these hydrocarbons. Compound I yielded benzene and triphenylmethane. The attempted hydrogenolysis of *m*-tolyltriphenylmethane and of 3-methyl-4-hydroxyphenyltriphenylmethane (III) indicated that the triphenylmethyl group would not be removed, under the conditions used, if it were on the aromatic nucleus.

In an attempt to characterize the triphenylmethyl aryl sulfides by using mercuric chloride, it was found that the addition of this reagent to an alcoholic solution of triphenylmethyl phenyl sulfide (I) produced mercury phenylmercaptide (IV) if the mercuric chloride was one-half molar with respect to I. If the mercuric chloride was in excess of equimolar quantities, the phenylmercaptomercuric chloride (V) was produced. The triphenylmethyl tolyl sulfides behaved in an analogous manner.

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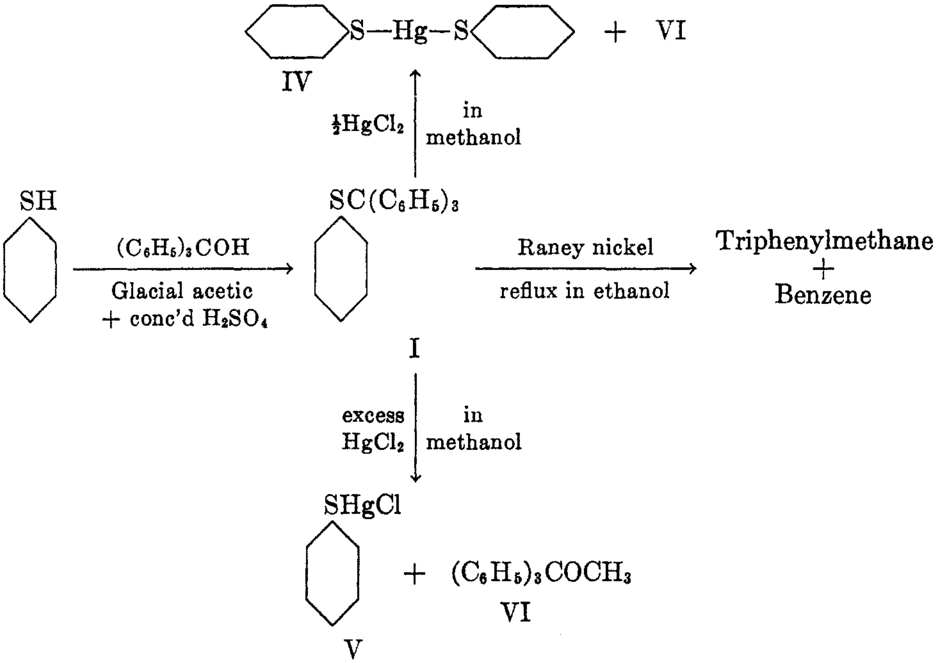
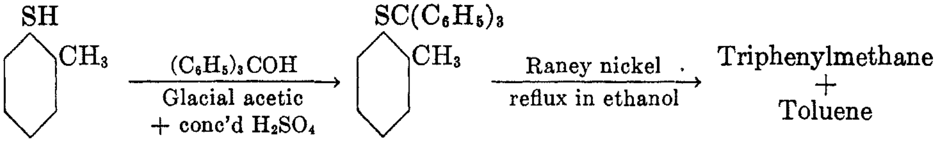
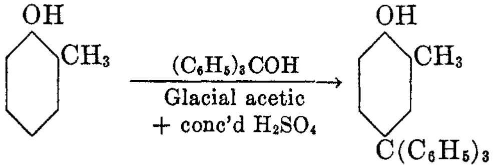
The melting points of Compounds IV and V have been reported (24, 25, 26). The melting points of the three isomeric mercury tolylmercaptides and of the tolylmercaptomercuric chlorides could not be found, although the preparation of several have been reported (26, 27, 28). These derivatives have been prepared by using the appropriate aryl mercaptan, and each was found to be identical to the compound obtained in a similar manner from the corresponding triphenylmethyl aryl sulfide. (See Tables III and IV.)


IV, I, V, VI


II


III

The cleavage of these sulfides by mercuric chloride at ordinary temperatures appears to be a displacement reaction: an electrophilic displacement on sulfur. When methanol was used as the reaction solvent, the triphenylmethyl cation and the methanol formed triphenylmethyl methyl ether (VI).

