Preparation of 1,3-Disubstituted-5-cyano-4,5-dihydropyrazoles via 1,3-Dipolar Cycloaddition of Nitrile Imine with Acrylonitrile†

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Oxidation of aldehyde 4-chloro-2, 3, 5, 6-tetrafluorophenylhydrazones (1) with [bis(acetoxy)iodo]benzene leads to the formation of nitrile imines (2) which can react *in situ* with acrylonitrile to produce 1-(4-chloro-2, 3, 5, 6-tetrafluorophenyl)-3-substituted-5-cyano-4, 5-dihydropyrazoles (3) in moderate to good yields. The structures of new compounds were fully confirmed by their spectral data and elemental analyses. A plausible reaction mechanism for the generation of nitrile imine is proposed.

Keywords 1,3-dipolar cycloaddition, nitrile imine, 4,5-dihydropyrazole derivative

Introduction

4,5-Dihydropyrazole derivatives have been studied extensively due to their diverse chemical reactivity, broad spectrum of biological activity and variety of industrial application.[1] In addition, it is known that 4,5-dihydropyrazole derivatives were useful compounds not only as intermediates in the synthesis of pyrazoles, but also as effective chemical bleaching agents, luminescent and fluorescent substances.[2] Thus, the synthesis of 4,5-dihydropyrazole derivatives is of current importance. These compounds were generally prepared via 1,3-dipolar cycloaddition reaction of nitrile imines with alkene.[3] Many methods have been reported for generating nitrile imine intermediates *in situ*, including the thermolysis or photolysis of either 2,5-diphenyl-tetrazole,[4] 3,5-disubstituted-3*H*-1,2,3,4-oxathiadiazolines,[5] 1,3,4-oxadiazolin-2-ones,[6] sydnones[7] or the sodium salt of α-nitroaldehyde hydrazones, pyridinium betaines.[8] The dehydrohalogenation of *N*-phenylbenzahydrazonyl halides by triethylamine has been elaborated as a valuable source of nitrile imine,[9] as has been the use of hydrazide with Ph_3PCl_2.[10] Dehydrogenation of an aldehyde hydrazone with Chloramine-T,[11] [bis(acetoxy)iodo]benzene,[12] polymer supported [bis(acetoxy)iodo]benzene,[13] lead tetraacetate[14] or mercuic acetate[15] also led to nitrile imines. Nitrile imine can also be formed by reaction of α-azobenzyl-hydroperoxide, which was formed on auto oxidation of an aldehyde hydrazone, with triethylamine.[16] These results prompted us to study the methodology employing aldehyde 4-chloro-2,3,5,6-tetrafluorophenylhydrazones. Herein, we wish to report the generation of nitrile imines from the oxidation of aldehyde 4-chloro-2, 3, 5, 6-tetrafluorophenylhydrazones with [bis(acetoxy)iodo]benzene *in situ*, and their simultaneous trapping with acrylonitrile to produce a series of 1-(4-chloro-2, 3, 5, 6-tetrafluorophenyl)-3-substituted-5-cyano-4,5-dihydropyrazole derivatives (**3**).

Results and discussion

Aldehyde 4-chloro-2,3,5,6-tetrafluorophenylhydrazones (**1**) were readily prepared by the reaction of alde-

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hyde and 4-chloro-2,3,5,6-tetrafluorophenylhydrazine in EtOH at room temperature. After recrystallization with petroleum-ethyl acetate twice, they were pure enough for use. Firstly, we examined the oxidation of **1** with [bis-(acetoxy)iodo]benzene in the presence of acrylonitrile (Scheme 1). It was found that, compared with reported method,[12] the reaction temperature was slightly higher. For example, after addition of [bis(acetoxy)iodo]benzene in CH_2Cl_2 to a solution of **1** in acrylonitrile at 0 ℃, the reaction was not completed by maintaining at 0 ℃ for 4 h. Then the ice-water bath was removed, the reaction temperature was gradually raised to room temperature. After 4 h stirring, the starting material **1** disappeared (monitored by TLC). General work afforded the expected 1-(4-chloro-2, 3, 5, 6-tetrafluorophenyl)-3-substituted-5-cyano-4,5-dihydropyrazole derivatives (**3**). It was noted that in the case of aliphatic aldehyde 4-chloro-2,3,5,6-tetrafluorophenylhydrazone (**1j**), the reaction occurred smoothly at 0 ℃ and was completed within 4 h.

