Reports of the Academy of Sciences of the USSR

Nik. A. NESMEYANOV and B. N. STRUNIN

1961

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Volume 137, No. 1

CHEMISTRY

Nik. A. NESMEYANOV and B. N. STRUNIN

SULFONATION OF ACYL AND CARBOMETHOXY DERIVATIVES OF FERROCENE

(Presented by Academician A. N. Nesmeyanov, 15 X 1960)

Recently we obtained 1-carboxyferrocene-1′-sulfonic acid and described a number of its derivatives ([1]). In the present work the sulfonation reaction has for the first time been extended to other ferrocene compounds.

1,1′-Dicarbomethoxyferrocene was successfully sulfonated with a solution of sulfuric anhydride in dichloroethane. To 0.025 mole of this ester in 50 ml of dichloroethane, a solution of 0.037 mole of sulfuric anhydride in the same solvent was added over the course of an hour at 0°. After stirring for one and a half hours at 20°, the reaction products were extracted with water, the excess sulfuric acid was precipitated with barium chloride, and the clear solution was evaporated in a stream of warm air almost to dryness. The remaining yellow crystals were washed on the filter with acetone and ether. Yield 60%, calculated on pure sulfonic acid I. However, the sulfonic acid contains a considerable admixture of its iron salt, formed upon partial destruction of ferrocene. Sulfonic acid I was identified in the form of its acid chloride. Acid chlorides of ferrocene-sulfonic acids are readily obtained by the following method.

ferrocene nucleus bearing SO_3H and $COOCH_3$ on one ring,
Fe I
and $COOCH_3$ on the other ring

To a suspension of 0.01 mole of the sulfonic acid (or of its lead salt) in 15 ml of dichloroethane, 0.05 mole of PCl_3 was added; after 30 min., 0.015 mole of PCl_5 was added in portions over 1 hour. After heating for one hour at 50-60°, the mixture was filtered; after cooling, the solution was treated with ice water, washed twice with water and with a 1% soda solution, dried over calcium chloride, and the solvent was removed in a stream of air. The acid chloride of ferrocene-1,1′-disulfonic acid was obtained in 95% yield (from its lead salt). The yield of the acid chloride of sulfonic acid I was 50%, calculated on the pure starting sulfonic acid. This acid chloride was recrystallized from ether, butyl alcohol, and a mixture of these solvents (1 : 1), after which it had m.p. 96-97°.

Found, %: C 42.17; 42.01; H 3.38; 3.34; Fe 14.01; 13.79; Cl 8.95; 8.77
$C_{14}H_{13}O_6ClFe$. Calculated, %: C 41.97; H 3.27; Fe 13.94; Cl 8.85

Already after the first recrystallization the melting point rises only insignificantly; this probably indicates that we are dealing with one of the two possible isomers that could have formed as a result of sulfonation.

It seemed possible that, upon sulfonation, 1,1′-diacetylferrocene would behave similarly to 1,1′-dicarbomethoxyferrocene. However, as a resul-

of this reaction* and subsequent treatment of its products with PCl_5, we were able to isolate only ferrocene-1,1′-disulfochloride in 25% yield (75% based on the 1,1′-diacetylferrocene that entered into the reaction).

$C_{10}H_8O_4S_2Cl_2Fe$.	Found, %:	C 31.60; 31.78;	H 2.11; 2.05;	Fe 14.63; 14.43;	Cl 18.90; 18.57
	Calculated, %:	C 31.55;	H 2.10;	Fe 14.58;	Cl 18.51

Thus, both acetyl groups were replaced by sulfogroups**. Most likely, a mixed anhydride is first formed according to the following scheme

[[chemical scheme: acetyl-substituted cyclopentadienyl system undergoing rearrangement to a mixed sulfonic-acetic anhydride, with substituents shown as $COCH_3$, S, O, and $OCOCH_3$]]

This anhydride is readily hydrolyzed during the subsequent treatment.

In the presence of bulkier radicals in the acyl substituents, such as phenyl or cyclohexyl, replacement of the acyl group by the sulfo group no longer occurs (probably owing to steric hindrance). 1,1′-Dibenzoylferrocene, when treated with sulfuric anhydride in dichloroethane (under the same conditions), remains unchanged; 1,1′-di-(hexahydrobenzoyl)-ferrocene is decomposed by 45%, and 40% of it is recovered unchanged. The latter of these ketones was obtained by us by the Friedel-Crafts method in 30% yield. M.p. 135-135.5° (from alcohol).

