N-1 Substituted Ethyl 4-Pyrazolecarboxylates: Synthesis and Spectroscopic Investigations

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The synthesis of various N-1 substituted ethyl 4-pyrazolecarboxylates *via* reaction of ethyl 2-formyl-3-oxopropionate (= ethoxycarbonylmalondialdehyde) with appropriately substituted hydrazines is described. Moreover, detailed nmr-spectroscopic investigations with the title compounds are presented.

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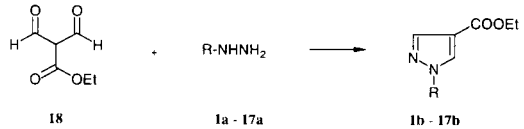
In the course of a program directed towards isosteric modification of biologically active molecules we became interested in (N-1 substituted) alkyl 4-pyrazolecarboxylates, which are assumed to be valuable synthetic building blocks in the construction of complex molecules containing the 1,2-diazole unit. For the synthesis of such type of compounds various methods have been reported in the literature [2-5]. One important strategy consists in the modification of appropriate functional groups attached to a preformed pyrazole system (such as, for instance, oxidation of 4-methylpyrazole and subsequent esterification of the obtained 4-pyrazolecarboxylic acid [6]; or removement of the amino group in alkyl 5-amino-4-pyrazolecarboxylates *via* diazotation and subsequent decomposition of the intermediate diazonium compounds [7]). Alternatively, pyrazole-ring formation *via* reaction of appropriately substituted 1,3-dielectrophiles with (substituted) hydrazines can provide an useful access to 4-pyrazolecarboxylates [8]. A synthesis belonging to the latter type is the reaction of the sodium salt of ethoxycarbonylmalondialdehyde (**18**) with hydrazine [9] or phenylhydrazine [10], respectively, leading to ethyl 4-pyrazolecarboxylate (**1b**) and ethyl 1-phenyl-4-pyrazolecarboxylate (**4b**). However, this method suffers from the disadvantage that the mentioned sodium salt of **18** cannot be purified sufficiently [10]. As exemplified by the preparation of ethyl 4-pyrazolecarboxylates **1b-17b** (Scheme 1) we here report on an improvement of the latter approach, employing ethoxycarbonylmalondialdehyde (**18**) and appropriate (substituted) hydrazines as the educts [11]. Compound **18** can be easily prepared from commercially available 3,3-diethoxypropionate following the procedure given in ref [13]. It is easy to handle and could be stored over longer periods without stability-problems.

Scheme 1



18 **1a - 17a** **1b - 17b**

No.	R	No.	R
1	H	10	Tosyl
2	Me	11	SO_2Mesityl
3	CH_2COOEt	12	2-Pyridinyl
4	Ph	13	6-Cl-3-Pyridazinyl
5	2-Tolyl	14	2-Pyrimidinyl
6	3-Tolyl	15	2-Pyrazinyl
7	4-Tolyl	16	2-Quinolinyl
8	4-Cl-C_6H_4	17	3-Phthalazinyl
9	SO_2Ph		

Synthesis.

The synthesis of pyrazoles **1b, 2b, 4b, 9b-16b** was carried out simply by treatment of the 1,3-dicarbonyl compound **18** with hydrazines **1a, 2a, 4a, 9a-16a** in ethanolic solution (0° to room temperature). The reaction products either precipitated from the reaction mixture or were obtained after evaporation of the solvent and subsequent chromatographic purification of the residue and/or crystallization from an appropriate solvent. In the preparation of the remaining esters **3b, 5b-8b** hydrochloride salts of hydrazines **3a, 5a-8a** were employed and the reaction mixtures were treated with sodium bicarbonate solution before the purification procedure. In contrast, treatment of ethoxycarbonylmalondialdehyde (**18**) with hydralazine hydrochloride (**17a**·HCl) in ethanolic solution did not result in the formation of the desired pyrazole derivative **17b**. From the complex reaction mixture product **19** could be isolated which was identified as 1-ethoxyphthalazine according to its mass spectrum (M^+, m/z = 174) and its ^{1}H-nmr and ^{13}C-nmr data. However, compound **17b** could be obtained upon treatment of hydralazine hydrochloride with sodium bicarbonate before addition of **18** and by employing methanol as the solvent.

Spectroscopic Investigations.

All ethyl 4-pyrazolecarboxylates obtained were characterized by ^{1}H-nmr spectra (Table 1), ^{13}C-nmr spectra, ir spectra and mass spectra. The ir spectra of compounds **1b-17b** exhibit strong absorption bands between 1700 and 1730 cm^{-1} due to the C=O stretching vibration. The mass spectra of compounds **2b-8b, 12b-17b** are characterized by fragmentation of the C-C bonds proceeding from the ester carbonyl-C atom, resulting in base peaks or peaks of high relative intensity of type M^+-45 (= M^+-OEt) and M^+-73 (= M^+-COOEt). With sulfonyl compounds **9b-11b**, cleavage of the S-N bond and the S-C bond plays a dominant role, reflected by base peaks of 77 (**9b**) and 91 (**10b**).

Table 1. ^{1}H-Nmr Data (δ, ppm) and NOE Data of Compounds **1b** - **17b**.

