BRIEF COMMUNICATIONS

BREAKDOWN OF THE FERROCENE NUCLEUS BY HYDROGENATION AND THE ACTION OF HALOGENS

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The study of the laws governing the replacement of the hydrogens of ferrocene (dicyclopentadienyliiron) [1] and its derivatives demands the development of a method for proving the structures of di- and poly-substituted ferrocenes [2]. The method of confirmatory synthesis from the corresponding substituted cyclopentadienes, carried out by Pauson [3] for di- and poly-phenylferrocenes and 1,1'-bisdiphenylmethylferrocene, is of little value for this purpose, not only because of the poor accessibility of cyclopentadiene derivatives, but also because the method is applicable only to the preparation of derivatives with hydrocarbon substituents. The most suitable method for proving the structures of poly-substituted ferrocenes depends on the rupture of the iron-carbon bond with formation of cyclopentane derivatives, this being effected by, for example, hydrogenation or the action of halogens. Woodward and coworkers [4] showed that ferrocene is not hydrogenated over reduced platinum oxide under normal conditions. Fischer [5] did not succeed in hydrogenating ferrocene in presence of a nickel catalyst at 150° and 150 atm.

In the present investigation we effected the breakdown of ferrocene and some of its derivatives by the action of bromine and chlorine and by hydrogenation with hydrogen in presence of Raney nickel under severe conditions.

EXPERIMENTAL

Ferrocene (30 g) was hydrogenated in cyclohexane (60 ml) in presence of Raney nickel in a rotating 500-ml autoclave for five hours at 200° and a further four hours at 340°. The initial hydrogen pressure was 120 atm, and the working pressure was 280 atm. Distillation through a 25-plate column gave 4.1 g of cyclopentane, b.p. 47-49° (745 mm), nD 1.4060, and d25 0.7440, and 3 g of a mixture of b.p. 36-47° (745 mm) and nD 1.4040, which, judging from its refractive index, consisted of cyclopentane and 5% of n-pentane [6]. For cyclopentane the literature [6] gives b.p. 48.7-48.8° (742.6 mm), nD 1.4060, and d25 0.7450. Some ferrocene (16.2 g) was recovered unchanged. The total yield of cyclopentane was 7 g (67% on the amount of ferrocene that reacted).

The yield of n-pentane was increased to 23% on the total amount of cyclopentane when freshly prepared Raney nickel was used. Reduction of the working pressure to 180 atm also increased the yield of n-pentane (to 7% of the total amount of cyclopentane), which is in accord with the results of Kazansky and Terentyeva [7], who showed that with increase in the pressure of hydrogen there was a rise in the temperature at which scission of the cyclopentane ring occurred in presence of a platinum or nickel catalyst.

Diacetylferrocene (28 g) was hydrogenated in alcohol (60 ml). The initial hydrogen pressure was 95 atm, and the working pressure was 240 atm. Heating was for one hour at 100°, two hours at 300°, and five hours at 345°. The products isolated were 9.2 g (35%) of ethylcyclopentane (distilled through a 25-plate column), b.p. 101.5-102.3°, nD 1.4202, and d25 0.7656, and 3.5 g (15% on the diacetylferrocene taken) of diethylferrocene [8]. For ethylcyclopentane the literature gives b.p. 100.5-101.5° (740 mm); nD 1.4202; d25 0.7654 [9]; b.p. 101-102° (747 mm) nD 1.4200; d25 0.7662 [10].

Ferrocenedicarboxylic acid was hydrogenated in the form of a solution of its sodium salt (4.3 g) in water (60 ml) for one hour at 180° and 2.5 hours at 265°. The initial hydrogen pressure was 122 atm, and the working pressure was 260 atm. The produce isolated was 2 g (65%) of cyclopentanecarboxylic acid, identified by
its p-bromopentacetyl ester, which melted, both alone and in admixture with an authentic sample, at 75-76°.

When ferrocene carboxylic acid was hydrogenated in cyclohexane (five hours at 269° and 200 atm), 37% of cyclopentane and a little ferrocene was obtained. Hydrogenation in alcoholic solution (30 g in 100 ml) resulted in the formation of cyclopentanecarboxylic acid (3.5 g, i.e. 14%) and its ethyl ester (5.2 g, i.e. 17%), b.p. 168.5-170°, \( \alpha \D 1.4362 \), and \( d^20 0.9504 \). For ethyl cyclopentanecarboxylate the literature [11] gives: b.p. 171.9° (737 mm); 89.3° (45 mm); \( \alpha \D 1.4360 \), \( d^20 0.9523 \).

