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Abstract

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OXYFERROCENES AND THEIR DERIVATIVES

We have already reported the synthesis of oxyferrocene (^{1}) from ferrocenylboric acid and haloferrocenes by the action of copper acetate. The ferrocenyl acetate formed in this reaction was hydrolyzed with alkali; oxyferrocene and a series of its ethers were obtained.

Ferrocenyl allyl ether is readily obtained by heating oxyferrocene with allyl bromide in acetone in the presence of potash. All our attempts to carry out the Claisen rearrangement showed that this compound is incapable of rearrangement. This is probably connected with the impossibility of a "quinoid" structure of ferrocene in the transition state. When ferrocenyl allyl ether is heated at 215—220° (under nitrogen), its decomposition to oxyferrocene is observed. Part of the ether remains unchanged. Claisen and Tietze (^{2}) had also indicated that allyl ethers of certain phenols (2,4-dimethyl-6-allylphenol and 2,4-dimethyl-6-propylphenol, where allyl rearrangement is impossible) on heating give the corresponding phenol with liberation of allene and diallyl. Ferrocenyl allyl ether does not rearrange even under the conditions of simultaneous acetylation of the allylic-rearrangement product described for the allyl ether of α-naphthohydroquinone (^{3}).

Table 1

Neutr., %	pH	pK	K
30	9.71	10.09	$8.12 \cdot 10^{-11}$
50	10.12	10.15	$7.15 \cdot 10^{-11}$
70	10.57	10.28	$5.30 \cdot 10^{-11}$

When ferrocenyl allyl ether is heated in diethylaniline in the presence of acetic anhydride, allylferrocenyl acetate is not formed; unchanged ferrocenyl allyl ether is recovered.

The considerations expressed above concerning the instability of the "quinoid" state in the ferrocene molecule are supported by experiments on the oxidation by air of the 1,1′-dioxyferrocene described below; in this process the molecule decomposes with liberation of an inorganic iron compound, and the cyclopentadienone formed is isolated as the dimer.

In the present work, the dissociation constants of oxyferrocene and phenol are also compared, and 1,1′-dioxyferrocene and its derivatives are described. The dissociation constants were calculated by the formula of Kumler (^{4}). The pH measurements were carried out with a glass electrode and an LP-5 potentiometer at 17° in 0.005 molar solutions of oxyferrocene and phenol in 5% alcohol, partially neutralized to 30, 50, and 70% with caustic soda. The data for oxyferrocene are given in Table 1.

Average values: for oxyferrocene $K = 6.9 \cdot 10^{-11}$, pK 10.17 ± 0.10; for phenol $K = 1.20 \cdot 10^{-10}$, pK 9.93 ± 0.05. Thus, oxyferrocene as an acid is weaker than phenol. The difference in pK values in the case of oxyferrocene (with increasing neutralization) is possibly due to the instability of the compound.

* *Note added in proof.* The just-published article by Fahrni, Habich, and Schmid (^{7}) establishes the migration of the allyl group of 2,4,6-trimethylphenyl allyl ether under the action of BCl_3 into the meta position. In this case as well, the authors propose formation of the quinoid form as the primary stage of the rearrangement.

Using 1,1′-ferrocenylenediboronic acid, we were able to synthesize derivatives of 1,1′-dioxyferrocene. 1,1′-Ferrocenylenediboronic acid reacts with copper acetate to form 1,1′-ferrocenylenediacetate (m.p. 55–56°) in 41% yield. The ester of 1,1′-dioxyferrocene is obtained in a considerably higher yield (83%) if, beforehand, one $B(OH)_2$ group in 1,1′-ferrocenylenediboronic acid is replaced by a halogen. In our preceding paper (^{5}) a method was given for preparing 1-(1′-haloferrocenyl)boronic acids. Under the action of copper acetate on the latter, both the halogen and the $B(OH)_2$ group are replaced by acetoxy groups. For the synthesis of 1,1′-ferrocenylenediacetate, 1,1′-dibromoferrocene may also be used

$$\begin{array}{c} (HO)_2BC_5H_4FeC_5H_4B(OH)_2 \\ XC_5H_4FeC_5H_4B(OH)_2 \\ XC_5H_4FeC_5H_4X \end{array} \xrightarrow{Cu[(OCOCH_2)_2]} (CH_3COOC_5H_4)_2Fe,$$

where X is a halogen.

