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SYNTHESIS OF ALKYL HEXAHYDROPYRAZINO-[1,2-*c*]PYRIMIDINE-9-CARBOXYLATES

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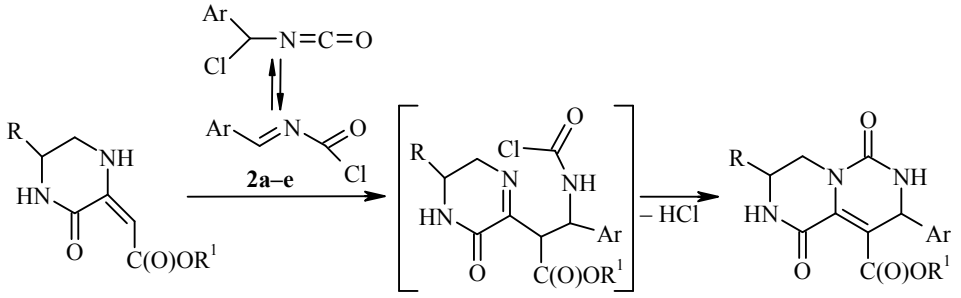
Cyclocondensation of 3-alkoxycarbonylmethylidenepiperazin-2-ones with α-chlorobenzyl isocyanates gave alkyl 8-aryl-1,6-dioxo-1,3,4,6,7,8-hexahydro-2H-pyrazino[1,2-c]pyrimidine-9-carboxylates. The use of 1-aryl-2,2,2-trifluoroethyl isocyanates in an analogous cyclization gave 6-aryl-1,8-dioxo-6-trifluoromethyl-1,3,4,6,7,8-hexahydro-2H-pyrazino[1,2-c]pyrimidine-9-carboxylates.

Keywords: 3-alkoxycarbonylmethylidenepiperazin-2-ones, 1-aryl-2,2,2-trifluoroethyl isocyanates, α-chlorobenzyl isocyanates, pyrazino[1,2-*c*]pyrimidine-9-carboxylates, cyclocondensation.

The pyrazino[1,2-c]pyrimidine heterocyclic system is characterized by pronounced pharmacological properties. In particular, 7-ethyl-2-methyloctahydro-6*H*-pyrazino[1,2-*c*]pyrimidin-6-one is the active component of the known antifilarial compound centperazine [1, 2]. In addition, there are found amongst substituted octahydropyrazino[1,2-*c*]pyrimidines compounds with high analgesic, anti-inflammatory, and anti-anorexic properties [3]. Recently, a series [4] of 1,6,8-trioxoperhydropyrazinopyrimidines has been proposed as novel, highly functionalized starting materials for peptidomimetics. It should be noted that the methods reported in the literature [1, 2, 5-7] for preparing pyrazino[1,2-*c*]pyrimidines are labor intensive and multistage and generally lead to the target materials in poor yields.



1a, 4a–e R = H, R^1 = Me; **1b, 4f–h** R = H, R^1 = Et; **1c, 4i** R = R^1 = Me; **1d, 4j** R = Me, R^1 = Et; **2a, 4a,i** Ar = Ph; **2b, 4b,f** Ar = 2-FC_6H_4; **2c, 4c,g,j** Ar = 3-BrC_6H_4; **2d, 4d** Ar = 4-$NO_2C_6H_4$; **2e, 4e,h** Ar = 3,4-$Cl_2C_6H_3$

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TABLE 1. Characteristics of Compounds **4a-j, 5a-d**

