Chemistry

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, S. S. CHURANOV

1958

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. N. NESMEYANOV, E. G. PEREVALOVA, S. S. CHURANOV
and O. A. NESMEYANOVA

REACTIONS OF FERROCENESULFONIC ACIDS

In a previous communication (1) we described the sulfonation of ferrocene by various sulfonating reagents and certain derivatives of ferrocenesulfonic acids. In the present work a number of other sulfur-containing substituted ferrocenes have been obtained, and an attempt has been made to carry out reactions involving replacement of the sulfo group.

On interaction of the lead salt of ferrocenedisulfonic acid, $Fe(C_5H_4SO_3)_2Pb \cdot 4H_2O$, with phosphorus trichloride, we obtained the monochloroanhydride $ClSO_2C_5H_4FeC_5H_4SO_3H$.

Phosphorus oxychloride with the lead salt of the diacid forms the dichloroanhydride of ferrocenedisulfonic acid, while the lead salt of the monosulfonic acid is oxidized to the ferricinium cation with the appearance of an intense dark-green coloration, which can be used as a qualitative test for distinguishing these acids.

From the barium salts it is not possible to obtain the chloroanhydrides of either the mono- or the disulfonic acid.

On heating ferrocenedisulfochloride with diethylamine, we obtained bis(diethylamide) of ferrocenedisulfonic acid, $Fe[C_5H_4SO_2N(C_2H_5)_2]_2$.

From ferrocenemonosulfochloride* there were prepared diethylamide**, the sodium salt of sulfinic acid, diferrocenyldisulfide, and thioferrocenol, isolated in the form of derivatives—the benzoate and the *S*-ferrocenylthioglycolic acid. In air, thioferrocenol is rapidly converted into the disulfide. The sodium salt of the sulfinic acid, under the action of $HgCl_2$, smoothly gives chloromercuriferrocene.

On reduction of the dichloroanhydride of ferrocenedisulfonic acid, a halogen-free substance was obtained which is probably a polymer of bis(disulfide), but this compound was not isolated in pure form.

In the infrared spectra of all the monosubstituted sulfur-containing ferrocene compounds obtained by us, there are characteristic maxima in the region of 1000 and 1110 cm^{-1}, indicating (3,4) the presence of a free cyclopentadienyl ring. These maxima are absent in all disubstituted sulfur derivatives of ferrocene, which confirms the earlier (1) suggestion made by us that the sulfo groups are located in different cyclopentadienyl rings.

Our attempts to replace the sulfo group by hydroxyl on fusion with alkali, by cyano under the action of potassium ferricyanide, and by a formyl group on heating with sodium formate were unsuccessful and led to complete destruction of the ferrocene nucleus with liberation of ferric hydroxide or ferric salt.

It was also not possible to effect hydrolysis of the sulfonic acids with formation of ferrocene. On prolonged heating in a strongly acidic solution, in the case of the monoacid, oxidation to a ferricinium-cation derivative is observed.

* The preparation of ferrocenemonosulfochloride was described by us in the previous communication ([1]).
** Diethylamide of ferrocenemonosulfonic acid was obtained by N. A. Nesmeyanov.

and subsequent decomposition. In the case of the disulfonic acid, decomposition with formation of ionic iron occurs in part already on evaporation of solutions not only of the free acid, but also of its salts. When an aqueous solution of the disulfonic acid is heated in a sealed tube for 6 h, more than 25% of the diacid decomposes, as shown by quantitative determination of ionic iron. Evidently, the stability of the bond of iron with the cyclopentadienyl rings is greatly decreased under the influence of sulfo groups in comparison with ferrocene.

Introduction of a sulfo group sharply decreases the capacity for further substitution in the same cyclopentadienyl ring and, to a considerably lesser extent, in the other ring. This is evidenced by the formation, on sulfonation of ferrocene ([1]), of ferrocenemonosulfonic acid in good yield, practically without admixture of the diacid. The marked passivation of the ferrocene nucleus toward further electrophilic substitution is also indicated by the fact that the trisulfonic acid cannot be obtained. The influence of the sulfo group on the reactivity of the ferrocene nucleus is similar to the influence of the acetyl group ([5]).

Experimental Part

Preparation of ferrocenendisulfonic acid dichloroanhydride. 12 g of the lead salt of ferrocenendisulfonic acid (containing $4H_2O$) and 30 ml of $POCl_3$ were heated for 40 min; the reaction mass was poured onto ice; the precipitate that formed was filtered off and extracted with dry dichloroethane (200 ml) in a Soxhlet extractor. The dichloroethane was distilled off until crystallization began. The crystals of ferrocenendisulfonic acid dichloroanhydride that separated on cooling to 0° were filtered off (weight 4.2 g). From the mother liquor a further 0.8 g of dichloroanhydride was isolated. Total yield 5 g (64% of theory).

