Academician A. N. NESMEYANOV, V. A. SAZONOVA, V. N. DROZD

and L. A. NIKONOVA

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. N. NESMEYANOV, V. A. SAZONOVA, V. N. DROZD and L. A. NIKONOVA

1-(1′-HALOFERROCENYL)BORIC ACIDS IN THE SYNTHESIS OF FERROCENE DERIVATIVES

As we have described previously, ferrocenylboric and 1,1′-ferrocenylenediboric acids ([1]) can be used for the synthesis of various ferrocene derivatives. Through 1,1′-ferrocenylenediboric acid, disubstituted ferrocene derivatives with identical substituents in the cyclopentadienyl rings have been obtained. Partial replacement of only one $B(OH)_2$ group by a halogen leads to 1-(1′-haloferrocenyl)boric acids—an interesting starting material for the synthesis of certain ferrocene derivatives with different substituents in the two cyclopentadienyl rings.

In the present work it is shown that, when the reaction of 1,1′-ferrocenylenediboric acid is carried out in a benzene–water mixture with cupric chloride or bromide, taken in an amount calculated for one $B(OH)_2$ group, 1-(1′-chloroferrocenyl)- and 1-(1′-bromoferrocenyl)boric acids are formed.

$$(HO)_2BC_5H_4FeC_5H_4B(OH)_2 \xrightarrow{CuX_2} XC_5H_4FeC_5H_4B(OH)_2,$$

where $X = Cl, Br$.

The structure of the 1-(1′-haloferrocenyl)boric acids was confirmed by obtaining from them the corresponding haloferrocenes after hydrolysis in the presence of zinc salts.

1-(1′-Haloferrocenyl)boric acids react, like arylboric acids, with mercury salts to form the corresponding mercury compounds of ferrocene: chloromercury 1-(1′-chloroferrocenyl)mercury and bromomercury 1-(1′-bromoferrocenyl)mercury, which are readily symmetrized by sodium thiosulfate to di-1-(1′-chloroferrocenyl)mercury and di-1,1′-(1′-bromoferrocenyl)mercury. By the action of iodine on these organomercury compounds of ferrocene, according to the method described for chloromercury ferrocenylmercury ([2]), we obtained the previously unknown 1′-chloro-1-iodoferrocene and 1′-bromo-1-iodoferrocene.

In an attempt to obtain the heteroannular chlorobromoferrocene by the action of cupric chloride on 1-(1′-bromoferrocenyl)boric acid, 1,1′-dichloroferrocene was

isolated:

$$BrC_5H_4FeC_5H_4B(OH)_2 \xrightarrow{CuCl_2} ClC_5H_4FeC_5H_4Cl.$$

This reaction confirms the ease, previously found by us, of halogen replacement in the ferrocene nucleus in the presence of copper salts ([3]).

Experimental Part

1-(1′-Chloroferrocenyl)boric acid. Into a flask equipped with a stirrer and a reflux condenser were placed 3.1 g of 1,1′-ferrocenylenediboric acid, moistened with 7 ml of methanol, and 4.7 g of $CuCl_2 \cdot 2H_2O$ (20% excess) in 75 ml of water and 60 ml of benzene were added. The mixture was boiled for 2.5 h, then cooled, and the unreacted 1,1′-ferrocenylenediboric acid was filtered off. The benzene layer was separated, and the aqueous layer was used for a repeated operation with the unreacted–

the precipitated 1,1′-ferrocenylenediboronic acid, with the addition of 70 ml of benzene. Then the aqueous layer was again separated from the benzene, saturated with NaCl, and extracted with ether. The benzene and ether extracts were combined and evaporated to 50 ml. 1-(1′-Chloroferrocenyl)boronic acid was extracted with a 10% KOH solution; the alkaline solution was washed twice with ether and acidified with 10% H_2SO_4. The precipitated 1-(1′-chloroferrocenyl)boronic acid was filtered off, washed with water, and dried over 65% H_2SO_4. Yield of 1-(1′-chloroferrocenyl)boronic acid: 1.56 g (52% of theory). The acid is sufficiently pure for further work. It crystallizes from water or aqueous alcohol; it has no sharp melting point, m.p. 159–161° (when the capillary is introduced into a preheated apparatus).

