Regioselective 1,3-Dipolar Cycloadditions of (1*Z*)-1-(Arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide Azomethine Imines to Acetylenic Dipolarophiles

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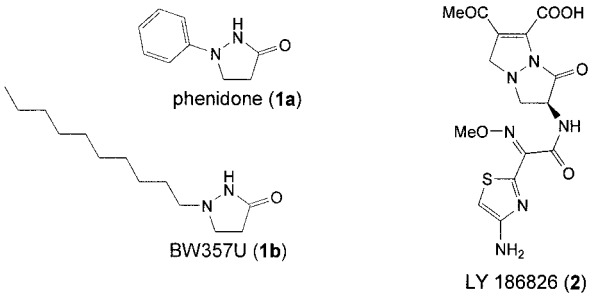
The 5,5-dimethylpyrazolidin-3-one (**4**), prepared from ethyl 3-methylbut-2-enoate (**3**) and hydrazine hydrate, was treated with various substituted benzaldehydes **5a**–**i** to give the corresponding (1*Z*)-1-(arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide azomethine imines **6a**–**i**. The 1,3-dipolar cycloaddition reactions of azomethine imines **6a**–**h** with dimethyl acetylenedicarboxylate (=dimethyl but-2-ynedioate; **7**) afforded the corresponding dimethyl pyrazolo[1,2-*a*]pyrazoledicarboxylates **8a**–**h**, while by cycloaddition of **6** with methyl propiolate (=methyl prop-2-ynoate; **9**), regioisomeric methyl pyrazolo[1,2-*a*]-pyrazolemonocarboxylates **10** and **11** were obtained. The regioselectivity of cycloadditions of azomethine imines **6a**–**i** with methyl propiolate (**9**) was influenced by the substituents on the aryl residue. Thus, azomethine imines **6a**–**e** derived from benzaldehydes **5a**–**e** with a single substituent or without a substituent at the *ortho*-positions in the aryl residue, led to mixtures of regioisomers **10a**–**e** and **11a**–**e**. Azomethine imines **6f**–**i** derived from 2,6-disubstituted benzaldehydes **5f**–**i** gave single regioisomers **10f**–**i**.

Introduction. – Since the beginning of a systematic work on the chemistry of substituted pyrazolidin-3-ones more than four decades ago, the importance of this initially relatively neglected type of heterocycle significantly rose in the last two decades (for a review on pyrazolidin-3-ones, see [1]). Pyrazolidin-3-ones are an important class of compounds that exhibit biological activity and a wide applicability for industrial and synthetic purposes. For example, phenidone (**1a**) and its derivatives and analogues such as BW357U (**1b**) are used as super-additive developers in photographic applications[1]) [2] and as inhibitors of cyclooxygenase, lipooxygenase, and γ-aminobutyrate transferase [3]. Another important pyrazolidinone is *Lilly*'s bicyclic pyrazolidinone **2**, which is a γ-lactam antibiotic [4]. On the other hand, pyrazolidin-3-ones and closely related homologues, perhydropyridazin-3-ones, can also serve either as building blocks, or as precursors for the preparation of β-turn mimics [5], azatropane derivatives [6], and natural products such as saxitoxin, celacinnine, and glidobactin antibiotics [7].

Previously, we have reported the stereoselective 1,3-dipolar cycloaddition reactions of azomethine imines derived from *rel*-(4*R*,5*R*)-4-(benzoylamino)-5-phenylpyrazolidin-3-one and on the utilization of *rel*-(4*R*,5*R*)-4-(benzoylamino)-5-phenylpyrazolidin-3-one in the synthesis of 3-(alkylamino)-3-phenyl- and 3-phenyl-3-(pyrazol-1-yl)-substituted alanine derivatives [8–11]. Recently, we reported an unusual two-step

[1]) There are many publications and patents on this topic. Just few examples are given in [2].



transformation of 5,5-dimethylpyrazolidin-3-one into an alkaloid-like tetracyclic system [12]. On the other hand, *Chuang* and *Sharpless* reported the preparation of N^4,N^4-disubstituted (4*S**,5*S**)-5-phenyl-4-aminopyrazolidin-3-ones and their stereoselective transformations into substituted 1*H*,5*H*-pyrazolo[1,2-*a*]pyrazol-1-one derivatives *via* N^4,N^4-disubstituted (4*S**,5*S**)-1-(arylmethylidene)-5-phenyl-4-amino-3-oxopyrazolidin-1-ium-2-ide azomethine imines as the key intermediates [13][2]).

