Journal of Organometallic Chemistry, 96 (1975) 271—274

THE SYNTHESIS OF 1,2-DIACETYL- AND 1,2-DIETHYLFERROCENES

A.N. NESMEYANOV, E.V. LEONOVA, N.S. KOCHETKOVA and A.I. MALKOVA
Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow B-312 (U.S.S.R.)

(Received March 5th, 1975)

Summary

A method is described for the preparation of 1,2-diacetylferrocene, in which ferrocene is acetylated with acetyl chloride in the presence of $AlCl_3$ in methylene chloride. Addition of the ferrocene to an excess of the acetylation mixture over a prolonged period was found to be most favourable. The 1,2-diacetylferrocene formed proved to be free of the 1,3-isomer. It was reduced with $LiAlH_4/AlCl_3$ to 1,2-diethylferrocene.

In this paper the synthesis is described of 1,2-diacetylferrocene by acetylation of ferrocene with acetyl chloride in the presence of $AlCl_3$ in CH_2Cl_2. The technique is attractive in that it is a rare example of formation of the 1,2-isomer without the other homoannular isomer. It has been reported [1,2] that 1,2-diacetylferrocene is formed as a minor (ca. 1%) admixture to the main product, 1,1'-diacetylferrocene, under the usual conditions of ferrocene diacetylation. 1,2-Diacetylferrocene described [1] was not isolated and the yield was estimated indirectly.

In our method of preparation we have changed the ratio of the reagents and the order in which they are mixed. The ferrocene/$AlCl_3$/CH_3COCl molar ratio selected was 1/10/10, and a solution of ferrocene in methylene chloride was added to the acetylating mixture. The rate at which the ferrocene is added also affects the yield of the 1,2-diacetyl derivative, the yield being higher the more prolonged the duration of the ferrocene introduction (see Table 1).

Thus, a prolonged excess of the acetylating mixture with respect to ferrocene is necessary in order that 1,2-disubstitution should occur in the same cyclopentadienyl (Cp) ring. Acetylation of formylferrocene gave [5] only 1,3-acetylformylferrocene, in other words, the homoannular substitution occurred in the 3-position. Consequently, the fact that 1,2-diacetylferrocene is formed during the acetylation of ferrocene may be explained by assuming that two acetyls add to the Cp ring simultaneously, rather than successively via an acetylferrocene intermediate. Indeed, electron and spatial factors would have led to the 1,3-iso-

TABLE 1

RATIO OF PRODUCTS AS A FUNCTION OF THE REACTION CONDITIONS

No.	Mixing order of reagents[a]	Addition time (h)	Percentage of products			Ref.
			Monoacetylferrocene	1,1'-Diacetylferrocene	1,2-Diacetylferrocene	
1	Direct	0.5	76.4	23.1	0.5	This work
2	Reverse	0.5	26.7	69.5	3.8	This work
			45.5	70.5	4.0	This work
3	Reverse	4.0	12.7	82.9	4.0	This work
			14.6	80.9	4.5	
4	Reverse	7.0	6.5	87.2	5.6	This work
			5.6	88.6	5.8	
5	Reverse[b]	7.0	2.8	88.9	8.9	This work
6	Reverse[c]	0.25	2.4	76.0	1.2	3
7	Direct		1.3	95.3	3.4	4

[a] Ferrocene/$AlCl_3$/CH_3COCl molar ratio: 1/2/2. V.V. Zhartovskaya, an undergraduate of the All-Union Correspondence-Course Polytechnical Institute, took part in these experiments. [b] Ferrocene/$AlCl_3$/CH_3COCl molar ratio: 1/10/10. [c] Ferrocene/$AlCl_3$/CH_3COCl molar ratio: 1/2.4/2.7. [d] Ferrocene/$AlCl_3$/CH_3COCl molar ratio: 1/2.3/2.8. [e] Found by an indirect method.

mer being formed as the predominant product in the latter case. We have not found any 1,3-diacetylferrocene in our reactions (Table 1) within the accuracy of the direct or indirect methods applied*. The starting mixture of diacetylferrocenes resulting from the acetylation (No. 5 in Table 1; Sample 1) was reduced by $LiAlH_4/AlCl_3$ to a mixture of the respective diethylferrocenes, and then analyzed by gas-liquid chromatography (GLC). This mixture contains nothing but 1,1'- and 1,2-diethylferrocenes. The total diacetylferrocenes mixture separated by thin-layer chromatography (TLC) gave a sample (Sample 2) that could possibly have contained the highest possible amount of the 1,3-isomer [6]. Sample 2 was reduced by $LiAlH_4/AlCl_3$ and analyzed by GLC [7]. This analysis did not reveal the presence of any 1,3-isomer. PMR spectra of Samples 1 and 2 gave no evidence of any 1,3-diacetylferrocene either. Consequently, the acetylation of ferrocene has given a mixture containing monoacetylferrocene and isomeric 1,1'- and 1,2-diacetylferrocenes. The yield of 1,2-diacetylferrocene was several times greater than that reported in ref. 1. Quantitative TLC analysis of the mixture has been made** (Al_2O_3, ether/water 60/1, 125 × 250 mm plates, 0.5 mm thick layers; R_F values: 1,1'-diacetylferrocene 0.19, 1,2-diacetylferrocene 0.32, acetylferrocene 0.68). The purity of 1,2-diacetylferrocene has been also tested [8] by PMR. An analytically pure sample was isolated by repeated chromatography. The resulting 1,2-diacetylferrocene was reduced by $LiAlH_4/AlCl_3$ to 1,2-diethylferrocene identical to an authentic sample.

