[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reactions of Two Diaryl Diselenides with Mercury(II) Chloride

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The reaction of diphenyl diselenide or di-(*o*-biphenylyl) diselenide with mercury(II) chloride in ethanol, isopropyl alcohol or di-isobutylcarbinol does not yield an addition compound of the type $Ar_2Se_2 \cdot 2HgCl_2$ as has been reported. Rather, compounds of the type ArSeHgCl are formed, probably by small amounts of selenophenols present in many samples of diaryl diselenides. The same type of product may be formed from the diselenide by prolonged heating in a reducing solvent. The reaction does not appear to be initiated by light.

An earlier communication described some complexes formed from diaryl selenoxides and mercury(II) halides.[1] It was reported that the formation of such adducts is not a general reaction, since only alkoxy-substituted selenoxides and dibenzoselenophene oxide gave evidence of reaction under the conditions described. Some years before, it had been noted[2] that certain diaryl selenides form brilliant yellow crystalline complexes when treated with the chloride or bromide (but not the iodide) of dipositive mercury. (Determinations of the exact compositions of the selenide adducts has not been possible since each adduct appears to form solid solutions with either or both of its components.) Again, evidence of complex formation was limited to the alkoxy-substituted selenides and dibenzoselenophene. In short, a selenide which exhibited basicity toward mercury(II) halides would yield, upon oxidation, a selenoxide which would also appear basic.

Since neither diphenyl selenide itself or diphenyl selenoxide appeared to form stable adducts with mercury(II) halides, we were led to question the early report by Bradt and Green[3] that diphenyl diselenide (which would be expected to be less basic than the monoselenide) forms a very stable adduct with mercury(II) chloride of formula $(C_6H_5)_2Se_2 \cdot 2HgCl_2$ when solutions of the two components are mixed. Repeating Bradt's experiments, we obtained a white solid, m.p. 189°, presumably the same as Bradt's "adduct," which was reported to melt at 188°. However, our yield was curiously small (less than 10%). Moreover, if the non-reacted diselenide was recovered, dissolved in alcohol, and treated with a fresh solution of mercury(II) chloride, practically no additional product was formed, although very small amounts could be obtained by prolonged refluxing. Since samples of diaryl diselenides often contain appreciable amounts of the corresponding selenophenols, it seemed possible that a reaction of selenophenol was being observed, rather than a reaction of the diselenide. This was confirmed by preparing the same product in excellent yield by treatment of freshly prepared selenophenol itself with mercury(II) chloride. From this evidence and from our analyses, we suggest that Bradt's compound was simply chloromercuriselenophenylate, $C_6H_5SeHgCl$, formed in the reaction

$$C_6H_5ScH + HgCl_2 \longrightarrow C_6H_5SeHgCl + HCl$$

The formation of very small amounts of the same product upon refluxing indicated, however, that the diselenide was being slowly reduced, presumably by the solvent. In view of other evidence that diselenides, like disulfides, dissociate into radicals at elevated temperatures[4] it appeared possible that such reduction occurred by transfer of a hydrogen atom from the solvent to a $C_6H_5Se\cdot$radical.

A preliminary study of this type of reduction has been made, using as solvents both isopropyl alcohol and diisobutylcarbinol. The compound di-(*o*-biphenylyl) diselenide was substituted in some cases for diphenyl diselenide; the tetra-aryl compound is more easily recovered from solution than is the di-aryl compound. Moreover, its degree of dissociation into radicals would presumably be greater than that for the di-aryl compound under similar conditions, for the more extended conjugated system should better accommodate the unpaired electron.

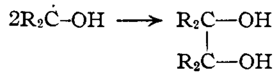
We have found no evidence that this reaction is initiated by light, either from a strong incandescent lamp or from the sun. The rate of the reaction is, however, temperature-dependent, since raising the reaction temperature from 82° to 172° results in about a fifteen-fold increase in yield of the $-SeHgCl$ compound.

