# Academician A. N. NESMEYANOV, V. A. SAZONOVA, A. V. GERASIMENKO,

N. S. SAZONOVA

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## Abstract

## Full Text

Academician A. N. NESMEYANOV, V. A. SAZONOVA, A. V. GERASIMENKO,
N. S. SAZONOVA

# PHOTOLYSIS OF SALTS OF $\alpha$-PYRIDYLFERROCENE

As is known, ferrocene is rather stable for an organometallic compound ([1]). We observed an extremely facile destruction of the ferrocene system under the action of light (at room temperature) using as an example $\alpha$-pyridylferrocene, the synthesis of which we described earlier ([2]).

If the methiodide of $\alpha$-pyridylferrocene in alkaline solution is subjected to the action of light (sunlight for several minutes or an ordinary 300-watt lamp at a distance of 25 cm for an hour), rupture of the bond between iron and the cyclopentadienyl rings occurs, with formation of N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (N-methyl-2-cyclopentadienylidene-pyridinium) and cyclopentadiene. Iron was found in the reaction mixture in inorganic form. The cyclopentadiene was isolated as cyclopentadienylthallium ([3]).

[reaction scheme]

To confirm the structure of the obtained N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine, it was synthesized from N-methyl-2-bromopyridinium iodide and sodium cyclopentadienide ([4]). A mixed sample of the two specimens melts without depression.

Orange N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine dissolves in dilute acids, giving colorless solutions. On alkalization, the orange substance is formed again. According to Berson and Evleth ([5]), protonation of N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine gives a mixture of two cations:

[reaction scheme]

On shaking a bright-orange ethereal solution of the "ylide" with an aqueous solution of chloroplatinic acid, we obtained a colorless precipitate of the chloroplatinate; the latter is rather unstable.

Photolysis of $\alpha$-pyridylferrocene also proceeds readily in solutions of various acids. Thus, in an aqueous solution of oxalic acid the ferrocene system is destroyed and iron oxalate precipitates.

## Experimental Part

1. **Methiodide of $\alpha$-pyridylferrocene.** $\alpha$-Pyridylferrocene (0.8 g) was dissolved in 3 ml of methyl iodide and left at room temperature.

temperature for several days. The red precipitate that separated was filtered off and washed several times with absolute ether. 1.21 g of α-pyridylferrocene methyl iodide was obtained. For purification the substance was dissolved in alcohol; the alcoholic solution was filtered and the methyl iodide was precipitated with ether. 0.99 g (80% of theory) of pure α-pyridylferrocene methyl iodide was obtained.

Found, %: C 47.44, H 4.24, Fe 13.87, N 3.49;
46.93; 4.04; 13.53; 3.49

$C_{16}H_{16}NFeJ$. Calculated, %: C 47.44; H 3.98; Fe 13.79; N 3.44

**2. Photolysis of α-pyridylferrocene methyl iodide** (the reaction is carried out under nitrogen). α-Pyridylferrocene methyl iodide (1 g) was dissolved in water and 20 ml of 10% NaOH was added. When irradiated with a lamp (300 W) at a distance of 25 cm for one hour, or under the action of sunlight, the resulting solution changes color from bright red to orange, and a precipitate forms. The reaction mixture was extracted with ether. The ether solution was washed with a small amount of water. The nitrogenous base was extracted from the ether with 10% $H_2SO_4$; both the aqueous layer and the ether layer thereby become colorless. On alkalization of the acidic solution an orange oil forms. It was extracted with benzene. The benzene was distilled off under nitrogen. 0.32 g of N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine was obtained (84% of theory). After recrystallization from hexane with benzene, m.p. 73–74.5°; literature data: m.p. 74.5–75° (4). A mixed sample with a specimen obtained from N-methyl-2-bromopyridinium iodide and sodium cyclopentadienide melts without depression.

Along with the "ylide," cyclopentadiene was isolated in the form of its Tl derivative. (Cyclopentadiene was removed from the reaction mixture by a stream of nitrogen into a TlOH solution.)

Found, %: C 22.22; H 2.06
$C_5H_5Tl$. Calculated, %: C 22.20; H 1.87

When the ether solution of N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine is shaken with an aqueous solution of chloroplatinic acid, a precipitate of the chloroplatinate forms. For purification the precipitate was dissolved, with heating, in nitromethane, the solution was filtered, and ether was added to it. The precipitated solid was filtered off, washed with ether, dried, and analyzed.

Found, %: C 36.06, 36.04; H 3.59, 4.04; Pt 27.08
$C_{11}H_{12}NPtCl_6$. Calculated, %: C 36.47; H 3.34; Pt 26.95

**Photolysis of α-pyridylferrocene in an aqueous solution of oxalic acid.** A solution of 0.15 g of α-pyridylferrocene and 0.1 g of oxalic acid in 35 ml of water was irradiated with an ordinary lamp (60 W) at a distance of 10 cm for 45 min, until the red color had completely disappeared. The yellow precipitate that separated was filtered off and washed with water and ether. 0.06 g of substance was obtained; its analysis corresponds to iron oxalate crystalline hydrate.

Found, %: C 13.49, H 2.48, Fe 31.45,
13.48; 2.54; 31.66

$FeC_2O_4 \cdot 2H_2O$. Calculated, %: C 13.35; H 2.24; Fe 31.04

Moscow State University
named after M. V. Lomonosov

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## CITED LITERATURE

1. T. J. Kealy, P. L. Pauson, *Nature*, **168**, 1039 (1951).

2. A. N. Nesmeyanov, V. A. Sazonova, A. V. Gerasimenko, DAN, **147**, 634 (1962).

3. E. O. Fischer, *Angew. Chem.*, **69**, 207 (1957).

4. J. A. Berson, E. M. Evleth, Z. Hamlet, *J. Am. Chem. Soc.*, **82**, 3793 (1960).

5. J. A. Berson, E. M. Evleth, *Chem. and Ind.*, **1961**, 1362.

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