No.	Sol-vent	Pyrazole [a] H-3	H-5	Ester-H [b] OCH_2	CH_3	Protons of R	Irrad. Reson.	NOE on
1b	[c]	8.06	8.06	4.31	1.35	9.00-7.00 (broad)	---	---
	[d]	8.07	8.07	4.19	1.24	13.00-10.00 (broad)	---	---
2b	[c]	7.88	7.85	4.28	1.33	3.91	NCH_3	H-5
	[d]	7.80	8.26	4.19	1.24	3.86	NCH_3	H-5
3b	[c]	7.92	7.97	4.27	1.31	4.89 (NCH_2), 4.22 (OCH_2), 1.26 (CH_3)	NCH_2	H-5
	[d]	7.86	8.33	4.21	1.25	5.11 (NCH_2), 4.17 (OCH_2), 1.19 (CH_3)	NCH_2	H-5
4b	[c]	8.10	8.40	4.34	1.38	7.75-7.25 (Ph)	Ph	H-5
	[d]	8.12	9.06	4.27	1.30	7.98-7.87 (Ph-2,6), 7.64-7.34 (Ph-3,4,5)	Ph	H-5
5b	[c]	8.10	8.08	4.34	1.37	7.37-7.26 (Ph), 2.25 (Ph-CH_3)	Ph	H-5
							Ph-CH_3	H-5
	[d]	8.09	8.58	4.26	1.29	7.39 (Ph), 2.18 (CH_3)	Ph	H-5
6b	[c]	8.09	8.38	4.34	1.37	7.53-7.19 (Ph), 2.43 (Ph-CH_3)	Ph	H-5
	[d]	8.10	9.03	4.26	1.29	7.76-7.12 (Ph), 2.37 (Ph-CH_3)	H-5	Ph
7b	[c]	8.08	8.36	4.34	1.37	7.64-7.55 (Ph-2,6), 7.31-7.21 (Ph-3,5), 2.39 (Ph-CH_3)	Ph	H-5
	[d]	8.09	9.00	4.26	1.29	7.85-7.74 (Ph-2,6), 7.35-7.25 (Ph-3,5), 2.34 (Ph-CH_3)	Ph-2,6	H-5
							H-5	Ph-2,6
8b	[c]	8.07	8.37	4.34	1.37	7.72-7.58 (Ph-2,6), 7.52-7.38 (Ph-3,5)	H-5	Ph-2,6
	[d]	8.13	9.10	4.27	1.30	8.02-7.87 (Ph-2,6), 7.66-7.51 (Ph-3,5)	H-5	Ph-2,6
							Ph-2,6	H-5
9b	[c]	8.05	8.57	4.31	1.34	8.11-8.00 (Ph-2,6), 7.72-7.54 (Ph-3,4,5)	---	---
	[d]	8.22	8.98	4.24	1.26	8.14-8.02 (Ph-2,6), 7.84-7.74 (Ph-3,4,5)	---	---
10b	[c]	8.03	8.55	4.30	1.33	7.97-7.87 (Ph-2,6), 7.40-7.30 (Ph-3,5), 2.43 (Ph-CH_3)	---	---
	[d]	8.19	8.94	4.23	1.25	8.00-7.90 (Ph-2,6) 7.54-7.44 (Ph-3,5) 2.39 (Ph-CH_3)	---	---
11b	[c]	8.00	8.64	4.33	1.36	7.01 (Ph-3,5), 2.65 (2,6-CH_3), 2.32 (4-CH_3)	---	---
	[d]	8.18	8.98	4.25	1.27	7.17 (Ph-3,5), 2.54 (2,6-CH_3), 2.29 (4-CH_3)	---	---
12b	[c]	8.11	9.03	4.34	1.37	8.44 (Py-6), 8.06-7.72 (Py-3,4), 7.25 (Py-5)	H-5	---
	[d]	8.18	8.95	4.25	1.28	8.50 (Py-6), 8.05-7.88 (Py-3,4), 7.44 (Py-5)	Py-3,4	H-5 [e]
13b	[c]	8.16	9.17	4.36	1.38	8.21 (pyridazine-4), 7.67 (pyridazine-5) [f]	H-5	---
	[d]	8.33	9.16	4.28	1.30	8.32 (pyridazine-4), 8.14 (pyridazine-5) [f]	---	---
14b	[c]	8.19	9.08	4.35	1.38	8.79 (pyrimid-3,5), 7.29 (pyrimid-4) [g]	---	---
	[d]	8.19	9.00	4.26	1.29	8.91 (pyrimid-3,5), 7.56 (pyrimid-4) [g]	---	---
15b	[c]	8.16	8.98	4.36	1.38	9.36 (pyra-3), 8.57 (pyra-5), 8.40 (pyra-6) [h]	---	---
	[d]	8.27	8.98	4.27	1.30	9.24 (pyra-3), 8.70 (pyra-5), 8.60 (pyra-6) [h]	pyrazine-3	---
							H-5	---
16b	[c]	8.16	9.26	4.38	1.41	8.38-7.45 (quinoline)	---	---
	[d]	8.24	9.13	4.28	1.31	8.59 (quinol-4), 8.19-7.51 (quinol-3,5,6,7,8)	H-5	---
17b	[c]	8.30	9.15	4.38	1.39	9.50 (phthal-4), 9.10 (phthal-8), 8.08-7.92 (phthal-5,6,7)	---	---
	[d]	8.38	9.09	4.31	1.32	9.78 (phthal-4), 8.65 (phthal-8), 8.36-8.06 (phthal-5,6,7)	H-5	---
							---	---

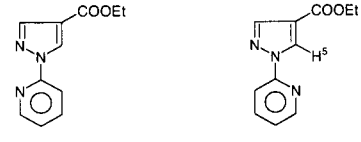
[a] Signals of pyrazole H-3 and H-5 appear either as singlets or as dublets with ^4J(H-3,H-5) ~ 0.5 Hz.
[b] $^3J(CH_3,OCH_2)$ ~ 7.1 Hz.
[c] Deuteriochloroform.
[d] Deuteriodimethyl sulfoxide.
[e] Weak enhancement.
[f] ^3J (Pyridazine H-4,H-5) = 9.1 Hz.
[g] ^3J (Pyrimidine H-4,H-6) = 4.9 Hz.
[h] ^3J (Pyrazine H-5,H-6) = 2.6 Hz, ^5J (Pyrazine H-3,H-6) = 1.3 Hz.

The ^{1}H-nmr data of compounds **1b-17b** are summarized in Table 1. As the utility of solvent effects for the discrimination between pyrazole H-3 and pyrazole H-5 has been reported in the literature [14,15], ^{1}H-nmr spectra were recorded in deuteriochloroform as well as in deuteriodimethyl sulfoxide solution. Under the acquisition parameters used (digital resolution 0.3 Hz/data point), the signals due to pyrazole H-3 and pyrazole H-5 appeared either as singlets or as doublets split by a small coupling constant ($^4J_{H\text{-}3/H\text{-}5} \sim 0.5$ Hz). For compounds **2b-8b**, homonuclear NOE-difference spectroscopy - which has been proven to be a useful tool for assignments in the pyrazole series [16] - turned out to be the method of choice to distinguish between pyrazole H-3 and H-5 signals. Particularly with compounds **2b, 3b** and **5b**, the spectra of which show the two pyrazole-H signals very close together (in deuteriochloroform), this technique enabled us to assign the mentioned resonances unambiguously. Thus, irradiation of the NCH_3, NCH_2, Ph, or Ph-CH_3-resonance, respectively, led to marked enhancements of the pyrazole H-5 signals, whereas the corresponding pyrazole H-3 lines remained unaffected. Except with *N*-methylpyrazole **2b** and 1-(2-tolyl)pyrazole **5b**, both showing the pyrazole H-3 resonance at lower field than the corresponding pyrazole H-5 signal (in deuteriochloroform), in all cases the relationship δ H-5 > δ H-3 was found to be valid. The upfield shift of the pyrazole H-5 signal in compound **5b** (δ 8.08 ppm in deuteriochloroform, δ 8.58 ppm in deuteriodimethyl sulfoxide) relative to δ H-5 of isomeric compounds **6b** (δ 8.38 ppm, δ 9.03 ppm) and **7b** (δ 8.36 ppm, δ 9.00 ppm) can be attributed to steric effects (shielding effect of the tolyl methyl group). A distinction between pyrazole H-3 and pyrazole H-5 in compounds **2b-10b** was also possible considering solvent effects according to the literature [14,15], as the signal of H-5 was found to be markedly more sensitive to a change of the solvent than that of pyrazole H-3 (compare Table 2). However, this rule is violated in cases of 1-heteroarylpyrazoles **12b, 13b** and **15b**, or it was found to be ambiguous with compounds **14b, 16b** and **17b**, having only very small differences between $\Delta\delta$ H-3 and $\Delta\delta$ H-5 (Table 2).

