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Abstract

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FERROCENE AZIDES

Studying the nucleophilic substitution of halide bound to a ferrocene nucleus in the presence of copper salts (^{1}), we found that the halide in bromo- and 1,1′-dibromoferrocenes can be replaced by an azido group. Bromoferrocene is converted almost quantitatively into ferrocenyl azide in the presence of Cu^{2+} and N_3^- ions in a dimethylformamide–water solution when the reaction is carried out for two days at room temperature:

$$C_5H_5FeC_5H_4Br \xrightarrow{Cu^{2+},\ N_3^-} C_5H_5FeC_5H_4N_3$$

Under the indicated conditions, 1,1′-dibromoferrocene does not undergo halide exchange at all; however, when an aqueous-alcoholic solution of the halide is boiled in the presence of Cu^{2+} and N_3^- ions for 6 min, 1,1′-ferrocenylenediazide $Fe(C_5H_4N_3)_2$ is formed in 31% yield. It should be noted that the relatively low yield of this reaction is explained by the thermal instability of ferrocene azides. On heating, along with decomposition, 1,1′-ferrocenylenediazide is converted in small amount into ferrocenyl azide, and the latter into ferrocene. The azides are also unstable to light, and they should be stored in a cool dark place.

Ferrocenyl azide and 1,1′-ferrocenylenediazide can also be synthesized by the reaction of a mixture of lithioferrocene and 1,1′-dilithioferrocene with tosyl azide, followed by alkaline treatment of the reaction mixture, without isolation of the triazenes formed as intermediates:

$$\begin{array}{c} C_5H_5FeC_5H_4Li \\ \\ Fe(C_5H_4Li)_2 \end{array} \xrightarrow[\text{2. } OH^-]{\text{1. } p\text{-}TosN_3} \begin{array}{c} C_5H_5FeC_5H_4N_3 \\ \\ Fe(C_5H_4N_3)_2 \end{array}$$

A similar method for the synthesis of azides is described in the review by Boyer and Canter (^{2}). On reduction of ferrocenyl azide with lithium aluminum hydride by the procedure proposed for azides by Boyer (^{3}), ferrocenylamine is formed in good yield. Ferrocenylamine was first obtained in our laboratory by the reaction of hydroxylamine *O*-ethers with ferrocenyl lithium (^{4}), and also by the action of hydrazine hydrate on *N*-ferrocenylphthalimide (^{5}) and by reduction of azoferrocene (^{6}); in other laboratories it was obtained by the Curtius reaction (^{7}) and by reduction of nitroferrocene (^{8}).

1,1′-Diaminoferrocene, obtained by catalytic reduction of 1,1′-bis(phenyldiazo)ferrocene (^{9}), had not been isolated in pure form and was identified only as a series of acyl derivatives. In our work, on reduction of 1,1′-ferrocenylenediazide with lithium aluminum hydride, solid 1,1′-diaminoferrocene was obtained; it crystallizes from a benzene–heptane mixture and rapidly oxidizes in air. It was identified as the dimethyl ester of 1,1′-ferrocenylenebiscarbamic acid:

$$\mathrm{Fe(C_5H_4N_3)_2} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Fe(C_5H_4NH_2)_2} \xrightarrow{\mathrm{ClCOOCH_3}} \mathrm{Fe(C_5H_4NHCOOCH_3)_2}$$

Ferrocenyl azide, like other organic azides, can add to a strained double bond, for example to the double bond of the dimethyl ester of exo-cis-3,6-endoxo-Δ^4-tetrahydrophthalic acid, with ob-

with formation of the corresponding triazoline:

[[chemical structural scheme: dimethyl acetylenedicarboxylate + $C_5H_5FeC_5H_4N_3 \longrightarrow$ ferrocenyl-substituted t

It was of interest, starting from azides, to synthesize triazenes of the ferrocene series, from which diazo compounds of ferrocene could be obtained by acidolysis of the triazene system according to the scheme:

$$\mathrm{C_5H_5FeC_5H_4N{=}N{-}NHR} \xrightarrow{\mathrm{H^+}} \mathrm{C_5H_5FeC_5H_4\overset{+}{N}{\equiv}N} + \mathrm{RNH_2}$$

