N-Substituted hepta(methoxycarbonyl)-3a,7a-dihydroindazoles as new sources for the generation of nitrile imines

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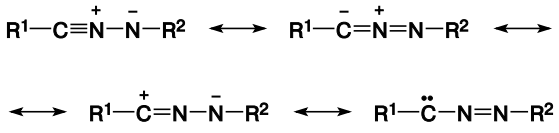
Thermal decomposition of *N*-substituted hepta(methoxycarbonyl)-3a,7a-dihydroindazoles proceeds through the elimination of hexamethyl benzenehexacarboxylate and results in the generation of 1-aryl-3-methoxycarbonylnitrile imines, which are intercepted by both the electron-withdrawing and electron-releasing olefins, for example, methyl acrylate, cyclopentene, vinylcyclopropane, or ethyl vinyl ether, to form the corresponding pyrazolines and pyrazoles. In the presence of propan-2-ol, the main process proceeds through the addition of nitrile imine to the O—H bond to form methyl 2-isopropoxy-2-[2-(4-methoxyphenyl)hydrazono]acetate.

Key words: 3a,7a-dihydroindazoles, nitrile imines, pyrazolines, pyrazoles, 1,3-dipolar addition, thermolysis.

Nitrile imines belong to the class of highly reactive 1,3-dipoles and, like aliphatic diazo compounds, are widely used in various 1,3-dipolar cycloaddition reactions to unsaturated compounds, which lead to the formation of pyrazolines, pyrazoles, and other heterocyclic compounds.[1—5] The electron state of nitrile imines is represented by four major resonance structures (propargylic, allenic, allylic, and carbene), the contribution of each of which can significantly change depending on the electronic properties of substituents.[5—8]



Due to the specificities of the electronic structure and, as a rule, higher reactivity as compared to diazo compounds, which are their structural isomers, nitrile imines can exhibit ambiphilic character, reacting with equal facility with multiple bonds of unsaturated compounds containing either electron-withdrawing, or electron-releasing substituents at the multiple bond.[2—4,9] Among various methods for the generation of nitrile imines, the following should be mentioned: 1,3-dehydrochlorination of chlorinated *N*-arylhydrazones (YC(Cl)=N—NHAr, Y = Ar, COOMe); thermolysis or photolysis of 2,5-disubstituted tetrazoles, sidnones, or 1,3,4-oxadiazol-5-ones; oxidation of aldehyde *N*-acyl- or *N*-hetaryl-substituted hydrazones,[1—5,9] as well as addition of electrophiles at the terminal nitrogen atom of metallated derivative of diazo compound, mainly used for the preparation of stable nitrile imines with bulky substituents in the molecule.[4,5,10]

In the present work, we found a new source of *N*-substituted 3-(methoxycarbonyl)nitrile imines **1**, formed during thermal decomposition of 1-aryl-3,3a,4,5,6,7,7a-hepta(methoxycarbonyl)-3a,7a-dihydroindazoles (**2**) and intercepted with unsaturated compounds or isopropyl alcohol.

