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Abstract

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α-FERROCENYLCARBONIUM SALTS

We have previously shown that, on treatment of a solution of diphenylferrocenylcarbinol in acetic acid with concentrated hydrochloric acid, destruction of the ferrocene system occurs with formation of 6,6-diphenylfulvene (^{1}).

We succeeded in isolating an intermediate reaction product—ferrichloride of diphenylferrocenylcarbonium. If chloric acid is used instead of HCl, diphenylferrocenylcarbonium perchlorate is formed. These salts are dark-blue crystalline substances, insoluble in ether and benzene and readily soluble in acetone and nitromethane. On addition of water to an acetone solution of the salt, instantaneous formation of diphenylferrocenylcarbinol is observed

$$\mathrm{Fc{-}C(C_6H_5)_2OH} \underset{\mathrm{H_2O}}{\rightleftarrows} [\mathrm{Fc{-}C^+(C_6H_5)_2}]\,\mathrm{X^-}, \qquad \mathrm{X = FeCl_4,\ ClO_4}$$

whereas on treatment with conc. HCl complete decomposition of the ferrocene molecule occurs (6,6-diphenylfulvene was isolated).

In 1959, diphenylferrocenylcarbonium perchlorate was described, obtained by condensation of ferrocene with ferrocenecarboxaldehyde or formic acid (^{2}). Recently, hexachloroantimonate (from the interaction of diphenylchloromethane with $SbCl_5$) and hexafluoroantimonate of diphenylcarbonium (from decomposition of the complex of diphenylacetic acid anhydrofluoride and SbF_5 in liquid SO_2) (^{3}) have been obtained; hexafluoroantimonates of dimethyl-, trimethyl-, and dimethylethylcarboniums, obtained from alkyl fluorides and SbF_5 in liquid SO_2, have also been described (^{4}).

The ease of formation of the α-ferrocenylmethyl cation is probably of the same order as that of the triphenylmethyl cation, since the rate of solvolysis of ferrocenylcarbinyl and methylferrocenylcarbinyl acetates is comparable with the rate of solvolysis of trityl acetate (^{5}). The increased stability of the α-ferrocenylcarbonium ion has been explained by overlap of the $3d$-orbital of the iron atom and the vacant orbital of the carbonium ion ($^{6-8}$).

We obtained comparatively stable salts of ferrocenylphenylcarbonium—the light-brown perchlorate and tetraphenylborate (from ferrocenylphenylcarbinol in acetic-acid solution by the action of $HClO_4$ and sodium tetraphenylborate, respectively)

$$\left[\mathrm{Fc{-}\overset{+}{C}HC_6H_5}\right]\mathrm{X^-}, \qquad \mathrm{X = ClO_4,\ B(C_6H_5)_4}$$

and investigated some of their properties.

Tetraphenylborate of ferrocenylphenylcarbonium, on dissolution in pyridine, gives tetraphenylborate of N-(ferrocenylphenylmethyl)pyridinium:

$$\text{ferrocenyl-}\mathrm{\overset{+}{C}HC_6H_5\ \ B(C_6H_5)_4^-} \xrightarrow{\mathrm{C_5H_5N}} \text{ferrocenyl-}\mathrm{CH(C_6H_5) - \overset{+}{N}C_5H_5\ \ B(C_6H_5)_4^-}$$

Thermal decomposition of ferrocenylphenylcarbonium tetraphenylborate in nitromethane at 50° leads to a mixture of approximately equal amounts of the diastereomers of 1,2-diphenyl-1,2-diferrocenylethane.

To explain the facile dimerization of α-ferrocenylcarbonium ions, the following scheme had previously been proposed (^{9,10}):

$$\text{ferrocenyl-}\mathrm{\overset{+}{C}HC_6H_5} \longrightarrow \text{ferrocenyl}^+ - \mathrm{\dot{C}HC_6H_5} \longrightarrow \text{ferrocenyl}^+ - \mathrm{CHC_6H_5 - CHC_6H_5} - \text{ferrocenyl}^+ \longrightarrow$$
$$\longrightarrow \text{ferrocenyl-}\mathrm{CHC_6H_5 - CHC_6H_5} - \text{ferrocenyl}$$

However, we found that the perchlorates of ferrocenylphenylcarbonium and diphenylferrocenylcarbonium are diamagnetic (according to ESR data), which is consistent with a carbonium-ion structure. It is possible that reduction of the ferrocenylphenylmethyl cation to the radical (which immediately dimerizes)

$$\text{ferrocenyl-}\mathrm{\dot{C}HC_6H_5}$$

occurs only on heating with the tetraphenylborate anion (biphenyl was isolated). On heating ferrocenylphenylcarbonium fluoroborate in nitromethane, smooth formation of 1,2-diphenyl-1,2-diferrocenylethane does not occur.

Experimental Part

1. Ferrichloride of diphenylferrocenylcarbonium. To a solution of 0.2 g of diphenylferrocenylcarbinol in 10 ml of glacial acetic acid, two drops of conc. HCl were added. Almost immediately a crystalline dark-blue precipitate separated; it was filtered off, washed with abs. ether, and dried in a vacuum desiccator. Yield: 0.10 g (33% of theory) of diphenylferrocenylcarbonium ferrichloride.

