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Abstract

Full Text

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DIFERROCENYLAMINE

In previous papers we described N-ethyl- and N-phenyldiferrocenylamines (^{1,2}). We obtained the acetyl derivative of diferrocenylamine by heating the sodium derivative of N-acetylferrocenylamine with bromoferrocene in the presence of Cu_2Br_2.

$$\text{N-acetylferrocenylamide sodium derivative} + \text{bromoferrocene} \xrightarrow[110-120^\circ]{Cu_2Br_2} \text{N-acetyldiferrocenylamine}$$

All attempts to hydrolyze the amide to diferrocenylamine by the usual methods gave no positive results. In this respect it differs from N-acetylphenylferrocenylamine. On boiling in alcohol with KOH, N-acetyldiferrocenylamine remains unchanged; upon prolonged heating it gradually decomposes; acid hydrolysis leads to rapid complete destruction of the ferrocene system.

Diferrocenylamine can be obtained by reductive cleavage of N-acetyldiferrocenylamine with lithium aluminum hydride,

$$\text{N-acetyldiferrocenylamine} \xrightarrow{LiAlH_4} \text{diferrocenylamine}$$

along with a small amount (8%) of ethyldiferrocenylamine

ethyldiferrocenylamine

Cleavage is predominant only if 0.25 mole of $LiAlH_4$ is taken per mole of amide; with a large excess of $LiAlH_4$, the cleavage and reduction reactions proceed with approximately equal yields.

Diferrocenylamine resembles diphenylamine in some properties. It is not extracted from benzene solutions by dilute acids, but dissolves in conc. HCl; it forms the hydrochloride when hydrogen chloride is passed into an ethereal solution of the amine. This is the basis, in the preparation of diferrocenylamine, for separating it from ethyldiferrocenylamine, which forms the hydrochloride with greater difficulty.

Diferrocenylamine is alkylated with triethyloxonium borofluoride.

$$\text{diferrocenylamine} \xrightarrow{(C_2H_5)_3OBF_4} \text{ethyl-diferrocenylamine}$$

On reduction with lithium aluminum hydride of N-acetyl- and N-benzoylferrocenylamines, ethylferrocenylamine is formed, respectively, in 94% yield, and benzylferrocenylamine in 86% yield; alkylation of the latter with triethyloxonium borofluoride gives ethylbenzylferrocenylamine. Schlegel and Fried (3), in describing the reaction of acetylferrocene oxime with $LiAlH_4$, give only very brief data on the reduction of N-acetylferrocenylamine.

Experimental Part

1. N-Acetyldiferrocenylamine. The reaction is carried out under nitrogen. To sodium ethylate, prepared from 0.11 g of sodium, 1 g of N-acetylferrocenylamine was added. After thorough mixing, the mixture was heated at 150° (oil-bath temperature) for 40 min; during this, the sodium derivative of N-acetylferrocenylamine was formed as a reddish-brown mass. The reaction mixture was cooled to 110–120°, 1.1 g of bromoferrocene and 1.1 g of Cu_2Br_2 were added, and it was heated at this temperature for one hour. The resulting solid black mass was extracted repeatedly with ether, the ether was distilled off, and the residue was chromatographed on Al_2O_3. Obtained:

Substance	Eluent	Amount, g
Ferrocene	Petroleum ether	0.28
Diferrocenyl	Same	0.08
Azoferrocene	Petroleum ether: ether (7:3)	0.01
N-Acetyldiferrocenylamine	Same	0.3–0.35
N-Acetylferrocenylamine	Ether	0.17

N-Acetyldiferrocenylamine is a yellow crystalline substance, soluble in ether and benzene; m.p. 176° (under nitrogen) after recrystallization from heptane.

Found, %: C 62.15; 62.06; H 4.90; 5.03; N 3.27; 3.40;
Fe 26.32; 26.13

$C_{22}H_{21}Fe_2NO$. Calculated, %: C 61.86; H 4.96; N 3.28;
Fe 26.15

2. Cleavage and reduction of N-acetyldiferrocenylamine with lithium aluminum hydride. Diferrocenylamine. To a solution of 0.25 g of N-acetyldiferrocenylamine in 100 ml of absolute ether (before the reaction, the absolute ether was distilled over $LiAlH_4$), 0.01 g of $LiAlH_4$ was added. The mixture was refluxed under nitrogen with mechanical stirring for 6 h. During this time, 0.01 g portions of $LiAlH_4$ were added twice to the reaction mixture; the course of the reaction was monitored by thin-layer chromatography on Al_2O_3;

refluxing was stopped when the N-acetyldiferrocenylamine had completely disappeared. The reaction mixture was carefully poured into water, the ether layer was separated, and the aqueous layer was extracted with ether; the ether extracts were combined, washed with 10% NaOH solution and with water. The ether was evaporated, and the residue was dried in a vacuum desiccator over KOH. A 0.23 g mixture of diferrocenylamine and ethyldiferrocenylamine was obtained. The amine mixture was dissolved in absolute ether and hydrogen chloride was passed through the ethereal solution. The precipitated hydrochloride was filtered off and washed with absolute ether. The filtrate was washed with alkali solution and water, and after removal of the ether the residue was chromatographed on Al_2O_3. Heptane eluted 0.02 g (8.3% of theory) of ethyldiferrocenylamine, m.p. 149–149.5° (see following

experiment). As the chromatogram shows (in a thin layer on Al_2O_3), the filtrate contains only ethyldiferrocenylamine.