In the IR spectrum of ferrocenylenediacetate there are no frequencies characteristic of an unsubstituted cyclopentadienyl ring of ferrocene. Hydrolysis of this compound (in a nitrogen atmosphere), followed by acidification or passage of CO_2, gives yellow needles of 1,1′-dioxyferrocene, extremely sensitive to air.

[[chemical scheme: 1,1'-dioxyferrocene $\xrightarrow{O_2}$ intermediate → oxidized product]]

The alkaline hydrolysate proved possible to use for obtaining derivatives of 1,1′-dioxyferrocene (1,1′-dimethoxyferrocene, 1,1′-ferrocenylenedibenzoate, 1,1′-ferrocenylenedibenzosulfonate, O,O′-(1,1′-ferrocenylene)diglycolic acid). All these derivatives of 1,1′-dioxyferrocene are stable in air.

Experimental Part

Ferrocenylallyl ether

A mixture of 0.30 g of oxyferrocene, 1.5 g of powdered potassium, and 0.5 ml of allyl bromide in 7 ml of abs. acetone was heated (under nitrogen) with stirring on a water bath for 2 h. Then the mixture was diluted with water and extracted with ether; the ether was filtered, thoroughly washed with 10% KOH and water, and evaporated. The resulting yellow oil crystallized on cooling. Yield: 0.30 g (84% of theory) of ferrocenylallyl ether with m.p. 26.5–28°; after recrystallization from methyl alcohol saturated with ferrocenylallyl ether at room temperature and cooled with dry ice with acetone, m.p. 28–30°.

Table 2

Compound	Yield, %	m.p., °C
$(CH_3OC_5H_4)_2Fe$	95	35–36
$(CH_3COOC_5H_4)_2Fe$	83	55–56
$(C_6H_5COOC_5H_4)_2Fe$	68	114–115
$(C_6H_5SO_2OC_5H_4)_2Fe$	72	119.5–120.5
$(HOOC{-}CH_2OC_5H_4)_2Fe$	76	168.5–169.5

$C_{13}H_{14}FeO$. Found, %: C 64.49; 64.62; H 5.90; 5.98; Fe 22.70; 22.78
Calculated, %: C 64.50; H 5.83; Fe 23.07

Ferrocenylallyl ether (0.55 g) was heated (under nitrogen) at 215–220° for half an hour. After cooling, ether and 10% KOH were added to the dark melt. The mixture was filtered from resin. The aqueous layer was separated and shaken with benzoyl chloride. Obtained was 0.17 g of ferrocenyl benzoate with m.p. 105–106°; after recrystallization from alcohol, m.p. 108.5–109.5°; mixed-

a mixed sample with an authentic sample melts without depression. The yellow oil remaining after evaporation of the ether was chromatographed on Al_2O_3 in a petroleum ether–benzene mixture. After removal of the solvent, the oil crystallized after some time. Obtained: 0.22 g, m.p. 21–23°. After recrystallization from hexane, m.p. 27–28°; a mixed sample with an authentic sample of ferrocenyl allyl ether melts at the same temperature.

Ferrocenoxyacetic acid. To 0.42 g of oxyferrocene in 3 ml of KOH solution was added a solution of 0.42 g of chloroacetic acid; the mixture was boiled for 3 h. (During the reaction it is ensured that the mixture remains alkaline.) After cooling, crystals of the potassium salt precipitated; the solution was acidified with 10% H_2SO_4 and shaken with ether until the salt precipitate disappeared. The ether was washed with water and evaporated. The remaining crystals were thoroughly dried in vacuo over P_2O_5. Obtained: 0.44 g (82% of theory) of ferrocenoxyacetic acid, m.p. 131–133°; after recrystallization from benzene, m.p. 136–137.5°.