Results and Discussion. – In continuation of our work on the chemistry of pyrazolidin-3-ones, we now report 1,3-dipolar cycloaddition sof (1*Z*)-1-(arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide azomethine imines **6a**–**i** with dimethyl acetylenedicarboxylate (= dimethyl but-2-ynedioate; **7**) and methyl propiolate (= methyl prop-2-ynoate; **9**). The 5,5-dimethyl pyrazolidin-3-one (**4**), prepared from ethyl 3-methylbut-2-enoate (**3**) and hydrazine hydrate [14], was treated with various substituted benzaldehydes **5a**–**i** to give the corresponding (1*Z*)-1-(arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide azomethine imines **6a**–**i** (*cf. Scheme 1*). The (*Z*)-configuration of the exocyclic C=N bond in azomethine imine **6b**, which is otherwise usual for oxopyrazolidiniumide azomethine imines [1], was confirmed by NMR spectroscopy (NOESY experiment, $d(\mathrm{H-C(1')\cdots Me-C(5)}) = 0.27$ nm). The 1,3-dipolar cycloadditions of 1,3-dipoles **6a**–**h** to dimethyl acetylenedicarboxylate (**7**) gave the corresponding dimethyl 1-aryl-6,7-dihydro-7,7-dimethyl-5-oxo-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylates (**8a**–**h**) in 70–97% yields. In the cycloadditions of azomethine imines **6a**–**i** with methyl propiolate (= methyl prop-2-ynoate; **9**), regioselectivity was found to be dependent on the substituents attached to the aryl residue. With azomethine imines **6a**–**e**, unsubstituted or monosubstituted at one of the *ortho*-positions of the benzene ring, *ca.* 3 : 1 mixtures of regioisomers **10a**–**e** and **11a**–**e** were formed. In the cases of **6a**,**b**,**e**, both regioisomers were separated, isolated, and fully characterized, whereas in the cases of **6c**,**d**, the minor isomers **11c**,**d** were only detected by ^{1}H-NMR. On the other hand, azomethine imines **6f**–**i**, substituted at both *ortho*-positions of the aromatic ring, afforded single regioisomers **10f**–**i** upon treatment with methyl propiolate (**9**) (*Scheme 1*).

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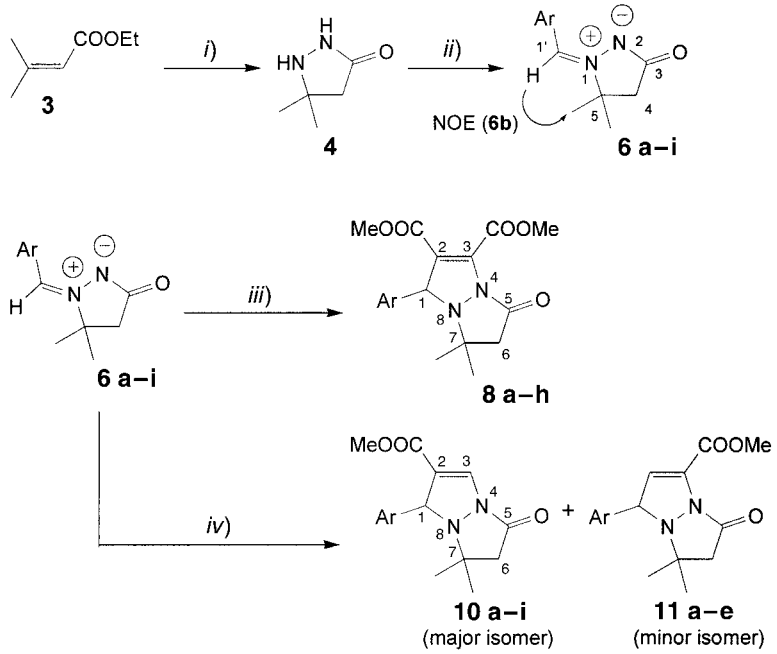
[2]) We are grateful to the referee for informing us about this article, which was published after submission of our manuscript. The numbering of the 1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole derivatives **7**–**10** in [13] should be revised (*cf.* numbering of **8a**–**h** in *Scheme 1*).

Scheme 1



	Ar	**10**/**11**[a])
5a, **6a**, **8a**, **10a**, **11a**	2-nitrophenyl	71 : 29
5b, **6b**, **8b**, **10b**, **11b**	4-nitrophenyl	67 : 33
5c, **6c**, **8c**, **10c**, **11c**	2-methoxyphenyl	70 : 30
5d, **6d**, **8d**, **10d**, **11d**	3,4,5-trimethoxyphenyl	75 : 25
5e, **6e**, **8e**, **10e**, **11e**	2,4-dichlorophenyl	80 : 20
5f, **6f**, **8f**, **10f**	2,6-dichlorophenyl	100 : 0
5g, **6g**, **8g**, **10g**	2,4,6-trimethylphenyl	100 : 0
5h, **6h**, **8h**, **10h**	2,4,6-trimethoxyphenyl	100 : 0
5i, **6i**, **10i**	2,6-dimethoxyphenyl	100 : 0

[a]) Determined by ^{1}H-NMR spectroscopy.

i) Hydrazine hydrate, EtOH, reflux. *ii*) ArCHO (**5a**–**i**), EtOH, CF_3COOH, r.t. *iii*) MeOOCC≡CCOOMe (**7**), 100–150°. *iv*) HC≡CCOOMe (**9**), 100–150°.

Spectroscopic and analytical data for compounds **6**–**11** are in accordance with the data for similar compounds described in [1]. Structures of compounds **6f** and **10g** were also confirmed by X-ray diffraction analysis (*Figs. 1* and *2*).

