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Abstract

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CHEMISTRY

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REACTIONS OF 1,1′-DIMETHYLFERROCENE

The influence of substituents (acetyl, ethyl, *p*-nitrophenyl, carboxyl groups, and sulfo groups) on the reactivity of the ferrocene nucleus has been noted previously ($^{1-6}$).

In the present work the reactions of 1,1′-dimethylferrocene have been investigated. Its metallation and acylation were studied.

Attempts to metallate 1,1′-dimethylferrocene with *n*-butyllithium under conditions in which this reaction is carried out for ferrocene (^{7}) gave no positive results: dimethylferrocene was recovered quantitatively unchanged. The methyl groups hinder the metallation of the ferrocene nucleus.

We used *n*-amylsodium as the metallating agent, which, in the case of ferrocene, as shown in the present work, gives higher yields of 1,1′-ferrocenedicarboxylic acid than phenyllithium. In addition, the use of phenyllithium is less convenient owing to the formation of considerable quantities of benzoic acid (^{7}).

In the metallation of 1,1′-dimethylferrocene with *n*-amylsodium, two reaction paths are possible—replacement of the hydrogen of the methyl group or of the hydrogen of the cyclopentadienyl rings. By analogy with toluene (^{8}), metallation in the methyl groups might have been expected. However, this possibility was not realized: metallation of 1,1′-dimethylferrocene with *n*-amylsodium takes place in the cyclopentadienyl rings. The principal reaction product (yield 52%) is dimethylferrocenedicarboxylic acid with m.p. 196–200°. Two further acids were isolated in small amounts. One of them is an isomer of dimethylferrocenedicarboxylic acid; the other was not investigated. All three acids give solid dimethyl esters and, consequently, none of them is di-(carboxymethyl)ferrocene, which forms a liquid dimethyl ester (^{9}). The relative positions of the methyl and carboxyl groups have not yet been established by us.

Acylation of dimethylferrocene was carried out by us with acetyl chloride in the presence of $AlCl_3$. The dark-red viscous liquid formed during acylation is a mixture of acylation products and the starting dimethylferrocene, which is readily separated chromatographically. The acylated products cannot be separated in this way. On prolonged standing of the mixture, diacetyldimethylferrocene crystallizes out, which by fractional crystallization is separated into two isomers. Comparison (by melting points) with the isomers of diacetyldimethylferrocene obtained by Reinhart and Motz ([10]) permits the assumption that the substances isolated by us are stereoisomeric 1,1′-dimethyl-2,2′-diacetylferrocenes.

From the liquid mixture remaining after removal of the crystals, monoacyldimethylferrocene was isolated chromatographically. On oxidation of this mixture with sodium hypochlorite, dimethylferrocenetricarboxylic acid was obtained, identified in the form of its trimethyl ester. After reduction of the same mixture with $LiAlH_4$, dimethyltriethylferrocene was isolated.

The formation of dimethylferrocenetricarboxylic acid and dimethyltriethylferrocene shows that, in the acylation of dimethylferrocene, in contrast to ferrocene, a triacylated product is formed. This indicates a considerable activation of the ferrocene nucleus under the influence of methyl groups in electrophilic substitution reactions.

The initial mixture of acylation products was then subjected to catalytic hydrogenation under pressure in the presence of Raney nickel (11), in order to establish the structure of the acylation products from the structure of the alkylcyclopentanes formed.

Upon fractionation on a column of the hydrogenation products, four alkylcyclopentanes were isolated: methylcyclopentane, two methylethylcyclopentanes, and an alkylcyclopentane with b.p. 151–152.5°, probably the methyl-diethylcyclopentane not described in the literature, formed from triacetyldimethylferrocene or diacetyldimethylferrocene in which both acetyl groups are located in one cyclopentadienyl ring. The formation, upon acylation of dimethylferrocene, of such a diacetyldimethylferrocene in comparatively high yield is quite possible as a result of the influence of the CH_3 groups, since in the acylation even of ferrocene itself, as is known (5), small amounts of 1,2-diacetylferrocene are obtained.

Experimental Part

Metallation of ferrocene with *n*-amylsodium.

To *n*-amylsodium, prepared from 11 g (0.48 g-at.) of sodium and 25.5 g (0.24 mole) of $n\text{-}C_5H_{11}Cl$ in absolute octane (8), 11 g (0.059 mole) of ferrocene was added. The reaction mixture was stirred for 3.5 hours while heating to 100° and was left overnight, then poured onto solid CO_2. After 1 hour, 50 ml of methanol and 300 ml of water were added. The octane was separated. The aqueous layer was washed with ether. The ethereal solution was combined with the octane solution. After removal of the solvents, 3.2 g was isolated (29% of the ferrocene introduced into the reaction).