We succeeded in synthesizing several diazoamino compounds of the ferrocene series. Thus, benzoldiazoaminoferrocene can be obtained by the reaction of phenylmagnesium bromide with ferrocenyl azide or, more conveniently, by the reaction of lithioferrocene with phenyl azide; owing to the well-known tautomerism of diazoamino compounds, in both cases one and the same substance is formed:

$$\mathrm{C_5H_5FeC_5H_4N_3} + \mathrm{C_6H_5MgBr} \longrightarrow \mathrm{C_5H_5FeC_5H_4N{=}NNHC_6H_5}$$
$$\mathrm{C_6H_5N_3} + \mathrm{C_5H_5FeC_5H_4Li} \longrightarrow \mathrm{C_5H_5FeC_5H_4NH{-}N{=}NC_6H_5}$$

Since in the metalation of ferrocene with butyllithium the reaction mixture also contains 1,1′-dilithioferrocene, the latter, reacting with phenyl azide, forms 1,1′-bis-benzoldiazoaminoferrocene:

$$\mathrm{Fe(C_5H_4Li)_2} + 2\mathrm{C_6H_5N_3} \longrightarrow \mathrm{Fe(C_5H_4N{=}NNHC_6H_5)_2}$$

The reaction of ferrocenyl azide with ferrocenyl lithium leads to the symmetrical triazene—diazoaminoferrocene:

$$C_5H_5FeC_5H_4N_3 + C_5H_5FeC_5H_4Li \longrightarrow C_5H_5FeC_5H_4N{=}NNHC_5H_4FeC_5H_5$$

These triazenes of ferrocene were used by us to obtain diazonium salts of the ferrocene series.

Experimental Part

1. Ferrocenyl azide. To a solution of 2.0 g of bromoferrocene in 60 ml of dimethylformamide were added solutions of 4 g of sodium azide in 10 ml of water and 0.70 g of cupric bromide in 3 ml of water, and the solution was left in the dark at room temperature; after 2 days the reaction mixture was extracted with ether, the ethereal solution was washed with water, dried over $MgSO_4$, and evaporated. This gave 1.68 g (98% of theory) of ferrocenyl azide, m.p. 53-54° (from hexane on cooling with a dry-ice-acetone mixture).

Found, %: C 53.23; 53.25; H 4.16; 4.14; Fe 24.56; 24.62; N 18.45; 18.61
$C_{10}H_9FeN_3$. Calculated, %: C 52.90; H 3.99; Fe 24.60; N 18.51;

2. 1,1′-Ferrocenylene diazide. To a boiling solution of 0.5 g of 1,1′-dibromoferrocene in 10 ml of alcohol were added solutions of 2 g of sodium azide in 5 ml of water and 0.35 g of cupric bromide in 2.5 ml of water, and the mixture was boiled on a water bath for 6 min. The dark reaction mixture was rapidly cooled, extracted with ether; the ethereal solution was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed in heptane on Al_2O_3, activity III; initially small amounts of ferrocene and ferrocenyl azide were eluted; the main, third band was 1,1′-ferrocenylene diazide. The solvent should be distilled off with moderate heating in vacuo; yield 0.12 g (31% of theory), m.p. 58.5-59° (from hexane on cooling with a dry-ice-acetone mixture).

Found, %: C 45.09; 45.26; H 3.28; 3.12; N 31.40
$C_{10}H_8FeN_6$. Calculated, %: C 44.81; H 3.01; N 31.36

Ferrocenyl azide and 1,1′-ferrocenylene diazide are yellow crystalline substances, readily soluble in organic solvents; they decompose on heating and in light.

