Synthesis and Spectroscopic Characterizations of both 1-Ethyl-4,8-dihydro-10-methoxy-3-methyl-8-R_1-6-R_2-dipyrazolo[3,4-*b*:4',3'-*f*]-[1,5]diazocin-5(1*H*)-ones and 1-Ethyl-1,4,8,9-tetrahydro-3,9-dimethyl-8-R_1-6-R_2-dipyrazolo[3,4-*b*:4',3'-*f*][1,5]diazocine-5,10-diones of Pharmaceutical Interest

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The non-selective methylation of compounds **3a-d** using ethereal diazomethane, allowed the synthesis of isomers **4** and **5** which were useful intermediates for the preparation, by a simple approach, of the title compounds **7** and **9**. A complete assignment of the chemical shifts to the carbon atoms of the compounds **7** and **9** was performed by different nmr experiments, such as DEPT and XHDEPT for one-bond C-H correlations and COLOC experiments for long-range C-H correlations.

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Introduction.

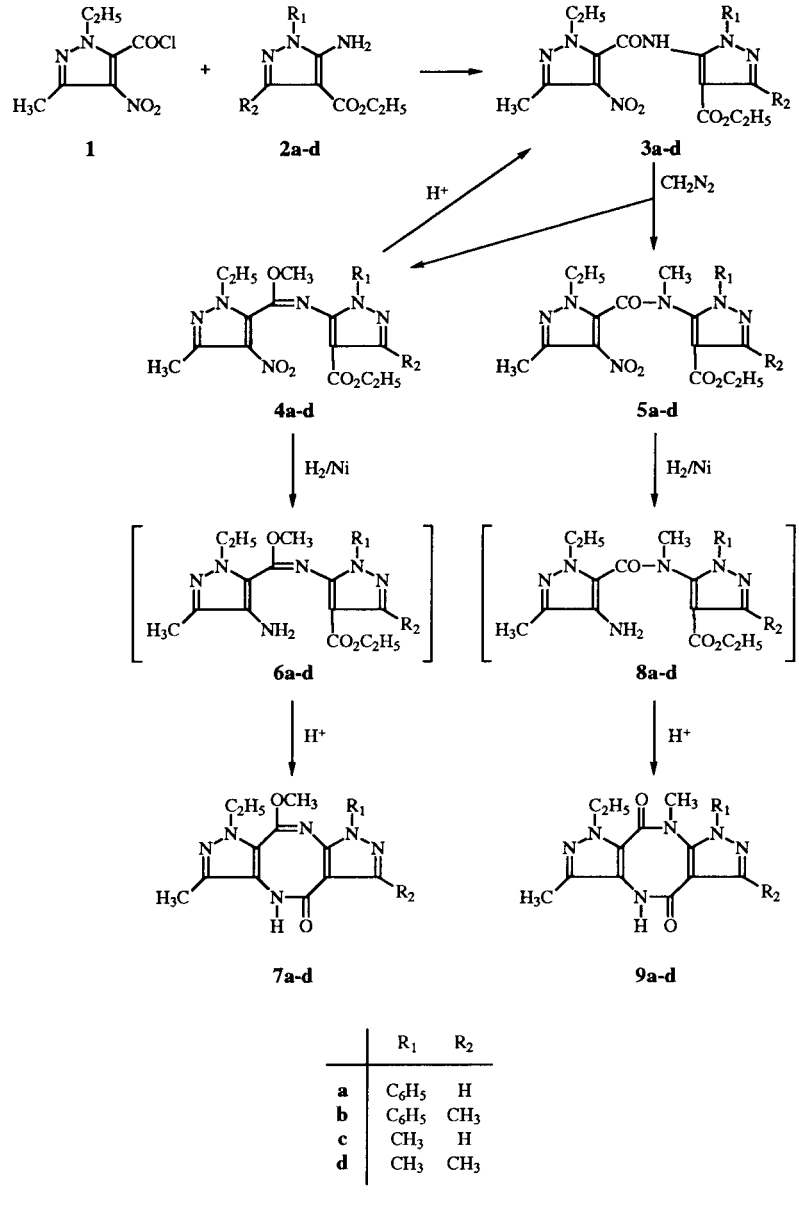
In the course of our investigation towards the design and synthesis of novel potentially active agents on CNS related to 8,9-dihydrodipyrazolo[3,4-*b*:4',3'-*f*][1,5]diazocin-10(1*H*)-one derivatives [1], compounds **3a-d** were needed as valuable key intermediates for the synthesis of model compounds **7a-d** and **9a-d**.

