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TRANSLATION

ALPHA-FERROCENYL CARBONIUM SALTS

By

A. N. Nesmeyanov, V. A. Sazonova, et al.

FOREIGN TECHNOLOGY DIVISION

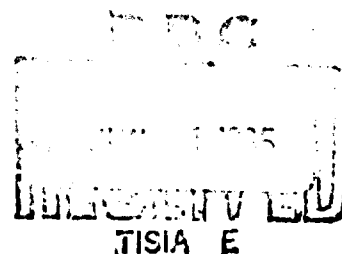
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UNEDITED ROUGH DRAFT TRANSLATION

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English pages: 7

SOURCE: AN SSSR. Doklady. (Russian), Vol. 160,
No. 2, 1965, pp. 355-358.

S/0020-065-160-002

(Acc. No. TP5001000)

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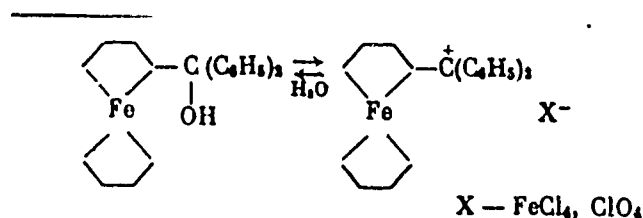
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ALPHA-FERROCENYLCARBONIUM SALTS

A. N. Nesmeyanov, V. A. Sazonova, et al.

We have shown before, that under the effect of concentrated hydrochloric acid on a solution of diphenylferrocenylcarbinol in acetic acid there is destruction of the ferrocene system and the formation of 6, 6-diphenylfulvene (1).

We have succeeded in separating an intermediate reaction product-ferrichloride diphenylferrocenylcarbonium. If, instead of HCl is taken perchloric acid, then a diphenylferrocenylcarbonium perchlorate is formed. These salts - dark-bluish crystalline substances, insoluble in ester and in benzene, well soluble in acetone and nitromethane. When water is added to the acetone solution of the salts is observed an instantaneous formation of diphenylferrocenylcarbonium

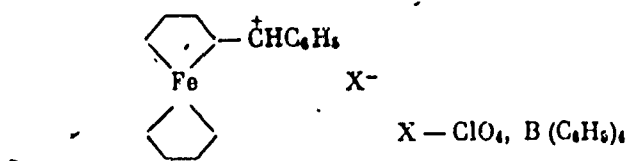


and during the action of concentrated HCL the ferrocene molecule suffers total decomposition (6, 6-diphenylfulvene is separated).

In 1959 was described diferrocenylcarbonium perchlorate, obtained during condensation of ferrocene with ferrocenylaldehyde or formic acid (2). Recently was obtained hexachloroantimonate (during reaction of diphenylchloromethane with SbCl_5) and hexafluoroantimonate of diphenylcarbonium (during decomposition of an acid fluoride complex of diphenylacetic acid and SbF_5 in liquid SO_2) (3), described were hexafluoroantimonates of dimethyl-trimethyl and dimethylethyl-carbonium, obtained from alkylfluorides and SbF_5 in liquid SO_2 (4).

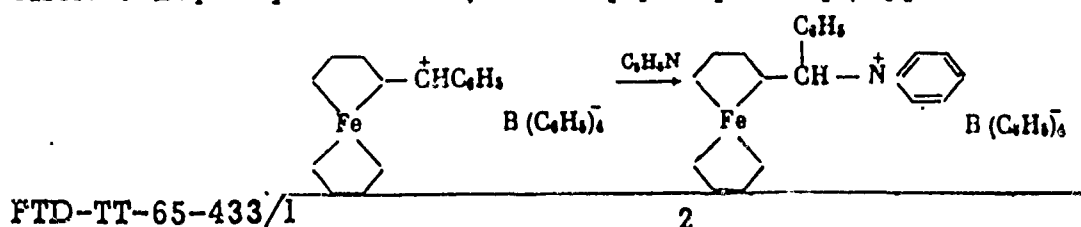
The easiness of the formation of alpha-ferrocenylmethyl cation is, probably of the very same order, as in case of triphenylmethyl cation since the rate of solvolysis of ferrocenylcarbiny- and methylferrocenylcarbinyacetates is comparable with the solvolysis rate of tritylacetate (5). The higher stability of alpha-ferrocenylcarbonium ion was explained in the overlapping of the 3d-orbit of the iron atom and vacant orbit of carbonium ion (6-8).

