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1,3-DIACETYLFERROCENE

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Summary

A method is described for the preparation of 1,3-diacetylferrocene, in which ethylferrocene is first acetylated with acetyl chloride in the presence of $AlCl_3$ in methylene chloride to a mixture of isomeric acetylethylferrocenes. This mixture is then subjected to thin-layer chromatography, a mixture of the 1,1'- and 1,3-derivatives free from the 1,2-isomer being obtained. After oxidation of this mixture with MnO_2 to a mixture of 1,1'- and 1,3-diacetylferrocenes, the isomers are separated by preparative thin-layer chromatography.

1,3-Derivatives of ferrocene can be obtained either by substitution in the cyclopentadienyl (Cp) ring [1] or by "direct synthesis" from 1,3-substituted cyclopentadienes [1]. We have used a known reaction, acetylation of ethylferrocene by acetyl chloride in the presence of $AlCl_3$ in CH_2Cl_2 [2]. The ethyl group activates 3-position in the ring [2-4] and thus facilitates homoannular electrophilic substitution, leading predominantly to the 1,3-isomer. The rate at which the reagents are added, the order in which they are mixed, and the reaction temperature have been found to affect both the total yield and the ratio of the isomers. A large excess of the acetylating agent with respect to ethylferrocene (EF) raises the yield of homoannular isomer. A constant excess of the acetylating mixture is guaranteed by mixing the reagents in the reverse order, that is, by adding the ethylferrocene solution to an equimolar $CH_3COCl/AlCl_3$ mixture over 7 h. If the addition time is 2 h, this "reverse mixing effect" will be less pronounced. As for the temperature effect, diacetylferrocene isomers* are formed at 30°C whereas the amount of unreacted ethylferrocene increases when the temperature is decreased to —50°C. The yield and the ratio of the isomers as a function of the reaction conditions are summarised in Table 1.

The optimal conditions for the formation of homoannular 1,2- and 1,3-

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* No diacetylation has been observed at 10°C.

TABLE 1

RATIO OF THE PRODUCTS AS A FUNCTION OF THE REACTION CONDITIONS

No.	Reaction conditions			Composition (%)^a				Ratio	
	Mixing order of reagents	Temp. (°C)	Addition time (h)	1,2-AEF A	1,3-AEF B	A + B	1,1'-AEF C	A/C	B/C
1	Direct	+30	2	13.6	42.4	56	44.0	0.31	0.96
2	Reverse	+30	2	11.3	43.5	54.8	45.2	0.25	0.960
3	Direct	+30	7	14.8	44.2	59	41.0	0.353	1.03
4	Reverse	+30	7	17.3	50	67.3	32.7	0.53	1.53
5	Direct	−5	2	12.1	44.3	56.4	43.6	0.27	0.97
6	Reverse	−5	2	12.7	44.2	56.9	43.1	0.284	0.99
7	Direct	5	7	14.4	47.7	62.1	37.9	0.38	1.26
8	Reverse	−5	7	20.2	56.3	76.5	23.5	0.86	2.39
9	Direct	−50	2	14.2	38.4	52.6	47.4	0.30	0.81
10	Reverse	−50	2	11.8	45.6	57.4	42.6	0.28	1.07
11	Direct	−50	7	14.5	41.4	55.9	44.1	0.33	0.94
12	Reverse	−50	7	12.3	49.3	61.6	38.4	0.32	1.28

^{a}A = 1,2-AEF: B = 1,3-AEF: C = 1,1'-AEF: AEF = acetylethylferrocene.

acetylethylferrocenes (AEF) are as follows: reverse mixing for 7 h at −5°C at an ethylferrocene/CH_3COCl/$AlCl_3$ molar ratio of 1/1/1.

The reaction products were analysed quantitatively by gas-liquid chromatography (GLC)*. The reaction products were separated by thin-layer chromatography (TLC) on Al_2O_3 plates (125 × 250 mm) using benzene/ether (6/1) as eluent. The GLC techniques were also used to test the TLC results. The adsorption properties of 1,1'- and 1,3-AEF are similar [5], so only their mixture has been isolated [R_F(EF) 0.91; R_F(1,2-AEF) 0.48; R_F(1,1'-AEF, 1,3-AEF) 0.32]. A 1,1'-AEF/1,3-AEF mixture free from 1,2-AEF has been obtained by repeated chromatography. Oxidation of the mixture with MnO_2 yields a mixture of 1,1'- and 1,3-diacetylferrocenes which have similar R_F values. The diacetyl mixture was separated by preparative TLC, both isomers forming a broad band. The homoannular isomer, however, lies mainly at the front. The sorbent was Al_2O_3, the eluent was an ether/water (60/1) mixture, the plate dimensions were 125 × 250 mm. The TLC separation was checked by a PMR method [4]. The isolated 1,3-diacetylferrocene contained 10% of the 1,1'-isomer.