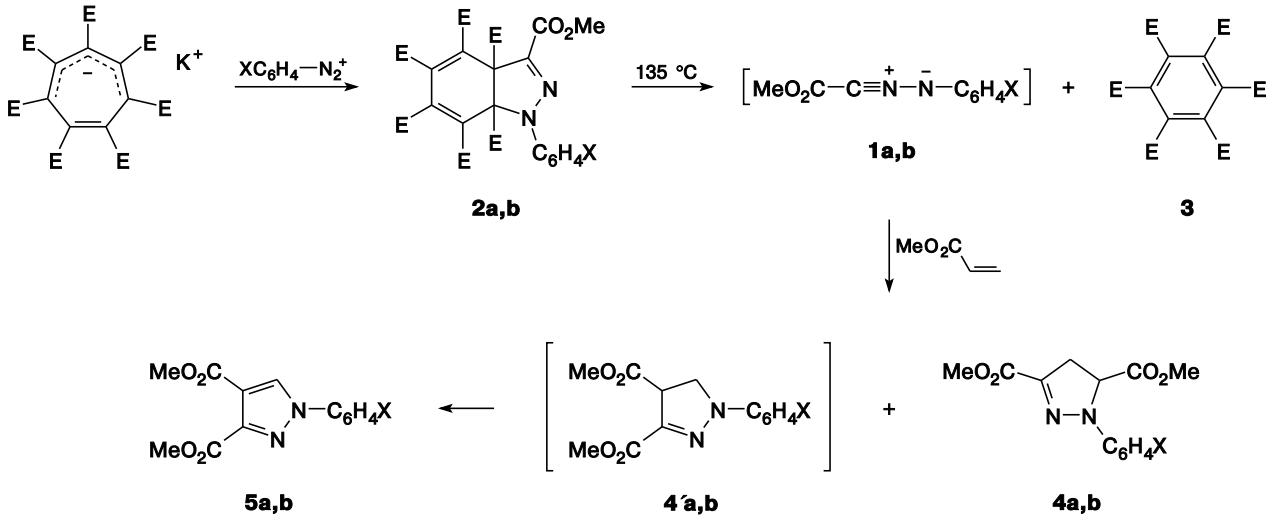
Results and Discussion

Recently,[11] while studying the reaction of hepta(methoxycarbonyl)cycloheptatrienylpotassium with aryldiazonium salts we suggested a new method for the synthesis of a number of substituted 3a,7a-dihydroindazoles **2**. It turned out that the latter undergo thermal decomposition at 130—140 °C with elimination of benzenehexacarboxylate **3** and generation of the intermediates, whose interception with unsaturated substrates indicates that they are nitrile imines **1** containing a methoxycarbonyl fragment at the carbon atom (Scheme 1). The experiments were carried out in sealed tubes under inert atmosphere by heating dihydroindazoles **2** with a 10-fold molar excess of an unsaturated compound or propan-2-ol. The unsaturated compounds were methyl acrylate, ethyl vinyl ether, cyclopentene, or vinylcyclopropane, and in all the cases, the reaction mixtures were diluted with a small amount of 1,4-dioxane for complete dissolution of **2**. For instance, thermolysis (135 °C, 10 h) of dihydroindazole **2a** in the presence of methyl acrylate leads, together with benzenehexacarboxylate **3**, to 1-(4-fluorophenyl)-2-pyrazoline-3,5-di-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1357—1362, July, 2010.

1066-5285/10/5907-1387

Scheme 1



E = CO_2Me; X = F (**a**), OMe (**b**)

carboxylate **4a** in 80% yield (see Scheme 1), whose formation is easily explained by the generation of nitrile imine **1a** and its regioselective addition to the double bond of methyl acrylate.

Recently,[9] an intermediate similar to **1a**, *viz.*, 1-(4-chlorophenyl)-3-(ethoxycarbonyl)nitrile imine, has been generated by photolytic dediazotization of 2-(4-chlorophenyl)-5-ethoxycarbonyltetrazole. It was trapped with methyl methacrylate as a result of 1,3-dipolar cycloaddition and also gave 5-substituted pyrazoline with high regioselectivity.

Thermolysis of dihydroindazole **2b** under analogous conditions in the presence of methyl acrylate, together with expected pyrazoline **4b**, additionally gave pyrazole-3,4-dicarboxylate **5b** (the total yield was 78%, the ratio was ~6 : 1) (see Scheme 1). The latter was identified* by comparison of ^1H and ^{13}C NMR spectra obtained by us with those given in the work.[12] The side formation of pyrazole **5b** apparently occurs due to the fact that nitrile imine **1b** reacts with methyl acrylate with lower regioselectivity than **1a**, whereas pyrazoline **4b´** resulted from this, in contrast to regioisomeric pyrazoline **4b**, undergoes rapid oxidation to pyrazole **5b**. After obtaining such a result, we studied in detail the composition of the products of the reaction of **2a** with methyl acrylate and made certain that, if the corresponding 1-(4-fluorophenyl)pyrazole-3,4-dicarboxylate **5a** is really present in the reaction mixture, then its amount does not exceed 1.5%, *i.e.*, is lower by an order of magnitude than on generation of methoxyphenyl-substituted intermediate **1b**.

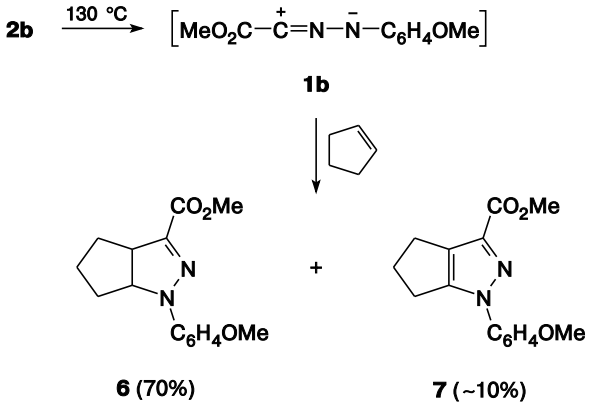
It should be noted that the lack of regiospecificity in the 1,3-dipolar cycloaddition reactions of nitrile imines to the multiple bonds of unsaturated compounds is not surprising. Thus, for example, if cycloaddition of diphenylnitrile imine to alkenes with electron-releasing substituents virtually entirely leads to 5-substituted 2-pyrazolines, then in the case of conjugated and electron-deficient dipolarophiles the fraction of 4-substituted regioisomers significantly increases.[2,13] The lack of regioselectivity is especially noticeable in the case of acetylene dipolarophiles. Thus, for example, cycloaddition of the same nitrile imines **1a,b** generated *in situ* by 1,3-dehydrochlorination of chlorinated *N*-arylhydrazones $MeO_2C—CCl=N—NHAr$ in the presence of methyl propiolate leads to isomeric pyrazole-3,4- and pyrazole-3,5-dicarboxylates in the ratio close to 1 : 1 (see Ref. 12).