Experimental

The experiments were carried out in an inert gas atmosphere.

---

* For the synthesis of 1,3-diacetylferrocene, see our paper [6].

** The reaction mixture cannot be analyzed by GLC quantitatively since 1,2-diacetylferrocene decomposes under the GLC conditions applied.

Synthesis of 1,2-acetylferrocene

$AlCl_3$ (15.8 g; 0.118 mol) in 25 ml CH_2Cl_2 was placed in a four-necked flask fitted with a stirrer, reflux condenser and dropping funnel. CH_3COCl (10 g; 0.127 mol) in 25 ml CH_2Cl_2 was added under vigorous stirring. Ferrocene (2 g) in 42 ml CH_2Cl_2 was added dropwise to the transparent solution at a rate of 6 ml/min at room temperature for 7 h. The mixture was maintained at room temperature for 4 h, decomposed with ice-cold water, the aqueous layer extracted with ether, the combined organic layers washed with water and dried over Na_2SO_4, and the solvent was removed to give 2.7 g (93%) of a dry residue. Two TLC cycles gave 0.24 g of a light yellow 1,2-acetylferrocene, m.p. 93-94°C.

Synthesis of Sample 1

Ferrocene acetylation was performed as described above. The aqueous layer was extracted with ether, the combined organic layers were washed with water, and dried over Na_2SO_4. The solvent was removed to give 2.6 g of Sample 1.

Synthesis of Sample 2

Ferrocene acetylation was carried out as described above. The dry residue (2.75 g) was separated by TLC. The front part of the 1,1'-diacetyl band (R_F 0.19) was collected. The alumina was treated with ether, the ether solutions were combined and the ether removed, to give 0.93 g of Sample 2.

Reduction of Sample 1

Absolute ether (30 ml) and $LiAlH_4$ (0.8 g) were placed in a flask fitted with a stirrer, reflux condenser, and dropping funnel, $AlCl_3$ (2.6 g) was added under vigorous stirring. The mixture was stirred for 15-20 min until a uniform system was formed. Sample 1 (2.6 g) in 150 ml absolute ether was added over 20-25 min. The reaction mixture was stirred until a yellow suspension was formed, this was decomposed with ice-cold water, the ether layer separated, the aqueous layer extracted with ether, the combined ether layers washed with water and dried over Na_2SO_4. The solvent was removed and the residue was chromatographed on an alumina column. A mixture of isomeric ethylferrocenes was eluted by heptane, a mixture of unreacted isomeric diacetylferrocenes by ether. The yield was 78.2%. The mixture of ethylferrocenes was analyzed by GLC (column length 45 m, diameter 0.25 mm, filled with Apiezon L, carrier gas nitrogen, isothermal analysis at 160°C). Nothing but 1,1'- and 1,2-diethylferrocenes were found.

Reduction of Sample 2

Sample 2 was reduced by $LiAlH_4$ (0.03 g) and $AlCl_3$ (0.1 g) in the way described in the preceding experiment. The yield of a mixture of isomeric diethylferrocenes was 89.1%. The mixture was analyzed by GLC as described above. No 1,3-diethylferrocene was found among the products of reduction of Sample 2.

Reduction of 1,2-diacetylferrocene

1,2-Diacetylferrocene (0.2 g) was reduced by $LiAlH_4$ (0.06 g) and $AlCl_3$ (0.2 g) as described for Sample 1. 1,2-Diethylferrocene (0.15 g; 81%) was obtained.

References

1 J.H. Richards and T.J. Curphey, Chem. Ind. (London), (1956) 1456.
2 P.L. Pauson, Quart. Rev., 9 (1955) 391.
3 M. Rosenblum and R.B. Woodward, J. Amer. Chem. Soc., 80 (1958) 5943.
4 P. Carty and M.F. Dove, J. Organometal. Chem., 21 (1970) 195.
5 M. Sato, M. Koda, I. Matayama and K. Hata, Bull. Chem. Soc. Jap., 43 (1970) 1142.
6 A.N. Nesmeyanov, E.V. Leonova, N.S. Kochetkova, A.I. Malkova and A.G. Makarovskaya, J. Organometal. Chem., 96 (1975) 275.
7 A.N. Nesmeyanov, L.P. Yur'eva, N.S. Kochetkova and S.V. Vitt, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 560.
8 A.N. Nesmeyanov, E.V. Leonova, E.I. Fedin, P.V. Petrovskii and N.S. Kochetkova, J. Organometal. Chem., 96 (1975) 279.