The method is applicable to not only aromatic aldehyde bearing electron-donating substituent or electron-withdrawing substituent, but also α,β-unsaturated aromatic aldehyde, fused aromatic aldehyde and heterocyclic aldehyde. However, in the case of **1j**, the yield of the product **3j** was rather lower, and this observation is in agreement with a previous report.[12] The reaction conditions and reaction results are summarized in Table 1.

It is known that 1,3-dipolar cycloaddition reaction of nitrile imines to acrylonitrile is a regioselective reaction, yielding 5-cyano-4,5-dihydropyrazoles exclusively.[9b] The structures of the products were fully confirmed by their elemental analyses and spectral data. For instance, in their ^{1}H NMR spectra, the 5-position proton in the 4,5-dihydropyrazole was found as triplet in the region δ 5.00—5.20, whereas the 4-position protons in the compound **3** were found as doublet in the region δ 3.50—3.70. However, it was noted that, in the case of compounds **3g**, **3i** and **3j**, the 5-position proton was found as doublet of doublet, whereas the 4-position protons were found as either doublet of doublet or ABX system. The mass spectra of compound **3** showed the strong molecular ion peak, and in most cases, it is the base peak. The ^{19}F NMR spectra of 4,5-dihydropyrazole showed a very similar pattern in the region δ −140— −141 and δ −146— −147 for the four fluorine atoms, respectively. In their IR spectra, all the products **3** showed the very strong C = N absorption at 1485—1493 cm^{-1}, which is the characteristic absorption of 4,5-dihydropyrazole **3**. However, the 5-position cyano group absorption was very weak. This is similar to the case of aliphatic cyano activated by a nitrogen atom or an oxygen atom in the α-position.[17]

A plausible mechanism for the generation of nitrile imines is analogous to the oxidation of the aldehyde hydrazones with lead tetracetate[12] as well as mercuric acetate[15] and is illustrated in Scheme 2.

Scheme 1

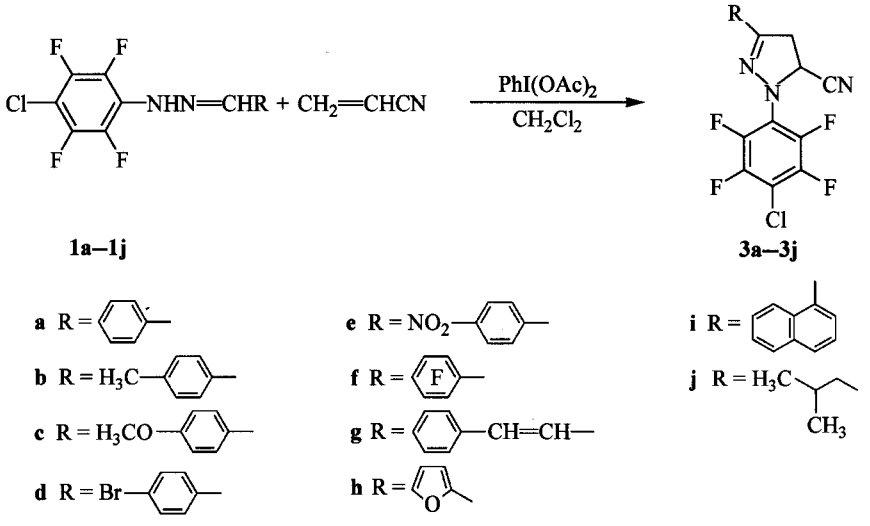
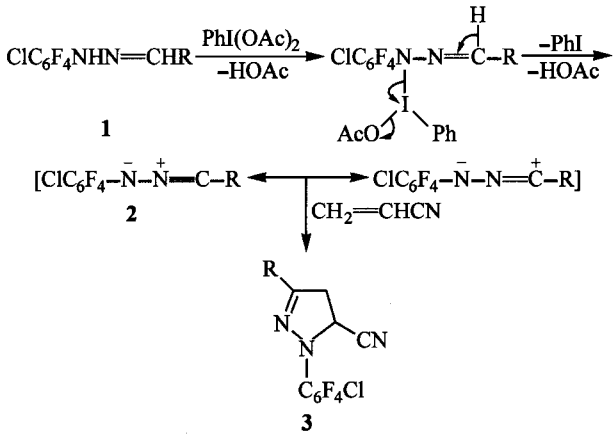


