

Study of reactions of pentafluorophenylhydrazine with activated enol ethers. Synthesis of *N*-pentafluorophenylpyrazoles

Dušan Bortňák,^a Michal Šoral,^b Martin Breza,^c Silvia Vlčková,^d Daniel Végh,^a
and Viktor Milata^{*a}

^a Department of Organic Chemistry, ^b Central Laboratories, and ^c Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského street 9, SK-812 37 Bratislava, Slovakia

^d Chemical Institute, Slovak Academy of Sciences, Dúbravská road 9, SK-845 38 Bratislava, Slovakia

E-mail: viktor.milata@stuba.sk

Dedicated to Prof. Jacek Mlochowski in appreciation of his 80th anniversary

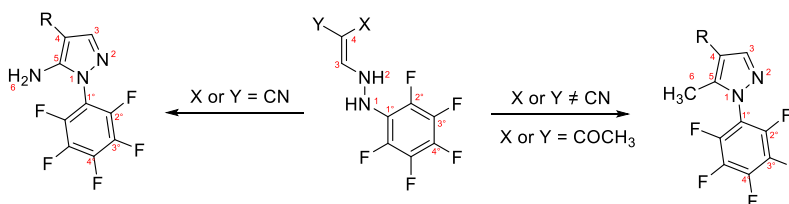
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Abstract

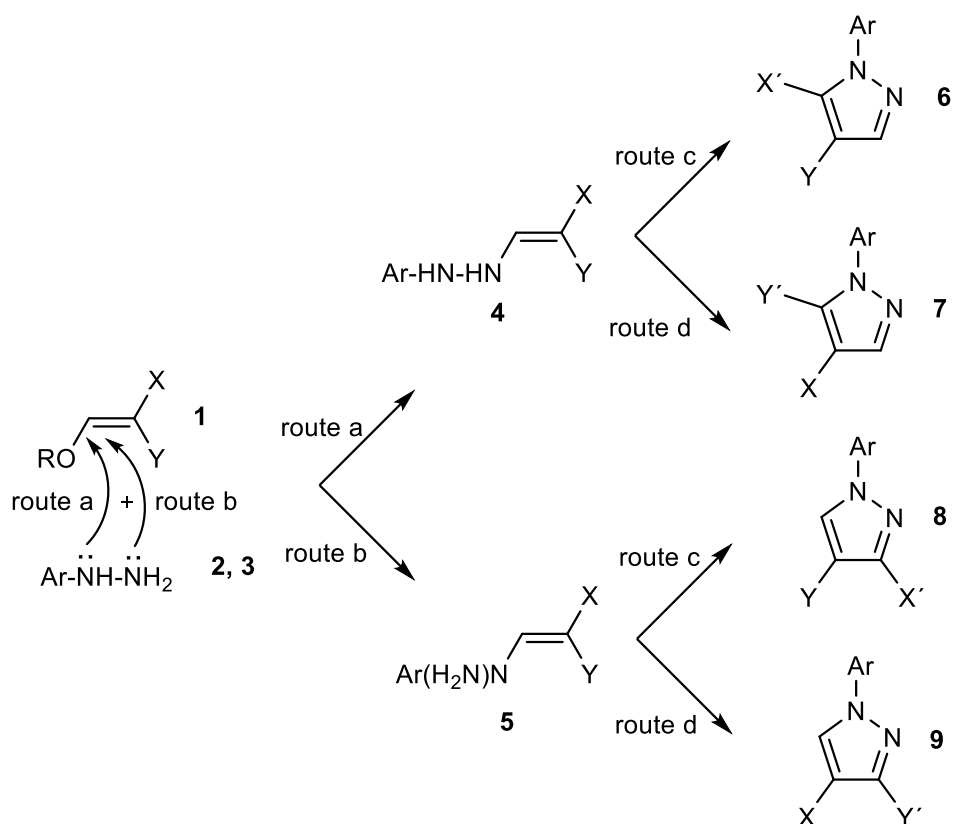
Activated enol ethers derived from methyl or ethyl acetoacetate/cyanoacetates or nitriles and pentane-2,4-dione react with pentafluorophenylhydrazine through the primary amino-group to afford pyrazoles bearing a preferred 5-amino- over 5-methyl- or 5-hydroxy-substituent in the resulting 4-substituted pyrazoles.



