Chemistry

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Abstract

Full Text

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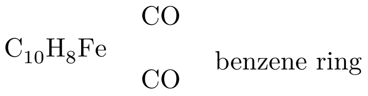
REACTIONS OF *o*-CARBOXYBENZOYLFERROCENE

Recently, two of us and Vol' kenau (^{1}) obtained *o*-carboxybenzoylferrocene by the interaction of ferrocene with the acid chloride of *o*-carbomethoxybenzoic acid in the presence of anhydrous aluminum chloride, followed by hydrolysis of the resulting *o*-carbomethoxybenzoylferrocene. The substance of composition $C_{36}H_{26}O_4Fe_2$, obtained by the action of sulfuric acid on *o*-carboxybenzoylferrocene and previously taken by us to be the ferrocene analog of anthraquinone,



$$C_{10}H_8Fe \begin{matrix} CO \\ \\ CO \end{matrix} \text{benzene ring} \quad (I) \quad (^2),$$

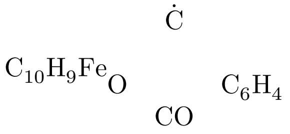
proved to have another structure, namely (II). Thus, the substance with structure (I) should be deleted from the list of those obtained.

Indeed, *o*-carboxybenzoylferrocene undergoes a series of interesting transformations under the action of concentrated sulfuric acid or acetic anhydride in the presence of catalytic amounts of sulfuric acid already at room temperature, forming 3,3′-diferrocenyl-3,3′-diphthalide according to the scheme:

$$C_{10}H_9Fe{-}CO{-}C_6H_4{-}COOH \xrightarrow[\substack{(CH_3CO)_2O \\ 1\ \text{drop} \\ H_2SO_4}]{H_2SO_4} \left[C_{10}H_9Fe{-}C(OH)\left(\begin{matrix} O \\ CO \end{matrix}\right) C_6H_4\right] + H^{\oplus} \longrightarrow$$

$$(C_{10}H_9Fe{-}C)_2\,[\text{phthalide rings with CO and O}] \quad (II)$$

3,3′-Diferrocenyl-3,3′-diphthalide is apparently obtained by dimerization of the intermediate radical (III)



$$C_{10}H_9Fe_{O} \begin{matrix} \dot{C} \\ \\ CO \end{matrix} C_6H_4 \quad (III)$$

As for the transformation, in an acidic medium, of α-hydroxyl derivatives of ferrocene (in the side chain) into a radical followed by dimerization, this is not the first case. The condensation of aldehydes with ferrocene in an acidic medium proceeds analogously (3–6). Apparently, all such transformations may proceed according to the scheme:

[reaction scheme]

[reaction scheme]

3,3′-Diferrocenyl-3,3′-diphthalide is a light-yellow powder with no sharp melting point; it darkens on heating in a sealed capillary above 250°. It is readily soluble in ether, less soluble in benzene and alcohol. Recrystallized from benzene. Molecular weight 645 (ebullioscopy, benzene).

To determine the structure of 3,3′-diferrocenyl-3,3′-diphthalide, a hydrolysis reaction was carried out with a concentrated aqueous solution of KOH on heating. The reaction proceeds not only with cleavage of the lactone ring, but also of the C—C bond of the diphthalide according to the scheme:

[reaction scheme]

(IV)

In the reaction products, with a total yield of 60%, both 3-ferrocenylphthalide (m.p. 137°) and *o*-carboxybenzoylferrocene (m.p. 186°) were found in equimolecular amounts. In addition, a deeper decomposition of the molecule also partially occurs, with destruction of the ferrocene system. Ionic iron was detected in the aqueous solution.

An interesting decomposition of 3,3′-diferrocenyl-3,3′-diphthalide occurs on heating it with metallic sodium in alcohol. The main reaction products here are likewise 3-ferrocenylphthalide (IV) (yield 37%) and *o*-carboxybenzylferrocene with m.p. 174° (yield about 30% of theory). 3-Ferrocenylphthalide was obtained by an independent synthesis during the Clemmensen reduction of *o*-carboxybenzoylferrocene. Along with the usual reduction product—*o*-carboxybenzylferrocene (m.p. 174°) (2)—a small amount of 3-ferrocenylphthalide was isolated (Table 1).

The 3-ferrocenylphthalide obtained by three different methods was identified by a mixed melting-point test and by IR spectra; it was characterized in the form of the 2,4-dinitrophenylhydrazone. Molecular weight 320 (benzene, cryoscopy).