Found, %: C 50.26; 50.44; H 3.70; 3.84; Fe 19.48; 19.69; Cl 26.28; 26.5
$\mathrm{C_{23}H_{19}Fe_2Cl_4}$. Calculated, %: C 50.23; H 3.66; Fe 20.31; Cl 25.79

2. Hydrolysis of diphenylferrocenylcarbonium ferrichloride. To a solution of 0.08 g of diphenylferrocenylcarbonium ferrichloride in abs. acetone, several drops of water were added; the solution at once changed from dark blue to yellow. After dilution with water, diphenylferrocenylcarbinol was extracted with ether. The ethereal solution was dried over $MgSO_4$, and after removal of the ether the residue was chromatographed on Al_2O_3. 0.04 g (74% of theory) of diphenylferrocenylcarbinol was obtained, m.p. 130°; a mixed sample with an authentic specimen melted without depression.

3. **6,6-Diphenylfulvene from diphenylferrocenylcarbonium ferrichloride.** To a solution of 0.08 g of diphenylferrocenylcarbonium ferrichloride in abs. acetone, three drops of conc. HCl were added; after 10 min the solution was poured into ether; the ethereal solution was washed with water, 10% KOH, and water, and dried over $MgSO_4$. After removal of the ether, the residue was chromatographed on Al_2O_3 in hexane. 0.02 g (60% of theory) of 6,6-diphenylfulvene was obtained; a mixed sample with an authentic specimen melted without depression.

4. **Diphenylferrocenylcarbonium perchlorate.** To a solution of 0.1 g of diphenylferrocenylcarbinol in 5 ml of glacial acetic acid, two drops of 70% $HClO_4$ were added. A dark-blue diphenylferrocenylcarbonium perchlorate precipitated; it was filtered off and washed with abs. ether. 0.07 g (57% of theory) of the salt was obtained. Diphenylferrocenylcarbonium perchlorate is insoluble in ether and benzene, readily soluble in acetone and nitromethane; it explodes on heating.

Found, %: Fe 12.70; 12.94 (after wet combustion, polarographically)

$C_{23}H_{19}FeClO_4$. Calculated, %: Fe 12.39

5. **Ferrocenylphenylcarbonium perchlorate.** To a concentrated solution of 0.1 g of ferrocenylphenylcarbinol in glacial acetic acid, two drops of 70% $HClO_4$ were added. A light-brown crystalline ferrocenylphenylcarbonium perchlorate precipitated; it was filtered off and washed with abs. ether. 0.08 g (63% of theory) of the salt was obtained, insoluble in ether and benzene, readily soluble in acetone and nitromethane.

Found, %: Fe 14.71; 15.17

$C_{17}H_{15}FeClO_4$. Calculated, %: Fe 14.91

6. **Ferrocenylphenylcarbonium tetraphenylborate.** To a solution of 0.14 g of ferrocenylphenylcarbinol in glacial acetic acid was added a solution of 0.17 g of sodium tetraphenylborate in glacial acetic acid. The light-brown precipitate that formed was filtered off and washed with glacial acetic acid and ether. 0.09 g (44% of theory) of ferrocenylphenylcarbonium tetraphenylborate was obtained. The salt gradually decomposes in air.

Found, %: C 82.67; H 6.07; Fe 9.63; B 1.86

$C_{41}H_{35}FeB$. Calculated, %: C 82.84; H 5.93; Fe 9.40; B 1.82

7. **Tetraphenylborate of N-(ferrocenylphenylmethyl)pyridinium.** To 0.09 g of ferrocenylphenylcarbonium tetraphenylborate, abs. pyridine was added; the solution was filtered; N-(ferrocenylmethyl)pyridinium tetraphenylborate was precipitated with abs. ether, filtered off, and washed with abs. ether. Yield 0.10 g (88% of theory), reprecipitated from abs. acetone with abs. ether; a yellow crystalline substance, insoluble in water.

Found, %: C 81.94; 81.78; H 6.15; 6.02; N 2.23; 2.34;
Fe 7.90; 7.78; B 1.51; 1.51

$C_{46}H_{40}FeBN$. Calculated, %: C 82.03; H 5.99; N 2.08;
Fe 8.29; B 1.67

8. **Thermal decomposition of ferrocenylphenylcarbonium tetraphenylborate.** The reaction was carried out in a stream of nitrogen. A solution of 1.5 g of ferrocenylphenylcarbonium tetraphenylborate in nitromethane was heated on a water bath at 50°; the color of the precipitate changed from brownish to light yellow. After cooling to room temperature, the precipitate was filtered off and washed with ether. The nitromethane and ethereal solutions were combined and washed with 10% KOH and water. The ether was distilled off; the residue and precipitate were combined and chromatographed on Al_2O_3.

Diphenyl was washed out with petroleum ether; the diastereomer 1,2-diphenyl-1,2-diferrocenylethane, mp 218° (from heptane), was washed out with a mixture of petroleum ether and benzene; yield 0.29 g (42% of theoretical). Lit.: mp 218-220° ([10]).

Found, %: C 74.10; 74.08; H 5.67; 5.47; Fe 19.81; 20.04
$C_{34}H_{30}Fe_2$. Calculated, %: C 74.20; H 5.50; Fe 20.30

The diastereomer with mp 275° (from nitromethane) was washed out with benzene; yield 0.32 g (46% of theoretical). Lit.: mp 276-278° ([10]).

Found, %: C 74.16; 74.15; H 5.51; 5.54; Fe 20.20; 20.07
$C_{34}H_{30}Fe_2$. Calculated, %: C 74.20; H 5.50; Fe 20.30

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