The nature of the solvent was a factor in the preparation of the mercury arylmercaptides. In methanol and ethanol they were produced in good yields. However, if benzene, ether, or ethyl acetate were used as reaction solvents, the corresponding arylmercaptomercuric chlorides precipitated instead. Lecher (24) showed that the mercury phenylmercaptide and phenylmercaptomercuric chloride were in equilibrium when in solution. $2\ C_6H_5SHgCl \rightleftarrows (C_6H_5S)_2Hg + HgCl_2$, Apparently certain solvents affect this equilibrium. The present authors have found this also obtains with respect to the tolyl derivatives.

EXPERIMENTAL

Specific examples are usually noted to illustrate the general procedures used in this work. Exceptions are noted. All temperatures are uncorrected.

Materials. The thiophenol, the isomeric thiocresols, the triphenyl carbinol, the triphenylchloromethane, and the boron trifluoride-ether complex were Eastman Kodak best grade chemicals.

TABLE I

PHYSICAL CONSTANTS OF THE TRIPHENYLMETHYL ARYL SULFIDES[a] $(C_6H_5)_3CSAr$

AR	M.P., °C.	LIT. M.P., °C. (REF.)	ANALYSES[b]					
			Calculated			Found		
			C	H	S	C	H	S
Phenyl	104–106	106 (1–5)	85.22	5.68	9.10	85.56	5.79	9.15
o-Tolyl	97–99[c]	145 (5)	85.25	6.01	8.74	85.15	6.28	8.53
m-Tolyl	90–92[c]	—	85.25	6.01	8.74	85.39	6.02	8.51
p-Tolyl	145–146	147 (5)	85.25	6.01	8.74	85.19	5.96	8.71

[a] Each compound was prepared by adding boron trifluoride-ether to a dry ethereal solution of the mercaptan and triphenylcarbinol (See preparation of Compound II). [b] Microanalyses by Schwarzkopf Microanalytical Lab., Middle Village, L. I., N. Y. [c] Mixture melting points using samples obtained from each of the four methods of preparation indicated no depression.

Triphenylmethyl o-tolyl sulfide (II). The procedure, using glacial acetic acid and conc'd sulfuric acid as the solvent, reported by Finzi and Bellavita (5) was employed in the preparation of several batches of the sulfide. The product from a typical preparation, yield (80%), had m.p. 97–99°.

An alternative method, using boron trifluoride as the acidic catalyst, was also used. Six grams (0.049 mole) of *o*-thiocresol and 12 g. (0.047 mole) of triphenylcarbinol were dissolved in 25 ml. of anhydrous ether. To this suspension was added 5 ml. of a boron triflouride-ether complex. The crude product was obtained after cooling the reaction mixture. Material remaining in solution was isolated by first washing the ethereal solution with alkali, then with water, and finally evaporating the ether layer. The crude sulfide was recrystallized twice from ethanol; yield 16.7 g. (97%) m.p. 97–99°.

Compound II was also prepared by using the methods reported by Lecher (2) and Knoll (4) for the preparation of Compound I. A typical preparation, yield (85%), had m.p. 96–98°.

The procedure (method 1) reported by Schorigen (8a) for the preparation of triphenylmethyl *o*-tolyl ether was followed to prepare II, except that sodium *o*-tolylmercaptide was used instead of sodium o-cresoxide. A typical preparation, yield (78%), had m.p. 96–98°.

Hydrogenolysis of II. The Raney nickel catalyst used in the experiments was prepared by using the procedure outlined by Mozingo (29), and stored under ethanol. II (6 g., 0.016 mole) and 25–30 g. of Raney nickel were added to 150 ml. of ethanol, and heated under reflux for two hours. Water (50 ml.) was added and the azeotropic mixture of ethanol, water, and toluene was removed by fractional distillation. An equal volume of a saturated solution of calcium chloride was added to the azeotropic mixture and the toluene separated. The yield of toluene was 1.0 ml. (0.86 g., 58%), b.p. 107–110°. The toluene was oxidized with alkaline permanganate to benzoic acid. A mixture melting point with an authentic sample showed no depression.

TABLE II

HYDROGENOLYSIS OF THE TRIPHENYLMETHYL ARYL SULFIDES[a]

AR	BENZENE		TOLUENE		TRIPHENYLMETHANE	
	Yield, %	B.P.,[b] °C.	Yield, %	B.P.,[b] °C.	Yield, %	M.P.,[c] °C.
Phenyl.....	60	78–80	—	—	97	90–92
o-Tolyl.....	—	—	58	107–110	82	91–92
m-Tolyl....	—	—	54	107–109	80	91–93
p-Tolyl.....	—	—	62	106–109	85	91–92

[a] Experimental data were checked by W. J. Plant, U. of Vt. [b] Boiling points were usually taken over sodium. [c] Mixed melting points were taken with an authentic sample.