Further we studied the reactivity of nitrile imines **1a**,**b** with respect to electron-releasing olefins. It turned out that thermolysis of dihydroindazole **2b** (130 °C, 10 h) in the presence of cyclopentene, similar to the case of methyl acrylate, leads to a predominant formation of bicyclic pyrazoline **6** (the yield was 70%) and a small amount of pyrazole **7** (Scheme 2) isolated in the individual state by column chromatography on SiO_2. It should be noted that the presence of pyrazoles **5b** and **7** was observed in the ^1H NMR spectra of the reaction mixtures even when the reaction was carried out under inert atmosphere. It cannot be excluded that their formation is due to the easy dehydrogenation of the corresponding 4-substituted pyrazolines upon the action of nitrile imine **1b** itself in the course of the reaction; at least, no oxidation of pyrazolines **4a,b**

* The ^{13}C NMR spectrum obtained by us significantly differs from that described in the work[12] in position of the signal for the methoxy group of the aryl fragment. Chemical shift δ 55.5 found by us seems more reasonable than the value δ 44.1 given by the authors.[12]

or **6** to pyrazoles was observed during chromatographic separation of the reaction mixture and their isolation.

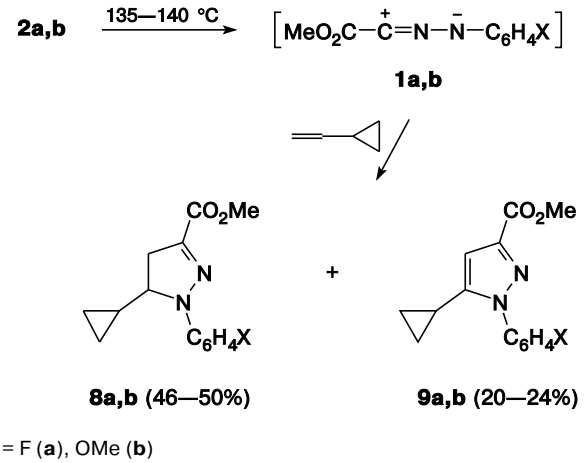
Scheme 2



Analogous transformations take place on the interception of nitrile imines with vinylcyclopropane. For instance, thermolysis of dihydroindazoles **2a** and **2b** at 135—140 °C in the presence of vinylcyclopropane leads, together with pyrazolines **8a,b**, to a significant amount of the corresponding pyrazoles **9a,b** (Scheme 3). In this case, NMR spectroscopy with the use of homo- and heteronuclear two-dimensional COSY, HMBC, and HSQC correlation spectra unambiguously showed that the cyclopropyl substituent in both pyrazoline **8b** and pyrazole **9b** is located on the C(5) atom of the heterocycle. The result obtained, as it was mentioned above, is in agreement with the fact that cycloaddition of nitrile imines to electron-saturated alkenes occurs with high regioselectivity, leading to the formation of 5-substituted 2-pyrazolines. At the same time, pyrazolines containing electron-releasing substituents apparently undergo much easier oxidation, that results in significant formation of pyrazoles **9a,b** independent on the nature of substituents in the phenyl fragment.

It is known[14] that the reaction of butyl vinyl ether with nitrile imine **1b**, generated by elimination of HCl from methyl [(4-methoxyphenyl)hydrazono]chloroacetate at 20 °C, gives a mixture of 5-butoxy-3-methoxycarbonyl-1-(4-methoxyphenyl)-2-pyrazoline and 3-methoxycarbonyl-1-(4-methoxyphenyl)pyrazole in 27 and 28% yields, respectively. During thermal decomposition (130 °C) of dihydroindazole **2a** in the presence of 50—60-fold excess of ethyl vinyl ether, the reaction also proceeds through the 1,3-dipolar cycloaddition of generated nitrile imine **1a** to the double bond of the substrate. The yield of 5-ethoxypyrazoline **10** is only 15—18%, whereas the major reaction product is pyrazole **11**, formed in ~60% yield from pyrazoline **10** as a result of elimination of ethanol (Scheme 4). In fact, an additional experiment showed that thermolysis

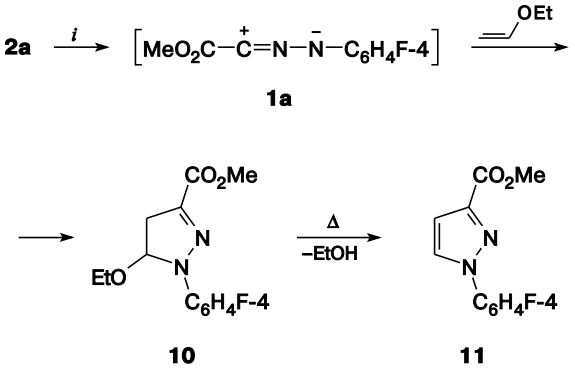
Scheme 3



X = F (**a**), OMe (**b**)

of pyrazoline **10** at 150 °C for 6 h leads to its entire conversion to pyrazole **11**.

