Synthesis of 3-Dialkylaminomethyl-5-methyl-4-substituted-1*H*-pyrazoles. Selective Functionalization of One Methyl Group *via N*-Nitration of 3,5-Dimethyl-4-substituted-1*H*-pyrazoles [1,2]

H. Lammers*

Laboratory for Organic Chemistry and Catalysis,
Julianalaan 136, 2628 BL Delft, The Netherlands

R. Vollinga, P. Zandbergen, P. Cohen-Fernandes and C. L. Habraken*

Leiden University Gorlaeus Laboratories, P.O. Box 9502,
2300 RA Leiden, The Netherlands
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Treatment of 4-substituted 3,5-dimethyl-1-nitro-1*H*-pyrazoles **1** and **10a-c** with secondary amines in acetonitrile, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), affords the novel dialkylaminomethyl-1*H*-pyrazoles **5**, **6**, **7**, **8**, **11a-c**, **12a-c** and **13a-c** in good to excellent yields. In this way one of the, in general, inert methyl groups of 3,5-dimethyl-4-substituted-1*H*-pyrazoles is functionalized creating a new synthetic route to azoles containing a coordinating substituent.

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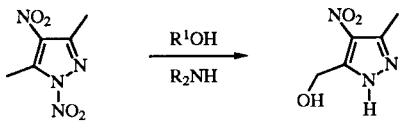
Introduction.

The design and synthesis of coordination compounds strongly depends on the availability of the desired ligands [3]. Model systems for Type 1 Copper proteins are copper coordination compounds with azole-containing ligands [4,5]. In addition, the possibility of chelate formation may be enhanced when a coordinating substituent near the donor atom is present in the azole [3]. Azoles possessing one or more methyl groups are the most easily synthesized [6]. Therefore functionalization of such a methyl group would create a method to synthesize azoles containing a coordinating substituent. However, it is well known that in general, functionalizations of methyl groups involve multi-step transformations. It is also nearly impossible to functionalize one methyl group only of two identical methyl groups present in one molecule [7,8].

N-Nitropyrazoles have proved to be versatile intermediates in organic synthesis. In previous work we have described the thermal *intra*-molecular rearrangement reaction affording 3-nitro-1*H*-pyrazoles in excellent yields [6,9-12]. We have also described the *cine* substitution reaction of 1,4-dinitro-1*H*-pyrazoles [6,9,13-15] which has been incorporated in model syntheses of formycin, pyrazofurin and other C-nucleosides by J. G. Buchanan [16,17].