In this paper we report a simple and quick approach to the title compounds. A common feature of all of these transformations (see Scheme) is the non-selective methylation of **3a-d** using ethereal diazomethane [2-3], in fact compounds **4a-d** and **5a-d** were obtained. Particularly, the structure of compounds **4**, was confirmed on the basis of chemical behavior, in fact all products **4**, in hydrochloric acid medium gave compounds **3**. Catalytic reduction, over Raney nickel, of compounds **4a-d** and **5a-d** afforded the products **6a-d** and **8a-d**, respectively, which were not isolated but directly converted, in acidic medium, into **7a-d** and **9a-d**, respectively.

The nmr spectra in deuteriodimethyl sulfoxide solutions of compounds **3**, **4** and **5** were in accord with the assigned structures. The ^1H and ^{13}C nmr chemical shifts are reported in Table 1. The assignment of the chemical shifts in the fully proton decoupled ^{13}C nmr spectra of all the examined compounds was made on the basis of both known substituent effects and DEPT-135 experiments and confirmed by ^{13}C-^1H heterocorrelated spectra which provided for both one-bond and long-range C-H interactions [4]. In particular, both ^1H and ^{13}C spectra of **4** and **5** were well characterized by the signals of the C(=N)OCH_3 and C(=O)NCH_3 sequences, respectively (Table 1). Also the signals of the neighboring carbon atoms showed marked differences in the two series of compounds, being the signals of C-5 and C-5' for **5** deshielded and shielded, respectively, of *ca.* 4 ppm with respect to the corresponding carbons for **4**, whereas the signal of C-4' for 5 resulted downfield shifted of *ca.* 7 ppm with respect to the signal of C-4' for **4**. In addition, both ^1H and ^{13}C nmr spectra of **5** showed doubled signals for each atom or group, providing evidence for the presence of two conformation isomers due to the partial double bond character of the C-N bond. Thus, two signals were detected for the NCH_3 carbon atom, the downfield one being more abundant in all derivatives. According to the literature [5], the downfield resonance was assigned to the conformer bearing the methyl group *anti* to the carbonyl. Also the carbonyl carbon resonance of the more abundant conformer resulted in a downfield shift with respect to the corresponding isomer. The relative abundances of the two conformers were 35:65 for **5a,b** and 20:80 for **5c,d**. Proton and carbon chemical shift values of the less abundant isomer are reported in parentheses in Table 1.

As expected, also the nmr spectra of **7** and **9** (Table 2) were characterized by the signals of the C(=N)OCH_3 and C(=O)NCH_3 groups, respectively. Once again the signals of C-5a and C-10a for **7** were deshielded when compared to the corresponding carbons for **9** and the signal of C-8a shielded for **7** with respect to **9**. A complete assignment of the chemical shifts to the carbon atoms in both **7** and **9** was possible performing different 2D nmr experiments, such as XHDEPT or COLOC sequences for one-bond or long-range C-H correlations, respectively. Thus, *e.g.*, COLOC experiments performed for **7** gave evidence of the C-H interactions of C-3a, C-5, C-5a and C-10a with the NH proton, together with interactions of either C-10a with *N*-methylene protons or C-3, C-3a and C-10a with the methyl protons at C-3, thus allowing the assignment of the signals of the quaternary carbon atoms C-3a and C-10a.

Lastly, it is noteworthy that the ^1H spectra of compounds **5a,b** exhibited two different signals for the protons of the *N*-ethyl group, which resulted from magnetic non-equivalence due to hindered rotation around to the N-C bond. Two



	R_1	R_2
a	C_6H_5	H
b	C_6H_5	CH_3
c	CH_3	H
d	CH_3	CH_3

different signals for the *N*-methylene protons appeared also in the proton spectra of both **7a,b** and **9c,d**. This behavior was observed in strictly correlated diazocine derivatives previously reported [1], for which a small increase in temperature produced coalescence of the signals.