The dichloroanhydride was recrystallized from a mixture of dichloroethane with CCl_4 (1:1). It is a yellow-orange crystalline substance, readily soluble in dichloroethane and benzene and slightly soluble in ether. On rapid heating above 150° the dichloroanhydride decomposes with a flash; in a sealed capillary it darkens above 135°.

Found, %:	C 31.87; 31.84; H 2.30; 2.29
$C_{10}H_8O_4S_2Cl_2Fe$. Calculated, %:	C 31.35; H 2.10

Preparation of ferrocenendisulfonic acid monochloroanhydride. 2.9 g of the lead salt of ferrocenendisulfonic acid were added with stirring to 20 ml of PCl_3. The mixture was boiled for 1 h. The yellow solution that formed was filtered off. The residue was heated with 10 ml of PCl_3 and 20 ml of dichloroethane. The undissolved portion was again filtered off and washed with dichloroethane. The bulk of the solvent and PCl_3 was distilled off in vacuo, and the residues were evaporated in a vacuum desiccator over caustic soda. The separated monochloroanhydride was washed with methyl alcohol and dried in a vacuum desiccator. Yield 0.65 g (36% of theory).

Ferrocenendisulfonic acid monochloroanhydride is a yellow powdery substance, decomposing on heating above 129°, poorly soluble in water.

Found, %:	C 33.60; 33.55;	H 2.44; 2.44;	Fe 15.25; 15.50
$C_{10}H_9O_5S_2ClFe$. Calculated, %:	C 32.99;	H 2.49;	Fe 15.32

Qualitative distinction of ferrocen sulfonic acids. 0.1–0.2 g of the lead salt of ferrocenendisulfonic acid is heated with 5 ml of PCl_3 to boiling, and the mixture is kept at this temperature for 3–5 min, and then poured onto ice. Formation of a reddish precipitate

the acid chloride after hydrolysis of all the PCl_3 is characteristic of the monoacid. The lead salt of ferrocenedisulfonic acid gives yellow solutions.

If $POCl_3$ is used, a precipitate appears in the case of the lead salt of the disulfonic acid, while the monoacid forms a green solution.

Preparation of bis(diethylamide) of ferrocenedisulfonic acid. 1 g of ferrocenedisulfonic acid chloride and 50 ml of diethylamine were heated for 6 hr to boiling. The crystals of bis(diethylamide) that separated on cooling were filtered off. Weight 0.4 g. On dilution of the diethylamine solution with water, another 0.7 g of substance was isolated.

The bis(diethylamide) of ferrocenedisulfonic acid was recrystallized from ethyl acetate with the addition of several drops of ethyl alcohol. It is a golden-yellow crystalline substance, readily soluble in organic solvents. M.p. 159–161°. Yield 92% of theory.

Found, %:	C 47.84; 47.87;	H 6.28; 6.34;	Fe 12.37; 12.41
$C_{18}H_{28}O_4N_2S_2Fe$. Calculated, %:	C 47.36;	H 6.18;	Fe 12.23

Preparation of diethylamide of ferrocenemonosulfonic acid. The substance was obtained similarly to the preceding one (heating for 3 hr). The yield was almost quantitative. The diethylamide of ferrocenemonosulfonic acid is a light-yellow crystalline substance, readily soluble in organic solvents and crystallizing from methyl alcohol and carbon tetrachloride. M.p. 91–92°.

Found, %: C 52.25; 52.33; H 6.09; 6.20; S 10.06; 9.71; Fe 17.61; 17.49
$C_{14}H_{19}O_2NSFe$. Calculated, %: C 52.37; H 5.96; S 9.97; Fe 17.40

Reduction of ferrocenemonosulfonic acid chloride.

A. Sodium salt of sulfinic acid. A mixture of 5 g of ferrocenesulfonyl chloride, 10 g of Zn dust, 150 ml of ether, and approximately 0.5 ml of water was boiled for 1 hr. The precipitate was then filtered off and heated for 10 min with a saturated solution of soda. On cooling of the filtered hot solution, the Na salt of the sulfinic acid separated (2 g), which was recrystallized from alcohol (contains $2H_2O$).

Found, %: C 39.09; 39.38; H 4.20; 4.26
$C_{10}H_{13}SO_4FeNa$. Calculated, %: C 38.98; H 4.25

B. S-Ferrocenylthioglycolic acid. A solution of 5 g of ferrocenesulfonyl chloride in abs. ether was gradually added to an ethereal solution of $LiAlH_4$, taken in excess. The mixture was heated for 1 hr and then poured into 200 ml of ice water acidified with 5 ml of conc. HCl. The ethereal solution containing thioferrocenol was separated, washed twice with water, and extracted with 10 ml of 20% NaOH. To the aqueous solution of sodium thioferrocenolate thus obtained, a saturated solution of monochloroacetic acid (taken in excess) in 20% NaOH was added. After 30 min the mixture was acidified and extracted with ether. The S-ferrocenylthioglycolic acid remaining after evaporation of the ether was recrystallized from aqueous alcohol. M.p. 109–110°. Yield 2.7 g (56% of theory).