$C_{24}H_{30}O_2Fe$.	Found, %:	C 71.42; 71.33;	H 7.58; 7.60;	Fe 13.61; 13.17
	Calculated, %:	C 70.94;	H 7.44;	Fe 13.74

We sulfonated acetylferrocene with dioxanesulfur trioxide in dichloroethane and obtained 1-acetylferrocene-1′-sulfonic acid in 50-60% yield. To a solution of 7 g of acetylferrocene in 50 ml of dichloroethane, at 0°, there was added a suspension of dioxanesulfur trioxide (from 3.1 g of dioxane and 3.0 g of SO_3) in 25 ml of dichloroethane. After standing for one hour at 0° and 5 hours at 20°, the reaction products were extracted with a minimal amount of water. The extracts were washed with chloroform, and the aqueous solution was evaporated to dryness in a stream of air. The residue was washed repeatedly with acetone, giving 2.3 g of golden crystals which, in all likelihood, were the iron salt of 1-acetylferrocene-1′-sulfonic acid; these were recrystallized from acetic acid.

$C_{24}H_{22}S_2O_8Fe_3 \cdot 5H_2O$.	Found, %:	C 38.11; 37.92;	H 4.04; 4.10;	S 8.28; 8.36;	Fe 22.93; 22.67
	Calculated, %:	C 37.93;	H 4.24;	S 8.24;	Fe 22.04

The acetone solution (after washing the crystals) contained free sulfonic acid. This solution was treated with an excess of diazomethane in ether. We obtained 2.4 g of the methyl ester of 1-acetylferrocene-1′-sulfonic acid. After three recrystallizations from methanol, m.p. 79.5–81°.

$C_{13}H_{14}SO_4Fe$.	Found, %:	C 48.40; 48.47;	H 4.36; 4.28;	S 9.82; 9.84;	Fe 17.70; 17.97
	Calculated, %:	C 48.49;	H 4.38;	S 9.95;	Fe 17.34

The IR spectrum of this ester shows that the sulfo group and the acetyl group are located in different rings of the ferrocene molecule. Upon sulfonation of acetylferrocene under harsher conditions (an excess of sulfuric anhydride, in dichloroethane, heating at 60–80°), together with 1-acetylferrocene-1′-sulfonic acid, ferrocene-1,1′-disulfonic acid is formed, identified in the form of its methyl ester.

Thus, ferrocene derivatives containing one electrophilic substituent (−COOH or $-COOCH_3$ [1], $-SO_3H$ [4], or $-COCH_3$) are smoothly sulfonated with dioxanesulfur trioxide in the cold; substitution in this case occurs in the free ring. If electrophilic substituents are present in both rings of ferrocene, the reaction is impeded. Thus, the ester of ferrocene-1,1′-dicarboxylic acid is sulfonated by sulfuric anhydride in dichloroethane, but not by dioxanesulfur trioxide. 1,1′-Diacetylferrocene is not sulfonated, but exchanges acetyl groups for sulfo groups; 1,1′-dibenzoyl- and 1,1′-di-(hexahydrobenzoyl)-ferrocenes are

---

* Reaction conditions: to 0.06 mole of 1,1′-diacetylferrocene in 150 ml of dichloroethane, 0.09 mole of SO_3 in 100 ml of dichloroethane was added with stirring (0°). After 2 hours at 0° and 2 hours at 20°, the reaction mixture was treated as described for the preparation of sulfonic acid I.

** A similar result was obtained by Kreckeler in 1886 in the sulfonation of acetophenone with pyrosulfuric acid (2,3).

not sulfonated. We were also unable to sulfonate ferrocene-1,1′-disulfochloride either with an excess of sulfuric anhydride in dichloroethane (boiling, 3 hours) or by heating (50°) with 40% oleum.

Moscow State University
named after M. V. Lomonosov

Received
26 X 1960

CITED LITERATURE

1. Nik. A. Nesmeyanov, O. A. Reutov, *Izv. AN SSSR, OKhN*, **1959**, No. 5, 926.
2. K. Krekeler, *Ber.*, **19**, 674 (1886).
3. K. Krekeler, *Ber.*, **19**, 2623 (1886).
4. A. N. Nesmeyanov, E. G. Perevalova, S. S. Churanov, *DAN*, **114**, 335 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.