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CHEMISTRY

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1964

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Abstract

Full Text

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FERROCENYLSULFONES. FERROCENYLMESITYLSULFONE UNDER THE CONDITIONS OF THE SMILES REARRANGEMENT

Recently we suggested that the transition state corresponding to the quinoid one in the benzene series is impossible for ferrocene; in particular, by this we explained the inability of ferrocenyl allyl ether to undergo the Claisen rearrangement ([1]). It is known that substitution by the S_N2 mechanism in the aromatic series presupposes a quinoid intermediate state. It could be assumed that reactions of this type are impossible for ferrocene. For this purpose we used the Smiles rearrangement of *o*-methyldiaryl sulfones in the presence of *n*-butyllithium, recently found by Truce and co-workers ([2]): it was found, for example, that mesityl phenyl sulfone rearranges in 98% yield into 2-benzyl-4,6-dimethylbenzenesulfinic acid. Since the Smiles rearrangement proceeds

$$C_6H_5SO_2{-}Mes \xrightarrow{n\text{-}C_4H_9Li} C_6H_5SO_2{-}C_6H_2(CH_3)_2CH_2Li \longrightarrow [C_6H_5{-}SO_2{-}C_6H_2(CH_3)_2CH_2] \longrightarrow LiSO_2{-}C$$

by an intramolecular S_N2 mechanism ([3]), on the basis of the foregoing one could expect that mesityl ferrocenyl sulfone would not rearrange.

To obtain sulfones of the ferrocene series we used the reaction of bromoferrocene with copper salts of arylsulfinic acids:

$$C_5H_5FeC_5H_4Br + Cu(SO_2Ar)_2 \rightarrow C_5H_5FeC_5H_4SO_2Ar.$$

The reaction proceeds readily even in the cold in a solution of dimethylformamide; thus phenyl ferrocenyl sulfone and diferrocenyl sulfone were smoothly obtained in yields $> 80\%$: the latter had previously been obtained in our laboratory by the reaction of diferrocenylmercury with benzenesulfonyl iodide and ferrocenesulfochloride, respectively ([4]). It should be noted that the copper salt of ferrocenesulfinic acid in a solution of dimethylformamide gradually decomposes with formation also of diferrocenyl sulfone and diferrocenyl. The reaction of bromoferrocene with the copper salt of mesitylenesulfinic acid proceeds less smoothly: bromoferrocene is mainly reduced to ferrocene; mesityl ferrocenyl sulfone is formed in only 7% yield, and diferrocenyl sulfone is formed as a byproduct.

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Therefore we had to seek another route for the synthesis of mesityl ferrocenyl sulfone. On heating a mixture of copper mesitylthiolate (I) with bromoferro-

in xylene at 130° for 40 min, mesitylferrocenyl sulfide is formed in 86% yield. Copper mesitylthiolate was obtained by us by adding an alcoholic solution of thiomesitol to Ilosvay' s reagent, which is more convenient than the previously proposed method for preparing copper mercaptides (5)—boiling an alcoholic solution of the mercaptan with copper oxide for several hours in a nitrogen atmosphere. It was not possible to oxidize mesitylferrocenyl sulfide to the corresponding sulfone with the commonly used oxidant, hydrogen peroxide in acetic acid: in an acidic medium, complete oxidation of the ferrocene nucleus proceeds very readily, with liberation of inorganic iron. Therefore, as oxidant we used a solution of hydrogen peroxide in methyl alcohol with addition of acetonitrile at pH > 7; this oxidant had previously been used by Payne et al. (6) for obtaining a series of olefin oxides, for oxidizing aniline to azoxybenzene, etc. The oxidation was carried out at 50°; along with mesitylferrocenyl sulfone (yield 62-28%, depending on the reaction time), the intermediately formed mesitylferrocenyl sulfoxide was also isolated:

$$C_5H_5FeC_5H_4Br + CuS\text{–}\langle C_6H_2(\overset{CH_3}{C}H_3)_2\rangle \xrightarrow{130^\circ} C_5H_5FeC_5H_4S\text{–}\langle C_6H_2(\overset{CH_3}{C}H_3)_2\rangle$$

$$\xrightarrow{H_2O_2+CH_3CN} C_5H_5FeC_5H_4SO\text{–}\langle C_6H_2(\overset{CH_3}{C}H_3)_2\rangle + C_5H_5FeC_5H_4SO_2\text{–}\langle C_6H_2(\overset{CH_3}{C}H_3)_2\rangle$$