Scheme 1

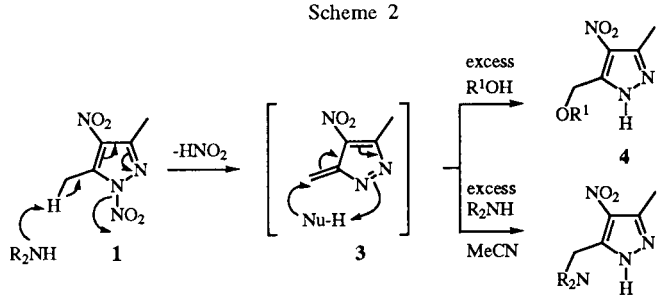


1 **2**

R^1 = methyl, ethyl or isopropyl
R_2NH = piperidine or morpholine

Earlier we reported [18] the facile conversion of 3,5-dimethyl-1,4-dinitro-1*H*-pyrazoles **1** to 3-hydroxymethyl-5-methyl-4-nitro-1*H*-pyrazole **2** by reacting **1** with secondary amines in alcoholic solution (see Scheme 1). The mechanism as proposed by Habraken and Bonser [18] involves an elimination-addition reaction (see Scheme 2). Deprotonation of **1** by the secondary amine results in formation of a diazafulvene intermediate **3**. Consecutive nucleophilic addition of a water molecule, formed by nitrosation of the amine with the generated nitrous acid then affords **2**. In addition, minor amounts of 3-alkoxymethyl derivatives **4** were obtained due to the addition of an alcohol molecule of the solvent (ROH) to the diazafulvene intermediate. Surprisingly no compounds were isolated resulting from the addition of the amine (R_2NH). However, when we reacted **1** with an excess of secondary amine in acetonitrile solution moderate yields of 3-dialkylaminomethyl-5-methyl-4-nitro-1*H*-pyrazoles **5-8** were obtained. The formation of **5-8** presumably proceeds also *via* the above described mechanism with, in this case, the secondary amine functioning as the base as

Scheme 2



1 **3** **4** **5-8**

Nu-H = R^1OH, R_2NH; R^1 = methyl, ethyl or isopropyl; **5**: R_2N = pyrrolidino; **6**: R_2N = piperidino; **7**: R_2N = morpholino and **8**: R_2N = diethylamino

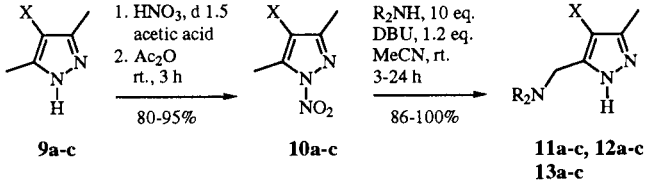
well as the nucleophile. These results prompted us to investigate this reaction more systematically.

Results and Discussion.

Treatment of the 4-bromo-3,5-dimethyl-1-nitro-1*H*-pyrazole **10a** with pyrrolidine and with piperidine afforded the corresponding dialkylaminomethyl-1*H*-pyrazoles **11a** and **12a** in excellent yields (97%). However, no reaction occurred upon reacting **10a** with morpholine. Morpholine (pK_a = 8.33) is much less basic than pyrrolidine and piperidine (pK_a = 11.27 and 11.12, respectively). Based upon our assumption that the first step concerns an elimination of nitrous acid (see Scheme 2), these results imply that the 5-methyl protons of **10a** are much less acidic than those of **1** and consequently the less basic morpholine fails to abstract a proton. Thus nitrous acid elimination and hence diazafulvene formation is precluded.

It is commonly believed that 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) is a non-nucleophilic strong base, which is well known for its good performance in elimination reactions [1,19,20]. We therefore then performed the reaction of **10a** with 10 equivalents of morpholine in acetonitrile using an additional amount of 1 equivalent of DBU to induce the diazafulvene formation. This resulted in a 100% yield of the pyrazole **13a**. Interestingly, the presence of 1 equivalent of DBU in the reaction mixtures of **10a** and pyrrolidine and of **10a** and piperidine resulted in much shorter reaction times. As a result of these findings we have developed a general and facile procedure for the conversion of the 4-halo-3,5-dimethyl-1*H*-pyrazoles **9a-c** to the 3-dialkylaminomethyl-5-methyl-4-halo-1*H*-pyrazoles **11a-c**, **12a-c**, and **13a-c** in almost quantitative yield (see Scheme 3). Structures of the new pyrazoles were determined by ^{1}H-nmr and ir spectroscopy, ms and elemental analysis.

Scheme 3



9a-c **10a-c** **11a-c, 12a-c 13a-c**

X = Br **9a-13a**; Cl **9b-13b** and I **9c-13c**
R_2N = pyrrolidino **11a-c**; piperidino **12a-c** and morpholino **13a-c**

In conclusion, this procedure provides the novel, potentially bidentate ligands 3-dialkylaminomethyl-5-methyl-4-substituted-1*H*-pyrazoles, by an attractively simple and short route. Moreover this methyl group functionalization once again demonstrates the versatility of the use of *N*-nitropyrazoles for specific conversions of pyrazoles [6,9-18].