Compounds **12b-17b** are characterized by an azine-nitrogen atom in the α-position to the carbon-atom attached to the pyrazole N-1. Due to stereoelectronic effects (repulsion between lone-pairs of pyrazole N-2 and azine N-1 in conformers similar to form **A** of **12b** in Scheme 2) for compounds **12b, 13b, 15b-17b** a conformation with the pyrazole N-2 and the azine N-1 in the *trans*-position (Scheme 2, form **B**) should be favored. This assumption could be confirmed by NOE-difference experiments: whereas with 1-arylpyrazoles **4b-8b** marked through-space connectivities between phenyl protons and pyrazole H-5 could be detected (see above), irradiation of appropriate azine-H resonances (located in *ortho*-position to the pyrazole substituent) in **12b, 13b, 15b-17b** either led to only very small NOEs on the signal of the corresponding pyrazole H-5 proton, or - in most cases - did not affect this resonance (compare NOE data in Table 1). Reversely, no enhancements on such azine-H resonances were obtained upon irradiation of the pyrazole H-5 lines. These findings provide a strong hint for a larger distance between pyrazole H-5 and the mentioned azine-protons [17] and thus for the presence of **12b-17b** in conformations similar to form **B** of **12b** in Scheme 2.

In addition, the chemical shifts of pyrazole H-5 in compounds **12b-17b** (in deuteriochloroform) are consistent with a *trans*-conformation of pyrazole N-2 and azine N-1: the marked downfield shifts of these resonances compared to δ H-5 of the remaining *N*-substituted pyrazole-4-carboxylates **2b-11b** can be attributed to the influence of the lone-pair of azine N-1 being spatially close [18].

Scheme 2



A 12b B

The preference of conformations with pyrazole N-2 *trans* to azine N-1 (similar to form **B** of **12b** in Scheme 2) for compounds **12b, 13b, 15b-17b** also follows from semi-

Table 2

Influence of the Solvent on the Chemical Shift of Pyrazole H-3 and Pyrazole H-5 in Compounds 2b-17b
[$\Delta\delta$ = δ (deuteriodimethyl sulfoxide) - δ (deuteriochloroform)]

	2b	**3b**	**4b**	**5b**	**6b**	**7b**	**8b**	**9b**	**10b**	**11b**
$\Delta\delta$ H-3	-0.08	-0.06	0.02	-0.01	0.01	0.01	0.06	0.17	0.16	0.18
$\Delta\delta$ H-5	0.41	0.36	0.66	0.50	0.65	0.64	0.73	0.41	0.39	0.34

	12b	**13b**	**14b**	**15b**	**16b**	**17b**
$\Delta\delta$ H-3	0.07	0.17	0.00	0.11	0.08	0.08
$\Delta\delta$ H-5	-0.08	-0.01	-0.08	0.00	-0.13	-0.06

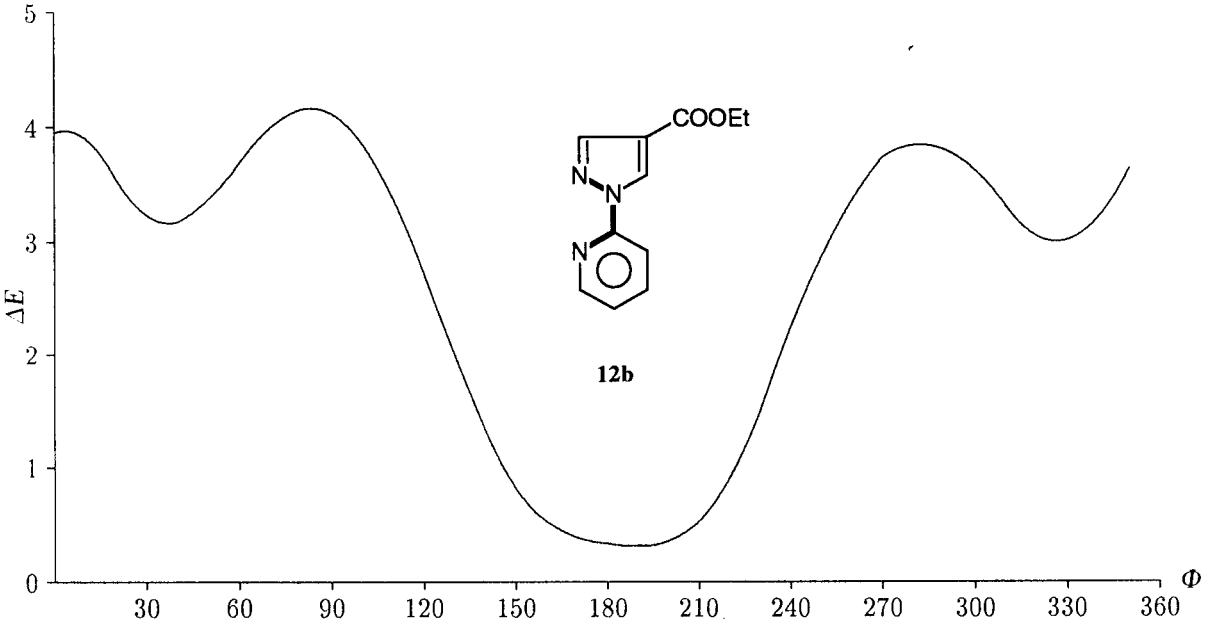


Figure 1. Dependence of energy (kcal/mole) from the dihedral angle ϕ (pyrazole N^2 - pyrazole N^1 - pyridine C^2 - pyridine N^1) in compound **12b** calculated with the AM1-method.