So far, we do not have a firm explanation for the regioselectivity of these cycloadditions. Since the ratios of the regioisomers formed from the dipole **6a** with an acceptor substituent and from **6c** with a donor substituent are the same, the electronic effects of the substituents at the aromatic ring seem to have a negligible effect on the regioselectivity (*cf. Scheme 1*). Presumably, the electronic distribution in azomethine imines **6a**–**i** is reflected at best by the resonance structures **6** and **6′** as the negative

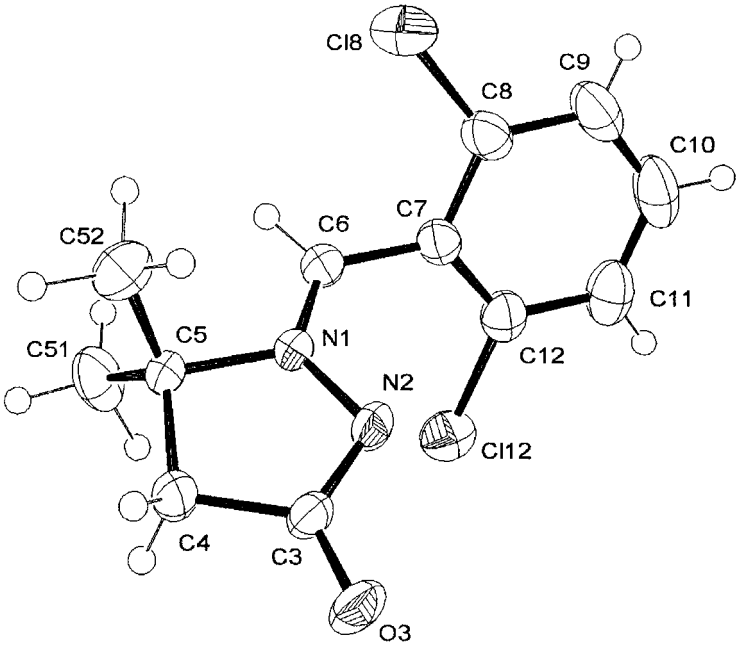


Fig. 1. *ORTEPIII View of the molecular structure of compound* **6f**, *showing the labelling of the non-H-atoms.* Ellipsoids are drawn at the 50% probability level.

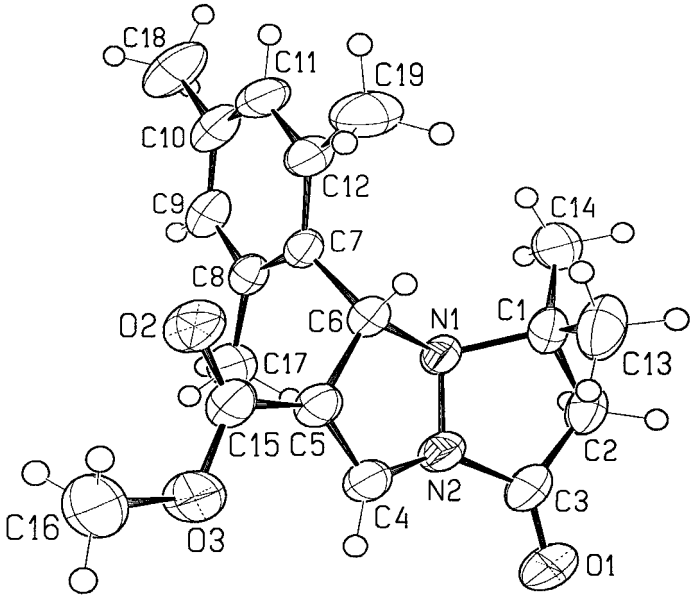
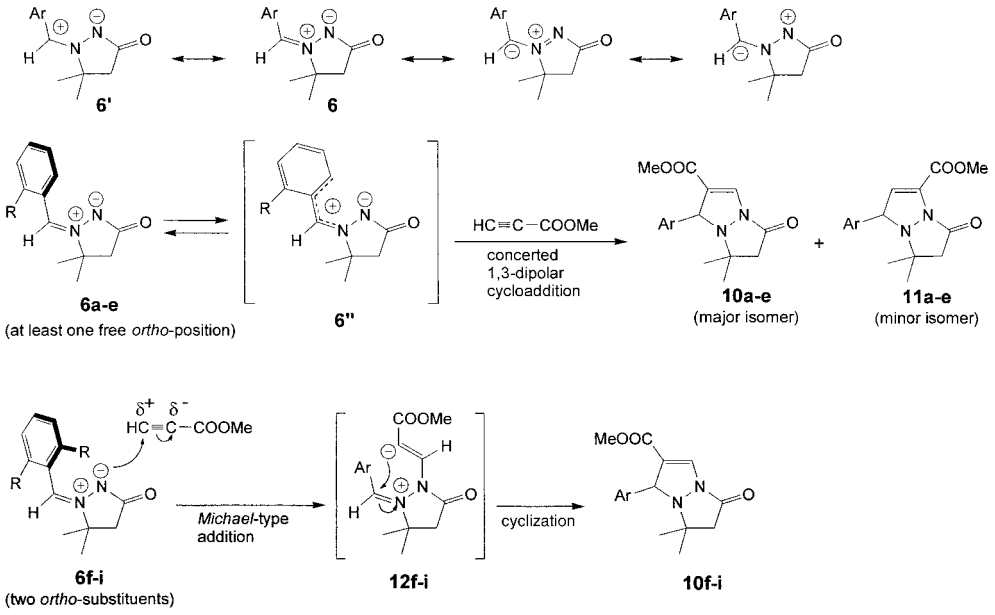


Fig. 2. *ORTEPII View of the molecular structure of compound* **10g**, *showing the labelling of the non-H-atoms.* Ellipsoids are drawn at the 50% probability level.

charge at the N(1) atom is stabilized by the carbonyl group (*Scheme 2*). In the case of at least one free *ortho*-position in the aromatic ring, the dipole can adopt a planar conformation **6″**, which allows both regioisomeric transition states. To the contrary, the planar conformation is not accessible in the case of two *ortho*-substituents; therefore, the transition state for the concerted 1,3-dipolar cycloaddition is prohibited. In this case, a two-step *Michael*-type mechanism is feasible. Consequently, the formation of mixtures of regioisomers **10a**–**e** and **11a**–**e** from *ortho*-unsubstituted or *ortho*-monosubstituted azomethine imines **6a**–**e** could be explained by the concerted 1,3-dipolar cycloaddition mechanism with the 'planar' dipole conformation **6″** as the reactive species, whereas the regiospecific formation of cycloadducts **10f**–**i** from *ortho*-disubstituted azomethine imines **6f**–**i** could be explained by a two-step *Michael*-type mechanism including the 'nonplanar' dipole conformation as the reactive species and dipolar adducts **12f**–**i** as intermediates (*Scheme 2*).

