Pseudoesters and Derivatives. XXV [1]. 1,3-Dipolar Cycloaddition of Diazomethane to 5-Methoxy-3-pyrrolin-2-ones

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Cycloaddition of diazomethane to pyrrolinones **1a,b,d,e** affords only one regioisomer as a mixture of the epimeric pyrrolopyrazolines **2** and **2'**. 4-Halo derivatives **1f,g** react with diazomethane to give the two possible regioisomers **2** and **3**. The regio- and stereochemistry of the adducts is evidenced by the ^{1}H-nmr data. The primary adducts originated from the halopyrrolinones suffer dehydrohalogenation to give aromatized products, which by further methylation give derivatives of type **7**, **8**, **10** and **11**.

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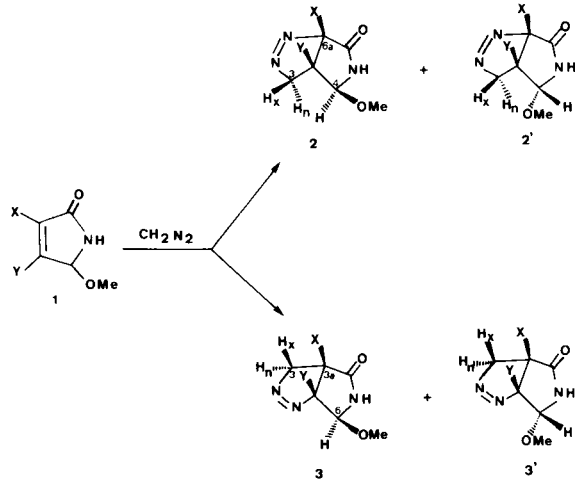
In previous papers [2-4] we reported on the application of 5-methoxyfuran-2(5*H*)-ones to the synthesis of other heterocyclic compounds, such as pyrrolinones and pyridazinones. Recently we have also shown [1,5] that methoxyfuranones and pyridazinones undergo 1,3-dipolar cycloaddition of diazomethane and these reactions provide valuable routes to several fused heterocyclic ring systems.

In the present paper these studies are extended to the cycloaddition of diazomethane to 5-methoxy-3-pyrrolin-2-ones **1a-g** which offers a possible quick entry into the relatively unknown pyrrolopyrazole ring system.

Scheme 1



Results and Discussion.

The 1,3-dipolar cycloaddition of diazomethane to methoxypyrrolinones is effected by treatment of the corresponding derivative of type **1** with an excess of ethereal diazomethane at −10° (Scheme 1). The reaction parallels that with 5-methoxy-2(5*H*)-furanones [1], although requires longer periods, even by using a great excess of ethereal diazomethane. The results of the reactions are summarized in Table 1.

Table 1

Cycloaddition of Diazomethane to 5-Methoxy-3-pyrrolin-2-ones

Substrate	X	Y	Time (days)	Products [a] 2	2'	3	3'
1a	H	H	7 [b]	70	30	—	—
1b	CH_3	H	30 [c]	55	45	—	—
1c	H	CH_3	— [d]	—	—	—	—
1d	Br	H	10 [b]	60	40	—	—
1e	Cl	H	10 [b]	60	40	—	—
1f	H	Br	30 [e]	(50) [f]		(50) [f]	
1g	H	Cl	40 [e]	(50) [f]		(50) [f]	

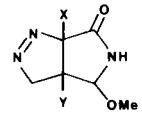
[a] Relative product distrubution (%) (^{1}H-nmr). [b] Time required for a total conversion. [c] Only a *ca.* 50% conversion is attained. [d] No reaction after 60 days. [e] Only a *ca.* 20-30% conversion is attained. [f] Determined from the pyrrolopyrazole derivatives formed by aromatization; only one epimer is formed.

The cycloaddition to 3- or 4-substituted-5-methoxy-3-pyrrolin-2-ones proceeds at a rate slower than that of the unsubstituted compound. Thus the 3-methyl-substituted pyrrolinone **1b** shows a lower reactivity compared to **1a** and only a partial conversion is attained, and in the case of 4-methyl-substituted pyrrolinone **1c** no trace of adduct is detected after 60 days. Similarly, the presence of halogen atoms at 3- or 4-position also decreases the reactivity compared to **1a**, although pyrrolinones **1d-g** are more reactive than the corresponding methylsubstituted derivatives.