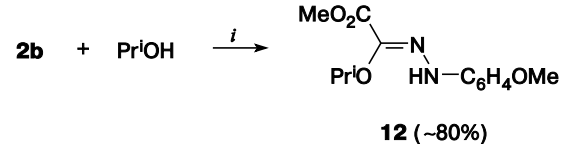
Scheme 4



i. 130 °C, 11 h

In addition to unsaturated substrates, alcohols also proved active interceptors of nitrile imines.[15,16] We showed that heating a solution of dihydroindazole **2b** in isopropyl alcohol in a sealed tube at 130 °C for 10 h leads to the formation of 2-hydrazono-2-isopropoxyacetate **12** in ~80% yield, the addition product of **1b** at the O—H bond of propan-2-ol (Scheme 5).

Scheme 5



i. 130 °C, 10 h

In conclusion, decomposition of 1-aryl-3,3a,4,5,6,7,7a-hepta(methoxycarbonyl)-3a,7a-dihydroindazoles **2** upon heating above 130 °C through the elimination of benzenehexacarboxylate **3** leads to the generation of intermediates corresponding to the structure of 1-aryl-3-methoxycarbonylnitrile imines **1**. The latter, similarly to nitrile imines generated by other methods, undergo the 1,3-dipolar addition reaction with unsaturated compounds containing either electron-withdrawing, or electron-releasing substituents at the double bond, as well as undergo addition at the O—H bond of aliphatic alcohols. In the case of electron-deficient olefins, the addition agrees with the propargylic or allenic form, whereas in the case of electron-enriched olefins, with the allylic form of nitrile imines.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 300 (300 and 75.5 MHz) and Bruker DRX-500 (500 MHz and 125.3 MHz, respectively) spectrometers for solutions in $CDCl_3$ containing 0.05% of Me_4Si as an internal standard; chemical shifts for ^{19}F are given relative to CCl_3F. Assignment of signals and determination of isomeric composition of compounds formed were made using homo- and heteronuclear two-dimensional COSY, HMBC, and HSQC correlation spectra. GLC-MS spectra were obtained on a Finnigan MAT DSQII instrument (EI, 70 eV, the temperature of the source of ions—trap of ions system was 200 °C) and Trace GC Ultra chromatograph equipped with a Thermo TR-5ms SQC column, 15 m×0.25 mm. IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. Thin-layer chromatography was performed on Silica gel 60 plates (Merck) with visualization in a chamber with iodine vapors. Column chromatography was used for preparative separations (silica gel 60, 0.040—0.063 mm, Merck) at the ratio substance—sorbent of ~1 : 100. Melting points were measured on a Nagema PHMK-05 apparatus.

1-(4-Fluorophenyl)- (**2a**) and 3,3a,4,5,6,7,7a-hepta(methoxycarbonyl)-1-(4-methoxyphenyl)-3a,7a-dihydroindazoles (**2b**) with the purity no less than 98% were obtained according to the described procedure.[11] Unsaturated compounds were distilled under inert atmosphere before use, solvents (chemically pure grade, >99.5%) were used without additional purification.

Thermolysis of 3a,7a-dihydroindazoles 2a,b in the presence of olefins (general procedure). A mixture of heptamethyl dihydroindazoleheptacarboxylate **2a** or **2b** (0.4 mmol), an unsaturated compound (4 mmol), and 1,4-dioxane (0.3 mL) was heated in a sealed tube under Ar at 130—140 °C for 10 h. The reaction mixture was analyzed by TLC and ^{1}H NMR spectroscopy. The major reaction products were isolated by column chromatography on SiO_2 using the benzene—EtOAc mixture as an eluent with the solvents gradient from 10 : 1 to 2 : 1. In all the cases, benzenehexacarboxylate **3** was eluted after the corresponding pyrazolines and pyrazoles.

