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Photoreactions of Metalloörganic Compounds of Mercury

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1,4-Butanediol was obtained in 40% yield when methanol solutions of 2-chloromercuriethanol ($ClHgCH_2CH_2OH$) were exposed to ultraviolet light. Solutions of the related bis-(2-chloromercuriethyl) ether ($ClHgCH_2CH_2OCH_2CH_2HgCl$) were stable under ultraviolet light. 1,6-Dioxacyclodecane ($O<(CH_2CH_2CH_2CH_2)_2>O$) was obtained in 25% yield when benzene solutions of 1,7-dioxa-4,10-dimercuracyclododecane ($O<(CH_2CH_2HgCH_2CH_2)_2>O$) were exposed to ultraviolet light.

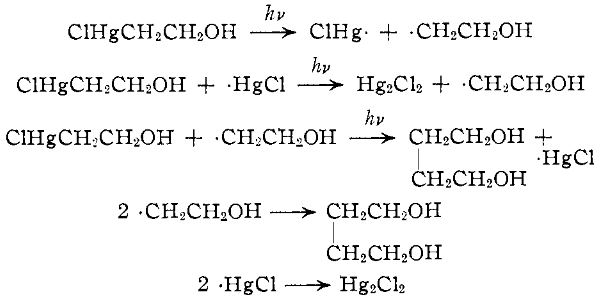
The photoreaction of several mercury compounds readily available from ethylene[1] was investigated briefly.

1,4-Butanediol is obtained in about 40% yield when a solution of 2-chloromercuriethanol[1] in methanol is illuminated with ultraviolet light. The mercury is recovered quantitatively as mercurous chloride. No reactions occur in benzene, pyridine or dimethylformamide solutions.

The related bis-(2-chloromercuriethyl) ether remains unaffected by ultraviolet light regardless of the solvent in which it is exposed.

1,7-Dioxa-4,10-dimercuracyclododecane,[2] readily prepared from bis-(2-chloromercuriethyl) ether and originally thought to be mercury diethylene oxide $Hg<(CH_2CH_2)_2>O$,[3] is converted to 1,6-dioxacyclodecane in 25% yield when exposed to ultraviolet light in benzene solution. The mercury is recovered quantitatively as metallic mercury. Some higher molecular weight by-products are also formed. This 1,6-dioxacyclodecane is identical with the recently reported "cyclic dibutanediol."[4]

A free radical mechanism explains satisfactorily the formation of 1,4-butanediol and mercurous chloride from 2-chloromercuriethanol under the influence of ultraviolet radiation or the radiation from a Van de Graaf generator if the reaction medium is methanol or water. The formation of



$$\mathrm{ClHgCH_2CH_2OH} \xrightarrow{h\nu} \mathrm{ClHg\cdot} + \mathrm{\cdot CH_2CH_2OH}$$

$$\mathrm{ClHgCH_2CH_2OH} + \mathrm{\cdot HgCl} \xrightarrow{h\nu} \mathrm{Hg_2Cl_2} + \mathrm{\cdot CH_2CH_2OH}$$

$$\mathrm{ClHgCH_2CH_2OH} + \mathrm{\cdot CH_2CH_2OH} \xrightarrow{h\nu} \begin{array}{l}\mathrm{CH_2CH_2OH} \\ | \\ \mathrm{CH_2CH_2OH}\end{array} + \mathrm{\cdot HgCl}$$

$$2\ \mathrm{\cdot CH_2CH_2OH} \longrightarrow \begin{array}{l}\mathrm{CH_2CH_2OH} \\ | \\ \mathrm{CH_2CH_2OH}\end{array}$$

$$2\ \mathrm{\cdot HgCl} \longrightarrow \mathrm{Hg_2Cl_2}$$

1,4-butanediol did not occur in several other solvents in which free radical promoted reactions customarily proceed well. Similarly, peroxides which induce free radical reactions failed to cause the formation of 1,4-butanediol. Thus, we have either a very limited case of a free radical reaction which proceeds only in a few selected solvents, or the condensation proceeds by another mechanism for which we can offer no full explanation. It may well proceed by a separation at the carbon–metal linkage and produce pseudo radicals which do not diffuse into the bulk of the reaction medium. The dimerization process is then affected by the nature of the solvent, either its polarity or its reactivity.