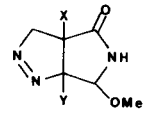
In principle, the reaction occurs to give only one regioisomer, which is formed as a mixture of the cycloadducts **2**

and **2′**, epimeric at C-4. The direction of the cycloaddition is the expected in accord with the early von Auwers rule [6] and with the results previously obtained in the corresponding methoxyfuranones [1]. Exceptions were found, however, with the 4-halo derivatives **1f,g**, which afford approximately equal quantities of both regioisomers, each of which appear as a single epimer (**2** or **2′** and **3** or **3′**), the stereochemistry of which has not been ascertained.

The regioselectivities obtained can be rationalized through a semiquantitative FMO approach [7] (Table 2). In fact, in all cases the stabilization energy calculated for the "normal" approach (A) is greater than that for the "inverse" orientation (B). The formation of both regioisomers occurs only in the 4-halopyrrolinones in which the stabilization energy difference is minimal ($\Delta\Delta E$ = 0.60 kcal/mol). The lower reactivity of the 3- and 4-substituted pyrrolinones compared to the unsubstituted case **1a** may be adscribed, as in the respective furanones [1], to greater steric interactions, not considered in the FMO method.



A



B

The structure of the cycloadducts is supported by the spectral data, particularly the ^{1}H-nmr. The adducts **2f,g**, or **2′f,g**, formed from the 4-halopyrrolinones are too unstable to be characterized by spectral means. Their formation, however, is evidenced by the isolation of the pyrrolopyrazolone **7**, originated by dehydrohalogenation and methylation of the primary unstable adducts.

Table 2

Stabilization Energies (kcal/mol) of Cycloaddition of Diazomethane to Pyrrolinones **1**

Pyrrolinone	ΔE_A	ΔE_B	ΔE_A-ΔE_B
1a	37.47	34.16	3.31
1b	37.12	33.99	3.13
1c	37.21	33.96	3.25
1e	43.73	38.65	5.08
1g	38.73	38.13	0.60

The stereochemistry of the adducts **2** and **2′** is assigned on the basis of the ^{1}H-nmr data (Table 3), using arguments similar to those which allowed the assignment of structure of the corresponding furopyrazoline derivatives [1]:

(i) A coupling constant $J_{3a,4}$ = 6.9-7.8 Hz indicates that H-3a and H-4 must be *cis* to each other (*endo* MeO-group, **2′**), whereas a coupling constant $J_{3a,4}$ = 0.0-1.0 Hz suggests a *trans* relationship (*exo* MeO-group, **2**).

(ii) An *exo* MeO-group causes a considerable deshielding of H-3x and H-6a. Similarly, the H-3n is largely deshielded by the anisotropy effect of an *endo* MeO-group.

(iii) The H-4 *endo* protons are shielded by the anisotropy effect of the N=N double bond.

The cycloadducts from **1a,b** are stable enough at room temperature, thus allowing the separation of the C-4 epimers **2a,b** and **2′a,b** and their full characterization by analytical and spectral data. In these cases no trace of spontaneous decomposition has been observed and nitrogen extrusion occurs only by thermal decomposition (above 100°) or photolysis [8].