Other transformations of *o*-carboxybenzoylferrocene, indicating the presence of ring-chain tautomerism similar to the tautomerism of *o*-benzoylbenzoic acid, are presented in the scheme:

$$\mathrm{C_{10}H_9FeCO{-}C_6H_5{-}COOH} \rightleftharpoons \mathrm{C_{10}H_9Fe{-}C(OH){-}C_6H_4{-}COO} \xrightarrow{(CH_3CO)_2O}$$

$$\rightarrow \mathrm{C_{10}H_9Fe{-}C(OCOCH_3){-}C_6H_4{-}COO}\ \mathrm{(V)} \xrightarrow{ROH}$$

$$\rightarrow \mathrm{C_{10}H_9Fe{-}C(OR){-}C_6H_4{-}COO} \xrightarrow[\text{or } H_2SO_4]{120^\circ,\ 130^\circ} \mathrm{(II)},$$

where (VI) $R = CH_3$; (VII) $R = C_2H_5$.

Table 1

Derivatives of 3-ferrocenylphthalide
$C_{10}H_9Fe—C(R)C_6H_4COO$

Compound	R	Yield, %	m.p., °C	Mol. wt. found	Mol. wt. calc.	C found, %	C calc., %	H found, %	H calc., %	Fe found, %	Fe calc., %	Substance from which recrystallized
(II)	$\varphi—C—C_6H_4—COO$*	87	decomp. 250	645	634	68.43; 68.50	68.13	4.36; 4.43	4.13	16.47; 16.37	17.61	Benzene
(IV)	H**	30-37	137	320	318	67.68; 67.64	67.92	4.42; 4.45	4.44	17.18; 17.37	17.61	Methanol
(V)	$-OCOCH_3$	89	125			63.48; 63.35	63.84	4.26; 4.20	4.28	15.02; 14.95	14.84	Heptane
(VI)	$-OCH_3$	94	128	357	348	65.52; 65.26	65.53	4.59; 4.66	4.63	15.69; 15.89	16.04	Methanol
(VII)	$-OC_2H_5$	close to quant.	135	380	362	65.80; 66.10	66.31	5.10; 4.97	5.00	15.15; 15.06	15.41	Ethanol

* $\varphi = C_{10}H_9Fe$.
** Dinitrophenylhydrazone m.p. 187° from a 1:1 benzene-petroleum ether mixture.

Upon hydrolysis of acetate (V) with water, 15% HCl, and 20% KOH, *o*-carboxybenzoylferrocene was obtained.

The mobility of the acetoxy group in 3-acetyl-3-ferrocenylphthalide (V) is characteristic. Exchange for methoxy and ethoxy groups occurs already upon prolonged standing in a solution of the corresponding alcohol at room temperature, or upon recrystallization from them.

On heating somewhat above 100°, and also under the action of H_2SO_4, 3-alkoxy- and 3-acetoxy-3-ferrocenylphthalides (V), (VI), and (VII) are converted into 3,3′-diferrocenyl-3,3′-diphthalide (II) (yield 85%).

The IR spectra of the 3-ferrocenylphthalide derivatives (II)–(VII) contain the frequencies of the unsubstituted ferrocene ring at 1000 and 1105 cm^{-1} and a very intense frequency in the region of 1760 cm^{-1} ($C = O$ stretching vibrations of γ-lactones).

The IR spectrum of phthalide (m.p. 73°), synthesized for comparison, likewise contains a frequency at 1760 cm^{-1}. The starting *o*-carboxybenzoylferrocene contains frequencies in the regions of 1652 and 1680 cm^{-1}.

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REFERENCES

1. A. N. Nesmeyanov, N. A. Vol' kenau, V. D. Vil' chevskaya, DAN, **111**, No. 2, 362 (1956).
2. A. N. Nesmeyanov, N. A. Vol' kenau, V. D. Vil' chevskaya, DAN, **118**, No. 3, 512 (1958).
3. V. Weinmayr, *J. Am. Chem. Soc.*, **77**, No. 11, 3009 (1955).
4. A. N. Nesmeyanov, I. I. Kritskaya, *Izv. AN SSSR, OKhN*, 1956, No. 2, 253.
5. A. N. Nesmeyanov, L. A. Kozitsina, B. Lokshin, I. I. Kritskaya, DAN, **117**, 433 (1957).
6. K. L. Rinehart, Ch. J. Michejda, *J. Am. Chem. Soc.*, **81**, No. 12, 3162 (1959).

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