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Abstract

Full Text

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DIAZO COMPOUNDS OF FERROCENE

It was shown earlier that ferrocenediazonium cannot be obtained by the action of nitrous acid on ferrocenylamine, owing to its destructive action on the ferrocene nucleus ([1]). The diazoamino compounds of ferrocene synthesized by us ([2]) make it possible to obtain diazo compounds of ferrocene by an indirect route, since it is known that diazoamino compounds undergo acidolysis with formation of a diazo compound and the corresponding amine.

Indeed, when diazoaminoferrocene is treated with conc. HCl in the range $-40, -20^\circ$, a violet solution is formed which already at -15° begins to evolve nitrogen; chloroferrocene and aminoferrocene were detected in the reaction mixture, which undoubtedly indicates the intermediate formation of the ferrocenediazonium cation:

$$C_5H_5FeC_5H_4N{=}NNHC_5H_4FeC_5H_5 \xrightarrow{H^+} C_5H_5FeC_5H_4N^+{\equiv}N{+}C_5H_5FeC_5H_4NH_2.$$

$$C_5H_5FeC_5H_4N^+{\equiv}N \xrightarrow{Cl^-} C_5H_5FeC_5H_4Cl + N_2$$

On analogous treatment of benzenediazoaminoferrocene with conc. HCl, a violet solution of ferrocenediazonium is also formed. Ferrocenediazonium couples with β-naphthol, giving a dark-green dye—1-ferrocenazo-2-naphthol—which confirms its existence:

$$C_5H_5FeC_5H_4N{=}NNHC_6H_5 \xrightarrow{H^+} C_5H_5FeC_5H_4N^+{\equiv}N + C_6H_5NH_2.$$

$$C_5H_5FeC_5H_4{-}N{=}N{-}_{\text{naphthyl}}^{\text{OH}}$$

1-Ferrocenazo-2-naphthol had previously been obtained by A. N. Nesmeyanov, E. G. Perevalova, and T. V. Nikitina by coupling β-naphthol with ferrocenediazotate, which is formed, together with other products, by the action of nitrogen dioxide on ferrocenyl lithium.

Acidolysis of benzenediazoaminoferrocene shows that its tautomeric equilibrium is shifted mainly toward 1-ferrocenyl-3-phenyltriazene,

$$C_5H_5FeC_5H_4N{=}NNHC_6H_5 \rightleftarrows C_5H_5FeC_5H_4NHN{=}NC_6H_5,$$

since among the reaction products no appreciable amounts of 1-benzolazo-2-naphthol were detected, which should be formed according to the scheme

$$C_5H_5FeC_5H_4NHN{=}NC_6H_5 \xrightarrow{H^+} C_5H_5FeC_5H_4NH_2{+}C_6H_5N^+{\equiv}N \rightarrow C_6H_5N{=}N{-}_{\text{naphthyl}}^{OH},$$

Actually, by analogy with ([3]), one should have expected that the C_6H_5 group, owing to its lower electron-donating ability in comparison with the $C_5H_5FeC_5H_4$ group ([4]), would favor an increase of the negative charge on nitrogen atom 3 in the intermediate anion

$$C_5H_5FeC_5H_4N{=}N{-}\overset{\ominus}{N}{-}C_6H_5$$

1 2 3

and thereby a shift of the tautomeric equilibrium toward 1-ferrocenyl-3-phenyltriazene.

Ferrocenediazonium has an increased ability (in comparison with phenyldiazonium) to enter into the nucleophilic substitution reaction S_N1. Thus, in solutions of hydrohalic acids HX ($X = Cl, Br, J$), already at -15° a gradual evolution of nitrogen begins, which is completely finished at -5°, and the yields of the corresponding haloferrocenes exceed 70%:

$$C_5H_5FeC_5H_4\overset{+}{N}{\equiv}N \xrightarrow{X^-} C_5H_5FeC_5H_4X + N_2.$$

In a solution of H_2SO_4, oxyferrocene is formed.

On treatment with conc. HCl at -40, -20°, 1,1′-bis-benzenediazoaminoferrocene gives a dark-violet solution containing 1,1′-ferrocenylene-bis-diazonium, since coupling with β-naphthol leads to the black-green dye ferrocene-1,1′-bis-((azo-1′)-2-naphthol). However, among the reaction products 1-benzeneazo-2-naphthol was also found:

$$Fe(C_5H_4N{=}N{-}NHC_6H_5)_2 \xrightarrow[2.\ \beta\text{-naphthol}]{1.\ H^+} Fe(C_5H_4N{=}N{-}C_{10}H_6OH)_2 + C_6H_5N{=}N{-}C_{10}H_6OH.$$

This indicates that at the moment of cleavage the molecule of the diazoamino compound contains the grouping $-NHN{=}NC_6H_5$.