The experimental facts which we present may offer valuable clues to other investigators in the field of metalloörganic compounds.

Discussion

The Reaction of 2-Chloromercuriethanol.—The reaction was studied primarily on 2-chloromercuriethanol, but the mercuriethanols where chlorine was replaced by bromine or iodine reacted in a similar manner. The coupling to 1,4-butanediol under the influence of ultraviolet light occurred best in methanol (40% yield), and nearly as well in dilute aqueous ammonia (27% yield). The reaction was noticeably temperature dependent. The reaction, if truly free radical, should have proceeded better in *t*-butyl alcohol than in methanol. Actually the yield in *t*-butyl alcohol was less than 10%.

Razuvaev[5] has reported that diethyl adipate was formed by the ultraviolet light irradiation of the dimethyl ester of β-mercuribispropionic acid better in benzene than in alcohols. In our case no reaction at all occurred in benzene (thiophene-free). Yet benzene could not be considered as a reaction inhibitor because the condensation proceeded in a mixture of one part of methanol (but not less) and seven parts of benzene. Other inoperative solvents were pyridine and dimethylformamide.

Mercurous chloride precipitated quickly and quantitatively when solutions of 2-chloromercuriethanol in isopropyl alcohol were exposed to ultraviolet light. However, only ethanol and acetone and no 1,4-butanediol were detected in the reaction mass. An aid to the quick reaction in isopropyl alcohol was the phenomenon that, in contrast to other solvents, the mercurous chloride did not coat the light coils but precipitated freely.

The addition of hydroquinone, a known free radical inhibitor, had no adverse influence upon the reaction under ultraviolet light. 1,4-Butanediol was formed and the reaction proceeded rapidly because the mercurous chloride precipitated freely without adhering to the light coils.

Exposure of methanol solutions of 2-chloromercuriethanol to the radiation from a 2 mev. Van de Graaf generator precipitated mercurous chloride quantitatively and a mixture of butanediol and

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(1) H. A. Hofmann and J. Sand, *Ber.*, **33**, 1340 (1900).

(2) D. Grdenic, *Acta Cryst.*, **5**, 367 (1952).

(3) J. Sand, *Ber.*, **34**, 2910 (1901).

(4) W. Reppe, *Ann.*, **596**, 1 (1955).

(5) G. A. Razuvaev, Yu. A. Oldekop and V. N. Latyaeva, *J. Gen. Chem. U.S.S.R.*, **24**, 261 (1954).

ethylene glycol was obtained. 1,4-Butanediol was not noticeably changed under this electron beam.

When methanolic solutions of 2-chloromercuriethanol were heated to 135° in the presence of peroxides, mercurous chloride was precipitated quantitatively, but only formaldehyde and no 1,4-butanediol could be detected in the reaction mass. In a similar experiment, but in the presence of traces of hydroquinone, only 19% of the expected amount of mercurous chloride was precipitated. No reaction took place when benzene or dimethylformamide solutions of 2-chloromercuriethanol were heated with peroxides.

The ultraviolet-catalyzed reaction in methanol was noticeably temperature dependent. The best yields were obtained at temperatures below 25°. At 45°, the reaction was rapid, but the yield of 1,4-butanediol was low, and acetaldehyde was present in the reaction mass.

