[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

# The Reactions between Mercury Diaryls and Diarylselenium Dihalides

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In previous work on the synthesis of aromatic selenonium salts[1] it was shown that triarylselenonium chlorides could be prepared by fusing together diarylselenium dichlorides and mercury diaryls. Since at that time the chief interest lay in the study of the selenonium salts, the mechanism of their synthesis was not worked out. The course of this reaction has now been studied.

Since mercury diaryls were found to react with diarylselenium dihalides in solution, the mechanism of this reaction was first investigated. Both diarylselenium dibromides and dichlorides were used, and the procedure was the same in all cases. The equimolecular amounts of the reagents shown in Table I were mixed in the dry state and treated with about 25 cc. of carbon disulfide. The mixture was shaken for five minutes at room temperature. The mercury diaryls dissolved at once; the dihalides somewhat more slowly. When the dibromides were used, a white precipitate began to appear almost immediately, and the red color of the dibromide faded. After shaking, the mixture was allowed to stand for five to ten minutes. Precipitation was then complete. In the case of the dichlorides, the precipitation required from one to three days before it was complete. The precipitate was filtered off and crystallized from benzene if necessary, though usually it was very pure. The carbon disulfide was distilled from the filtrate and the residue dissolved in ether. A little aryl mercuric halide which remained undissolved was added to the main precipitate. The ether was then distilled off and the residue fractionated.

TABLE I

| | Starting Compounds | | | | Reaction Products | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | $R_2Hg$ R = | Amt., g. | $R_2SeX_2$ R = | Amt., g. | $R_2Se$ R = | Amt., g. | Yld., % | RX R = | Amt., g. | Yld., % | RHgX R = | Amt., g. | Yld., % |
| 1 | Tol.[a] | 1.8 | Tol.[b] | 2.1 | Tol. | 1.2[c] | 97 | Tol.[b] | 0.5[c] | 62 | Tol.[b] | 1.5 | 85 |
| 2 | Tol. | 0.76 | Ph.[b] | 0.79 | .. | .. | .. | Tol.[b] | .15 | 44 | Tol.[b] | 0.66 | 89 |
| 3 | Ph. | .70 | Tol.[b] | .84 | Tol. | 0.37 | 71 | Ph.[b] | .27 | 87 | Ph.[b] | .71 | 100 |
| 4 | Ph. | .70 | Ph.[b] | .78 | Ph. | .37 | 80 | Ph.[b] | .07 | 23 | Ph.[b] | .67 | 94 |
| 5 | Tol. | .90 | Tol.[d] | .80 | Tol. | .50 | 82 | .. | .. | .. | Tol.[d] | .60 | 78 |

[a] Tol. = *p*-tolyl; Ph. = phenyl. [b] X = Br. [c] The amounts of selenide and bromotoluene were determined in separate experiments. [d] X = Cl.

The reactions which were studied quantitatively are summarized in Table I. The three reactions which correspond for the dichlorides to reactions 2 to 4 for the dibromides were studied only qualitatively, but the analogous reaction products were identified in each case.

Di-*p*-tolyl selenide, phenyl and *p*-tolyl mercuric bromides and chlorides were identified by mixed melting points with the known compounds; diphenyl selenide was converted to the dibromide for identification; *p*-bromotoluene was oxidized to *p*-bromobenzoic acid which was proved by mixed melting point; and bromobenzene was identified by conversion to *p*-nitrobromobenzene, and by mixed melting point of the latter with an authentic specimen.

It is therefore evident that the course of the reaction can be represented by the following general equation

$$R_2Hg + R_2SeX_2 = RHgX + RX + R'_2Se$$

where X is a halogen. The ease with which the selenium dihalides, especially the dibromides, halogenate the mercury compounds is noteworthy.

The reaction was next tried in acetone. When diaryl selenium dibromides were dissolved alone in this solvent, the powerful effect of bromoacetone on the eyes soon became apparent, and the red color faded from the solution. Evaporation of the solvent left diaryl selenides, which were identified as described above. The reaction occurred more rapidly in the case of di-*p*-tolylselenium dibromide than when diphenylselenium dibromide was used. This bromination of the solvent rendered study of the reaction with mercury diaryls unsatisfactory.