Compound	Empirical formula	Found, % / Calculated, %			$[M+H]^+$	mp, °C	Yield, %
		C	H	N			
4a	$C_{15}H_{15}N_3O_4$	59.44 / 59.80	5.16 / 5.02	14.09 / 13.95	302	290–292	72
4b	$C_{15}H_{14}FN_3O_4$	56.21 / 56.43	4.48 / 4.42	12.94 / 13.16	320	268–270	80
4c	$C_{15}H_{14}BrN_3O_4$	47.72 / 47.39	3.58 / 3.71	11.26 / 11.05	381	263–265	78
4d	$C_{15}H_{14}N_4O_6$	52.29 / 52.03	3.96 / 4.07	16.30 / 16.18	347	280–282	73
4e	$C_{15}H_{13}Cl_2N_3O_4$	48.91 / 48.67	3.67 / 3.54	11.52 / 11.35	370	288–290	70
4f	$C_{16}H_{16}FN_3O_4$	57.84 / 57.66	4.78 / 4.84	12.77 / 12.61	334	263–265	71
4g	$C_{16}H_{16}BrN_3O_4$	48.51 / 48.75	3.96 / 4.09	10.86 / 10.66	395	273–275	65
4h	$C_{16}H_{15}Cl_2N_3O_4$	50.31 / 50.02	4.05 / 3.94	11.11 / 10.94	384	260–262	63
4i	$C_{16}H_{17}N_3O_4$	61.17 / 60.94	5.36 / 5.43	13.09 / 13.33	316	> 300	65
4j	$C_{17}H_{18}BrN_3O_4$	49.81 / 50.02	4.53 / 4.44	10.16 / 10.29	409	282–284	69
5a	$C_{16}H_{13}F_4N_3O_4$	49.38 / 49.62	3.54 / 3.38	11.01 / 10.85	388	> 300	56
5b	$C_{17}H_{16}F_3N_3O_4$	53.09 / 53.27	4.35 / 4.21	10.83 / 10.96	384	280–282	39
5c	$C_{17}H_{16}F_3N_3O_4$	53.48 / 53.27	4.14 / 4.21	11.05 / 10.96	384	285–287	45
5d	$C_{17}H_{15}F_4N_3O_4$	50.61 / 50.88	3.64 / 3.77	10.61 / 10.47	402	288–290	62

With the aim of developing an efficient method for the synthesis of polyfunctional pyrazino[1,2-*c*]-pyrimidines as key starting materials in a rational search for bioactive compounds, we have proposed a convenient method for preparing novel pyrazino[1,2-*c*]pyrimidine-9-carboxylic acid derivatives. This route is based on the previously tested [8-10] principle of forming the pyrimidine ring *via* condensation of [–C=C–N–] binucleophiles and [–C–N=C–] bielectrophiles using the scheme given above. Initially for this task, we selected the preparatively available [11-13] 3-alkoxycarbonylmethylidenepiperazin-2-ones **1a-d** as the first and the α-chloroalkyl isocyanates **2a-e**, **3a-c** as the second.

It was found that refluxing the methylidene-substituted piperazin-2-ones **1a-d** with the α-chlorobenzyl isocyanates **2a-e** in dichloromethane is accompanied by formation of good yields of the alkyl 8-aryl-1,6-dioxo-1,3,4,6,7,8-hexahydro-2*H*-pyrazino[1,2-*c*]pyrimidine-9-carboxylates **4a-j** (Table 1). It is most likely that this reaction occurs by initial addition of the nucleophilic carbon atom of the exocyclic alkoxycarbonyl- methylidene group of compounds **1a-d** to the C=N bond of the *N*-chloroformylimino form [14] of the isocyanates **2a-e** *via* a diazadiene mechanism [15] to yield the intermediates **A** (which then cyclize to the target compounds **4a-j**).

