Academician A. N. NESMEYANOV, N. A. VOL' KENAU, and V. D. VIL' CHEVSKAYA

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Abstract

Full Text

Academician A. N. NESMEYANOV, N. A. VOL' KENAU, and V. D. VIL' CHEVSKAYA

INTRAMOLECULAR ACYLATION IN THE FERROCENE SERIES

CYCLIZATION OF γ-FERROCENYL-SUBSTITUTED ACIDS AND KETO ACIDS

In a previous communication (^{1}), using as an example the synthesis of di(ketotetrahydroindenyl)iron from di(ω-carboxypropyl)ferrocene, we demonstrated the possibility of intramolecular acylation in the ferrocene series. The present work is an extension and continuation of the first communication. It is devoted to the cyclization of monosubstituted ferrocene derivatives.

By the reaction of ferrocene with the acid chloride of β-carbomethoxypropionic acid, we obtained β-carbomethoxypropionylferrocene, and from it—β-carboxypropionylferrocene.

Attempts to cyclize β-carboxypropionylferrocene by the action of polyphosphoric or sulfuric acid were unsuccessful. Under mild conditions the substance was recovered unchanged, while under severe conditions it was destroyed.

β-Carboxypropionylferrocene was reduced by the Clemmensen method to ω-carboxypropylferrocene. The latter, like di(ω-carboxypropyl)ferrocene, cyclized readily on heating with polyphosphoric acid. As a result, ketotetrahydroindenylcyclopentadienyliron was formed. The structure of the latter was proved: a) by obtaining a derivative at the keto group; b) by bromination, which led to pentabromocyclopentane, i.e., revealed the presence in the molecule of an unsubstituted cyclopentadienyl ring; c) by the infrared spectrum,* which confirmed the presence of an unsubstituted ring (frequencies: 1008 and 1106 cm^{-1}).

We also investigated the cyclization of *o*-carboxybenzoylferrocene. The starting *o*-carboxybenzoylferrocene was obtained by the reaction of ferrocene with the acid chloride of *o*-carbomethoxybenzoic acid, followed by hydrolysis of the resulting *o*-carbomethoxybenzoylferrocene.

In contrast to the ferrocene-substituted keto acids of the aliphatic series, *o*-carboxybenzoylferrocene cyclizes readily with both polyphosphoric and concentrated sulfuric acids. Under the same conditions *o*-carbomethoxybenzoylferrocene also cyclizes.

Thus, a complete analogy with benzene derivatives is observed. It is known that benzoylpropionic acid does not cyclize, whereas *o*-benzoylbenzoic acid readily structure I

Figure 1: structure I

forms anthraquinone simply upon heating ([2]).

Investigation of the structure of the cyclization product showed that it has structure I, since it forms pentabromocyclopentane upon bromination and its infrared spectrum contains lines characteristic of an unsubstituted cyclopentadienyl ring (frequencies: 1003 and 1107 cm^{-1}).

The above results confirm the conclusion made in the previous communication ([1]): β-ferrocenyl-substituted carboxylic acids undergo intramolecular acylation into the same cyclopentadienyl ring in which the substituent already stands.

This applies even to *o*-carboxybenzoylferrocene, in which this ring—

[*] The spectra cited in this work were recorded by L. A. Kazitsyna and B. V. Lokshin.

is somewhat deactivated by the CO group already present in it. β-Carboxypropionylferrocene does not cyclize at all.

Whether this is explained by the fact that a chain of four carbon atoms is not long enough to connect the two cyclopentadienyl rings of ferrocene, or whether the free ring is also somewhat deactivated by the first CO group,^(3) is a question that will be resolved by further investigation.

Experimental Part

1. Preparation of β-carbomethoxypropionylferrocene. To a solution of 10 g (0.051 mole) of ferrocene in 100 ml of carbon disulfide was added a solution of 7 g (0.05 mole) of $AlCl_3$ and 8 g (0.05 mole) of β-carbomethoxypropionic acid chloride in 25 ml of abs. ether. After heating for one hour, the carbon disulfide was decanted, and the residue was decomposed with ice and HCl. The precipitate that separated was recrystallized twice from petroleum ether with benzene (3:1). In this way 5.2 g (32% of theoretical) of β-carbomethoxypropionylferrocene was obtained—an orange substance with m.p. 60°. The substance is readily soluble in alcohol, ether, benzene, $CHCl_3$, and moderately soluble in heptane.

Found, %:	C 59.94; 60.15;	H 5.13; 5.31;	Fe 18.74; 18.56
$C_{15}H_{16}O_3Fe$. Calculated, %:	C 60.00;	H 5.33;	Fe 18.66

The method is general for the preparation of monoacylferrocenes.

2. Preparation of β-carboxypropionylferrocene. 6.4 g of β-carbomethoxypropionylferrocene were heated for 5 h with 30 ml of a 30%

aqueous KOH solution. From the resulting alkaline solution, after acidification, 5.6 g (92.5% of theoretical) of β-carboxypropionylferrocene was isolated—a red-orange substance with m.p. 149–150° after recrystallization from 50% methyl alcohol.

