Soviet-era science, translated into English

CHEMISTRY

Academician A. N. NESMEYANOV, V. A. SAZONOVA, V. I. ROMANENKO

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.68130

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. N. NESMEYANOV, V. A. SAZONOVA, V. I. ROMANENKO

DERIVATIVES OF FERROCENYLAMINE

We have previously described the alkylation of ferrocenylamine with triethyloxonium borofluoride (^{1}). In the present work it is shown that, under the action of bromoferrocene on the sodium derivative of diphenylamine in the presence of CuBr, diphenylferrocenylamine is formed

$$\mathrm{BrFc} + (\mathrm{C_6H_5})_2\mathrm{NNa} \xrightarrow[120^\circ]{\mathrm{CuBr}} \mathrm{FcN}(\mathrm{C_6H_5})_2$$

Diphenylferrocenylamine is a typical tertiary aromatic amine; it does not form salts even with strong acids.

Monophenylferrocenylamine is obtained by heating bromoferrocene with the sodium derivative of acetanilide in the presence of CuBr

$$\mathrm{BrFc} + \mathrm{C_6H_5N(Na)COCH_3} \xrightarrow{\mathrm{CuBr}} \mathrm{FcN(C_6H_5)COCH_3} \longrightarrow \mathrm{FcNH(C_6H_5)}$$

The secondary amine is not extracted from solutions in organic solvents by dilute hydrochloric acid; with concentrated HCl (or when hydrogen chloride is passed through a heptane solution of phenylferrocenylamine) it gives the hydrochloride; with benzoyl chloride, the benzoyl derivative of monophenylferrocenylamine is formed.

In an attempt to obtain monophenylferrocenylamine by the interaction of ferrocenylamine with iodobenzene in the presence of CuI under ordinary conditions (heating in an ampoule for 2 hr at 120°), we isolated azoferrocene.

Further investigation showed that ferrocenylamine is readily oxidized by atmospheric oxygen in benzene solution at room temperature in the presence of CuBr or CuCl. For aromatic amines the oxidation reaction in the presence of a pyridine complex with CuCl or of copper acetate has been studied in detail (^{2,3,4}).

Ferrocenylamine is oxidized within 15 min to the extent of 36% to azoferrocene. The latter had previously been obtained by the action of ferrocenyl lithium on nitrogen oxide (^{5}). With more prolonged passage of air through a benzene solution of ferrocenylamine in the presence of CuBr, the oxidation of the amine to azoferrocene can be carried out quantitatively.

SovietRxiv

$$\mathrm{FcNH_2} \xrightarrow{O_2} \mathrm{FcN{=}NFc}$$

Investigation of the reaction mixture by thin-layer chromatography on Al_2O_3 in benzene showed that no reaction products other than azoferrocene are formed.

Substituents in the ferrocene nucleus affect the rate of the oxidation process of amines. Thus, 1-(1′-chloroferrocenyl)amine is oxidized to heteroannular dichloroazoferrocene with more difficulty than ferrocenylamine to azoferrocene.

$$\mathrm{ClC_{10}H_8FeNH_2} \xrightarrow{O_2} \mathrm{ClC_{10}H_8Fe{-}N{=}N{-}FeC_{10}H_8Cl}$$

1-(1′-Chloroferrocenyl)amine was obtained from 1-(1′-chloroferrocenyl)boronic acid and copper phthalimide in pyridine solution by the procedure described by us earlier for ferrocenyl- and arylboronic acids (6).

$$\mathrm{ClC_{10}H_8FeB(OH)_2} \rightarrow \mathrm{ClC_{10}H_8FeN(CO)_2C_6H_4} \rightarrow \mathrm{ClC_{10}H_8FeNH_2}$$

Since 1-(1′-chloroferrocenyl)amine is oxidized more slowly than ferrocenylamine, it is readily purified from admixtures of the latter. 1-(1′-Chloroferrocenyl)amine is a yellow crystalline substance, m.p. 116°. Its acetyl derivative melts at 124.5°.

Experimental Part

1. Diphenylferrocenylamine. To molten diphenylamine (2 g) was added 0.06 g of sodium, and the mixture was heated under nitrogen at 300° until the sodium had completely dissolved. The melt was then cooled to 90°, and 0.5 g of bromoferrocene and 1.5 g of CuBr were added to it. The mixture was thoroughly stirred and heated at 120° for one hour. After cooling, the reaction mixture was extracted repeatedly with petroleum ether; then a stream of HCl was passed through the resulting solution to remove diphenylamine. The precipitated diphenylamine hydrochloride was filtered off, and from the filtrate, after removal of the solvent, 0.44 g (67% of theory) of diphenylferrocenylamine was obtained as an oil rapidly crystallizing on cooling; the test for halogen was negative. In those cases where bromoferrocene does not react completely, it is readily separated chromatographically on Al_2O_3. Diphenylferrocenylamine is recrystallized from alcohol or heptane as orange crystals, m.p. 82°.

