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Reaction of Substituted 6,8-Dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylates and 6,8-Dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylates with *N*-Fluoropyridinium Tetrafluoroborate*

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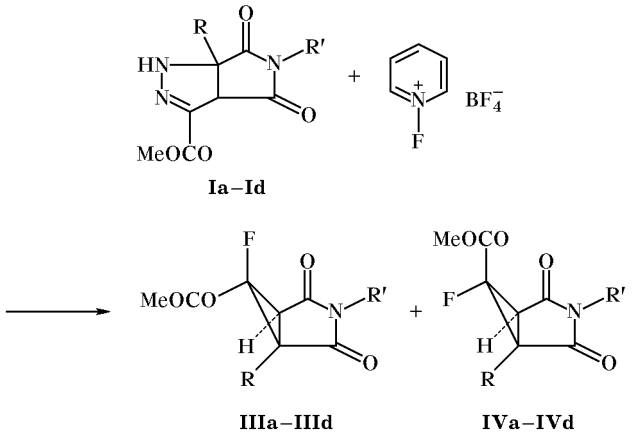
Abstract—Substituted 6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylates react with *N*-fluoropyridinium tetrafluoroborate to give mixtures of *exo* and *endo* isomers of 6-fluoro-2,4-dioxo-3-azabicyclo[3.1.0]-hexane-6-carboxylates. Analogous reaction of 6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylates results in formation of *syn,anti*-isomeric 1-fluoro-4,6-dioxo-5-azaspiro[2.4]heptane-1-carboxylates.

The most widely used methods for preparation of 1-fluorocyclopropanecarboxylates are the following: (1) reaction of carbon dioxide with lithium derivatives of 1-fluorocyclopropanes which are in turn obtained by treatment of 1-bromo-1-fluorocyclopropanes with organolithium compounds [1]; (2) reaction of olefins with fluoro(alkoxycarbonyl)carbene generated from bromo(fluoro)alkoxycarbonylmethyl(phenyl)mercury [2]; and (3) reaction of diazo compounds with α-fluoroacrylic acid esters [3]. 1-Fluorocyclopropanecarboxylates were also synthesized by addition of dichlorocarbene to α-fluoroacrylate [4] and by oxidation of perfluorinated olefins having a cyclopropane fragment [5]. The reaction of substituted 6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylates and 6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylates with halogens (chlorine and bromine) yields derivatives of 1-halocyclopropanecarboxylates [6, 7].

In the present work we examined the reaction of 7-aryl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylates **Ia**–**Id** and 6,8-dioxo-1,2,7-triazaspiro-[4.4]non-2-ene-3-carboxylates **IIa** and **IIb** with *N*-fluoropyridinium tetrafluoroborate as a source of electrophilic fluorine species [8]. The reaction of pyrrolopyrazoles **Ia**–**Id** with *N*-fluoropyridinium tetrafluoroborate was performed in acetonitrile at 80°C (reaction time 150 h; TLC monitoring). As a result, we obtained 10–15% (70–77% with respect to the reacted compound **I**) of 6-fluoro-2,4-dioxo-3-azabicyclo[3.1.0]hexane-6-carboxylates as mixtures of *exo* (**IIIa**–**IIId**) and *endo* isomers (**IVa**–**IVd**). The isomer ratio was 1.3:1 (**a**), 1:1.5 (**b**), 1.2:1 (**c**), and 1.2:1 (**d**) (Scheme 1).

Scheme 1.



I, **III**, **IV**, R = R′ = 4-$CH_3C_6H_4$ (**a**); R = 4-$CH_3C_6H_4$, R′ = 4-ClC_6H_4 (**b**); R = 4-ClC_6H_4, R′ = Ph (**c**); R = 4-ClC_6H_4, R′ = 4-$CH_3C_6H_4$ (**d**).