EXPERIMENTAL

Melting points were measured in open capillary tubes, using a Buchi-Tottoli immersion apparatus, and are uncorrected. The ir spectra were recorded on a Perkin-Elmer Infracord 137 spectrophotometer as nujol mulls. The ^1H and ^{13}C nmr spectra were recorded on a Bruker AC 250 spectrometer operating in FT mode at 250.13 and 62.89 MHz, respectively, in 0.1 *M* dimethyl sulfoxide-d_6 solutions on a switchable $^1H/^{13}C$ 5 mm probe. TMS was used as an internal standard. The ^{13}C nmr chemical shift values were measured from proton fully decoupled spectra. The assignment was supported by both DEPT-135 and 2D C-H correlation experiments. Typical conditions for ^1H nmr spectra were: spectral width 3760 Hz; number of data points 16 K, giving a digital resolution of 0.5 Hz/point; pulse width 6.6 μs (flip angle 90°); acquisition time 2.1 s. No exponential line broadening function was used. Typical conditions for ^{13}C nmr spectra were: spectral width 11320 Hz; number of data points 32 K (zero-filled to 64 K), giving a digital resolution of 0.4 Hz/point; pulse width 3 μs (flip angle of 90° was 6.3 μs); acquisition time 1.4 s; relaxation delay 2.2 s; number of scans 1 K. Exponential multiplication equivalent to a line broadening of 1.0 Hz was applied to the FIDs before Fourier transformation. Two-dimensional nmr experiments were performed using the standard Bruker pulse sequences XHDEPT.AUR and COLOC.AUR, for one-bond (160.0 or 130.0

Table 1

^{13}C and ^{1}H NMR Chemical Shift Values of Compounds **3-5** [a]

	3a	**3b**	**3c**	**3d**	**4a**	**4b**	**4c**	**4d**	**5a**	**5b**	**5c**	**5d**
C-3	144.5	144.4	144.5	144.4	144.7	144.8	144.7	144.7	145.1 (144.3)	145.2 (144.3)	145.4 (144.4)	145.3 (144.5)
C-4	129.8	129.7	130.1	130.1	129.5	129.7	129.9	130.0	129.6 (129.2)	129.6 (129.3)	129.8 (129.4)	129.6 (129.2)
C-5	135.7	135.6	136.0	136.0	130.3	130.5	130.8	131.0	134.4 (133.5)	134.5 (133.5)	135.0 (134.1)	135.0 (134.3)
C-3'	141.4 8.21	150.0	139.8 7.92	148.6	141.1 7.87	149.4	139.5 7.59	147.8	141.9 8.24 (141.4) (8.09)	151.0	140.1 7.97 (140.2) (7.78)	148.9 (149.0)
C-4'	109.6	107.5	108.0	105.6	101.9	100.7	100.7	99.1	109.0 (110.0)	107.0 (107.5)	108.0 (108.3)	105.5 (106.2)
C-5'	135.9	136.3	136.1	136.6	144.5	145.0	145.0	145.6	140.6 (139.5)	141.3 (140.0)	140.3 (140.2)	140.7 (140.7)
CO	157.2	157.0	157.2	157.1					159.4 (158.3)	159.4 (158.3)	159.8 (159.2)	159.6 (159.0)
NH	11.59	11.46	11.51	11.44								
NCH_3									37.9 3.50 (37.7) (3.13)	38.2 3.48 (37.6) (3.12)	37.3 3.24 (35.8) (3.41)	37.1 3.19 (35.2) (3.36)
C=N					152.9	152.4	153.3	152.8				
OCH_3					56.3 4.08	56.2 4.06	56.1 4.18	56.0 4.14				
N1$CH_2$$CH_3$	46.1 4.16	46.0 4.05	46.2 4.31	46.2 4.29	47.5 4.06	47.3 4.04	47.7 4.18	47.5 4.15	45.2 2.99 [b] (46.1) (4.33)	45.2 2.93 [b] (46.3) (4.31)	46.2 4.27 (46.8) (4.30)	46.1 4.24 (46.5) (4.29)
N1$CH_2$$CH_3$	15.1 1.33	15.0 1.29	15.0 1.43	14.9 1.42	14.3 1.41	14.3 1.36	14.2 1.46	14.2 1.43	14.7 1.03 [c] (14.5) (1.39)	14.7 1.02 [c] (14.9) (1.40)	14.7 1.44 (14.5) (1.36)	14.6 1.40 (14.4) (1.32)
C-3CH_3	13.2 2.47	13.2 2.45	13.1 2.51	13.1 2.50	13.1 2.35	13.1 2.35	13.0 2.34	13.0 2.35	13.1 2.45 (12.7) (2.29)	13.3 2.45 (12.8) (2.29)	13.2 2.53 (12.7) (2.30)	13.1 2.51 (12.7) (2.30)
$CO_2CH_2CH_3$	161.4	162.1	161.4	162.2	161.7	162.5	161.9	162.7	161.3 (160.7)	162.2 (161.8)	161.4 (161.2)	162.0 (161.8)
$CO_2CH_2CH_3$	60.1 4.30	59.9 4.27	59.7 4.24	59.5 4.22	59.5 4.06	59.4 4.04	59.3 3.99	59.1 3.99	60.4 4.31 (60.4) (4.34)	60.3 4.32 (60.3) (4.32)	60.1 4.27 (60.2) (4.18)	59.8 4.24 (59.9) (4.19)
$CO_2CH_2CH_3$	14.2 1.30	14.1 1.29	14.2 1.26	14.1 1.26	14.0 1.14	14.0 1.18	14.1 1.10	14.1 1.14	14.1 1.32 (14.0) (1.35)	14.1 1.34 (14.0) (1.37)	14.1 1.30 (14.0) (1.24)	14.1 1.29 (14.0) (1.23)
R_1 = Ph: C-1	137.6	137.5			138.1	138.0			137.2 (136.7)	137.3 (136.6)		
C-2,6	124.8 7.57	124.7 7.54			123.6 7.70	123.5 7.64			125.0 7.57 (123.8) (7.17)	125.0 7.55 (123.8) (7.15)		
C-3,5	129.3 7.57	129.2 7.54			128.8 7.54	128.8 7.51			129.4 7.57 (129.9) (7.57)	129.3 7.55 (130.0) (7.55)		
C-4	128.9 7.57	128.6 7.54			127.6 7.42	127.4 7.39			129.4 7.57 (129.3) (7.57)	129.6 7.60 (129.2) (7.55)		
R_1 = CH_3			36.0 3.83	35.6 3.74			35.0 3.68	34.5 3.58			35.8 3.87 (35.9) (3.68)	35.3 3.77 (35.7) (3.56)
R_2 = CH_3		14.4 2.45		14.2 2.35		14.5 2.27		14.4 2.16		14.4 2.49 (14.3) (2.35)		14.2 2.37 (13.9) (2.20)