Dimethyl 1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (4a) was obtained from dihydroindazole **2a** (0.24 g) and methyl acrylate (0.34 g). The yield of compound **4a** was 90 mg (80%), colorless crystals, m.p. 124—125 °C (from C_6H_6—AcOEt, 10 : 1). Found (%): C, 55.74; H, 4.60; N, 10.08; F, 6.74. $C_{13}H_{13}FN_2O_4$. Calculated (%): C, 55.71; H, 4.68; N, 10.00; F, 6.78. MS (EI), m/z (I_{rel} (%)): 280 $[M]^+$ (73), 249 $[M - OMe]^+$ (17), 221 $[M - CO_2Me]^+$ (65), 189 (100), 177 (54), 135 (45), 122 (75), 109 (62), 95 (85), 75 (75), 59 (45). IR, ν/cm^{-1}: 2952, 1752 and 1724 (2 COO), 1564, 1512, 1440. ^{1}H NMR ($CDCl_3$), δ: 3.34 (dd, 1 H, H_a(4), ^2J = 18.5 Hz, ^3J = 7.0 Hz); 3.56 (dd, 1 H, H_b(4), ^2J = 18.5 Hz, ^3J = 13.5 Hz); 3.76, 3.90 (both s, 3 H each, 2 OMe); 4.92 (dd, 1 H, H(5), J = 7.0 Hz, J = 13.5 Hz); 7.00 (dd, 2 H, H_m, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,F}$ = 8.5 Hz); 7.08 (dd, 2 H, CH_o, $^3J_{H,H}$ = 9.5 Hz, $^3J_{H,F}$ = 4.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 37.3 (C(4)); 52.4, 53.0 (2 OMe); 62.7 (C(5)); 115.4 (d, C_o, $^3J_{C,F}$ = = 8.0 Hz); 116.0 (d, C_m, $^2J_{C,F}$ = 23.0 Hz); 138.3 (C(3)); 138.90 (d, C_{ipso}, $^4J_{C,F}$ = 2.0 Hz); 158.4 (d, C_p, $J_{C,F}$ = 243 Hz); 162.4, 170.4 (2 COO). ^{19}F NMR ($CDCl_3$), δ: −122.8 (tt, ^3J = 8.5 Hz, ^4J = 4.5 Hz).

Dimethyl 1-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (4b) and dimethyl 1-(4-methoxyphenyl)-1*H*-pyrazole-3,5-dicarboxylate (5b). Dihydroindazole **2b** (0.25 g) and methyl acrylate (0.34 g) gave a mixture of pyrazoline **4b** and pyrazole **5b** (91 mg, ~78%, the ratio was ~6 : 1 according to the ^{1}H NMR spectrum) as slightly yellowish fusible crystals, m.p. 25—28 °C, which were unseparable under these conditions.

Compound **4b**. GLC-MS (EI), m/z (I_{rel} (%)): 292 $[M]^+$ (78), 233 $[M - CO_2Me]^+$ (80), 201 (100), 189 (36), 174 (58), 134 (40), 107 (35). ^{1}H NMR ($CDCl_3$), δ: 3.31 (dd, 1 H, H_a(4), ^2J = 18.5 Hz, ^3J = 7.0 Hz); 3.53 (dd, 1 H, H_b(4), ^2J = 18.5 Hz, ^3J = 13.5 Hz); 3.73, 3.77, 3.87 (all s, 3 H each, 3 OMe); 4.92 (dd, 1 H, H(5), J = 7.0 Hz, J = 13.5 Hz); 6.85, 7.08 (both d, 2 H each, H_o, H_m, ^3J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 37.1 (C(4)); 52.3, 52.9 (2 COOMe); 55.6 (OMe); 62.94 (C(5)); 114.6, 115.5 (C_o, C_m); 136.4 (C(3)); 137.1 (C_{ipso}); 155.12 (C_p); 162.6, 170.7 (2 COO).

Compound **5b** (see Ref. 12). ^{13}C NMR ($CDCl_3$), δ: 52.3, 53.5, 55.5 (3 OMe); 113.8 (C_m); 114.7 (C(5)); 115.6 (C(4)); 127.4 (C_o); 131.6 (C_{ipso}); 144.7 (C(3)); 157.5 (C_p); 161.8, 162.2 (2 COO).

Methyl 1-(4-methoxyphenyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[*c*]pyrazole-3-carboxylate (6) and methyl 1-(4-methoxyphenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate (7). Dihydroindazole **2b** (0.25 g) and cyclopentene (0.27 g) gave pyrazoline **6** (76 mg, 70%) and pyrazole **7** (11 mg, 10%).