Keywords: Pentafluorophenylhydrazine, 4,5-disubstituted-1-pentafluorophenylpyrazole, ¹H, ¹³C, ¹⁹F NMR

Introduction

Enol ethers are a wide group of very reactive organic systems¹ which, with the introduction of one or two electron withdrawing groups¹ to the alkoxy group, produce push-pull systems. The alkoxy group can then be replaced by various mono-, bi- or trifunctional nucleophiles,² thus producing acyclic products, cyclic or polycyclic (hetero)cycles such as quinolines/quinolones, pyrazoles/pyrazolones, isoxazoles/isoxazolones, pyrimidines/pyrimidones, benzenes, etc.³ In the case of two non-equivalent electron withdrawing groups ('unsymmetrical enol ethers') cyclisation can give rise to two isomeric products and when a monosubstituted hydrazine is used the number of final products is theoretically doubled and indeed, in some cases all four possible products have been isolated (Scheme 1).⁴⁻⁶



2: Ar = C₆H₅, 3 - 9: Ar = C₆F₅

X, Y, X', Y' for 1, 4 - 9 (OH or NH₂ can exist also in their tautomeric forms^{7,8})

1, 4 - 9	X	X'	Y	Y'	R for 1
a	CN	NH ₂	CN	NH ₂	Et
b	COCH ₃	CH ₃	COCH ₃	CH ₃	Et
c	COOCH ₃	OH	COOCH ₃	OH	Me
d	COOC ₂ H ₅	OH	COOC ₂ H ₅	OH	Et
e	CN	NH ₂	COCH ₃	CH ₃	Et
f	CN	NH ₂	COOCH ₃	OH	Me
g	CN	NH ₂	COOC ₂ H ₅	OH	Et
h	COCH ₃	CH ₃	COOCH ₃	OH	Me
i	COCH ₃	CH ₃	COOC ₂ H ₅	OH	Et

Scheme 1. Reaction of enol ethers with arylhydrazines.

Recently we studied the reaction of pentafluorophenylhydrazine with 2-ethoxymethylene-3-oxobutanenitrile and isolated an intermediate enehydrazine (2-pentafluorophenylhydrazinylmethylene-3-oxobutanenitrile) due to the lower nucleophilicity of the second nitrogen in comparison with phenylhydrazine⁵ (route a). In continuation we have now studied the reaction of the monosubstituted hydrazine (pentafluorophenylhydrazine **3**) with enoethers **1a-d,f-i** and the chemoselectivity of the cyclisation reaction in the case of 'unsymmetrical' enol ethers **1f-i**. Aminonitrile **6a** has been previously reported,⁹ but no data were given.

Results and Discussion

Quantum-chemical calculations

Standard geometry optimizations of the compounds under study at DFT level of theory using hybrid B3LYP functional¹⁰ and cc-pVDZ basis sets^{11,12} were performed using the Gaussian03 program package.¹³ Their stability was confirmed by vibrational analysis (no imaginary vibrations). Frontier electron densities (FED) of individual atoms in the highest occupied molecular orbital (HOMO) and in the lowest unoccupied molecular orbital (LUMO) were evaluated as the corresponding net electron populations and used as reactivity indices of these atoms in nucleophilic and electrophilic reactions, respectively.