empirical molecular orbital calculations (AM1) [19]. For compound **12b**, the dependence of energy from the distorsion of the two heteroaromatic rings (characterized by the dihedral angle ϕ of pyrazole N^2 - pyrazole N^1 - pyridine C^2 - pyridine N^1) is displayed in Figure 1. The conformation with lowest energy had ϕ = 189° (heat of formation ΔH_f, 27.08 kcal/mole). For pyrazoles **13b, 15b** and **16b** the corresponding trajectories are very similar, geometry-optimized conformations had $\phi_{N\text{-}N\text{-}C\text{-}N}$ = 183° (**13b**, ΔH_f, 45.20 kcal/mole), 188° (**15b**, ΔH_f, 39.65 kcal/mole) and 181° (**16b**, ΔH_f, 51.92 kcal/mole). As expected, the *N*-phthalazinylpyrazole **17b** is characterized by a very strong dependence of energy from the distorsion of the two heteroaromatic rings due to steric reasons [difference between conformations with lowest energy ($\phi_{N\text{-}N\text{-}C\text{-}N}$ = 224°) and highest energy (ϕ = 5°) ~ 26.4 kcal/mole]. The most stable conformation of **4b** was found to have a 30.5° distorsion of pyrazole system and phenyl ring (ΔH_f, 13.68 kcal/mole). This result agrees well with the value of 32° obtained for 1-phenylpyrazole (the des-ethoxycarbonyl congener of **4b**) employing EHT-calculations [20].

Figure 1

From the ^{13}C-nmr spectra of compounds **2b-17b** the following general trends can be derived: regarding the chemical shifts of the pyrazole-C atoms the relationship δ C-3 > δ C-5 > δ C-4 is valid. An increase in the electron-withdrawing capability of the N-1 substituent leads to a downfield shift of the pyrazole C-3 and C-4 resonances (particularly for δ C-3 in sulfonyl derivatives **9b-11b**), whereas for δ pyrazole C-5 also steric conditions play a role (compare **5b**, $\delta_{C\text{-}5}$ 133.6 ppm; **6b**, $\delta_{C\text{-}5}$ 129.8 ppm; **7b**, $\delta_{C\text{-}5}$ 129.6 ppm). Also the spin coupling constants ^{1}J(pyrazole C-3,H-3) and ^{1}J(pyrazole C-5,H-5) increase with increasing electron-withdrawing properties of the N-1 substituent (for instance **2b**, $^1J_{C3,H3}$ = 189.3 Hz, $^1J_{C5,H5}$ = 189.9 Hz; **9b**, $^1J_{C3,H3}$ = 193.4 Hz, $^1J_{C5,H5}$ = 198.6 Hz). In general, $^1J_{C5,H5}$ was larger than $^1J_{C3,H3}$, with $^1J_{C5,H5}$ being more sensitive to a change of the N-1 substituent than $^1J_{C3,H3}$. The geminal pyrazole-C,H spin coupling constant $^2J_{C4,H3}$ was found to be larger than $^2J_{C4,H5}$; for the vicinal coupling constants the relationship $^3J_{C3,H5} > {}^3J_{C5,H3}$ is valid. All these observations are in full agreement with literature data for 1-substituted [21] and 1,4-disubstituted pyrazoles [22].

EXPERIMENTAL

Melting points were determined on a Reichert-Kofler hot-stage microscope and are uncorrected. The ir spectra (potassium bromide pellets) were recorded on a Jasco IRA-1 spectrophotometer or on a Perkin-Elmer FTIR 1605 spectrometer. The mass spectra (glc/ms) were obtained on a Hewlett-Packard 5890A/5970B-MSD instrument (EI, 70 eV); the high-resolution mass spectrum of compound **15b** was recorded on a Finnigan MAT 8230 instrument. The nmr spectra were recorded on a Bruker AC 80 spectrometer (80.13 MHz for ^{1}H, 20.15 MHz for ^{13}C). The solvent signal was used as an internal standard which was related to tetramethylsilane with δ 7.26 ppm (^{1}H, chloroform), δ 2.49 ppm (^{1}H, dimethyl sulfoxide) and 77.0 ppm (^{13}C, deuteriochloroform). Assignments of ^{13}C-chemical shifts are based on multiplicity selection by the J-modulated spin-echo technique [23], on selec-

tive heteronuclear decoupling experiments irradiating unambiguously assigned ^{1}H-nmr lines, on coupling information derived from fully ^{1}H-coupled ^{13}C-nmr spectra (obtained with the "gated decoupling" mode) and on comparison with literature data [4,21,22]. For the acquisition parameters of the NOE-difference experiments see ref [24]. Conformational analyses (single point calculations starting from the structure with optimized geometry) were carried out using the semi-empirical AM1-method [19] as implemented in the HyperChem™ program-package [25]. Column chromatographic separations were performed on Merck Kieselgel 60 (70-230 mesh).

Hydrazines **1a-12a** and **17a** (or their hydrochloride salts, respectively) are commercially available, the remaining substituted hydrazines were prepared according to the literature: **13a** [26], **14a** [27], **15a** [28], **16a** [29]. Ethoxycarbonylmalondialdehyde (**18**) was obtained following the procedure given in ref [13].

General Procedure for the Preparation of Ethyl 4-Pyrazolecarboxylates **1b-16b**.

To a stirred solution of 288 mg (2 mmoles) of ethyl 2-formyl-3-oxopropionate (= ethoxycarbonylmalondialdehyde) (**18**) in 2 ml of ethanol 2 mmoles of the appropriate hydrazines, **1a, 2a, 4a, 9a-16a**, or hydrazine hydrochlorides, **3a**·HCl, **5a**·HCl-**8a**·HCl in 10 ml of ethanol were added dropwise at 0°. After the addition was complete, the mixture was allowed to reach ambient temperature where stirring was continued for 1 day. Subsequent workup was carried out as described in the following.

Ethyl 1*H*-Pyrazole-4-carboxylate (**1b**).

The residue obtained after evaporation of ethanol was subjected to column chromatography (eluent: dichloromethane-ethyl acetate, 9:1) to afford 241 mg (86%) of colorless crystals, mp 72-74° (lit [9] mp 76-78°).

Ethyl 1-Methyl-1*H*-pyrazole-4-carboxylate (**2b**).