[a] Chemical shift values are given in ppm downfield from internal TMS in DMSO-d_6 solutions. The values in parentheses are for the less abundant isomer (20-35%). [b] In the proton spectra recorded at 23° two different resonances are detected for the methylene protons: **5a**, 2.85 and 3.13 ppm; **5b**, 2.74 and 3.12 ppm. [c] In the proton spectra recorded at 23° two different resonances are detected for the methyl protons: **5a**, 0.97 and 1.08 ppm; **5b**, 0.96 and 1.08 ppm.

Table 2

^{13}C and ^{1}H NMR Chemical Shift Values of Compounds **7** and **9** [a]

	7a	**7b**	**7c**	**7d**	**9a**	**9b**	**9c**	**9d**
C-3	141.5	141.4	141.3	141.3	141.3	141.3	140.8	140.8
C-3a	122.7	122.5	122.7	122.7	120.6	120.6	120.5	120.6
NH	9.48	9.36	9.08	9.08	9.77	9.71	9.54	9.46
C-5	165.6	165.7	165.9	166.3	163.8	164.1	164.3	164.7
C-5a	107.3	105.0	105.8	103.4	112.4	110.1	110.9	108.4
C-6	141.1	149.0	139.0	147.1	139.4	147.7	137.4	145.7
	7.85		7.49		7.91		7.58	
C-8a	142.5	142.9	142.6	143.2	138.5	138.6	138.8	139.0
C-10	156.8	156.6	156.4	156.3	160.4	160.4	160.3	160.3
C-10a	126.0	126.2	126.2	126.5	129.6	129.7	129.8	129.9
N-1-CH_2CH_3	46.1	45.9	46.0	46.0	45.4	45.3	45.3	45.2
	4.10 [b]	4.07 [b]	4.04	4.05	4.19	4.18	4.08 [b]	4.07 [b]
N-1-CH_2CH_3	15.3	15.3	15.1	15.1	15.3	15.4	15.4	15.4
	1.26	1.21	1.25	1.24	1.40	1.39	1.25	1.23
C-3 CH_3	10.5	10.5	10.4	10.4	10.5	10.5	10.3	10.3
	2.18	2.13	2.09	2.10	2.14	2.13	2.06	2.04
R_1 = Ph: C-1	138.2	138.1			137.6	137.5		
C-2,6	124.3	123.9			123.9	123.7		
	7.56	7.51			7.40	7.35		
C-3,5	128.9	128.8			129.9	129.9		
	7.56	7.50			7.64	7.61		
C-4	127.6	127.2			129.1	128.8		
	7.43	7.45			7.55	7.52		
$R_1 = CH_3$			34.6	34.1			36.2	35.7
			3.64	3.57			3.76	3.66
$R_2 = CH_3$		13.0		12.8		12.5		12.2
		2.25		2.14		2.26		2.11
NCH_3					35.1	35.0	35.6	35.5
					2.82	2.80	3.34	3.30
OCH_3	55.6	55.5	55.2	55.2				
	3.97	3.94	4.10	4.10				

