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Reactions of arene- and pyridinecarbaldehydes with ferrocenyl-4,5-dihydropyrazoles afforded 1-arylmethyl- and 1-pyridylmethyl-3,5-aryl(ferrocenyl)pyrazoles. Their structures were established based on spectroscopic methods and, for 4-[(3,5-diferrocenylpyrazol-1-yl)methyl]pyridine, based on X-ray diffraction analysis.

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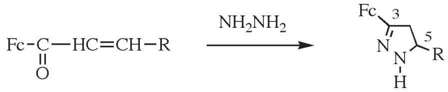
Introduction.

An increased interest in the synthesis and studies of biological activities of pyrazole derivatives possessing often a set of valuable pharmacological properties combined with a moderate action on a living organism has been observed in recent years. These properties include anti-inflammatory, anti-rheumatic, analgesic, and anti-psychotic activities. In addition, compounds of the pyrazole series have demonstrated their usefulness in pathological states and cardiovascular and gastrointestinal disorders [1–3]. In our opinion, the incorporation of an iron-containing ferrocene substituent into a pyrazole molecule will enlarge the spectrum of valuable characteristics. Ferrocene compounds are known not to possess high toxicities, many of them manifest haemopoietic, anti-inflammatory, analgesic, and antitumor activities [4–7].

Syntheses of pyrazoles are mainly based on reactions of 1,3-diketones with hydrazines or on oxidation of 2-pyrazolines. Both these methods are virtually inapplicable to the preparation of ferrocenylpyrazoles, since 1,3-diketones with ferrocenyl substituents are usually hardly accessible, and oxidative methods can result in destruction of the metallocene substituent.

In the present work, we have studied the reactions of ferrocenyl-4,5-dihydropyrazoles with aromatic aldehydes aiming at the development of a convenient method for the synthesis of ferrocenylpyrazoles.

Scheme 1



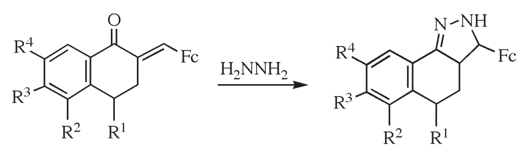
1a-f **2a-f**

R= Ph (a), *p*-BrC_6H_4- (b), *p*-$MeOC_6H_4$- (c), *p*-FC_6H_4- (d), 2-Py (e), Fc (f)
Fc= $C_5H_5FeC_5H_4$-

Results and Discussion.

3- And 5-ferrocenyl-4,5-dihydropyrazoles (**2a-f** and **4a-f**) were used as the starting compounds. These in turn were prepared by condensation of ferrocenyl enones (**1a-f**) and (**3a-f**) with hydrazine hydrate (Schemes 1 and 2).

Scheme 2



3a-f **4a-f**

$R^1= R^2 = R^3= R^4=$ H (a), $R^1=$ Me, $R^2 = R^3= R^4=$ H (b)
$R^2 =$ OMe, $R^1 = R^3= R^4=$ H (c), $R^3=$ OMe, $R^1 = R^2 = R^4=$ H (d)
$R^4=$ OMe, $R^1 = R^2= R^3=$ H (e), $R^2= R^4 =$ Me, $R^1= R^3=$ H (f)

The ferrocenyl-4,5-dihydropyrazoles **2a-f** and **4a-f** were obtained as yellow crystalline compounds stable in dry state. Dihydropyrazoles **2a-f** were relatively stable in acetone solutions that allowed their characterization by ^1H NMR spectroscopy (Table 1). Compounds **4a-f** decompose rapidly in $(CH_3)_2CO$, CH_3CN, $CHCl_3$, CH_2Cl_2, *etc*. solutions with the formation of starting enones **3a-f**. Therefore, their ^1H NMR spectra could not be obtained. All 4,5-dihydropyrazoles **2a-f** and **4a-f** were characterized by IR spectra and Mp (Table 4). Also elemental analysis data were obtained for dihydropyrazoles **2d** and **2e** (Table 3).

We have found that dihydropyrazoles react with aromatic aldehydes (benzaldehyde, *p*-bromobenzaldehyde, *p*-methoxybenzaldehyde, *p*-fluorobenzaldehyde, 2-pyridinecarbaldehyde, and 4-pyridinecarbaldehyde) at 100-120 °C (~20 min) to yield 1-arylmethyl(ferrocenyl)pyrazoles (**5a-j**) and (**6a-f, 7b-f, 8c**) (Schemes 3 and 4).