Table 1. Selected electronic structure data of C₆H₅-NHNH₂ (**2**) and C₆F₅-NHNH₂ (**3**)

Atom	Atomic charge	FED	
		HOMO	LUMO
C₆H₅-NH-NH₂ (2)			
N(central)	-0.169	0.265	0.006
N(terminal)	-0.100	0.012	0.009
Orbital energy [eV]	-	-0.203	-0.004
C₆F₅-NH-NH₂ (3)			
N(central)	-0.136	0.265	0.022
N(terminal)	-0.109	0.026	0.025
Orbital energy [eV]	-	-0.203	-0.024

Quantum-chemical calculations indicate the highest nucleophilic character of the N(central) atom based on FED HOMO reactivity indices (see Table 1) which is equal for both compounds. The nucleophilic character of the N(terminal) atom is significantly lower and *ca.* twice higher in the case of the fluorinated aromatic ring. Higher nucleophilic character of N(central) atoms in comparison with the N(terminal) ones is also supported by their higher negative charges. The electrophilic character of both N atoms in phenylhydrazine based on FED LUMO reactivity indices is very small, unlike its fluorinated analogue where both N atoms exhibit nearly equal reactivity indices, which are *ca.* three times higher than for phenylhydrazine. The low HOMO-LUMO energy separation of both compounds (*ca.* 0.2 eV) indicates their high reactivity.

Reactivity of pentafluorophenylhydrazine **3**

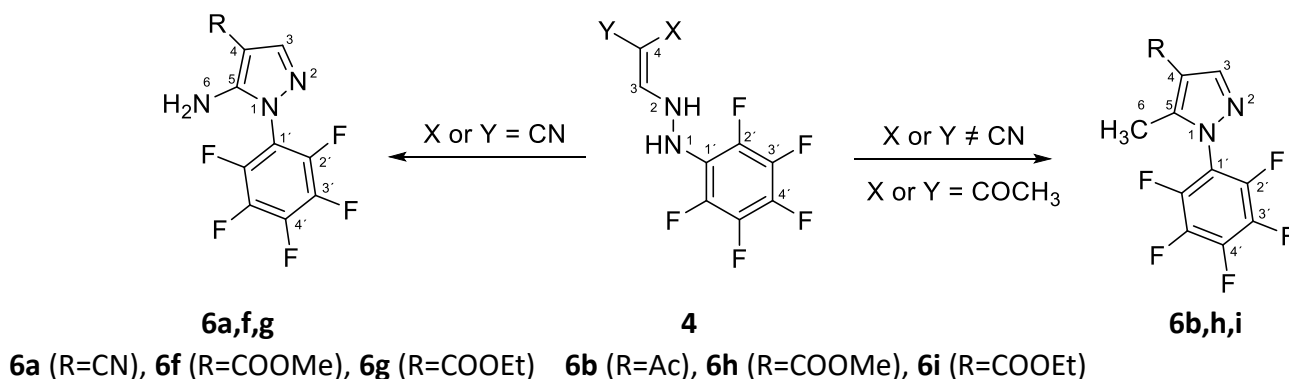
According to quantum-chemical calculations, the arylhydrazines **2**, **3** are highly reactive and there is no large difference between their reactivities. However, cyclisation in the case of phenylhydrazine **2** occurs to the cyano group (thus producing a 5-amino-4-acetylpyrazole) while with pentafluorophenylhydrazine **3** the

cyclisation is to the acetyl group (producing the 5-methyl-4-cyanopyrazole derivative **7e**)⁵. Another interesting fact is that, in the case of the reaction of **1e** with **3** we were able to isolate the intermediate enehydrazine **4e** and on the basis of ¹H NMR analysis (two different doublets) to establish that the first nucleophilic attack was through the terminal (primary) amino group of the pentafluorophenylhydrazine **3** (route a) and therefore the succeeding cyclisation should produce **6** or **7** and not **8** or **9**. These facts motivated us to study the reactivity of pentafluorophenylhydrazine with various enol ethers **1** displaying moderate reactivity.¹⁴

Under the chosen reaction conditions (reflux in methanol or ethanol for the appropriate time) we were never able to detect any other product than that of nucleophilic substitution through the terminal (primary) amino group (no route b and subsequent routes c,d in Scheme 1). In some cases we were able to isolate intermediate **4** (**4d** and **4c**) confirming nucleophilic substitution at the terminal amino group (**4d** was obtained in almost quantitative yield, **4c** in only 64% yield). The lower yield of **4c** is perhaps due to the lower boiling temperature of methanol (Table 2).