The residue obtained after evaporation of ethanol was subjected to column chromatography (eluent: dichloromethane-ethyl acetate, 9:1) to afford 256 mg (83%) of **2b** [30,31] as a colorless oil; ^{13}C-nmr (deuteriochloroform): δ 162.6 (C=O), 140.6 (pyrazole C-3, ^1J = 189.3 Hz, ^3J = 6.9 Hz), 133.0 (pyrazole C-5, ^1J = 189.9 Hz, $^3J_{C5,H3}$ = 3.2 Hz, $^3J_{C5,Me}$ = 2.7 Hz), 114.9 (pyrazole C-4, $^2J_{C4,H3}$ = 8.6 Hz, $^2J_{C4,H5}$ = 7.2 Hz), 59.7 (OCH_2, ^1J = 147.1 Hz, ^2J = 4.4 Hz), 38.8 (NCH_3, ^1J = 140.5 Hz), 14.0 (CH_3, ^1J = 126.9 Hz, ^2J = 2.6 Hz); ms: m/z (%) 154 (M^+, 14), 126 (35), 110 (10), 109 (100).

Ethyl 4-Ethoxycarbonyl-1*H*-pyrazole-1-acetate (**3b**).

The residue obtained after evaporation of ethanol was dissolved in 20 ml of dichloromethane and treated with saturated sodium bicarbonate solution. The organic layer was separated, dried and evaporated to dryness. The residue was subjected to Kugelrohr-distillation to afford 235 mg (52%) of a colorless oil, bp 140°/0.03 mbar; ^{13}C-nmr (deuteriochloroform): δ 166.8 (CH_2-*C*O), 162.4 (pyrazole-CO), 141.1 (pyrazole C-3, ^1J = 190.5 Hz, $^3J_{C3,H5}$ = 7.1 Hz), 134.0 (pyrazole C-5, ^1J = 191.5 Hz, $^3J_{C5,H3}$ = 3.3 Hz, $^3J_{C5,NCH2}$= 3.3 Hz), 115.8 (pyrazole C-4, $^2J_{C4,H3}$ = 8.8 Hz, $^2J_{C4,H5}$ = 6.8 Hz), 61.8 ($CH_2COO\mathit{C}H_2$, ^1J = 148.5 Hz, ^2J = 4.3 Hz), 59.9 (pyrazole-COO*C*H_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 53.0 (NCH_2, ^1J = 142.0 Hz), 14.0 (CH_3, ^1J = 126.9 Hz, ^2J = 2.6 Hz), 13.8 (CH_3, ^1J = 127.2 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1754 (CH_2C=O), 1715 (pyrazole-C=O); ms: m/z (%) 226 (M^+, 21), 198 (41), 182 (10), 181 (74), 154 (14), 153 (100), 126 (12), 125 (45), 95 (13), 81 (10), 80 (11), 53 (15), 52 (13).

Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.39; H, 6.35; N, 12.22.

Ethyl 1-Phenyl-1*H*-pyrazole-4-carboxylate (**4b**).

The precipitated material was filtered off and washed with cold ethanol. The remaining solution was evaporated and the residue was recrystallized from ethanol to yield a second crop of **4b**. Overall, 255 mg (59%) of almost colorless crystals were obtained, mp 97° (lit [7,10] mp 99-100°, lit [12] mp 96-97°); ^{13}C-nmr (deuteriochloroform): δ 162.5 (C=O), 141.9 (pyrazole C-3, ^1J = 191.0 Hz, $^3J_{C3,H5}$ = 7.3 Hz), 139.2 (Ph C-1), 129.8 (pyrazole C-5, ^1J = 191.3 Hz, $^3J_{C5,H3}$ = 3.5 Hz), 129.3 (Ph C-3,5), 127.2 (Ph C-4), 119.3 (Ph C-2,6), 116.7 (pyrazole C-4, $^2J_{C4,H3}$ = 8.8 Hz, $^2J_{C4,H5}$ = 6.7 Hz), 60.1 (OCH_2, ^1J = 147.3 Hz, ^2J = 4.4 Hz), 14.2 (CH_3, ^1J = 127.0 Hz, ^2J = 2.5 Hz); ms: m/z (%) 216 (M^+, 46), 188 (30), 172 (17), 171 (100), 77 (21), 51 (11).

Ethyl 1-(2-Methylphenyl)-1*H*-pyrazole-4-carboxylate (**5b**).

The residue obtained after evaporation of ethanol was taken up in 20 ml of dichloromethane; the resulting solution was washed with saturated sodium bicarbonate solution, dried and evaporated to dryness. The residual oil was subjected to Kugelrohr-distillation to afford 239 mg (52%) of a yellowish liquid, bp 140°/0.025 mbar; ^{13}C-nmr (deuteriochloroform): δ 162.7 (C=O), 141.3 (pyrazole C-3, ^1J = 190.5 Hz, $^3J_{C3,H5}$ = 7.0 Hz), 138.9 (Ph C-1), 133.6 (pyrazole C-5, ^1J = 191.5 Hz, $^3J_{C5,H3}$ = 3.6 Hz), 133.4 (Ph C-2), 131.1 (Ph C-3), 128.8 (Ph C-4), 126.4 (Ph C-5), 125.7 (Ph C-6), 115.7 (pyrazole C-4, $^2J_{C4,H3}$ = 8.6 Hz, $^2J_{C4,H5}$ = 7.3 Hz), 60.0 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 17.7 (Ph-CH_3, ^1J = 128.2 Hz), 14.1 (ester CH_3, ^1J = 127.0 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1715 (C=O); ms: m/z (%) 231 (15), 230 (M^+, 100), 229 (30), 201 (18), 185 (60), 157 (36), 156 (22), 130 (27), 129 (15), 91 (16), 65 (18).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.16. Found: C, 68.02; H, 6.18; N, 12.05.

Ethyl 1-(3-Methylphenyl)-1*H*-pyrazole-4-carboxylate (**6b**).

Workup was carried out as described above for the preparation of compound **5b**. Instead of Kugelrohr-distillation, the solid residue was purified by recrystallization from ethanol to afford 138 mg (30%) of yellow crystals, mp 55-56°; ^{13}C-nmr (deuteriochloroform): δ 162.6 (C=O), 141.8 (pyrazole C-3, ^1J = 190.8 Hz, $^3J_{C3,H5}$ = 7.2 Hz), 139.5 (Ph C-3), 139.1 (Ph C-1), 129.8 (pyrazole C-5, ^1J = 191.2 Hz, $^3J_{C5,H3}$ = 3.6 Hz), 129.1 (Ph C-5), 128.0 (Ph C-4), 120.0 (Ph C-2), 116.6 (pyrazole C-4, $^2J_{C4,H3}$ = 9.0 Hz, $^2J_{C4,H5}$ = 6.5 Hz), 116.3 (Ph C-6), 60.1 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 21.2 (Ph-CH_3, ^1J = 126.9 Hz), 14.2 (ester CH_3, ^1J = 127.0 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1705 (C=O); ms: m/z (%) 230 (M^+, 53), 202 (27), 186 (18), 185 (100), 91 (15), 65 (12).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.16. Found: C, 67.59; H, 5.92; N, 12.16.