Table 1

^{1}H NMR Spectral Data of Compounds **2a-f**, **5a-j**, **6a-f**, **7b-f**, **8c** (δ, J/Hz)

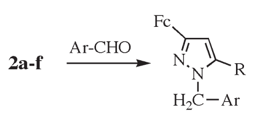
No.	C_5H_5 (s)	C_5H_4 (m)	CH_3, CH, CH=,	CH_2	Ar, NH
2a	4.13 (5H)	4.29 (2H), 4.54 (1H), 4.60 (1H)	4.84 (dd, 1H, J = 9.0, 10.5 Hz)	2.83 (dd, 1H, J = 9.0, 15.0 Hz), 3.36 (dd, 1H, J = 10.5, 15.0 Hz)	6.48 (bs, 1H)
2b	4.16 (5H)	4.32 (2H), 4.49 (1H), 4.62 (1H)	4.93 (dd, 1H, J = 8.7, 10.4 Hz)	2.85 (dd, 1H, J = 8.7, 15.3 Hz), 3.42 (dd, 1H, J = 10.4, 15.3 Hz)	6.44 (bs, 1H), 6.97 (d, 2H, J = 8.7 Hz), 7.18 (d, 2H, J = 8.7 Hz)
2c	4.14 (5H)	4.27 (2H), 4.32 (1H), 4.45 (1H)	3.84 (s, 1H), 4.86 (dd, 1H, J = 7.5, 10.5 Hz)	2.86 (dd, 1H, J = 7.5, 15.7 Hz), 3.43 (dd, 1H, J = 10.5, 15.7 Hz)	6.35 (bs, 1H), 6.88 (d, 2H, J = 9.0 Hz), 7.29 (d, 2H, J = 9.0 Hz)
2d	4.15 (5H)	4.22 (2H), 4.29 (1H), 4.37 (1H)	4.68 (dd, 1H, J = 6.3, 9.9 Hz)	2.74 (dd, 1H, J = 6.3, 14.7 Hz), 3.38 (dd, 1H, J = 9.9, 14.7 Hz)	6.28 (bs, 1H), 7.02 (d, 2H, J = 8.7 Hz), 7.32 (d, 2H, J = 8.7 Hz)
2e	4.12 (5H)	4.31 (2H), 4.64 (2H)	4.73 (dd, 1H, J = 7.2, 10.2 Hz)	2.78 (dd, 1H, J = 7.2, 15.6 Hz), 3.48 (dd, 1H, J = 10.2, 15.6 Hz)	6.31 (bs, 1H), 6.96 (m, 1H), 7.50 (m, 2H), 8.51 (m, 1H)
2f	4.13 (5H), 4.21 (5H)	4.16 (4H), 4.31 (2H), 4.56 (2H)	4.52 (dd, 1H, J = 3.9, 10.5 Hz)	2.84 (dd, 1H, J = 3.9, 15.9 Hz), 3.22 (dd, 1H, J = 10.5, 15.9 Hz)	5.61 (bs, 1H)
5a	4.10 (5H)	4.28 (2H), 4.74 (2H)	6.42 (s, 1H)	5.37 (bs, 2H)	7.04 (m, 2H), 7.20-7.42 (m, 8H)
5b	4.10 (5H)	4.27 (2H), 4.73 (2H)	6.39 (s, 1H)	5.33 (bs, 1H)	7.02-7.54 (m, 9H)
5c	4.09 (5H)	4.26 (2H), 4.73 (2H)	3.82 (s, 3H), 6.35 (s, 1H)	5.33 (bs, 2H)	6.90 (d, 2H, J = 9.0 Hz), 7.05 (m, 2H), 7.20-7.31 (m, 3 H), 7.26 (d, 2H, J = 9.0 Hz)
5d	4.10 (5H)	4.29 (2H), 4.74 (2H)	6.38 (s, 1H)	5.33 (bs, 2H)	7.03 (m, 2H), 7.06 (d, 2H, J = 8.7 Hz), 7.09 (d, 2H, J = 8.7 Hz), 7.30 (m, 3H)
5e	4.08 (5H), 4.10 (5H)	4.25 (2H), 4.27 (2H), 4.38 (2H), 4.74 (2H)	6.43 (s, 1H)	5.54 (bs, 2H)	7.05-7.36 (m, 5H)
5f	4.09 (5H)	4.28 (2H), 4.72 (2H)	6.38 (s, 1H)	5.28 (bs, 2H)	6.93-7.03 (m, 4H), 7.19 (d, 2H, J = 8.4 Hz), 7.53 (d, 2H, J = 8.4 Hz)
5g	4.09 (5H)	4.29 (2H), 4.72 (2H)	6.37 (s, 1H)	5.28 (bs, 2H)	6.93-7.31 (m, 8H)
5h	4.06 (5H)	4.26 (2H), 4.74 (2H)	6.60 (s, 1H)	5.45 (bs, 2H)	6.97 (m, 1H), 7.25 (m, 1H), 7.38-7.49 (m, 3H), 7.55 (m, 2H), 7.74 (m, 1H), 8.52 (m, 1H)
5i	4.09 (5H)	4.29 (2H), 4.76 (2H)	6.74 (s, 1H)	6.07 (bs, 2H)	6.71 (m, 1H), 7.09 (m, 1H), 7.18 (m, 1H), 7.51 (m, 1H), 7.61 (m, 1H), 7.71 (m, 1H), 8.52 (m, 1H), 8.56 (m, 1H)
5j [a]	4.10 (5H), 4.12 (5H)	4.27 (2H), 4.29 (2H), 4.31 (2H), 4.73 (2H)	6.45 (s, 1H)	5.51 (bs, 2H)	6.96 (d, 2H, J = 6.0 Hz), 8.56 (d, 2H, J = 6.0 Hz)
6a	4.12 (5H)	4.28 (2H), 4.40 (2H)	3.79 (s, 3H)	2.99 (m, 4H), 5.64 (bs, 2H)	6.86 (d, 2H, J = 9.0 Hz), 7.03 (d, 2H, J = 9.0 Hz), 7.18-7.30 (m, 4H)
6b	4.11 (5H)	4.22 (2H), 4.40 (2H)	1.34 (d, 3H, J = 6.9 Hz), 3.19 (m, 1H), 3.79 (s, 3H)	2.84 (dd, 1H, J = 5.7, 15.0 Hz), 3.10 (dd, 1H, J = 6.0, 15.0 Hz); 5.63 (bs, 2H)	6.87 (d, 2H, J = 8.7 Hz), 7.01 (d, 2H, J = 8.7 Hz), 7.28 (m, 3H), 7.91 (m, 1H)
6c	4.12 (5H)	4.28 (2H), 4.41 (2H)	3.79 (s, 3H), 3.88 (s, 3H)	2.95 (m, 2H), 3.04 (m, 2H), 5.63 (bs, 2H)	6.83 (dd, 1H, J = 0.9, 8.1 Hz), 6.87 (d, 2H, J = 8.7 Hz), 7.02 (d, 2H, J = 8.7 Hz), 7.24 (t, 1H, J = 8.1 Hz), 7.5 (dd, 1H, J = 0.9, 8.1 Hz)
6d	4.12 (5H)	4.28 (2H), 4.39 (2H)	3.79 (s, 3H), 3.84 (s, 3H)	2.98 (m, 4H), 5.62 (bs, 2H)	6.82 (s, 1H), 6.84 (d, 1H, J = 7.8 Hz), 6.87 (d, 2H, J = 9.0 Hz), 7.02 (d, 2H, J = 9.0 Hz), 7.81 (d, 1H, J = 7.8 Hz)