The acyclic structural pattern of **4c,d** was easily recognized from the ¹H NMR spectra – the methine proton signal at position 3 was split by a ³J_{HH} coupling with a neighboring proton from one of the present N-H pairs. The peak shapes excluded the possibility that the reactions proceeded via route b yielding analogues **5c,d** (see Scheme 1). The narrow peaks of the N-H proton signals (related to their sufficiently slow exchange rate and ordinary T2* relaxation times) enabled the observation of heteronuclear correlations with nearby ¹³C nuclei (²J_{CH} and ³J_{CH}), thus explicitly proving the linkage between the perfluorinated and non-fluorinated part of the molecules. The methyl ester and ethyl ester moieties in **4c** and **4d**, respectively, were also proved by the analysis of HMBC correlations (Table 5).

Cyclisation of (un)isolated intermediate in the reaction mixture can take place through the same functional group in the case of symmetrically-substituted derivatives **4a-d** (X=Y) and thus only a single product can arise. In a successful cyclisation giving products **6c**, **6d** we tried to enhance the nucleophilicity of the secondary amino group by addition of sodium ethoxide in ethanol under reflux, but we isolated only traces of the desired products. If we used potassium carbonate in boiling water the product was isolated in 22-26% yields. Heating in toluene, xylene or DMSO led to decomposition of the starting compound and no product was detected. In the case of differently substituted derivatives **4e-i** enehydrazine intermediates can exist as geometrical isomers which could not be isolated due to the low energy barrier of their isomerization.⁶ Upon thermal cyclisation, these enehydrazines gave a single product: in the case of cyano-substituted enehydrazines (**4a,f,g**) only the corresponding 5-aminopyrazoles were formed. If no cyano group is present, cyclisation to the acetyl group is observed and 5-methylpyrazoles were obtained (Scheme 2).



Scheme 2. Cyclisation of arylaminoenhydrazines **4**.

Non-cyclised intermediates (**4c,d**) have slightly lower melting points in comparison with their cyclized products (**6c,d**). In the compounds **4c,d** the melting point of the corresponding methyl ester has higher melting point in comparison with ethyl ester. This tendency is reversed for cyclic pyrazoles **6h/i** and **6f/g**.

HRMS spectra were used instead of elemental analysis (Table 2). Typically, electrospray ionization registered the protonated cation of the molecule. Differences between measured m/z and calculated values are stated in ppm units.

Table 2. Physico-chemical properties of the prepared compounds **4c**, **4d** and **6a-h**

Comp. No.	Solvent ^a	M. p. (°C)	Yield (%)	Reaction scale (mmol)	HRMS [M+H] ⁺ (Da)	Calc. [M+H] ⁺ (Da) ^b	Delta (ppm)
4c	Methanol (Hexane)	110-114	64	1.010	341.05579	341.05552	0.78
4d	Ethanol	62-63	96	1.514	369.08673	369.08682	-0.26
6a	Ethanol (Toluene)	93-96	72	2.524	275.03525	275.03506	0.67
6b	Ethanol	53-55	90	2.524	291.05501	291.05513	-0.41
6c	Water	130-133	22	2.5	309.02912	309.02931	-0.61
6d	Water	68-70	26	2.5	323.04472	323.04496	-0.74
6f	Methanol (Toluene)	168-171	65	1.010	308.04543	308.04529	0.44
6g	Ethanol (2:3 EtOAc: Hexanes)	170-174	56	1.010	322.06078	322.06094	-0.51
6h	Methanol	60-62	98	3.4	307.04998	307.05005	-0.21
6i	Ethanol (Toluene)	< 250	69	2.524	321.06570	321.06570	0.015

^a Reaction solvent (recrystallization solvent if appropriate or eluent if chromatographed).

^b Calc. [M+H]⁺ were obtained using XCalibur software with consideration of m/z value of electron (0.000 548 579 909 43(23)).