TABLE III

MERCURY ARYLMERCAPTIDES $(ArS)_2Hg$

AR	YIELD, %	M.P., °C.[a]	ANALYSES, HG[b]	
			Calc'd	Found
FROM THE ARYL MERCAPTANS				
Phenyl...........	98	150–152[c]	47.92	47.10
o-Tolyl...........	95	170–173	44.92	44.92
m-Tolyl..........	90	126–129	44.92	44.62
p-Tolyl...........	92	163–166	44.92	43.82
FROM THE TRIPHENYLMETHYL ARYL SULFIDES				
Phenyl...........	95	150–153	47.92	47.77
o-Tolyl...........	93	169–172	44.92	44.69
m-Tolyl..........	90	127–130	44.92	44.76
p-Tolyl...........	97	162–165	44.92	44.79

[a] Mixture melting points were taken with the corresponding product from the triphenylmethyl aryl sulfide. The colorless mercaptides produced clear, colorless melts. [b] Analyses were done by C. A. Blood, U. of Vt. Procedure employed was similar to that reported by Faragher, *et al.* (18). [c] Lecher (24) reported m.p. 150–153°.

The residue remaining after removal of the azeotrope was filtered while hot and triphenylmethane was isolated from the filtrate either by addition of water or by removal of about half of the ethanol by distillation. Yield, 3.2 g., (82%), m.p. 91–92°.

Treatment of m-tolyltriphenylmethane with Raney nickel. The hydrocarbon was prepared by using the method of Iddles and Hussey (32). To 60 ml. of ethanol was added 10–12 g.

of Raney nickel and 0.5 g. (0.0015 mole) of *m*-tolyltriphenylmethane and the mixture was heated under reflux for 4½ hours. The nickel was removed and the filtrate concentrated by evaporation. The starting material was recovered quantitatively; m.p. 161–163°.

Treatment of compound III with Raney nickel. Compound III was prepared by using the method described by Iddles, *et al.* (11). To 100 ml. of ethanol was added 15–17 g. of Raney nickel and 1.5 g. of III and the mixture was heated under reflux for four hours. Most of the ethanol was then removed by distillation and ether added to extract the organic material. After boiling the ethereal suspension for 30 minutes, it was filtered and the ether removed. The crude material was recrystallized from ethanol; yield, 1.4 g., (93%), m.p. 182–183°. A mixture melting point with a sample of III gave no depression.

MERCURY ARYLMERCAPTIDES

(a) *From the aryl mercaptans.* A solution containing 0.004 mole of mercuric chloride in 10 ml. of ethanol was slowly added at room temperature to 0.008 mole of the mercaptan in 50 ml. of ethanol. The mercaptide precipitated almost immediately, and completely on cooling. It was purified by recrystallization from ethanol or ethyl acetate. Several preparations yielded products that did not require purification. Preparations using methanol as the reaction solvent yielded the same products as with ethanol..

TABLE IV

ARYLMERCAPTOMERCURIC CHLORIDES ArSHgCl

AR	YIELD, %	M.P., °C.[a]	ANALYSES, HG[b]	
			Calc'd	Found
FROM THE ARYL MERCAPTANS				
Phenyl	90	190–192[c]	58.13	57.78
o-Tolyl	86	178–180	55.86	55.45
m-Tolyl	90	187–189	55.86	55.16
p-Tolyl	92	225–226	55.86	55.60
FROM THE TRIPHENYLMETHYL ARYL SULFIDES				
Phenyl	92	189–191	58.13	57.96
o-Tolyl	94	177–179	55.86	55.58
m-Tolyl	92	188–190	55.86	55.66
p-Tolyl	91	225–227	55.86	55.60

[a] The pale yellow mercaptomercuric chlorides partially melted and decomposed leaving a residue of mercurous chloride (24). Mixture melting points were taken as noted in Table III. [b] Same as in Table III. [c] Lecher reported m.p. 188–191.5° (24).

(b) *From the triphenylmethyl aryl sulfides.* A solution containing 0.0014 mole of mercuric chloride in 10 ml. of ethanol was added to 0.0027 mole of the sulfide in 100–150 ml. of ethanol, either warm or at room temperature. The mercaptide commenced to precipitate within a minute and was isolated and purified as described in section (a). Methanol was also used as the reaction solvent. With both ethanol and methanol, the solvent was warmed to put the sulfide into solution.