Table 1 (continued)

No.	C_5H_5 (s)	C_5H_4 (m)	CH_3, CH, CH=,	CH_2	Ar, NH
6e	4.10 (5H)	4.18 (2H), 4.41 (2H)	3.77 (s, 3H), 3.82 (s, 3H)	2.97 (m, 4H), 5.60 (bs, 2H)	7.00–7.73 (m, 7H)
6f	4.11 (5H)	4.28 (2H), 4.40 (2H)	2.32 (s, 3H), 2.33 (s, 3H), 3.78 (s, 3H)	2.96 (m, 4H), 5.63 (bs, 2H)	6.85 (d, 2H, J = 8.7 Hz), 6.94 (s, 1H), 7.01 (d, 2H, J = 8.7 Hz), 7.63 (s, 1H)
7b	4.09 (5H)	4.26 (2H), 4.38 (2H)	1.31 (d, 3H, J = 6.9 Hz), 3.21 (m, 1H)	2.84 (dd, 1H, J = 6.0, 15.0 Hz), 3.11 (dd, 1H, J = 6.0, 15.0 Hz), 5.70 (bs, 2H)	7.7 (m, 2H), 7.22-7.37 (m, 6H), 7.91 (m, 1H)
7c	4.10 (5H)	4.26 (2H), 4.38 (2H)	3.88 (s, 3H)	2.97 (m, 2H), 3.04 (m, 2H), 5.70 (bs, 2H)	6.82 (dd, 1H, J = 0.9, 8.1 Hz), 7.8 (m, 2H), 7.24 (d, 1H, J = 0.9 Hz), 7.32 (d, 1H, J = 8.1 Hz), 7.34-7.40 (m, 3H)
7d	4.12 (5H)	4.29 (2H), 4.38 (2H)	3.84 (s, 3H)	2.97 (m, 4H), 5.86 (bs, 2H)	6.83 (m, 3H), 7.20 (m, 1H), 7.61 (m, 1H), 7.82 (d, 1H, J = 8.7 Hz), 8.64 (d, 1H, J = 4.8 Hz)
7e	4.09 (5H)	4.21 (2H), 4.41 (2H)	3.82 (s, 3H)	2.95 (m, 4H), 5.58 (bs, 2H)	6.87 (s, 1H), 7.02-7.69 (m, 7H)
7f	4.18 (5H)	4.56 (2H), 4.97 (2H)	2.35 (s, 3H), 2.42 (s, 3H)	2.97 (m, 2H), 3.36 (m, 2H), 5.86 (bs, 2H)	7.15 (s, 1H), 7.40 (m, 1H), 7.90 (m, 1H), 8.35 (s, 1H), 8.63 (m, 1H), 8.90 (m, 1H)
8c [b]	4.12 (5H)	4.29 (2H), 4.37 (2H)	3.88 (s, 3H)	2.96 (m, 2H), 3.04 (m, 2H), 5.66 (bs, 2H)	6.83 (dd, 1H, J = 0.9, 8.4 Hz), 7.03 (d, 2H, J = 8.1 Hz), 7.05 (d, 2H, J = 8.1 Hz), 7.25 (dd, 1H, J = 7.5, 8.4 Hz), 7.54 (dd, 1H, J = 0.9, 7.5 Hz)