[a] Chemical shift values are given in ppm downfield from internal TMS in DMSO-d_6 solutions. [b] In the proton spectra recorded at 23° two different resonances are detected for the methylene protons: **7a**, 4.09 and 4.11 ppm; **7b**, 4.06 and 4.08 ppm; **9c**, 4.04 and 4.12 ppm; **9d**, 4.02 and 4.12 ppm.

Hz) and long-range (6.5 or 3.0 Hz) C-H interactions, respectively. Mass spectra were recorded on a Jeol JMS-01-SG-2 spectrometer at 75 eV (100 μA). Elemental analyses were determined by labo. de Chimie Pharmaceutique—service de microchimie—Dr. H. Eder, Université de Geneve, Suisse.

General Procedure for the Synthesis of 1-Ethyl-3-methyl-4-nitro-*N*-(1-R_1-3-R_2-4-carbethoxy-1*H*-pyrazol-5-yl)-1*H*-pyrazole-5-carboxamides **3a-d**.

A solution of **1** (10 mmoles), aminopyrazoles **2a-d** (10 mmoles) in toluene (100 ml) was refluxed for 7 hours. The solvent was then evaporated under reduced pressure and the residue was recrystallized from ethanol.

Compound **3a** ($R_1 = C_6H_5$, R_2 = H) was obtained in a yield of 48%, mp 158-159°; ir: 3220 (NH), 1720, 1690 (CO) cm^{-1}.

Anal. Calcd. for $C_{19}H_{20}O_5N_6$: C, 55.33; H, 4.89; N, 20.38. Found: C, 55.42; H, 4.86; N, 20.32.

Compound **3b** ($R_1 = C_6H_5$, $R_2 = CH_3$) was obtained in a yield of 52%, mp 145-146°; ir: 3200 (NH), 1710-1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{20}H_{22}O_5N_6$: C, 56.33; H, 5.20; N, 19.71. Found: C, 56.12; H, 5.22; N, 19.87.

Compound **3c** ($R_1 = CH_3$, R_2 = H) was obtained in a yield of 54%, mp 165-166°; ir: 3210 (NH), 1720, 1690 (CO) cm^{-1}.

Anal. Calcd. for $C_{14}H_{18}O_5N_6$: C, 47.99; H, 5.18; N, 23.99. Found: C, 47.77; H, 5.25; N, 24.07.

Compound **3d** ($R_1 = CH_3$, $R_2 = CH_3$) was obtained in a yield of 58%, mp 177-178°; ir: 3210 (NH), 1710, 1690 (CO) cm^{-1}.

Anal. Calcd. for $C_{15}H_{20}O_5N_6$: C, 49.44; H, 5.53; N, 23.07. Found: C, 49.30; H, 5.37; N, 23.22.

General Procedure for the Synthesis of Ethyl 5-[[(1-Ethyl-3-methyl-4-nitro-1*H*-pyrazol-5-yl)methoxymethylene]amino]-1-R_1-3-R_2-1*H*-pyrazole-4-carboxylates **4a-d** and 1-Ethyl-*N*,3-dimethyl-4-nitro-*N*-(1-R_1-3-R_2-4-carbethoxy-1*H*-pyrazol-5-yl)-1*H*-pyrazole-5-carboxamides **5a-d**.