The Reaction of Bis-(2-halomercuriethyl) Ethers.—Solutions of bis-(2-chloromercuriethyl) ether in numerous solvents showed the same strong absorption in the ultraviolet range as did those of 2-chloromercuriethanol. Yet under no condition of illumination did the chloro, bromo or iodo compounds react and mercurous halides were never formed. When an alkaline solution of bis-(2-chloromercuriethyl) ether in aqueous isopropyl alcohol was illuminated with ultraviolet light, the mercury was precipitated quantitatively as metallic mercury, but the only reaction products to be detected were ethyl ether and acetone. When a methanolic solution of bis-(2-chloromercuriethyl) ether was heated with dicumyl peroxide to 135°, some metallic mercury was precipitated, but other reaction products could not be isolated or identified. No reaction occurred in benzene, pyridine or dimethylformamide. Neither was any reaction observed under the 2 mev. Van de Graaf generator in pyridine solutions of the chloro, bromo or iodo compounds, nor when an aqueous suspension of the bis-(2-iodomercuriethyl) ether was irradiated.

The Photolysis of 1,7-Dioxa-4,10-dimercuracyclododecane.—J. Sand[3] had reduced bis-(2-chloromercuriethyl) ether with stannous chloride and had heated the resulting reaction product to 140° in ether. He had obtained a compound C_4H_8OHg which he had called mercury diethylene oxide. Based on our molecular weight determinations, however, and the investigations of Grdenic,[2] that compound actually was the 1,7-dioxa-4,10-dimercuracyclododecane. This compound reacted readily in benzene under ultraviolet light to give 1,6-dioxacyclodecane.

The nuclear magnetic resonance spectrum showed the expected two peaks of equal intensity. The structure has been confirmed on the basis of the following comparison.

CHEMICAL SHIFT (CPS.)[a]

Compound	C-CH_2-O	C-CH_2-C	Intensity ratio
1,6-Dioxacyclodecane	−54	−132	1.0
Tetrahydrofuran	−56	−131	1.0
1,4-Dioxane	−50	. . .	. .

[a] The chemical shifts were measured at a frequency of 40 m.c. *versus* water as reference.

The shifts are good to perhaps ±5 cycles/sec. Thus, the C–CH_2–O and C–CH_2–C resonances for the unknown compound are essentially identical with those of the reference compounds. The nearly complete identity of the spectra of 1,6-dioxacyclodecane and of tetrahydrofuran was unexpected. It appears that the ring strain in tetrahydrofuran has practically no effect on the electron densities around the protons.

Acknowledgment.—We are indebted to Dr. R. C. Ferguson for preparing and interpreting the n.m.r. spectrum.

Experimental

Formation of 1,4-Butanediol.—A solution of 2-chloromercuriethanol (42 g.)[1] in anhydrous methanol (700 cc.) was illuminated at 20–25° in a nitrogen atmosphere in a cylindrical glass vessel containing a quartz coil filled with mercury vapor.[6] (All experiments using ultraviolet light were made in this equipment and were carried out in a nitrogen atmosphere.)

Within a few minutes after the light was turned on, a white suspension was formed and the quartz coils became loosely coated with mercurous chloride. This coating had to be brushed off frequently to keep the reaction continuing. The reaction was judged complete when the quartz coil remained uncoated for two hours. The reaction time was about 40 hours. Upon filtration, an essentially quantitative yield of mercurous chloride was obtained.

Pyridine (100 cc.) was added to the methanolic filtrate and the methanol was removed by distillation. The 1,4-butanediol was precipitated as its bis-*p*-nitrobenzoate and the yield of 1,4-butanediol was calculated from the amount of 1,4-butanediol bis-(*p*-nitrobenzoate) as 40% of theory. The crystallized *p*-nitrobenzoate, m.p. 172°, was identical with one prepared from a commercial source of 1,4-butanediol of a freezing point of 17.6° which had been shown to be free of isomers by an infrared analysis. The crude 1,4-butanediol bis-(*p*-nitrobenzoate) melted from 167–170° and the butanediol isolated from it was shown by infrared analysis to contain about 10% of 1,3-butanediol.