^{19}F NMR (282 MHz, $CDCl_3$): [a] δ = -38.38 (sept., J = 5.6 Hz, 1F) ppm; [b] δ = -38.93 (sept., J = 6.2 Hz, 1F) ppm.

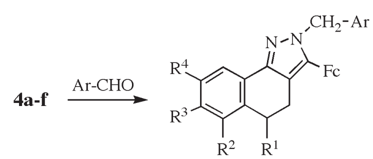
Scheme 3



5a-j

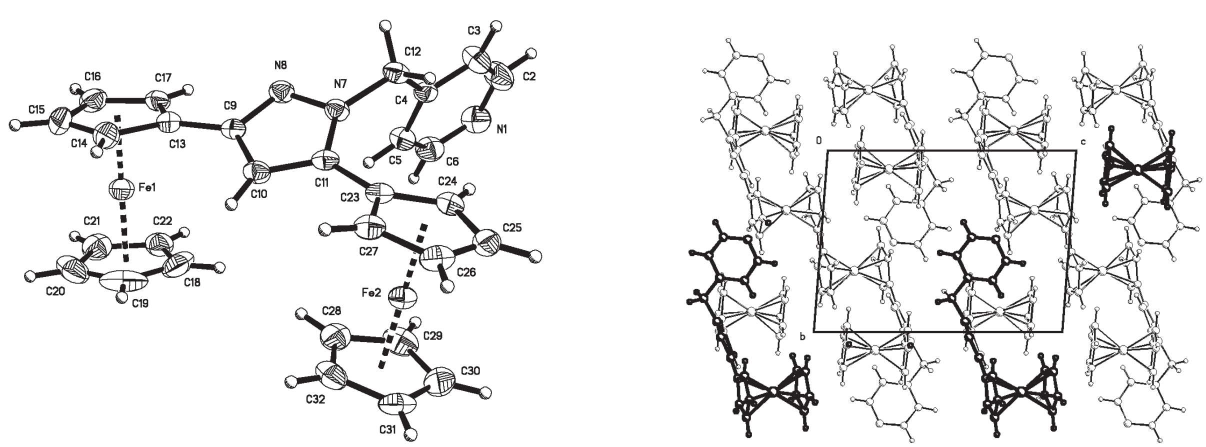
R = Ar = Ph- (a); R = *p*-BrC_6H_4-, Ar = Ph- (b); R = *p*-$MeOC_6H_4$-, Ar = Ph- (c);
R = *p*-FC_6H_4-, Ar = Ph-, (d); R = Fc-, Ar = Ph- (e);
R = *p*-BrC_6H_4-; Ar = *p*-FC_6H_4- (f); R = Ar = *p*-FC_6H_4- (g); R = Ph-, Ar = 2-Py- (h)
R = Ar = 2-Py- (i); R = Fc-, Ar = 4-Py- (j)

Scheme 4



6a-f; **7a-f**; **8c**

Ar = p-$MeOC_6H_4$- (**6a-f**),
Ar = Ph- (**7b, c, e**),
Ar = 2-Py- (**7d, f**),
Ar = p-FC_6H_4- (**8c**)



(a) (b)

Figure 1. (a) Crystal structure of **5j**. Selected bond lengths (Å): N(7)-N(8) = 1.357(3); N(8)-C(9) = 1.337(3); C(10)-C(9) = 1.396(3); N(7)-C(11) = 1.365(3); C(11)-C(10) = 1.369(4); C(12)-N(7) = 1.449(3); C(9)-C(13) = 1.454(4); C(11)-C(23) = 1.459(4). Selected bond angles (°): C(11)-N(7)-N(8) = 112.3(2); N(8)-N(7)-C(12) = 117.0(2); N(8)-C(9)-C(10) =110.7(3); N(7)-N(8)-C(9) = 104.8(2); C(11)-N(7)-C(12) = 130.3(2); N(8)-C(9)-C(13) = 119.3(2); C(11)-C(10)-C(9) = 106.6(2); N(7)-C(11)-C(10) = 105.6(2); N(7)-C(11)-C(23) = 124.2(3). (b) Crystal packing of **5j**.