We obtained relatively stable salts of ferrocenylcarbonium-bright-brownish perchlorate and tetraphenylborate (from ferrocenylphenylcarbinol in an acetic acid solution during the action of HClO_4 and tetraphenylboronsodium respectively)



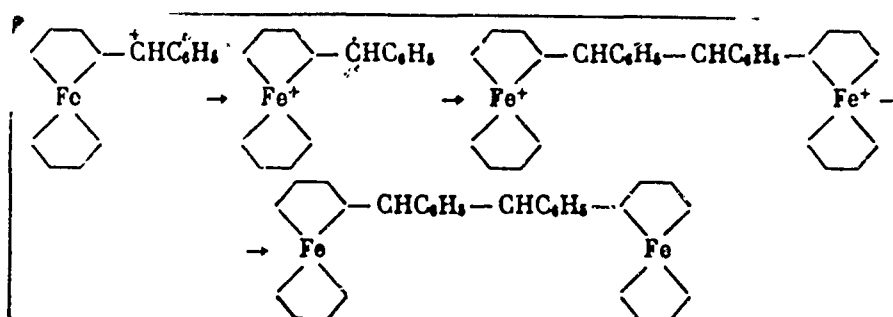
and we investigated some of its properties.

Tetraphenylborate of ferrocenylphenylcarbonium when dissolved in pyridine offers tetraphenylborate N-(ferrocenylphenylmethyl)-pyridinium

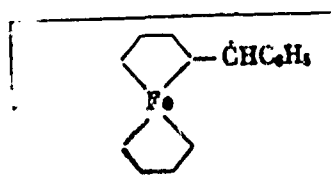


Thermal decomposition of tetraphenylborate of ferrocenylphenylcarbonium in nitromethane at 50° leads to a mixture of approximately equal amounts of diastereomers 1, 2-diphenyl-1, 2-diferrocenylethane.

To explain the easy doubling of alpha-ferrocenylcarbonium ions was previously introduced the following scheme (9, 10):



But, we have found that ferrocenylphenylcarbonium perchlorates and diphenylferrocenylcarbonium perchlorates are diamagnetic (according to E.P.R. = electron paramagnetic resonance data) which is in conformity with carbonium-ion structure. It is possible that reduction of ferrocenylphenylmethyl cation into a radical (which doubles immediately)



takes place only during the heating of the tetraphenylborate-with an ion (diphenyl was separated). When heating borofluoride of ferrocenylphenylcarbonium in nitromethane there is no smooth formation of 1, 2-diphenyl - 1, 2-diferrocenylethane.

Experimental part.

1. Ferrichloride of diphenylferrocenylcarbonium. To a solution of 0.2 g diphenylferrocenylcarbinol in 10 ml of icy acetic acid were added two droplets of concentrated HCl. Almost immediately precipitated a crystalline dark-bluish residue, which was filtered, washed in absolute ether and desiccated in a vacuum-exsiccator. Obtained were 0.10 g (33% of theoretical) ferrichloride of diphenylferrocenylcarbonium.

Found %: C 50,26; 50,44; H 3,84; Fe 19,48; 19,69; Cl 26,28; 26,5 $C_{22}H_{19}Fe_2Cl_4$ Calculated %: C 50,23; H 3,66 Fe 20,31 Cl,79.

2. Hydrolysis of ferrichloride of diphenylferrocenylcarbonium. To a solution of 0.08 g ferrichloride diphenylferrocenylcarbonium in absolute acetone were added several drops of water; the solution from dark-bluish immediately turned yellow. After diluting with water diphenylferrocenylcarbinol was extracted with ether. The ether solution was desiccated with $MgSO_4$ and after removing the ether the residue was chromatographed on Al_2O_3 . Obtained were 0.04 g (74% of theoretical) diphenylferrocenylcarbinol, melting point 130° ; the mixed sample with the known sample melts without depression.

