

THE PREPARATION AND STUDY OF SOME ORGANOMERCURIC DERIVATIVES OF NEOBARENES (*m*-CARBORANES)

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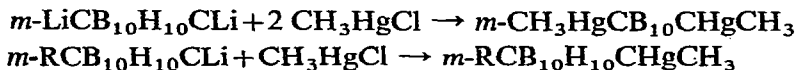
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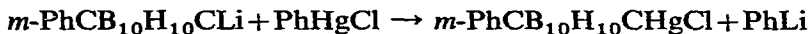
It has previously been shown in our laboratory¹ that some properties of barenylmercury compounds such as high thermal stability, great resistance to protonic acids and weak tendency to disproportionation are similar to the properties of pentafluoro-² and pentachlorophenylmercury compounds³. It was assumed that these properties of the organomercuric derivatives of barenes are conditioned by the unusual co-ordination state of the barenic carbon atom bonded to the mercury atom, by steric hindrance and the strong inductive electron-withdrawing effect of the barenic system. In the present paper, we describe the preparation of some neobarenylmercury compounds and discuss their properties. It is known^{4,5} that the neobarenyl group (neobarene, *m*-C₂B₁₀H₁₂) exhibits a weaker electron-withdrawing effect than the barenyl group (barene, *o*-C₂B₁₀H₁₂). We considered that a comparison of the properties of mercuric derivatives of barenes and neobarenes would permit a more exact determination of the electron-withdrawing effect on the properties of the C-Hg bond in this class of compounds. Symmetrical neobarenylmercury compounds are easily formed by the action of the lithium derivatives of neobarenes on mercuric chloride:



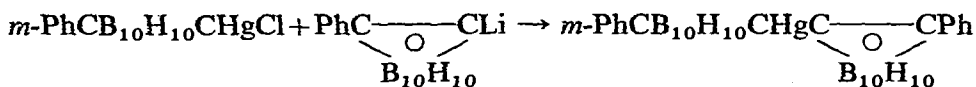
Mixed methyl compounds are readily prepared by the action of lithiumneobarenes on methylmercuric chloride:



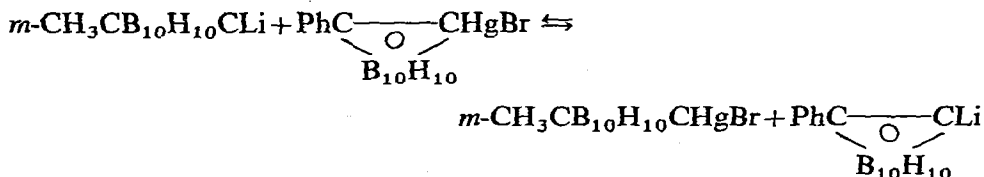
In the reaction of phenylneobarenyllithium with phenylmercuric chloride in benzene solution, phenyl(phenylneobarenyl)mercury was obtained together with small amounts of bis(phenylneobarenyl)mercury and diphenylmercury. The amount of two latter compounds increases in the presence of THF. It seems that bis(phenylneobarenyl)mercury and diphenylmercury are formed according to the following exchange reaction:



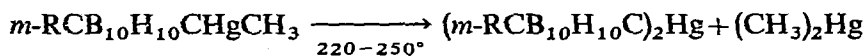
Phenyl(phenylneobarenyl)mercury can be obtained in good yield from phenylneobarenylmercuric halide and phenylmagnesium bromide. Phenylneobarenyl(phenylbarenyl)mercury was prepared from phenylneobarenylmercuric chloride and phenylbarenyllithium:



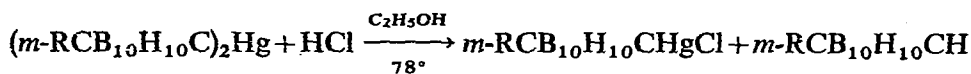
However, in the reaction of methylneobarenylmercuric bromide with phenylbarenyllithium or methylneobarenyllithium with phenylbarenylmercuric bromide, a mixture of methylneobarenyl(phenylbarenyl)mercury, bis(methylneobarenyl)mercury and bis(phenylbarenyl)mercury is formed. It is probable that the two latter compounds are formed also as the result of an exchange reaction as follows:



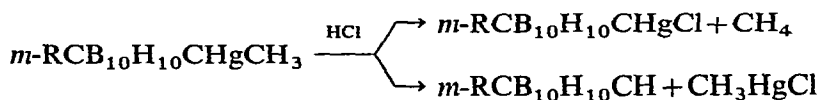
A study of neobarenylmercury compounds shows that they are distinguishable from alkyl- and aryl-mercurials and are similar in many respects to organomercury compounds containing a strong electron-withdrawing group (e.g., perfluoroalkyl-, pentafluorophenyl- and ethynyl-). Symmetrical neobarenylmercury compounds such as bis(methylneobarenyl)- and bis(phenylneobarenyl)mercury possess a high thermal stability; they were unchanged after several hours heating at 250–275°—similar to bis(phenylbarenyl)mercury¹ and bis(pentafluorophenyl)mercury². That the neobarenyl groups in the mercuric derivatives of neobarenes are strong electron acceptors toward the mercury atom is borne out by the polarographic reduction measurement of bis(methylneobarenyl)mercury; the half-wave potential obtained (in dimethylformamide) was $E_{1/2} = -1.36$ V. The half-wave potential obtained previously¹ for bis(dimethylbarenyl)mercury was $E_{1/2} = -0.80$ V and for diphenylmercury, $E_{1/2} = -2.60$ V. These data indicate that the polarity of the C–Hg bond in neobarenic compounds is considerably larger than the polarity of the C–Hg bond in diarylmercurials but is smaller than the polarity of the C–Hg bond in barenic compounds. Mixed compounds—methyl(methylneobarenyl)- and methyl(phenylneobarenyl)mercury—also show considerable thermal stability; they are, however, completely symmetrized on heating at 220–250°:



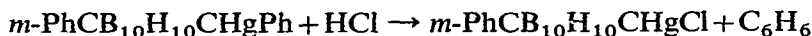
In contrast to dialkyl- and diaryl-mercurials, which react easily with protonic acids, symmetrical neobarenylmercury compounds are quite resistant to hydrogen chloride. The rupture of the C–Hg bond in bis(methylneobarenyl)- and bis(phenylneobarenyl)mercury takes place slowly only on prolonged boiling in alcoholic hydrogen chloride:



However, this reaction proceeds more easily than in case of bis(phenylbarenyl)mercury¹. In the reaction of methyl(methylneobarenyl)- and methyl(phenylneobarenyl)mercury with alcoholic hydrogen chloride under reflux there is a more extensive splitting of the CH₃–Hg bond and less splitting of the Hg–neobarenyl bond:

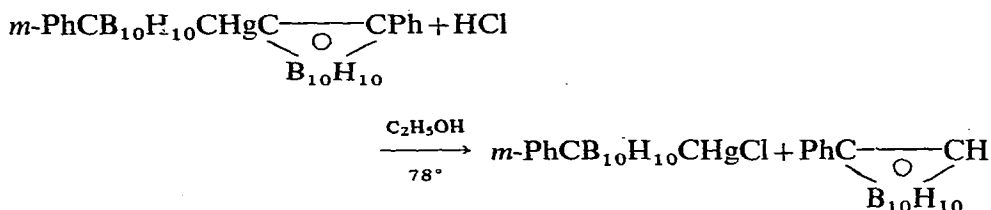


Methyl(phenylbarenyl)mercury gives with alcoholic hydrogen chloride only phenylbarene and no methane¹. The action of alcoholic hydrogen chloride on phenyl-(phenylneobarenyl)mercury under reflux results in phenylneobarenylmercuric chloride and benzene:

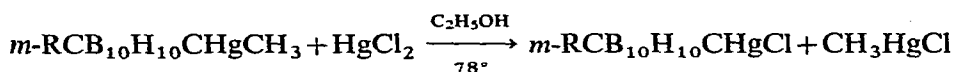
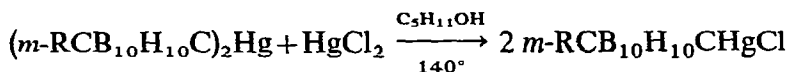


The above results indicate that, in spite of the high polarity of the Hg-neobarenyl bond, the neobarenyl group stands near the methyl group in the Kharasch series.