Found, %:	C 55.59; 55.39	H 4.77; 4.78;	Fe 21.50; 21.56
$C_{12}H_{12}FeO_3$. Calculated, %:	C 55.41;	H 4.65;	Fe 21.48

1,1′-Ferrocenylenediacetate. a) To a hot solution of 2 g of 1-(1′-bromoferrocenyl)boronic acid was added a solution of 5.4 g of copper acetate. The mixture was heated to boiling. A red precipitate of cuprous oxide formed. After cooling, the mixture was extracted with ether; the ether was washed with water, 5% KOH, and water, and evaporated. Obtained: 1.62 g (83% of theory) of 1,1′-ferrocenylenediacetate, m.p. 50–52°. After recrystallization from hexane, m.p. 55–56°.

Analogously, from 0.83 g of 1-(1′-chloroferrocenyl)boronic acid and 2.2 g of copper acetate, 0.66 g of 1,1′-ferrocenylenediacetate (70% of theory) was obtained.

b)* To a hot suspension of 2 g of 1,1′-ferrocenylenediboronic acid in 400 ml of water was added a solution of 5.8 g of copper acetate. The mixture was heated for 40 min on a boiling water bath. A red precipitate formed. The 1,1′-ferrocenylenediacetate was extracted with ether; the ether was washed with alkali and water and evaporated. The residue (0.92 g) was dried, washed on the filter with petroleum ether. After evaporation of the petroleum ether, 0.90 g (41% of theory) of 1,1′-ferrocenylenediacetate was obtained, m.p. 48–51°; after recrystallization from hexane, m.p. 54.5–55.5°. A mixed sample with the sample obtained in experiment (a) melts without depression.

Found, %:	C 55.63; 55.55;	H 4.72; 4.70;	Fe 18.63; 18.58
$C_{14}H_{14}FeO_4$. Calculated, %:	C 55.66;	H 4.67;	Fe 18.49

Hydrolysis of 1,1′-ferrocenylenediacetate (in a nitrogen atmosphere). 1,1′-Ferrocenylenediacetate is readily hydrolyzed upon heating with 10% KOH for 10 min on a water bath. Upon acidification of the hydrolysate or passage of CO_2, yellow crystals of 1,1′-dioxyferrocene precipitate; these are extremely unstable in air. After washing with water and dissolving in alkali, the 1,1′-dioxyferrocene was benzoylated by the Schotten–Baumann method, giving 1,1′-ferrocenylenedibenzoate.

Oxidation of 1,1′-dioxyferrocene. A stream of dry air was passed for 1.5 h through an ethereal solution of 1,1′-dioxyferrocene obtained by hydrolysis of 0.80 g of 1,1′-ferrocenylenediacetate. The brown precipitate that formed was filtered off and washed with ether. The precipitate dissolved almost completely in dilute HCl. The solution gives a reaction for Fe^{3+} with KCNS. The ethereal extract was washed with a small amount of water, 1% KOH, and water, and the ether was evaporated. The remaining crystals were sublimed in vacuo. Obtained: 0.06 g (14% of theory, calculated on the 1,1′-ferrocenylenediacetate taken) of the dimer of cyclopentadienone 4,7-methano-3a,4,7,7a-tetrahydroindenedione-1,8, m.p. 96-98°. Literature data: m.p. 101-101.5°; 96-98° ([6]). A mixed sample with an authentic sample melts without depression.

* Carried out jointly with A. V. Gerasimenko.

1,1′-Ferrocenylene dibenzoate was obtained by benzoylation of the hydrolysate of 0.3 g of 1,1′-ferrocenylene diacetate in 6 ml of 10% KOH with benzoyl chloride (0.5 ml). Yield 0.29 g (68% of theory), m.p. 108-110°; after recrystallization from alcohol, m.p. 114-115°.