Table 2

[13]C-NMR Spectral Data of Compounds **5b**, **c**, **e**, **f**, **h-j**, **6a-d**, **7b-d**, **8c** (δ, ppm)

No.	C_5H_5	C_5H_4	$C_{ipso}Fc$	CH_3	CH, CH=	Ar	CH_2	C
5b	69.52	66.63, 68.56	78.33	-	104.29	126.34 (2C), 127.42, 128.6 (2C), 130.27 (2C) 131.81 (2C)	53.08	122.84, 129.56, 137.79, 143.73, 150.53
5c	69.45	66.58, 68.39	78.63	55.28	103.82	114.0 (2C), 126.36 (2C), 127.2, 128.47 (2C), 130.0 (2C)	52.82	123.0, 138.15, 144.8, 150.2, 159.74
5e	69.46, 69.60	66.51, 68.18, 68.42, 68.88	74.68, 78.49	-	103.32	125.95 (2C), 127.2, 128.62 (2C)	53.10	138.24, 142.18, 149.97
5f	69.48	66.61, 68.58	78.15	-	104.45	115.33, 115.62, 128.08, 128.2, 130.25 (2C), 131.86 (2C)	52.44	122.93, 129.47, 143.68, 150.7, 160.45, 163.72
5h	70.14	67.3, 69.02	79.86	-	104.69	121.89, 123.17, 129.34, 129.5 (2C), 129.56 (2C), 137.57, 159.0	55.45	131.59, 145.95, 151.18, 158.96
5i	69.51	66.62, 68.55	78.17	-	104.36	120.54, 121.76, 122.4, 122.47, 136.6, 136.62, 148.9, 149.3	56.37	142.65, 149.43, 150.5, 158.77
5j	69.03, 69.45	66.5, 68.15, 68.55, 69.03	74.25, 78.06	-	103.70	121.08 (2C), 150.04 (2C)	52.03	142.51, 147.32, 150.67
6a	69.37	67.9, 68.68	74.99	55.28	-	114.11 (2C), 122.32, 126.77, 127.19 (2C), 127.28, 128.17	20.61, 29.89, 52.98	115.12, 130.09, 130.59, 136.35, 136.67, 147.64, 158.77
6b	69.36	67.71, 68.04, 68.63, 68.66	74.99	21.63, 55.27	34.95	114.11 (2C), 122.48, 126.65, 126.96, 127.11 (2C), 127.56	28.30, 53.02	113.67, 129.0, 130.59, 137.34, 141.26, 147.15,158.74
6c	69.38	67.90, 68.66	75.02	55.28, 55.54	-	109.46, 114.10 (2C), 115.06, 127.04, 127.18 (2C)	19.96, 21.68, 52.96	124.55, 130.6 (2C), 131.07, 136.6, 147.6, 156.77, 158.74
6d	69.42	67.91, 68.71	75.19	55.25, 55.28	-	111.93, 113.98, 114.10 (2C), 123.56, 127.18 (2C)	20.64, 30.27, 52.85	114.28, 123.08, 130.68, 136.57, 138.14, 147.6, 158.74, 159.03
7b	69.34	67.65, 68.01, 68.65, 68.68	74.86	21.65	34.05	122.48, 125.85 (2C), 126.65, 126.97, 127.18, 127.6, 128.72 (2C)	28.29, 53.52	113.67, 128.95, 137.5, 138.58, 141.26, 147.22
7c	69.38	67.86, 68.68	74.89	55.53	-	109.5, 115.05, 125.92 (2C), 127.05, 127.17, 128.7 (2C),	19.95, 21.67, 53.46	124.56, 131.02, 136.74, 138.58 (2C), 147.67, 156.78
7d	69.38	67.87, 68.84	74.61	55.45	-	112.02, 114.04, 120.96, 122.24, 123.6, 137.12, 149.32	20.64, 30.21, 55.31	114.62, 122.92, 136.99, 138.29, 148.03, 158.73, 159.18
8c	69.41	67.82, 68.76	74.83	55.53	-	109.55, 115.00, 115.46, 115.74, 127.09, 127.58, 127.69	52.78	115.21, 124.59, 139.89, 134.19, 134.24, 136.70, 147.84, 156.8

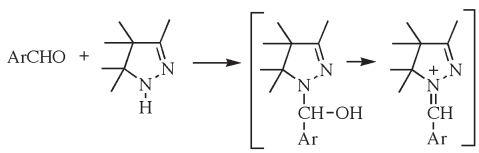
The [1]H NMR spectra of compounds **5a-j**, **6a-f**, **7b-f** and **8c** contain each a broadened two-proton singlet of the -NCH_2-group at δ 5.30 - 5.60 ppm. The [1]H NMR spectra of monocyclic pyrazoles **5a-j** contain also a singlet of an olefinic proton at δ 6.00 - 6.05 (Table 1). Data from [13]C NMR spectra of compounds **5a-j** suggest the presence of –CH_2– and –CH= groups and of carbon atoms bearing no hydrogen (Table 2).

The structure of one of the reaction products, namely, 3,5-diferrocenyl-1-(4-pyridyl)methylpyrazole (**5j**), was confirmed by X-ray diffraction analysis of a single crystal prepared by crystallization from chloroform. The general view of the molecule **5j** and its principal characteristics are given in Figure 1a, the crystal packing is shown in Figure 1b; these require no special comments.