Scheme 2



Experimental Part

General. 5,5-Dimethylpyrazolidin-3-one (**4**) was prepared according to the procedure described in [14]. Ratios of regioisomers **10a**–**i** and **11a**–**i** were determined in the following manner: after completion of the reaction, volatile components were evaporated and the ^{1}H-NMR spectra of the residue recorded. All starting materials were commercially available (in most cases from *Fluka*) and purified according to the standard techniques. Column chromatography (CC): silica gel (*Fluka*, silica gel *60*; column dimensions 40 × 5 cm). TLC: alu foils coated with silica gel *60 F 254* (0.2 mm; *Merck*). M.p.: *Kofler* micro hot stage. IR: *Perkin-Elmer-1310* spectrophotometer. ^{1}H- and ^{13}C-NMR: *Bruker-Avance DPX-300* spectrometer. Elemental analyses: *Perkin-Elmer CHN Analyser 2400*.

(1Z)-1-(Arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide Azomethine Imines **6a–i**: *General Procedure.* CF_3COOH (1 ml) was added to a stirred mixture of 5,5-dimethyl pyrazolidin-3-one (**4**; 1.14 g, 10 mmol), substituted benzaldehyde **5a–i** (10 mmol), and anh. EtOH (40 ml). The mixture was stirred at r.t. for 3–72 h. Volatile compounds were evaporated, Et_2O (30 ml) added to the residue, and the precipitate collected by filtration: azomethine imines **6a–i**.

(1Z)-5,5-Dimethyl-1-[(2-nitrophenyl)methylidene]-3-oxopyrazolidin-1-ium-2-ide (**6a**). From 2-nitrobenzaldehyde (**5a**) (24 h): 2.10 g (85%). M.p. 194–196° (EtOH). IR (KBr): 1670 (C=O). ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.78 (*s*, 2 Me–C(5)); 2.78 (*s*, 2 H–C(4)); 7.60 (*ddd*, *J* = 8.3, 7.5, 0.8, 1 arom. H); 7.68 (*s*, H–C(1′)); 7.76 (*ddd*, *J* = 7.9, 7.5, 1.1, 1 arom. H); 8.14 (*dd*, *J* = 8.3, 1.1, 1 arom. H); 9.06 (*dd*, *J* = 7.9, 1.1, 1 arom. H of Ph). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.26): C 58.29, H 5.29, N 16.99; found: C 58.02, H 5.50, N 16.98.

(1Z)-5,5-Dimethyl-1-[(4-nitrophenyl)methylidene]-3-oxopyrazolidin-1-ium-2-ide (**6b**). From 4-nitrobenzaldehyde (**5b**) (3 h): 2.30 g (93%). M.p. >270° (EtOH). IR (KBr): 1680 (C=O). ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.68 (*s*, 2 Me–C(5)); 2.63 (*s*, 2 H–C(4)); 7.93 (*s*, H–C(1′)); 8.30 (*d*, *J* = 9.0, 2 arom. H); 8.59 (*d*, *J* = 9.0, 2 arom. H). Anal. calc. for $C_{12}H_{13}N_3O_3$ (247.26): C 58.29, H 5.29, N 16.99; found: C 58.01, H 5.14, N 16.92.

(1Z)-1-[(2-Methoxyphenyl)methylidene]-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide (**6c**). From 2-methoxybenzaldehyde (**5c**) (72 h): 2.11 g (91%). M.p. 160–165° (PhMe). IR (KBr): 1650 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.71 (*s*, 2 Me–C(5)); 2.73 (*s*, 2 H–C(4)); 3.92 (*s*, MeO); 6.93 (*dd*, *J* = 8.3, 0.8, 1 arom. H); 7.06 (*ddd*, *J* = 7.9, 7.5, 0.8, 1 arom. H); 7.44 (*ddd*, *J* = 8.3, 7.5, 1.9, 1 arom. H); 7.64 (*s*, H–C(1′)); 9.25 (*dd*, *J* = 7.9, 1.9, 1 arom. H). Anal. calc. for $C_{13}H_{16}N_2O_2$ (232.29): C 67.22, H 6.94, N 12.06; found: C 67.26, H 6.93, N 12.18.

(1Z)-5,5-Dimethyl-3-oxo-1-[(3,4,5-trimethoxyphenyl)methylidene]pyrazolidin-1-ium-2-ide (**6d**). From 3,4,5-trimethoxybenzaldehyde (**5d**) (24 h): 2.87 g (98%). M.p. 134–136° (heptane/EtOH 5:1). IR (KBr): 1660 (C=O). ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.63 (*s*, 2 Me–C(5)); 2.56 (*s*, 2 H–C(4)); 3.76, 3.83 (2*s*, 1:2, 3 MeO); 7.71 (*s*, H–C(1′)); 7.84 (*s*, 2 arom. H). Anal. calc. for $C_{15}H_{20}N_2O_4$ (292.34): C 61.63, H 6.89, N 9.58; found: C 61.69, H 6.99, N 9.77.