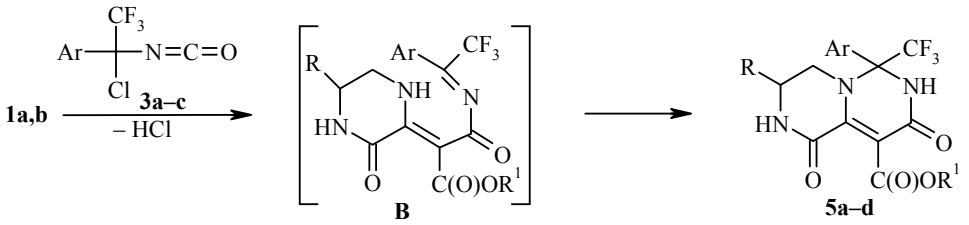
When studying the reaction of piperazin-2-ones **1a,b** with the 1-aryl-2,2,2-trifluoroethyl isocyanates **3a-c** we obtained a qualitatively different result. Hence refluxing the reagents in toluene gave the 6-aryl-1,8-dioxo-6-trifluoromethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrazino[1,2-*c*]pyrimidine-9-carboxylic acid esters **5a-d**. With the previously revealed [6] dependence of the reaction of isocyanates of type **3a-c** and *N*-substituted

TABLE 2. ^{1}H NMR Spectra of Compounds **4a-j, 5a-d***

Compound	Chemical shifts, δ, ppm (*J*, Hz)
4a	3.36-3.48 (3H, m, CH_2, CH); 3.50 (3H, s, CH_3); 3.76-3.83 (1H, m, CH); 5.07 (1H, d, *J* = 2.1, H-8); 7.24-7.35 (5H, m, H Ar); 7.82 (1H, d, *J* = 2.1, H-7); 8.49 (1H, s, H-2)
4b	3.34-3.44 (3H, m, CH_2, CH); 3.47 (3H, s, CH_3); 3.78-3.84 (1H, m, CH); 5.33 (1H, d, *J* = 2.2, H-8); 7.08-7.32 (4H, m, H Ar); 7.76 (1H, d, *J* = 2.2, H-7); 8.49 (1H, s, H-2)
4c	3.32-3.44 (3H, m, CH_2, CH); 3.50 (3H, s, CH_3); 3.75-3.81 (1H, m, CH); 5.11 (1H, d, *J* = 2.1, H-8); 7.22-7.48 (4H, m, H Ar); 7.90 (1H, d, *J* = 2.1, H-7); 8.54 (1H, s, H-2)
4d	3.36-3.47 (3H, m, CH_2, CH); 3.49 (3H, s, CH_3); 3.79-3.86 (1H, m, CH); 5.25 (1H, d, *J* = 2.2, H-8); 7.54 (2H, d, *J* = 9.0, H Ar); 8.09 (1H, d, *J* = 2.2, H-7); 8.20 (2H, d, *J* = 9.0, H Ar); 8.55 (1H, s, H-2)
4e	3.34-3.49 (3H, m, CH_2, CH); 3.50 (3H, s, CH_3); 3.76-3.82 (1H, m, CH); 5.12 (1H, d, *J* = 2.1, H-8); 7.24-7.28 (1H, m, H Ar); 7.45 (1H, d, *J* = 2.4, H Ar); 7.55 (1H, d, *J* = 7.6, H Ar); 7.91 (1H, d, *J* = 2.1, H-7); 8.54 (1H, s, H-2)
4f	0.99 (3H, t, *J* = 7.0, CH_3); 3.33-3.48 (3H, m) and 3.81-3.97 (3H, m, $3CH_2$); 5.36 (1H, d, *J* = 2.0, H-8); 7.21-7.37 (4H, m, H Ar); 7.83 (1H, d, *J* = 2.0, H-7); 8.54 (1H, s, H-2)
4g	1.05 (3H, t, *J* = 7.5, CH_3); 3.26-3.32 (3H, m, CH_2, CH); 3.76-3.96 (3H, m, CH_2O, CH); 5.09 (1H, d, *J* = 2.1, H-8); 7.28-7.47 (4H, m, H Ar); 7.86 (1H, d, *J* = 2.1, H-7); 8.51 (1H, s, H-2)
4h	1.02 (3H, t, *J* = 7.0, CH_3); 3.37-3.47 (3H, m, CH_2, CH); 3.75-3.98 (3H, m, CH_2O, CH); 5.19 (1H, d, *J* = 2.1, H-8); 7.30 (1H, d, *J* = 8.0, H Ar); 7.52 (1H, s, H Ar); 7.64 (1H, d, *J* = 8.0, H Ar); 7.95 (1H, d, *J* = 2.1, H-7); 8.57 (1H, s, H-2)
4i	1.11-1.18 (3H, m, CH_3); 2.78-2.98 (1H, m, CH); 3.57 and 3.60 (3H, two s, CH_3O); 3.62-3.85 (2H, m, CH_2); 5.07 and 5.12 (1H, two d, *J* = 2.0, H-8); 7.24-7.37 (5H, m, H Ar); 7.82 and 7.86 (1H, two d, *J* = 2.0, H-7); 8.55 (1H, s, H-2)
4j	1.02-1.08 (3H, m, CH_3); 1.16-1.19 (3H, m, CH_3); 2.86-3.01 (1H, m) and 3.59-3.92 (4H, m, CH, CH_2, CH_2O); 5.05 and 5.11 (1H, two d, *J* = 2.0, H-8); 7.28-7.45 (4H, m, H Ar); 7.87 and 7.90 (1H, two d, *J* = 2.0, H-7); 8.56 (1H, s, H-2)
5a	2.86-3.34 (4H, m, CH_2); 3.59 (3H, s, CH_3O); 7.34-4.41 (2H, m, H Ar); 7.70-7.75 (2H, m, H Ar); 8.80 (1H, s, NH); 8.99 (1H, s, NH)
5b	2.37 (3H, s, CH_3); 2.84-3.28 (4H, m, CH_2); 3.60 (3H, s, CH_3O); 7.30 (2H, d, *J* = 7.2, H Ar); 7.52 (2H, d, *J* = 7.2, H Ar); 8.70 (1H, s, NH); 8.83 (1H, s, NH)
5c	1.24 (3H, t, *J* = 6.5, CH_3); 2.84-3.32 (4H, m, CH_2); 4.08 (2H, q, *J* = 6.5, CH_2O); 7.36-7.42 (2H, m, H Ar); 7.64-7.70 (3H, m, H Ar); 8.72 (1H, s, NH); 8.90 (1H, s, NH)
5d	1.25 (3H, t, *J* = 6.5, CH_3); 2.88-3.35 (4H, m, CH_2); 4.10 (2H, q, *J* = 6.5, CH_2O); 7.29-7.35 (2H, m, H Ar); 7.71-7.74 (2H, m, H Ar); 8.70 (1H, s, NH); 8.90 (1H, s, NH)