Found, %: C 45.53; 45.40; H 3.72; 3.77; Cl 13.76; 13.49;
Fe 20.76; 20.85; B 4.02; 4.04

$C_{10}H_{10}ClFeBO_2$. Calculated, %: C 45.45; H 3.81; Cl 13.42;
Fe 21.13; B 4.09

1-(1′-Bromoferrocenyl)boronic acid. Similarly, from 4 g of 1,1′-ferrocenylenediboronic acid, 6 ml of methanol, 8 g of $CuBr_2$ in 120 ml of water, and 100 ml of benzene, 2.9 g of 1-(1′-bromoferrocenyl)boronic acid (65% of theory) was obtained. The substance is recrystallized from water or aqueous alcohol. On determination of the melting point it softens at about 137°, solidifies again, and melts at 155–157°.

Found, %: C 38.85; 39.03; H 3.22; 3.37; B 3.50; Br 25.42;
Fe 18.05

$C_{10}H_{10}BrFeBO_2$. Calculated, %: C 38.89; H 3.26; B 3.50; Br 25.88; Fe 18.09

Hydrolysis of 1-(1′-haloferrocenyl)boronic acids. To 0.16 g of 1-(1′-chloroferrocenyl)boronic acid in 50 ml of water was added 0.25 g of $ZnCl_2$. On heating with steam, chloroferrocene distilled off; it was extracted with ether, and the ether was evaporated. This gave 0.10 g of chloroferrocene (79% of theory), m.p. 52–54°; after recrystallization from alcohol, m.p. 57–58°; a mixed sample with authentic chloroferrocene melted without depression.

Similarly, on hydrolysis of 0.20 g of 1-(1′-bromoferrocenyl)boronic acid in the presence of 0.4 g of zinc bromide in 40 ml of water, 0.15 g of bromoferrocene (88% of theory) was obtained, m.p. 28.5–30.5°; after recrystallization from methanol, m.p. 32–33°; a mixed sample with authentic bromoferrocene melted without depression.

Chloro-1-(1′-chloroferrocenyl)mercury. To a hot solution of 0.27 g of 1-(1′-chloroferrocenyl)boronic acid in 5 ml of alcohol and 50 ml of water was added an aqueous-acetone solution of 0.28 g of mercuric chloride. A yellow precipitate formed. The mixture was heated for another 5 min; the precipitate was filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. This gave 0.41 g (88% of theory) of chloro-1-(1′-chloroferrocenyl)mercury, m.p. 141–143°; after recrystallization from acetone, m.p. 144.5–145°.

Found, %: C 26.48; 26.55; H 1.78; 1.92; Cl 15.58; 15.49; Hg 43.41; 43.54; Fe 12.33; 12.38

$C_{10}H_8Cl_2HgFe$. Calculated, %: C 26.36; H 1.77; Cl 15.57; Hg 44.04; Fe 12.26

Bromo-1-(1′-bromoferrocenyl)mercury. Similarly, from 0.30 g of 1-(1′-bromoferrocenyl)boronic acid and 0.36 g of $HgBr_2$, 0.46 g of bromo-1-(1′-bromoferrocenyl)mercury was obtained (84% of theory), m.p.

142.5–145°; after recrystallization from acetone, m.p. 146.5–147°.

Found, %: C 22.17; 22.15; H 1.41; 1.48; Br 29.20; 29.15;
Hg 36.31; 36.37; Fe 10.39; 10.62

$C_{10}H_8Br_2HgFe$. Calculated, %: C 22.06; H 1.48; Br 29.35;
Hg 36.84; Fe 10.26

These mercury compounds are yellow crystalline substances, soluble in acetone, benzene, and chloroform; less readily in ether and alcohol.

Di-1-(1′-chloroferrocenyl)mercury. Chloro-1-(1′-chloroferrocenyl)mercury (0.33 g), moistened with acetone, was shaken for several hours with 20 ml of a

50% solution of sodium thiosulfate; then di-1-(1′-chloroferrocenyl)mercury was filtered off, washed with water, and dried over P_2O_5. Yield 0.21 g (95% of theory), m.p. 146–147°; after recrystallization from a mixture of xylene and hexane (with rapid cooling of the solution), m.p. 151–152°.