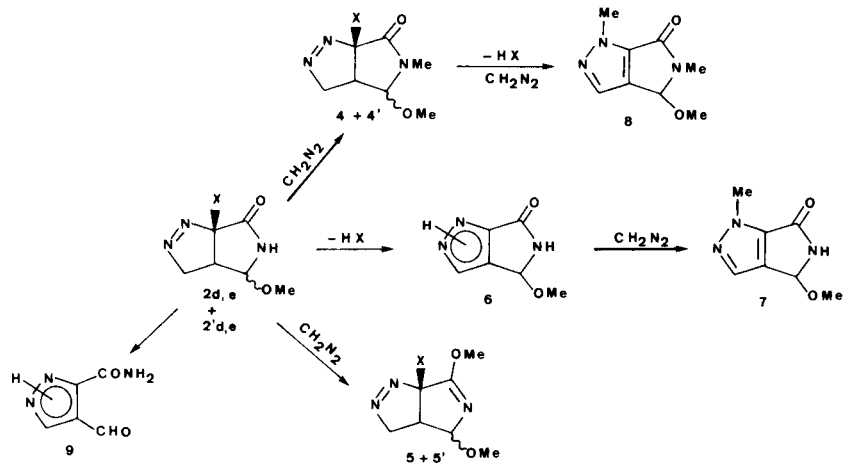
Table 3

^{1}H-NMR Chemical Shifts and Coupling Constants of Adducts **2** and **3**

Adduct	H-3x	H-3n	X	Y	H-4 (H-6)	OMe	$J_{X,Y}$	$J_{Y,4}$	$J_{Y,3x}$	$J_{Y,3n}$	$J_{X,3x}$	$J_{X,3n}$	$J_{3x,3n}$
2a	4.98	4.57	5.65	2.68	4.52	3.36	8.3	1.0	10.2	4.9	−1.1	−2.6	−18.7
2′a	4.38	5.28	5.26	3.04	4.79	3.32	8.9	6.9	9.2	2.3	−2.3	−2.4	−18.7
2b	5.03	4.53	(1.75) [a]	2.31	4.47	3.36	—	0.0	10.1	4.9	—	—	−18.7
2′b	4.38	5.24	(1.51) [a]	2.65	4.75	3.33	—	7.0	8.2	2.3	—	—	−18.3
2d	5.13	4.79	—	2.90	4.65	3.34	—	0.0	9.5	4.0	—	—	−19.1
2′d	4.49	5.32	—	3.28	4.89	3.41	—	7.8	7.8	1.6	—	—	−18.7
2e	5.19	4.76	—	2.80	4.60	3.42	—	0.0	9.5	4.1	—	—	−19.1
2′e	4.56	5.36	—	3.13	4.90	3.36	—	6.9	7.8	1.7	—	—	−18.7
3f (or **3′f**)	4.61	5.13	3.08	—	(5.30)	3.61	—	—	—	—	7.6	0.0	−18.6
3g (or **3′g**)	4.65	5.14	3.02	—	(5.30)	3.62	—	—	—	—	7.7	1.1	−18.8

[a] Me signals.

Scheme 2



In contrast, the adducts from halopyrrolinones are unstable at room temperature, thus avoiding the separation of the epimers, the characterization of which has only been effected on the basis of the spectral data.

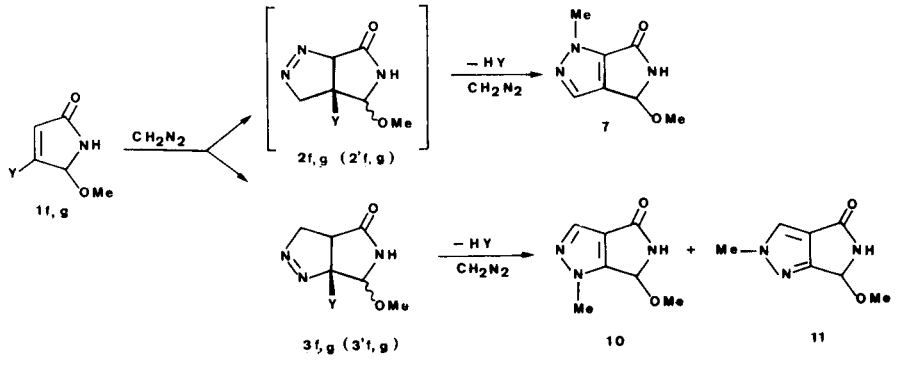
Furthermore, when the cycloaddition to the 3-halopyrrolinones **1d,e** is effected for prolonged reaction periods, in the presence of a great excess of diazomethane, the primary adducts are converted into the *N*-methyl derivatives **4** + **4′** or the *O*-methyl ethers **5** + **5′** (Scheme 2). The *N*-methylpyrazolines of type **4** are not stable enough to be isolated and their presence has been deduced from the ^{1}H-nmr spectrum of the crude reaction mixture, which shows signals at δ 2.88/2.93 and 2.89/2.93 attributable to the N-CH_3 groups of the pyrazolines **4d** + **4′d** and **4e** + **4′e**, respectively. The remaining signals overlap with those of the initial adduct; therefore, a complete analysis of the spectrum was not possible.