(c) *Other reaction solvents.* By using ether, ethyl acetate or benzene as reaction solvents, it was not possible to prepare pure mercury mercaptides both from the mercaptans and the triphenylmethyl aryl sulfides. In each attempt the corresponding arylmercaptomercuric chloride precipitated instead. In a typical run, 0.5 g. of thiophenol in 10 ml. of ethyl acetate was mixed with 0.6 g. of mercuric chloride in 5 ml. of ethyl acetate. The crystals that separated in the cold were washed with cold solvent. Yield, 0.6 g., (79%), m.p. 188–190°. A mixture melting point with a sample of phenylmercaptomercuric chloride (V) prepared in ethanol gave no depression. Using the same procedure, but with ether as the solvent, 0.6 g. of V, m.p. 187–189°, was obtained.

(d) *Isolation of triphenylmethyl methyl ether* (VI). The isolation of pure VI as the by-product, using methanol as the solvent, was rather tedious. It did not seem practical to attempt to get pure VI from each run since it was established that VI was the by-product in the formation of the arylmercaptomercuric chlorides from the sulfides. However, by-products were obtained that were without doubt impure VI.

ARYLMERCAPTOMERCURIC CHLORIDES

(a) *From the aryl mercaptans.* A solution containing 0.012 mole of mercuric chloride in 10 ml. of ethanol was added at room temperature to 0.008 mole of the aryl mercaptan in 100–150 ml. of ethanol, either warm or at room temperature. The purification of the crude product was the same as for the arylmercaptides, except that 1.0 g. of mercuric chloride was added to the recrystallization solvent to suppress conversion to the mercaptide. Methanol was also used as the reaction solvent and the products were the same as with ethanol.

(b) *From the triphenylmethyl aryl sulfides.* A solution containing 0.004 mole of mercuric chloride in 10 ml. of ethanol was added to 0.0027 mole of the sulfide in 100–150 ml. of ethanol, either warm or at room temperature. The isolation of the pure product was the same as in (a). With methanol as the solvent, the products were identical to those produced in ethanol.

(c) *Other reaction solvents.* Ether, acetone, or ethyl acetate could be substituted for ethanol and methanol as reaction solvents. However, yields were lower and appeared to vary in proportion to the volume of solvent used. The best yields were obtained by using 10–15 ml. of solvent for 0.5 g. of the mercaptan or 1.0 g. of the sulfide. The products isolated were identical with those obtained in ethanol as shown by mixture melting points.

(d) *Isolation of triphenylmethyl methyl ether* (VI). Two grams of mercuric chloride in 5 ml. of methanol was added to 1.0 g. of triphenylmethyl *o*-tolyl sulfide (II) in 50 ml. of warm methanol. The reaction yielded 0.95 g. (97%) of *o*-tolylmercaptomercuric chloride, m.p. 177–179°. To the filtrate was added 200 ml. of water in order to precipitate VI, which was recrystallized from dilute methanol. Yield, 0.6 g., (81%), m.p. 94–96°. Norris and Cresswell (30) reported m.p. 95.5–96° and Hatt (31) reported m.p. 96–96.5°.

A sample of VI was prepared by adding 2 g. of mercuric chloride in 5 ml. of methanol to 1.0 g. of triphenylmethyl chloride in 75 ml. of methanol. The mixture, after 20 minutes, was poured into 200 ml. of water. The crude material was recrystallized from dilute methanol. Yield, 0.9 g., (91%), m.p. 93.5–95°. This product was used to make mixture melting points with each of the samples of VI isolated during the preparation of the four mercaptomercuric chlorides from the respective sulfides. No depressions in melting points were noted.

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SUMMARY

1. Triphenylmethyl *o*-tolyl sulfide was prepared and found to melt at 97–99°. Finzi and Bellavita (5) reported m.p. 145°. Triphenylmethyl *m*-tolyl sulfide, not reported in the literature, was prepared.

2. Hydrogenolysis of the triphenylmethyl aryl sulfides with Raney nickel yielded the expected hydrocarbons.

3. Mercuric chloride cleaved the triphenylmethyl aryl sulfides to produce the

mercury arylmercaptides or the arylmercaptomercuric chlorides, depending on the reaction solvent and the quantity of mercuric chloride used.

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