Table 1

3-Dialkylaminomethyl-5-methyl-4-substituted-1*H*-pyrazoles

Compound	X	R_2N	Reaction time (h)	Yield (%)	mp (°C)
5	NO_2	pyrrolidino	2.5	59	121-123
6	NO_2	piperidino	1.5	48	136-138
7	NO_2	morpholino	2	77	yellow oil
8	NO_2	diethylamino	2	14	red oil
11a	Br	pyrrolidino	4	89	93-95
12a	Br	piperidino	5	86	129-131
13a	Br	morpholino	24	100	77-78
11b	Cl	pyrrolidino	3.5	86	96-97
12b	Cl	piperidino	5.5	87	119-120
13b	Cl	morpholino	24	100	oil
11c	I	pyrrolidino	3	91	115
12c	I	piperidino	5	87	132-133
13c	I	morpholino	24	91	117-118

Table 2

Spectroscopic Data of New Compounds

Compound	ms (70 eV) m/z	1H nmr, δ [a] CH_3	CH_2	α-CH_2	β-CH_2	γ-CH_2
5	211, 140	2.56	4.13	2.74	1.88	
6	224, 207, 84	2.28	3.60	2.48	1.56	1.48
7	227, 209, 110, 86	2.58	3.98	2.64	3.78	
8	212, 195, 72, 29	2.56	4.04	2.68	1.08 (2 x CH_3)	
11a	245, 243, 244, 242, 70	2.26	3.68	2.62	1.82	
12a	259, 257, 84	2.28	3.61	2.48	1.56	1.48
13a	261, 259, 180, 175, 173, 86	2.28	3.56	2.54	3.74	
11b	201, 199, 164, 129, 70	2.24	3.68	2.61	1.82	
12b	215, 213, 178, 129, 84	2.21	3.49	2.45	1.58	1.45
13b	217, 215, 180, 129, 86	2.22	3.54	2.52	3.72	
11c	291, 164, 70	2.26	3.66	2.62	1.82	
12c	305, 221, 178, 84	2.24	3.44	2.42	1.56	1.45
13c	308, 221	2.28	3.54	2.53	3.73	

[a] Deuteriochloroform, tetramethylsilane as the internal standard.

EXPERIMENTAL

The ^{1}H-nmr spectra were recorded on a JEOL FX 200 FT NMR spectrometer (tetramethylsilane as internal standard). The ir spectra were recorded as potassium bromide discs or neat using a Pye Unicam SP3-200 spectrometer. The ms spectra were obtained using a ITD ion trap detector (gc-ms), HP5985A (ms) and a TSQ (lc-ms) spectrometer with EI ionization, electron beam energy 70 eV, source temperature 423 K. Element analyses were performed by Mikroanalytisches Labor Pascher, Bonn, Germany. Melting points were obtained on a Büchi Melting Point Apparatus (open capillary tubes) and are uncorrected. Prior to recrystallization most compounds were purified by a short column technique on silica H (Merck 7736) according to Stahl as described by Hunt and Rigby [21]. The eluents used were chloroform/ethyl acetate/methanol = 9/5/1 for **5-8** and **11b-13b** and 20/10/3 for **11c-13c**. Spraying with a Rhodamine B solution (0.05% in ethanol) was used for the detection of nitropyrazoles on tlc (chloroform/ethyl acetate/methanol = 9/5/1). In the case of *N*-

nitropyrazoles the purple coloured spots, characteristic for all nitropyrazoles, turn yellow on standing. Spraying with *o*-toluidine/potassium iodide (0.05 *N*) (1/1) was used after chlorination for the detection of 1-*H*-unsubstituted pyrazoles [22]. The tlc plates used were from Schleicher and Schuell F 1500/LS 254. All solvents used for column chromatography, reactions and crystallizations were purified according to standard procedures. All chemicals were high grade commercial products used as received from the suppliers. Compounds **1** [1,18], **9a** [23] and **9c** [23] were synthesized according to literature procedures. Compound **9b** was prepared from 3-chloro-2,4-pentanedione and hydrazine [23,24].