Found, %: C 59.09; 58.93; H 4.97; 4.89; Fe 18.50; 18.48
$C_{14}H_{14}O_3Fe$. Calculated, %: C 58.74; H 4.89; Fe 19.58

3. Preparation of ω-carboxypropylferrocene. 1 g of β-carboxypropionylferrocene was reduced with a tenfold excess of amalgamated zinc and hydrochloric acid in glacial acetic acid (heating for 5 h). As a result, 0.89 g (97.8% of theoretical) of ω-carboxypropylferrocene was obtained, with m.p. 117–118° after recrystallization from petroleum ether with benzene (1:1).

Found, %: C 61.85; 61.94; H 5.80; 5.93; Fe 20.22; 20.39
$C_{14}H_{16}O_2Fe$. Calculated, %: C 61.76; H 5.88; Fe 20.58

4. Cyclization of ω-carboxypropylferrocene. 2.1 g of ω-carboxypropylferrocene were mixed with polyphosphoric acid (from 8 ml of H_3PO_4, sp. gr. 1.695, and 16 g of P_2O_5) and left for 3 days at room temperature, and then heated for 1 h at 50–60°. The reaction mixture was then decomposed with alkali and ice, and the cyclization product was extracted with ether. 1.05 g (56.4% of theoretical) of ketotetrahydroindenyl-cyclopentadienyl-iron was obtained —a yellow crystalline substance with m.p. 84° after recrystallization from petroleum ether.

Found, %: C 66.12; 66.01; H 5.61; 5.53; Fe 22.15; 22.08
$C_{14}H_{14}OFe$. Calculated, %: C 66.14; H 5.51; Fe 22.04

A semicarbazone of ketotetrahydroindenyl-cyclopentadienyl-iron was obtained, with m.p. 198–198.5°.

Found, %: C 57.88; 57.83; H 5.64; 5.53; Fe 18.05; 17.95; N 13.6; 13.36
$C_{15}H_{17}ON_3Fe$. Calculated, %: C 57.87; H 5.46; Fe 18.00; N 13.5

5. Preparation of o-carbomethoxybenzoylferrocene. o-Carbomethoxybenzoylferrocene was obtained from 15 g (0.08 mole) of ferrocene in 150 ml of carbon disulfide, 15.9 g (0.08 mole) of o-carbometh—

oxybenzoic acid and 21 g (0.158 mole) of $AlCl_3$ in 60 ml of abs. ether under the same conditions as β-carbomethoxypropionylferrocene. Yield of product

23.2 g (82.8% of theory), m.p. 138° after recrystallization from 50% methanol and then from heptane (literature data: 134–135° (^{1})). The substance gives no depression of the melting point with *o*-carbomethoxybenzoylferrocene obtained by esterification of *o*-carboxybenzoylferrocene (^{1}).

6. **Preparation of *o*-carboxybenzoylferrocene.** *o*-Carboxybenzoylferrocene was obtained by hydrolysis of *o*-carbomethoxybenzoylferrocene under the conditions described in experiment 2, in 95% yield. The red-orange substance had decomp. temp. 183–184° after recrystallization from water with CH_3OH (1 : 3) (cf. (^{1})).

Found, %: C 65.10; 65.11; H 4.25; 4.16; Fe 15.92; 16.04
$C_{18}H_{14}O_3Fe$. Calculated, %: C 64.68; H 4.22; Fe 16.71

The potassium salt of *o*-carboxybenzoylferrocene, like the sodium salt (^{1}), is only slightly soluble in water and, on hydrolysis, precipitates from solution as shiny orange crystals.

7. **Reduction of *o*-carboxybenzoylferrocene.** 1 g of *o*-carboxybenzoylferrocene was reduced with a twentyfold excess of amalgamated zinc and hydrochloric acid, with gradual addition of the latter over 10 hr while heating.

The product, recrystallized from methanol with water (3 : 1), melted at 173–174°. Yield of *o*-carboxybenzylferrocene 0.82 g (86% of theory).

Found, %: C 67.41; 67.37; H 5.07; 5.14; Fe 17.62; 17.45
$C_{18}H_{16}O_2Fe$. Calculated, %: C 67.5; H 5.00; Fe 17.45

8. **Cyclization of *o*-carbomethoxybenzoylferrocene.** 3 g of *o*-carbomethoxybenzoylferrocene, mixed with 10 ml of concentrated sulfuric acid, were left for 10 hr at room temperature. Then, with thorough cooling, the reaction mixture was neutralized and the product extracted with ether. 1.45 g (54% of theory) of a yellow crystalline substance was obtained, not melting above 300°. The substance is soluble in benzene, alcohol, and toluene, and can be recrystallized from xylene.

Found, %: C 68.36; 68.22; H 4.05; 4.02; Fe 17.19; 17.17
$C_{18}H_{12}O_2Fe$. Calculated, %: C 68.38; H 3.83; Fe 17.66

The same product was obtained in 34% yield by cyclization, under the above conditions, of *o*-carboxybenzoylferrocene. Cyclization with the aid of polyphosphoric acid led to the same result.

9. **Bromination of the cyclization products of ω-carboxypropylferrocene and *o*-carboxybenzoylferrocene.** Bromination of both products was carried out identically.

The substance to be brominated was dissolved in CCl_4, a solution of bromine in CCl_4 was added to it, and the mixture was boiled for 1–2 hr. After removal of the $FeBr_3$ precipitate, the chloroform solution was evaporated and the oily portion of the residue was washed out with ether; the remaining crystalline pentabromocyclopentane was recrystallized from alcohol, m.p. 103–104° (literature data (^{4}): 103–104°). The product was identified by the melting point of a mixed sample with an authentic specimen.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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