When mesitylferrocenyl sulfide is treated with an equimolecular amount of *n*-butyllithium in ether, as in the case of phenyl mesityl sulfone, an intense red coloration appears, indicating the formation of a lithium-organic compound of the benzylic type, i.e., according to Truce, metalation of a lateral methyl group of the sulfone. If the resulting solution is treated with D_2O after 6 min, then in the spectrum of the isolated deuterated mesitylferrocenyl sulfone the absorption band of the stretching vibrations of the C—D bond is found at 2194 cm^{-1}. The C—D stretching vibrations in decadeuteroferrocene occur at 2354 cm^{-1} (7), and in monodeuteroferrocene at 2320 cm^{-1} (monodeuteroferrocene was obtained by us by hydrolysis of the dibutyl ester of ferrocenylboronic acid with D_2O in the presence of zinc chloride). In ω-deuterotoluene the C—D stretching vibrations occur at 4.59 μ (2179 cm^{-1}) (8), and in C_6H_5CHDY at 4.5-4.7 μ (2220-2130 cm^{-1}) (9). All these data very probably indicate that, on metalation of mesitylferrocenyl sulfone, as in the case of phenyl mesityl sulfone, lithium enters the lateral methyl group.

If the reaction mixture is left for several hours, the coloration fades and a yellow precipitate separates, which proved to be the lithium salt of ferrocenesulfinic acid; part of the starting sulfone was recovered from the ether solution. Cleavage

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of sulfones by such nucleophilic agents as KOH, sodium piperidide, alkali metals in liquid amines, and triphenylsilyllithium is known (10); here we are probably dealing with a similar cleavage of mesitylferrocenyl sulfone under the action of organolithium compounds, possibly even intramolecularly. No products of the Smiles rearrangement were detected. The data obtained thus cast doubt on the possibility of nucleophilic substitution in the ferrocene series by the usual S_N2 mechanism.

Experimental Part*

1. Phenylferrocenyl sulfone. A solution of 0.9 g of bromoferrocene and 1.6 g of the copper salt of benzenesulfinic acid in 60 ml of dimethylformamide was left for two days at room temperature. Then 50 ml of water was added, the solution was extracted with ether, and the ether layer was washed with water, 10% KOH, water, 10% H_2SO_4, and water, dried over $MgSO_4$, and the ether was distilled off. This gave 0.31 g (82% of theory) of phenylferrocenyl sulfone, m.p. 153.5-154° (from alcohol or hexane). The earlier m.p. (145-146°), reported by our laboratory ([4]), was too low.

Found, %: C 58.90, 59.00; H 4.29, 4.23; S 9.52, 9.70; Fe 16.97, 16.68

$C_{16}H_{14}FeSO_2$. Calculated, %: C 58.91; H 4.32; S 9.83; Fe 17.12

The IR spectrum contains two strong absorption bands at 1143 and 1307 cm^{-1}, characteristic of sulfones.

The reaction was also carried out by heating the reaction mixture on a boiling water bath; 0.87 g (78% of theory) of phenylferrocenyl sulfone was obtained.

2. Diferrocenyl sulfone. a) A solution of 0.15 g of bromoferrocene and 0.30 g of the copper salt of ferrocenesulfinic acid in 10 ml of dimethylformamide was left for two days at room temperature. The precipitated diferrocenyl sulfone (0.15 g) was filtered off and washed with dimethylformamide and water. The mother liquor was diluted with water and extracted with chloroform; the chloroform was washed with water, dried over $MgSO_4$, and distilled off; the residue was chromatographed on Al_2O_3 in benzene, giving an additional 0.06 g of diferrocenyl sulfone; total yield 0.21 g (85% of theory), m.p. 270-273° (decomp.) (from benzene). Lit.: m.p. 270-275° (decomp.) ([4]).

b) A solution of 100 mg of the copper salt of ferrocenesulfinic acid in 1 ml of diphenylformamide was left for two days at room temperature. Then the reaction mixture was diluted with water and extracted with chloroform; the chloroform extracts were washed with water, dried over $MgSO_4$, and the chloroform was distilled off; the residue was chromatographed on Al_2O_3: heptane eluted 6 mg of diferrocenyl, and benzene eluted 18 mg of diferrocenyl sulfone.