The structure of esters **IIIa**–**IIId** and **IVa**–**IVd** was determined on the basis of their elemental analyses

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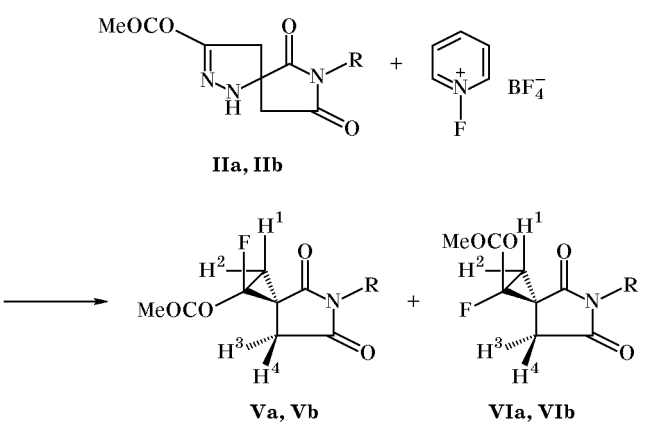
and spectral data. The IR spectra of these compounds contain an absorption band at 1720 cm^{-1} due to carbonyl stretching vibrations. *endo* Isomers **IVa**–**IVd** show in the ^1H NMR spectrum a doublet signal at δ 3.50 ppm with a coupling constant J_{HF} of 15 Hz (*cis*), which belongs to proton in the bridgehead position. No splitting of the corresponding signal was observed in the spectra of *exo* isomers **IIIa**–**IIId**, for the *trans*-constant J_{HF} is too small. In the ^{19}F NMR spectra of esters **III** and **IV**, a doublet signal from the fluorine atom in the *endo* isomer was present at δ_F –172 ppm (J_{FH} = 15 Hz), and a singlet fluorine signal of the *exo* isomer appeared at δ_F –199 ppm. The ^{13}C NMR spectra contained doublets from C^1, C^5, and C^6 at δ_C 47, 35, and 86 ppm (J = 13, 13, 260 Hz) for *exo* isomers **IIIa**–**IIId** and at δ_C 46, 36, and 81 ppm (J = 13, 13, 260 Hz) for *endo* isomers **IVa**–**IVd**. These data indicate that the fluorine atom is located at the three-membered ring.

By reaction of spiro pyrazoles **IIa** and **IIb** with *N*-fluoropyridinium tetrafluoroborate we obtained 12–18% of methyl 1-fluoro-4,6-dioxo-5-azaspiro[2.4]-heptan-1-carboxylates as mixtures of *syn* (**Va**, **Vb**) and *anti* isomers (**VIa**, **VIb**) at a ratio of 1.4:1 (**a**) and 2.0:1 (**b**) (Scheme 2).

Scheme 2.



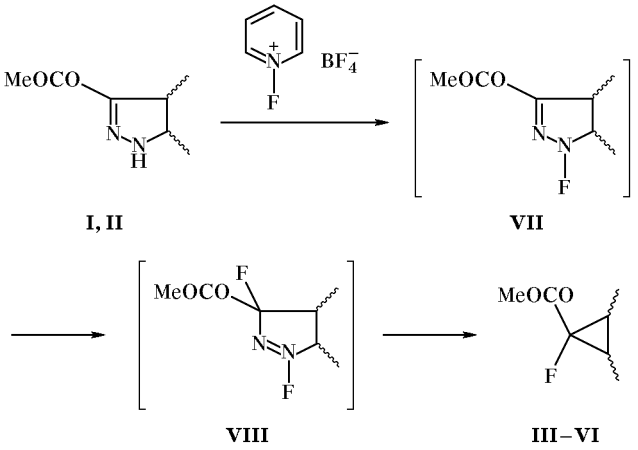
II, **V**, **VI**, R = Ph (**a**), 4-ClC_6H_4 (**b**).