Found %: C 67.65; 67.53; H 4.39; 4.49; Fe 12.88; 12.97

$C_{24}H_{18}FeO_4$. Calculated %: C 67.63; H 4.26; Fe 13.10

1,1′-Ferrocenylene dibenzenesulfonate was obtained from 0.3 g of 1,1′-ferrocenylene diacetate after hydrolysis and treatment with benzenesulfonyl chloride (0.5 ml). Yield 0.36 g (72% of theory), m.p. 114.5-116.5°; after recrystallization from alcohol, m.p. 119.5-120.5°.

Found %: C 52.87; 52.92; H 3.68; 3.57; Fe 11.00; 11.23; S 12.53; 12.40

$C_{22}H_{18}FeO_6S_2$. Calculated %: C 53.02; H 3.64; Fe 11.21; S 12.87

1,1′-Dimethoxyferrocene was obtained analogously to methoxyferrocene. To a solution of 0.70 g of 1,1′-ferrocenylene diacetate and 3 ml of dimethyl sulfate in 20 ml of absolute methanol, 7.5 ml of 50% KOH was added dropwise. The mixture was boiled for one hour; then diluted with water and extracted with ether. The ether was washed with water and evaporated. 0.54 g (95% of theory) of 1,1′-dimethoxyferrocene was obtained, m.p. 31.5-33°; after recrystallization from hexane saturated with 1,1′-dimethoxyferrocene at 30° and cooled with dry ice with acetone, m.p. 35-36°.

Found %: C 58.39; 58.58; H 5.87; 5.91; Fe 22.71; 22.47

$C_{12}H_{14}FeO_2$. Calculated %: C 58.55; H 5.73; Fe 22.70

O,O′-(1,1′-Ferrocenylene)diglycolic acid. To the hydrolysate of 0.50 g of 1,1′-ferrocenylene diacetate in 6 ml of 10% KOH was added a solution of 1.0 g of chloroacetic acid in 10% KOH. The mixture was boiled for 3 hours, the medium being kept alkaline. After cooling, upon acidification there precipitated the sparingly soluble acid potassium salt of the corresponding acid, which was filtered off, washed with ether, and recrystallized from water.

Found %:	C 45.46; 45.36; H 3.78; 3.77
$C_{14}H_{13}FeO_6K$. Calculated %:	C 45.18; H 3.52

It gives a reaction for the potassium ion with sodium tetraphenylborate.
To isolate the free acid, the acidic solution together with the precipitate is shaken with ether; the salt precipitate gradually disappears, and the acid passes into the ether. The aqueous acidic green solution is reduced with sodium sulfite or thiosulfate, saturated with NaCl, and extracted with ether; the combined ether extracts are washed with a small amount of water; after evaporation of the ether the remaining crystals are dried over P_2O_5. 0.42 g (76% of theory) of O,O′-(1,1′-ferrocenylene)diglycolic acid is obtained, m.p. 160-163°; after recrystallization from water and thorough drying in vacuum over P_2O_5, m.p. 168.5-169.5°.

Found %:	C 50.53; 50.44; H 4.37; 4.30; Fe 16.91; 16.92
$C_{14}H_{14}FeO_6$. Calculated %:	C 50.33; H 4.22; Fe 16.72

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CITED LITERATURE

1. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **129**, No. 5, 1060 (1959).
2. L. Claisen, E. Tietze, A., **449**, 81 (1926).
3. L. F. Fieser, W. P. Campbell, E. M. Fry, J. Am. Chem. Soc., **61**, 2206 (1939).
4. W. D. Kumler, J. Am. Chem. Soc., **60**, 859 (1938).
5. A. N. Nesmeyanov, V. A. Sazonova et al., DAN, **131**, No. 5, 1088 (1960).
6. C. H. DePuy, B. W. Ponder, J. Am. Chem. Soc., **81**, 4629 (1959); C. H. DePuy, E. F. Zaweski, J. Am. Chem. Soc., **81**, 4920 (1959).
7. P. Fahrni, A. Habich, H. Schmid, Helv. chim. acta, **43**, 448 (1960).