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Abstract

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Photolysis of Ferrocene Derivatives

We have observed that certain ferrocene derivatives are readily destroyed under the action of light. Thus, the hydroxide of N-methyl-2-ferrocenylpyridinium decomposes in sunlight into N-methyl-2-cyclopentadienylidene-pyridinium, cyclopentadiene, and Fe^{2+} (1). Ferrocene derivatives with substituents bearing a positive charge adjacent to the cyclopentadienyl ring behave similarly (in acidic solutions—ferrocenylamine, ethylferrocenylamine, diethylferrocenylamine, acetylferrocene and its oxime) (2); cleavage of the iron–carbon bonds also readily occurs in the diphenylferrocenylcarbonium ion, with formation of 6,6-diphenylfulvene (3).

In the present work it is shown that other nitrogen-containing ferrocene compounds also possess similar properties (methyl iodide salt of α-quinolylferrocene, triethylferrocenylammonium hydroxide) as does ferrocene-1,1′-disulfonic acid.

α-Quinolylferrocene, together with 1,1′-di-(α-quinolyl)-ferrocene, was obtained by the action of a mixture of lithium- and 1,1′-dilithioferrocenes on quinoline.* With methyl iodide, α-quinolylferrocene gives the methyl iodide salt. The latter, under the action of light, undergoes destruction to N-methyl-2-cyclopentadienylidene-1,2-dihydroquinoline (along with it, α-quinolylferrocene is formed in larger quantity).

N-methyl-2-ferrocenylquinolinium $\longrightarrow$ N-methyl-2-cyclopentadienylidene-1,2-dihydroquinolinium

N-Methyl-2-cyclopentadienylidene-1,2-dihydroquinoline had previously been obtained by Meerwein and co-workers (5) by condensation of 1-methylquinolone-2 diethyl acetal with cyclopentadiene.

The violet acidic aqueous solutions of α-quinolylferrocene are decolorized under the action of light.

Triethylferrocenylammonium hydroxide decomposes in light to triethylammonium cyclopentadienylide,

triethylferrocenylammonium hydroxide $\longrightarrow$ triethylammonium cyclopentadienylide, isolated in the form of the tetraphenylborate. Spooncer (^{6}) obtained an analogous compound—trimethylammonium cyclopentadienylide—by Hofmann reaction from trans-1,2-bis-(trimethylammonium)-3-cyclopentene diiodide.

* By the time our work on the synthesis of quinolylferrocenes was completed, an article appeared reporting the preparation of these compounds (^{4}).

Addition of a proton to the cyclopentadienyl anion in triethylammonium cyclopentadienylide can give three cations:

[[chemical structure]] [[chemical structure]] [[chemical structure]]

The question of the structure of the salt—the tetraphenylborate of triethylcyclopentadienylammonium—still remains unresolved. For N-methyl-2-cyclopentadienylidene-pyridinium it is known that protonation gives a mixture of cations (7)

[[chemical structure]] [[chemical structure]]

Destruction of the ferrocene system under the action of light is also characteristic of ferrocene compounds with other substituents, for example with a sulfo group. Thus, an aqueous yellow solution of ferrocene-1,1′-disulfonic acid, when irradiated with a 300-W lamp at a distance of 15 cm for 6 h, is completely decolorized

[[chemical structure of ferrocene-1,1'-disulfonic acid]] $\longrightarrow ((C_5H_5SO_3)_2Fe)_x$.

If concentrated solutions of ferrocene-1,1′-disulfonic acid are irradiated, the iron salt of ferrocene-1,1′-disulfonic acid precipitates; after isolation, washing, and redissolution in water, it decomposes on irradiation to $[(C_5H_5SO_3)_2Fe]_x$ and iron(II) hydroxide.

Experimental Part

α-Quinolyl- and 1,1′-di-(α-quinolyl)ferrocenes*. Ferrocene (8.8 g) is metallated in the usual way with *n*-butyllithium, prepared from 3.8 g of lithium and 21 ml of *n*-butyl chloride. To the mixture of lithium- and 1,1′-dilithioferrocenes is added 16 ml of freshly distilled quinoline; the reaction mixture is heated on a water bath for 5 h under nitrogen and, after cooling, decomposed with water. The ether layer is separated and washed with water several times. After removal of the solvent in vacuo, the residue is chromatographed on Al_2O_3. Heptane elutes unreacted ferrocene; a heptane-ether mixture (1:1) elutes α-quinolylferrocene, 3.2 g (21.6% of theoretical), and benzene elutes 1,1′-di-(α-quinolyl)ferrocene, 1.4 g (6.7% of theoretical).

To obtain analytically pure quinolylferrocenes, they are heated for 15 min in nitrobenzene. α-Quinolylferrocene was obtained with m.p. 139-140° (from alcohol). Literature data: m.p. 139-141° (4).

Found, %: C 72.87, 73.01; H 4.79, 4.76; N 4.42, 4.29; Fe 17.80, 17.68
$C_{19}H_{15}NFe$. Calculated, %: C 72.87; H 4.83; N 4.47; Fe 17.79

1,1′-Di-(α-quinolyl)ferrocene melts at 209°. Literature data: m.p. 209-211° (4).