Thus, the reaction of pyrazolines **2a-f** and **4a-f** with aromatic aldehydes occurs as an intramolecular oxidation of the pyrazoline ring into pyrazole with concomitant reduction of an exocyclic functionality into the methylene group.

The following putative reaction schemes seem to rationalize the formation of the pyrazoles **5a-j**, **6a-f**, **7b-f** and **8c**. The addition of a pyrazoline with an unsubstituted –NH group to the carbaldehyde results in a cation **9** (Scheme 5).

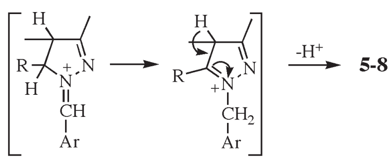
Scheme 5



9

This may be followed by either: *i*) an intramolecular 1,3-hydride shift from C(5) of the mesomeric cation **9** and formation of an isomeric cation **10**. The latter is stabilized by elimination of a proton to afford an aromatic system of pyrazoles **5**, **6**, **7** or **8** (Scheme 6).

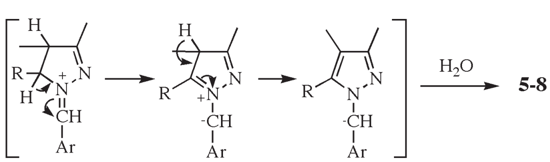
Scheme 6



9 **10**

ii) or the intermolecular shift of electron pairs with elimination of a proton and formation of a bipolar or a carbanionic intermediate **11**. The latter is stabilized by abstracting a proton from the environment (Scheme 7).

Scheme 7

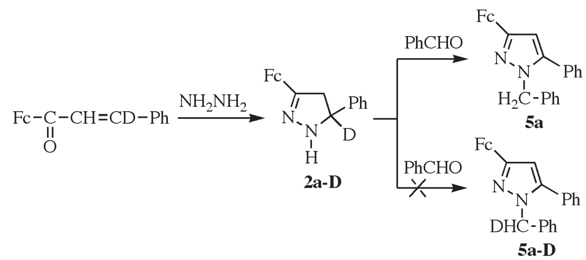


9 **11**

In our opinion, the latter direction is preferable. The results of an experiment with 5-deuteriopyrazoline **2a-D** (Scheme 8) seem to support this conclusion.

Data from the ^{1}H NMR spectrum revealed complete absence of the deuterium atoms in the reaction product. Hence, the reaction is not accompanied by the 1,3-hydride shift, the proton being rather abstracted from the environment.

Scheme 8



Thus, the reaction described may be regarded as a convenient method for the synthesis of *N*-substituted pyrazoles with ferrocenyl substituents in the ring together with other groups.

Biological assays of compounds **5c-j**, **6a-f**, **7b-d**, **f** and **8c** revealed sufficiently high antiviral activities for compounds **5b**, **d**, **f**, **i**, **6a**, **6c** and anti-inflammatory activities for compounds **5a**, **5f**, **6c**, **7f**, **8c**.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $(CD_3)_2CO$ (compounds **2a-f**) and $CDCl_3$ (compounds **5a-j**, **6a-f**, **7b-f** and **8c**) with Me_4Si as the internal standard. The NMR spectroscopic data are listed in Tables 1 and 2. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elemental Analysis system GmbH was used for elemental analyses. The mass spectrometric data, data from elemental analyses, yields, and melting points of the compounds obtained are given in Table 3. Column chromatography was carried out on alumina (Brockmann activity III).

The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; acetylferrocene, 98%; benzaldehyde, 99%; 4-bromobenzaldehyde, 99%; 4-fluorobenzaldehyde, 98%; p-anisaldehyde, 98%; α-tetralone, 98%; 4-methyl-1-tetralone, 97%; 5-methoxy-1-tetralone, 97%; 6-methoxy-1-tetralone, 99%; 7-methoxy-1-tetralone, 99%; 5,7-dimethyl-1-tetralone, 97%; 4-pyridinecarboxaldehyde, 97%; 2-pyridinecarboxaldehyde, 99%.

3-Aryl-1-ferrocenylprop-2-enones **1a-f** and 2-Ferrocenylmethylidenetetralones **3a-f**.

These were prepared by condensation of acetylferrocene with arenecarbaldehydes in aqueous-ethanolic alkali [8-10]. 2-Ferrocenylmethylidenetetralones **3a-f** were prepared by condensation of ferrocenecarbaldehyde with tetralones in aqueous-ethanolic alkali [11]. The physical and ^{1}H NMR spectroscopic characteristics of compounds **1a-f** and **3a-f** were in accord with the literature data [8-11].

Ferrocenyl-4,5-dihydropyrazoles **2a-f** and **4a-f**.