The new *N*-nitropyrazoles **10a-c** were synthesized according to the procedures as described previously [11,25]. The *N*-nitropyrazoles were stored under anhydrous conditions to prevent hydrolysis.

4-Bromo-3,5-dimethyl-1-nitro-1*H*-pyrazole **10a**.

This compound was obtained as colorless crystals, mp 47-52° dec; ir: ν *N*-NO_2 1610 and 1267 cm^{-1}; ^{1}H-nmr: δ 2.30 (s, 3H, 3-CH_3), 2.68 (s, 3H, 5-CH_3); hrms: m/e Calcd. for $C_5H_6{}^{79}BrN_3O_2$: 218.9643. Found: 218.9632.

4-Chloro-3,5-dimethyl-1-nitro-1*H*-pyrazole **10b**.

This compound was obtained as colorless crystals, mp 54-57° dec; ir: ν *N*-NO_2 1611 and 1270 cm^{-1}; ^{1}H-nmr: δ 2.29 (s, 3H, 3-CH_3), 2.61 (s, 3H, 5-CH_3); hrms: m/e Calcd. for $C_5H_6{}^{35}ClN_3O_2$: 175.0148. Found: 175.0152.

4-Iodo-3,5-dimethyl-1-nitro-1*H*-pyrazole **10c**.

This compound was obtained as colorless crystals, mp 83-85° dec; ir: ν *N*-NO_2 1608 and 1261 cm^{-1}; ^{1}H-nmr: δ 2.30 (s, 3H, 3-CH_3), 2.68 (s, 3H, 5-CH_3); hrms: m/e Calcd. for $C_5H_6IN_3O_2$: 266.9504. Found: 266.9516.

3-Dialkylaminomethyl-4-halo-5-methyl-1*H*-pyrazoles **11a-c**, **12a-c**, and **13a-c**.

General Procedure A.

To a solution of the 4-halo-3,5-dimethyl-1-nitro-1*H*-pyrazole **10a-c** (3.2 mmoles, 1 equivalent) in acetonitrile (10 ml) in a round bottom flask (100 ml) equipped with magnetic stirrer and addition funnel, a solution of DBU (0.58 g, 3.84 mmoles, 1.2 equivalents) dissolved in the secondary amine (32 mmoles, 10 equivalents) was added dropwise. The reaction mixture was stirred at room temperature until the *N*-nitropyrazole could no longer be detected on tlc. Water (20 ml) and a solution of sulfamic acid (15 equivalents) in water (30 ml) were added to the organic phase. After refluxing for 0.5 hour and evaporating the solvent, the crude product was dissolved in water (50 ml) and washed with chloroform. The water layer was neutralized with sodium carbonate (*p*H = 7-8) and extracted with chloroform (3 x 25 ml). The combined organic phases were dried on magnesium sulfate. The solvent was evaporated and the crude product was chromatographed. Compounds **11a-b**, **13a** and **13c** were recrystallized from petroleum ether (80-100°). Compounds **12a-c** and **11c** were recrystallized from ethanol/water (1/9) and water, respectively. After column chromatography **13b** was obtained as a colourless oil which was not purified any further.

3-Dialkylaminomethyl-5-methyl-4-nitro-1*H*-pyrazoles **5-8**.

General Procedure B.

A round bottom flask (100 ml) containing the secondary amine (30 mmoles, 1 equivalent), was equipped with magnetic stirrer, addition funnel, and thermometer. A solution of **1** (0.6 g, 3 mmoles, 1 equivalent) in acetonitrile (10 ml) was added dropwise while the temperature of the reaction mixture was kept below 30°. To complete the reaction this reaction mixture was stirred at 25° until the *N*-nitropyrazole could no longer be detected on tlc. See procedure A for the work-up procedure. Compounds **5** and **6** were recrystallized from petroleum ether (80-100°) and ethanol/water, respectively. After column chromatography, compound **7** was obtained as a red oil which was further purified by boiling in ethanol with Norit. After column chromatography, compound **8** was obtained as a red oil which could not be purified any further. Infrared spectra (potassium bromide) for compounds **5-8** showed characteristic absorptions at ν 1360 and 1580 cm^{-1} (C-NO_2). Reaction details and spectroscopic data of compounds **5-8**, **11a-c**, **12a-c** and **13a-c** are summarized in Table 1 and Table 2, respectively.