3. Ferrocenyl azide and 1,1′-ferrocenylene diazide (from tosyl azide). The reaction is carried out under N_2. To a solution of 7.4 g of ferrocene in 70 ml of abs. tetrahydrofuran was added an ethereal solution of butyllithium (from 23 ml of butyl bromide and 3 g of lithium in 70 ml of abs. ether); the mixture was stirred at room temperature for 5 h, and then added over 30 min to a solution of 24 g of tosyl azide in 50 ml of abs. ether. The reaction mixture was left overnight, then decomposed with ~150 ml of 10% KOH; the organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on Al_2O_3 in heptane: ferrocene is eluted first, the second band is ferrocenyl azide, 1.70 g (28% of theory), and the third is 1,1′-ferrocenylene diazide, 0.31 g (6% of theory).

4. Reduction of ferrocene azides. Ferrocenylamine and 1,1′-diaminoferrocene. a) On reduction of 0.80 g of ferrocenyl azide with 0.40 g of $LiAlH_4$ in ethereal solution under N_2, 0.51 g (72% of theory) of ferrocenylamine was obtained, mp 153-155°. Literature data: mp 153-154° (^{4}), 155° (^{7}); it was also identified as the N-acetyl derivative; b) from 0.14 g of 1,1′-ferrocenylene diazide and 0.15 g of $LiAlH_4$ in 10 ml of abs. ether was obtained (under N_2) 0.07 g (62% of theory) of 1,1′-diaminoferrocene; a yellow crystalline substance, crystallizing from a heptane—benzene mixture, rapidly oxidized in air. A solution of 1,1′-diaminoferrocene in 5 ml of abs. benzene was treated with 1 ml of methyl chloroformate, and after 5 min, with cooling, with 1.8 ml of triethylamine. After 30 min the reaction mixture was poured into water and extracted with ether. The ether-benzene solution was washed with solutions of $NaHCO_3$ and H_2SO_4, dried over $MgSO_4$, and evaporated. After recrystallization of the residue from methanol, 0.05 g (50% of theory) of the dimethyl ester of 1,1′-ferrocenylene-bis-carbamic acid was obtained, mp 176-178°; literature data: mp 177-178° (^{9}).

Found %: N 8.17
$C_{14}H_{16}FeN_2O_4$. Calculated %: N 8.43

5. Dimethyl ester of exo-cis-4,5-(N-ferrocenyltriazolino)-3,6-endoxohexahydrophthalic acid. A solution of 0.25 g of ferrocenyl azide and 0.23 g of the dimethyl ester of exo-cis-3,6-endoxo-Δ^4-tetrahydrophthalic acid in 4 ml of ethyl acetate was left for several days in the dark at room temperature. The solvent was distilled off, and the residue was chromatographed on Al_2O_3; chloroform elutes 0.36 g (75% of theory) of the dimethyl ester of exo-cis-4,5-(N-ferrocenyltriazolino)-3,6-endoxohexahydrophthalic acid, mp 153.5-154° (from benzene).

Found %: C 54.58; 54.53; H 4.88; 4.92; Fe 12.92; 12.89; N 9.59; 9.72
$C_{20}H_{21}FeN_3O_5$.
Calculated %: C 54.68; H 4.82; Fe 12.72; N 9.57

6. Benzenediazoaminoferrocene (from ferrocenyl azide). To phenylmagnesium bromide (from 0.4 ml of bromobenzene and 0.04 g of magnesium in 4 ml of abs. ether) was added a solution of 0.30 g of ferrocenyl azide in 5 ml of abs. ether; the mixture was stirred for 40 min, decomposed with NH_4Cl solution, and the ethereal solution was dried over $MgSO_4$ and evaporated. The residue was chromatographed on Al_2O_3; heptane elutes insignificant amounts of ferrocenyl azide, bromobenzene, and diphenyl, while benzene elutes benzenediazoaminoferrocene, yield 0.30 g (74% of theory), dark-ruby crystals (from hexane), mp 120-122° (with decomposition) (in an evacuated capillary).

