[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF DIALKYL MERCURY COMPOUNDS FROM THE GRIGNARD REAGENT. II. THE RELATIVE STABILITY OF THE CARBON-MERCURY LINKAGE IN DIALKYL MERCURY COMPOUNDS

BY C. S. MARVEL AND H. O. CALVERY

Received December 8, 1922

In a previous paper[1] suitable conditions were described for the preparation of several simple dialkyl mercury compounds from the corresponding Grignard reagents and mercuric chloride. The compounds studied contain the linkage, RCH_2-Hg-, in almost every case. The one exception is mercury di-*iso*propyl which contains the linkage, R_2CH-Hg-. Since there is considerable difference in the stability of various compounds containing the carbon-mercury union, it seemed desirable to extend this method of preparing dialkyl mercury compounds to include substances with the linkages, R_2CH-Hg- and R_3C-Hg-. It would then be possible to study in closely related compounds the stability of the carbon-mercury union when mercury is attached to a primary, a secondary or a tertiary alkyl radical.

Very few data have appeared in the literature concerning secondary alkyl mercury compounds. Mercury di-*iso*propyl,[2] mercury di-*sec*-butyl[3] and mercury dicyclohexyl [4] are the only compounds of this type that have been described. No mention has been made of the stability of the true dialkyl mercury compounds. The cyclohexyl derivatives are unstable to light and heat and reduce acid solutions of silver and gold salts.[4]

Nothing is known concerning compounds containing mercury attached to a tertiary alkyl group, since none has been prepared. Kharasch and Stavely[5] have obtained compounds of the type, CH_3COCR_2-Hg-CR_2-$COCH_3$, by decomposing the mercury salts of substituted aceto-acetic acids. They have found that this type of mercury compound is unstable toward heat, easily losing mercury to give a diketone.

By use of the Grignard reagent it has been possible to prepare compounds containing mercury attached to secondary and tertiary alkyl groups. The conditions for the preparation of the secondary alkyl mercury compounds are identical with those described in the previous paper.[1] The tertiary alkyl mercury compounds are best obtained by allowing the Grignard reagent to react with the mercuric halide at room temperature.

---

[1] THIS JOURNAL, **44**, 153 (1922).

[2] Ref. 1; *C. A.*, **16**, 3062 (1922).

[3] *Ber.*, **39**, 3628 (1906).

[4] *Ibid.*, **47**, 1655 (1914).

[5] Paper read before the Organic Section of the American Chemical Society at the Pittsburgh Meeting, 1922.

Two reactions of the dialkyl mercury compounds were studied to determine the relative stability of the carbon-mercury linkage when mercury is attached to a primary, a secondary or a tertiary alkyl group. These reactions are represented by the following equations: $\text{R-Hg-R} + \text{HCl} \longrightarrow \text{R-Hg-Cl} + \text{R-H}$; $\text{R-Hg-R} \xrightarrow{\text{heat}} \text{R-R} + \text{Hg}$.

These reactions were carried out with the 3 isomeric compounds, mercury di-*n*-butyl, mercury di-*sec*-butyl and mercury di-*tert*-butyl. The results clearly show that the carbon-mercury linkage is much more readily broken when mercury is attached to a tertiary alkyl group than when it is attached to a secondary alkyl group. This latter linkage is more readily broken than when mercury is attached to a primary alkyl group. This decrease in stability of the carbon-mercury linkage in the series, RCH_2-Hg-, R_2CH-Hg-, R_3C-Hg-, is not surprising and it agrees with the facts already known concerning the alcohols, halides and other compounds. Thus it is much easier to eliminate the hydroxyl group of a tertiary alcohol than that of a secondary alcohol, and this is more easily removed than is a primary alcohol group.

Experimental Part

Mercury Di-*sec*-butyl.[6]—The Grignard reagent, prepared from 12 g. of magnesium and 75 g. of *sec*-butyl bromide in 500 cc. of dry ether, was treated with 45 g. of mercuric chloride. The reaction mixture was refluxed for 8 hours and then worked up as described in the earlier paper.[1] The yield of mercury di-*sec*-butyl boiling at 93–96° under 18 mm. pressure was 35 g. (66% yield); d_{20}^{20}, 1.763; n_D^{20}, 1.511.

Analysis. Subs., 0.500: CO_2, 313 cc. (25°, 750 mm.). Calc. for $C_8H_{18}Hg$: C, 30.57. Found: 30.68.