$C_{22}H_{19}FeN$.	Found, %:	C 74.40, 74.43; H 5.38, 5.51; N 3.85, 3.91; Fe 15.92, 15.78
	Calculated, %:	C 74.80; H 5.42; N 3.97; Fe 15.81

2. Monophenylferrocenylamine. To the sodium derivative of acetanilide, prepared from 0.75 g of acetanilide and sodium ethylate (from 0.13 g of sodium), were added 1 g of bromoferrocene and 1 g of CuBr, and the mixture was heated under nitrogen at 120° for 1 hour. The reaction mixture was extracted with ether, the ether was evaporated, and the residue was chromatographed on Al_2O_3. This gave 0.26 g of a mixture of ferrocene and bromoferrocene, 0.03 g of diferrocenyl upon elution with petroleum ether; the mixture of acetanilide with the acetyl derivative of monophenylferrocenylamine was washed with ether. This mixture was hydrolyzed by boiling in alcoholic solution (15 ml of alcohol) in the presence of 1 g of KOH. After hydrolysis, the alcoholic solution was diluted with water and extracted with ether. Aniline was extracted from the ethereal solution with 10% HCl, and then a small amount of conc. HCl was added; the hydrochloride of monophenylferrocenylamine precipitated, from which 0.40 g of amine was obtained (38% of theory, calculated on the bromoferrocene taken). Monophenylferrocenylamine is recrystallized from aqueous alcohol, m.p. 69.5–70.5°.

$C_{16}H_{15}FeN$. Found, %: C 69.64, 69.72; H 5.51, 5.41; N 5.26, 5.28; Fe 19.97, 19.73
Calculated, %: C 69.34; H 5.46; N 5.06; Fe 20.15

N-Benzoylphenylferrocenylamine. Benzoylation of 0.07 g of phenylferrocenylamine with benzoyl chloride in 10% KOH gave 0.09 g (92% of theory) of *N*-benzoylphenylferrocenylamine, m.p. 177° (under nitrogen); recrystallized from heptane.

Found, %: C 72.10, 72.00; H 5.11, 4.97; N 3.67, 3.92; Fe 14.66, 14.52
$C_{23}H_{19}FeNO$. Calculated, %: C 72.46; H 5.02; N 3.67; Fe 14.65

3. 1-(1′-Chloroferrocenyl)phthalimide. A mixture of 2 g of 1-(1′-chloroferrocenyl)boric acid and 4 g of copper phthalimide in 20 ml of pyridine was heated with constant shaking for 7–10 min, until the green color disappeared and a brown color appeared. The mixture was diluted with water and extracted with ether. The ether layer was washed with 10% KOH, water, 10% H_2SO_4 (until complete removal of pyridine), then again with water and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on Al_2O_3. Heptane eluted chloroferrocene, 0.84 g (50% of theory), m.p. 58–59°; a mixed sample with a known specimen melted without depression; benzene eluted 1-(1′-chloroferrocenyl)phthalimide, 0.87 g (31.6% of theory), m.p. 164.5-165.5° (from a benzene–heptane mixture).

Found, %: C 59.32, 59.51; H 3.38, 3.39; N 3.83, 3.87; Fe 15.21, 15.44; Cl 9.20, 9.01
$C_{18}H_{12}FeClNO_2$. Calculated, %: C 59.13; H 3.31; N 3.83; Fe 15.27; Cl 9.69

4. 1-(1′-Chloroferrocenyl)amine. A solution of 0.2 g of 1-(1′-chloroferrocenyl)phthalimide and 1 ml of hydrazine hydrate in 6 ml of alcohol was heated for half an hour. After cooling, the solution was diluted with water and extracted with ether. The ether layer was washed with water, 10% KOH, again with water, and the amine was extracted with 10% H_2SO_4; on alkalization of the acidic solution, a yellow precipitate of the amine separated, which was extracted with ether. The ethereal solution was washed with a small amount of water and the solvent was removed in vacuo. This gave 0.13 g of 1-(1′-chloroferrocenyl)amine (97% of theory). (To remove possible impurities of ferrocenylamine, air was passed for 5 min through a solution of 0.64 g of amine, obtained from several experiments, in 30 ml of benzene in the presence of 2 g of CuBr; the color immediately changed from yellow to cherry-red. The CuBr precipitate was filtered off, and 1-(1′-chloroferrocenyl)amine was extracted from the benzene solution with 10% H_2SO_4.)