3-Methyl-4-nitro-5-pyrrolidinomethyl-1*H*-pyrazole **5**.

Recrystallization from petroleum ether (80-100°) afforded white needles, mp 121.5-123°; ir: ν *C*-NO_2 1595 and 1361 cm^{-1}; ^{1}H-nmr: δ 1.88 (m, 4H, -CH_2CH_2-), 2.56 (s, 3H, 3-CH_3), 2.74 (m, 4H, -CH_2NCH_2-), 4.13 (s, 2H, CH_2); ms: m/e 211 (M+H, 100%), 140 (M- C_4H_8N).

Anal. Calcd. for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.6; O, 15.2. Found: C, 51.46; H, 6.85; N, 26.4; O, 15.2.

3-Methyl-4-nitro-5-piperidinomethyl-1*H*-pyrazole **6**.

Recrystallization from ethanol water (1/2) afforded white needles, mp 136-138°; ir: ν *C*-NO_2 1578 and 1360 cm^{-1}; ^{1}H-mnr: δ 1.48 (m, 2H, CH_2), 1.56 (m, 4H, $2CH_2$), 2.28 (s, 3H, 3-CH_3), 2.48 (m, 4H, -CH_2NCH_2-), 3.6 (s, 2H, CH_2); ms: m/e 224 (M), 207 (M-OH), 84 (C_5H_8N, 100%); hrms: m/e Calcd. for $C_{10}H_{16}N_4O_2$: 224.1273. Found: 224.1285.

Anal. Calcd. for $C_{10}H_{16}N_4O_2$: C, 53.36; H, 7.19; N, 24.99; O, 14.27. Found: C, 53.34; H, 7.23; N, 25.0; O, 14.14.

3-Methyl-5-morpholinomethyl-4-nitro-1*H*-pyrazole **7**.

After column chromatography (silica 60H, Merck 7736) the red oil was further purified by boiling in ethanol with norit. The yellow oil was kept under nitrogen at -15°; ir: ν *C*-NO_2 1585 and 1360 cm^{-1}; ^{1}H-nmr: δ 2.58 (s, 3H, CH_3), 2.64 (m, 4H, -CH_2NCH_2-), 3.78 (m, 4H, -CH_2OCH_2-), 3.98 (s, 2H, CH_2); ms: m/e 227 (M+H), 209 (M-OH), 110 ($C_4H_4N_3O$), 86 (C_4H_8NO, 100%), 56 (C_4H_8); hrms: m/e Calcd. for $C_9H_{14}N_4O_3$: 226.1066. Found: 226.1063.

Anal. Calcd. for $C_9H_{14}N_4O_3$: C, 47.78; H, 6.24; O, 21.2. Found: C, 48.2; H, 6.43; O, 21.2.

3-Diethylaminomethyl-5-methyl-4-nitro-1*H*-pyrazole **8**.

Column chromatography (silica 60H, Merck 7736) gave a red oil; ir: ν *C*-NO_2 1580 and 1350 cm^{-1}; ^{1}H-nmr: δ 1.08 (t, 6H, 2 CH_3), 2.56 (s, 3H, 5-CH_3), 2.68 (q, 4H, -CH_2NCH_2-), 4.04 (s, 2H, CH_2); ms: m/e 212 (M), 195 (M-OH), 72 ($C_4H_{10}N$), 29 (C_2H_5, 100%); hrms: m/e Calcd. for $C_9H_{16}N_4O_2$: 212.1273. Found: 212.1285.