***sec*-Butyl Mercuric Chloride.**—Mercury di-*sec*-butyl was dissolved in alcohol and treated with aqueous hydrochloric acid. In a short time *sec*-butyl mercuric chloride separated as an oil which could be frozen to a white solid by cooling the reaction mixture in an ice- and salt-bath. After recrystallization from alcohol the product melts at 30.5°. It is necessary to cool the alcohol very thoroughly in order to obtain the crystals.

Analysis. Subs., 0.5000: CO_2, 166.9 cc. (25°, 750 mm.). Calc. for C_4H_9HgCl: C, 16.44. Found: 16.48.

***sec*-Butyl Mercuric Bromide.**—This was prepared as was the compound just described except that hydrobromic acid was used. The *sec*-butyl mercuric bromide melts at 39°.

Analysis. Subs., 0.500: CO_2, 144.7 cc. (25°, 742 mm.). Calc. for C_4H_9HgBr: C, 14.24. Found: 13.83.

Mercury Di-*sec*-octyl.—The Grignard reagent prepared from 8 g. of magnesium and 70 g. of *sec*-octyl bromide (2-bromo-octane) in 500 cc. of dry ether was treated with 21 g. of mercuric chloride. The reaction mixture was boiled under a reflux condenser for 6 hours and was then worked up in the usual manner. The product could not be distilled even under 3 mm. pressure on account of decomposition with the formation of free mercury. The crude product weighed 48 g. (52% yield); d_{20}^{20}, 1.338; n_D^{20}, 1.334.

---

[6] Most of the work on the *sec*-butyl derivatives was done by A. O. Beckman.

Analysis showed that the product was not entirely pure and contained some hydrocarbon and free mercury.

Analysis. Subs., 0.5000: CO_2, 462.8 cc. (23°, 746 mm.). Calc. for $C_{16}H_{39}Hg$: C, 45.07. Found: 43.76.

***sec*-Octyl Mercuric Bromide.**—The Grignard reagent was prepared from *sec*-octyl bromide and then treated with a slight excess of mercuric bromide. Water was added, the ether layer separated and evaporated. The *sec*-octyl mercuric bromide after recrystallizing from alcohol melted at 98°.

Analysis. Subs., 0.5000: CO_2, 236.6 cc. (0°, 760 mm.). Calc. for $C_8H_{17}HgBr$: C, 24.42. Found: 25.08.

Mercury Di-*tert*-butyl.—The Grignard reagent was prepared from 6 g. of magnesium and 35 g. of *tert*-butyl bromide in 500 cc. of dry ether. The solution of Grignard reagent was then transferred to a 2-neck flask fitted with a mechanical stirrer and a stopper carrying a calcium chloride tube. The stirrer was started and 20 g. of mercuric bromide was added in portions by removing the stopper carrying the calcium chloride tube. This addition required about three quarters of an hour. The flask was cooled in a pan of water to avoid decomposition of the reaction product. The stirring was continued for 6 to 8 hours. Water was then added and the ether layer separated, washed with water and dried over calcium chloride. The ether was allowed to evaporate spontaneously. As the solution became more concentrated, a considerable amount of *tert*-butyl mercuric bromide crystallized. This was separated. When all of the ether had evaporated, the residue was distilled under reduced pressure. The yield of mercury di-*tert*-butyl was about 2 g. (9%) boiling at 78–82° under 5 mm. pressure. Considerable decomposition occurred even under these conditions and the final product contained some hydrocarbon as is indicated by the analysis; d_{20}^{20}, 1.749; n_D^{20}, 1.521.

Analysis. Subs., 0.5000: CO_2, 291 cc. (0°, 760 mm.). Calc. for $C_8H_{18}Hg$: C, 30.57. Found: 31.20.

***tert*-Butyl Mercuric Bromide.**—The Grignard reagent prepared from *tert*-butyl bromide was treated in the cold with an excess of mercuric bromide. After about 1 hour the reaction mixture was decomposed with water, the ether layer separated and dried over calcium chloride. The ether was then allowed to evaporate. When the product was heated even in a solvent, it decomposed, giving mercurous bromide. It could not be recrystallized. The melting point was determined by dipping capillary tubes containing the substance into an oil-bath heated to various temperatures. It melts with decomposition at 106°. Bright sunlight causes very rapid decomposition.