* ^{19}F NMR spectra, δ, ppm: **5a** -111.49 (1F, s, 4-FC_6H_4), -75.49 (3F, s, CF_3); **5b** -74.50 (3F, s, CF_3); **5c** -74.99 (3F, s, CF_3); **5d** -111.07 (1F, s, 4-FC_6H_4), -75.02 (3F, s, CF_3).

aminocrotonates in mind, it can be reliably proposed that, in this case, a *C*-carbamoylation occurs of the enamine fragment of compounds **1a,b** to form the intermediate *N*-alkylidenecarbamoyl structured products **B** which tend to cyclize to the products **5a-d** at increased temperature. Such a scheme is confirmed by the observation of lowered yields of compounds **5b** (Ar = 4-MeC_6H_4) and **5c** (Ar = Ph) due to the decreased electrophilicity of the azomethine bond in the intermediates **B** resulting from the effect of the indicated donor aryl substituents.



5a,b R = H, R^1 = Me; **5c,d** R = H, R^1 = Et; **3a, 5c** Ar = Ph; **3b, 5a,d** Ar = 4-FC_6H_4; **3c, 5b** Ar = 4-MeC_6H_4

The composition and structure of the synthesized compounds was confirmed from elemental analysis, chromato-mass spectra, and from their IR, ^{1}H NMR, and ^{13}C NMR spectra. For compounds **4a-j,** the formation of a partially hydrogenated pyrimidine ring is indicated by the presence in the ^{1}H NMR spectra of doublets for the H-7 and H-8 protons in the ranges 7.82-8.09 and 5.07-5.33 ppm with spin-spin coupling 2.0-2.2 Hz and by the C-8 atom signals in the ^{13}C NMR spectra at 50-56 ppm (Table 2).

