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Abstract

Full Text

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ALKYLATION OF FERROCENYLAMINE

Previously we observed the destruction of the ferrocene system under the action of light, using salts of α-pyridylferrocene as an example ([1]). Assuming that substituents carrying a positive charge on an atom bonded to the cyclopentadienyl ring cause cleavage of the iron–carbon bonds, we undertook a study of the salts of ferrocenylamine and alkylated ferrocenylamines. As is known, ferrocenylamine can be obtained by various methods: by the interaction of ferrocenyl lithium with the benzyl ether of hydroxylamine ([2]), from ferrocene carboxylic acid azide by the Curtius reaction ([3]), by catalytic reduction of phenylazoferrocene ([4]), azoferrocene ([5]), and nitroferrocene ([6,7]), by replacement of halogen in haloferrocene with a phthalimido group followed by hydrolysis ([8]), and by reduction of ferrocenyl azide ([9]).

Alkylation of ferrocenylamine, however, has not been described. In the present work it is shown that ferrocenylamine is very readily alkylated by triethyloxonium borofluoride

$$C_5H_5FeC_5H_4NH_2 \xrightarrow{(C_2H_5)_3OBF_4} C_5H_5FeC_5H_4NHC_2H_5.$$

The reaction is carried out without solvent; ferrocenylamine is mixed, with cooling, with a slight excess of triethyloxonium borofluoride, followed by treatment of the reaction mixture with alkali solution. Ethylferrocenylamine is formed in 77% yield; its hydrochloride and N-ethyl-N-ferrocenyl-*p*-toluenesulfonamide were obtained. Monoethylferrocenylamine is then, under the same conditions, readily alkylated to diethylferrocenylamine (yield 95%); its hydrochloride and iodoethylate were obtained.

$$C_5H_5FeC_5H_4NHC_2H_5 \xrightarrow{(C_2H_5)_3OBF_4} C_5H_5FeC_5H_4N(C_2H_5)_2.$$

As expected, diethylferrocenylamine, as well as monoethylferrocenylamine and ferrocenylamine, in an aqueous solution of an acid—oxalic acid—under the action of light (under nitrogen) are gradually destroyed with formation of iron oxalate, the diethyl compound more rapidly, then the monoethyl compound, and ferrocenylamine more slowly. Still more readily under the action of light the hydroxide of triethylferrocenylammonium is destroyed (in aqueous solutions). In acidic

aqueous solutions, under the action of light, acetylferrocene and its oxime are destroyed.

These reactions, as well as their products, are being studied by us.

Experimental Part

Ethylferrocenylamine. Ferrocenylamine (1.05 g) is mixed with triethyloxonium borofluoride (1.19 g) with cooling by ice water. The reaction proceeds very rapidly with self-heating. The reaction mixture is decomposed with 10% KOH solution and extracted with ether. The ethereal extracts are washed with 10% KOH solution, water, and dried over $MgSO_4$. After removal of the solvent in vacuo, a reddish-brown oil remains, crystallizing upon addition of hexane and cooling. The precipitated crystals are filtered off and washed several times with hexane. Obtained: 0.9 g (77% of theory) of ethylferrocenylamine, m.p. 54–55°. For purification the amine is dissolved in 10% H_2SO_4; the acidic solution is filtered and 10% KOH solution is added. The precipitated ethylferrocenylamine is filtered off, washed with water, and dried in a vacuum desiccator. M.p. 56.5–58°. Sublimes in vacuo.

Found, %: C 62.71, 62.78; H 6.75, 6.87; Fe 24.90, 24.91; N 6.02, 6.26
$C_{12}H_{15}FeN$. Calculated, %: C 62.91; H 6.60; Fe 24.38; N 6.11

Ethylferrocenylamine is a yellow crystalline substance, readily soluble in alcohol, ether, and benzene.

On chromatography of the residue on Al_2O_3, ethylferrocenylamine decomposes; 0.08 g (6% of theory) of diethylferrocenylamine, m.p. 35.5–36.5° (see below), is eluted with hexane.

Ethylferrocenylamine hydrochloride. When a stream of dry HCl is passed through an ethereal solution of ethylferrocenylamine, the hydrochloride is isolated quantitatively.

Found, %: C 54.13, 54.32; H 6.17, 6.16; N 5.60, 5.42; Fe 21.09, 21.08
Cl 13.50, 13.36
$C_{12}H_{16}FeNCl$. Calculated, %: C 54.25; H 6.07; N 5.27; Fe 21.08
Cl 13.35

N-Ethyl-N-ferrocenyl-*p*-toluenesulfonamide. A solution of 0.100 g of ethylferrocenylamine and 0.105 g of *p*-toluenesulfonyl chloride in 1 ml of abs. pyridine is heated on a water bath for 1 hour. After cooling, water is added to the reaction mixture and extraction with ether is carried out. The ethereal extracts are washed with water, 10% H_2SO_4, again with water, and dried over $MgSO_4$. After removal of the solvent, the residue is chromatographed on Al_2O_3. Ether elutes 0.16 g (98% of theory) of N-ethyl-N-ferrocenyl-*p*-toluenesulfonamide. M.p. 105–105.5° (from heptane).

Found, %: C 59.83, 59.85; H 5.46, 5.55; Fe 14.70, 14.83; N 3.57, 3.79
$C_{19}H_{21}FeNSO_2$. Calculated, %: C 59.54; H 5.52; Fe 14.57; N 3.65

Diethylferrocenylamine. Ethylferrocenylamine (0.86 g) is mixed with 0.83 g of triethyloxonium borofluoride while cooling with ice water. The reaction mixture is worked up in the same way as in the preparation of ethylferrocenylamine. 0.93 g (95% of theory) of diethylferrocenylamine is obtained. Red crystalline substance. M.p. 35.5–36.5° (from alcohol). Sublimes in vacuum.

Found, %: C 65.04, 65.31; H 7.20, 7.44; N 5.46, 5.47; Fe 22.09, 22.32
$C_{14}H_{19}FeN$. Calculated, %: C 65.39; H 7.48; N 5.44; Fe 21.72

When a stream of dry hydrogen chloride is passed through an ethereal solution of diethylferrocenylamine, a yellow precipitate of the hydrochloride is quantitatively formed; this hydrochloride is still less stable than ethylferrocenylamine hydrochloride.

Triethylferrocenylammonium iodide. On standing for 3 days (in the dark), light-yellow crystals separate from a solution of 0.3 g of diethylferrocenylamine in 1 ml of ethyl iodide; these are filtered off and washed with ether. For purification, the crystals are dissolved in alcohol, the solution is filtered, and the salt is precipitated by addition of ether.

Found, %: C 46.34, 46.41; H 5.89, 5.97; Fe 13.35, 13.15;
N 3.42, 3.63; J 30.44, 30.41
$C_{16}H_{24}FeNJ$. Calculated, %: C 46.51; H 5.85; Fe 13.55;
N 3.39; J 30.72

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.