The aqueous layer was acidified with conc. HCl. The precipitated 1,1′-ferrocenedicarboxylic acid was filtered off, washed with hot water and hot benzene. Yield 11.5 g (68% of theoretical, or practically quantitative if calculated on the ferrocene that entered into reaction). The dimethyl ester of the 1,1′-ferrocenedicarboxylic acid obtained has m.p. 114–115° and gives no depression of m.p. with an authentic sample (12).

Preparation of 1,1′-dimethylferrocene.

1,1′-Dimethylferrocene was prepared by the interaction of methylcyclopentadienyllithium* with $FeCl_3$ in ethereal solution. Yield 37% of theoretical. M.p. 32.5–33° (from petroleum ether on cooling to −20°); d_4^{35} 1.2349; n_D^{35} 1.5900.

Metallation of 1,1′-dimethylferrocene with *n*-amylsodium.

The metallation of 1,1′-dimethylferrocene (4.4 g; 0.0205 mole) was carried out as described for ferrocene. 1.2 g (27%) of dimethylferrocene was recovered unchanged.

The acid mixture obtained was extracted with hot benzene and ether. The residue was dimethylferrocenedicarboxylic acid. Yield 3 g (52% of theoretical). Decomp. temp. 196–200° (from alcohol).

Found, %: C 55.96; 56.03; H 4.97; 5.04; Fe 18.99; 18.91
$C_{14}H_{14}O_4Fe$. Calculated, %: C 55.62; H 4.63; Fe 18.54.

Dimethyl ester, m.p. 106–107° (from petroleum ether and methanol). IR spectrum (in Vaseline oil)**: 828; 854; 908; 940; 983; 1044; 1101; 1195; 1226; 1300; 1384; 1400; 1560; 1712 cm^{-1}.

Found, %: C 58.41; 58.33; H 5.65; 5.58
$C_{16}H_{18}O_4Fe$. Calculated, %: C 58.18; H 5.45.

* For providing methylcyclopentadiene we express our gratitude to N. I. Shuikin and T. I. Naryshkina.
** The IR spectra were recorded by L. A. Kazitsyna and B. V. Lokshin.

From the benzene-ether extracts, 0.2 g of isomeric dimethylferrocenedicarboxylic acid was isolated (washed with hot water and ether), m.p. above 220° (from alcohol).

Found, %: C 55.97; 56.12; H 4.86; 4.96; Fe 18.41; 18.33
$C_{14}H_{14}O_4Fe$. Calculated, %: C 55.62; H 4.63; Fe 18.54.

On treatment of the acid with diazomethane, an ester was obtained with m.p. 81-82°. IR spectrum (in Vaseline oil): 832; 851; 906; 942; 982; 1044; 1099; 1151; 1193; 1220; 1308; 1392; 1460; 1560; 1712 cm^{-1}.

From the ether with which the acid had been washed, a small amount of acid with m.p. 132-140° was isolated; the methyl ester has m.p. 75-76°.

Acylation of 1,1′-dimethylferrocene. To a mixture of 13.3 g (0.1 mole) of $AlCl_3$, 40 ml of CS_2, and 8 ml (0.1 mole) of CH_3COCl, over the course of 2 h with vigorous stirring in a nitrogen atmosphere,* there was added 8 g (0.034 mole) of 1,1′-dimethylferrocene dissolved in 40 ml of CS_2. Stirring was then continued for 20 min at room temperature and for 1.5 h with heating to gentle boiling. After this, the reaction mass was cooled with ice water. The CS_2 layer, which had become almost colorless, was decanted, and the residue was treated with cooled 1% HCl and then extracted with ether. From the ether extracts, 8.4 g of a mixture of acylation products and unreacted 1,1′-dimethylferrocene was obtained; these were dissolved in a mixture of petroleum ether and benzene (1 : 3) and separated chromatographically on Al_2O_3. There were three bands on the column. From the lower yellow band, 1.3 g (16%) of the starting 1,1′-dimethylferrocene was eluted with petroleum ether. The middle raspberry-colored band was eluted with absolute benzene. This gave 0.3 g of a raspberry-colored substance, insoluble in conc. HCl, unlike acylated dimethylferrocene. The substance was not studied further.

The last band (dark red) was eluted with methanol. This gave 5.9 g of a liquid mixture of acylated dimethylferrocenes, in which, by the various methods described below, monoacetyldimethylferrocene, three diacetyldimethylferrocenes, and triacetyldimethylferrocene were detected.