Analysis. Subs., 0.250: CO_2, 66.1 cc. (0°, 760 mm.). Calc. for C_4H_9HgBr: C, 14.24. Found: 14.16.

Mercury Di-*tert*-amyl.—The Grignard reagent, prepared from 12 g. of magnesium and 80 g. of *tert*-amyl bromide in 500 cc. of dry ether, was treated with 40 g. of mercuric bromide. The procedure was exactly like that described under the preparation of mercury di-*tert*-butyl. The yield of mercury di-*tert*-amyl before distillation was 9 g. (21%). When distilled in 2- to 3-g. portions the compound boils at 80–84° under 5 mm. pressure. Considerable decomposition occurs even under these conditions; d_{20}^{20}, 1.649; n_D^{20}, 1.492.

Analysis. Subs., 0.5000: CO_2, 356.4 cc. (25°, 750 mm.). Calc. for $C_{10}H_{22}Hg$: C, 35.29. Found: 34.6

***tert*-Amyl Mercuric Bromide.**—This compound was obtained in the same manner as was described for *tert*-butyl mercuric bromide. It can be recrystallized from alcohol if the solution is not heated above 50°. The melting point of the pure product is 82°.

Analysis. Subs., 0.5000: CO_2, 177.1 cc. (25°, 743 mm.). Calc. for $C_5H_{11}HgBr$: C, 17.1. Found: 17.0.

Index of Refraction of Other Dialkyl Mercury Compounds.—Previous workers have never recorded the values for the indices of refraction of the liquid mercury compounds. These values have been determined on all of the dialkyl compounds which were available. The following values were observed at 20°: mercury dimethyl, 1.532; mercury diethyl, 1.543; mercury di-*n*-propyl, 1.517; mercury di-*iso*propyl, 1.532; mercury di-*n*-butyl, 1.504.

Stability of the Dialkyl Mercury Compounds toward Hydrochloric Acid.—One-half g. samples of each of the 3 dibutyl mercury derivatives were placed successively in a small flask and treated with 10 cc. of conc. hydrochloric acid. A delivery tube connected the flask to a nitrometer in which the butane that was formed was collected and measured. The time required for the reaction of the dibutyl compound with hydrochloric acid to give butane and butyl mercuric chloride was noted. The experiments were carried out at 26°. The reaction between mercury di-*n*-butyl and hydrochloric acid was complete in 12 to 13 minutes; mercury di-*sec*-butyl reacted in about 6 minutes; mercury di-*tert*-butyl reacted in about 2 minutes.

Mercury di-*iso*propyl was compared with mercury di-*n*-propyl in the same way. The *iso*propyl compound reacted in 28 to 30 minutes, while the *n*-propyl compound required 50 to 55 minutes.

Stability of the Mercury Dibutyl Compounds Towards Heat.—In attempting to prepare mercury di-*tert*-butyl it was found that this compound was very unstable toward heat and easily decomposed to give metallic mercury. It has often been observed that other dialkyl mercury compounds decompose when heated to temperatures around 200°, giving metallic mercury and a hydrocarbon.

One-cc. samples of each of the 3 mercury dibutyl compounds were placed in small test-tubes and heated in a water-bath at 40°. The temperature of the bath was maintained at approximately this point for about 30 minutes. During this time the sample of mercury di-*tert*-butyl completely decomposed, giving metallic mercury. That decomposition was complete was shown by the fact that after removal of the mercury no further decomposition occurred when the sample was heated over a flame. The samples of mercury di-*n*-butyl and mercury di-*sec*-butyl showed no signs of decomposition after heating for 1 hour at 40°.

No temperature was found at which mercury di-*n*-butyl was stable and mercury di-*sec*-butyl decomposed. However, when samples of these compounds were heated at 110° in an oil-bath, mercury di-*sec*-butyl showed signs of decomposition within 2 minutes, whereas no mercury separated from mercury di-*n*-butyl until this temperature was maintained for 3 to 4 minutes.

Summary

1. The reaction between the Grignard reagent and mercuric halides has been applied to the preparation of dialkyl mercury compounds containing secondary and tertiary alkyl groups.

2. The reactions with heat and with acids indicate that the carbon-mercury linkage in R_3C-Hg- is more easily broken than that in R_2CH-Hg- and this in turn more easily than that in RCH_2-Hg-.

URBANA, ILLINOIS