

A CONVENIENT METHOD FOR THE PREPARATION OF BIS(CYCLOPENTADIENYL)MERCURY IN HIGH YIELD

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Bis(cyclopentadienyl)mercury has previously been prepared from sodium cyclopentadienide and mercuric chloride in 20% yield¹ and from thallium cyclopentadienide and mercuric chloride in 97% yield.²

During a study of the reactions of some metal oxides, it was observed that yellow mercuric oxide readily dissolved at room temperature in a mixture containing monomeric cyclopentadiene and a primary amine. When the solution was centrifuged to remove a small quantity of insoluble material and evaporated, the pale buff solid residue was found to be pure bis(cyclopentadienyl)mercury in yields of 85% or better.

Primary amines of low molecular weight and correspondingly low boiling points were preferred, since they could be readily removed after the reaction. For instance, both *n*-propylamine and isopropylamine gave equally good results. Secondary amines were unsuitable, because they led to other reaction products and in the presence of tertiary amines no apparent reaction took place. When liquid ammonia was used, yields of bis(cyclopentadienyl)mercury of 90% or better were obtained when the mixture was vigorously stirred to overcome solubility problems.

Bis(cyclopentadienyl)mercury is sensitive to light, moisture, atmospheric oxygen, and heat, and precautions have to be taken to exclude them during reaction and storage. The pure product, even when stored protected from light and moisture, gradually turned grey and became insoluble in solvents like pyridine or diethyl ether. Any unchanged compound could be recovered by extraction with diethyl ether. The purity of several preparations was checked by elementary analysis, by the melting point, and by the i.r. spectrum which agreed with the one reported.¹

Experimental

Materials

Mercuric oxide (yellow, B.P.) from May & Baker was used. *n*-Propylamine and isopropylamine were dried over solid sodium hydroxide and redistilled; the fractions with b.p. 48–52°/760 mm and 34–40°/760 mm respectively were collected. Freshly cracked monomeric cyclopentadiene was used in all preparations.

Bis(cyclopentadienyl)mercury

Procedure A.—Mercuric oxide (2.17 g, 0.01 mole) was added in several portions to cyclopentadiene (10 ml, 0.12 mole) and *n*-propylamine or isopropylamine (6 ml) and the mixture

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¹ Wilkinson, G., and Piper, T. S., *J. inorg. nucl. Chem.*, 1956, **2**, 32.

² Nesmeyanov, A. N., Materikova, R. B., and Kochetkova, N. S., *Izv. Akad. Nauk SSSR (Ser. Khim.)*, 1963, No. 7, 1334.

shaken with exclusion of light. The reaction mixture became warm and a yellow solution formed quickly which was centrifuged in a stoppered tube. The solvent was evaporated under nitrogen at reduced pressure at room temperature. The yields of several preparations varied between 85 and 90%; m.p. 83–84° (with decomposition) (Found: C, 36.1; H, 3.2. Calc. for $C_{10}H_{10}Hg$: C, 36.3; H, 3.1%).

Procedure B.—Mercuric oxide (10.8 g, 0.05 mole) and cyclopentadiene (30 ml, 0.36 mole) were stirred vigorously with dry ice–acetone cooling while ammonia was condensed into the mixture. Gradually partial solution occurred, the ammonia layer turned green, and the orange mercuric oxide changed to a pale yellow solid. About 30 ml of ammonia were collected and the stirring continued for 1 hr. After completion of the reaction, nitrogen was passed into the mixture without further cooling until the ammonia and excess cyclopentadiene were volatilized. The last traces of volatile matter were removed under vacuum at room temperature. The yield depended on the completeness of the conversion and was 90% or better. The product could be purified from any unchanged mercuric oxide by extraction with diethyl ether (Found: C, 36.2; H, 3.1%).