Found, %: C 52.19; H 4.38; S 11.60; Fe 20.20
$C_{12}H_{12}SO_2Fe$. Calculated, %: C 52.39; 52.23; H 4.45; 4.39; S 11.12; 11.03; Fe 20.06; 20.00

In addition, 0.9 g of diferrocenyldisulfide was isolated.

B. Diferrocenyldisulfide. On distilling off the ether from the solution of thioferrocenol obtained as described in experiment B, there was isolated

with good yield, diferrocenyl disulfide, identical with that synthesized by us previously (2) from diferrocenylmercury.

G. Thioferrocenyl benzoate. 0.98 g of diferrocenyl disulfide was heated for 1 hour with an excess of an ethereal solution of $LiAlH_4$. The reaction mixture was then worked up as described in experiment B. Benzoyl chloride was then gradually added to the solution of thioferrocenol in 10% NaOH, with vigorous shaking, until the solution was almost completely decolorized. The precipitated thioferrocenyl benzoate was extracted with ether and, after removal of the ether, recrystallized from butyl alcohol. M.p. 138–139°. Yield 1.33 g (92% of theoretical).

Found, %: C 63.36; H 4.38; Fe 17.30
$C_{17}H_{14}SOFe$. Calculated, %: C 62.91; 62.64; H 4.36; 4.33; Fe 17.45; 17.42

Hydrolysis of ferrocenylsulfonic acids. 2.0696 g of ferrocenylsulfonic acid (contains $4H_2O$; m.p. 123–125° in a sealed capillary*) was dissolved in 25 ml of water and heated in a sealed tube at 100° for 6 hours. The solution was then diluted with water (no ferrocene separated), and ionic iron was precipitated with ammonia. The weight of iron oxide after ignition was 0.1051 g. Consequently, 26% of the original sulfonic acid had decomposed.

Ferrocenylsulfonic acid itself contains no ionic iron and gives no precipitate on treatment with ammonia.

Infrared spectra of sulfur-containing ferrocene compounds. The infrared spectra were recorded on a single-beam IKS-11 spectrometer with recording of the spectrum on an EPP-09, in the narrow region from 970 to 1250 cm^{-1}, using sodium chloride prisms and cells. The substances were taken as suspensions in Vaseline oil**.

Ferrocenemonosulfonic acid: 1000; 1018; 1065; 1107; 1166; 1172. Lead salt of ferrocenemonosulfonic acid: 1011; 1047; 1109; 1125; 1137; 1224. Methyl ester of ferrocenemonosulfonic acid: 1004; 1018; 1030; 1106; 1149; 1176; 1200. Ferrocenemonosulfonyl chloride: 999; 1017; 1032; 1110; 1140; 1180; 1202.

Ferrocendisulfonic acid: 832; 1013; 1049; 1092; 1129; 1157; 1223; 1228. Lead salt of ferrocenyl disulfonic acid: 1009; 1043; 1059; 1153. Dimethyl ester of ferrocenyl disulfonic acid: 985; 1021; 1035; 1151; 1182; 1202.

Ferrocenyl disulfonyl chloride: 1023; 1035; 1146; 1176; 1202.
Monochloroanhydride of ferrocenyl disulfonic acid: 1013; 1022; 1037; 1083; 1149 cm^{-1}.

Moscow State University
named after M. V. Lomonosov

Received
16 I 1958

REFERENCES

1. A. N. Nesmeyanov, E. G. Perevalova, S. S. Churanov, DAN, **114**, 335 (1957).

2. A. N. Nesmeyanov, E. G. Perevalova, O. A. Nesmeyanova, DAN, **119**, No. 2 (1958).

3. P. L. Pauson, Quart. Rev. Lond. Chem. Soc., **9**, 391 (1955).

4. A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin, I. I. Kritskaya, DAN, **117**, 433 (1957).

5. A. N. Nesmeyanov, E. G. Perevalova et al., Izv. AN SSSR, OKhN, **1957**, 638.

* In our preceding communication (1), for ferrocenylsulfonic acid a m.p. of 80-90° was given; this is the melting point of a hydrate whose composition is lower in water content; in the present article the melting point of ferrocenemonosulfonic acid is given (117-118° in a sealed capillary).

** We express our gratitude to L. A. Kazitsyna and B. V. Lokshin for their help in recording the spectra.

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