Table 1 Preparation of compounds **3**

Entry	R	Condition[a]		Product	Yield (%)[b]
		T (℃)	t (h)		
1	C_6H_5 –	0→r.t.	4	**3a**	57
2	p-$CH_3C_6H_4$ –	0→r.t.	4	**3b**	54
3	p-$CH_3OC_6H_4$ –	0→r.t.	4	**3c**	50
4	p-BrC_6H_4 –	0→r.t.	4	**3d**	53
5	p-$O_2NC_6H_4$ –	0→r.t.	4	**3e**	55
6	C_6F_5 –	0→r.t.	4	**3f**	74
7	$C_6H_5CH=CH$ –	0→r.t.	4	**3g**	47
8	furfuryl-	0→r.t.	4	**3h**	57
9	naphthyl-1-	0→r.t.	4	**3i**	53
10	*iso*-butyl-	0	4	**3j**	21

[a] All reactions were carried out in CH_2Cl_2. [b] Isolated yield based on **1**.

Scheme 2



In summary, a series of 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-substituted-5-cyano-4,5-dihydropyrazoles (**3**) was prepared by oxidation of aldehyde 4-chloro-2,3,5,6-tetrafluorophenylhydrazones (**1**) with [bis(acetoxy)iodo]benzene in the presence of acryonitrile. A further chemical transformation of the new compounds **3** is under investigation.

Experimental

Melting points were measured on a Temp-Melt apparatus and are uncorrected. Solvents were dried before use. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian-Mercury 300 instrument or a Bruker AM-300 spectrometer with TMS or TFA ($\delta_{CFCl_3} = \delta_{TFA} + 76.8$) as the internal and external standards and the up field as negative. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Lower resolution mass spectra or high resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 or a Finnigan MAT-8430 instrument respectively. Elemental analyses were performed by this Institute. [Bis(acetoxy)iodo]benzene was purchased from Acros.

General procedure for the preparation of 4,5-dihydropyrazoles

[Bis(acetoxy)iodo]benzene (2 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise at 0 ℃ to a stirred solution of 2 mmol of aldehyde 4-chloro-2,3,5,6-tetrafluorophenylhydrazone (**1**) in 5 mL of acrylonitrile. After addition, the ice-water bath was removed and the reaction temperature was gradually raised to room temperature. The disappearance of starting material **1** was about 4 h at room temperature. The reaction mixture was then concentrated under vacuum. To the residue was added 20 mL of CH_2Cl_2 and the organic layer was washed with 5% aq. Na_2CO_3 solution (10 mL), H_2O (10 mL), and dried with anhydrous $MgSO_4$. The crude material, after evaporation of the solvent, was purified by column chromatography on silica gel using petroleum-ethyl acetate (9∶1, V∶V) as eluent. The reaction yields are showed in Table 1.

1-(4-Chloro-2,3,5,6-tetrafluoro)phenyl-3-phenyl-5-cyano-4,5-dihydropyrazole (**3a**) M.p. 158—160 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.70 (d, J = 8.4 Hz, 2H), 5.14 (t, J = 8.4 Hz, 1H), 7.43—7.46 (m, 5H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −140.4 (d, J = 15 Hz, 2F), −146.3 (d, J = 15 Hz, 2F); IR (KBr) ν: 1493, 1084 cm^{-1}; MS (70 eV) m/z (%): 355/353 (M^+, 33/93), 328/326 (M^+ − HCN, 34/100), 199/197 ($ClC_6F_4N^+$, 28/84), 162 ($C_6F_4N^+$, 66), 77 ($C_6H_5^+$, 69). Anal. calcd for $C_{16}H_8ClF_4N_3$: C 54.31, H 2.26, N 11.88; found C 54.48, H 2.46, N 11.80.