Ethyl 1-(4-Methylphenyl)-1*H*-pyrazole-4-carboxylate (**7b**).

After workup as described above for the preparation of compound **6b** and recrystallization from ethanol 396 mg (86%) of colorless crystals were obtained, mp 101-102°; ^{13}C-nmr (deuteriochloroform): δ 162.6 (C=O), 141.7 (pyrazole C-3, ^1J = 190.8 Hz, $^3J_{C3,H5}$ = 7.2 Hz), 137.1 (Ph C-4), 136.9 (Ph C-1), 129.8 (Ph C-3,5), 129.6 (pyrazole C-5, ^1J = 191.1 Hz, $^3J_{C5,H3}$ = 3.5 Hz), 119.2 (Ph C-2,6), 116.5 (pyrazole C-4, $^2J_{C4,H3}$ = 8.8 Hz, $^2J_{C4,H5}$ = 6.7 Hz),

60.1 (OCH_2, ^1J = 147.3 Hz, ^2J = 4.4 Hz), 20.7 (Ph-CH_3, ^1J = 126.7 Hz), 14.2 (ester CH_3, ^1J = 126.9 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1700 (C=O); ms: m/z (%) 231 (11), 230 (M^+, 67), 202 (26), 186 (18), 185 (100), 91 (14), 65 (10).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.16. Found: C, 67.62; H, 5.98; N, 12.13.

Ethyl 4-Chlorophenyl-1*H*-pyrazole-4-carboxylate (**8b**).

After workup as described for the preparation of compound **4b** and recrystallization from chloroform 341 mg (68%) of colorless crystals were obtained, mp 127-128° (lit [7] mp 127-129°); ^{13}C-nmr (deuteriochloroform): δ 162.4 (C=O), 142.1 (pyrazole C-3, ^1J = 191.3 Hz, $^3J_{C3,H5}$ = 7.3 Hz), 137.7 (Ph C-1), 132.8 (Ph C-4), 129.7 (pyrazole C-5, ^1J = 191.5 Hz, $^3J_{C5,H3}$ = 3.6 Hz), 129.5 (Ph C-3,5), 120.4 (Ph C-2,6), 117.1 (pyrazole C-4, $^2J_{C4,H3}$ = 8.8 Hz, $^2J_{C4,H5}$ = 6.4 Hz), 60.3 (OCH_2, ^1J = 147.5 Hz, ^2J = 4.4 Hz), 14.2 (CH_3, ^1J = 127.0 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1700 (C=O); ms: m/z (%) 250/252 (M^+, 63/21), 222/224 (34/12), 205/207 (100/30), 111 (14), 75 (14).

Ethyl 1-Benzenesulfonyl-1*H*-pyrazole-4-carboxylate (**9b**).

After workup as described for the preparation of compound **4b** and recrystallization from diisopropyl ether 420 mg (75%) of colorless crystals were obtained, mp 110-111°; ^{13}C-nmr (deuteriochloroform): δ 161.3 (C=O), 145.0 (pyrazole C-3, ^1J = 193.4 Hz, $^3J_{C3,H5}$ = 7.6 Hz), 136.1 (Ph C-1), 135.0 (Ph C-4), 133.9 (pyrazole C-5, ^1J = 198.6 Hz, $^3J_{C5,H3}$ = 3.6 Hz), 129.5 (Ph C-3,5), 128.3 (Ph C-2,6), 117.7 (pyrazole C-4, $^2J_{C4,H3}$ = 9.1 Hz, $^2J_{C4,H5}$ = 6.7 Hz), 60.8 (OCH_2, ^1J = 148.0 Hz, ^2J = 4.4 Hz), 14.1 (CH_3, ^1J = 127.2 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1710 (C=O); ms: m/z (%) 280 (M^+, 4), 236 (10), 235 (70), 216 (64), 188 (65), 172 (15), 171 (60), 141 (95), 77 (100).

Anal. Calcd. for $C_{12}H_{12}N_2O_4S$: C, 51.42; H, 4.32; N, 9.99. Found: C, 51.15; H, 4.13; N, 9.98.

Ethyl 1-(4-Toluenesulfonyl)-1*H*-pyrazole-4-carboxylate (**10b**).

After workup as described for the preparation of compound **4b** and recrystallization from diisopropyl ether 371 mg (63%) of colorless crystals were obtained, mp 78-79°; ^{13}C-nmr (deuteriochloroform): δ 161.3 (C=O), 146.5 (Ph C-4), 144.8 (pyrazole C-3, ^1J = 193.3 Hz, $^3J_{C3,H5}$ = 7.6 Hz), 133.7 (pyrazole C-5, ^1J = 198.4 Hz, $^3J_{C5,H3}$ = 3.4 Hz), 132.9 (Ph C-1), 130.0 (Ph C-3,5), 128.3 (Ph C-2,6), 117.4 (pyrazole C-4, $^2J_{C4,H3}$ = 9.1 Hz, $^2J_{C4,H5}$ = 6.7 Hz), 60.7 (OCH_2, ^1J = 147.8 Hz, ^2J = 4.4 Hz), 21.5 (Tos CH_3, ^1J = 127.5 Hz, ^3J = 4.3 Hz), 14.0 (CH_3, ^1J = 127.1 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1710 (C=O); ms: m/z (%) 294 (M^+, 1), 249 (29), 231 (13), 230 (89), 202 (41), 186 (16), 185 (67), 155 (32), 91 (100), 65 (32).

Anal. Calcd. for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79; N, 9.52. Found: C, 52.80; H, 4.60; N, 9.43.

Ethyl 1-(2,4,6-Trimethylbenzenesulfonyl)-1*H*-pyrazole-4-carboxylate (**11b**).