The ^1H NMR spectra of esters **V** and **VI** contain signals from the 1-H and 2-H protons in the cyclopropane ring, δ, ppm (J_{HH}, J_{HF}, Hz): **Va**: 2.55 d.d (1-H, 6, 19), 2.05 d.d (2-H, 6, 10); **VIa**: 2.62 d.d (1-H, 7, 12), 1.87 d.d (2-H, 7, 18); **Vb**: 2.56 d.d (1-H, 7, 19), 2.06 d.d (2-H, 7, 10); **VIb**: 2.64 d.d (1-H, 7, 10), 1.89 d.d (2-H, 7, 17); and doublet signals belonging to the 3-H and 4-H methylene protons in the pyrrole ring: *syn* isomers: δ 2.90 (3-H, J = 19 Hz) and 3.10 ppm (4-H, J = 19 Hz); *anti* isomers: δ 2.90 (3-H, J = 19 Hz) and 3.30 ppm (4-H, J = 19 Hz). The 4-H signal is displaced downfield due to steric effect of the electron-acceptor *syn*-substituent in the cyclopropane ring (fluorine atom in *anti* isomers **VI** and methoxycarbonyl group in *syn* isomers **V**). In the ^{13}C NMR spectra of compounds **Va**, **Vb**, **VIa**, and **VIb** we observed doublet signals from carbon atoms of the cyclopropane ring, δ_C, ppm (J_{CF}, Hz): **Va**, **Vb**: 24.2 d (C^2, 10), 33.1 d (C^3, 9), 79.5 d (C^1, 256); **VIa**, **VIb**: 22.4 d (C^2, 8), 32.2 d (C^3, 12), 80.0 d (C^1, 238). The methylene group (C^7H_2) gives rise to a singlet at δ_C 35.0 ppm in the spectra of *syn* isomers **V** and to a doublet at δ_C 33.2 ppm (J = 7 Hz) in the spectra of *anti* isomers **VI**. It is seen that the C^7 signal is split into doublet when the methylene group and fluorine atom are located at the same side of the cyclopropane ring plane. An analogous pattern was observed in the ^{13}C NMR spectra of 1-fluoro-2-methylcyclopropanecarboxylic acid derivatives, where the methyl group in the *Z* isomers gives rise to a doublet (J_{CF} = 5.2 Hz), while that in the *E* isomers appears as a singlet [4]. The relative substituent configuration in the molecule of ester **Va** was proved by X-ray analysis (see figure). According to the X-ray diffraction data, the ester and imide ring methylene group are located at the same side of the cyclopropane ring plane. Table contains the principal bond lengths and bond and dihedral angles in molecule **Va**.

Fluorocyclopropanes **Vb** and **VIb** were also formed in a very poor yield (4 and 2%, respectively) in the reaction of spiro pyrazole **IIb** with (difluoroiodo)-benzene ($PhIF_2$).

Presumably, the mechanism of formation of fluorocyclopropanecarboxylates is analogous to that proposed in [6, 7] for chloro- and bromocyclopropanes. Electrophilic fluorination of pyrazole derivatives **I** and

Scheme 3.



Some bond lengths (*d*) and bond (ω) and dihedral angles (φ) in the molecule of methyl *syn*-1-fluoro-4,6-dioxo-5-phenyl-5-azaspiro[2.4]heptane-1-carboxylate (**Va**)

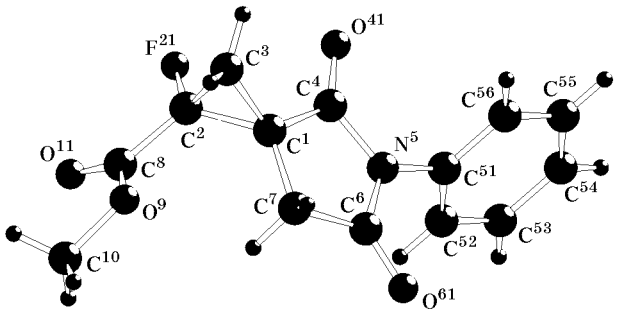
Bond	*d*, Å	Bond angle	ω, deg	Dihedral angle	φ, deg
C^1-C^2	1.526 (3)	$C^6N^5C^4$	112.8 (1)	$C^4C^1C^2F^{21}$	–2.1 (2)
C^1-C^3	1.506 (2)	$C^4N^5C^{51}$	122.5 (1)	$C^3C^1C^2F^{21}$	107.3 (2)
C^1-C^4	1.498 (2)	$C^4C^1C^3$	119.1 (1)	$C^7C^1C^2F^{21}$	–139.6 (2)
C^1-C^7	1.512 (2)	$C^4C^1C^7$	107.1 (1)	$C^4C^1C^2C^3$	–109.4 (2)
C^2-C^3	1.480 (3)	$C^3C^1C^7$	124.9 (1)	$C^7C^1C^2C^3$	113.1 (2)
$F^{21}-C^2$	1.367 (2)	$C^4C^1C^2$	116.4 (1)	$C^4C^1C^2C^8$	137.1 (2)
O^9-C^8	1.325 (3)	$C^3C^1C^2$	58.4 (1)	$C^3C^1C^2C^8$	–113.5 (2)
$O^{11}-C^8$	1.205 (2)	$F^{21}C^2C^3$	116.9 (1)	$C^7C^1C^2C^8$	–0.3 (3)
O^9-C^{10}	1.450 (2)	$F^{21}C^2C^8$	110.0 (1)	$F^{21}C^2C^3C^1$	–106.7 (2)
C^6-C^7	1.506 (2)	$C^3C^2C^8$	123.7 (2)	$C^8C^2C^3C^1$	110.1 (2)
$O^{41}-C^4$	1.202 (2)	$F^{21}C^2C^1$	116.6 (1)	$C^4C^1C^3C^2$	104.7 (2)
$O^{61}-C^6$	1.209 (2)	$C^3C^2C^1$	60.1 (1)	$C^7C^1C^3C^2$	–112.4 (2)
N^5-C^6	1.388 (2)	$C^8C^2C^1$	121.6 (1)	$C^6N^5C^4O^{41}$	176.2 (2)
N^5-C^4	1.403 (2)	$O^{41}C^4N^5$	124.8 (1)	$C^{51}N^5C^4O^{41}$	–7.0 (3)
N^5-C^{51}	1.438 (2)	$O^{41}C^4C^1$	128.5 (2)	$C^6N^5C^4C^1$	–3.4 (2)
C^2-C^8	1.495 (3)	$O^{61}C^6N^5$	124.9 (2)	$C^{51}N^5C^4C^1$	173.1 (1)
		$N^5C^6C^7$	108.8 (1)	$C^3C^2C^4O^{41}$	–25.7 (3)
		$C^6C^7C^1$	104.2 (1)	$C^7C^1C^4O^{41}$	–174.5 (2)