(1Z)-1-[(2,4-Dichlorophenyl)methylidene]-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide (**6e**). From 2,4-dichlorobenzaldehyde (**5e**) (24 h): 2.30 g (85%). M.p. 180–184° (Et_2O). IR (KBr): 1670 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.77 (*s*, 2 Me–C(5)); 2.77 (*s*, 2 H–C(4)); 7.39 (*dd*, *J* = 8.7, 1.9, 1 arom. H); 7.50 (*d*, *J* = 1.9, 1 arom. H); 7.52 (*s*, H–C(1′)); 9.36 (*d*, *J* = 8.7, 1 arom. H). Anal. calc. for $C_{12}H_{12}Cl_2N_2O$ (271.15): C 53.16, H 4.46, N 10.33; found: C 52.92, H 4.44, N 10.31.

(1Z)-1-[(2,6-Dichlorophenyl)methylidene]-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide (**6f**). From 2,6-dichlorobenzaldehyde (**5f**) (24 h): 2.43 g (90%). M.p. 246–248° (Et_2O). IR (KBr): 1650 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.79 (*s*, 2 Me–C(5)); 2.77 (*s*, 2 H–C(4)); 7.18 (*s*, H–C(1′)); 7.29–7.37 (*m*, 3 arom. H). Anal. calc. for $C_{12}H_{12}Cl_2N_2O$ (271.15): C 53.16, H 4.46, N 10.33; found: C 53.05, H 4.66, N 10.17.

(1Z)-5,5-Dimethyl-3-oxo-1-[(2,4,6-trimethylphenyl)methylidene]pyrazolidin-1-ium-2-ide (**6g**). From 2,4,6-trimethylbenzaldehyde (**5g**) (48 h): 2.17 g (89%). M.p. 206–210° (PhMe). IR (KBr): 1660 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.75 (*s*, 2 Me–C(5)); 2.22, 2.28 (2*s*, 2:1, $Me_3C_6H_2$); 2.75 (*s*, 2 H–C(4)); 6.86 (*s*, 2 arom. H); 7.35 (*s*, H–C(1′)). Anal. calc. for $C_{15}H_{20}N_2O$ (244.34): C 73.74, H 8.25, N 11.46; found: C 73.91, H 8.23, N 11.40.

(1Z)-5,5-Dimethyl-3-oxo-1-[(2,4,6-trimethoxyphenyl)methylidene]pyrazolidin-1-ium-2-ide (**6h**). From 2,4,6-trimethoxybenzaldehyde (**5h**) (24 h): 2.72 g (93%). M.p. 206–207° (PhMe). IR (KBr): 1650 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.72 (*s*, Me–C(5)); 2.99 (*s*, H–C(4)); 3.85, 3.86 (2*s*, 1:2, 3 MeO); 6.11 (*s*, 2 arom. H); 7.56 (*s*, H–C(1′)). Anal. calc. for $C_{15}H_{20}N_2O_4$ (292.34): C 61.63, H 6.89, N 9.58; found: C 61.31, H 6.97, N 9.74.

(1Z)-1-[(2,6-Dimethoxyphenyl)methylidene]-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide (**6i**). From 2,6-dimethoxybenzaldehyde (**5i**) (24 h): 2.26 g (86%). M.p. 195–199° (Et_2O). IR (KBr): 1650 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.72 (*s*, 2 Me–C(5)); 2.75 (*s*, 2 H–C(4)); 3.85 (*s*, 2 MeO); 6.55 (*d*, *J* = 8.3, 2 arom. H); 7.20 (*s*, H–C(1′)); 7.34 (*t*, *J* = 8.3, 1 arom. H). Anal. calc. for $C_{14}H_{18}N_2O_3$ (262.31): C 64.10, H 6.92, N 10.68; found: C 64.03, H 7.07, N 10.40.

*Dimethyl 1-Aryl-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H*-pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylates* **8a–h**: *General Procedure.* A mixture of dimethyl acetylenedicarboxylate (**7**; 1.2 ml, 10 mmol) and (1*Z*)-1-(arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide **6a–h** (10 mmol) in an appropriate solvent (PhMe, xylene, or PhOMe; 40 ml) was heated under reflux for 20 min to 4 h. Volatile components were evaporated, the residue was triturated with Et_2O or $^iPr_2O$, and the precipitate was collected by filtration; cycloadducts **8a–h**.

*Dimethyl 6,7-Dihydro-7,7-dimethyl-1-(2-nitrophenyl)-5-oxo-1*H,5H*-pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8a**). From **6a** (xylene, 20 min): 3.55 g (91%). M.p. 164–166° ($^iPr_2O$). ^{1}H-NMR (300 MHz, $CDCl_3$):

1.25 (*s*, 1 Me–C(7)); 1.36 (*s*, 1 Me–C(7)); 2.43 (*d*, *J* = 15.8, 1 H–C(6)); 2.87 (*d*, *J* = 15.8, 1 H–C(6)); 3.53 (*s*, MeOOC–C(2)); 3.97 (*s*, MeOOC–C(3)); 6.44 (*s*, H–C(1)); 7.42 (*ddd*, *J* = 8.7,8.3, 1.5, 1 arom. H); 7.64 (*ddd*, *J* = 8.7, 7.5, 1.1, 1 arom. H); 7.77 (*dd*, *J* = 7.9, 1.1, 1 arom H); 7.89 (*dd*, *J* = 7.9, 1.5, 1 arom. H). Anal. calc. for $C_{18}H_{19}N_3O_7$ (389.37): C 55.53, H 4.92, N 10.79; found: C 55.47, H 4.87, N 10.47.