The *O*-methyl derivatives **5** + **5′** can be separated by flash chromatography but are not stable enough for a microanalysis to be obtained. It is also to note that, under the reaction conditions, the primary adducts **2d,e** + **2′d,e** and their *N*-methyl derivatives **4** + **4′** readily eliminate HX to give the corresponding pyrrolopyrazole derivatives, which are further *N*-methylated to the stable pyrrolopyrazolones **7** and **8**, respectively.

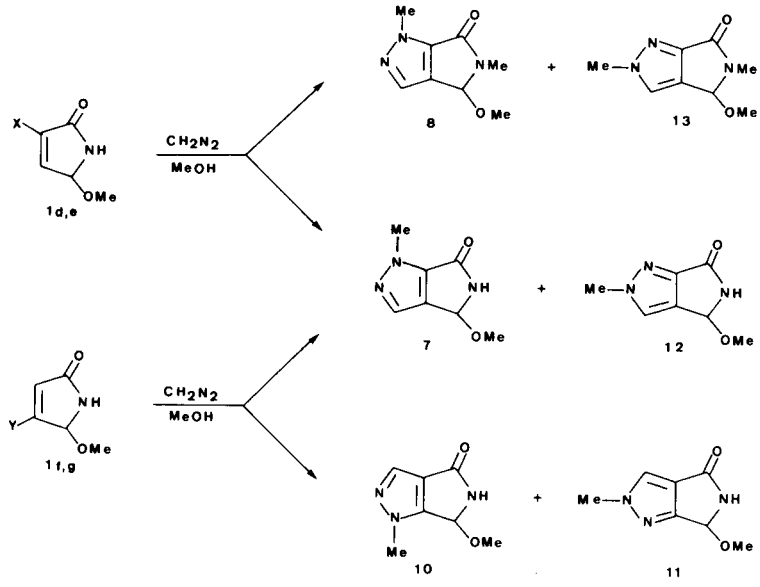
The adducts **2d,e** and **2′d,e** are also unstable to silica gel and during the chromatographic separation are converted to the pyrrolopyrazole derivative **6** by dehydrohalogenation. Moreover, spontaneous or acid catalyzed dehydrohalogenation of **2d,e** and **2′d,e** is accompanied by cleavage of the pyrrolinone ring to yield the pyrazole derivative **9**, identical with an authentic sample [9].

The adducts **2f,g**, or **2′f,g**, presumably originated by cycloaddition of diazomethane to the 4-halopyrrolinones

Scheme 3



Scheme 4



1f,g, have not been detected and by dehydrohalogenation followed by methylation are converted to the pyrrolopyrazole derivative **7** (Scheme 3), which confirms their formation. In contrast, the corresponding regioisomeric cycloadducts **3f,g**, originated from an inverse orientation of the partners, are stable enough to be characterized by the ^{1}H-nmr spectra. In this case, however, only one stereoisomer is formed, although in absence of the coupling constant $J_{3a,4}$ a decission between the epimers was not possible. The adducts undergo dehydrohalogenation and further methylation to give the *N*-methyl derivatives **10** and **11**.

It should be noted that when the above cycloadditions of diazomethane to the halopyrrolinones are carried out in methanol with an excess of ethereal diazomethane, at $-10°$, the reactions proceed more rapidly than in the absence of methanol. Furthermore, the primary cycloadducts are converted directly into isomeric mixtures of the corresponding *N*-methylated pyrrolopyrazole derivaties (Scheme 4). Thus, the cycloaddition to 3-halopyrrolinones was complete within 4-5 days yielding mainly the pyrrolopyrazole derivatives **7** and **8**, accompanied by small amounts of their isomers **12** and **13**, with a different position of the *N*-methylation. Under the same conditions, the cycloaddition to 4-halopyrrolinones is only completed after 30 days, and the "normal" adducts are converted into the *N*-methylpyrazoles **7** and **12**, whereas those from an "inverse" cycloaddition give rise to the *N*-methylpyrazoles **10** and **11**.

