

Properties of Phenylferrocene

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Abstract

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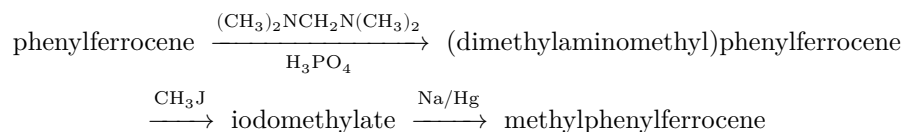
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PROPERTIES OF PHENYLFERROCENE

An alkyl group bonded to a ferrocene nucleus facilitates subsequent electrophilic substitution; in this case, the cyclopentadienyl ring to which it is attached is activated more strongly ⁽¹⁻⁴⁾. A phenyl group, with respect to a ferrocenyl group, is electron-accepting, as we first showed by comparing the basicity constant of *n*-ferrocenylaniline and the ionization constant of *n*-ferrocenylphenol with the constants of the corresponding benzene derivatives ⁽⁵⁾.

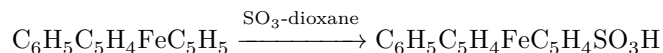
Rosenblum's data ⁽⁶⁾ on the acylation of phenylferrocene confirm our results: the phenyl group, like other electron-accepting substituents, has a deactivating effect on the electrophilic substitution of the hydrogens of the ferrocene nucleus.

In the present work we investigated the aminomethylation, sulfonation, and nitration of phenylferrocene, and also carried out competitive acetylation of phenylferrocene (with ferrocene). Aminomethylation of phenylferrocene was carried out with tetramethyldiaminomethane in the presence of phosphoric acid. In this process, (*N,N*-dimethylaminomethyl)phenylferrocene was obtained. In the IR spectrum of the crude product there are absorption bands in the region of 1000 and 1100 cm⁻¹; however, the intensity of the bands is low. Apparently, the homoannular isomer is formed in small amount. (*N,N*-Dimethylaminomethyl)phenylferrocene was converted into the iodomethylate and reduced with sodium amalgam to methylphenylferrocene. From the reaction products a heteroannular methylphenylferrocene was isolated in 70% yield, calculated on the aminomethylated phenylferrocene.



This indicates that the heteroannular isomer was the principal component of the initial mixture of *N,N*-dimethylaminomethylphenylferrocenes and, consequently, that aminomethylation of phenylferrocene proceeds predominantly in the free cyclopentadienyl ring.

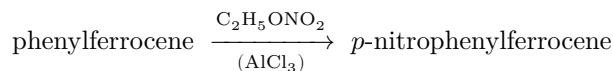
On sulfonating phenylferrocene with dioxane sulfur trioxide under the conditions for the formation of ferrocenemonosulfonic acid, we obtained 1, 1'-phenylferrocenesulfonic acid.



The acid was isolated in the form of the lead salt. The formation of a heteroannular sulfonic acid also indicates the lower reactivity of the cyclopentadienyl ring bonded to phenyl.

The deactivating influence of the phenyl group on the ferrocenyl nucleus is clearly manifested in the Friedel-Crafts reaction. Thus, on acylation of a mixture of phenylferrocene and ferrocene with acetyl chloride in the presence of aluminum chloride (all components were taken in a molar ratio of 1 : 1 : 1), we obtained acetylferrocene in a yield of 25% of theory, and a mixture of acetylphenylferrocenes in a yield of only 5%; at the same time, 64% of phenylferrocene and 30% of ferrocene were recovered unchanged. Consequently, ferrocene is acetylated considerably more readily than phenylferrocene.

We carried out the nitration of phenylferrocene with ethyl nitrate in carbon disulfide in the presence of AlCl_3 and obtained *p*-nitrophenylferrocene in a yield of 13% of theory.



It should be noted that the main amount of *p*-nitrophenylferrocene and part of the unreacted phenylferrocene are isolated in the unoxidized form (and not in the form of the cation). Obviously, the nitration reaction proceeds with the phenylferrocene itself, and not with its cation. At the same time, the preservation of the ferrocenyl nucleus under these conditions is noteworthy, probably as a consequence of its somewhat reduced ability, in comparison with ferrocene, to oxidize to the cation. Ferrocene itself cannot be nitrated under these conditions.

Our attempts to nitrate ferrocene with various reagents, including nitronium borofluoride, were unsuccessful. In all cases ferrocene was oxidized to the cation, which is inert in electrophilic substitution reactions (⁷).