In turn, the ^{1}H NMR spectra of compounds **4i,j**, with the two asymmetric carbon centers at the C-3 and C-8 atoms, show doubling of the signals for virtually all of the substituents pointing to their existence as an approximately equal amount of two diastereomers.

The solid state IR spectra (KBr tablets) of compounds **4a-j** show three sets of bands in the C=O group absorption region for the C(O)OR^1, NHC(O), and NC (O)NH groups (Table 3). The two latter bands overlap strongly with one another and the lower-frequency band appears as a shoulder on the higher. The NH group absorption region is characterized by two sets of bands. In dichloromethane solution, the lower-frequency band for the C=O group absorption is lost but the medium- and higher-frequency bands remain unchanged. In the NH group absorption region, the NH bands characteristic for the solid state disappear and a new band at 3410-3415 cm^{-1} appears. It is thus very likely that the solid state of the studied compounds exist as associates involving both NHC(O) groups. The carbamoyl group of the pyrazine ring is bound in an associate to the carbamoyl group of another molecule and the ureido NHC(O) fragment of the pyrimidine ring with the ureido group of another molecule.

TABLE 3. IR Spectra of Compounds **4a-j**, **5a-d**

Compound	ν, cm^{-1}				
	NHC(O)	NHC(O)	C(O)OR^1	N–H	
	KBr			KBr	CH_2Cl_2
4a	1677	1689	1725	3080, 3210	3410
4b	1677	1689	1729	3079, 3205	3412
4c	1685	1695	1730	3085, 3210	3414
4d	1677	1687	1722	3080, 3210	3412
4e	1675	1687	1725	3070, 3200	3415
4f	1679	1690	1726	3080, 3210	3412
4g	1686	1693	1730	3085, 3210	3414
4h	1677	1688	1723	3080, 3215	3415
4i	1680	1690	1725	3080, 3210	3410
4j	1685	1695	1728	3080, 3210	3412
5a	1645	1680	1720	3130, 3220	
5b	1640	1670	1720	3115, 3220	
5c	1645	1675	1720	3120, 3230	
5d	1640	1675	1725	3125, 3220	

TABLE 4. ^{13}C NMR Spectra of Compounds **4a–h, 5a–d**

Compound	Chemical shifts, δ, ppm (*J*, Hz)										
	CH_3	C-3,4	CH_2O	C-8	C-9	CF_3	C_{Ar}	C-9a	C-6	C(O)O	C-1
4a	52.3	38.6; 40.6	—	55.8	112.5	—	127.1; 128.6; 129.2; 131.0	142.1	151.9	159.2	167.7
4b	52.3	38.6; 41.0	—	50.4	111.0	—	116.0; 125.4; 129.0; 129.1; 130.7; 159.7 (d, J_{C-F} = 244.5)	151.8	159.1	160.9	167.3
4c	52.4	38.6; 40.8	—	55.1	111.6	—	122.3; 126.3; 128.0; 130.0; 131.0; 131.4	144.7	151.7	159.0	167.5
4d	54.5	38.1; 41.1	—	51.9	110.6	—	123.8; 128.0; 131.2; 147.2	148.6	151.1	158.4	166.8
4e	54.6	38.6; 40.8	—	52.4	111.2	—	127.6; 129.4; 131.2; 131.4; 131.5; 131.6	143.1	151.6	158.9	167.4
4f	13.47	38.2; 41.1	60.3	50.0	111.0	—	115.4; 124.8; 128.6; 130.0; 130.1; 159.4 (d, J_{C-F} = 246.5)	130.2	151.3	158.5	166.7
4g	14.04	38.6; 41.1	60.8	55.4	112.2	—	122.2; 126.3; 130.0; 130.7; 131.3; 131.4	144.6	151.7	158.9	166.9
4h	13.48	37.8; 40.7	60.3	54.3	111.1	—	127.2; 128.9; 130.4; 130.6; 130.8; 131.0	142.5	151.1	158.3	166.2
5a	51.6	38.2; 43.5	—	157.9	102.8	124.6 (q, J = 296.8)	115.8 (d, J_{C-F} = 22.6); 130.3; 130.8; 62.6 (d, J_{C-F} = 251.2)	142.0	78.2 (q, J = 29.2)	160.1	165.2
5b	51.1	38.2; 43.4	—	157.7	102.8	124.3 (q, J = 298.1)	127.8; 129.1; 131.6; 139.5	141.6	78.2 (q, J = 29.6)	159.9	164.9
5c	13.41	38.2; 43.4	59.9	157.7	103.2	124.8 (q, J = 298.1)	127.3; 128.5; 129.9; 134.6	141.4	78.4 (q, J = 30.2)	159.9	164.4
5d	13.47	38.2; 43.4	59.9	157.7	103.8	124.8 (q, J = 296.8)	115.7 (d, J_{C-F} = 21.4); 130.2; 130.8; 62.6 (d, J_{C-F} = 249.0)	141.5	77.9 (q, J = 30.2)	160.0	164.4