The assignment of the position of *N*-methylation in compounds **8/13**, **7/12** and **10/11** was based on changes in chemical shift of the pyrazole proton in going from chloroform to DMSO as solvent. Thus, 2-Me substituted derivatives show variations of *ca.* 0.5 ppm, while in 1-Me substituted these variations are small (0.02-0.11), in accord with previous results in other disubstituted pyrazoles [9].

EXPERIMENTAL

Melting points have been determined on a Kofler hot stage and are uncorrected. The ir spectra were recorded on a Perkin-Elmer model 257 grating spectrometer, ν values in cm^{-1} and the ^{1}H-nmr spectra on a Varian EM-390 or a Bruker WM 200 SY, in deuteriochloroform solutions (unless otherwise stated), using TMS (δ = 0 ppm) as the internal reference. Mass spectra were recorded on a Hewlett-Packard GC-MS 5985 System. Silica gel Merck 60 (70-230 mesh), 60 (230-400 mesh) and DC-Alufolien 60 F_{254} were used for conventional, flash column chromatography and analytical tlc, respectively.

The eigenvalues and eigenvectors (energies and coefficients) of FMO of pyrrolinones have been obtained from a CNDO/2 program running on an IBM 360/65 computer, using standard bond lengths and dihedral angles. The corresponding bondings for diazomethane and β values have been taken from Houk [7].

Cycloaddition of Diazomethane to 5-Methoxy-3-pyrrolin-2-ones **1**. General Procedure.

To a solution of the pyrrolinone **1** (5 mmoles) in diethyl ether (10 ml), cooled to $-10°$, was added a cold ethereal solution of diazomethane (10 ml, containing 0.3 mmole/ml). The reaction was kept at $-10°$ during the period indicated in Table 1 (for prolonged reaction times, additional portions of diazomethane solution were periodically added). The solvent was removed and the mixture of stable epimers was separated by column chromatography (ethyl acetate-chloroform 2:1).

3a,6a-Dihydro-4-*exo*-methoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**2a**).

This compound (60% yield) had mp 144-145° (from chloroform-petroleum ether); ir (Nujol): 3200, 3100 (NH), 1710 (C=O), 1555 (N=N) cm^{-1}; ms: (m/z) 155 (M$^+$), 126, 124, 112, 96, 68 (100%).

Anal. Calcd. for $C_6H_9O_2N_3$: C, 46.45; H, 5.80; N, 27.09. Found: C, 46.59; H, 5.78; N, 26.77.

3a,6a-Dihydro-4-*endo*-methoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**2'a**).

This compound (25% yield) had mp 174° (from chloroform-petroleum ether); ir (Nujol): 3260 (NH), 1730, 1700 (C=O), 1540 (N=N) cm^{-1}; ms: (m/z) 155 (M^+), 126, 124, 112, 96, 68 (100%).

Anal. Calcd. for $C_6H_9O_2N_3$: C, 46.45; H, 5.80; N, 27.09. Found: C, 46.70; H, 5.60; N, 27.20.

3a,6a-Dihydro-4-*exo*-methoxy-6a-methyl-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**2b**).

This compound (44% yield based on consumed **1b**) had a mp 80-83° (from chloroform-petroleum ether); ir (Nujol): 3720 (NH), 1700 (C=O), 1560 (N=N) cm^{-1}; ms: (m/z) 169 (M^+), 138, 126, 110 (100%), 83, 82, 80.

Anal. Calcd. for $C_7H_{11}O_2N_3$: C, 49.70; H, 6.51; N, 24.85. Found: C, 49.78; H, 6.81; N, 24.43.

3a,6a-Dihydro-4-*endo*-methoxy-6a-methyl-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**2'b**).

This compound (26% yield, based on consumed **1b**) had a mp 104-105° (from chloroform-petroleum ether); ir (Nujol): 3200, 3110 (NH), 1715 (C=O), 1550 (N=N) cm^{-1}; ms: (m/z) 169 (M^+), 126, 110 (100%), 94, 83, 82, 80.

Anal. Calcd. for $C_7H_{11}O_2N_3$: C, 49.70; H, 6.51; N, 24.85. Found: C, 50.00; H, 6.68; N, 24.68.

The halogenated adducts **2d-g** are unstable at room temperature. They were identified by the ^{1}H-nmr spectrum of the crude mixture (Table 3) and through the products originated by methylation and aromatization described below.