4-Bromo-3-methyl-5-pyrrolidinomethyl-1*H*-pyrazole **11a**.

Recrystallization from petroleum ether (80-100°) afforded yellow needles, mp 93.5-95°; ^{1}H-nmr: δ 1.82 (m, 4H, -CH_2CH_2-), 2.26 (s, 3H, 3-CH_3), 2.62 (m, 4H, -CH_2NCH_2-), 3.68 (s, 2H, CH_2); ms: m/z 245 (M ^{81}Br), 244 (M ^{81}Br-H), 243 (M ^{79}Br), 242 (M ^{79}Br-H), 70 (C_4H_8N, 100%).

Anal. Calcd. for $C_9H_{14}BrN_3$: C, 44.28; H, 5.78; Br, 32.7; N, 17.2. Found: C, 43.85; H, 5.78; Br, 32.5; N, 17.2.

4-Bromo-3-methyl-5-piperidinomethyl-1*H*-pyrazole **12a**.

Recrystallization from ethanol water (1/1) afforded white needles, mp 129-131°; ^{1}H-nmr: δ 1.48 (m, 2H, CH_2), 1.56 (m, 4H, $2CH_2$), 2.28 (s, 3H, 3-CH_3), 2.48 (m, 4H, -CH_2NCH_2-), 3.6 (s, 2H, CH_2); ms: m/e 259 (M ^{81}Br), 257 (M ^{79}Br), 84 ($C_5H_{10}N$, 100%); hrms: m/e Calcd. for $C_{10}H_{16}{}^{79}BrN_3$: 257.0528. Found: 257.0516.

Anal. Calcd. for $C_{10}H_{16}BrN_3$: C, 46.30; H, 6.31; Br, 30.9; N, 16.1. Found: C, 46.68; H, 6.27; Br, 30.7; N, 16.3.

4-Bromo-3-methyl-5-morpholinomethyl-1*H*-pyrazole **13a**.

Recrystallization from petroleum ether (60-80°) afforded light crystals, mp 76.5-78°; ^{1}H-nmr: δ 2.28 (s, 3H, CH_3), 2.54 (m, 4H, -CH_2NCH_2-), 3.56 (s, 2H, CH_2), 3.74 (m, 4H, -CH_2OCH_2-); ms: m/e 261 (M ^{81}Br), 259 (M ^{79}Br), 180 (M-Br), 175 (M ^{81}Br-C_4H_8NO), 173 (M ^{79}Br-C_4H_8NO), 86 (C_4H_8NO, 100%).

Anal. Calcd. for $C_9H_{14}BrN_3O$: C, 41.55; H, 5.43; Br, 30.7; N, 16.2. Found: C, 41.17; H, 5.43; Br, 31.1; N, 16.2.

4-Chloro-3-methyl-5-pyrrolidinomethyl-1*H*-pyrazole **11b**.

Recrystallization from petroleum ether (80-100°) afforded white crystals, mp 95.5-97°; ir: ν *C*-Cl 1093 cm^{-1}; ^{1}H-nmr: δ 1.82 (m, 4H, 2 CH_2), 2.24 (s, 3H, 3-CH_3), 2.61 (m, 4H, -CH_2NCH_2-), 3.68 (s, 2H, CH_2); ms: m/e 201 (M ^{37}Cl), 199 (M ^{35}Cl), 164 (M-Cl), 129 (M-C_4H_8N), 70 (C_4H_8N, 100%).

Anal. Calcd. for $C_9H_{14}N_3Cl$: C, 54.14; H, 7.07; Cl, 17.8; N, 21.0. Found: C, 53.95; H, 7.03; Cl, 17.9; N, 21.0.

4-Chloro-3-methyl-5-piperidinomethyl-1*H*-pyrazole **12b**.

