

SHORT  
COMMUNICATIONS

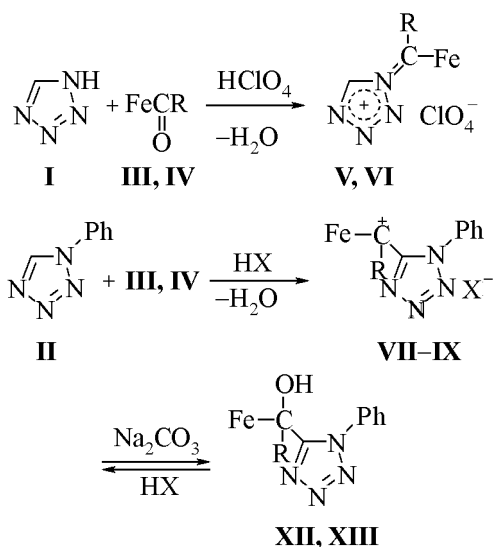
## Synthesis of Salts of $\alpha$ -Ferrocenyl Carbocations Containing Tetrazole

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We reported formerly on the synthesis of  $\alpha$ -ferrocenyl-alkylated tetrazolium salts [1] that may be useful in various practical respects [2, 3]. In this study we carried out new reactions of tetrazoles **I**, **II** with carbonyl derivatives of ferrocene, formyl- and acetylferrocene (**III**, **IV**), in the presence of strong mineral acids. It was established that the mentioned substrates react in equimolar amounts at room temperature in the medium of phosphorus oxychloride with addition of 72% perchloric acid. The reaction gave rise to the respective crystalline dark-violet immonium salts **V**, **VI** perchlorates, and dark-blue perchlorates of  $\alpha$ -ferrocenylmethyl cations **VII**, **VIII**. A similar reaction product was obtained as tetrafluoroborate **IX** in reaction of aldehyde **III** with tetrazole **II** at heating the reagents in a mixture of glacial acetic acid and acetic anhydride in the presence of 45% tetrafluoroboric acid.

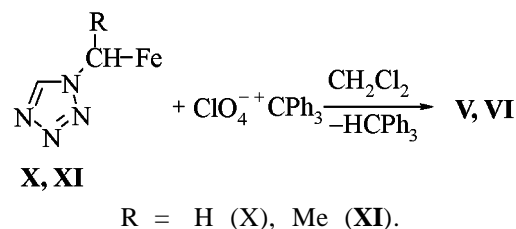


Fc = C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>; R = H (**III**, **V**, **VII**, **IX**, **XII**), Me (**IV**, **VI**, **VIII**, **XIII**); X = ClO<sub>4</sub> (**VII**, **VIII**), BF<sub>4</sub> (**IX**).

The structure of compounds **V-IX** was confirmed by UV, IR, <sup>1</sup>H NMR spectra, and also by independent synthesis and chemical transformations.

Thus the UV spectra of salts **V-IX** are characterized by several absorption maxima and are similar to the UV spectra of the other salts of this type containing ferrocenyl core [4, 5]. The most characteristic is the presence of an absorption band in the longwave range at 558-615 nm belonging to electron transition  $\pi \rightarrow \pi^*$  [5] in the chromophore system from the ferrocenyl core to the cationic center. This fact confirms the ionic structure of salts obtained.

IR and <sup>1</sup>H NMR spectra (Table 1) also are consistent with the assumed structure of salts **V-IX**. However these data are not sufficient for unambiguous identification of the isomeric composition of salts **V**, **VI** obtained since in the literature are not enough data for solution of this problem. Therefore we synthesized authentic 1-isomers of compounds **V**, **VI** by dehydrogenation of known [6, 7] 1-ferrocenylalkyl-tetrazoles (**X**, **XI**) effected by triphenylmethyl cation perchlorate playing the role of hydride ion acceptor. The corresponding procedure was developed before [8].



As a result we obtained salts **V**, **VI** in 65-83% yield; the samples by the physical constants and spectral characteristics (Table 1) were identical to those previously prepared. Thus in the reactions of carbonyl compounds of ferrocene **III**, **IV** with tetrazole **I** in the presence of acid arise only 1-isomers.