Methylation and Aromatization of the Halogenated Cycloadducts.

An excess of cold ethereal diazomethane was added to the cycloaddition mixture (at −10°), prepared in accord with the general procedure. The mixture was kept at −10° for 10-30 days (as indicated in each case) and the solvent was removed *in vacuo*. The crude mixture was analyzed by ^{1}H-nmr and the residue chromatographed on silica gel under pressure (petroleum ether-ethyl acetate-methanol 5:4:1).

The adducts **2d** + **2'd**, after 10-15 days, were converted to a crude mixture which contained compounds **5d**, **5'd**, **7** and **8** (described below), recovered **2d** + **2'd** and small amounts of their *N*-methyl derivatives **4d** [shows a signal at δ 2.88 (3H, NMe)] and **4'd** [shows a signal at 2.93 (3H, NMe)]. After chromatography the following compounds were isolated:

6a-Bromo-3a,6a-dihydro-4-*exo*,6-dimethoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazole (**5d**).

This compound was isolated in 5% yield as a liquid; ir (film): 1725 (C=O), 1645 (C=N), 1530 (N=N) cm^{-1}; ^{1}H-nmr: 4.83 (s, 1H, H-4), 4.80 (d, 1H, H-3x, $J_{3a,3x}$ = 2.6 Hz), 4.62 (d, 1H, H-3n, $J_{3a,3n}$ = 2.3 Hz), 4.02 (s, 3H, OMe-6), 3.51 (s, 3H, OMe-4), 2.96 (m, 1H, H-3a); ms: (m/z) 249, 247 (M^+), 206, 204, 162, 160, 149, 140, 84 (100%).

6a-Bromo-3a,6a-dihydro-4-*endo*,6-dimethoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazole (**5'd**).

This compound was isolated in 3% yield as a liquid; ir (film): 1725 (C=O), 1645 (C=N), 1530 (N=N) cm^{-1}; ^{1}H-nmr: 5.13 (d, 1H, H-4, $J_{3a,4}$ = 6.3 Hz), 5.06 (dd, 1H, H-3n, $J_{3x,3n}$ = −19.2 Hz), 4.73 (dd, 1H, H-3x, $J_{3a,3x}$ = 9.2 Hz), 3.98 (s, 3H, OMe-6), 3.49 (s, 3H, OMe-4), 3.15 (m, 1H, H-3a); ms: (m/z) 249, 247 (M^+), 206, 204, 162, 160, 149, 140, 84 (100%).

Satisfactory combustion analysis of the individual isomers **5d** and **5'd** could not be obtained due to easy decomposition by further chromatographic purification. However, an epimeric mixture **5d** + **5'd** obtained as an oil by chromatography (petroleum ether-ethyl acetate 1:2) of the crude reaction mixture gave satisfactory analytical data:

Anal. Calcd. for $C_7H_{10}BrO_2N_3$: C, 33.87; H, 4.03; N, 16.93. Found: C, 34.02; H, 4.17; N, 16.65.

4-Methoxy-4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**6**).

This compound (9% yield) had a mp 203-204° (from methanol); ir (Nujol): 3190, 3130 (NH), 1725, 1685 (C=O) cm^{-1}; ^{1}H-nmr (DMSO-d_6): 8.43 (br s, 1H, NH); 7.87 (s, 1H, H-3), 5.76 (s, 1H, H-4), 3.16 (s, 3H, OMe-4); ms: (m/z) 153 (M^+), 122 (100%), 94, 67.

Anal. Calcd. for $C_6H_7O_2N_3$: C, 47.05; H, 4.57; N, 27.48. Found: C, 47.05; H, 4.65; N, 27.19.

4-Methoxy-1-methyl-4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**7**).

This compound (35% yield) had a mp 137° (from chloroform-petroleum ether); ir (Nujol): 3230 (NH), 1710 (C=O) cm^{-1}; ^{1}H-nmr: 7.45 (s, 1H, H-3), 5.85 (s, 1H, H-4), 4.02 (s, 3H, NMe-1), 3.22 (s, 3H, OMe-4); (DMSO-d_6): 8.86 (br s, 1H, NH), 7.47 (s, 1H, H-3), 5.65 (s, 1H, H-4), 3.86 (s, 3H, NMe-1), 3.19 (s, 3H, OMe-4); ms: (m/z) 167 (M^+), 136 (100%), 123, 81, 68.