Five mmoles of **3a-d** were stirred with diazomethane (ether solution, 50 ml) for 1 hour and then allowed to stand at room temperature overnight. The ethereal liquor was decomposed with acetic acid and then evaporated to give a residue which was subjected to flash chromatography on Merck Kieselgel 60 (column, 3 x 45 cm), prepacked in petroleum ether 40-70°. Elution of the column with increasing amounts of ethyl acetate in petroleum ether 40-70°, gave the isomeric products **4** and **5**.

Compound **4a** ($R_1 = C_6H_5$, R_2 = H) was obtained in a yield of 73% (elution with petroleum ether-ethyl acetate, 95:5), mp 157-158° (from ethanol); ir: 1730, 1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{20}H_{22}O_5N_6$: C, 56.33; H, 5.20; N, 19.71. Found: C, 56.39; H, 5.31; N, 19.85.

Compound **5a** ($R_1 = C_6H_5$, R_2 = H) was obtained in a yield of 19% (elution with petroleum ether-ethyl acetate, 80:20), mp

165-166° (from ethanol); ir: 1715, 1685 (CO) cm^{-1}.

Anal. Calcd. for $C_{20}H_{22}O_5N_6$: C, 56.33; H, 5.20; N, 19.71. Found: C, 56.25; H, 5.35; N, 19.91.

Compound **4b** ($R_1 = C_6H_5$, $R_2 = CH_3$) was obtained in a yield of 58% (elution with petroleum ether-ethyl acetate, 90:10), mp 125-126° (from ethanol); ir: 1710, 1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{21}H_{24}O_5N_6$: C, 57.26; H, 5.49; N, 19.08. Found: C, 57.32; H, 5.37; N, 19.24.

Compound **5b** ($R_1 = C_6H_5$, $R_2 = CH_3$) was obtained in a yield of 38% (elution with petroleum ether-ethyl acetate, 80:20), mp 120-121°; ir: 1700, 1670 (CO) cm^{-1}.

Anal. Calcd. for $C_{21}H_{24}O_5N_6$: C, 57.26; H, 5.49; N, 19.08. Found: C, 57.36; H, 5.28; N, 19.29.

Compound **4c** ($R_1 = CH_3$, $R_2 = H$) was obtained in a yield of 40% (elution with petroleum ether-ethyl acetate, 80:20), mp 105-106° (from ethanol); ir: 1700, 1670 (CO) cm^{-1}.

Anal. Calcd. for $C_{15}H_{20}O_5N_6$: C, 49.44; H, 5.53; N, 23.07. Found: C, 49.55; H, 5.42; N, 23.28.

Compound **5c** ($R_1 = CH_3$, $R_2 = H$) was obtained in a yield of 46% (elution with petroleum ether-ethyl acetate, 70:30), mp 138-140° (from ethanol); ir: 1710, 1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{15}H_{20}O_5N_6$: C, 49.44; H, 5.53; N, 23.07. Found: C, 49.49; H, 5.63; N, 23.15.

Compound **4d** ($R_1 = CH_3$, $R_2 = CH_3$) was obtained in a yield of 27% (elution with petroleum ether-ethyl acetate, 75:25), mp 95-96° (from ethanol); ir: 1700, 1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{16}H_{22}O_5N_6$: C, 50.78; H, 5.86; N, 22.21. Found: C, 50.65; H, 5.79; N, 22.10.

Compound **5d** ($R_1 = CH_3$, $R_2 = CH_3$) was obtained in a yield of 32% (elution with petroleum ether-ethyl acetate, 60:40), mp 175-176° (from ethanol); ir: 1700-1680 (CO) cm^{-1}.

Anal. Calcd. for $C_{16}H_{22}O_5N_6$: C, 50.78; H, 5.86; N, 22.21. Found: C, 50.83; H, 5.95; N, 22.34.

Hydrolysis of **4a-d**.

Two mmoles of **4a-d** in ethanol (40 ml) were refluxed with 10% aqueous hydrochloric acid (10 ml) for 10 hours. Then the solution was concentrated to small volume and a solid product precipitated, which was identical in all respects with the compounds **3a-d** (mp, ir, tlc).

General Procedure for the Synthesis of 1-Ethyl-4,8-dihydro-10-methoxy-3-methyl-8-R_1-6-R_2-dipyrazolo[3,4-*b*:4',3'-*f*][1,5]diazocin-5(1*H*)-ones **7a-d**.

