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THE INTERACTION OF FERROCENE AND ITS DERIVATIVES WITH AROMATIC COMPOUNDS

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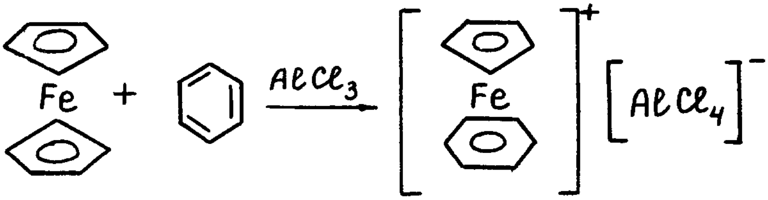
The exchange of cyclopentadienyl rings for the other ligands had not been known for ferrocene till now.

In the present work we have succeeded in performing such exchange reaction (1). On warming (80-165°) of ferrocene with aromatic hydrocarbons in the presence of two-, fourfold excess of $AlCl_3$ and equimolecular quantity of aluminium powder one cyclopentadienyl group is replaced for aromatic ring. As a result one-charged arene-cyclopentadienyl-iron-cation arises, which can be isolated in the form of tetraphenylborate. The aluminium powder prevents ferrocene from being oxydized to the ferricinium-cation.



We did not manage to substitute both cyclopentadienyl rings in ferrocene.

Thus, we have obtained in 30-66% yields tetraphenylborates of the following cations: benzene-cyclopentadienyl-iron, dec.p. 250-251° x), (found: C, 81.29, 81.29; H, 6.13, 6.06; Fe, 11.04, 10.53; $C_{35}H_{31}BFe$ requires C, 81.10; H, 6.03; Fe, 10.77); mesitylene-cyclopentadienyl-iron, m.p. 257-258° dec., (found: C, 81.04, 81.12; H, 6.65, 6.64; Fe, 9.98, 9.88; $C_{38}H_{37}BFe$ requires C, 81.44; H, 6.65; Fe, 9.96); tetralin-cyclopentadienyl-iron, m.p. 237.5-238.5° dec., (found: C, 82.02, 81.75; H, 6.39, 6.62; Fe, 9.88, 9.66; $C_{39}H_{37}BFe$ requires C, 81.84; H, 6.52; Fe, 9.76).

Oxidation of mesitylene-cyclopentadienyl-iron-tetraphenylborate by potassium permanganate produced trimesic acid as a result; this proves the presence of mesitylene in π-complex molecule.

Mesitylene- (2) and benzene-cyclopentadienyl-iron-cations (2,3) were obtained earlier by interaction of mesitylene and benzene respectively with $[C_5H_5Fe(CO)_2]Cl$.

We have shown that substituted ferrocenes can also exchange ligands. Thus 1,1'-diethyl- and 1,1'-diacetyl-ferrocenes react with mesitylene to give respectively ethylcyclopentadienyl-mesitylene-iron-tetraphenylborate, m.p. 245.5-

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x) All the substances, described in this paper, can be melted only in fused capillaries, placed in a block 30-40° before melting point.

246.5° dec., (found: C, 81.69, 81.55; H, 7.10, 6.93; Fe, 9.82, 9.24; $C_{40}H_{41}BFe$ requires C, 81.65; H, 7.02; Fe, 9.49), and acetyl-cyclopentadienyl-mesitylene-iron-tetraphenylborate, m.p. 197-198° dec., (found: C, 79.90, 79.74; H, 6.75, 6.70; Fe, 9.41, 9.52; $C_{40}H_{39}OBFe$ requires C, 79.75; H, 6.52; Fe, 9.27).

A substituent in cyclopentadienyl ring of ferrocene compound influences strongly the exchange reaction. Electron withdrawing groups make it difficult, electron repeling groups facilitate it. Thus diacetylferrocene is less active and diethylferrocene more active than ferrocene itself is.

By the action of mesitylene and $AlCl_3$ on acetylferrocene the acetylcyclopentadienyl-mesitylene-iron is mainly formed. The major product from ethylferrocene is the cyclopentadienyl-mesitylene-iron.

All tetraphenylborates obtained are yellow cristalline solids comparatively well soluble in acetone, dichloroethane, acetonitrile and nitromethane, insoluble in petroleum ether, benzene and ether. Acetylcyclopentadienyl-mesitylene-iron-tetraphenylborate is lightly orange solid, soluble in ethanol. Tetraphenylborates in solid state resist on action of air oxygen and are affected by day light. Arene-cyclopentadienyl-iron-cations are rather stable in acid medium, less stable in alkaline medium.

By the action of iodine in the presence of KI on the solutions of benzene-, mesitylene- and tetralin-cyclopentadienyl-iron in hydrochloric acid black polyiodides have formed. The iodine content in these polyiodides is indefinite.

Reduction of polyiodides with Na_2SO_3 or $Na_2S_2O_4$ in boiling ethanol have led to iodides of benzene-cyclopentadienyl-iron, m.p. 230-230.5° dec., (found: C, 40.30, 40.29; H, 3.46, 3.33; I, 39.06, 38.86; Fe, 17.17, 17.08; $C_{11}H_{11}FeI$ requires C, 40.53; H, 3.40; I, 38.93; Fe, 17.13); mesitylene-cyclopentadienyl-iron, m.p. 220-222° dec., (found: C, 45.53, 45.59; H, 4.44, 4.70; I, 34.83, 34.70; Fe, 15.11, 14.98; $C_{14}H_{14}FeI$ requires C, 45.68; H, 4.65; I, 34.49; Fe, 15.17), and tetralin-cyclopentadienyl-iron, m.p. 207-208° dec., (found: C, 47.18, 47.41; H, 4.46, 4.44; I, 33.30, 33.87; Fe, 15.09, 14.89; $C_{15}H_{17}FeI$ requires C, 47.40; H, 4.51; I, 33.40; Fe, 14.70). All the iodides are yellow crystalline solids, extremely soluble in water, CH_3OH and C_2H_5OH, soluble in acetone, moderately soluble in dichloroethane and $CHCl_3$. They are highly unstable in the light.

For benzene-cyclopentadienyl-iron-cation we have also obtained reddish-violet triiodide, $\left[C_5H_5FeC_6H_6\right]^+\left[I_3\right]^-$, dec.p. 226-227° (found: C, 23.17, 23.15; H, 2.04, 1.97; I, 65.50, 65.59; Fe, 9.70, 9.81; $C_{11}H_{11}I_3Fe$ requires C, 22.81; H, 1.91; I, 65.67; Fe, 9.63). Triiodide is formed by partial reduction of polyiodide, by the action of an excess of KI on the polyiodide and by treatment of $\left[C_5H_5FeC_6H_6\right]I$ with I_2.

By thermal decomposition (230-300°) tetraphenylborates and iodides of arene-cyclopentadienyl-iron-cations give ferrocene.

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