II gives *N*-fluorodihydropyrazoles **VII** which undergo rearrangement into 3-fluoro-3-methoxycarbonyl-3,4-dihydro-2*H*-pyrazoles **VIII**. The latter lose nitrogen molecule to give final cyclopropane derivatives **III**–**VI** (Scheme 3).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from 2% solutions in $CHCl_3$. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-300 instrument at 300 and 75 MHz, respectively, using $CDCl_3$ as solvent. The ^{19}F NMR spectra were obtained on a Bruker HA-500 spectrometer at 475 MHz using $CDCl_3$ as solvent and CCl_3F as reference. The purity of compounds was checked, and the reaction mixtures were analyzed, by TLC on Silufol UV-254 plates.

Methyl 6-fluoro-2,4-dioxo-1,3-bis(4-tolyl)-3-azabicyclo[3.1.0]hexane-6-carboxylate (IIIa/IVa). A mixture of 0.8 g (2.1 mmol) of methyl 6,8-dioxo-1,7-bis(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (**Ia**) and 0.5 g (2.7 mmol) of *N*-fluoropyridinium tetrafluoroborate in 20 ml of acetonitrile was heated for 150 h at 80°C under argon, the progress of the reaction being monitored by TLC. The solvent was distilled off under reduced pressure, and a mixture of diethyl ether with methylene chloride was added to the residue. The precipitate (unreacted ester **Ia** and *N*-fluoropyridinium tetrafluoroborate) was filtered off and washed with ether. The filtrate was evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (2:1, by volume) as eluent. Yield 0.1 g (13%). mp 109–111°C. IR spectrum, ν, cm^{-1}: 920, 1020, 1100, 1170, 1320, 1380, 1450, 1500, 1720 v.s, 3050. ^1H NMR spectrum, δ, ppm (*J*, Hz): **IIIa**: 2.39 s (6H), 3.65 s (3H), 3.84 s (1H), 7.12–7.52 (8H); **IVa**: 2.43 s (6H), 3.52 d (1H, 15), 3.95 s (3H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): **IIIa**: 21.5 (CH_3); 35.4 d (C^5, 13); 46.7 d (C^1, 13); 85.0 d (C^6, 260); 126.1; 128.9 d (2); 129.2, 130.4, 130.5, 139.1, 139.5, 139.8 (C_{arom}); 163.4 d (27); 168.3 d (5); 169.1 d (5) (C=O); **IVa**:



Structure of the molecule of methyl *syn*-1-fluoro-4,6-dioxo-5-phenyl-5-azaspiro[2.4]heptane-1-carboxylate (**Va**) according to the X-ray diffraction data.

21.5 (CH_3); 35.6 d (C^5, 12); 45.7 d (C^1, 12); 81.4 d (C^6, 250); 125.8, 129.0, 129.3, 130.2, 130.3, 139.0, 139.4, 140.1 (C_{arom}); 165.8 d (26); 168.3 d (5); 169.1 d (5) (C=O). ^{19}F NMR spectrum, δ_F, ppm (J_{FH}, Hz): **IIIa**: –199.7 s; **IVa**: –171.9 d (15). Found, %: C 68.52; H 5.07; N 3.69. $C_{21}H_{18}FNO_4$. Calculated, %: C 68.66; H 4.94; N 3.81.