Recrystallization from ethanol water (1/9) afforded white crystals, mp 119-120.5°; ^{1}H-nmr: δ 1.45 (m, 2H, CH_2), 1.58 (m, 4H, $2CH_2$), 2.21 (s, 3H, 3-CH_3), 2.45 (m, 4H, -CH_2NCH_2-), 3.49 (s, 2H, CH_2); ms: m/e 215 (M ^{37}Cl), 213 (M ^{35}Cl), 178 (M-Cl), 129 (M-$C_5H_{10}N$), 84 ($C_5H_{10}N$, 100%).

Anal. Calcd. for $C_{10}H_{16}N_3Cl$: C, 56.2; H, 7.55; Cl, 16.6; N, 19.7. Found: C, 56.2; H, 7.48; Cl, 17.0; N, 20.0.

4-Chloro-3-methyl-5-morpholinomethyl-1*H*-pyrazole **13b**.

Column chromatography (silica 60H, Merck 7736) gave a colorless oil; ^{1}H-nmr: δ 2.22 (s, 3H, 3-CH_3), 2.52 (m, 4H, -CH_2NCH_2-), 3.54 (s, 2H, CH_2), 3.72 (m, 4H, -CH_2OCH_2-); ms: m/e 217 (M ^{37}Cl), 215 (M ^{35}Cl), 180 (M-Cl), 129 (M-C_4H_8NO, 100%), 86 (C_4H_8NO).

Anal. Calcd. for $C_9H_{14}N_3ClO$: C, 50.12; H, 6.54. Found: C, 49.85; H, 6.84.

4-Iodo-3-methyl-5-pyrrolidinomethyl-1*H*-pyrazole **11c**.

Recrystallization from water afforded white crystals, mp 115°; ^{1}H-nmr: δ 1.82 (m, 4H, $2CH_2$), 2.26 (s, 3H, 3-CH_3), 2.62 (m, 4H, -CH_2NCH_2-), 3.66 (s, 2H, CH_2); ms: m/e 291 (M), 164 (M-I), 95 (M-I-C_4H_8N), 70 (C_4H_8N, 100%).

Anal. Calcd. for $C_9H_{14}N_3I$: C, 37.13; H, 4.85; I, 43.59; N, 14.4. Found: C, 36.96; H, 4.79; I, 43.52; N, 14.4.

4-Iodo-3-methyl-5-piperidinomethyl-1*H*-pyrazole **12c**.

Recrystallization from ethanol water (1/9) afforded white crystals, mp 132-133.5°; ^{1}H-nmr: δ 1.45 (m, 2H, CH_2), 1.56 (m, 4H, $2CH_2$), 2.24 (s, 3H, 3-CH_3), 2.42 (m, 4H, -CH_2NCH_2-), 3.44 (s, 2H, CH_2); ms: m/e 305 (M), 221 (M-$C_5H_{10}N$), 178 (M-I), 84 ($C_5H_{10}N$, 100%).

Anal. Calcd. for $C_{10}H_{16}N_3I$: C, 39.36; H, 5.28; I, 41.6; N, 13.8. Found: C, 39.25; H, 5.28; I, 41.4; N, 13.8.

4-Iodo-3-methyl-5-morpholinomethyl-1*H*-pyrazole **13c**.

Recrystallization from petroleum ether (80-100°) afforded white crystals, mp 117-118°; ^{1}H-nmr: δ 2.28 (s, 3H, CH_3), 2.53 (m, 4H, -CH_2NCH_2-), 3.54 (s, 2H, CH_2), 3.73 (m, 4H, -CH_2OCH_2-); ms: m/e 308 (M+H), 221 (M-C_4H_8NO, 100%).

Anal. Calcd. for $C_9H_{14}N_3IO$: C, 35.2; H, 4.59; I, 41.3; N, 13.7; O, 5.21. Found: C, 35.5; H, 4.73; I, 41.2; N, 13.5; O, 5.27.

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