Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

A CONVENIENT PROCEDURE FOR THE CONVERSION OF MONO-ORGANOMERCURY COMPOUNDS, RHgX, TO DIORGANOMERCURIALS

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(Received November 14th, 1969)

SUMMARY

Monoorganomercury acetates, halides, hydroxides, etc. (RHgX) are converted in nearly quantitative yield to the diorganomercurials, R_2Hg, by treatment with polyethyleneimine (Dow "PEI-6", mol.wt. 600) in the presence of water. The inorganic mercury species, HgX_2, produced in this disproportionation process are held in solution in the form of their polyethyleneimine complex, from which metallic mercury may be recovered by reduction with sodium borohydride.

INTRODUCTION

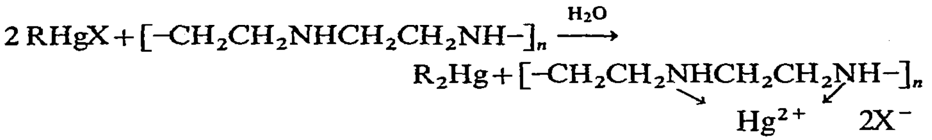
Many procedures are available for effecting the disproportionation of monoorganomercury compounds (eqn. 1)[1,2]. However, not all of them are generally applicable and not all of them are applicable to the rapid, quantitative, large-scale preparation of R_2Hg compounds from RHgX derivatives. We have discovered a new procedure for effecting the disproportionation reaction (eqn. 1) which is very easily carried out

$$2\,RHgX \rightarrow R_2Hg + HgX_2 \qquad (1)$$

and gives nearly quantitative yields of very pure diorganomercury compounds and which, furthermore, is capable of large-scale application. The recently reported dicobalt octacarbonyl-catalyzed synthesis of aromatic ketones by the reaction of diarylmercury compounds with gaseous carbon monoxide at atmospheric pressure[3] is a process to which our new redistribution procedure can be most effectively coupled.

RESULTS AND DISCUSSION

When a monoaryl- or a monoalkylmercury derivative is dispersed in an excess of an anhydrous polyamine such as ethylenediamine, diethylenetriamine or any of the polyethyleneimines (Dow PEI) and water is added to the mixture, spontaneous disproportionation occurs. In the case of arylmercuric derivatives, the diarylmercury compound precipitates while the inorganic mercury species which is formed remains in solution as the polyamine complex. Eqn. 2 describes this process for the case of the



$$2\,RHgX + [\!-CH_2CH_2NHCH_2CH_2NH-]_n \xrightarrow{H_2O} R_2Hg + [\!-CH_2CH_2NHCH_2CH_2NH-]_n \cdot Hg^{2+}\ 2X^- \quad (2)$$

polyethyleneimine. The reaction mixtures become warm due to the heat of hydration of the polyamine and warming of the mixtures to not above 50° for 1 hour results in the formation of the diarylmercurial in practically quantitative yield. The product is recovered by filtering, washing with water and drying. Excellent purities generally are obtained. Temperatures above 50° should be avoided since some reduction of the inorganic mercury complex to metallic mercury occurs. Mercury metal can be recovered quantitatively from the Hg^{II}–polyamine complexes by reduction with sodium borohydride.

Dimethylmercury is conveniently prepared by this general procedure on a large scale. The product is easily recovered from the reaction mixture by codistillation with water (a process during which much of the inorganic mercury product is reduced), separating the bottom product layer from the distillate and drying.

In these disproportionation reactions Dow Chemical Company "PEI-6", a polyethyleneimine of mol.wt. 600, gives the best results: yields of 95% or better and excellent purities. Ethylenediamine converted phenylmercuric acetate to diphenylmercury in only 28% yield under the mild conditions used, while diethylenetriamine gave diphenylmercury in 40% yield. This procedure does not appear to be applicable to olefin mercuration products. Thus (2-methoxycyclohexyl)mercuric chloride was not converted to the symmetrical mercurial by PEI-6/H_2O, but rather was deoxymercurated by the action of this reagent.

EXPERIMENTAL

Starting materials

The RHgX starting materials were obtained from Wood Ridge Chemical Division, Ventron Corp., or Alfa Inorganics, Inc.

Conversion of phenylmercuric acetate to diphenylmercury

One g of phenylmercuric acetate was dispersed in 3 g of Dow PEI-6, a polyethyleneimine with mol.wt. 600, and 10 ml of water was added. The temperature of the mixture increased spontaneously to *ca.* 50°. At the same time, the phenylmercuric acetate disproportionated to give a light, flocculent suspension of diphenylmercury. The mixture was allowed to stand for 1 h, then was filtered to remove the solid. The latter was washed with water and dried in air to give 0.5 g (94%) of diphenylmercury, m.p. 120–124° (m.p. of pure material, 122°). The filtrate retained the rest of the mercury as the soluble PEI-6–mercuric acetate complex.

Conversion of methylmercuric acetate to dimethylmercury

Thirty ml of an acetic acid solution of 53 mmol of methylmercuric acetate was mixed with an aqueous solution (40 ml) containing 33% of PEI-6. After the exothermic reaction had subsided, the reaction mixture was distilled over a temperature range of 73–94° at atmospheric pressure. The distillate separated into two liquid layers. The bottom layer, 9.15 g, was dried over anhydrous potassium carbonate. Gas chromatography indicated that it was dimethylmercury of better than 99% purity, and its infrared spectrum was identical with that of an authentic sample.

Caution: Dimethylmercury is toxic; this preparation should be carried out in a good hood.

Table 1 lists further examples.

TABLE 1

DIORGANOMERCURIALS BY DISPROPORTIONATION OF MONOORGANOMERCURY DERIVATIVES WITH "PEI-6" AND WATER

RHgX	Wt. (g)	PEI-6 (g)	H_2O (ml)	Product	Yield (%)	Hg (%) found (calcd.)	M.p.
PhHgOAc	1	3	10	Ph_2Hg	94	58.0 (58.1)	122
PhHgOH	1	3	100	Ph_2Hg	86	58.3 (58.1)	122.5
PhHgBr	1	3	10	Ph_2Hg	91		121–123.5
p-MeC_6H_4HgOAc	5	15	200	(p-$MeC_6H_4)_2Hg$	98	52.3 (52.2)	
$Me_2C_6H_3HgOAc$ (mixed isomers)	5	15	200	$(Me_2C_6H_3)_2Hg$	98	48.9 (48.8)	
2,4,6-$Me_3C_6H_2HgOAc$	5	15	200	(2,4,6-$Me_3C_6H_2)_2Hg$	97	45.4 (45.5)	240.5–241.5
MeHgOAc (in HOAc)	1524	1090	2000	Me_2Hg	75		B.p. 92–94°

ACKNOWLEDGEMENTS

We wish to acknowledge the valuable laboratory assistance of E. G. Cadmus, Wood Ridge Chemical Div., Ventron Corporation, Dr. Bernd Schneider, Alfa Inorganics, Inc., and Dr. Ralph J. Spohn, M.I.T.

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