Compound **6**, lemon crystals, m.p. 90—91 °C (from hexane—C_6H_6, 5 : 1). Found (%): C, 65.56; H, 5.76; N, 10.18. $C_{15}H_{18}N_2O_3$. Calculated (%): C, 65.68; H, 6.61; N, 10.21. MS (EI), m/z (I_{rel} (%)): 274 $[M]^+$ (100), 259 $[M - Me]^+$ (20), 243 $[M - OMe]^+$ (6), 215 $[M - CO_2Me]^+$(40). ^{1}H NMR ($CDCl_3$), δ: 1.40, 1.20 (both m, 1 H each, H_2C(5)); 1.82—2.14 (m, 4 H, 2 CH_2); 3.77, 3.85 (both s, 3 H each, 2 OMe); 3.93, 4.78 (both m, 1 H each, H(3a), H(6a)); 6.84, 7.13 (both d, 2 H each, H_o, H_m, ^3J = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 24.4 (C(5)); 33.2, 34.4 (C(4), C(6)); 49.4 (C(3a)); 51.9 (CO_2Me); 55.6 (OMe); 67.2 (C(6a)); 114.5, 115.4 (C_o, C_m); 135.9 (C_{ipso}); 140.1 (C(3)); 154.6 (C_p); 163.5 (COO).

Compound **7**, a yellowish wax-like mass. MS (EI), m/z (I_{rel} (%)): 272 $[M]^+$ (100), 257 $[M - Me]^+$ (20), 241 $[M - OMe]^+$ (20), 229 (20), 213 $[M - CO_2Me]^+$(32). ^{1}H NMR ($CDCl_3$), δ: 2.65 (m, 2 H, H_2C(5)); 2.86, 2.96 (both br.t, 2 H each, 2 CH_2, ^3J = 7.3 Hz); 3.84, 3.93 (both s, 3 H each, 2 OMe); 6.95 (d, 2 H, 2 H_m, ^3J = 8.9 Hz); 7.59 (d, 2 H, 2 H_o, ^3J = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.5, 23.9 (C(4), C(6)); 30.9 (C(5)); 52.0 (CO_2Me); 55.6 (OMe); 114.5 (C_m); 121.9 (C_o); 131.3 (C(3a)); 132.2 (C_{ipso}); 132.4 (C(3)); 150.1 (C(6a)); 158.6 (C_p); 163.6 (COO).

Methyl 5-cyclopropyl-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (8a) and methyl 5-cyclopropyl-1-(4-fluorophenyl)-1*H*-pyrazole-3-carboxylate (9a). Dihydroindazole **2a** (0.24 g) and vinylcyclopropane (0.27 g) gave pyrazoline **8a** (53 mg, ~50%) and pyrazole **9a** (23 mg, 22%), each of which is enriched with the major substance by 93—95%.

Compound **8a**. IR, ν/cm^{-1}: 2958, 1700 (COO), 1508. MS (EI), *m/z* (I_{rel} (%)): 262 $[M]^+$ (10), 221 (5), 189 (16), 177 (10), 122 (12), 109 (100). ^{1}H NMR ($CDCl_3$), δ: 0.26, 0.41, 0.52, 0.65 (all m, 1 H each, CH_2CH_2); 1.07 (m, 1 H, CH in *cyclo*-C_3H_5); 3.03 (dd, 1 H, H_a(4), ^2J = 17.9 Hz, ^3J = 6.0 Hz); 3.31 (dd, 1 H, H_b(4), ^2J = 17.9 Hz, ^3J = 12.0 Hz); 3.90 (s, 3 H, OMe); 4.09 (ddd, 1 H, H(5), ^3J = 6.0 Hz, 7.9 Hz, J = 12.0 Hz); 7.00 (dd, 2 H, H_m, $^3J_{H,H}$ = 9.1 Hz, $^3J_{H,F}$ = 8.6 Hz); 7.24 (dd, 2 H, H_o, $^3J_{H,H}$ = = 9.1 Hz, $^4J_{H,F}$ = 4.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 1.9, 6.3 (CH_2CH_2); 15.3 (CH in *cyclo*-C_3H_5); 37.9 (C(4)); 52.2 (OMe); 66.2 (C(5)); 115.7 (d, C_m, $^2J_{C,F}$ = 22.5 Hz); 117.8 (d, C_o, $^3J_{C,F}$ = = 8.0 Hz); 137.8 (d, C_{ipso}, $^4J_{C,F}$ = 2.2 Hz); 138.5 (C(3)); 160.0 (COO); 160.1 (d, C_p, $^1J_{C,F}$ = 242 Hz). ^{19}F NMR ($CDCl_3$), δ: −122.8 (tt, ^3J = 8.6 Hz, ^4J = 4.5 Hz).