The formation of the 1,8-dioxopyrazino[1,2-*c*]pyrimidine-9-carboxylic acid derivatives **5a-d** agrees with ^{19}F NMR spectroscopic data in which the presence of CF_3 group fluorine atoms indicates its position in an aminal N–C(CF_3)Ar–NH fragment [16, 17]. The ^{13}C NMR spectroscopic signals for the C-6 atom appears as a quartet indicating its tetracoordinate character [18].

Hence regioselective cyclocondensations of 3-alkoxycarbonylmethylidenepiperazin-2-ones with chlorobenzyl isocyanates appears to be a convenient method for the synthesis of the structurally related 1,6-dioxo- and 1,8-dioxopyrazino[1,2-*c*]pyrimidine-9-carboxylates and these are promising subjects for further chemical biological investigation.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument as KBr tablets and in dichloromethane. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer (500 and 125 MHz respectively) for solutions in DMSO-d_6 with TMS as internal standard. ^{19}F NMR spectra were taken on a Varian Gemini-2000 spectrometer (188 MHz) using DMSO-d_6 with CCl_3F as internal standard. Chromato-mass spectra were obtained on an Agilent 1100 series instrument. Zorbax SB-C18 column, 1.8 μ, 4.6×15 mm. Ionization method: atmospheric pressure chemical ionization.

3-Alkoxycarbonylmethylidenepiperazin-2-ones **1a-d** were synthesized by method [11]. The α-chlorobenzyl isocyanates **2a-e** and 1-aryl-1-chloro-2,2,2-trifluoroethyl isocyanates **3a-c** were obtained by methods [9] and [19] respectively.

Alkyl 8-Aryl-1,6-dioxo-1,3,4,6,7,8-hexahydro-2*H*-pyrazino[1,2-*c*]pyrimidine-9-carboxylates (4a-j). The isocyanate **2** (2.0 mmol) in dichloromethane (5 ml) was added to a solution of the corresponding piperazine **1** (2.0 mmol) in dichloromethane (20 ml) and refluxed for 1.5 h. The reaction mixture was cooled and the precipitated product was filtered off, dried, and crystallized from ethanol.

Alkyl 6-Aryl-1,8-dioxo-6-trifluoromethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrazino[1,2-*c*]pyrimidine-9-carboxylates 5a-d. The corresponding isocyanate **3** (2.0 mmol) in toluene (5 ml) was added to a solution of the corresponding piperazine **1** (2.0 mmol) in toluene (15 ml) and refluxed for 9 h. The reaction mixture was cooled and the precipitate was filtered off, dried, and crystallized from ethanol.

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