Found %: C 63.53; 63.38; H 4.96; 4.94; Fe 18.35; 18.44; N 13.82; 14.06
$C_{16}H_{15}FeN_3$.
Calculated %: C 62.97; H 4.96; Fe 18.30; N 13.77

7. **Benzoldiazoaminoferrocene and 1,1′-bis-benzoldiazoaminoferrocene** (from phenyl azide). The reaction is carried out under N_2. To a solution

of 25.5 g of ferrocene in 125 ml of abs. tetrahydrofuran is added a solution of butyllithium (from 16 ml of butyl bromide and 3 g of lithium in 125 ml of abs. ether), and the mixture is stirred at room temperature for 5 h. Then, with ice cooling, a solution of 7.5 g of phenyl azide in 25 ml of abs. ether is rapidly added. The solution becomes blood-red. The mixture is stirred for 1 h, poured into water, the organic layer is washed with water, dried over $MgSO_4$, and evaporated. The residue is triturated with Al_2O_3 and chromatographed. Heptane elutes unreacted ferrocene, benzene elutes benzoldiazoaminoferrocene, and tetrahydrofuran elutes 1,1′-bis-benzoldiazoaminoferrocene. To avoid resinification, the solvents should be distilled off from the triazene fractions in vacuo on a water bath at a temperature not above 40°. Benzoldiazoaminoferrocene was recrystallized from a benzene–hexane mixture (1:2), yield 10.9 g (57% of theory, calculated on phenyl azide); in melting point it is identical with that obtained from ferrocenyl azide. 1,1′-Bis-benzoldiazoaminoferrocene, yield 3.2 g (24% of theory, calculated on phenyl azide), brownish-red crystals (from benzene), depending on the rate of heating spontaneously decomposes at 145–150° (in an evacuated capillary).

Found, %: C 62.58; 62.49; H 4.86; 4.71; Fe 12.78; 12.58; N 19.55; 19.72
$C_{22}H_{20}FeN_6$.
Calculated, %: C 62.28; H 4.75; Fe 13.16; N 19.81.

8. **Diazoaminoferrocene.** The reaction is carried out under N_2. To a solution of 2.55 g of ferrocene in 15 ml of abs. tetrahydrofuran is added an ethereal solution of butyllithium (from 1.6 ml of butyl bromide and 0.3 g of lithium in 15 ml of abs. ether), and the mixture is stirred at room temperature for 5 h. Then, with ice cooling, a solution of 0.5 g of ferrocenyl azide in abs. ether is added; the solution becomes blood-red. After half an hour of stirring, the reaction mixture is poured into water; the organic layer is washed with water, dried over $MgSO_4$, and evaporated. The residue is washed on the filter with hexane to remove unreacted ferrocene and recrystallized from a benzene–hexane mixture. Obtained 0.75 g of brownish-red crystals of diazoaminoferrocene, decomp. temp. 150–152° (in vacuo).

Found, %: C 58.28; 58.41; H 4.72; 4.71; Fe 26.88; 26.73; N 9.99; 10.19
$C_{20}H_{19}Fe_2N_3$.
Calculated, %: C 58.15; H 4.64; Fe 27.04; N 10.17.

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CITED LITERATURE

1. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **130**, 1030 (1960); **137**, 102 (1961).
2. J. H. Boyer, F. C. Canter, Chem. Revs., **54**, 1 (1954).
3. J. H. Boyer, J. Am. Chem. Soc., **73**, 5865 (1951).
4. A. N. Nesmeyanov, E. G. Perevalova et al., DAN, **102**, 535 (1955).
5. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **126**, 1004 (1959).
6. A. N. Nesmeyanov, E. G. Perevalova, T. V. Nikitina, Tetrahedron Letters, No. 1, 1 (1960).
7. F. S. Arimoto, A. H. Haven, J. Am. Chem. Soc., **77**, 6295 (1955).
8. H. Grubert, K. L. Rinehart, Tetrahedron Letters, No. 12, 16 (1959); J. F. Helling, H. Shechter, Chem. and Ind., **1959**, 1157.
9. G. R. Knox, P. L. Pauson, J. Chem. Soc., **1961**, 4615.

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