Compound **9a**. IR, ν/cm^{-1}: 2958, 1724 (COO), 1516. MS (EI), *m/z* (I_{rel} (%)): 260 $[M]^+$ (10), 229 $[M - OMe]^+$ (90), 213 (10), 201 $[M - COOMe]^+$ (12), 161 (12), 134 (15), 105 (50), 95 (100). ^{1}H NMR ($CDCl_3$), δ: 0.81, 1.01 (both m, 2 H each, CH_2CH_2); 1.74 (tt, 1 H, CH in *cyclo*-C_3H_5, J_{cis} = 8.5 Hz, J_{trans} = = 5.2 Hz); 3.95 (s, 3 H, OMe); 6.50 (s, 1 H, H(4)); 7.18 (dd, 2 H, H_m, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,F}$ = 8.3 Hz); 7.60 (dd, 2 H, H_o, $^3J_{H,H}$ = = 9.0 Hz, $^4J_{H,F}$ = 4.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.5 (CH in *cyclo*-C_3H_5); 9.1 (CH_2CH_2); 52.1 (OMe); 105.3 (C(4)); 116.1 (d, C_m, $^2J_{C,F}$ = 22.7 Hz); 127.3 (d, C_o, $^3J_{C,F}$ = 8.3 Hz); 135.6 (d, C_{ipso}, $^4J_{C,F}$ = 2.2 Hz); 143.6 (C(3)); 147.9 (C(5)); 162.4 (d, C_p, $^1J_{C,F}$ = 248 Hz); 162.9 (COO). ^{19}F NMR ($CDCl_3$), δ: −113.3 (tt, ^3J = 8.3 Hz, ^4J = 4.8 Hz).

Methyl 5-cyclopropyl-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (8b) and methyl 5-cyclopropyl-1-(4-methoxyphenyl)-1*H*-pyrazole-3-carboxylate (9b). Dihydroindazole **2b** (0.25 g) and vinylcyclopropane (0.27 g) gave pyrazoline **8b** (53 mg, 48%) and pyrazole **9b** (26 mg, 24%).

Compound **8b**, colorless crystals, m.p. 112—113 °C (from C_6H_6—AcOEt, 10 : 1). Found (%): C, 65.31; H, 6.50; N, 10.01. $C_{15}H_{18}N_2O_3$. Calculated (%): C, 65.68; H, 6.61; N, 10.21. MS (EI), *m/z* (I_{rel} (%)): 274 $[M]^+$ (100), 259 $[M - Me]^+$ (10), 243 $[M - OMe]^+$ (8), 233 (15), 215 $[M - CO_2Me]^+$ (5), 201 (50), 189 (12), 174 (20), 160 (15), 146 (17), 134 (20), 122 (90). ^{1}H NMR ($CDCl_3$), δ: 0.24, 0.38, 0.50, 0.62 (all m, 1 H each, CH_2CH_2); 1.07 (m, 1 H, CH in *cyclo*-C_3H_5); 3.01 (dd, 1 H, H_a(4), ^2J = 18.0 Hz, ^3J = 6.1 Hz); 3.29 (dd, 1 H, H_b(4), ^2J = 18.0 Hz, ^3J = 12.0 Hz); 3.80, 3.87 (both s, 3 H each, 2 OMe); 4.06 (ddd, 1 H, H(5), ^3J = 6.1 Hz, ^3J = 8.0 Hz, ^3J = 12.0 Hz); 6.86 (d, 2 H, H_m, ^3J = 9.0 Hz); 7.23 (d, 2 H, H_o, ^3J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 1.8, 6.3 (CH_2CH_2); 15.2 (CH in *cyclo*-C_3H_5); 37.5 (C(4)); 52.1 (CO_2Me); 55.6 (OMe); 66.8 (C(5)); 114.3 (C_m); 118.3 (C_o); 137.0 (C(3)); 137.4 (C_{ipso}); 155.2 (C_p); 163.6 (COO).

Compound **9b**. MS (EI), *m/z* (I_{rel} (%)): 272 $[M]^+$ (100), 257 $[M - Me]^+$ (20), 241 $[M - OMe]^+$ (35), 225 (45), 213 $[M - CO_2Me]^+$ (25), 197 (22), 121 (33), 108 (25), 92 (37). ^{1}H NMR ($CDCl_3$), δ: 0.78, 0.98 (both m, 2 H each, CH_2CH_2); 1.73 (tt, 1 H, CH in *cyclo*-C_3H_5, J_{cis} = 8.5 Hz, J_{trans} = 5.1 Hz); 3.87 and 3.91 (both s, 3 H each, 2 OMe); 6.98 (d, 2 H, H_m, ^3J = 8.9 Hz); 7.50 (d, 2 H, H_o, ^3J = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.6 (CH in *cyclo*-C_3H_5); 9.0 (CH_2CH_2); 52.1 (CO_2Me); 55.6 (OMe); 104.9 (C(4)); 114.2 (C_m); 126.9 (C_o); 132.6 (C_{ipso}); 143.2 (C(3)); 147.9 (C(5)); 159.7 (C_p); 163.4 (COO).

Methyl 5-ethoxy-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (10) and methyl 1-(4-fluorophenyl)-1*H*-pyrazole-3-carboxylate (11). Dihydroindazole **2a** (0.24 g, 0.4 mmol) and ethyl vinyl ether (1.73 g, 24 mmol) after separation by column chromatography on SiO_2 (benzene—EtOAc, 8 : 1) gave a mixture of **10** and **11** (30 mg, molar ratio 1 : 0.7) and pyrazole **11** (41 mg), the total yield of which was ~60%.