Found, %: C 37.57; 37.56; H 2.63; 2.60; Cl 11.06; 11.20;
Hg 31.00; 31.03; Fe 17.84; 17.92

$C_{20}H_{16}Cl_2HgFe_2$. Calculated, %: C 37.55; H 2.52; Cl 11.09;
Hg 31.38; Fe 17.47

Di-1-(1′-bromoferrocenyl)mercury. Similarly, from 0.35 g of bromo-1-(1′-bromoferrocenyl)mercury in 20 ml of a 50% solution of sodium thiosulfate, 0.245 g (94% of theory) of di-1-(1′-bromoferrocenyl)mercury was obtained, m.p. 134–135°. After recrystallization from nitromethane, m.p. 135–136°.

Found, %: C 32.93; 33.28; H 2.04; 2.10; Br 21.69; 21.83;
Hg 27.23; 27.34; Fe 15.13; 15.45

$C_{20}H_{16}Br_2HgFe_2$. Calculated, %: C 32.97; H 2.24; Br 21.94;
Hg 27.54; Fe 15.33

Symmetrical 1-(1′-haloferrocenyl)mercury compounds partially decompose on heating in solutions of xylene or nitromethane. Thus, after heating a xylene solution of di-1-(1′-bromoferrocenyl)mercury, bromoferrocene was isolated; therefore they crystallize with large losses.

1′-Chloro-1-iodoferrocene. To a solution of 1.00 g of chloro-1-(1′-chloroferrocenyl)mercury in 10 ml of hot xylene was added a hot solution of 3 g of iodine in 10 ml of xylene. After cooling, the black precipitate that separated was filtered off, washed with alcohol, and shaken in a separatory funnel with a solution of 45 g of sodium thiosulfate in 200 ml of water and ether. The yellow ethereal solution was filtered, the ether evaporated; 0.49 g of 1′-chloro-1-iodoferrocene was obtained (64% of theory), m.p. 38–40°. Its saturated solution in methanol at 40° is cooled with a mixture of dry ice in acetone, giving yellow crystals with m.p. 42–44°.

Found, %: C 34.63; 34.83; H 2.27; 2.35; Fe 16.28; 16.44;
sum of halogens —47.19; 47.24

$C_{10}H_8ClJFe$. Calculated, %: C 34.67; H 2.33; Fe 16.12;
sum of halogens —46.87

1′-Chloro-1-iodoferrocene is readily soluble in organic solvents.

1′-Bromo-1-iodoferrocene. Similarly, from 0.80 g of bromo-1-(1′-bromoferrocenyl)mercury in 10 ml of xylene and 3 g of iodine in 10 ml of xylene, 0.44 g (76% of theory) of 1′-bromo-1-iodoferrocene was obtained, m.p. 25–26°; upon cooling the saturated methanolic ···

from a solution of 1′-bromo-1-iodoferrocene, yellow crystals with m.p. 28–30° were obtained.

Found, %: C 30.62; 30.53; H 2.21; 2.22; Fe 13.87; 14.13

$C_{10}H_8BrJFe$. Calculated, %: C 30.73; H 2.06; Fe 14.19

1′-Bromo-1-iodoferrocene is readily soluble in organic solvents.

Action of cupric chloride on 1-(1′-bromoferrocenyl)boronic acid. 1,1′-Dichloroferrocene. A mixture of 1 g of 1-(1′-bromoferrocenyl)boronic acid and 1.7 g of cupric chloride in 120 ml of water was placed in a flask for steam distillation. After steam distillation, the 1,1′-dichloroferrocene was extracted with ether, and the ether was evaporated. 0.60 g of 1,1′-dichloroferrocene with m.p. 72–74° was obtained; after recrystallization from alcohol, m.p. 75–77°; a mixed sample with an authentic specimen melted without depression; analysis for C and H corresponds to dichloroferrocene.

Moscow State University
named after M. V. Lomonosov

Received
7 I 1960

CITED LITERATURE

1. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **126**, No. 5 (1959).

2. A. N. Nesmeyanov, E. G. Perevalova, O. A. Nesmeyanova, DAN, **100**, No. 6 (1955).

3. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **129**, No. 5 (1959); DAN, **130**, No. 5 (1960).

Note: Figure translations are in progress. See original paper for figures.