Two possible products formed by oxidation of the carbinols used as solvents come to mind, the corresponding ketones and the corresponding pinacols. In searching for the ketones using conditions under which very small amounts could be detected, we found no appreciable ketone to be formed from the reaction of either of the carbinols. The formation of the pinacols is therefore a strong possibility, but the difficult analytical problem of detecting small amounts of pinacol in the presence of large amounts of the parent carbinol has prevented us from confirming this alternative. Therefore, in the provisional mechanism suggested below for this reaction, the final step is the most suspect

$$ArSe{-}SeAr \xrightarrow{\text{heat}} 2\ ArSe\cdot$$

$$ArSe\cdot + R_2CHOH \longrightarrow ArSeH + R_2\dot{C}{-}OH$$

$$ArSeH + HgCl_2 \longrightarrow ArSeHgCl + HCl$$



$$2R_2\dot{C}{-}OH \longrightarrow \begin{array}{c} R_2C{-}OH \\ | \\ R_2C{-}OH \end{array}$$

Experimental

Materials.—Isopropyl alcohol (City Chemical) and diisobutylcarbinol (Carbide and Carbon) were twice distilled through a helix-packed column having a theoretical plate value of 6; the initial and final fifths of the distillates from

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[1] E. S. Gould and J. D. McCullough, THIS JOURNAL, **73**, 3196 (1951).

[2] J. D. McCullough, K. Jung and E. S. Gould, unpublished results.

[3] W. E. Bradt and J. F. Green, *J. Org. Chem.*, **1**, 540 (1936).

[4] A. Schoenberg and co-workers, *Ber.*, **66B**, 237 (1933).

both distillations were discarded. Diphenyl diselenide and di-(*o*-biphenylyl) diselenide were prepared by methods previously described.[5,6] Mercury(II) chloride (Mallinckrodt Analytical Reagent Grade) was used as received.

Reactions in Isopropyl Alcohol.—Eight solutions, each containing 1.5 g. of diphenyl diselenide and 2.6 g. of mercury(II) chloride in 50 cc. of isopropyl alcohol, were refluxed for four hours. Four of these solutions had no direct illumination, whereas four were placed directly beside a 1000-watt G.E. lamp. The solutions were then cooled, filtered and the precipitates formed were washed with a very small volume of ether to dissolve any diselenide which might have precipitated. The precipitates were dried and weighed, and the filtrates were refluxed for a second 4-hour period under the same conditions, recooled, refiltered, then refluxed for a third 4-hour period. In a typical case, the weights of precipitates from an "unlit" sample were: 170 mg. after the first four hours, 35 mg. after the second four hours, and 21 mg. after the third four hours. Similarly, for a typical illuminated sample, 180 mg. of precipitate was recovered after the first reflux period, 120 mg. after the second, and 27 mg. after the third. Although there was considerable variation in the weights of precipitate formed from the various samples, the yields for the illuminated reactions were neither systematically greater nor less than those for the unilluminated reactions. The product, a white solid, m.p. 189°, was practically insoluble in organic solvents at room temperature (unlike mercury(II) halide complexes of monoselenides and selenoxides), but dissolved in aqueous KCN. It was recrystallized with some difficulty from boiling toluene or boiling nitrobenzene.

Anal. Calcd. for $C_6H_5SeHgCl$: Se, 20.2; Hg, 51.1; Cl, 9.1. Found: Se, 19.8; Hg, 50.8; Cl, 8.9.

A similar set of eight experiments was run, using solutions having 1.9 g. of di-(*o*-biphenylyl) diselenide and 2.1 g. of mercury(II) chloride in 50 cc. of isopropyl alcohol. Although the yields of solid from this set of reactions tended to be slightly greater than for diphenyl diselenide, the trend in results was the same, and again there was no systematic increase of yield for the illuminated mixtures. The solid product, glistening white crystalline plates, melted at 183°.

Anal. Calcd. for $C_{12}H_9SeHgCl$: Se, 16.9; Hg, 42.9; Cl, 7.8. Found: Se, 16.6; Hg, 40.7; Cl, 7.6.

Reactions in Di-isobutylcarbinol.—Six solutions, each containing 1.0 g. of di-(*o*-biphenylyl) diselenide and 1.5 g. of mercury(II) chloride in 50 cc. of freshly distilled di-isobutylcarbinol were refluxed for a period of four hours. Two of these were kept in the dark, two were illuminated with a 1000-watt lamp, and the remaining two were illuminated by sunlight. Within a few minutes after heating, all solutions darkened, becoming almost opaque. The solutions were cooled, then filtered. There was far more solid formed than was the case with the reaction in isopropyl alcohol. Almost all of the solid dissolved in boiling toluene; the crystalline product obtained by cooling the toluene solution was the same as that from the reaction in isopropyl alcohol. The small residue insoluble in toluene was a mixture of mercury(I) chloride and elemental mercury; an additional small amount of mercury(I) chloride sublimed on the inside of the reflux condenser during the reaction. The yields (80 ± 10%) were in all cases higher than those from the reactions in isopropyl alcohol, and again there was no evidence that the yields were increased by illumination. The mercury and mercury(I) chloride arose from direct reaction between the carbinol and mercury(II) chloride. Similar amounts (about 20 mg. of each) were formed when the carbinol and the chloride were refluxed together in the absence of diselenide.