However, no corresponding chlorination occurred with diarylselenium dichlorides. In the cold, these reacted with mercury diaryls just as they did in carbon disulfide solution. When,

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[1] Leicester and Bergstrom, THIS JOURNAL, **53**, 4428 (1931).

however, the reaction mixture was refluxed, a second reaction was observed. Thus, when diphenylselenium dichloride and mercury diphenyl were heated in acetone, a compound precipitated which was insoluble in boiling benzene, and could thus be separated from the phenyl mercuric chloride which was also formed. The amount of this new compound produced increased as the time of refluxing was lengthened. The substance was not very soluble in alcohol, but could be crystallized from this solvent in short needles, m. p. 259–260° (uncorrected). When it was treated with sodium hydroxide solution, mercuric oxide was precipitated. Triphenylselenonium chloride was isolated from the filtrate by the method previously described.[1] The compound was thus the double salt, triphenylselenonium chloride–mercuric chloride, a fact which was proved by comparing it with a sample of the double salt prepared directly from mercuric chloride and triphenylselenonium chloride. The behavior of the two substances was identical.

The reactions described above, with the exception of the second step in hot acetone, obviously differ from that which was previously observed in the fusion of the mercury and selenium compounds, since no selenonium salt was formed. Therefore, a more detailed study of the fusion of di-*p*-tolylselenium dichloride and mercury di-*p*-tolyl was made. This reaction has been earlier described[1] (p. 4434) but the proportions of the reagents there used were determined empirically. When an equimolecular mixture of the two compounds was heated to 140–150°, it fused to a brown liquid which cooled to a thick tar. When this was treated with ether, it was converted to a yellow powder. A hot benzene extract of the latter gave crystals of *p*-tolyl mercuric chloride when it cooled. The material which did not dissolve in benzene crystallized from alcohol in granular crystals, m. p. 216–217°. These gave mercuric oxide and tri-*p*-tolylselenonium chloride when they were treated with sodium hydroxide.

When a mixture of 0.76 g. of mercury di-*p*-tolyl and 1.30 g. of di-*p*-tolylselenium dichloride, a ratio of 1:2, was fused and treated as above, no *p*-tolymercuric chloride was isolated. However, from the ether extract was obtained di-*p*-tolyl selenide, and the odor of *p*-chlorotoluene was noticed. A yield of 1.29 g. or 98% of the mercuric chloride double salt, m. p. 216–217°, was obtained. When this was worked up in the usual way, it gave 86% of the tri-*p*-tolylselenonium salt which was identified by conversion to the iodide.

These facts show that the reaction which took place in carbon disulfide and cold acetone also occurred in the fusion, but that a further reaction then occurred between the aryl mercuric chloride, which now was not removed from the sphere of the reaction, and a second molecule of diarylselenium dichloride. The two steps in the reaction are

$$(CH_3C_6H_4)_2SeCl_2 + (CH_3C_6H_4)_2Hg = (CH_3C_6H_4)_2Se + CH_3C_6H_4Cl + CH_3C_6H_4HgCl$$

$$CH_3C_6H_4HgCl + (CH_3C_6H_4)_2SeCl_2 = (CH_3C_6H_4)_3SeCl\cdot HgCl_2$$

The occurrence of the second step in hot acetone is no doubt due to the solubility of the aryl mercuric chlorides in this solvent.

For further proof of the occurrence of the second reaction, equimolecular mixtures of di-*p*-tolylselenium dichloride and *p*-tolyl mercuric chloride were fused at 150–160° for one minute. The liquid bubbled at first, and became dark red-brown. It cooled to a hard solid. This was converted to an orange powder by stirring under ether. The ether extract contained a very small amount of an oily product which was not identified. A yield of 73% of tri-*p*-tolylselenonium chloride–mercuric chloride, m. p. 215–216°, was obtained.

Entirely analogous results were obtained by fusing together equimolecular amounts of diphenylselenium dichloride with *p*-tolyl mercuric chloride, and of di-*p*-tolylselenium dichloride with phenyl mercuric chloride. In the latter case, the selenonium iodide and picrate prepared from the reaction product had low melting points, as had been found for the corresponding products from the fusion of di-*p*-tolylselenium dichloride with mercury diphenyl.

## Summary

1. In carbon disulfide solution, mercury diaryls react with diarylselenium dihalides to form aryl mercuric halides, aryl halides and diaryl selenides.
2. In the fusion of mercury diaryls and diarylselenium dichlorides, aryl mercuric chlorides are produced, and these react with more diarylselenium dichloride to form the mercuric chloride double salt of a triarylselenonium chloride.
3. In acetone solutions, diarylselenium dibromides brominate the solvent, and diarylselenium dichlorides in the cold react as in carbon disulfide and when heated, as in the fusion reactions.

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