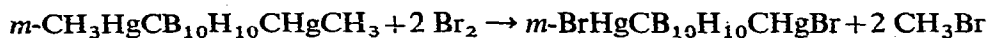
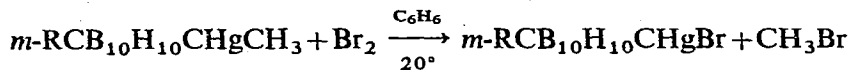
Phenylneobarenyl(phenylbarenyl)mercury reacts with alcoholic hydrogen chloride on prolonged heating with preferential cleavage of a phenylbarenyl group to phenylbarene:



Dessy and Kim concluded that the rate of cleavage of a group from mercury by hydrogen chloride depends on the electron density at the mercury-bonded carbon atom⁶. The nature of neobarenic carbon atoms and barenic carbon atoms is very similar. On this basis, the above result indicates that the electron density on the mercury-bonded carbon atom of a neobarenyl group is lower than with the barenyl group. It should also be noted that the rates of cleavage of phenyl and methyl groups from mercury by hydrogen chloride in phenyl- and methyl(neobarenyl)mercurials are slower than in diphenyl- and dimethylmercury, respectively. Neobarenylmercury compounds react with mercuric chloride more easily than barenylmercury compounds but much more slowly than dialkyl- and diaryl-mercurials:



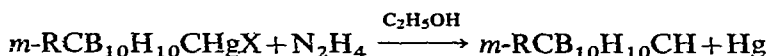
In the reaction of methyl(methylneobarenyl)- and methyl(phenylneobarenyl)-mercury and 1,7-bis(methylmercury)neobarene with bromine in benzene solution only, the CH₃-Hg bond is broken, the Hg-neobarenyl bonds are unaffected:



The cleavage of the CH₃-Hg bond in neobarenyl compounds by bromine proceeds

more easily than the cleavage of $\text{CH}_3\text{-Hg}$ bond in methyl(phenylborenyl)mercury¹, probably because it is bonded with the weaker electron-withdrawing power of the neoborenic system. The ionic character of the Hg-Cl(Br) bond in neoborenyl compounds is apparently greater compared to borenyl compounds, and neoborenyl-mercuric halides are less soluble in hydrocarbons than borenylmercuric halides. Bis(methylneoborenyl)- and bis(phenylneoborenyl)mercury react very slowly with bromine in benzene solution; furthermore, this reaction is accompanied by side reactions resulting in the evolution of hydrogen bromide.

Neoborenylmercuric halides are resistant to the action of symmetrizing agents such as potassium cyanide and potassium iodide on heating in ethanol solution. The action of symmetrizing agents, such as hydrazine, on methylneoborenylmercuric bromide and phenylneoborenylmercuric chloride in alcoholic solution gives metallic mercury, methylneoborene and phenylneoborene only:



When methylneoborenylmercuric chloride and phenylneoborenylmercuric bromide are refluxed in methoxyethanol solution, metallic mercury and methylneoborene and phenylneoborene are formed.

The results of the present study of the action of some electrophilic reagents on neoborenylmercury compounds, and the previous data¹ show that the properties of borenyl- and neoborenyl-mercurials are sufficiently similar, that the major causes defining the character of electrophilic substitution at the borenic and neoborenic carbon atoms, must be identical. It is undoubtedly the weaker electron-withdrawing effect of the neoborenyl group that exerts an appreciable influence on the properties of the Hg-neoborenic bond. It seems, therefore, that neoborenylmercury compounds react more easily with electrophilic reagents than borenylmercury compounds. The preferential cleavage of the Hg-borenic bond in phenylneoborenyl(phenylborenyl)mercury by hydrogen chloride shows that the stronger electron-withdrawing borenyl group apparently decreases in this compound the reactivity of the Hg-neoborenic bond. The question about the electron density on mercury-bonded borenic and neoborenic carbon atoms cannot be solved on the grounds of the relative rates of the cleavage of borenyl and neoborenyl groups by hydrogen chloride, as the mechanism of this reaction in the case of these compounds is unknown.

EXPERIMENTAL

Bis(methylneoborenyl)mercury

To a stirred solution of methylneoborenyllithium⁵ (from 3.2 g of methylneoborene and 1.35 g of butyllithium) in benzene (35 ml) was added mercuric chloride (2.8 g) in dry THF. The mixture was refluxed for 2 h, cooled, treated with 20 ml of water and filtered from a small amount of metallic mercury. The organic layer was separated and dried over CaCl_2 . After the solvent had been removed, the residue was recrystallized from hexane and heated *in vacuo*. 3.6 g (69%) of bis(methylneoborenyl)mercury, m.p. 185–186°, was obtained. (Found: C, 13.98; H, 4.92; B, 42.11; Hg, 37.65. $\text{C}_6\text{H}_{26}\text{B}_{20}\text{Hg}$ calcd.: C, 13.98; H, 5.09; B, 42.00; Hg, 38.93%.)