These were obtained according to the known procedure [12] by reactions of the enones **1a-f** and **3a-f**, respectively, with hydrazine hydrate in ethanol. The reaction products that precipitated (**2a-f** and **4a-f**) were collected by filtration, washed with ethanol and dried *in vacuo*. Their yields ranged from 60 to 70% and the mp's corresponded to the literature data [8–12].

Table 3

Yields, Mp, Elemental Analysis and MS Data for the Synthesized Compounds

No.	Yield, %	Mp, °C	Found, % Calcd., %					Molecular formula	MS, *m/z* (M^+)
			C	H	Fe	Br, F	N		
2d	71	102-103	65.39	4.87	16.13	5.37	8.11	$C_{19}H_{17}FFeN_2$	348
			65.54	4.92	16.04	5.46	8.04		
2e	69	143-144	65.37	5.08	16.93	-	12.57	$C_{18}C_{17}FeN_3$	331
			65.28	5.18	16.86		12.68		
5a	65	113-114	74.42	5.44	13.51	-	6.47	$C_{26}H_{22}FeN_2$	418
			74.65	5.30	13.35		6.70		
5b	70	168-169	62.65	4.43	11.12	15.84	5.42	$C_{26}H_{21}BrFeN_2$	497
			62.81	4.26	11.23	16.07	5.63		
5c	64	134-135	72.51	5.21	12.63	-	6.09	$C_{27}H_{24}FeN_2O$	448
			72.33	5.40	12.46		6.25		
5d	63	127-128	71.69	5.03	12.58	4.53	6.29	$C_{26}H_{21}FFeN_2$	436
			71.57	4.85	12.80	4.36	6.42		
5e	67	175-176	68.61	5.11	21.07	-	5.14	$C_{30}H_{26}Fe_2N_2$	526
			68.47	4.98	21.23		5.32		
5f	64	154-156	60.45	4.06	10.73	-	5.25	$C_{26}H_{20}BrFFeN_2$	515
			60.61	3.91	10.84		5.44		
5g	65	149-151	68.95	4.27	12.45	8.19	6.33	$C_{26}H_{20}F_2FeN_2$	454
			68.74	4.44	12.30	8.36	6.16		
5h	66	179-180	71.47	4.89	13.47	-	9.86	$C_{25}H_{21}FeN_3$	419
			71.61	5.05	13.32		10.02		
5i	67	146-147	68.68	4.64	13.42	-	13.14	$C_{24}H_{20}FeN_4$	420
			68.59	4.79	13.29		13.33		
5j	63	172-173	65.97	4.92	21.03	-	8.09	$C_{29}H_{25}Fe_2N_3$	527
			66.06	4.78	21.19		7.97		
6a	66	150-151	73.24	5.72	11.59	-	5.67	$C_{29}H_{26}FeN_2O$	474
			73.43	5.53	11.77		5.90		
6b	64	168-169	73.49	5.94	11.70	-	5.97	$C_{30}H_{28}FeN_2O$	488
			73.77	5.78	11.44		5.73		
6c	67	198-199	71.58	5.42	10.84	-	5.29	$C_{30}H_{28}FeN_2O_2$	504
			71.43	5.60	11.07		5.55		
6d	63	165-167	71.55	5.43	10.88	-	5.29	$C_{30}H_{28}FeN_2O_2$	504
			71.43	5.60	11.07		5.55		
6e	66	172-173	71.61	5.51	11.19	-	5.64	$C_{30}H_{28}FeN_2O_2$	504
			71.43	5.60	11.07		5.55		
6f	65	155-156	74.29	5.87	11.30	-	5.35	$C_{31}H_{30}FeN_2O$	502
			74.11	6.02	11.12		5.57		
7b	65	151-152	75.87	5.93	12.34	-	6.23	$C_{29}H_{26}FeN_2$	458
			76.00	5.72	12.18		6.10		
7c	64	148-149	73.61	5.34	12.01	-	5.72	$C_{29}H_{26}FeN_2O$	474
			73.43	5.53	11.77		5.90		
7d	68	229-230	70.97	5.11	11.99	-	8.66	$C_{28}H_{25}FeN_3O$	475
			70.75	5.30	11.75		8.83		
7e	65	152-153	73.21	5.74	11.61	-	5.69	$C_{29}H_{26}FeN_2O$	474
			73.43	5.53	11.77		5.90		
7f	67	187-189	73.74	5.59	11.59	-	8.69	$C_{29}H_{27}FeN_3$	473
			73.58	5.75	11.80		8.87		
8c	66	158-159	70.56	5.29	11.49	3.69	5.88	$C_{29}H_{25}FFeN_2O$	492
			70.74	5.12	11.34	3.86	5.69		

Reaction of Benzaldehyde with 3-Ferrocenyl-5-phenyl-4,5-dihydropyrazole **2a**.