In the IR spectra (Table 3) only selected characteristic vibrations are presented: for **6a** of the cyano group (2228 cm⁻¹), for **6a,f,g** of the amino groups the presence of which confirms cyclisation in these cases through cyano groups and having intramolecular hydrogen bond between hydrogen of the amino group and oxygen atom of the carbonyl of the alkoxy carbonyl group for **6f,g** evident from the frequency of the carbonyl group (comparison **6f,g** with **6h,i**) (Figure 1). Ester groups without this hydrogen bond (derivatives **6h,i**) had peaks about 5 cm⁻¹ higher frequency due to weak hydrogen bond of the previous compounds **6f,g**. Methyl esters had these frequencies higher than ethyl esters. Absorption bands corresponding to C-F were found between 1000 – 1400 cm⁻¹. Amino tautomers of **6a,e,f,g** were indicated with no evidence for the tautomeric imino form.⁶ UV spectra showed absorption bands between 220 – 240 nm belonging to pentafluorophenyl and pyrazole units which are not coplanar but twisted out of plane.

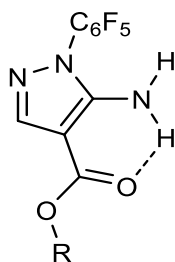


Figure 1. Intramolecular hydrogen bond in compounds **6f,g**.

Table 3. IR and UV spectra of the compounds **4c**, **4d** and **6a-d,f-i**

Compd.	IR (cm ⁻¹)	UV, nm	
		(log ε, m ² mol ⁻¹)	
4c	3318, 3236, 1733, 1614, 1519, 1441, 1382, 1263, 1189, 1102, 1067, 1027, 970	220	280
		(3.26)	(3.40)
4d	3244, 1695, 1648, 1519, 1247, 1068, 1016, 969	219	280
		(3.24)	(3.37)
6a	3352, 3146, 2228, 1077, 996	226	-
		(3.35)	
6b	1691, 1264, 1175, 1132	244	-
		(3.30)	
6c	1707, 1620, 1514, 1371, 1247, 1083, 990	222	266
		(3.13)	(2.41)
6d	1697, 1608, 1512, 1377, 1344, 1303, 1184	216	-
		(3.29)	
6f	3289, 3218, 1694, 1616, 1480, 1445, 1398, 1345, 1321, 1296, 1248, 1201, 1161, 1092, 1015	210	281
		(2.65)	(2.86)
6g	3363, 1684, 1629, 1483, 1418, 1383, 1306, 1220, 1106, 1068	226	252
		(3.22)	(3.07)
6h	1698, 1512, 1377, 1344, 1303, 1184, 1082, 988	221	268
		(3.27)	(2.53)
6i	1691, 1653, 1574, 1525, 1258, 1174, 1132, 1064, 1033, 992	210	313
		(2.99)	(2.67)

Table 4. NMR spectra of pyrazoles **6** (δ in ppm, multiplicity, coupling constants in Hz, numbering according Scheme 2)