*Dimethyl 6,7-Dihydro-7,7-dimethyl-1-(4-nitrophenyl)-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8b**). From **6b** (xylene, 4 h): 3.77 g (97%). M.p. 167–168° (heptane/EtOH 5:2). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 1 Me–C(7)); 1.30 (*s*, 1 Me–C(7)); 2.43 (*d*, *J* = 15.8, 1 H–C(6)); 2.87 (*d*, *J* = 15.8, 1 H–C(6)); 3.61 (*s*, MeOOC–C(2)); 3.98 (*s*, MeOOC–C(3)); 5.61 (*s*, H–C(1)); 7.68 (*d*, *J* = 8.8, 2 arom. H); 8.22 (*d*, *J* = 8.8, 2 arom. H). Anal. calc. for $C_{18}H_{19}N_3O_7$ (389.37): C 55.53, H 4.92, N 10.79; found: C 55.36, H 4.80, N 10.81.

*Dimethyl 6,7-Dihydro-1-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8c**). From **6c** (xylene, 2 h): 3.10 g (83%). M.p. 104–105° (^{i}Pr$_2$O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*s*, 1 Me–C(7)); 1.31 (*s*, 1 Me–C(7)); 2.34 (*d*, *J* = 15.4, 1 H–C(6)); 2.79 (*d*, *J* = 15.8, 1 H–C(6)); 3.57 (*s*, MeOOC–C(2)); 3.88 (*s*, *Me*OC$_6$H$_4$); 3.98 (*s*, MeOOC–C(3)); 6.02 (*s*, H–C(1)); 6.89 (*d*, *J* = 8.3, 1 arom. H); 6.98 (*dd*, *J* = 7.9, 7.5, 1 arom. H); 7.26 (*m*, 1 arom. H); 7.36 (*dd*, *J* = 7.5, 1.9, 1 arom. H). Anal. calc. for $C_{19}H_{22}N_2O_6$ (374.40): C 60.95, H 5.92, N 7.48; found: C 60.98, H 5.98, N 7.37.

*Dimethyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(3,4,5-trimethoxyphenyl)-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8d**). From **6d** (xylene, 30 min): 3.82 g (88%). M.p. 147–149° (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21 (*s*, 1 Me–C(7)); 1.27 (*s*, 1 Me–C(7)); 2.41 (*d*, *J* = 15.7, 1 H–C(6)); 2.88 (*d*, *J* = 15.7, H–C(6)); 3.63 (*s*, MeOOC–C(2)); 3.84, 3.88 (2*s*, 1:2, 3 *Me*OC$_6$H$_2$); 3.97 (*s*, MeOOC–C(3)); 5.45 (*s*, H–C(1)); 6.68 (*s*, 2 arom. H). Anal. calc. for $C_{21}H_{26}N_2O_8$ (434.45): C 58.06, H 6.03, N 6.45; found: C 58.01, H 6.21, N 6.48.

*Dimethyl 1-(2,4-Dichlorophenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8e**). From **6e** (PhMe, 25 min): 2.91 g (70%). M.p. 76–79° (heptane). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 1 Me–C(7)); 1.34 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.8, 1 H–C(6)); 2.80 (*d*, *J* = 15.8, H–C(6)); 3.59 (*s*, MeOOC–C(2)); 3.98 (*s*, MeOOC–C(3)); 6.07 (*s*, H–C(1)); 7.29 (*dd*, *J* = 8.7, 1.9, 1 arom. H); 7.36 (*d*, *J* = 1.9, 1 arom. H); 7.52 (*d*, *J* = 8.7, 1 arom. H). Anal. calc. for $C_{18}H_{18}Cl_2N_2O_5$ (413.26): C 52.31, H 4.39, N 6.78; found: C 52.27, H 4.36, N 6.76.

*Dimethyl 1-(2,6-Dichlorophenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8f**). From **6f** (PhOMe, 3 h): 3.18 g (77%). M.p. 152–153° (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 1 Me–C(7)); 1.40 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.8, 1 H–C(6)); 2.83 (*d*, *J* = 15.8, 1 H–C(6)); 3.59 (*s*, MeOOC–C(2)); 3.97 (*s*, MeOOC–C(3)); 6.54 (*s*, H–C(1)); 7.17 (*dd*, *J* = 8.3, 7.9, 1 arom. H); 7.32 (*dd*, *J* = 8.3, 1.1, 1 arom. H); 7.33 (*dd*, *J* = 7.9, 1.1, 1 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 19.7; 24.9; 49.4; 52.2; 53.9; 62.4; 65.7; 112.0; 128.5; 129.9; 131.1; 134.6; 135.9; 136.2; 137.4; 159.9; 163.0; 166.6. Anal. calc. for $C_{18}H_{18}Cl_2N_2O_5$ (413.26): C 52.31, H 4.39, N 6.78; found: C 52.33, H 4.34, N 6.48.

*Dimethyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(2,4,6-trimethylphenyl)-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8g**). From **6g** (PhMe, 90 min): 3.15 g (82%). M.p. 114–115° (heptane). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.07 (*s*, 1 Me–C(7)); 1.36 (*s*, 1 arom. Me); 2.24 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.8, 1 H–C(6)); 2.46 (*s*, 1 arom. Me); 2.48 (*s*, 1 arom. Me); 2.80 (*d*, *J* = 15.8, 1 H–C(6)); 3.57 (*s*, MeOOC–C(2)); 3.96 (*s*, MeOOC–C(3)); 6.06 (*s*, H–C(1)); 6.78 (*s*, 1 arom. H); 6.83 (*s*, 1 arom. H). Anal. calc. for $C_{21}H_{26}N_2O_5$ (386.45): C 65.27, H 6.78, N 7.25; found: C 65.22, H 6.94, N 7.06.

*Dimethyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(2,4,6-trimethoxyphenyl)-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2,3-dicarboxylate* (**8h**). From **6h** (xylene, 20 min): 3.13 g (72%). M.p. 186–188° (EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.18 (*s*, 1 Me–C(7)); 1.30 (*s*, 1 Me–C(7)); 2.31 (*d*, *J* = 15.5, 1 H–C(6)); 2.82 (*d*, *J* = 15.5, 1 H–C(6)); 3.57 (*s*, MeOOC–C(2)); 3.79, 3.82 (2*s*, 2:1, 1 arom. Me); 3.96 (*s*, MeOOC–C(3)); 6.09 (*s*, H–C(1)); 6.12 (*s*, 2 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 18.9; 24.3; 49.1; 51.6; 53.2; 55.2; 55.7; 56.1; 65.5; 91.4; 109.8; 115.1; 135.0; 160.6; 161.1; 163.4; 167.7. Anal. calc. for $C_{21}H_{26}N_2O_8$ (434.45): C 58.06, H 6.03, N 6.45; found: C 58.14, H 6.12, N 6.74.

*Methyl 1-Aryl-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylates* **10a–i** *and Methyl 1-Aryl-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-3-carboxylates* **11a–e**: *General Procedure.* A mixture of methyl propiolate (**9**; 0.5 ml, 6 mmol) and (1*Z*)-1-(arylmethylidene)-5,5-dimethyl-3-oxopyrazolidin-1-ium-2-ide **6a–i** (5 mmol) in an appropriate solvent (PhMe, xylene, or PhOMe; 20 ml) was heated under reflux for 1–8 h. Volatile components were evaporated to afford mixtures of isomers **10a–e** and **11a–e** or single regioisomers **10f–i**. Regioisomers **10a**, **b**, **e** and **11a**, **b**, **e** were then separated by CC. In the cases of mixtures of **10c**, **d** and **11c**, **d**, the minor isomers **11c**,**d** were detected by ^{1}H-NMR spectroscopy. In the case of **10f–i**, the residue was triturated with an appropriate solvent to give the pure compounds.

*Methyl 6,7-Dihydro-7,7-dimethyl-1-(2-nitrophenyl)-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10a**) *and Methyl 6,7-Dihydro-7,7-dimethyl-1-(2-nitrophenyl)-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-3-carboxylate* (**11a**). From **6a** (PhMe, 1 h), after CC (Et_2O).

Data of Major Isomer **10a**: Yield: 0.930 g (56%). M.p. 110–115° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23 (*s*, 1 Me–C(7)); 1.31 (*s*, 1 Me–C(7)); 2.44 (*d*, *J* = 15.8, 1 H–C(6)); 2.88 (*d*, *J* = 15.8, 1 H–C(6)); 3.56 (*s*, MeOOC–C(2)); 6.38 (*d*, *J* = 1.5, H–C(1)); 7.41 (*ddd*, *J* = 1.5, 7.5, 7.9, 1 arom. H); 7.51 (*d*, *J* = 1.5, H–C(3)); 7.62 (*ddd*, *J* = 1.2, 7.5, 7.5, 1 arom. H); 7.77 (*dd*, *J* = 1.2, 7.9, 1 arom. H); 7.85 (*dd*, *J* = 1.5, 7.9, 1 arom. H). Anal. calc. for $C_{16}H_{17}N_3O_5$ (331.33): C 58.00, H 5.17, N 12.68; found: C 58.25, H 5.36, N 12.68.

Data of Minor Isomer **11a**: Yield: 0.174 g (11%). M.p. 180–185° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, 1 Me–C(7)); 1.24 (*s*, 1 Me–C(7)); 2.42 (*d*, *J* = 15.7, 1 H–C(6)); 2.98 (*d*, *J* = 15.7, 1 H–C(6)); 3.85 (*s*, MeOOC–C(3)); 5.95 (*d*, *J* = 2.5, H–C(1)); 6.07 (*d*, *J* = 2.3, H–C(2)); 7.47 (*ddd*, *J* = 1.5, 7.5, 7.9, 1 arom. H); 7.73 (*ddd*, *J* = 1.2, 7.5, 7.5, 1 arom. H); 8.01 (*dd*, *J* = 1.2, 7.9, 1 arom. H); 8.22 (*dd*, *J* = 1.5, 7.9, 1 arom. H). Anal. calc. for $C_{16}H_{17}N_3O_5$ (331.33): C 58.00, H 5.17, N 12.68; found: C 58.06, H 5.37, N 12.54.

*Methyl 6,7-Dihydro-7,7-dimethyl-1-(4-nitrophenyl)-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10b**) *and Methyl 6,7-Dihydro-7,7-dimethyl-1-(4-nitrophenyl)-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-3-carboxylate* (**11b**). From **6b** (PhOMe, 1 h), after CC ($CHCl_3$/MeOH 25 : 1).