Bis(phenylneobarenyl)mercury

To a stirred solution of phenylneobarenyllithium (from 4.4 g of phenylneobarene) in benzene, was added mercuric chloride (2.8 g) in THF. The mixture was refluxed for 2 h and treated as above. 5.9 g (81%) of bis(phenylneobarenyl)mercury, m.p. 178–179° (from heptane), was obtained. (Found: C, 30.39; H, 4.92; Hg, 31.16. $C_{16}H_{30}B_{20}Hg$ calcd.: C, 30.08; H, 4.72; Hg, 31.40%.)

Methyl(methylneobarenyl)mercury

To a solution of methylneobarenyllithium (from 3.2 g of methylneobarene) in benzene (35 ml) and ether (15 ml), was added methylmercuric chloride (5.6 g). The mixture was refluxed for 2 h. 5.7 g (75%) of methyl(methylneobarenyl)mercury, m.p. 123–124° (from hexane), was obtained. (Found: C, 12.79; H, 4.37; B, 29.33; Hg, 53.13. $C_4H_{16}B_{10}Hg$ calcd.: C, 12.88; H, 4.32; B, 29.01; Hg, 53.79%.)

Methyl(phenylneobarenyl)mercury

To a benzene solution of phenylneobarenyllithium (from 4.4 g of phenylneobarene) was added methylmercuric chloride (5.5 g). The mixture was heated for 2 h. 7.1 g (82%) of methyl(phenylneobarenyl)mercury, m.p. 140–141° (from hexane–benzene) was obtained. (Found: C, 24.73; H, 4.40; B, 25.06; Hg, 45.87. $C_9H_{18}B_{10}Hg$ calcd.: C, 24.85; H, 4.16; B, 24.87; Hg, 45.45%.)

1,7-Bis(methylmercury)neobarene

A mixture of dilithiumneobarene (from 1.5 g of neobarene) and methylmercuric chloride (5.5 g) in benzene (25 ml) and THF (10 ml), was refluxed for 2 h. 3.3 g (58%) of 1,7-bis(methylmercury)neobarene, m.p. 235–237° (from benzene–heptane), was obtained. (Found: C, 8.28; H, 2.75; B, 18.82; Hg, 70.01. $C_4H_{16}B_{10}Hg_2$ calcd.: C, 8.37; H, 2.79; B, 18.85; Hg, 70.07%.)

Phenyl(phenylneobarenyl)mercury

To 40 ml of a stirred benzene solution of phenylneobarenyllithium (from 2.2 g of phenylneobarene) was added 3.1 g of phenylmercuric chloride. The mixture was heated at 40° for 3 h. 2.8 g (56%) of phenyl(phenylneobarenyl)mercury, m.p. 138–140° (from hexane–benzene), was obtained. (Found: C, 34.70; H, 4.43; B, 21.43; Hg, 39.41. $C_{14}H_{20}B_{10}Hg$ calcd.: C, 33.83; H, 4.03; B, 21.75; Hg, 40.35%.)

Similarly, the reaction of phenylneobarenyllithium with phenylmercuric chloride in the presence of THF gave, together with phenyl(phenylneobarenyl)mercury, bis(phenylneobarenyl)mercury, m.p. 178–179°, and diphenylmercury, m.p. 125°.

Phenylneobarenyl(phenylbarenyl)mercury

A mixture of phenylbarenyllithium (from 0.6 g of phenylbarene) and phenylneobarenylmercuric chloride (1.3 g) in benzene (10 ml) was stirred and refluxed for 1 h. 1.1 g (60%) of phenylneobarenyl(phenylbarenyl)mercury, m.p. 159–160° (from heptane), was obtained. (Found: C, 30.02; H, 5.16; B, 34.13; Hg, 30.80. $C_{16}H_{30}B_{20}Hg$ calcd.: C, 30.08; H, 4.72; B, 33.80; Hg, 31.40%.)