Comp.	6a	6b	6c	6d	6f	6g	6h	6i
Solvent	DMSO- <i>d</i> ₆	CDCl ₃	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆	CDCl ₃	CDCl ₃
1'- ¹³ C	112.10 m	113.58 td, 14.6, 4.6	112.13 m	112.28 m	112.55 m	112.57 m	113.8 m	113.7 m
2'- ¹⁹ F	-145.51 m	-145.75 m	-146.32 m	-146.26 m	-145.62 m	-145.63 m	-146.04 m	-144.73 m
2'- ¹³ C ¹ J _{CF}	144.25 m, 252.8	143.63 dddd, 255.8, 11.8, 7.7, 3.7	143.23 m, 252.1	143.26 m, 254.3	144.27 m	144.27 m, 250.5	143.79 m, 256.1	143.57 m, 255.7
3'- ¹⁹ F	-161.84 m	-161.20 m	-161.67 m	-161.79 m	-162.09 m	-162.13 m	-161.08 m	-160.10 m
3'- ¹³ C ¹ J _{CF}	137.70 m, 249.7	137.78 m, 251.1	137.54 m, 249.3	137.51 m, 252.5	137.67 m	137.67 m, 249.5	137.78 m, 255.5	137.62 m, 253.2
4'- ¹⁹ F	-152.53 tt, 22.7, 2.4	-151.34 tt, 21.2, 2.4	-151.90 t, 22.7	-152.13 m	-153.10 t, 22.8	-153.13 t, 22.7	-151.82 t 21.4	-150.18 tt, 21.4, 2.3
4'- ¹³ C ¹ J _{CF}	142.01 254.3	142.29 dtt, 258.2, 13.4, 4.5	141.67 m, 239.2	141.56 m, 253.6	141.82 m	141.80 m, 253.7	142.33 m	142.08 m, 258.1
3- ¹ H	7.92 s	7.94 s	7.96 s	7.92 s	7.82 s	7.80 s	7.86 s	8.13 s
3- ¹³ C	144.04 s	143.39 s	143.01 s	142.93 s	142.58 s	142.50 s	143.32 s	143.17 s
4- ¹³ C	72.06 s	120.82 s	94.90 s	94.87 s	93.15 s	93.36 s	112.87 s	113.02 s
5- ¹³ C	154.14 s	145.78 s	156.70 s	157.13 s	152.42 s	152.47 s	146.46 s	146.13 s
6- ¹ H	7.19 s	2.28 s	-	-	6.77 s	6.74 s	2,28 s	2,47 s
6- ¹³ C	- 114.21 s	10.52 s 192.56 s	162.33 s 50.83 s	162.14 s 59.32 s	- 163.25 s	- 162.94 s	9.99 s 163.02 s	9.82 s 162.41 s
Other signals		2.297 s	3.74 s	4.21 q, 7.1Hz	3.731 s	4.22 q, 7.1 Hz	5.354 s	4.35 q, 7.1Hz
		28.12 s		1.27 t, 7.1Hz	50.62 s	59.09 s	50.80 s	13.58 s
				14.37 s		1.27 t, 7.1		1.39 t 7.1
						14.48 s		13.58 s

Table 5. NMR spectra of enhydrazines **4c**, **4d** (δ in ppm, multiplicity, coupling constants in Hz, numbering according to Scheme 2)

Comp.	4c	4d
Solv.	DMSO- <i>d</i> ₆	DMSO- <i>d</i> ₆
1'- ¹³ C	121.08	123.35
	td, 11.7, 3.9	td, 10.7, 2.2
2'- ¹⁹ F	-154.32	-155.42
	m	m
2'- ¹³ C	139.76	138.42
	m (¹ J _{CF} = 247.0)	m (¹ J _{CF} = 244.2)
3'- ¹⁹ F	-161.74	-164.77
	m	m
3'- ¹³ C	137.99	137.34
	(¹ J _{CF} = 251.4)	m (¹ J _{CF} = 245.9)
4'- ¹⁹ F	-161.20	-167.53
	m	tt, 23.1, 4.2
4'- ¹³ C	137.75	134.98
	m (¹ J _{CF} = 251.0)	m (¹ J _{CF} = 244.9)
1- ¹ H	6.34	8.79
	s	t, 2.2
2- ¹ H	10.06	10.30
	d, 10.9	d, 11.8
3- ¹ H	8.32	8.10
	d, 10.9	d, 11.8
3- ¹³ C	161.05	159.68
	s	s
4- ¹³ C	91.11	88.96
	s	s
5- ¹³ C	165.25	166.54
	s	s
Other signal(s)	3.74, s	4.12, q, 7.1
	51.45, s	59.23, s
	169.00, s	1.21, t, 7.1
	3.78, s	14.28, s
	51.63, s	164.69, s
		4.07, q, 7.1
		59.19, s
		1.20, t, 7.1
	14.28, s	

Initially the identification of **6a-h** was hampered by the lack of evidence about the precise order of the pyrazole ring substituents, as well as the unavailability of heteronuclear correlations between the pyrazole and the pentafluorophenyl group. Thanks to the good solubility of 3-methylpyrazoles **6b,h,i** in chloroform it

was possible to prepare concentrated samples for measurements of uncommon spectra. The measurement and analysis of an INADEQUATE spectrum from a sample of **6b** offered an unambiguous proof of the reaction path c.