A solution of alkali was added to the hydrochloride precipitate, and the amine was extracted with ether. The ether was evaporated, and the residue was washed with a small amount of hexane. This gave 0.16 g (70% of theory) of chromatographically pure diferrocenylamine.

Diferrocenylamine is a yellow crystalline substance, readily soluble in ether, alcohol, and benzene, and sparingly soluble in hexane; m.p. 152–153° (under nitrogen). It crystallizes from aqueous alcohol or hexane.

Found, %: C 62.48; 62.50; H 5.17; 5.07; N 3.76; 3.72; Fe 28.63; 28.30
$C_{20}H_{19}Fe_2N$. Calculated, %: C 62.38; H 4.97; N 3.64; Fe 29.01

Mass-spectrometric investigation of the vapors of diferrocenylamine confirmed the results obtained.*

3. **Ethyldiferrocenylamine.** To a solution of 0.05 g of diferrocenylamine in dry methylene chloride was added 0.1 g of triethyloxonium fluoroborate. The reaction mixture was left at room temperature for 5–10 min, and then, after addition of a 10% NaOH solution, was extracted with ether. The ether was removed, and the residue was chromatographed on Al_2O_3. Ethyldiferrocenylamine was eluted with hexane. This gave 0.03 g (56% of theory) of ethyldiferrocenylamine.

Found, %: C 63.63; 63.81; H 5.78; 5.61; N 3.36; 3.54; Fe 26.91; 27.10
$C_{22}H_{23}Fe_2N$. Calculated, %: C 63.96; H 5.61; N 3.39; Fe 27.04

Ethyldiferrocenylamine is readily soluble in organic solvents, crystallizes from hexane, m.p. 149–149.5° (under nitrogen); a mixed sample with the specimen obtained in the preceding experiment melts without depression.

4. **Benzylferrocenylamine.** To 0.1 g of $LiAlH_4$ in 10 ml of anhydrous tetrahydrofuran was added dropwise a solution of 0.5 g of N-benzoylferrocenylamine in 40 ml of anhydrous tetrahydrofuran. The mixture was boiled under nitrogen with stirring for 6 h. During this

time a further 0.1 g of $LiAlH_4$ was added. The course of the reaction was followed by thin-layer chromatography on Al_2O_3; the reaction was stopped when the N-benzoylferrocenylamine had reacted completely. The reaction mixture was carefully decomposed with water and extracted with ether. The ethereal solution was washed with KOH solution and with water, and then extracted with 10% HCl; on alkalinization a precipitate of the amine separated, which was extracted with ether. The ethereal solution was dried with KOH. The ether was distilled off. This gave 0.41 g (86% of theory) of benzylferrocenylamine, m.p. 125° (from hexane).

Found, %: C 70.40; 70.29; H 6.07; 6.02; N 4.99, 4.98; Fe 19.26; 19.44
$C_{17}H_{17}FeN$. Calculated, %: C 70.12; H 5.89; N 4.81; Fe 19.18

Benzoyl derivative of benzylferrocenylamine. Benzylferrocenylamine was benzoylated according to Schotten–Baumann; from 0.35 g of the amine, 0.4 g (81% of theory) of N-benzoylbenzylferrocenylamine was obtained. For purification, the benzoyl derivative was passed in ether through a small column of Al_2O_3. M.p. 134.5-135° (from alcohol).

Found, %: C 72.87; 72.98; H 5.57; 5.55; N 3.57; 3.44;
Fe 14.08; 14.22
$C_{24}H_{21}FeNO$. Calculated, %: C 72.92; H 5.36; N 3.54;
Fe 14.16

5. **Ethylbenzylferrocenylamine.** To a solution of 0.35 g of benzylferrocenylamine in 4 ml of dry methylene chloride was added 0.6 g of triethyloxonium fluoroborate. The mixture was heated to boiling for 5 min, then 10% NaOH was added and the amine was extracted with ether. The ethereal solu-

the solution was washed with water, the ether was removed in vacuo, and the residue was chromatographed on Al_2O_3. This gave 0.31 g (81% of theory) of ethylbenzylferrocenylamine, m.p. 48–48.5° (from aqueous alcohol).

Found, %: C 71.62; 71.66; H 6.63; 6.66; N 4.65; 4.59; Fe 17.52; 17.57
$C_{19}H_{21}FeN$. Calculated, %: C 71.48; H 6.63; N 4.39; Fe 17.50

6. Ethylferrocenylamine. To 0.04 g of $LiAlH_4$ in 10 ml of abs. ether was added a suspension of 0.18 g of N-acetylferrocenylamine in 40 ml of abs. ether. The reaction mixture was boiled under nitrogen with continuous stirring for 3 h. Water was then carefully added. The ether layer was separated, washed with KOH solution and with water, and the amine was extracted with 10% HCl. On alkalization, a precipitate of the amine separated, which was extracted with ether. The ether was removed in vacuo. This gave 0.16 g (94% of theory) of ethylferrocenylamine, m.p. 56.5–58°; a mixed sample with a specimen obtained

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earlier by alkylation of ferrocenylamine with triethyloxonium tetrafluoroborate melted without depression.

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