The residue obtained after evaporation of ethanol was subjected to column chromatography (eluent: dichloromethane) to afford 97 mg (15%) of colorless crystals, mp 97-98°; ^{13}C-nmr (deuteriochloroform): δ 161.7 (C=O), 145.5 (Ph C-4), 144.2 (pyrazole C-3, ^1J = 193.1 Hz, $^3J_{C3,H5}$ = 7.6 Hz), 141.5 (Ph C-2,6), 133.3 (pyrazole C-5, ^1J = 197.9 Hz, $^3J_{C5,H3}$ = 3.6 Hz), 132.4 (Ph C-3,5), 129.9 (Ph C-1), 116.5 (pyrazole C-4, $^2J_{C4,H3}$ = 9.1 Hz, $^2J_{C4,H5}$ = 6.7 Hz), 60.8 (OCH_2, ^1J = 147.7 Hz, ^2J = 4.4 Hz), 22.9 (Ph 2,6-CH_3, ^1J = 129.6 Hz, ^3J = 6.1 Hz), 21.1 (Ph 4-CH_3, ^1J = 127.4 Hz, ^3J = 4.4 Hz), 14.2 (ester CH_3, ^1J = 127.1 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1725 (C=O); ms: m/z (%) 322 (M^+, 11), 277 (25), 258 (27), 257 (88), 229 (21), 214 (15), 213 (100), 212 (43), 185 (17), 184 (11), 183 (10), 134 (40), 119 (76), 118 (71), 117 (44), 115 (15), 103 (18), 95 (12), 91 (40), 77 (17).

Anal. Calcd. for $C_{15}H_{18}N_2O_4S$: C, 55.89; H, 5.63; N, 8.69. Found: C, 55.86; H, 5.72; N, 8.60.

Ethyl 1-(2-Pyridinyl)-1*H*-pyrazole-4-carboxylate (**12b**).

After workup and purification as described for the preparation of compound **1b**, 239 mg (55%) of yellowish crystals were obtained, mp 68-70°; ^{13}C-nmr (deuteriochloroform): δ 162.5 (C=O), 150.5 (pyridine C-2), 148.0 (pyridine C-6), 142.5 (pyrazole C-3, ^1J = 190.9 Hz, $^3J_{C3,H5}$ = 7.4 Hz), 138.6 (pyridine C-4), 129.8 (pyrazole C-5, ^1J = 196.1 Hz, $^3J_{C5,H3}$ = 3.4 Hz), 122.1 (pyridine C-5), 116.6 (pyrazole C-4), 112.5 (pyridine C-3), 60.1 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 14.1 (ester CH_3, ^1J = 126.9 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1705 (C=O); ms: m/z (%) 217 (M^+, 38), 189 (55), 173 (15), 172 (100), 145 (57), 78 (61), 51 (16).

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 60.92; H, 5.28; N, 19.26.

Ethyl 1-(6-Chloro-3-pyridazinyl)-1*H*-pyrazole-4-carboxylate (**13b**).

The precipitated product was filtered off, washed with ethanol and recrystallized from chloroform. Evaporation of ethanol and recrystallization of the resulting residue gave a second crop of **13b**. Totally, 445 mg (88%) of cream crystals were obtained, mp 208-210°; ^{13}C-nmr (deuteriochloroform): δ 162.2 (C=O), 155.4 (pyridazine C-3), 153.4 (pyridazine C-6, assignment may be interchanged with that of pyridazine C-3), 143.9 (pyrazole C-3), 130.7 (pyridazine C-5), 130.5 (pyrazole C-5), 120.3 (pyridazine C-4), 118.5 (pyrazole C-4), 60.8 (OCH_2), 14.3 (CH_3); ir: cm^{-1} 1713 (C=O); ms: m/z (%) 252/254 (M^+, 43/15), 224/226 (88/29), 207/209 (100/37), 180/182 (59/20).

Anal. Calcd. for $C_{10}H_9ClN_4O_2$: C, 47.54; H, 3.59; N, 22.17. Found: C, 47.27; H, 3.31; N, 21.94.

Ethyl 1-(2-Pyrimidinyl)-1*H*-pyrazole-4-carboxylate (**14b**).

The precipitated product was filtered off and washed with ethanol. The mother liquor was evaporated and the residue was purified by column chromatography (eluent: dichloromethane-ethyl acetate, 9:1). Totally, 166 mg (38%) of colorless crystals were obtained, mp 108-111°; ^{13}C-nmr (deuteriochloroform): δ 161.8 (C=O), 158.5 (pyrimidine C-4,6, ^1J = 184.3 Hz, ^2J = 3.5 Hz, ^3J = 5.6 Hz), 154.8 (pyrimidine C-2), 143.3 (pyrazole C-3, ^1J = 192.1 Hz, $^3J_{C3,H5}$ = 7.7 Hz), 131.8 (pyrazole C-5, ^1J = 197.0 Hz, $^3J_{C5,H3}$ = 3.4 Hz), 119.2 (pyrimidine C-5, ^1J = 170.7 Hz, ^2J = 7.7 Hz), 117.2 (pyrazole C-4, $^2J_{C4,H3}$ = 9.0 Hz, $^2J_{C4,H5}$ = 6.9 Hz), 60.0 (OCH_2, ^1J = 147.5 Hz, ^2J = 4.4 Hz), 13.8 (CH_3, ^1J = 127.0 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1719 (C=O); ms: m/z (%) 218 (M^+, 24), 203 (14), 190 (61), 174 (15), 173 (100), 146 (48), 79 (41), 53 (17).

Anal. Calcd. for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.67. Found: C, 55.32; H, 4.69; N, 25.41.

Ethyl 1-(2-Pyrazinyl)-1*H*-pyrazole-4-carboxylate (**15b**).

The residue obtained after evaporation of ethanol was subjected to column chromatography (eluent: dichloromethane-ethyl acetate, 9:1) to afford 288 mg (66%) of yellow crystals, mp 126-127°; ^{13}C-nmr (deuteriochloroform): δ 162.1 (C=O), 146.6 (pyrazine C-2), 143.3 (pyrazole C-3, ^1J = 191.9 Hz, $^3J_{C3,H5}$ = 7.5 Hz), 142.7 (pyrazine C-5, ^1J = 185.5 Hz, ^2J = 10.1 Hz, ^3J = 10.1 Hz), 141.8 (pyrazine C-6, ^1J = 185.0 Hz, ^2J = 11.7 Hz, ^4J = 1.0 Hz), 135.6 (pyrazine C-3, ^1J = 192.9 Hz, ^2J = 10.3 Hz, ^4J = 1.2

Hz), 130.3 (pyrazole C-5, ^1J = 196.7 Hz, $^3J_{C5,H3}$ = 3.4 Hz), 117.5 (pyrazole C-4, $^2J_{C4,H3}$ = 9.0 Hz, $^2H_{C4,H5}$ = 6.9 Hz), 60.4 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 14.1 (CH_3, ^1J = 127.0 Hz, ^2J = 2.6 Hz); ir: cm^{-1} 1715 (C=O); ms: m/z (%) 218 (M^+, 43), 203 (11), 190 (69), 174 (16), 173 (100), 146 (34), 79 (24), 52 (14); hrms: Calcd. for $C_{10}H_{10}N_4O_2$ (M^+): 218.080376. Found: 218.08047 ± 0.0022.