1-(4-Chloro-2,3,5,6-tetrafluoro)phenyl-3-(4-methylphenyl)-5-cyano-4,5-dihydropyrazole (**3b**) M.p. 126—127 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.40 (s, 3H), 3.67 (d, J = 6.0 Hz, 2H), 5.12 (t, J = 6.0 Hz, 1H), 7.24 (d, J = 6.0 Hz, 2H), 7.57 (d, J = 6.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −140.5 (d, J = 14 Hz, 2F), −146.3 (d, J = 14 Hz, 2F); IR (KBr) ν: 1485, 1105 cm^{-1}; MS (70 eV)

m/z (%): 369/367 (M^+, 33/100), 199/197 ($ClC_6F_4N^+$, 18/55), 162 ($C_6F_4N^+$, 60), 91 ($CH_3C_6H_4^+$, 29). Anal. calcd for $C_{17}H_{10}ClF_4N_3$: C 54.51, H 2.72, N 11.43; found C 55.73, H 2.78, N 11.49.

1-(4-*Chloro*-2, 3, 5, 6-*tetrafluoro*) *phenyl*-3-(4-*methoxyphenyl*)-5-*cyano*-4,5-*dihydropyrazole* (**3c**) M.p. 135—136 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.66 (d, J = 7.8 Hz, 2H), 3.86 (s, 3H), 5.10 (t, J = 7.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −141.7 (d, J = 13 Hz, 2F), −147.4 (d, J = 13 Hz, 2F); IR (KBr) ν: 1488, 1258, 1174 cm^{-1}; MS (70 eV) *m/z* (%): 385/383 (M^+, 26/75), 199/197 ($ClC_6F_4N^+$, 10/30), 162 ($C_6F_4N^+$, 61), 133 ($CH_3OC_6H_4CN^+$, 100). Anal. calcd for $C_{17}H_{10}ClF_4N_3O$: C 53.19, H 2.61, N 10.95; found C 53.35, H 2.73, N 11.01.