Generally the presence of five fluorine atoms on the pentafluorophenyl group resulted in the formation of complicated multiplet patterns in the standard proton-decoupled ^{13}C NMR spectra (Tables 4, 5). The $^1J_{\text{CF}}$ and $^nJ_{\text{CF}}$ couplings causing these multiplets were exploited in order to obtain ^{19}F -heterocorrelated 2D NMR spectra – these served for the exact assignment of the atoms in the perfluorinated group and for the precise extraction of chemical shifts in cases when ^{19}F -decoupled ^{13}C NMR spectra were not measured. It was noted that the pyrazoles **6a-h** provide ^{19}F NMR spectra with a characteristic motif, in which the fluorine in the *para*-position resonates at a higher frequency than the fluorine in the *meta*-position. The cyclisation has a dramatic effect on the ^{19}F NMR shifts as the acyclic derivatives **4c,d** and similar acyclic derivatives yield ^{19}F NMR spectra with a shift of the *para*-fluorine signal towards lower resonance frequencies. This detailed analysis revealed that ^{19}F NMR is an accessible (especially when a NMR probe with a double-tuned high frequency channel is available) and seemingly reliable indicator in the reaction pathway of pentafluorophenyl derivatives described in Scheme 1.

Conclusions

Quantum chemical calculations confirm that the reactivity of the two amine groups in pentafluorophenylhydrazine is not reversed in comparison with those in phenylhydrazine and there is no difference in principle between them. In some cases we were able to isolate an intermediate thus confirming this. Cyclisation of the intermediate enhydrazines gave chemoselectively 5-amino-1-pentafluorophenylpyrazoles or 5-methyl-1-pentafluorophenylpyrazoles. If a cyano or acetyl group is not present (**1c,d**: X = Y = COOMe or COOEt), cyclisation gave a 5-hydroxy/5-oxopyrazole.

Experimental Section

General. All NMR spectra were obtained using a Varian VNMRS 600 MHz spectrometer (operating frequencies 599.76 MHz (^1H), 150.83 MHz (^{13}C) and 564.25 MHz (^{19}F)) equipped by an inverse triple resonance probe and a standard tuneable X/H probe with the possibility to tune the high frequency channel to the resonance frequency of ^{19}F . These spectra include standard ^1H , ^{13}C , ^{19}F , ^{19}F -decoupled ^{13}C spectra (bridged WALTZ16 decoupling), non-uniform sampled HSQC spectra with gradient coherence selection, HMBC with gradient coherence selection, ^{19}F - ^{13}C HSQC ($^1J_{\text{CF}}$ set to 250 Hz) spectra and ^{19}F - ^{13}C HMBC spectra with gradient coherence selection ($^nJ_{\text{CF}}$ set to 15 Hz) and one ^{13}C - ^{13}C INADEQUATE spectrum. Tetramethylsilane was used for the calculation of the ^1H and ^{13}C chemical shift scales and correctly referenced using the (residual) solvent signals (2.50 and 39.52 ppm for DMSO and 7.26 and 77.00 ppm for chloroform). CFCl_3 was used for the calculation of the ^{19}F chemical shift scale; in order to correctly reference the ^{19}F chemical shift scale an automatic referencing mechanism exploiting the ^2H signal of the deuterated solvent was used. ATR IR spectra were recorded on Perkin-Elmer FT-IR spectrometer Spectrum Two UTa (ZnSe). UV-vis spectra were measured on two-beam UV-vis spectrometer Specord® 250 Plus (Analytik Jena). HRMS data were recorded on high resolution mass spectrometer Orbitrap Elite (Thermo Scientific) with resolution 240 000 for m/z 200. For

ionization of samples we used electrospray with voltage set at 4.0kV and sheath gas flow at 5 unit. Melting points were measured on Boetius micro hot stage and are uncorrected. CC were performed using 60 μ m silicagel, TLC by UV 256 plates from Merck.