The dihydropyrazole **2a** (0.66 g, 2 mmol) was added with stirring to benzaldehyde (0.53 g, 5 mmol) at 110 °C. The mixture was stirred at 110 - 120 °C for 20 min, and the excess of benzaldehyde was removed by steam-distillation. The residue was chromatographed on alumina (hexane – dichloromethane, 10:1) to yield 0.55 g (65%) of 1-benzyl-3-ferrocenyl-5-phenylpyrazole (**5a**), yellow powder, mp 113 -114 °C.

5-Aryl-1-arylmethyl-3-ferrocenylpyrazoles (**5b-j**) were obtained similarly.

Reaction of Benzaldehyde with 3-Ferrocenyl-5-methyl-3,3a,4,5-tetrahydro-2*H*-benzo[*g*]indazole (**4a**).

The condensation of compound **4a** (0.74 g, 2 mmol) with benzaldehyde (0.53 g, 5 mmol) was carried out at 100 - 120 °C for 30 min. Subsequent work-up of the reaction mixture as described above and column chromatography (Al_2O_3, hexane - dichloromethane, 7:1) afforded 2-benzyl-3-ferrocenyl-5-methyl-4,5-dihydro-2*H*-

Table 4

IR Spectral Data and Mp of Compounds **2a-f** and **4a-f**

No.	ν, cm^{-1}	Mp, °C
2a	698, 737, 777, 832, 866, 1026, 1099, 1313, 1414, 1449, 1492, 1595, 1658, 2927, 3027, 3089, 3280	167-168 [13]
2b	691, 832, 878, 961, 1012, 1079, 1230, 1290, 1380, 1462, 1508, 1601, 1661, 1912, 2953, 3087, 3230	66-67 [13]
2c	695, 780, 825, 939, 1024, 1050, 1235, 1273, 1319, 1403, 1450, 1490, 1601, 1650, 2934, 3089, 3270	89-90 [13]
2d	685, 837, 878, 879, 1012, 1077, 1230, 1291, 1381, 1464, 1509, 1603, 1660, 1911, 2954, 3089, 3228	102-103
2e	672, 812, 862, 942, 997, 1032, 1101, 1284, 1318, 1368, 1412, 1489, 1553, 1600, 1656, 2861, 2981, 3080, 3298	143-144
2f	623, 664, 739, 819, 997, 1024, 1102, 1232, 1312, 1399, 1487, 1614, 2944, 3090, 3272	191-192 [14]
4a	667, 746, 814, 937, 1001, 1103, 1194, 1302, 1353, 1390, 1460, 1590, 1625, 2834, 2865, 2931, 3079, 3289	168-170 [11]
4b	666, 743, 820, 938, 1002, 1104, 1202, 1300, 1356, 1396, 1456, 1595, 1630, 2831, 2865, 2940, 3082, 3274	172-174 [11]
4c	633, 793, 825, 939, 1024, 1057, 1154, 1235, 1319, 1354, 1403, 1450, 1604, 1652, 2836, 2939, 3089, 3270	184-186 [11]
4d	641, 801, 813, 928, 1020, 1051, 1148, 1240, 1320, 1360, 1411, 1460, 1600, 1640, 2824, 2928, 3072, 3281	191-193 [11]
4e	637, 789, 815, 927, 1024, 1050, 1151, 1235, 1312, 1359, 1402, 1454, 1601, 1637, 2831, 2935, 3072, 3280	283-284 [11]
4f	662, 739, 818, 941, 1001, 1105, 1201, 1310, 1352, 1402, 1454, 1593, 1634, 2835, 2944, 3082, 3281	202-203 [11]

benzo[*g*]indazole **6a** as a yellow powder, yield 0.53 g (64%), mp 151-152 °C.

2-Arylmethyl-3-ferrocenyl-4,5-dihydro-2*H*-benzo[*g*]indazoles **6b-f**, **7b-f** and **8c** were obtained similarly.

Determination of the Crystal Structure.

The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD diffractometer. The structure of compound **5j** was solved by the direct method (SHELXS) and refined using full-matrix least-squares on F^2.

Crystal data for $C_{29}H_{25}Fe_2N_3$ (5j): M = 527.22 g·mol^{-1}, triclinic P$\bar{1}$, a = 9.172(1), b = 10.683(1), c = 13.292(1) Å, α = 91.997(1), β = 94.562(1), γ = 115.111(1)°, V = 1172.2(2) $Å^3$, T = 293(2) K, Z = 2, ρ = 1.494 Mg/m^3, λ (Mo - Kα) = 0.71073 Å, F(000) = 544, absorption coefficient 1.261 mm^{-1}, index ranges -10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15, scan range 2.11 ≤ θ ≤ 25.03°, 4128 independent reflections, R_{int} = 0.0438, 13938 total reflections, 307 refinable parameters, final R indices [I > 2σ(I)] R_1 = 0.0401, wR_2 = 0.0590, R indices (all data) R_1 = 0.0600, wR_2 = 0.0619, largest difference peak and hole 0.597/-0.282 e·$Å^{-3}$.

Supplementary Material.

CCDC-233322 (for **5j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, UK: Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk].

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