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Abstract

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SOME OBSERVATIONS ON THE CHEMISTRY OF FERROCENE

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On the basis of recent indications ([1]), using readily available dioxane as solvent and, for better grinding, employing a cast-iron reactor, we succeeded in obtaining ferrocene in a yield of up to 90% of theory (see experiment 1). Very simply and in good yield (75%) a cobalt analogue was obtained in the form of $(C_5H_5)_2Co^+Br_3^-$ (experiment 2), and ferrocene was almost quantitatively converted into the ferricinium salt $(C_5H_5)_2Fe^+FeCl_4^-$ (experiment 3).

Attempts to synthesize 1,1′-dinitroferrocene by the reaction of $FeCl_2$ with sodium nitrocyclopentadienate did not lead to a positive result, probably because of the insufficient nucleophilicity of the initial cyclopentadiene derivative. As is known, attempts to nitrate ferrocene likewise have not been successful ([2,3])—only its conversion into the ferricinium cation was established. We observed that, for dilute nitric acid, this process proceeds practically by an autocatalytic reaction with nitrogen dioxide:

$$(C_5H_5)_2Fe + \cdot NO_2 \rightarrow (C_5H_5)_2Fe^+ + NO_2^-,$$

$$NO_2^- + 2HNO_3 \rightarrow 2 \cdot NO_2 + NO_3^- + H_2O.$$

In the presence of hydrazine, oxidation almost ceases; additions of urea act weakly. Judging by the external signs and the appearance of iron cations, the action of nitric acid on the ferricinium cation in the presence of NO_2 upon heating leads to the transformation products of nitrocyclopentadiene.

The reaction of ferrocene with nitrating agents, for example with nitrosyl tetrafluoroborate $NO^+BF_4^-$, proceeded with liberation of a radical-like nitrogen oxide:

$$(C_5H_5)_2Fe + NO^+ \rightarrow (C_5H_5)_2Fe^+ + \cdot NO.$$

In a similar way, in the first stage there should proceed the interaction of ferrocene with NO_2^+ from various nitrating agents. We also observed the formation of the ferricinium cation upon the action on ferrocene of solutions of

aluminum chloride in thionyl chloride, phosphorus trichloride, phosphorus oxychloride, probably through reaction with cations of the type $SOCl^+$, PCl_2^+.

When ferrocene was treated for 2 days with ethyl nitrate in the presence of sodium ethoxide or sodium tert-butoxide in a solution of the corresponding alcohol, formation was observed of considerable amounts of sodium nitrocyclopentadienate and, after treatment with water, of iron oxides:

$$(C_5H_5)_2Fe + RONO_2 \xrightarrow[(H2O)]{RONa} 2C_5H_4NO_2^-Na^+ + Fe(OH)_2 + 2ROH.$$

In the absence of an alkoxide, the reaction with ethyl nitrate did not proceed, even in acetic anhydride solution. It is possible that the activating action of al-

the alcoholate in this reaction is based on its formation of complexes with ferrocene through interaction with the cationoid Fe atom

$$(C_5H_5)_2[Fe+ : OC_4H_9 \rightarrow (C_5H_5)_2 \overset{-\delta}{Fe} \cdots : OC_4H_9$$

and on the resulting increase in the nucleophilicity of the C_5H_5 residues, bringing them still closer to the state of the $C_5H_5^-$ anion. The free cyclopentadienate ion, as is known, reacts rapidly under similar conditions with formation of the nitro derivative ([4]).

Previously, cleavage of this kind of the ferrocene system was observed in the study of the interaction of diethylferrocene with aryldiazonium cations ([5]); moreover, it must be assumed that solvation of the cationoid iron atom also played a noticeable role in the transition stages of these reactions.

Using data from earlier investigations ([6,7]) and carrying out sulfonation of ferrocene in acetic anhydride at 0° for 2.5 hours, we were able to obtain the disulfonic acid in yields up to 80% of theory; however, in this case too the formation of iron cations was observed. The action of *p*-nitrophenyldiazonium salts on solutions of the disulfonic acid caused very considerable cleavage of the nucleus.

The possibility of formylating ferrocene with *N*-methylformanilide by the Vilsmeier method was indicated by a number of authors in 1957-1958 ([8–11]), and in two of these papers methods were described for preparing ferrocene aldehyde $C_5H_5FeC_5H_4$—CHO ([10,11]). The method we developed in the same period for preparing ferrocene aldehyde, when comparatively tested, proved more convenient than those described earlier. Contrary to the assertions of the authors of one of the papers ([11]), which became known to us later, we observed that ethereal solutions of ferrocene aldehyde give a bisulfite compound, and this found application in our method. The reaction was accompanied by formation of the ferricinium cation and decomposition of the nucleus. The aldehyde was used for preparing a series of dyes.

We give a description of several experiments.

1. Into a cast-iron reactor of 1 l capacity were charged 36 g of $FeCl_3$, 200 ml of absolute dioxane, and 18 g of Fe powder. In a stream of nitrogen the mixture was boiled for 4 hours with a reflux condenser and with stirring. Toward the end the dioxane was distilled off in vacuo; to the $FeCl_2$ residue was added a mixture of 160 ml of diethylamine and 84 ml of freshly distilled cyclopentadiene. After 5 hours of stirring with an anchor stirrer, the mixture was left overnight and stirred again for 2 hours at 50–55°. The diethylamine was distilled off, and the residue was subjected to steam distillation—at first a little oil ($C_{10}H_{12}$) passed over, and then ferrocene. There was obtained 52.8 g of $(C_5H_5)_2Fe$, m.p. 174°—86.2% of theory based on $FeCl_3$. The yield in a glass reactor, owing to insufficient stirring, was somewhat lower. Small additions of water or the use of triethylamine likewise led to a decrease in yield.