Anal. Calcd. for $C_7H_9O_2N_3$: C, 50.30; H, 5.39; N, 25.15. Found: C, 50.23; H, 5.46; N, 25.28.

4-Methoxy-1,5-dimethyl-4*H*-pyrrolo[3,4-*c*]pyrazol-6-one (**8**).

This compound was isolated in 15% yield as a liquid; ir (film): 1710 (C=O) cm^{-1}; ^{1}H-nmr: 7.42 (s, 1H, H-3), 5.62 (s, 1H, H-4), 4.02 (s, 3H, NMe-1), 3.02 (s, 3H, OMe-4), 2.92 (s, 3H, NMe-5); (DMSO-d_6): 7.53 (s, 1H, H-3), 5.69 (s, 1H, H-4), 3.93 (s, 3H, NMe-1), 2.99 (s, 3H, OMe-4), 2.86 (s, 3H, NMe-5); ms: (m/z) 181 (M^+), 166, 150 (100%), 137, 123, 68.

Anal. Calcd. for $C_8H_{11}O_2N_3$: C, 53.03; H, 6.07; N, 23.20. Found: C, 52.74; H, 6.03; N, 23.36.

The adducts **2e** + **2'e**, after 10-15 days, were converted to a crude mixture which contained compounds **5e**, **5'e** (described below), **6**, **7**, **8** (described above), recovered **2e** + **2'e** and small amounts of their *N*-methyl derivatives **4e** [shows a signal at δ 2.89 (3H, NMe)] and **4'e** [shows a signal at δ 2.93 (3H, NMe)]. After chromatography the following compounds were isolated:

6a-Chloro-3a,6a-dihydro-4-*exo*,6-dimethoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazole (**5e**).

This compound was isolated in 4% yield as a liquid; ir (film): 1725 (C=O), 1650 (C=N), 1545 (N=N) cm^{-1}; ^{1}H-nmr: 4.77 (d, 1H, H-3x, $J_{3a,3x}$ = 5.7 Hz), 4.76 (s, 1H, H-4), 4.48 (d, 1H, H-3n, $J_{3a,3n}$ = 2.3 Hz), 3.95 (s, 3H, OMe-6), 3.44 (s, 3H, OMe-4), 2.78 (m, 1H, H-3a); ms: (m/z) 205, 203 (M^+), 162, 160, 149, 140 (100%), 97.

6a-Chloro-3a,6a-dihydro-4-*endo*,6-dimethoxy-3*H*,4*H*-pyrrolo[3,4-*c*]pyrazole (**5'e**).

This compound was isolated in 2% yield as a liquid; ir (film): 1725 (C=O), 1650 (C=N), 1545 (N=N) cm^{-1}; ^{1}H-nmr: 5.08 (d, 1H, H-4, $J_{3a,4}$ = 6.4 Hz), 5.04 (dd, 1H, H-3n, $J_{3a,3n}$ = 3.8 Hz, $J_{3x,3n}$ = −19.3 Hz), 4.67 (dd, 1H, H-3x, $J_{3a,3x}$ = 9.1 Hz), 3.91 (s, 3H, OMe-6), 3.43 (s, 3H, OMe-4), 2.97 (m, 1H, H-3a); ms: (m/z) 203, 205 (M^+), 160, 162, 149 (100%), 140, 97.

Satisfactory combustion analysis of the isomers **5e** and **5'e** could not be obtained due to easy decomposition by further chromatographic purification.

The adducts **2f**(or **2'f**) + **3f** (or **3'f**), after 20-30 days, were converted to a crude mixture which was separated by chromatography to afford recovered **3f**(or **3'f**), and compounds **7** (30%), **10** (12%) and **11** (12%), the yields being based on consumed **1f**.

6-Methoxy-1-methyl-6*H*-pyrrolo[3,4-*d*]pyrazol-4(5*H*)-one (**10**).