A mixture of **4a-d** (5 mmoles) in ethanol (100 ml) and 1 g of W-2 Raney-nickel was hydrogenated in a Parr apparatus at 45-50 psi for 24 hours at room temperature. Removal of the catalyst and evaporation of the solvent gave a residue which was treated with toluene (40 ml), acetic acid (2 ml) and refluxed for 30 hours. After evaporation of the solvent under reduced pressure, the residue was washed with 5% sodium bicarbonate solution and then recrystallized from ethanol.

Compound **7a** ($R_1 = C_6H_5$, $R_2 = H$) was obtained in a yield of 50%, mp 230-231°; ir: 3150 (NH), 1680 (CO) cm^{-1}; ms: m/z 350 (molecular ion).

Anal. Calcd. for $C_{18}H_{18}O_2N_6$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.85; H, 5.33; N, 24.07.

Compound **7b** ($R_1 = C_6H_5$, $R_2 = CH_3$) was obtained in a yield of 38%, mp 247-248°; ir: 3160 (NH), 1670 (CO) cm^{-1}; ms: m/z 364 (molecular ion).

Anal. Calcd. for $C_{19}H_{20}O_2N_6$: C, 62.62; H, 5.53; N, 23.06. Found: C, 62.70; H, 5.65; N, 23.19.

Compound **7c** ($R_1 = CH_3$, $R_2 = H$) was obtained in a yield of 50%, mp 266-267°; ir: 3200 (NH), 1650 (CO) cm^{-1}; ms: m/z 288 (molecular ion).

Anal. Calcd. for $C_{13}H_{16}O_2N_6$: C, 54.15; H, 5.59; N, 29.15. Found: C, 54.27; H, 5.63; N, 29.28.

Compound **7d** ($R_1 = CH_3$, $R_2 = CH_3$) was obtained in a yield of 38%, mp 255-256°; ir: 3160 (NH), 1670 (CO) cm^{-1}; ms: m/z 302 (molecular ion).

Anal. Calcd. for $C_{14}H_{18}O_2N_6$: C, 55.61; H, 6.00; N, 27.80. Found: C, 55.63; H, 6.24; N, 27.92.

General Procedure for the Synthesis of 1-Ethyl-1,4,8,9-tetrahydro-3,9-dimethyl-8-R_1-6-R_2-dipyrazolo[3,4-*b*:4',3'-*f*][1,5]diazocine-5,10-diones **9a-d**.

A mixture of **5a-d** (5 mmoles) in ethanol (100 ml) and 1 g of W-2 Raney-nickel was hydrogenated in a Parr apparatus at 45-50 psi for 24 hours at room temperature. Removal of the catalyst and evaporation of the solvent left a crude product which was treated with toluene (40 ml), acetic acid (2 ml) and refluxed for 15 hours. After evaporation to dryness under reduced pressure, the residue was washed with 5% sodium bicarbonate solution and recrystallized from ethanol.

Compound **9a** ($R_1 = C_6H_5$, $R_2 = H$) was obtained in a yield of 58%, mp 239-240°; ir: 3150 (NH), 1660 (CO) cm^{-1}; ms: m/z 350 (molecular ion).

Anal. Calcd. for $C_{18}H_{18}O_2N_6$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.66; H, 5.03; N, 23.85.

Compound **9b** ($R_1 = C_6H_5$, $R_2 = CH_3$) was obtained in a yield of 39%, mp 264-265°; ir: 3100 (NH), 1675 (CO) cm^{-1}; ms: m/z 364 (molecular ion).

Anal. Calcd. for $C_{19}H_{20}O_2N_6$: C, 62.62; H, 5.53; N, 23.06. Found: C, 62.58; H, 5.51; N, 23.12.

Compound **9c** ($R_1 = CH_3$, $R_2 = H$) was obtained in a yield of 66%, mp 273-274°; ir: 3200 (NH), 1670 (CO) cm^{-1}; ms: m/z 288 (molecular ion).

Anal. Calcd. for $C_{13}H_{16}O_2N_6$: C, 54.15; H, 5.59; N, 29.15. Found: C, 54.10; H, 5.54; N, 29.27.

Compound **9d** ($R_1 = CH_3$, $R_2 = CH_3$) was obtained in a yield of 60%, mp 302-303°; ir: 3190 (NH), 1670 (CO) cm^{-1}; ms: m/z 302 (molecular ion).

Anal. Calcd. for $C_{14}H_{18}O_2N_6$: C, 55.61; H, 6.00; N, 27.80. Found: C, 55.36; H, 6.14; N, 27.84.

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