2. To a mixture of 1.86 g of ferrocene, 10 ml of HCl of sp. gr. 1.19, and 20 ml of ether, with stirring and passage of O_2, were added dropwise 10 ml of a saturated solution of crystalline hydrate $FeCl_3$. Precipitation of ferricinium ferritetrachloride $(C_5H_5)_2Fe^+FeCl_4^-$ soon began. After two hours the salt was filtered off with suction and washed with concentrated HCl—the yield was close to theoretical.

3. 5.5 g of ground $CoBr_2$ (obtained by dissolving $CoCO_3$ in 48% HBr, evaporating, and drying in vacuo) was mixed with 10 ml of diethylamine and 5 ml of cyclopentadiene—warming to 42° and thickening occurred. The next day the amine was distilled off, the residue was treated with 30 ml of water while heating; in this process $(C_5H_5)_2Co$, with evolution of H_2, passed into the cobalticinium cation. The reaction mixture was then filtered from impurities and a solution of 2 ml of Br_2 in 30 ml of HBr was added. The perbromide $(C_5H_5)_2Co^+Br_3$ was filtered off with suction at 10° and washed with a solution of Br_2 in HBr—the yield of dry salt was 8.4 g (75% of theory).

4. Into a four-necked reactor were charged 5.4 g of N-methylformanilide and 4 ml of $POCl_3$; then, at 38° and with vigorous stirring over the course of 30 min, 3.72 g of ferrocene was added, after which the mixture was kept for 2 h at 50°. After cooling to 20°, 25 g of ice water was added, and then, after 2 h, 50 ml of ether, 10 g of Na_2SO_3, and 20 ml of 40% $NaHSO_3$. After stirring, the mixture was left overnight; the bisulfite compound was filtered off, washed several times with ether, and converted into the aldehyde by heating with 80 ml of 10% H_2SO_4 at 50° for 30 min.; hydrolysis in the presence of soda gave unsatisfactory results. The aldehyde can also be isolated by heating with formalin. The yield of the primary product (m.p. 88-90°) was 90-95% of theory; after recrystallization from aqueous alcohol, 2.63 g of pure aldehyde was isolated in the form of reddish-orange leaflets with m.p. 120° (56% of theory). When working on a larger scale, the quantities of $POCl_3$ and N-methylformanilide can be reduced. The use of dimethyl- and diethylformamide requires an increase in the reaction

temperature and gives a lower yield.

$C_{11}H_{10}OFe$.	Found %: C 61.65; H 4.79; Fe 26.00
	Calculated %: C 61.68; H 4.67; Fe 26.16

Absorption maxima in the UV: 228; 270; 342; 462 mμ.

Azomethine dyes (anils) were synthesized by heating the aldehyde with amines in alcohol; in particular, with aminoazobenzene, brownish-red crystals with m.p. 133.5–134° were obtained; with *o*-toluidine, brown lustrous crystals with m.p. 105–107°; with mesidine, dark-brown crystals with m.p. 85–86°; with *p*-anisidine, orange crystals with m.p. 104.5–105°.

5. A bright-green polymethine dye was obtained, for example, by stirring for 20 h a mixture of 2.14 g of the aldehyde, 1.7 g of 1,3,3-trimethyl-2-methyleneindoline (I), and 5 ml of CH_3COOH. The condensation product was isolated by dissolving the mixture in 120 ml of water and salting out with sodium chloride—4 g with m.p. 59°. Repeated dissolution in water and salting out did not change the m.p. The chloride was readily converted into the perchlorate, bromide, rhodanide, and iodide; the latter crystallizes well from aqueous alcohol—lustrous dark-green crystals with a violet sheen.

$C_{23}H_{24}NJFe$.	Found %: C 55.93; H 5.08; N 2.76; J 25.31; Fe 10.86
	Calculated %: C 55.53; H 4.82; N 2.82; J 25.53; Fe 11.26

The same dye was synthesized by condensation of perchlorate I with the aldehyde in 10 ml of ethyl alcohol in the presence of 8 drops of piperidine at 80° for 3 h. Absorption maxima in alcohol: 420, 620 mμ.

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REFERENCES CITED

1 G. Wilkinson, F. Cotton, J. Birmingham, J. Inorg. Nucl. Chem., 2, 95 (1956).
2 P. L. Pauson, Quart. rev., 9, 391 (1955).
3 A. N. Nesmeyanov, E. G. Perevalova, Khim. nauka i prom., 3, 152 (1958).
4 J. Thiele, Ber., 33, 670 (1900).
5 A. N. Nesmeyanov et al., Izv. AN SSSR, OKhN, 1957, 638.
6 V. Weinmayer, J. Am. Chem. Soc., 77, 3009 (1955).
7 A. N. Nesmeyanov, E. G. Perevalova, S. S. Churanov, DAN, 114, 335 (1957).
8 G. D. Broadhead, J. M. Osgerby, P. L. Pauson, Chem. Ind., 1957, 209.

9 M. Rosenblum, Chem. Ind., 1957, 72.
10 P. J. Graham et al., J. Am. Chem. Soc., 79, 3416 (1957).
11 G. D. Broadhead, J. M. Osgerby, P. L. Pauson, J. Chem. Soc., 1958, 650.

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