Compound **10**. GLC-MS (EI), *m/z* (I_{rel} (%)): 266 $[M]^+$ (50), 235 $[M - OMe]^+$ (10), 221 $[M - OEt]^+$ (70), 190 (60), 177 (30), 109 (100). ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, Me, ^3J = 7.0 Hz); 3.18—3.39 (m, 4 H, H_2C(4), OCH_2); 3.89 (s, 3 H, OMe); 5.83 (dd, 1 H, H(5), ^3J = 3.5 Hz, ^3J = 8.7 Hz); 7.01 (dd, 2 H, H_m, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,F}$ = 8.2 Hz); 7.30 (dd, 2 H, H_o, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,F}$ = 4.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 15.0 (Me); 37.0 (C(4)); 52.3 (OMe); 59.1 (OCH_2); 88.8 (C(5)); 115.8 (d, C_m, $^2J_{C,F}$ = 22.5 Hz); 116.2 (C_o, $^3J_{C,F}$ = 8.0 Hz); 138.0 (d, C_{ipso}, $^4J_{C,F}$ = 2.3 Hz); 139.0 (C(3)); 158.1 (d, C_p, $^1J_{C,F}$ = 243 Hz); 162.7 (COO).

Compound **11**, colorless crystals, m.p. 101—102 °C (from C_6H_6). Found (%): C, 60.24; H, 4.08; N, 12.51. $C_{11}H_9FN_2O_2$. Calculated (%): C, 60.00; H, 4.12; N, 12.72. MS (EI), *m/z* (I_{rel} (%)): 220 $[M]^+$ (50), 189 $[M - OMe]^+$ (71), 162 (25), 134 (45), 107 (40), 95 (100). IR, ν/cm^{-1}: 2960, 1724 (COO), 1522, 1504. ^{1}H NMR ($CDCl_3$), δ: 3.99 (s, 3 H, OMe); 5.83 (dd, 1 H, H(5), ^3J = 3.5 Hz, ^3J = 8.7 Hz); 7.00 (d, 1 H, H(4), ^3J = 2.4 Hz); 7.17 (dd, 2 H, H_m, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,F}$ = 8.1 Hz); 7.71 (dd, 2 H, H_o, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,F}$ = 4.9 Hz); 7.88 (d, 1 H, H(5), ^3J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 52.2 (OMe); 110.6 (C(4)); 116.4 (d, C_m, $^2J_{C,F}$ = 22.7 Hz); 122.1 (C_o, $^3J_{C,F}$ = 8.5 Hz); 136.0 (d, C_{ipso}, $^4J_{C,F}$ = 2.2 Hz); 144.9 (C(3)); 147.9 (C(5)); 161.8 (d, C_p, $^1J_{C,F}$ = = 244 Hz); 162.6 (COO). ^{19}F NMR ($CDCl_3$), δ: −114.7 (tt, ^3J = = 8.1 Hz, ^4J = 4.9 Hz).

Methyl 2-isopropoxy-2-(4-methoxyphenyl)hydrazonoacetate (12). A mixture of dihydroindazole **2b** (0.18 g, 0.3 mmol) and Pr^iOH (3 mL) was heated for 10 h in a sealed tube under Ar at 130 °C. After evaporation of propan-2-ol, the target product was isolated by column chromatography on SiO_2 (benzene—EtOAc, 2 : 1). Hydrazone **12** (76 mg) was obtained with admixture of benzenehexacarboxylate **3** (9—10%) as a colorless oil. MS (EI), *m/z* (I_{rel} (%)): 266 $[M]^+$ (10), 224 (15), 164 (60), 149 (15), 137 (18), 122 (100), 84 (60). ^{1}H NMR ($CDCl_3$), δ: 1.35 (d, 6 H, 2 Me, ^3J = 7.0 Hz); 3.78, 3.87 (both s, 3 H each, 2 OMe); 4.88 (sept, 1 H, OCH, ^3J = 7.0 Hz); 6.85 (m, 2 H, H_m, ^3J = 9.0 Hz); 7.08 (m, 2 H, H_o, ^3J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 23.0 (2 Me); 52.5 (CO_2Me); 55.7 (OMe); 74.7 (OCH); 114.7 and 114.8 (C_o and C_m); 135.5 (C_{ipso}); 137.0 (C=N); 154.6 (C_p); 160.7 (COO).

The authors are grateful to Yu. A. Strelenko (IOCh RAS) for the methodical help in recording ^{1}H and ^{13}C NMR spectra on a Bruker DRX-500 spectrometer.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-00636).

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Received December 24, 2009;
in revised form February 24, 2010