Anal. Calcd. for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.67. Found: C, 55.33; H, 4.58; N, 25.69.

Ethyl 1-(2-Quinolinyl)-1*H*-pyrazole-4-carboxylate (**16b**).

The residue obtained after evaporation of ethanol was subjected to column chromatography (eluent: dichloromethane-ethyl acetate, 3:1) to afford 315 mg (59%) of **16b** [32] as yellowish crystals, mp 86-87°; ^{13}C-nmr (deuteriochloroform): δ 162.5 (C=O), 149.1 (quinoline C-2), 146.2 (quinoline C-8a), 142.7 (pyrazole C-3, ^1J = 191.1 Hz, $^3J_{C3,H5}$ = 7.5 Hz), 138.9 (quinoline C-4, ^1J = 163.7 Hz, ^3J = 4.8 Hz), 130.2 (quinoline C-8, ^1J = 161.2 Hz, ^3J = 9.0 Hz, ^2J = 1.3 Hz), 130.1 (pyrazole C-5, ^1J = 196.3 Hz, $^3J_{C5,H3}$ = 3.3 Hz), 128.4 (quinoline C-7, ^1J = 163.4 Hz, ^3J = 6.7 Hz), 127.5 (quinoline C-5, ^1J = 161.1 Hz, ^3J = 7.1 Hz, ^3J = 3.8 Hz), 127.1 (quinoline C-4a), 126.2 (quinoline C-6, ^1J = 162.1 Hz, ^3J = 7.9 Hz), 117.0 (pyrazole C-4, $^2J_{C4,H3}$ = 8.8 Hz, $^2J_{C4,H5}$ = 7.2 Hz), 111.9 (quinoline C-3, ^1J = 171.8 Hz), 60.3 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 14.3 (CH_3, ^1J = 127.0 Hz, ^2J = 2.4 Hz); ir: cm^{-1} 1710 (C=O); ms: m/z (%) 268 (18), 267 (M^+, 100), 239 (32), 223 (16), 222 (78), 195 (33), 128 (42), 101 (10).

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.32; H, 4.75; N, 15.67.

Ethyl 1-(1-Phthalazinyl)-1*H*-pyrazole-4-carboxylate (**17b**).

To a stirred solution of 393 mg (2 mmoles) 1-hydrazinophthalazine (hydralazine) hydrochloride in 10 ml of methanol, 200 mg of sodium bicarbonate was added and the mixture was cooled to 0°. Then 288 mg (2 mmoles) of **18** in 3 ml of methanol was added dropwise and the resulting mixture was stirred at room temperature for one day. The residue obtained after evaporation of methanol was taken up in 20 ml of dichloromethane and was then washed with 20 ml of water. After drying, dichloromethane was evaporated and the residue (429 mg) was purified by column chromatography (eluent: dichloromethane-ethyl acetate, 2:3) to afford 215 mg (40%) of yellowish crystals, mp 118-119°; ^{13}C-nmr (deuteriochloroform): δ 162.1 (C=O), 151.4 (phthalazine C-4, ^1J = 182.3 Hz, ^3J = 3.1 Hz), 149.9 (phthalazine C-1), 143.2 (pyrazole C-3, ^1J = 191.7 Hz, $^3J_{C3,H5}$ = 7.5 Hz), 133.7 (pyrazole C-5, ^1J = 196.8 Hz, $^3J_{C5,H3}$ = 3.2 Hz), 133.1 and 132.8 (phthalazine C-6 and C-7 [33]), 128.8 (phthalazine C-4a), 126.2 and 125.8 (phthalazine C-5 and C-8 [33]), 120.3 (phthalazine C-8a), 116.6 (pyrazole C-4, $^2J_{C4,H3}$ = 8.5 Hz, $^2J_{C4,H5}$ = 7.2 Hz), 60.3 (OCH_2, ^1J = 147.4 Hz, ^2J = 4.4 Hz), 14.1 (CH_3, ^1J = 127.0 Hz, ^2J = 2.5 Hz); ir: cm^{-1} 1730 (C=O); ms: m/z (%) 269 (10), 268 (M^+, 100), 240 (11), 239 (29), 223 (38), 196 (74), 195 (85), 169 (10), 129 (19), 102 (14).

Anal. Calcd. for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.51; N, 20.88. Found: C, 62.64; H, 4.70; N, 20.83.

Reaction of Ethoxycarbonylmalondialdehyde (**18**) with Hydralazine Hydrochloride (**17a**·HCl) in Ethanolic Solution.

To a solution of **18** (288 mg, 2 mmoles) in 2 ml of ethanol, a solution of **17a** (393 mg, 2 mmoles) in 10 ml of ethanol was added dropwise at 0° and the mixture was stirred at room temperature for one day. The residue obtained after workup as described for the preparation of compound **5b** was subjected to column chromatography (eluent: dichloromethane-ethyl acetate, 4:6). Amongst several unidentified products 100 mg (29%) of 1-ethoxyphthalazine (**19**) [34] were obtained as a yellowish oil which slowly solidified on standing; ^{1}H-nmr (deuteriochloroform): δ 9.15 (s, 1H, phthalazine H-4), 8.29-8.16 (m, 1H, phthalazine H-8), 7.88-7.75 (m, 3H, phthalazine H-5,6,7), 4.73 (q, J = 7.1 Hz, 2H, OCH_2), 1.54 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C-nmr (deuteriochloroform): δ 160.0 (phth C-1), 147.4 (phth C-4), 131.8 and 131.6 (phth C-6,C-7 [33]), 128.2 (phth C-4a), 125.3 and 122.5 (phth C-5,C-8 [33]), 119.5 (phth C-8a), 63.0 (OCH_2), 14.2 (CH_3); ms: m/z (%) 174 (M^+, 12), 159 (29), 147 (12), 146 (100), 130 (18), 129 (10), 118 (16), 103 (55), 90 (13), 89 (40), 63 (19).

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