Tetrahedron Letters No. 17, pp.13-15, 1959. Pergamon Press Ltd. Printed in Great Britain.

HYDROXYFERROCENE

A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd
U.S.S.R. Academy of Sciences, Moscow

(Received 24 September 1959)

BENSON and LINDSEY[1] had synthesized bis-(1- hydroxy-3-methylcyclopentadienyl) iron by treating 3-methyl- 2 cyclopentenone in liquid ammonia with sodium amide and ferrous chloride.

We succeeded in preparing hydroxy ferrocene via ferrocenylboric acid.[2] The reaction of the latter with copper acetate resulted in ferrocenyl acetate (59 per cent yield) and biferrocenyl (21 per cent yield), the reaction with copper propionate taking the same course.

$$\varphi B(OH)_2 + 2Cu(OCOR)_2 + 2H_2O \rightarrow \varphi OCOR + 3RCOOH + Cu_2O + H_3BO_3$$

$$2\varphi B(OH)_2 + 2Cu(OCOR)_2 + 3H_2O \longrightarrow \varphi\text{-}\varphi + 4RCOOH + Cu_2O + 2H_3BO_3$$

with $R = CH_3, C_2H_5$; φ = ferrocenyl $C_5H_5FeC_5H_4$.

It is known from the literature[3] that phenylboric acid is oxidized by

---

[1] R. E. Benson and R. V. Lindsey, J. Amer. Chem. Soc. 79, 5471 (1957).

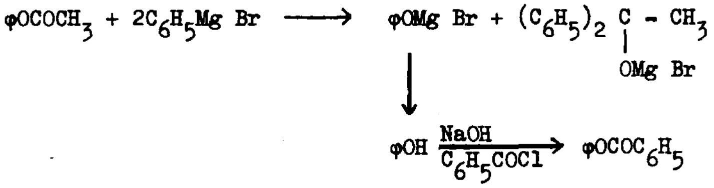
[2] A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd, Dokl. Akad. Nauk S.S.S.R. 126, No. 5, 1004 (1959).

[3] Z. Holzbecher, Chem. listy 46, 17 (1952).

Compound	Formula	M.p. (°C)	Found			Calculated		
			C	H	Fe	C	H	Fe
1. Hydroxyferrocene	$C_5H_5FeC_5H_4OH$	166-170	59.48	5.06	27.60	59.45	4.99	27.65
2. Methoxyferrocene	$C_5H_5FeC_5H_4OCH_3$	39.5-40.5	61.18	5.81	25.44	61.14	5.60	25.85
3. Ferrocenyl acetate	$C_5H_5FeC_5H_4OCOCH_3$	64.5-66	59.00	4.98	22.80	59.03	4.96	22.88
4. Ferrocenyl propionate	$C_5H_5FeC_5H_4OCOC_2H_5$	30-31	60.40	5.66	21.61	60.50	5.47	21.64
5. Ferrocenyl benzoate	$C_5H_5FeC_5H_4OCOC_6H_5$	108.5-109.5	66.79	4.71	18.25	66.70	4.61	18.24
6. Ferrocenyl benzosulphonate	$C_5H_5FeC_5H_4OSO_2C_6H_5$	90-90.5	56.07	4.16	16.53	56.15	4.12	16.32

copper acetate to phenol, whereas O - and m - nitrophenylboric acids are oxidized to 2,2' and 3,3' -dinitrobiphenyl, respectively.

The structure of ferrocenyl acetate has been proved by its reaction with phenylmagnesium bromide.



$$\varphi OCOCH_3 + 2C_6H_5Mg\,Br \longrightarrow \varphi OMg\,Br + (C_6H_5)_2\underset{\substack{|\\ OMg\,Br}}{C} - CH_3$$

$$\downarrow$$

$$\varphi OH \xrightarrow[C_6H_5COCl]{NaOH} \varphi OCOC_6H_5$$

Hydroxyferrocene or ferrocenol can be isolated from alkaline solutions, just as phenol, by treatment with carbon dioxide. It is a yellow crystalline substance, decomposing within several days when exposed to air but stable in nitrogen; m.p. 166-170°C (in nitrogen).

Hydroxyferrocene has also been obtained by the hydrolysis of ferrocenyl acetate in alcohol-alkaline medium. Besides hydroxyferrocene the following derivatives have been synthesized.

Hydroxyferrocene is soluble in ether, alcohols, and chloroform, but insoluble in benzene; its esters are readily soluble in organic solvents. Other properties of hydroxyferrocene are being studied.