1-(4-*Chloro*-2, 3, 5, 6-*tetrafluoro*) *phenyl*-3-(4-*bromophenyl*)-5-*cyano*-4, 5-*dihydropyrazole* (**3d**) M.p. 131—133 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.67 (d, J = 8.4 Hz, 2H), 5.15 (t, J = 8.4 Hz, 1H), 7.59—7.52 (m, 4H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −140.2 (d, J = 20 Hz, 2F), −146.4 (d, J = 20 Hz, 2F); IR (KBr) ν: 1490, 1166, 1100 cm^{-1}; MS (70 eV) *m/z* (%): 435/433/431 (M^+, 26/100/79), 199/197 ($ClC_6F_4N^+$, 23/75), 162 ($C_6F_4N^+$, 58). Anal. calcd for $C_{16}H_7BrClF_4N_3$: C 44.39, H 1.62, N 9.71; found C 44.77, H 1.80, N 9.73.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-(4-*nitrophenyl*)-5-*cyano*-4,5-*dihydropyrazole* (**3e**) M.p. 159—160 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.75 (d, J = 9.0 Hz, 2H), 5.24 (t, J = 9.0 Hz, 1H), 7.85 (d, J = 9.0 Hz, 2H), 8.31 (d, J = 9.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −140.7 (d, J = 14 Hz, 2F), −147.3 (d, J = 14 Hz, 2F); IR (KBr) ν: 1490, 1166, 1100 cm^{-1}; MS (70 eV) *m/z* (%): 401/399 (M^+ + 1, 30/91), 400/398 (M^+, 38/95), 373/371 (M^+ − HCN, 17/42), 199/197 ($ClC_6F_4N^+$, 34/100), 162 ($C_6F_4N^+$, 60). Anal. calcd for $C_{16}H_7ClF_4N_4O_2$: C 48.18, H 1.76, N 14.05; found C 48.28, H 1.96, N 14.14.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-(*pentafluorophenyl*)-5-*cyano*-4,5-*dihydropyrazole* (**3f**) M.p. 128—130 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.77 (d, J = 6.6 Hz, 2H), 5.16 (t, J = 6.6 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz,) δ: −137.6 (d, J = 20 Hz, 2F), −139.7 (d, J = 13 Hz, 2F), −146.1 (d, J = 13 Hz, 2F), −150.3 (t, J = 20 Hz, 1F), −160.4 (t, J = 20 Hz, 2F); IR (KBr) ν: 1493, 1084 cm^{-1}; MS (70 eV) *m/z* (%): 445/443 (M^+, 20/59), 199/197 ($ClC_6F_4N^+$, 29/86), 185/183 ($ClC_6F_4^+$, 13/34), 162 ($C_6F_4N^+$, 100). Anal. calcd for $C_{16}H_3ClF_9N_3$: C 43.29, H 0.68, N 9.47; found C 43.52, H 0.83, N 9.47.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-*styryl*-5-*cyano*-4,5-*dihydropyrazole* (**3g**) M.p. 197—199 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.58 (dd, J = 10.2, 6.6 Hz, 2H), 5.11 (dd, J = 10.2, 6.6 Hz, 1H), 6.78 (d, J = 16.5 Hz, 1H), 7.11 (d, J = 16.5 Hz, 1H), 7.34—7.51 (m, 5H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −141.2 (d, J = 14 Hz, 2F), −147.3 (d, J = 14 Hz, 2F); IR (KBr) ν: 1491, 1157, 1075 cm^{-1}; MS (70 eV) *m/z* (%): 382/380 (M^+ + 1, 28/91), 381/379 (M^+, 46/100), 354/352 (M^+ − HCN, 23/51), 199/197 ($ClC_6F_4N^+$, 5/13), 162 ($C_6F_4N^+$, 28); Anal. calcd for $C_{18}H_{10}ClF_4N_3$: C 56.92, H 2.63, N 11.07; found C 57.06, H 2.78, N 11.08.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-(*furfur*-2-*yl*)-5-*cyano*-4,5-*dihydropyrazole* (**3h**) M.p. 138—139 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.66 (d, J = 8.1 Hz, 2H), 5.09 (t, J = 8.1 Hz, 1H), 6.53—6.55 (m, 1H), 6.87 (d, J = 3.6 Hz, 1H), 7.55—7.56 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −141.3 (d, J = 14 Hz, 2F), −147.0 (d, J = 14 Hz, 2F); IR (KBr) ν: 1492, 1257, 1174, 1004 cm^{-1}; MS (70 eV) *m/z* (%): 345/343 (M^+, 34/100), 199/197 ($ClC_6F_4N^+$, 22/69), 162 ($C_6F_4N^+$, 67), 132 ($M^+ - ClC_6F_4N_2$, 42). Anal. calcd for $C_{14}H_6ClF_4N_3O$: C 48.91, H 1.75, N 12.23; found C 49.21, H 1.94, N 12.24.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-(*naphth*-1-*yl*)-5-*cyano*-4,5-*dihydropyrazole* (**3i**) M.p. 177—178 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz,) δ: 3.82—3.99 (m, ABX system, 2H), 5.18 (dd, J = 10.5, 5.4 Hz, 1H), 7.48—7.68 (m, 4H), 7.89—7.95 (m, 2H), 9.14—9.16 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −141.3 (d, J = 14 Hz, 2F), −147.6 (d, J = 14 Hz, 2F); IR (KBr) ν: 1493, 1122, 1098 cm^{-1}; MS (70 eV) *m/z* (%): 406/404 (M^+ + 1, 8/20), 405/403 (M^+, 41/100), 378/376

(M^+ – HCN, 13/39). Anal. calcd for $C_{20}H_{10}ClF_4N_3$: C 59.48, H 2.48, N 10.41; found C 59.50, H 2.53, N 10.39.

1-(4-*Chloro*-2,3,5,6-*tetrafluoro*)*phenyl*-3-*isobutyl*-5-*cyano*-4,5-*dihydropyrazole* (**3j**) Sticky oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.02 (dd, J = 6.6, 2.4 Hz, 6H), 1.93—2.06 (m, J = 6.6 Hz, 1H), 2.32 (d, J = 7.5 Hz, 2H), 3.23 (dd, J = 9.6, 6.3 Hz, 2H), 4.89 (dd, J = 9.6, 6.3Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: –141.8 (d, J = 14 Hz, 2F), –147.1 (d, J = 14 Hz, 2F); IR (liquid film) ν: 2960, 1493, 1148 cm^{-1}; MS (70 eV) m/z (%): 335/333 (M^+, 24/71), 292/290 ($M^+ - C_3H_7$, 42/100), 266/264 ($M^+ - C_3H_7 - CN$, 14/42), 199/197 ($ClC_6F_4N^+$, 18/51), 162 ($C_6F_4N^+$, 48), 43 ($C_3H_7^+$, 59). HRMS calcd for $C_{14}H_{12}ClF_4N_3$ 333.06559, found 333.06231.

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