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Abstract

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REACTIONS OF *o*-CARBOXYBENZOYLFERROCENE

In previous papers devoted to the reactions of *o*-carboxybenzoylferrocene (^{1,2}), we noted the distinctive behavior of this substance in the presence of catalytic amounts of sulfuric acid, polyphosphoric acid, etc. Under the action of these acids, a series of transformations takes place, accompanied by radical cleavage and leading, ultimately, to 3,3-(diferrocenyl-3,3)-diphthalide. The present work is devoted to the study of the reactions of *o*-carboxybenzoylferrocene with nucleophilic reagents.

When *o*-carboxybenzoylferrocene is treated with phosphorus trichloride, a substance is formed which, in its properties, strongly resembles the so-called "Boyd chloroanhydride" (^{3,4}). Apparently, *o*-carboxybenzoylferrocene reacts here in its cyclic form II.

$$\text{(I)} \rightleftarrows \text{II} \xrightarrow{\text{PCl}_3} \text{(IIIa) or (IIIb)}$$

The structure of the substance thus obtained was confirmed by its elemental analysis, measurement of molecular weight, and infrared spectral data. The latter contains frequencies in the regions 1000, 1103, 480, 580, 1250, 1280, 1300, and 1790 cm^{-1} (very intense). Thus, the substance contains a free cyclopentadienyl nucleus and a lactone ring. The frequencies 480-580 cm^{-1} may be assigned to P—Cl vibrations. However, on the basis of the infrared spectra it is impossible to say with certainty whether the substance has the pentavalent (IIIa) or trivalent (IIIb) type of structure.

The product is stable toward the action of air, water, and alkali. On heating with dilute acetic acid, however, destruction of the molecule occurs with liberation of the initial *o*-carboxybenzoylferrocene. Apparently, in this case one must assume the transformation of the "ring" lactone structure into a "chain" ketone structure. Under the action of an alcohol in the presence of triethylamine, only one chlorine atom is replaced by an ethoxy group. An attempt to replace the second chlorine atom by an ethoxy group under analogous conditions did not lead to the desired result. Interaction with sodium alcoholate leads to the formation of small amounts of 3-ferrocenylphthalidylphosphinic acid.

The reactions of *o*-carboxybenzoylferrocene with nucleophilic reagents—thiophenol and phenol—in the presence of phosphoric acid are of interest. In this process, S- and O-substituted and 3-ferrocenylphthalides are formed. In the case of thiophenol the reaction proceeds according to the scheme:

$$\textit{o}\text{-carboxybenzoylferrocene} \rightleftarrows \text{cyclic lactone form} \xrightarrow[H_3PO_4]{C_6H_5SH} \text{3-(phenylthio)-3-ferrocenylphthalide}$$

An attempt to carry out the same reactions in the absence of H_3PO_4 gave no positive results. Apparently, the first stage of the reaction is the formation of an α-ferrocenylmethyl cation of the type:

[structural formula]

with subsequent attack by the nucleophilic agent at the cationoid center. Thus, these reactions are a new example of an α-ferrocenylmethylation reaction. The detailed study of methods for the preparation and properties of ferrocenylmethylcation salts is the subject of work by one of us and V. A. Sazonova (^{5}). The structure of 3-ferrocenyl-3-thiophenylphthalide is confirmed by elemental-analysis data, as well as by IR-spectral data. The IR spectrum of this substance contains frequencies in the regions 1000, 1107, and 1785 cm^{-1}. Thus, the presence of a lactone ring may be considered proved. The IR spectrum of 3-ferrocenyl-3-phenoxyphthalide, obtained in an analogous reaction of *o*-carboxybenzoylferrocene with phenol, contains frequencies in the regions 1000, 1100, 1125, 1725, and 1730 cm^{-1}. Interpretation of these data requires a more detailed study of the IR and UV spectra in solutions.

1. To 5 g (0.014 mole) of *o*-carboxybenzoylferrocene was added dropwise 15 ml of freshly distilled PCl_3. The mixture was left overnight. The excess PCl_3 was carefully removed in the vacuum of a water-jet pump. The residue, in the form of yellow needles (5.55 g) (85% of theory), was washed with petroleum ether and recrystallized from dry heptane, m.p. 131°C with decomposition. Repeated recrystallization did not change the melting point.

Found, %: C 50.05, 50.03; H 3.12, 3.20; Cl 16.26, 16.00,
Fe 12.61, 12.43; P 7.56, 7.34

$C_{18}H_{13}FeO_3PCl_2$. Calculated, %: C 49.99; H 2.99; Cl 16.20;
Fe 12.78; P 7.12

Mol. wt.: found 386 (benzene, cryoscopy), calculated 435.14.

2. A mixture of 2 g (0.004 mole) of (III) and 10 ml of dilute CH_3COOH (1:5) was left overnight and then heated for 15 min at 80°. The red solution was decanted, and the crystalline residue was extracted three times with acetic

acid (1:1). The acid-insoluble black residue contains inorganic iron salts. From the acetic-acid solutions, on standing, yellow crystals precipitated. Weight 0.1 g, m.p. 188-189°C with decomposition. A mixed sample with *o*-carboxybenzoylferrocene gave no depression of the melting point. The acetic-acid mother liquors were combined, neutralized with alkali, and acidified with HCl. The precipitate that formed was separated, thoroughly washed with cold water, and dried. Weight 0.71 g, m.p. 188-189°. A mixed sample with *o*-carboxybenzoylferrocene gave no depression of the m.p. The total yield of *o*-carboxybenzoylferrocene was 0.81 g (53% of theory).