3. Mesitylferrocenyl sulfone. To a solution of 1.5 g of bromoferrocene in 100 ml of dimethylformamide was added 4.9 g of the copper salt of mesitylenesulfinic

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acid, and the reaction mixture was left for two days at room temperature, being shaken from time to time. Then 100 ml of water was added, the precipitate was filtered off and washed on the filter with benzene; the filtrate was extracted with benzene, and the benzene extracts were combined and washed with water, 10% KOH, water, 10% H_2SO_4, and water, dried over $MgSO_4$; the benzene was distilled off, and the residue was chromatographed on Al_2O_3. Heptane eluted a mixture, 0.71 g (68% of theory), of ferrocene and mesitylene; a benzene-heptane mixture (6:4) eluted 0.14 g (7% of theory) of mesitylferrocenyl sulfone, m.p. 148-149° (from hexane or alcohol).

Found, %: C 62.14, 62.29; H 5.50, 5.58; S 8.63, 8.6; Fe 15.52, 15.51

$C_{19}H_{20}FeSO_2$. Calculated, %: C 61.96; H 5.47; S 8.71; Fe 15.17

The IR spectrum contains two strong absorption bands at 1137 and 1309 cm^{-1}, characteristic of sulfones. Benzene eluted 0.07 g of diferrocenyl sulfone.

4. Mesitylferrocenyl sulfide. A solution of 0.75 g of thiomesitol in alcohol was added with stirring to Ilosvay's reagent prepared from 1.5 g of copper sulfate; the white precipitate that formed was filtered off, washed with methanol and absolute ether, and dried in a vacuum desiccator: 0.90 g (96% of theory) of copper mesitylthiolate was obtained. A mixture of 0.75 g of bromoferrocene and 0.90 g of mesitylthiolate

* Carried out with the participation of T. Yu. Frid.

copper was heated in an ampoule on an oil bath at 130° for 40 min. After cooling, the reaction mixture was placed on an Al_2O_3 column, and mesityl ferrocenyl sulfide was washed off with heptane; yield 0.84 g (86% of theory), m.p. 85.5-86.5° (from alcohol).

Found, %: C 67.93; 67.98; H 6.00, 5.95; S 9.55; 9.47; Fe 16.52; 16.53
$C_{19}H_{20}FeS$. Calculated, %: C 67.86; H 5.99; S 9.53; Fe 16.61.

5. Oxidation of mesityl ferrocenyl sulfide. To a solution of 0.4 g of mesityl ferrocenyl sulfide in 160 ml of absolute methanol, placed in a flask with a reflux condenser and heated to 50°, with stirring there were added 12 ml of acetonitrile, 4 ml of 0.1 N KOH solution, and 4 ml of 28% H_2O_2 (pH 9). During the reaction the change in pH was carefully monitored and, by adding KOH solution, it was not allowed to fall below pH 7. After 2.5, 5.5, and 20 h, further 4-ml portions of 28% H_2O_2 were added (25 h total). The solution was then diluted with water and extracted with ether; the ether layer was washed with water, dried over $MgSO_4$, and the ether was distilled off. The residue was chromatographed on Al_2O_3. Heptane eluted traces of the starting sulfide; benzene gave 0.27 g (62% of theory) of mesityl ferrocenyl sulfone, and chloroform gave 0.09 g (21% of theory) of mesityl ferrocenyl sulfoxide, m.p. 126-127° (from hexane).

Found, %: C 64.80, 64.79; H 5.82; 5.68; S 9.09; 8.93; Fe 16.00; 15.75
$C_{19}H_{20}FeSO$. Calculated, %: C 64.78; H 5.72; S 9.10; Fe 15.85.

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When the reaction time was reduced to 9 h, 26% of the starting sulfide was recovered, mesityl ferrocenyl sulfone was obtained in 28% yield, and mesityl ferrocenyl sulfoxide in 32% yield.

6. Interaction of mesityl ferrocenyl sulfone with *n*-butyllithium. To a solution of 0.55 g (1.5 mmole) of mesityl ferrocenyl sulfone in 16 ml of absolute ether under N_2 was added 5 ml of 0.4 N ethereal solution of *n*-butyllithium, and the reaction mixture was left overnight at room temperature. The dark-red solution gradually became pale, and a yellow precipitate of the lithium salt of ferrocenesulfinic acid formed. The latter was filtered off (0.20 g), washed with ether, dissolved in water, and, for identification, converted by treatment with sublimate into ferrocenylmercuric chloride, m.p. 192–194°, identical by mixed melting point and by Rf on Al_2O_3 in chloroform with an authentic sample. From the ethereal solution, after chromatography on Al_2O_3 in a benzene–heptane (6:4) mixture, 0.21 g of the starting sulfone was isolated.

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Received
2 VII 1964

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