Methyl 3-(4-chlorophenyl)-6-fluoro-2,4-dioxo-1-(4-tolyl)-3-azabicyclo[3.1.0]hexane-6-carboxylate (IIIb/IVb) was synthesized in a similar way from 0.8 g (2 mmol) of methyl 7-(4-chlorophenyl)-6,8-dioxo-1-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (**Ib**) and 0.45 g (2.4 mmol) of *N*-fluoropyridinium tetrafluoroborate. Yield 0.09 g (11%). mp 119–121°C. IR spectrum, ν, cm^{-1}: 1020, 1090, 1160, 1320, 1390, 1440, 1490, 1720 v.s, 3050. ^{1}N NMR spectrum, δ, ppm (*J*, Hz): **IIIb**: 2.37 s (3H), 3.64 s (3H), 3.84 s (1H), 7.22–7.48 (8H); **IVb**: 2.43 s (3H), 3.53 d (1H, 15), 3.94 s (3H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): **IIIb**: 21.7 (CH_3); 35.4 d (C^5, 13); 46.8 d (C^1, 13); 84.8 d (C^6, 261); 128.2, 129.6, 130.0, 130.2, 130.3, 130.5, 135.2, 140.0 (C_{arom}); 163.2 d (26), 165.8 d (6), 171.2 d (6) (C=O); **IVb**: 21.7 (CH_3); 35.6 d (C^5, 12); 45.8 d (C^1, 12); 81.2 d (C^6, 253); 128.1, 129.7, 129.8, 129.9, 130.2, 130.7, 135.0, 140.2 (C_{arom}); 165.7 d (25), 165.8 d (6), 171.2 d (6) (C=O). ^{19}F NMR spectrum, δ_F, ppm (J_{FH}, Hz): **IIIb**: –199.6 s; **IVb**: –172.2 d (15). Found, %: C 61.83; H 4.10; N 3.49. $C_{20}H_{15}ClFNO_4$. Calculated, %: C 61.95; H 3.90; N 3.61.

Methyl 1-(4-chlorophenyl)-6-fluoro-2,4-dioxo-3-phenyl-3-azabicyclo[3.1.0]hexan-6-carboxylate (IIIc/IVc) was synthesized in a similar way from 1 g (2.6 mmol) of methyl 1-(4-chlorophenyl)-6,8-dioxo-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (**Ic**) and 0.5 g (2.7 mmol) of *N*-fluoropyridinium tetrafluoroborate. Yield 0.09 g (9%). mp 159–161°C. IR spectrum, ν, cm^{-1}: 1020, 1090, 1160, 1310, 1380, 1450, 1500, 1590, 1730 v.s, 3050. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): **IIIc**: 3.65 s (3H), 3.85 s (1H), 7.24–7.45 (9H); **IVc**: 3.52 d (1H, 15), 3.93 s (3H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): **IIIc**: 35.3 d (C^5, 13); 46.2 d (C^1, 13); 85.4 d (C^6, 263); 126.2, 128.6, 128.7, 128.8 d (2), 129.0, 130.6, 131.1, 136.1 (C_{arom}); 163.1 d (26), 167.7 d (6), 168.5 d (6) (C=O); **IVc**: 35.6 d (C^5, 12); 45.1 d (C^1, 12); 81.2 d (C^6, 252); 126.0, 128.4, 128.5, 128.9, 129.7, 130.5 d (2), 132.1, 136.3 (C_{arom}); 165.4 d (25), 167.7 d (6), 168.5 d (6) (C=O). ^{19}F NMR spectrum, δ_F, ppm (J_{FH}, Hz): **IIIc**: –199.4 s; **IVc**: –171.8 d (15). Found, %: C 60.93; H 3.68; N 3.61. $C_{19}H_{13}SlFNO_4$. Calculated, %: C 61.06; H 3.51; N 3.81.