Experimental Part

Aminomethylation of phenylferrocene. To a mixture of 70 ml of glacial CH_3COOH and 4 g of H_3PO_4 , sp. gr. 1.735, cooled to 10° , there was gradually added 2.25 g (0.019 mole) of tetramethyldiaminomethane, and then 4 g (0.015 mole) of phenylferrocene. The reaction mixture was stirred in a stream of nitrogen for one hour at room temperature and for 10 hr at $110\text{--}115^\circ$; after this it was diluted with twice its volume of water, and the unreacted phenylferrocene

(1.5 g) was extracted with benzene. A 40% solution of NaOH was added to the acidic solution, and (N,N-dimethylaminomethyl)phenylferrocene was extracted with ether. After removal of the ether, 2.6 g of aminomethylated phenylferrocene was obtained as a viscous dark reddish-brown oil. The yield was 54% of theory, calculated on the phenylferrocene taken into the reaction, and 86%, calculated on the phenylferrocene that entered into the reaction.

(N,N-Dimethylaminomethyl)phenylferrocene was distilled in vacuo. B.p. 150–160°/3 mm; n_D^{20} 1.6315.

Found, %: C 72.09; 72.05; H 6.85; 6.87; N 4.83; 4.85
 $C_{19}H_{21}NFe$. Calculated, %: C 71.48; H 6.63; N 4.39

In the IR spectrum of the obtained (N,N-dimethylaminomethyl)phenylferrocene there are weak absorption bands in the region of 1000 and 1100 cm^{-1} ; consequently, a mixture of hetero- and homoannular isomers is formed.*

Iodomethylate of (N,N-dimethylaminomethyl)phenylferrocene was obtained by adding CH_3I to a solution of 3.2 g of aminomethylated phenylferrocene in absolute CH_3OH (or in benzene) and

* In the distilled product the absorption in this region is considerably less intense than in the undistilled product.

after 15 min with a large amount of dry ether. 4.3 g (yield almost quantitative) of the iodomethylate was obtained, a yellow crystalline substance. Decomp. temp. 70–75°.

Found, %: C 51.77; H 5.40; Fe 12.50; N 2.87
 $C_{20}H_{24}N_2Fe$. Calculated, %: C 52.09; H 5.25; Fe 12.12; N 3.04

In the IR spectrum of the iodomethylate obtained from distilled (N,N-dimethylaminomethyl)-phenylferrocene, absorption in the region of 1000 and 1100 cm^{-1} is absent; consequently, the substituent groups are located in different cyclopentadienyl rings.

1,1'-Methylphenylferrocene. An aqueous solution of 4.3 g (0.0093 mole) of the iodomethylate of (N,N-dimethylaminomethyl)-phenylferrocene* was added to sodium amalgam prepared from 24 g of sodium and 24 ml of mercury. The mixture was heated at 80–90° for 4 h. Methylphenylferrocene was extracted with petroleum ether and purified chromatographically on Al_2O_3 , and then recrystallized from petroleum ether and from ethyl alcohol. Yield 1.8 g (71% of theory). M.p. 88.5–89.5°.

Found, %: C 73.69; 73.63; H 6.00; 5.92; Fe 19.86; 20.12
 $C_{12}H_{14}Fe$. Calculated, %: C 73.93; H 5.83; Fe 20.22

A mixed sample with 1,1'-methylphenylferrocene, obtained by us earlier (8), by arylation of methylferrocene, melted without depression. The IR spectra of both preparations are identical; absorption in the region of 1000 and 1100 cm^{-1} is

absent. The free cyclopentadienyl ring is detected by means of the IR spectrum only in the substance isolated from the mother liquors.

Sulfonation of phenylferrocene. To a solution of 10 g (0.038 mole) of phenylferrocene in 100 ml of dichloroethane, 10 g (0.060 mole) of freshly prepared dioxanesulfur trioxide was added with ice cooling. After an hour the cooling was removed and the reaction mixture was left for 24 h. The sulfonic acids were then extracted with water.

By addition of lead carbonate to the aqueous solution of phenylferrocenesulfonic acid, its lead salt was obtained, crystallizing with four molecules of water.

Found, %: C 39.99; 39.68; H 3.97; 3.75

$C_{32}H_{34}O_{10}S_2Fe_2Pb$. Calculated, %: C 39.96; H 3.67

In the IR spectrum of the lead salt, absorption in the region of 1000 and 1100 cm^{-1} is absent; consequently, the phenyl and sulfo groups are located in different cyclopentadienyl rings.