Experimental Part

1. Acidolysis of diazoaminoferrocene. Ferrocenediazonium. To 5 ml of conc. HCl, cooled to −40°, 0.3 g of diazoaminoferrocene was added. On slow warming to −20° and dissolution of the crystals, a violet solution of ferrocenediazonium gradually forms. Already at −15° evolution of nitrogen begins, ending at −5°; at the same time crystals of chloroferrocene precipitate. The reaction mixture was diluted with water and extracted with ether; the ethereal solution was washed with water, 10% KOH (to remove traces of oxyferrocene), and water, dried over $MgSO_4$, and evaporated. Obtained: 0.12 g (72% of theory) of chloroferrocene, m.p. 57–58° (from methanol); with an authentic sample ([5]) it gives no depression of the melting point. The mother liquor was neutralized and extracted with ether; ferrocenylamine was extracted from the ether solution with 10% HCl and precipitated with 10% KOH. Obtained: 0.09 g (62% of theory) of ferrocenylamine, m.p. 154–155° (from heptane). Literature data: m.p. 153–155° ([5]), 155° ([6]).

2. Acidolysis of benzenediazoaminoferrocene. Ferrocenediazonium

a) **With hydrochloric acid.** Analogously to the preceding experiment, on treatment of 1.0 g of benzenediazoaminoferrocene with 15 ml of conc. HCl, 0.55 g (76% of theory) of chloroferrocene was isolated. In the mother liquor only traces of ferrocenylamine were found.

b) **With hydrobromic and hydriodic acids.** Similarly to chloroferrocene, from 1.0 g of benzenediazoaminoferrocene and 15 ml of conc. HBr or HJ there were obtained 0.61 g (70% of theory) of bromoferrocene, m.p. 32–33° (from methanol), or 0.73 g (72% of theory) of iodoferrocene, m.p. 42–44° (from methanol); no depression of the melting point with authentic samples was observed. Literature data: bromoferrocene, m.p. 32–33° ([5]); iodoferrocene, m.p. 44–45° ([7]), 43–45° ([8]).

c) **With sulfuric acid.** To 8 ml of 40% H_2SO_4, cooled to −40°, under nitrogen, 0.5 g of benzenediazoaminoferrocene and 10 ml of absolute ether were added, and the mixture was gradually warmed to room temperature. After the evolution of nitrogen had ceased, extraction with ether was carried out; the ether extracts were washed with water, and oxyferrocene was extracted with 10% KOH. Oxyferrocene was identifi-

in the form of ferrocenyl benzoate. 0.15 g (30% of theory) of ferrocenyl benzoate was obtained, m.p. 108.5-109.5° (from alcohol); with an authentic sample [9] it gives no depression of the melting point.

1-Ferrocenazo-2-naphthol. To 8 ml of conc. HCl, cooled to −40°, was added 0.5 g of benzenediazoaminoferrocene. After formation at −20°, as described above, of the violet solution of ferrocenediazonium, the solution was cooled to −40° and poured, with stirring, into a solution cooled to −5° of 0.5 g of β-naphthol in 60 ml of 10% KOH. A dark-green precipitate separated almost immediately. The reaction mixture was extracted with ether; the ethereal solu-

tion was washed with water, 10% H_2SO_4, and water, dried over $MgSO_4$, and the ether was distilled off. The residue was dissolved in a benzene–heptane mixture and chromatographed on Al_2O_3. Heptane first elutes chlorferrocene—yield 0.10 g (28% of theory), then benzene (or a heptane–benzene mixture) elutes the dark-green band of 1-ferrocenazo-2-naphthol, 0.28 g (48% of theory), and then benzene elutes unreacted benzenediazoaminoferrocene, 0.06 g.

1-Ferrocenazo-2-naphthol crystallizes from ether as dark-green crystals with m.p. 151–152° (in an evacuated capillary), gives dark-violet solutions in organic solvents, and is insoluble in alkalis.

$C_{20}H_{16}FeN_2O$.	Found %:	C 67.64;	67.58;	H 4.69;	4.81;	Fe 15.65,	15.86;	N 7.86	
	Calculated %:	C 67.44;		H 4.53;		Fe 15.68;		N 7.87	

4. Ferrocene-1,1′-bis-(⟨azo 1⟩ -2-naphthol). To 5 ml of conc. HCl, cooled to −40°, was added 0.3 g of 1,1′-bis-benzenediazoaminoferrocene. On trituration and gradual warming to −20°, the substance dissolves with formation of a dark-violet solution. After ∼ 15 min the solution was again cooled to −40° and poured, with stirring, into a solution of 0.6 g of β-naphthol in 40 ml of 10% KOH, cooled to −5°. The reaction mixture was extracted with ether; the ethereal solution was washed with water and dried over $MgSO_4$. The ether was distilled off; the residue was dissolved in benzene and chromatographed on Al_2O_3. Benzene-heptane (1:1) first elutes about 0.01 g of 1-ferrocenazo-2-naphthol (green band), and then the red band of 1-benzenazo-2-naphthol, 0.05 g (35% of theory), m.p. 130–131° (from alcohol); with an authentic sample it gives no depression of the melting point.

Ferrocene-1,1′-bis-(⟨azo 1⟩ -2-naphthol) is adsorbed on Al_2O_3, forming a dark-green band, which is eluted with benzene, the solution being colored a deep violet; yield of substance 0.09 g (24% of theory). It crystallizes from benzene as black lustrous crystals with decomposition point 212–213° (in an evacuated capillary).

$C_{30}H_{22}FeN_4O_2$.	Found %:	C 68.34,	68.53;	H 4.31;	4.29;	Fe 10.76,	10.54;	N 10.57;	10.75
	Calculated %:	C 68.45;		H 4.21;		Fe 10.61;		N 10.65	

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