Methyl 1-(4-chlorophenyl)-6-fluoro-2,4-dioxo-3-(4-tolyl)-3-azabicyclo[3.1.0]hexan-6-carboxylate (IIId/IVd) was synthesized in a similar way from 0.56 g (1.4 mmol) of methyl 1-(4-chlorophenyl)-6,8-dioxo-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylate (**Id**) and 0.31 g (1.7 mmol) of *N*-fluoropyridinium tetrafluoroborate. Yield 0.08 g (15%). mp 132–134°C. IR spectrum, ν, cm^{-1}: 920, 1020, 1100, 1180, 1320, 1390, 1440, 1520, 1600, 1720 v.s, 3050. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): **IIId**: 2.40 s (3H), 3.65 s (3H), 3.84 s (1H), 7.13–7.53 (8H); **IVd**: 2.40 s (3H), 3.53 d (1H, 15), 3.95 s (3H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): **IIId**: 21.5 (CH_3); 35.4 d (C^5, 13); 46.2 d (C^1, 13); 84.6 d (C^6, 262); 126.0, 128.7, 129.7, 130.3 d (5), 131.7, 132.1, 136.0, 139.7 (C_{arom}); 163.2 d (26), 167.9 d (6), 168.8 d (6) (C=O); **IVd**: 21.5 (CH_3); 35.5 d (C^5, 12); 45.1 d (C^1, 12); 81.0 d (C^6, 252); 125.8, 128.8, 129.4, 129.6 d (4), 131.3 d (2), 132.8 d (2), 136.2, 139.4 (C_{arom}); 165.4 d (25), 167.9 d (6), 168.8 d (6) (C=O). ^{19}F NMR spectrum, δ_F, ppm (J_{FH}, Hz): **IIId**: –199.5 s; **IVd**: –171.7 d (15). Found, %: C 61.86; H 4.01; N 3.58. $C_{20}H_{15}ClFNO_4$. Calculated, %: C 61.95; H 3.90; N 3.61.

Methyl 1-fluoro-4,6-dioxo-5-phenyl-5-azaspiro-[2.4]heptane-1-carboxylate (Va/VIa). A mixture of 0.78 g (2.7 mmol) of methyl 6,8-dioxo-7-phenyl-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (**IIa**) and 0.5 g (2.7 mmol) of *N*-fluoropyridinium tetrafluoroborate in 25 ml of acetonitrile was heated for 180 h at 80°C under argon (TLC). The solvent was distilled off under reduced pressure, 20 ml of a 1:1 diethyl ether–methylene chloride mixture was added, and the mixture was heated for 20 min under reflux. It was then cooled for 1 h in a refrigerator, and the organic phase was separated by decanting from the viscous residue which, according to the TLC data, contained unreacted compound **IIa** and *N*-fluoropyridinium tetrafluoroborate together with tarry products. The solvent was evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (1.6:1, by volume) as eluent. We thus isolated 0.06 g (7%) of compound **Va**, mp 172–173°C, and 0.04 g (5%) of isomer **VIa**, mp 124–125°C. IR spectrum, ν, cm^{-1}: **Va**: 870, 910, 980, 1060,1090, 1180 s, 1330, 1390, 1450, 1510, 1600, 1720 v.s, 3050; **VIa**: 870, 920, 980, 1110, 1180 s, 1320, 1390, 1450, 1510, 1600, 1720 v.s, 3050; ^{1}H NMR spectrum, δ, ppm (*J*, Hz): **Va**: 2.05 d.d (1H, 6, 10), 2.55 d.d (1H, 6, 19), 2.91 d (1H, 19), 3.08 d (1H, 19), 3.95 s (3H), 7.27–7.53 (5H); **VIa**: 1.87 d.d (1H, 7, 18), 2.62 d.d (1H, 7, 12), 2.92 d (1H, 19), 3.29 d (1H, 19), 3.87 s (3H), 7.27–7.53

(5H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): **Va**: 24.2 d (C^2, 10); 33.1 d (C^3, 9); 35.0 (C^7); 54.0 (OCH_3); 79.8 d (C^1, 256); 126.8, 129.0, 129.9, 132.1 (C_{arom}); 167.3 d (23), 171.8, 173.7 (C=O); **VIa**: 22.3 d (C^2, 8); 32.3 d (C^3, 12); 33.4 d (C^7, 7); 53.9 (OCH_3); 80.4 d (C^1, 238); 126.7, 129.2, 129.8, 132.0 (C_{arom}); 164.6 d (27), 173.2, 173.4 d (3) (C=O). Found, %: C 60.84; H 4.58; N 5.08 (**Va**); C 60.86; H 4.52; N 5.12 (**VIa**). $C_{14}H_{12}FNO_4$. Calculated, %: C 60.65; H 4.36; N 5.05.