Another six solutions, prepared as specified above, were heated at 100°. Two of these were unilluminated, two were illuminated with the 1000-watt lamp, and two were illuminated in sunlight. The yields ofso lids fell into the range 45 ± 5%, and again illumination had no appreciable effect. Direct reaction between the carbinol and the chloride did not occur at this temperature. A third set of six solutions was heated at 83°; here, the yields of solids lay in the range 5 ± 1%, and again yields were not increased by illumination.

Attempts to Detect Ketones.—A 10-ml. portion of the solvent remaining after each reaction was distilled off and treated successively with acidified 2,4-dinitrophenylhydrazine reagent and methanolic potassium hydroxide. The appearance of the deep red color, characteristic of the anion of the ketone dinitrophenylhydrazones indicated that some ketone was formed in the reaction, but the same red color appeared in the distillates from samples of carbinols which had been heated alone for four hours (presumably the ketones were formed by air oxidation). The quantity of the colored ion obtained from the reaction mixture was compared spectrophotometrically with that obtained merely by heating the solvent. The two amounts of ketone formed were essentially the same, and ketone formation could be cut down to a mere trace by carrying out the refluxing under a blanket of nitrogen. The quantity of ketone formed by refluxing a solution of mercury(II) chloride in diisobutylcarbinol for four hours was about 50% greater than that formed in the reaction of chloride, diselenide, and carbinol.

Chloromercuriselenophenylate.—A mixture of 0.5 g. of diphenyl diselenide, 2.0 g. of zinc dust and 1.0 g. of sodium hydroxide was heated in 25 cc. of methanol for two hours. The solution faded from orange to almost colorless, indicating reduction to the anion of selenophenol. The mixture was very rapidly filtered, acidified with dilute sulfuric acid, and added to a methanolic solution of mercury(II) chloride. The white precipitate obtained was recrystallized from boiling toluene. The yield was 1.0 g. (80%); the product melted at 188° and did not depress the m.p. of the solid formed in the reactions between diphenyl diselenide and mercury(II) chloride.

2-(Chloromercuriseleno)-biphenyl was prepared in the same way, using 1.0 g. of di-(*o*-biphenylyl) diselenide. The yield was 1.8 g. (90%); the product did not depress the m.p. of the solid formed by the reactions of the diselenide with mercury(II) chloride in isopropyl alcohol and in diisobutylcarbinol.

Analyses.—The method for selenium analyses was described in an earlier paper from this Laboratory.[7]

Mercury was determined as follows: the sample was dissolved in concd. nitric acid, then treated with excess 6 *N* potassium hydroxide, precipitating most of the mercury as the red oxide. A few drops of tin(II) chloride solution was added to the filtrate, reducing the remaining mercury to the element. The elemental mercury was combined with the mercury(II) oxide precipitated in the first step and the two precipitates were dissolved in concentrated nitric acid. The mercury was titrated thiocyanometrically by the method of Swift.[8]

To determine chlorine, the sample was dissolved in concd. nitric acid, and an excess of 6 *N* KOH was added to remove most of the mercury as the oxide. The precipitate was washed with water and the washings added to the filtrate. The filtrate was acidified with nitric acid and the chloride titrated by the Volhard method.[9] The determinations of both mercury and chloride were standardized using known amounts of mercury(II) chloride in the presence of the diselenides. By careful control of conditions, it was possible, using the procedures described, to detect 97 ± 1% of the mercury and 92 ± 1% of the chloride. Both "recovery factors" were used to obtain the analytical data given.

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[6] J. D. McCullougb, T. W. Campbell and E. S. Gould, *ibid.*, **72**, 5753 (1950).

[7] E. S. Gould, *Anal. Chem.*, **23**, 1502 (1951).

[8] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1940, p. 268.

[9] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 303.