3. To a mixture of 6 ml of abs. alcohol and 1 g (0.009 mole) of triethylamine in 60 ml of abs. ether, with stirring, was added a suspension of 2 g (0.004 mole) of III and 50 ml of abs. ether. The suspension was added at such a rate that the mixture boiled uniformly. Then the reaction mass was left overnight. The triethylamine hydrochloride that precipitated on standing was separated. Weight 0.85 g (70% of theory). The solution was thoroughly washed with water. The solvent was evaporated, and the residue was recrystallized from a benzene-heptane mixture (1:1). The yellow crystals that precipitated were separated, dried, m.p. 145-146°C with decomposition. Weight 0.48 g (24% of theory).

Found, %: C 54.31, 53.90; H 4.12, 4.15; Cl 7.41, 7.42;
Fe 12.3; P 6.87

$C_{20}H_{18}FePO_4Cl$. Calculated, %: C 54.03; H 4.08; Cl 7.98;
Fe 12.58; P 6.97

4. The reaction of 0.6 g (0.001 mole) of the product with m.p. 145-146° with 1 g (0.009 mole) of $N(C_2H_5)_3$ was carried out under conditions analogous to those of the preceding experiment. The starting product, m.p. 131-139°, was recovered; after recrystallization from a benzene-heptane mixture (1:1) it melted at 145-146° with decomposition.

5. A mixture of 1 g (0.0028 mole) of I, 10 ml of H_3PO_4, and 10.7 g (0.097 mole) of thiophenol was left overnight. It was then heated for 10 min at 50° and poured onto ice. The aqueous and thiophenol layers were separated. The thiophenol layer was thoroughly washed with water, 10% alkali, and again with water. The solution was poured into a dish, the solvent was evaporated, and the oily residue was dissolved in methylene chloride. The latter was washed with 15% $NaOH$, water, dried over Na_2SO_4, and then the solvent was evaporated. The residue, twice recrystallized from a benzene-petroleum ether mixture (1:3), melted at 145-144.5°. Weight 1.03 g. The aqueous layer was extracted with methylene chloride. The latter was washed with water, 15% $NaOH$, water, and dried over Na_2SO_4. After evaporation of the solvent, yellow crystals with m.p. 139-143° were isolated. After recrystallization from a benzene-petroleum ether mixture (1:3), it melted at 144.5-145°. Weight 0.2 g. Thus, 1.23 g (97% of theory)

of yellow crystalline product was isolated.

Found, %: C 67.79, 67.82; H 4.33, 4.42; Fe 12.46, 12.23
$C_{24}H_{18}FeSO_2$. Calculated, %: C 67.62; H 4.25; Fe 13.10

6. The reaction of 1 g (0.0028 mole) of *o*-carboxybenzoylferrocene with 10.7 g (0.097 mole) of thiophenol was carried out analogously to the preceding experiment. After workup of the reaction mixture, the starting acid, *o*-carboxybenzoylferrocene (m.p. 188-189°), was isolated. A mixed sample with an authentic preparation of *o*-carboxybenzoylferrocene showed no depression of the melting point.

7. To a melt of 5 ml of H_3PO_4 were added 5 g (0.053 mole) of phenol and 1 g (0.002 mole) of *o*-carboxybenzoylferrocene. The mixture was heated on a water bath for 7 h at 50-60°. The reaction mixture was transferred to ice and extracted with methylene chloride. The methylene chloride solution was washed with water and 15% $NaOH$ until the alkaline solution became colorless, and dried over Na_2SO_4. After evaporation of the solvent the residue crystallized. M.p. 188-200°. The product was recrystallized from a benzene-petroleum ether mixture (1:1), m.p. 250° with decomposition. Weight of 3,3′-diferrocenyldiphthalide 0.06 g.

Found, %: C 68.20, 68.41; H 4.32, 4.26; Fe 17.43, 17.25
$(C_{18}H_{19}FeO_2)_2$. Calculated, %: C 68.38; H 4.11; Fe 17.65

On cooling, yellow crystals precipitated from the solution, m.p. 180° with decomposition, weight 0.54 g (41% of theory).

Found, %: C 70.46, 70.41; H 4.34, 4.35; Fe 13.25, 13.12
$C_{24}H_{18}FeO_3$. Calculated, %: C 70.26; H 4.42; Fe 13.61

The product is soluble in common organic solvents.

8. A mixture of 1 g (0.002 mole) of *o*-carboxybenzoylferrocene and 5 g (0.053 mole) of phenol was heated under the conditions of the preceding experiment. After workup, the starting *o*-carboxybenzoylferrocene, m.p. 188-189°, was isolated. A mixed sample with an authentic synthesized product showed no depression of the melting point.

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