Other Observations Concerning Reactions of 2-Chloromercuriethanol. Reactions Under Ultraviolet Light.—Hydroquinone (0.42 g.) was added to a charge similar to that described above and almost as soon as the light was turned on, the mercurous chloride started to precipitate as a voluminous white solid which did not adhere to the light coils. The reaction was therefore complete in a few hours, and 1,4-butanediol was obtained in 23% yield. The recovery of mercurous chloride was quantitative. Aldehydes could not be detected in the solution.

p-Quinone (0.42 g.) was added to a similar charge and 1,4-butanediol was isolated in 30% yield. The mercurous chloride adhered unusually strongly to the light coil in this experiment. Aldehydes could not be detected in the solution and the mercurous chloride was again isolated essentially quantitatively.

A solution of 2-chloromercuriethanol (42 g.) in methanol (750 cc.) containing 25 cc. of 28% aqueous ammonium hydroxide was irradiated in the usual manner at 20–25°. The mercury was recovered quantitatively as mercurous oxide. The reaction was finished in less than 14 hours because the mercurous oxide did not coat the light coils. Formaldehyde was present in the finished reaction mass and was identified as the 2,4-dinitrophenylhydrazone. 1,4-Butanediol was isolated in about 40% yield.

A solution of 2-chloromercuriethanol (42 g.) in water (750 cc.) containing 20 cc. of 28% ammonia was exposed to ultraviolet light and 1,4-butanediol was obtained in 27% yield. The mercury was precipitated as mercurous oxide and metallic mercury. Aldehydes could not be detected.

A solution of 2-chloromercuriethanol (21 g.) in thiophene-free benzene (700 cc., dried over silica gel) was irradiated with ultraviolet light at 50–55°. The solution remained perfectly clear for 5 hours indicating that mercurous chloride had not been formed. Absolute methanol then was added gradually. The precipitation of mercurous chloride

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[6] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949). A vessel of this type is being manufactured by the Wakefield Industries, Inc., Skokie, Ill.

started only after 105 cc. of methanol had been added over a period of about two hours. All of the mercurous chloride had been precipitated after about 40 hours of irradiation. The 1,4-butanediol was isolated by distillation (2 g., b.r. 110–115° (9 mm.)). A second fraction (3 g., b.p. about 200° (2 mm.)), $C_6H_{10}O$, also was obtained but was not further investigated.

Anal. Calcd. for $C_6H_{10}O$: C, 73.3; H, 10.2. Found: C, 73.2; H, 9.5.

A solution of 2-chloromercuriethanol (8 g.) in *t*-butyl alcohol (600 cc.) which was free of isobutyl alcohol and *sec*-butyl alcohol and contained but traces of *n*-butyl alcohol (based on an infrared analysis) was irradiated for 26 hours when no more mercurous chloride precipitated. The alcoholic filtrate was distilled and 1 g. of distillate, b.r. 110–120° (15 mm.), was obtained. Based on an infrared analysis, it was 1,4-butanediol containing some 1,3-butanediol (less than 10%).

Reactions under the Van de Graaf Generator.—A solution of 2-chloromercuriethanol (31 g.) in about 600 cc. of methanol was put into four Petri dishes (16 cm. diameter). The dishes were covered with aluminum foil and cooled in a tray with ice. The entire assembly was passed sixty-five times through the electron beam from 10 mev. Van de Graaf, equal to an exposure of 7 minutes and 40 seconds. The mercurous chloride had been quantitatively precipitated by that time. The reaction products were isolated from pyridine as the bis-(*p*-nitrobenzoates) as described in the preceding experiments. A mixture of the bis-(*p*-nitrobenzoates) of 1,4-butanediol and ethylene glycol was obtained. Only the ethylene glycol bis-(*p*-nitrobenzoate) was separated in a pure state by crystallization. Identical results were obtained when this reaction was run in the presence of air or in a nitrogen atmosphere. It also was determined that under the reaction conditions employed methanol was converted to ethylene glycol (1 g. from 250 cc. of methanol in 65 passes), and that 1,4-butanediol dissolved in water remained unchanged when exposed to the electron beam.