The reaction of methylneobarenyllithium with phenylbarenylmercuric bromide

A mixture of methylneobarenyllithium (from 0.3 g of methylneobarene) and

phenylbarenylmercuric bromide (0.9 g) in benzene (5 ml) and 2 ml of THF was stirred and refluxed for 1 h. Thin-layer chromatography on alumina enabled bis(methylneobarenyl)mercury, methylneobarenyl(phenylbarenyl)mercury and bis(phenylbarenyl)mercury to be detected. The latter was isolated, m.p. 261–263°.

Similarly, treatment of phenylbarenyllithium with methylneobarenylmercuric bromide gave the same three compounds.

The symmetrization of methyl(methylneobarenyl)mercury

Methyl(methylneobarenyl)mercury (0.8 g) was heated at 220–250° for 2 h. A small quantity of the starting material was sublimed. The residue was recrystallized from hexane to give bis(methylneobarenyl)mercury, m.p. 185–186°.

Similarly, when methyl(phenylneobarenyl)mercury was heated, bis(phenylneobarenyl)mercury, m.p. 178–179°, was obtained.

Cleavage of methyl(methylneobarenyl)mercury with hydrogen chloride

A solution of methyl(methylneobarenyl)mercury (1.0 g) in ethanol (15 ml) and concentrated hydrochloric acid (3 ml) was heated for 6 h. The disappearance of the starting material and the presence of a small amount of methylneobarene was ascertained by means of thin-layer chromatography on alumina. Ethanol was evaporated *in vacuo* and the residue was recrystallized from benzene to give methylneobarenylmercuric chloride, m.p. 251–252°. (Found: C, 8.98; H, 3.43; Cl, 9.15. $C_3H_{13}B_{10}ClHg$ calcd. C, 9.16; H, 3.21; Cl, 9.05%.)

Cleavage of methyl(phenylneobarenyl)mercury with hydrogen chloride

The cleavage of methyl(phenylneobarenyl)mercury by a procedure similar to that used for methyl(methylneobarenyl)mercury gave a small amount of phenylneobarene and phenylneobarenylmercuric chloride, m.p. 210–211°. (Found: C, 20.80; H, 3.40; Cl, 8.13. $C_8H_{15}B_{10}ClHg$ calcd.: C, 21.10; H, 3.32; Cl, 7.81%.)

Cleavage of phenyl(phenylneobarenyl)mercury with hydrogen chloride

A solution of phenyl(phenylneobarenyl)mercury (0.7 g) in ethanol (15 ml) and concentrated hydrochloric acid (3 ml) was heated for 4 h. The disappearance of the starting material and phenylneobarene were ascertained by means of thin-layer chromatography. 0.55 g of phenylneobarenylmercuric chloride, m.p. 209–210°, was obtained.

Cleavage of bis(phenylneobarenyl)mercury with hydrogen chloride

The cleavage of bis(phenylneobarenyl)mercury by a procedure similar to that used for methyl(methylneobarenyl)mercury, after 12 h gave the initial compound, phenylneobarene and phenylneobarenylmercuric chloride, m.p. 209–211°.

Cleavage of phenylneobarenyl(phenylbarenyl)mercury with hydrogen chloride

A solution of phenylneobarenyl(phenylbarenyl)mercury (0.8 g) in ethanol (20 ml) and concentrated hydrochloric acid (3 ml) was refluxed for 12 h. The presence of phenylbarene and a negligible amount of phenylneobarene were detected by means of thin-layer chromatography. Ethanol was evaporated *in vacuo* and the residue was twice recrystallized from benzene to give phenylneobarenylmercuric chloride, m.p. 209–211°.

The reaction of methyl(phenylneobarenyl)mercury with mercuric chloride

A solution of methyl(phenylneobarenyl)mercury (2 g) and mercuric chloride (1.5 g) in *n*-butanol was refluxed for 6 h. Butanol was evaporated *in vacuo*, the residue was washed with diluted hydrochloric acid and water and dried. On recrystallization from benzene, phenylneobarenylmercuric chloride (1.4 g, 60%) m.p. 210–211°, was obtained.

Similarly, methyl(methylneobarenyl)mercury and mercuric chloride gave methylneobarenylmercuric chloride (72%), m.p. 251–252°.

The reaction of bis(phenylneobarenyl)mercury with mercuric chloride

A solution of bis(phenylneobarenyl)mercury (1.0 g) and mercuric chloride (1.0 g) in *n*-amyl alcohol was refluxed for 12 h. 1.2 g (84%) of phenylneobarenylmercuric chloride, m.p. 210–211°, was obtained.