General procedure for reaction of pentafluorophenylhydrazine with enol ethers

The pentafluorophenylhydrazine **3** and corresponding enol ether **1a-i** were mixed (1:1) in ethanol or methanol (corresponding to the alkoxy group of the enol ether (R in Scheme 1), 10 mL per 10 mmol) and heated under reflux 2-6 hour (TLC control). The reaction mixture was cooled, solvent evaporated and an appropriate method used for separating the product. Products **6b**, **6h**, **4d** were separated immediately after cooling of the reaction mixture by filtration followed by recrystallization from an appropriate solvent to obtain analytically pure compounds.

Analytical data for all obtained compounds are summarized in Table 2 and IR and UV spectra in Table 3, NMR data in Tables 4, 5 .

Preparation of 4-methoxycarbonylpyrazol-3-one (6c) and 4-ethoxycarbonylpyrazol-3-one (6d). The pentafluorophenylhydrazine **3** and corresponding enol ether **1c/d** were mixed (1:1) and heated in water (50 mL) with an equivalent of potassium carbonate at reflux for two hours (TLC). The mixture was cooled, washed with ethyl acetate and then acidified to pH 2 (5N hydrochloric acid). The resultant precipitate was filtered off, washed with water and dried under vacuum. The obtained sample was pure enough for analysis.

Acknowledgements

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References

1. Milata V.; Rádl S.; Voltrová S. in *Science of Synthesis*, 32.5.3. Product Subclass: Enol Ethers (acyclic, cyclic, i.e. endocyclic C=C-O- unit). Georg Thieme Verlag: Stuttgart, 2008; pp 589-756.
2. Saloň J.; Milata V.; Gatial A.; Prónayová N.; Leško J.; Černuchová P.; Vo-Thanh G.; Loupy A. *Eur. J. Org. Chem.* **2005**, 22, 4870.
<http://dx.doi.org/10.1002/ejoc.200500298>
3. Milata, V. in Dialkyl Alkoxymethylenemalonates, *Aldrichimica Acta* **2001**, 34, 20.
<http://www.sigmaaldrich.com/ifb/acta/v34/acta-vol34-2001.html#30>.
4. McFadden, H. G.; Huppatz, J. L. *Aust. J. Chem.* **1991**, 44, 1263.
<http://dx.doi.org/10.1071/CH9911263>
5. Černuchová, P.; Vo-Thanh, G.; Milata, V.; Loupy, A.; Jantová, S.; Theiszová, M.; *Tetrahedron* **2005**, 61, 5379.
<http://dx.doi.org/10.1016/j.tet.2005.03.066>
6. Tarabová D.; Šoralová S.; Breza M.; Fronc M.; Holzer W.; Milata V. *Beilstein J. Org. Chem.* **2014**, 10, 752.
<http://dx.doi.org/10.3762/bjoc.10.70>

7. Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda P. "The Tautomerism of Heterocycles" in *Advances in Heterocyclic Chemistry*, Vol. 76, Academic Press: New York, 1976, pp 157-32.
8. Minkin, V. I.; Garnovskii, A. D.; Elguero, J.; Katritzky, A. R.; Denisko, O. V. "Tautomerism of Heterocycles: Five-Membered Rings with Two or More Heteroatoms" in *Advances in Heterocyclic Chemistry*, Suppl. 1, Academic Press: New York 2000; p 655.
9. McFadden, H. G.; Huppatz, J. L.; Couzens, M. *Pest. Sci.* **1992**, *36*, 247.
<http://dx.doi.org/10.1002/ps.2780360311>
10. Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648.
<http://dx.doi.org/10.1063/1.464913>
11. Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1993**, *98*, 1358.
<http://dx.doi.org/10.1063/1.464303>
12. Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. Jr. *J. Chem. Phys.* **1999**, *110*, 7667.
<http://dx.doi.org/10.1063/1.478678>
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. *et al.*, Gaussian 03 (Revision C1), Gaussian, Pittsburgh, PA, 2006.
14. Al-Shaar, A. H. M.; Gilmour, D. W.; Lythgoe, D. J.; McClenaghan, I.; Ramsden, C. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2789.
<http://dx.doi.org/10.1039/P19920002789>