Diacetyldimethylferrocene. On standing for 1 month, 5.9 g of the mixture of dimethylferrocene acylation products at a temperature from −10 to −12° deposited 0.5 g of an orange-red crystalline substance, which was purified chromatographically on Al_2O_3. M.p. 93-94°. On recrystallization from methanol (deposits on standing for 24 h at 0–5°), diacetyldimethylferrocene with m.p. 87.5–88.5° was obtained.

Found, %: C 64.09; 64.14; H 6.00; 6.11
$C_{16}H_{18}O_2Fe$. Calculated, %: C 64.45; H 6.09.

From the mother liquor, diacetyldimethylferrocene was isolated with m.p. 98.5–99.5°.

Found, %: C 64.63; 64.66; H 6.17; 6.14; Fe 18.72
$C_{16}H_{18}O_2Fe$. Calculated, %: C 64.45; H 6.09; Fe 18.73.

These substances are probably stereoisomeric 1,1′-dimethyl-2,2′-diacetylferrocenes, for which Rinehart and Motz[10] give m.p. 84–86° and 102–103°.

Monoacetyldimethylferrocene. The mixture of acylation products remaining after separation of diacetyldimethylferrocene was dissolved in a mixture of petroleum ether and benzene (1 : 1) and passed through a column with Al_2O_3. The portion eluted with CH_3OH was chromatographed once more. Monoacetyldimethylferrocene was isolated in the form of a reddish-brown oil.

Found, %: C 65.47; 65.34; H 6.36; 6.54
$C_{14}H_{16}OFe$. Calculated, %: C 65.61; H 6.29.

* When the reaction is carried out in air, a dark powdery substance containing halide and insoluble in organic solvents and acids is sometimes formed.

The semicarbazone of monoacetyldimethylferrocene has m.p. 147-150° (recrystallized from C_2H_5OH-water).

Found, %: C 57.29; 57.08; H 6.03; 6.03; Fe 18.13; 18.00
$C_{15}H_{19}N_3OFe$. Calculated, %: C 57.52; H 6.12; Fe 17.83.

1,1′-Dimethylferrocenetricarboxylic acid. 1 g of the mixture of acylation products, after separation of diacetyldimethylferrocene, was dissolved in 5 ml of methanol and oxidized with sodium hypochlorite ([5]). 0.35 g of the acylated product was recovered. 0.06 g of dimethylferrocenetricarboxylic acid was isolated (washed with hot benzene); its trimethyl ester melts at 83–84° (from benzene and from alcohol).

Found, %: C 55.60; 55.62; H 5.19; 5.20
$C_{18}H_{20}O_6Fe$. Calculated, %: C 55.69; H 5.19.

1,1′-Dimethyltriethylferrocene. 1.5 g of acylated dimethylferrocene (after separation of diacetyldimethylferrocene) was reduced with $LiAlH_4$ ([7]). From the resulting mixture, dimethyltriethylferrocene was isolated chromatographically—a reddish-brown oily substance. It changes rapidly in air.

Found, %: C 72.33; 72.19; H 8.45; 8.55; Fe 19.11; 18.54
$C_{18}H_{28}Fe$. Calculated, %: C 72.49; H 8.78; Fe 18.73.

Hydrogenation ([11]). 16 g of acylated dimethylferrocene (unreacted dimethylferrocene having been removed chromatographically), 60 ml of C_2H_5OH, and 4 ml of Raney Ni were charged into an autoclave. The initial H_2 pressure was 95 atm. Hydrogenation was carried out for 1 hour at 110-120°, 4 hours at 230°, and 2 hours at 250-280°. The reaction products were extracted with ether. The ether solution was thoroughly washed with water to remove alcohol and dried. Removal of the ether and distillation of the reaction products were carried out on a 35-theoretical-plate column. Decalin was used as the hold-up liquid.

Methylcyclopentane was isolated (2 ml), b.p. 69.5-71.5°/750 mm, n_D^{20} 1.4100; d_4^{20} 0.7496, and two methylethylcyclopentanes (0.9 ml each), b.p. 120-121°/750 mm, n_D^{20} 1.4218; d_4^{20} 0.7681 and b.p. 125-125.5°, n_D^{20} 1.4261.

The lower-boiling methylethylcyclopentane may be, judging from the constants ([13]), the trans-1,2- or cis-1,3-isomer. The second methylethylcyclopentane is probably the cis-1,2-isomer ([13]).

In addition, 1.0 ml of alkylcyclopentane was obtained, having b.p. 151-152.5°/750 mm; n_D^{20} 1.4428; this is probably methyldiethylcyclopentane, not described in the literature.

Found, %: C 85.68; 85.84; H 14.34; 14.37
$C_{10}H_{20}$. Calculated, %: C 85.71; H 14.38.

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