Found, %: C 76.52, 76.43; H 4.68, 4.58; N 6.12, 6.23; Fe 12.70, 12.53
$C_{28}H_{11}N_2Fe$. Calculated, %: C 76.37; H 4.58; N 6.36; Fe 12.68

Iodomethylate of α-quinolylferrocene. To a solution of 1 g of α-quinolylferrocene in 3 ml of dimethylformamide was added 3 ml of methyl iodide. After standing for three days at room temperature, from the solution

* Carried out jointly with A. V. Gerasimenko.

with the addition of ether, the iodmethylate of α-quinolylferrocene was precipitated—0.45 g (30% of theory). The iodmethylate is a dark-violet crystalline substance, unstable to light in solutions; it is recrystallized from aqueous alcohol.

Found, %: C 50.26, 50.34; H 4.29, 4.30; N 3.06, 3.27; I 26.89, 26.63; Fe 11.90, 11.54
$C_{20}H_{18}NFeI \cdot H_2O$. Calculated, %: C 50.76; H 4.20; N 2.96; I 26.82; Fe 11.80

Photolysis of α-quinolylferrocene iodmethylate. A solution of 0.16 g of α-quinolylferrocene iodmethylate in 75 ml of water (for better wetting, 2 ml of alcohol was added), when irradiated under nitrogen with a 70 W lamp for 1.5 h, or when left in sunlight, changes color from violet to orange. The reaction mixture is extracted with ether, the ethereal solution is washed with a small amount of water, the ether is distilled off under nitrogen, and the residue is chromatographed on Al_2O_3. With a heptane–ether mixture (1:1), α-quinolylferrocene is eluted, 0.06 g (57% of theory), and with ether—N-methyl-2-cyclopentadienylidene-1,2-dihydroquinoline, 0.01 g (14% of theory), m.p. 168° (from heptane). Literature data: m.p. 172° (^{5}).

Found, %: N 6.96
$C_{15}H_{13}N$. Calculated, %: N 6.76

Photolysis of triethylferrocenylammonium hydroxide. To an aqueous solution of 0.13 g of triethylferrocenylammonium iodide, freshly precipitated silver oxide is added; after repeated shaking the precipitate is filtered off, and the filtrate is irradiated with a 150 W lamp at a distance of 10 cm for 4 h. During irradiation, iron hydroxide precipitates from the solution and is filtered off. The filtrate is washed with ether and extracted with chloroform. The chloroform solution, initially colorless, turns violet in air; therefore it is quickly washed with 5% acetic acid. Upon addition of an aqueous solution of sodium tetraphenylborate to the acetic-acid solution, a white precipitate of triethylcyclopentadienylammonium tetraphenylborate forms; it is filtered off, washed repeatedly with water, dried in a vacuum desiccator over P_2O_5, and reprecipitated from nitromethane with ether. Obtained: 0.07 g (45% of theory).

Found, %: C 86.70, 86.70; H 8.40, 8.32; N 2.98, 3.08; B 2.48, 2.18
$C_{35}H_{40}NB$. Calculated, %: C 86.58; H 8.30; N 2.83; B 2.23

The molecular weight of triethylcyclopentadienylammonium tetraphenylborate was determined (cryoscopically, in nitrobenzene). Mol. wt.: found 224.7, 229.5; calculated 485.5. The salt is completely ionized in nitrobenzene.

Photolysis of ferrocene-1,1′-disulfonic acid. a) A solution of 0.3 g of ferrocene-1,1′-disulfonic acid, obtained by Weinmayr' s method ([8]), in 3.5 ml of water is irradiated under nitrogen with a 300 W lamp at a distance of 15 cm for 6 h until complete decolorization. From the resulting solution, upon addition of acetone, a colorless iron salt of cyclopentadienesulfonic acid separates as an oil, which crystallizes upon shaking. The precipitate is quickly washed with acetone and ether, and then reprecipitated from an aqueous solution with acetone. Obtained: 0.21 g (64% of theory).

Found, %: C 26.87, 26.71; H 5.09, 4.87; Fe 12.67, 12.91; S 13.43, 13.48
$C_{10}H_{10}FeS_2O_6 \cdot 6H_2O$. Calculated, %: C 26.44; H 4.87; Fe 12.30; S 14.12

The salt is readily soluble in water and gives a reaction for divalent iron. Investigation of the structure of the salt is continuing.

b) A solution of 3.36 g of ferrocene-1,1′-disulfonic acid in 3.5 ml of water is irradiated under nitrogen with a 300 W lamp. Fifteen minutes after the start of irradiation, golden-yellow crystals begin to precipitate from the solution; after three hours of irradiation they are filtered off, washed with an aqueous alcohol solution (1 : 2), and dried over P_2O_5. This is the crystalline hydrate of the iron salt of ferrocene-1,1′-disulfonic acid. The salt is soluble in water and gives a reaction for divalent iron.

Found, %: C 25.48, 25.70; H 3.71, 3.41; Fe 23.42, 23.83; S 12.91, 13.10
$C_{10}H_8Fe_2S_2O_6 \cdot 4H_2O$. Calculated, %: C 25.44; H 3.41; Fe 23.66; S 13.58

c) A solution of 0.1 g of the iron salt of ferrocene-1,1′-disulfonic acid in 4.5 ml of water is irradiated with a 300 W lamp until the solution is completely decolorized. The precipitated iron hydroxide is filtered off, and the iron salt of cyclopentadienesulfonic acid is precipitated from the filtrate with acetone.

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