**Table 1.** IR and  $^1\text{H}$  NMR spectra of compounds **V–IX**, **XII**, **XIII**

Compd. no.	IR spectrum, $\nu$ , $\text{cm}^{-1}$			$^1\text{H}$ NMR spectrum, $\delta$ , ppm
	Ht	Fc	$\text{ClO}_4^- (\text{BF}_4^-)$ $\text{C}=\text{N}^+$	
<b>V</b>	3120, 1032, 982	3000, 1412, 1002, 828, 485	1100, 620, 1620	10.84 s (1H, $\text{H}^5$ ), 9.82 s (1H, $\text{N}=\text{CH}$ ), 5.32 m (2H, $\text{C}_5\text{H}_4$ ), 4.69 s (5H, $\text{C}_5\text{H}_5$ ), 4.56 m (2H, $\text{C}_5\text{H}_4$ )
<b>VI</b>	3125, 1042, 1017, 978	2980, 1415, 1000, 832, 488	1100, 622, 1622	10.63 s (1H, $\text{H}^5$ ), 5.28 m (2H, $\text{C}_5\text{H}_4$ ), 4.72 s (5H, $\text{C}_5\text{H}_5$ ), 4.61 m (2H, $\text{C}_5\text{H}_4$ ), 2.21 s (3H, $\text{CH}_3$ )
<b>VII</b>	1045, 1022, 982	2980, 1412, 1002, 838, 485	1095, 620	7.61–7.93 m (5H, $\text{C}_6\text{H}_5$ ), 7.34 s (1H, CH), 6.24 m (2H, $\text{C}_5\text{H}_4$ ), 4.83 s (5H, $\text{C}_5\text{H}_5$ ), 4.75 m (2H, $\text{C}_5\text{H}_4$ )
<b>VIII</b>	1048, 1018, 978	2980, 1414, 1001, 835, 480	1100, 621	7.60–7.87 m (5H, $\text{C}_6\text{H}_5$ ), 6.18 m (2H, $\text{C}_5\text{H}_4$ ), 5.03 s (5H, $\text{C}_5\text{H}_5$ ), 4.92 m (2H, $\text{C}_5\text{H}_4$ ), 2.25 s (3H, $\text{CH}_3$ )
<b>IX</b>	1042, 1020, 980	3000, 1415, 1000, 825, 485	(1085)	7.62–7.92 m (5H, $\text{C}_6\text{H}_5$ ), 7.15 s (1H, CH), 6.22 m (2H, $\text{C}_5\text{H}_4$ ), 4.85 s (5H, $\text{C}_5\text{H}_5$ ), 4.75 m (2H, $\text{C}_5\text{H}_4$ )
<b>XII</b>	1518, 1245, 1082, 1048, 1022, 978	3000, 1412, 1100, 830, 480	3430 (OH)	7.28–7.52 m (5H, $\text{C}_6\text{H}_5$ ), 4.68 s (1H, CH), 4.18 m (4H, $\text{C}_5\text{H}_4$ ), 4.01 s (5H, $\text{C}_5\text{H}_5$ ), 2.76 s (1H, OH)
<b>XIII</b>	1509, 1262, 1082, 1052, 1021, 982	3000, 1415, 1105, 1000, 828, 480	3420 (OH)	7.26–7.48 m (5H, $\text{C}_6\text{H}_5$ ), 4.16 m (4H, $\text{C}_5\text{H}_4$ ), 4.00 s (5H, $\text{C}_5\text{H}_5$ ), 2.72 s (1H, OH), 1.97 s (3H, $\text{CH}_3$ )

**Table 2.** Yields, melting points, and elemental analyses of compounds **V–IX**, **XII**, **XIII**

Compd. no.	Yield, %	mp, $^{\circ}\text{C}$	Found, %		Formula	Calculated, %	
			Fe	N		Fe	N
<b>V</b>	76	161–163 <sup>a</sup>	15.03	15.12	$\text{C}_{12}\text{H}_{11}\text{ClFeN}_4\text{O}_4$	15.24	15.28
<b>VI</b>	52	156–158 <sup>a</sup>	14.56	14.84	$\text{C}_{13}\text{H}_{13}\text{ClFeN}_4\text{O}_4$	14.68	14.72
<b>VII</b>	65	165–167 <sup>a</sup>	12.28	12.51	$\text{C}_{18}\text{H}_{15}\text{ClFeN}_4\text{O}_4$	12.62	12.67
<b>VIII</b>	48	161–164 <sup>a</sup>	12.36	12.29	$\text{C}_{19}\text{H}_{17}\text{ClFeN}_4\text{O}_4$	12.23	12.27
<b>IX</b>	40	188–190 <sup>b</sup>	13.08	13.07	$\text{C}_{18}\text{H}_{15}\text{BF}_4\text{FeN}_4$	12.99	13.03
<b>XII</b>	54	138–139	15.42	15.58	$\text{C}_{18}\text{H}_{16}\text{FeN}_4\text{O}$	15.51	15.56
<b>XIII</b>	48	125–126	14.87	14.91	$\text{C}_{19}\text{H}_{18}\text{FeN}_4\text{O}$	14.93	14.97

<sup>a</sup> With explosion. <sup>b</sup> With decomposition.