3.6, 6-Diphenylfulvene from diphenylferrocenylcarbonium ferrichloride. To a solution of 0.08 g of diphenylferrocenylcarbonium ferrichloride in absolute acetone were added three droplets of concentrated HCl; within 10 minutes the solution was poured into ether; the ether solution was washed with water, 10% KOH, water, desiccated with $MgSO_4$. After removing the ether the residue was chromatographed on Al_2O_3 in hexane. Obtained were 0.02 g (60% of theoretical) 6, 6-diphenylfulvene; the mixed probe with known sample melts without depression.

4. Perchlorate of diphenylferrocenylcarbonium. To a solution of 0.1 g diphenylferrocenylcarbinol in 5 ml of icy acetic acid were added two droplets of 70% HClO_4 . A dark-bluish perchlorate of diphenylferrocenylcarbonium has settled, which was filtered off, washed with absolute ether. Obtained were 0.07 g (57% of theoretical) of salt. Perchlorate of diphenylferrocenylcarbonium is insoluble in ether and benzene, well soluble in acetone and nitromethane; explodes when heated.

Found %: Fe 12.70; 12.94 (after wet combustion, polarographically) $\text{C}_{23}\text{H}_{19}\text{FeClO}_4$. Calculated %: Fe 12.39.

5. Ferrocenylphenylcarbonium perchlorate. To a concentrated solution of 0.1 ferrocenylphenylcarbinol in icy acetic acid were added two droplets of 70% HClO_4 , a bright-brown crystalline ferrocenylphenylcarbonium perchlorate settled, which was filtered, washed in absolute ether. Obtained were 0.08 g (63% of theoretical) salts, insoluble in ether and benzene, well soluble in acetone and nitromethane.

Found %: Fe 14.71; 15.17 $\text{C}_{17}\text{H}_{15}\text{FeClO}_4$; calculated %: Fe 14.91.

6. Tetraphenylborate of ferrocenylphenylcarbonium. To a solution of 0.14 g of ferrocenylphenylcarbinol in icy acetic acid was added a solution of 0.17 g tetraphenylborsodium in icy acetic acid. The settled bright-brownish residue was filtered, washed in icy acetic acid and ether. Obtained were 0.09 g (44% of theoretical) of tetraphenylborate of ferrocenylphenylcarbonium. When exposed to air the salt decomposes gradually.

Found %: C 82.67; H 6.07; Fe 0.63; B 1.86 $\text{C}_{41}\text{H}_{35}\text{FeB}$.

Calculated %: C 82.84; H 5.93; Fe 9.40; B 1.82

7. Tetraphenylborate N - (ferrocenylphenylmethyl)-pyridine. To a 0.09 g solution of tetraphenylborate of ferrocenylphenylcarbonium was added absolute ether, filtered and washed with ether. Yield 0.10 g (88% of theoretical), resettled from absolute acetone with absolute ether; the 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

8. Thermal decomposition of ferrocenylphenylcarbonium tetraphenylborate. The reaction was carried out in a nitrogen stream. A solution of 1.5 g of ferrocenylcarbonium tetraphenylborate in nitromethane was heated over a water bath at 50° , the color of the residue changed here from brownish to bright yellow. After cooling to room temperature the residue was filtered and washed with ether. Nitromethane and ether solutions (ester. solutions) were combined and washed with 10% KOH and water. The ether (ester) was distilled, the settling and residue were combined and chromatographed on Al_2O_3 . With petroleic ether was washed out the diphenyl; the mixture of the petroleic ether with benzene was used for washing out the diastereomer 1, 2-diphenyl-1, 2-diferrocenylethane with melting point of 218° (from heptane), yield 0.29g (42% of theoretical liter. melting point $218-220^{\circ}$ (10).

Found %: C 74.101 74.08; H 5.67; Fe 19.81; 20.04 $C_{34}H_{30}Fe_2$

Calculated %: C 74.20; H 5.50 Fe 20.30

With benzene was washed out the diastereomer with melting point of 275° (from nitromethane), yield 0.32 g (46% of theoretical). Literat. melt. pt $276-278^{\circ}$

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

The M. V. Lomonosov Moscow State Univers.

Submitted: Aug. 2, 1964

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