Experimental

The experiments were carried out in an inert gas atmosphere.

Acetylation of ethylferrocene

Direct mixing, (t is 2.7 h, T is 30°, −5°, −50°C). Ethylferrocene (0.5 g; 2.34×10^{-3} mol) in 10 ml CH_2Cl_2 was placed in a flask fitted with a stirrer, thermometer, and dropping funnel. A mixture of CH_3COCl (0.3 g; 3.82×10^{-3} mol), and CH_2Cl_2 (7 ml) was added at a constant rate for t h at the temperature T°C.

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The mixture was maintained at the reaction temperature for 30 min, decomposed with ice-cold water, after which the organic layer was separated and washed 5-7 times with 50-70 ml portions of distilled water. The washings were combined with the aqueous layer; this was treated with Na_2SO_3 until the blue solution turned colourless, and washed 3-4 times with 20-30 ml portions of benzene and ether. The combined organic solutions were dried with Na_2SO_4 and evacuated to the residual volume of 300 ml. A 100 ml portion of the latter solution was evaporated to constant weight, another 100 ml portion was evaporated to dryness, diluted with 0.5 ml benzene containing 0.020 g of analytically pure ferrocene and analysed by GLC. The results are given in Table 1.

GLC analyses were made on a Shandon chromatograph (glass column, 1% NPGA on Chromosorb W-AW, carrier gas argon, β-ionisation detection). The temperature was programmed at 85° to 230°C at 5°C/min.

Reverse mixing (t is 2.7 h, T is 30°, —5°, —50°C). Acetyl chloride (0.3 g; 3.82×10^{-3} mol) in 7 ml CH_2Cl_2, and then $AlCl_3$ (0.4 g; 3×10^{-3} mol) in 7 ml CH_2Cl_2 were placed in a three-necked flask fitted with a stirrer, thermometer, and dropping funnel. Ethylferrocene (0.5 g) in 7 ml CH_2Cl_2 was added at the reaction temperature T°C at a constant rate for t h. The reaction mixture was maintained at the reaction temperature for 30 min, decomposed with ice-cold water, and treated as described above.

Synthesis of a mixture of 1,1'- and 1,3-acetylethylferrocenes

Acetyl chloride (2.1 g) in 40 ml CH_2Cl_2 and $AlCl_3$ (2.0 g) in 45 ml CH_2Cl_2 were placed in the flask described above. Ethylferrocene (2.1 g) in 47 ml CH_2Cl_2 was added to the light yellow solution at —5°C at a constant rate for 7 h. The reaction mixture was maintained at —5°C for 30 min, decomposed with ice-cold water, and the organic and aqueous layers treated as described above. The organic layer was then evaporated to dryness, to give 2.03 g (80%) of a dry residue containing 1.71 g (80%) of a mixture of 1,1'- and 1,3-acetylethylferrocenes. TLC separation of the residue gave 0.95 g of the mixture of isomers.

Activated MnO_2

Two hundred ml of a 5% solution of $KMnO_4$ were added dropwise to 250 ml of a 5% solution of manganese sulphate at 50-60°C over 2 h. The mixture was left at 45-50°C overnight. The precipitate was filtered off, washed with distilled water until the filtrate was colourless, and then dried to constant weight at 110-120°C for 8-10 h to give 0.23 g (60.6%) of MnO_2.

Synthesis of 1,3-diacetylferrocene

A mixture of 1,1'- and 1,3-acetylethylferrocenes (0.45 g), MnO_2 (1.43 g), and 50 ml $CHCl_3$ was placed in a three-necked flask fitted with a stirrer and reflux condenser. The mixture was stirred vigorously at 62°C for 17 days. More MnO_2 [0.71 g; the total amount was 2.14 g (2.47×10^{-2} mol)] was added on the 13th day. The solution was separated, washed several times with ether, the solvent was removed from the combined solutions, to give 0.47 g of dry residue. TLC separation gave 0.13 g of unreacted 1,1'- and 1,3-AEF and 0.1 g of 1,3-diacetylferrocene containing 10% of the 1,1'-isomer. The R_F values were 0.88 and 0.52 for 1,1'- and 1,3-AEF and 1,1'- and 1,3-diacetylferrocenes, respectively.

References

1 E.V. Leonova, N.S. Kochetkova and A.M. Vainberg, Zh. Org. Khim., 7 (1971) 1912.

2 M. Rosenblum and R.B. Woodward, J. Amer. Chem. Soc., 80 (1958) 5443.

3 D.W. Slocum and C.R. Ernst, Advan. Organometal. Chem., 10 (1972) 79.

4 A.N. Nesmeyanov, E.V. Leonova, E.I. Fedin, P.V. Petrovskii and N.S. Kochetkova, J. Organometal. Chem., 96 (1975) 279.

5 P. Carty and M.F. Dove, J. Organometal. Chem., 28 (1971) 125.