Similarly, bis(methylneobarenyl)mercury and mercuric chloride gave methylneobarenylmercuric chloride (86%), m.p. 251–252°.

Methylneobarenylmercuric bromide

(1) A solution of methyl(methylneobarenyl)mercury (2.4 g) and bromine (1.04 g) in benzene (8 ml) was allowed to stand at 20° for 5 h. The crystals that separated were recrystallized from benzene. 2.6 g (92%) of methylneobarenylmercuric bromide, m.p. 233–234°, was obtained. (Found: C, 8.25; H, 2.94; Br, 18.50. $C_3H_{13}B_{10}BrHg$ calcd.: C, 8.24; H, 2.97; Br, 18.30%.)

(2) A solution of bis(methylneobarenyl)mercury (0.5 g) and bromine (0.16 g) in benzene (5 ml) was allowed to stand at 20° for 5 days. The solution slowly decolourised, and some hydrogen bromide was evolved. After recrystallization of the separated crystals from benzene, methylneobarenylmercuric bromide, m.p. 233–235°, was obtained.

Phenylneobarenylmercuric bromide

(1) A solution of methyl(phenylneobarenyl)mercury (2 g) and bromine (0.87 g) in 8 ml of benzene was refluxed for 5 min. The solution was cooled and the separated crystals were recrystallized from benzene. Phenylneobarenylmercuric bromide (2.2 g, 93%), m.p. 213–214°, was obtained. (Found: C, 19.52; H, 3.15; B, 21.77; Br, 16.02; Hg, 39.24. $C_8H_{15}B_{10}BrHg$ calcd.: C, 19.22; H, 3.02; B, 21.64; Br, 16.02; Hg, 40.12%.)

(2) Bis(phenylneobarenyl)mercury (0.6 g) and bromine (0.15 g) in benzene (5 ml) was allowed to stand for 5 days. Hydrogen bromide was evolved. Phenylneobarenylmercuric bromide, m.p. 212–214°, was obtained.

1,7-Bis(bromomercuric)neobarene

A solution of 1,7-bis(methylmercury)neobarene (1.0 g) and bromine (0.6 g) in benzene was refluxed for 10 min, cooled and filtered. The solid residue was washed with hot toluene; 1,7-bis(bromomercuric)neobarene (0.9 g, 73%), m.p. 314–316°, was obtained. (Found: C, 3.87; H, 1.50; B, 16.16; Br, 21.67; Hg, 56.77. $C_2H_{10}B_{10}Br_2Hg_2$ calcd.: C, 3.42; H, 1.42; B, 15.40; Br, 22.80; Hg, 57.00%.)

The reaction of phenylneobarenylmercuric bromide with hydrazine

A solution of phenylneobarenylmercuric bromide (1.0 g) and hydrazine (1.0 ml) in ethanol (10 ml) was heated for 10 min. Metallic mercury was formed. Thin-layer chromatography on alumina was used to ascertain the absence of the starting material and bis(phenylneobarenyl)mercury, and the presence of phenylneobarene. Phenylneobarene (0.3 g), m.p. 55–56°, was isolated from the reaction mixture.

The reaction of methylneobarenylmercuric chloride and hydrazine was carried out in a similar manner. Bis(methylneobarenyl)mercury was not detected in the reaction mixture. Methylneobarene was isolated.

ACKNOWLEDGEMENT

We are indebted to S.A. Soshka for polarographic measurements.

SUMMARY

The preparation of symmetrical and mixed neobarenylmercury compounds is described. Organomercuric derivatives of neobarenes react with electrophilic reagents (*e.g.*, hydrogen chloride, mercuric chloride, bromine) under more vigorous conditions than dialkyl- and diaryl-mercurials but more easily than barenylmercury compounds. Neobarenylmercury compounds show high thermal stability: however, methyl(methylneobarenyl)- and methyl(phenylneobarenyl)-mercury at 250° are symmetrized to give the corresponding bis(neobarenyl)mercurials. The reaction of phenylneobarenyl(phenylbarenyl)mercury with hydrogen chloride results in the preferential cleavage of a phenylbarenyl group as phenylbarene. The action of hydrazine on neobarenylmercuric halides gives metallic mercury and the corresponding neobarenes.

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