1-(1′-Chloroferrocenyl)amine is a yellow crystalline substance, readily soluble in ether and benzene, less soluble in hexane; m.p. 116° (under nitrogen) after two recrystallizations from hexane.

Found, %: C 51.35, 51.49; H 4.38, 4.17; N 6.07, 5.92; Fe 23.65, 23.45; Cl 15.25, 14.97
$C_{10}H_{10}FeNCl$. Calculated, %: C 51.00; H 4.28; N 5.95; Fe 23.72; Cl 15.05

N-Acetyl-1-(1′-chloroferrocenyl)amine. A mixture of 0.09 g of 1-(1′-chloroferrocenyl)amine, 1.5 ml of acetic anhydride, and 1.5 ml of absolute pyridine was allowed to stand for 3 h. The mixture was then diluted with water and extracted with ether. The ethereal solution was washed repeatedly with acid, then with water, and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on Al_2O_3. Benzene eluted the acetyl derivative of 1-(1′-chloroferrocenyl)amine; 0.11 g was obtained, m.p. 124.5° (under nitrogen) after recrystallization from a benzene–heptane mixture.

Found, %: C 52.01, 51.89; H 4.48, 4.49; N 5.05; Fe 20.17, 20.16; Cl 12.77, 12.63
$C_{12}H_{12}FeNOCl$. Calculated, %: C 51.93; H 4.36; N 5.05; Fe 20.12; Cl 12.78

5. Azoferrocene. a) Air was passed for 15 min through a solution of 0.1 g of ferrocenylamine in 10 ml of benzene in the presence of 0.22 g of CuBr; the color changed from yellow to violet. The CuBr precipitate was filtered off, and unreacted ferrocenylamine, 0.063 g (63% of theory), was extracted from the benzene solution with 10% HCl. After removal of the benzene, 0.030 g was obtained

azoferrocene (36% of theory). Azoferrocene was recrystallized from benzene, m.p. 255.5° (under nitrogen). Literature data: m.p. 256–258° (5). A mixed sample with an authentic specimen melts without depression.

b) Air was passed for 4 h through a solution of 0.1 g of ferrocenylamine in 5 ml of benzene in the presence of 0.22 g of CuBr. The work-up was the same as in the preceding experiment. Ferrocenylamine was not isolated. 0.093 g (99% of theory) of azoferrocene was obtained.

7. **Dichloroazoferrocene.** a) On oxidation of 0.077 g of 1-(1′-chloroferrocenyl)amine in 8 ml of benzene in the presence of 0.2 g

SovietRxiv

of CuBr for 15 min, 0.062 g (80.5% of theory) of the amine and 0.005 g (6.5% of theory) of dichloroazoferrocene were recovered.

b) Air was passed for 5 h through a solution of 0.2 g of 1-(1′-chloroferrocenyl)amine in 5 ml of benzene in the presence of 0.5 g of CuBr. 0.02 g (10% of theory) of 1-(1′-chloroferrocenyl)amine and 0.10 g (50.5% of theory) of dichloroazoferrocene were isolated.

Dichloroazoferrocene crystallizes from a mixture of benzene and heptane, m.p. 166° (under nitrogen).

Found, %: C 51.56, 51.69; H 3.48, 3.47; N 6.15, 6.13; Cl 15.27, 15.06; Fe 23.76, 23.36
$C_{20}H_{16}Fe_2Cl_2N_2$, calculated, %: C 51.44; H 3.45; N 6.00; Cl 15.19; Fe 23.93

Received
29 IV 1964

CITED LITERATURE

1. A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, DAN, **152**, 1358 (1963).
2. A. P. Terent' ev, Ya. D. Mogilyanskii, DAN, **103**, 91 (1955); ZhOKh, **28**, 1959 (1958); **31**, 326 (1961).
3. Keizo Kinoschita, Bull. Chem. Soc. Japan, **32**, 777 (1959); Chem. Abstr., **55**, 19741d (1961).
4. G. Engelsma, E. Havinga, Tetrahedron, **2**, 289 (1958).
5. A. N. Nesmeyanov, E. G. Perevalova, T. V. Nikitina, DAN, **138**, 1118 (1961).
6. A. N. Nesmeyanov, V. A. Sazonova et al., Izv. AN SSSR, OKhN, **1962**, 2073.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.