**(1-Phenyltetrazol-5-yl)ferrocenyl carbocation tetrafluoroborate (IX).** To 0.214 g (1 mmol) of formylferrocene (**III**) and 0.146 g (1 mmol) of 1-phenyltetrazole (**II**) in 3 ml of mixture of glacial acetic acid (2 ml) and acetic anhydride (1 ml) was carefully added dropwise 0.18 ml of 45%  $\text{HBF}_4$ . The reaction mixture was stirred for 6 h at 80–85 $^{\circ}\text{C}$ . After cooling 20 ml of anhydrous ethyl ether was added, and the mixture was left overnight at 4–5 $^{\circ}\text{C}$ . The separated precipitate of salt **IX** was filtered off, washed with 15 ml of ether, and dried in a vacuum-desiccator over  $\text{P}_2\text{O}_5$ . Yield 0.194 g.

**(1-Phenyltetrazol-5-yl)ferrocenylcarbinols (XII, XIII).** To a solution of 1 mmol of salt **VII–IX** in 10 ml of chloroform was added 15 ml of 10% water

solution of  $\text{Na}_2\text{CO}_3$ , and the mixture was vigorously stirred for 1–1.5 h at room temperature. Then the organic layer was separated, and the water layer was extracted with ether (2  $\times$  30 ml). The combined organic solutions were washed with water, dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and evaporated in a vacuum. The residue was dissolved in 10 ml of benzene–methanol mixture, 4:1, and applied to a chromatographic column packed with alumina. On removing the solvent carbinols **X**, **XI** were crystallized from methanol–water mixture, 3:1. Yields, physical constants, and elemental analyses of compounds **V–IX**, **XII**, **XIII** are given in Table 2.

In keeping with the cationic nature of compounds **V–IX** it was presumable that they would be fairly

reactive electrophilic reagents in reactions with nucleophilic substrates. Actually at the contact of the solutions of the compounds in chloroform with the water solution of sodium carbonate or of alkali the reaction mixture practically immediately changes the color, and from immonium salts **V**, **VI** form initial compounds **I**, **III**, **IV**, from carbenium salts **VII–IX** arise the corresponding ferrocenylcarbinols **XII**, **XIII** that by treatment with acids HX are easily converted into the initial salts. The structure of compounds **XII**, **XIII** is confirmed by IR and  $^1\text{H}$  NMR spectra (Table 1).

**1- $\alpha$ -Ferrocenylmethinetetrazolium perchlorate (V).** To a mixture of 0.214 g (1 mmol) of formylferrocene and 0.07 g (1 mmol) of tetrazole (**I**) in 2.5 ml of  $\text{POCl}_3$  was cautiously added dropwise 0.1 ml of 72%  $\text{HClO}_4$ , and the reaction mixture was stirred for 2–3 h at room temperature. Then 10 ml of anhydrous ethyl ether was added, and the mixture was left overnight at 4–5°C. The separated precipitate of perchlorate **V** was filtered off, washed with 15 of ether, and dried in a vacuum-desiccator over  $\text{P}_2\text{O}_5$ . Yield 0.278 g.

**(1-Phenyltetrazol-5-yl)ferrocenyl carbocations perchlorates (VII, VIII).** To a mixture of 1 mmol of formyl- or acetylferrocene (**III**, **IV**) and 1 mmol of 1-phenyltetrazole (**II**) in 3 ml  $\text{POCl}_3$  was cautiously added dropwise 0.1 ml of 72%  $\text{HClO}_4$ , and the reaction mixture was stirred for 5–6 h at room temperature. Then 10 ml of anhydrous ethyl ether was added, and the mixture was left overnight at 4–5°C. The separated precipitate of perchlorate **VII**, **VIII** was

filtered off, washed with 15 of ether, and dried in a vacuum-desiccator over  $\text{P}_2\text{O}_5$ .

IR spectra were recorded on spectrophotometers UR-20 and IKS-29 from KBr pellets or from mulls in mineral oil. UV spectra were measured in dichloromethane on spectrometer SF-46.  $^1\text{H}$  NMR spectra were registered on spectrometer Bruker WP-200 SY (200.13 MHz) in  $\text{CF}_3\text{COOD}$  for salts **V–IX** or deuterioacetone for alcohols **XII**, **XIII**, internal reference HMDS.

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