Reactions in Presence of Free Radical Generators.—Solutions of 2-chloromercuriethanol in methanol and in benzene (14 g. in 200 cc. of solvents) were refluxed for 20 hours in the presence of free radical generators. Benzoyl peroxide (1 g.) in methanol gave 22% of theory of mercurous chloride while no reaction occurred in benzene. With dicumyl peroxide (1 g.) or α,α'-azobisbutyronitrile (1 g.), no precipitate was formed in either solvent. The reactions in methanol were repeated in closed glass lined vessels. Dicumyl peroxide at 100° and 6 hours precipitated mercurous chloride in 25% yield; at 135° and 6 hours, the mercurous chloride was precipitated quantitatively. In the latter case, formaldehyde was found in the reaction mass, but 1,4-butanediol could not be detected. α,α'-Azobisbutyronitrile gave only 10% yield of mercurous chloride under similar reaction conditions. It previously had been established that under these reaction conditions 2-chloromercuriethanol was completely stable in the absence of peroxides.

When hydroquinone (0.005 mole) was present in a solution of 2-chloromercuriethanol (0.1 mole) and dicumyl peroxide (0.002 mole) in methanol (300 cc.), only 17% of mercurous chloride was precipitated in 6 hours at 135°.

When dimethylformamide or benzene was used as solvent, mercurous chloride was not precipitated at 135° in the presence of dicumyl peroxide.

When water was the solvent, a 40% yield of mercurous chloride was obtained.

2-Bromomercuriethanol and 2-iodomercuriethanol were tried in place of 2-chloromercuriethanol in some of the above tests with essentially the same results.

Observations Concerning the Reaction of Bis-(2-mercuriethyl) Ether.—Solutions of the bis-(2-chloro-, 2-bromo-2-iodomercuriethyl) ethers in pyridine (the only organic solvent in which they showed reasonable solubility) did not precipitate mercurous halides, or form any sort of a mercury precipitate when exposed to ultraviolet light. Neither was a precipitate formed when aqueous alkaline solutions of 2-bis-(2-chloromercuriethyl) ether were irradiated. A reaction occurred, however, when bis-(2-chloromercuriethyl) ether (54 g.) was dissolved in water (400 cc.) containing sodium hydroxide (14 g.) and isopropyl alcohol (300 cc., acetone-free). A slow current of nitrogen was passed through the liquid (20–25°) and cooled in CO_2 traps to condense any tetrahydrofuran that might have been formed. Within a few minutes after the light was turned on, metallic mercury started to precipitate. No further precipitate appeared to form after about six hours, but the illumination was continued overnight. Essentially a quantitative recovery of mercury was obtained. The alkaline filtrate was fractionated. Ethyl ether (2 cc.) and acetone (5 cc.) were isolated and positively identified. A small fraction of distillate (1 cc.) was collected in the range of 60–70°, but this fraction did not contain tetrahydrofuran (based on infrared analysis).

No reaction occurred when pyridine solutions of bis-(2-chloromercuriethyl) ether, or the 2-bromo and 2-iodo analog, were passed through the electron beam as previously described. A suspension of finely pulverized bis-(2-iodomercuriethyl) ether was suspended in water in Petri dishes and the dishes were passed through the electron beam. Mercurous iodide was not precipitated.

1,6-Dioxacyclodecane.—A solution of 1,7-dioxa-4,10-dimercuracyclododecane (30 g., m.p. 148°)[3] in dry, thiophene-free benzene was illuminated in a nitrogen atmosphere at 40–45°. Metallic mercury precipitated steadily until no more mercury compound could be detected in solution after 24 hours.

Upon fractionation, 1,6-dioxacyclodecane (4 g., 25% of theory) was obtained as a colorless oil distilling at 60° (9.5 mm.). A viscous colorless oil was left in the distillation flask.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.12; mol. wt., 144. Found: C, 66.8; H, 11.1; mol. wt., 142.

A nuclear magnetic study gave data in agreement with the postulated structure. An ether made (after considerable difficulty) by a synthesis reported recently[4] showed an infrared spectrum identical with that of the 1,6-dioxacyclodecane.

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