Methyl 5-(4-chlorophenyl)-1-fluoro-4,6-dioxo-5-azaspiro[2.4]heptane-1-carboxylate (Vb/VIb). *a*. The procedure was the same as that described above for compound **Va**/**VIa**. From 0.71 g (2.2 mmol) of methyl 7-(4-chlorophenyl)-6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylate (**IIb**) and 0.5 g (2.7 mmol) of *N*-fluoropyridinium tetrafluoroborate we obtained 0.08 g (12%) of compound **Vb**, mp 178–179°C, and 0.04 g (6%) of isomer **VIb**, mp 104–105°C. IR spectrum, ν, cm^{-1}: **Vb**: 870, 910, 980, 1020, 1100, 1160 s, 1320, 1380, 1450, 1500, 1720 v.s, 3050; **VIb**: 870, 920, 980, 1020, 1100, 1180 s, 1320, 1380, 1450, 1500, 1720 v.s, 3050. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): **Vb**: 2.06 d.d (1H, 7, 10), 2.56 d.d (1H, 7, 19), 2.91 d (1H, 19), 3.08 d (1H, 19), 3.93 s (3H), 7.28 d (2H, 8), 7.47 d (2H, 8); **VIb**: 1.89 d.d (1H, 7, 17), 2.64 d.d (1H, 7, 10), 2.95 d (1H, 19), 3.32 d (1H, 19), 3.87 s (3H), 7.26 d (2H, 8), 7.48 d (2H, 8). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): **Vb**: 24.2 d (C^2, 10); 33.0 d (C^3, 9); 34.8 (C^7); 53.9 (OCH_3); 79.7 d (C^1, 256); 128.0, 129.8, 130.5, 134.9 (C_{arom}); 167.2 d (23), 171.5, 173.3 (C=O); **VIb**: 22.4 d (C^2, 8); 32.2 d (C^3, 12); 33.3 d (C^7, 7); 53.8 (OCH_3); 80.2 d (C^1, 238); 128.0, 129.7, 130.5, 135.0 (C_{arom}); 164.7 d (27), 172.9, 173.2 d (3) (C=O). Found, %: C 53.78; H 3.83; N 4.56 (**Vb**); C 53.95; H 3.64; N 4.47 (**VIb**). $C_{14}H_{11}ClFNO_4$. Calculated, %: C 53.95; H 3.56; N 4.49.

b. A polyethylene vessel was charged with a suspension of 1.4 g of (dichloroiodo)benzene ($PhICl_2$) [9] and 1.4 g of yellow mercury oxide in 13 ml of methylene chloride, and 1.3 ml of 48% HF was carefully added with stirring. The mixture was vigorously stirred for 10 min, an additional 0.4 g of yellow mercury oxide was added, and the mixture was stirred for 15 min. The organic phase was separated by decanting, the residue was washed with 7 ml of methylene chloride, and the organic fractions were combined. The resulting solution of (difluoroiodo)benzene was used in further syntheses without additional purification. A polyethylene vessel was charged with a solution of 0.54 g (1.7 mmol) of compound **IIb** in 30 ml of methylene chloride, the solution was cooled to 0°C, and the above solution of (difluoroiodo)benzene was added with stirring over a period of 20 min. The cooling bath was removed, and the mixture was stirred for 4 h at room temperature. The mixture was then washed with two portions of a solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (1.6 : 1, by volume) as eluent. We isolated 0.02 g (4%) of compound **Vb** and 0.01 g (2%) of **VIb**.

X-Ray diffraction data of compound Va. Monoclinic crystals; $C_{14}H_{12}FNO_4$, *M* 277.25; crystal habit $0.60 \times 0.50 \times 0.30$ mm; unit cell parameters: a = 9.2014(9), b = 6.8317(7), c = 20.437(2) Å; α = 90.00, β = 94.41(0), γ = 90.00°; V = 1280.88(20) $Å^3$; Z = 4; d_{calc} = 1.438 g/cm^{-3}; μ = 0.078 mm^{-1}; space group $P2_1/c$ (no 14); F(000) = 576; irradiation source MoK_α, λ = 0.71073 Å; graphite monochromator. The complete set of data was included into the Cambridge Structural Database (CCDC-186671).

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