Unreacted phenylferrocene was not detected in the reaction products.

Competitive acetylation of ferrocene and phenylferrocene. A solution of 1.4 ml (0.02 mole) of acetyl chloride and 2.66 g (0.02 mole) of $AlCl_3$ in 10 ml of abs. ether was added over 20 min with stirring to a solution of 3.72 g (0.02 mole) of ferrocene and 5.42 g (0.02 mole) of phenylferrocene in 100 ml of CS_2 . Stirring was continued for 45 min at room temperature and for 30 min with heating on a water bath. The reaction was carried out in a stream of pure nitrogen.

The cooled reaction mixture was poured onto ice (300 g) mixed with 2 ml of conc. HCl. The aqueous layer was separated, reduced with Na_2SO_3 , and extracted with ether. The ether extracts were combined with the carbon disulfide layer, washed with 2N NaOH and water, and dried over Na_2SO_4 . The residue after removal of the solvent in vacuo was dissolved in a mixture (1:1) of petroleum ether and benzene and chromatographed on Al_2O_3 . Ferrocene and phenylferrocene were eluted with petroleum ether; acetylferrocene and acetylated phenylferrocenes, with a mixture (1:1) of petroleum ether and benzene. 1.1 g (30% of the amount taken) of ferrocene was isolated, m.p. and mixed-sample m.p. 173–174°; 3.35 g

* Obtained from undistilled aminomethylated phenylferrocene.

(64%) phenylferrocene, m.p. and mixed m.p. 109–110°; 1.15 g (25% yield) acetylferrocene, m.p. and mixed m.p. 83–84°, and 0.3 g (5%) of a mixture of acetylphenylferrocenes, m.p. 69–73°.

Found, %: C 71.40; 71.57; H 5.50; 5.40; Fe 17.96; 18.18

$C_{18}H_{16}OFe$. Calculated, %: C 71.07; H 5.30; Fe 18.36

In the IR spectrum of the mixture there is weak absorption at 1106 and 1002 cm^{-1} . From the mixture of acetylphenylferrocenes, by repeated fractional crys-

tallization from a mixture of petroleum ether and ether (2:1), the heteroannular acetylphenylferrocene was isolated. M.p. 88.5–89.5°. Literature data ⁽⁶⁾: m.p. 92.5–93.5°. In the IR spectrum, frequencies in the region of 1000 and 1100 cm⁻¹ are absent.

Found, %: C 71.31; 71.30; H 5.43; 6.51; Fe 18.20; 18.06
C₁₈H₁₆OFe. Calculated, %: C 71.07; H 5.30; Fe 18.36

Nitration of phenylferrocene. To a mixture of 2.62 g (0.01 mole) of phenylferrocene, 13.5 g (0.1 mole) of AlCl₃, and 50 ml of CS₂, with stirring over 10 min, a solution of 1 ml (0.1 mole) of ethyl nitrate in 25 ml of CS₂ was added. A dark precipitate formed, and the carbon disulfide became decolorized. The carbon disulfide was decanted, and the residue was treated with 2 N HCl. The precipitate was filtered off, washed with water, dried, and extracted with ether until the extracts were colorless. The ether was distilled off; the residue was dissolved in petroleum ether and chromatographed on Al₂O₃. There was isolated (elution was carried out with petroleum ether) 0.1 g of the starting phenylferrocene, m.p. and mixed m.p. 109–110°, and 0.35 g of *p*-nitrophenylferrocene, m.p. 167–168°; a mixed sample with *p*-nitrophenylferrocene obtained by us earlier ⁽⁹⁾ by arylation of ferrocene melted without depression.

The hydrochloric acid solution was reduced with SnCl₂ (50 g). The brown precipitate that formed was filtered off, washed with water, dried, and extracted with petroleum ether. The solution was chromatographed on Al₂O₃. An additional 0.15 g of phenylferrocene, m.p. 109–110°, and 0.05 g of *p*-nitrophenylferrocene, m.p. 167–168°, were obtained.

In all, 0.25 g (9.5% of the amount taken) of phenylferrocene and 0.40 g of *p*-nitrophenylferrocene were isolated; yield 13.0% of theoretical, calculated on the total phenylferrocene used in the reaction, and 14.2%, calculated on the phenylferrocene that reacted.

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