Bis-p-nitrophenylferrocene (12 g) was hydrogenated in cyclohexane (130 ml) for one hour at 142°, three hours at 195°, one hour at 250°, and three hours at 326°. The initial hydrogen pressure was 120 atm, and the working pressure was 280 atm if the autoclave was heated rapidly, there was an explosion. The product isolated was 1.3 g (15.3%) of cyclopentylcyclohexane, b.p. 75-76° (6 mm), \( \alpha \D 1.4750 \) and \( d^20 0.8818 \). For cyclopentylcyclohexane the literature gives: b.p. 214°; 225-227°, \( \alpha \D 1.4728, 1.4767 \); \( d^20 0.8780 \), 0.8813 [12,13].

Apart from cyclopentylcyclohexane, an appreciable amount of light-brown resin was formed; this substance was insoluble in water and in ether, but soluble in chloroform; it contained nitrogen and iron and rapidly underwent change in the air. The yield of cyclopentylcyclohexane could not be increased, and resin formation could not be reduced, by more prolonged hydrogenation (there are references in the literature to difficulties met in the hydrogenation of aromatic amines in presence of Raney nickel [14]).

Thus, the formation of ethylcyclopentane, cyclopentanecarboxylic acid, and cyclopentylcyclohexane by the hydrogenation of diacetylferrrocene, sodium ferrocenedicarboxylate, and bis-p-nitrophenylferrocene, respectively, provides the first chemical proof that in these compounds the substituents are in different rings of the ferrocene nucleus.

We effected the breakdown of the ferrocene nucleus also by means of bromine and chlorine. We have previously reported that treatment of ferrocene with bromine in boiling carbon tetrachloride gives pentabromo-cyclopentane [15]. When ferrocene (1 mole) was treated with bromine (6.5 moles) in boiling carbon tetrachloride, a 70% yield was obtained of pentabromocyclopentane, m.p. 103-104° (crystallized from alcohol and carbon tetrachloride). When the amount of bromine or the duration of heating was increased, the yield of pentabromocyclopentane was increased to 80-82%, but a mixture of stereoisomers, m.p. 83-101°, was formed. Found %: C 13.39, 13.30; H 1.09, 1.08; Br 85.75 85.52. Calculated %: C 12.92; H 1.08; Br 85.96.

Breakdown of the ferrocene nucleus can be effected also by means of chlorine. Chlorine was passed at room temperature into a solution of ferrocene (1.80 g) in carbon tetrachloride (40 ml) for two hours, and pentachlorocyclopentane was obtained in 62% yield on the amount of ferrocene that reacted (3% of ferrocene remained in the form of a cation). It was found that the yield of pentachlorocyclopentane was raised to 90% by gradually adding a solution of 3.72 g of ferrocene in carbon tetrachloride (20 ml) to an ice-cold saturated solution of chlorine in carbon tetrachloride (80 ml) and then passing chlorine at 0° for two hours. Pentachlorocyclopentane crystallizes from 70% alcohol and can be readily sublimed in a vacuum; m.p. 38-39°. Found %: C 24.72, 24.66; H 2.17, 2.20. Calculated %: C 24.76; H 2.06.

Ferrocene is stable to the action of iodine. After a solution of ferrocene and iodine in acetic acid had been boiled for one hour, the ferrocene was recovered unchanged (the ferrocene-iodine complex was reduced with sodium thiosulfate).

The bromine method of breaking down the ferrocene nucleus was applied to ferrocene carboxylic and ferrocenedicarboxylic acids. Treatment of ferrocene carboxylic acid with bromine (boiling for one hour in carbon tetrachloride) resulted in its complete breakdown with formation of a mixture of pentabromocyclopentane isomers, m.p. 80-100°, in 44% yield (an isomer of m.p. 103-104° was isolated after one chromatographic treatment on silica gel) and also a bromine-containing carboxylic acid which decomposed when heated to 90° with gas evolution and blackening. This substance was readily soluble in ether, alcohol, and benzene, but insoluble in petroleum ether; its structure was not established.

Found %: C 25.80, 25.80; H 1.98, 2.15; Br 62.81, 62.96.

When ferrocene carboxylic acid was broken down with bromine, only the above-described bromine-containing carboxylic acid was isolated. No pentabromocyclopentane could be detected, even when the reaction product was subjected to chromatographic separation.