This compound had mp 174-177° (from ethyl acetate-benzene); ir (Nujol): 3200, 3115 (NH), 1720, 1680 (C=O) cm^{-1}; ^{1}H-nmr: 7.58 (s, 1H, H-3), 5.93 (s, 1H, H-6), 3.91 (s, 3H, NMe-1), 3.25 (s, 3H, OMe-6); (DMSO-d_6): 8.42 (br s, 1H, NH), 7.55 (s, 1H, H-3), 5.92 (s, 1H, H-6), 3.83 (s, 3H, NMe-1), 3.26 (s, 3H, OMe-6); ms: (m/z) 167 (M^+), 136 (100%), 122, 109, 81, 68.

Anal. Calcd. for $C_7H_9O_2N_3$: C, 50.30; H, 5.39; N, 25.15. Found: C, 50.29; H, 5.38; N, 25.14.

6-Methoxy-2-methyl-6*H*-pyrrolo[3,4-*d*]pyrazol-4(5*H*)-one (**11**).

This compound had mp 184° (from ethyl acetate-benzene); ir (Nujol): 3180, 3100 (NH), 1710, 1660 (C=O) cm^{-1}; ^{1}H-nmr: 7.57 (s, 1H, H-3), 5.82

(s, 1H, H-6), 3.99 (s, 3H, NMe-2), 3.33 (s, 3H, OMe-6); (DMSO-d_6): 8.46 (br s, 1H, NH), 7.99 (s, 1H, H-3), 5.68 (s, 1H, H-6), 3.92 (s, 3H, NMe-2), 3.20 (s, 3H, OMe-6); ms: (m/z) 167 (M^+), 136 (100%), 123, 109, 81, 68.

Anal. Calcd. for $C_7H_9O_2N_3$: C, 50.30; H, 5.39; N, 25.15. Found: C, 50.37; H, 5.55; N, 25.11.

Cycloaddition of Diazomethane to Halopyrrolinones **1d-g** in Methanol-Ether.

To a solution of the pyrrolinone **1d-g** (5 mmoles) in methanol, cooled to $-10°$, was added a cool ethereal solution of diazomethane (20 ml, containing 0.3 mmole/ml). The reaction was kept at $-10°$ for 4-5 days (cycloadducts **1d,e**) or 20-30 days (cycloadducts **1f,g**). The solvent was removed and the residue was chromatographed under pressure on silica gel (ethyl acetate-chloroform 2:1).

From pyrrolinones **1d,e**, the main components were the pyrazoles **7** (56%) and **8** (28%) accompanied by minor amounts of the isomeric pyrazoles **12** (9%) and **13** (5%).

4-Methoxy-2-methyl-4*H*-pyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (**12**).

This compound had a mp 133-134° (from chloroform-petroleum ether); ir (Nujol): 3220, 3110 (NH), 1730, 1710 (C=O) cm^{-1}; ^{1}H-nmr: 7.37 (s, 1H, H-3), 5.95 (s, 1H, H-4), 4.03 (s, 3H, NMe-2), 3.23 (s, 3H, OMe-4); (DMSO-d_6): 8.82 (br s, 1H, NH), 7.82 (s, 1H, H-3), 5.71 (s, 1H, H-4), 3.93 (s, 3H, NMe-2), 3.17 (s, 3H, OMe-4); ms: (m/z) 167 (M^+), 136 (100%), 125, 109, 95, 81, 69.

Anal. Calcd. for $C_7H_9O_2N_3$: C, 50.30; H, 5.39; N, 25.15. Found: C, 50.06; H, 5.48; N, 25.38.

4-Methoxy-2,5-dimethyl-4*H*-pyrrolo[3,4-*c*]pyrazol-6-one (**13**).

This compound was isolated as a liquid; ir (film): 3100 (NH), 1710 (C=O) cm^{-1}; ^{1}H-nmr: 7.40 (s, 1H, H-3), 5.70 (s, 1H, H-4), 4.00 (s, 3H, NMe-2), 3.00 (s, 6H, OMe-4, NMe-5); ms: (m/z) 181 (M^+), 165, 150 (100%), 137, 123, 109, 81, 68.

Anal. Calcd. for $C_8H_{11}O_2N_3$: C, 53.03; H, 6.09; N, 23.20. Found: C, 52.75; H, 6.14; N, 22.97.

From pyrrolinones **1f,g** the pyrazoles **7** (42%), **12** (3%) and **10**+**11** (55%) were isolated.

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