Data of Major Isomer **10b**: Yield 0.730 g (44%). M.p. 119–120° ($CHCl_3$/MeOH 25 : 1). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, Me–C(7)); 1.25 (*s*, Me–C(7)); 2.44 (*d*, *J* = 15.8, 1 H–C(6)); 2.89 (*d*, *J* = 15.8, H–C(5)); 3.64 (*s*, MeOOC–C(2)); 5.58 (*d*, *J* = 1.2, H–C(1)); 7.53 (*d*, *J* = 1.2, H–C(3)); 7.69 (*d*, *J* = 8.8, 2 arom. H); 8.21 (*d*, *J* = 8.8, 2 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 19.3; 25.2; 49.5; 52.0; 64.3; 65.0; 115.9; 124.0; 129.3; 130.4; 148.0; 149.6; 164.1; 166.9. Anal. calc. for $C_{16}H_{17}N_3O_5$ (331.33): C 58.00, H 5.17, N 12.68; found: C 58.23, H 5.36, N 12.58.

Data of Minor Isomer **11b**: Yield 0.296 g (18%). M.p. 101–102° ($CHCl_3$/MeOH, 25 : 1). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, 1 Me–C(7)); 1.29 (*s*, 1 Me–C(7)); 2.43 (*d*, *J* = 15.7, 1 H–C(6)); 2.98 (*d*, *J* = 15.7, 1 H–C(6)); 3.87 (*s*, MeOOC–C(3)); 5.50 (*d*, *J* = 2.5, H–C(1)); 5.87 (*d*, *J* = 2.5, H–C(2)); 7.65 (*d*, *J* = 8.7, 2 arom. H); 8.24 (*d*, *J* = 8.7, 2 arom. H). Anal. calc. for $C_{16}H_{17}N_3O_5$ (331.33): C 58.00, H 5.17, N 12.68; found: C 57.96, H 5.02, N 12.73.

*Methyl 6,7-Dihydro-1-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10c**). From **6c** (PhMe, 3 h), after CC (Et_2O).

Data of Major Isomer **10c**: Yield 0.320 g (20%). M.p. 112–114° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.17 (*s*, 1 Me–C(7)); 1.27 (*s*, 1 Me–C(7)); 2.37 (*d*, *J* = 15.4, 1 H–C(6)); 2.81 (*d*, *J* = 15.4, 1 H–C(6)); 3.61 (*s*, MeOOC–C(2)); 3.88 (*s*, *Me*OC_6H_4); 6.02 (*d*, *J* = 1.5, H–C(1)); 6.89 (*dd*, *J* = 1.1, 8.3, 1 arom. H); 6.97 (*ddd*, *J* = 1.1, 7.5, 7.5, 1 arom. H); 7.26 (*ddd*, *J* = 1.7, 7.5, 8.3, 1 arom. H); 7.35 (*dd*, *J* = 1.5, 7.5, 1 arom. H); 7.57 (*d*, *J* = 1.5, H–C(3)). Anal. calc. for $C_{17}H_{20}N_2O_4$ (316.35): C 64.54, H 6.37, N 8.86; found: C 64.88, H 6.35, N 8.90.

Data of Minor Isomer **11c**: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.48 (*s*, 1 Me–C(7)); 2.97 (*d*, *J* = 15.4, 1 H–C(6)); 3.13 (*d*, *J* = 15.4, 1 H–C(6)); 3.76 (*s*, MeOOC–C(3)).

*Methyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(3,4,5-trimethoxyphenyl)-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10d**). From **6d** (PhMe, 2 h), after CC (Et_2O).

Data of Major Isomer **10d**: Yield 0.885 g (47%). M.p. 105–107° (Et_2O). ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.21 (*s*, 1 Me–C(7)); 1.22 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.7, 1 H–C(6)); 2.89 (*d*, *J* = 15.7, 1 H–C(6)); 3.66 (*s*, MeOOC–C(2)); 3.84, 3.87 (2*s*, 1 : 2, 1 arom. MeO); 5.41 (*d*, *J* = 1.2, H–C(1)); 6.69 (*s*, 2 arom. H); 7.50 (*d*, *J* = 1.2, H–C(3)). Anal. calc. for $C_{19}H_{24}N_2O_6$ (376.41): C 60.63, H 6.43, N 7.44; found: C 60.79, H 6.60, N 7.49.

Data of Minor Isomer **11d**: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.18 (*s*, 1 Me–C(7)); 1.29 (*s*, 1 Me–C(7)); 5.33 (*d*, *J* = 2.6, H–C(1)); 5.93 (*d*, *J* = 2.6, H–C(2)).

*Methyl 1-(2,4-Dichlorophenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10e**) *and Methyl 1-(2,4-Dichlorophenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,*5*H-*pyrazolo[1,2-*a*]pyrazole-3-carboxylate* (**11e**). From **6e** (PhMe, 2 h), after CC (Et_2O).

Data of Major Isomer **10e**: Yield 1.156 g (65%). M.p. 140–148° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, 1 Me–C(7)); 1.30 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.8, 1 H–C(6)); 2.82 (*d*, *J* = 15.8, 1 H–C(6)); 3.62 (*s*, MeOOC–C(2)); 6.03 (*d*, *J* = 1.5, H–C(1)); 7.27 (*dd*, *J* = 2.0, 7.9, 1 arom. H); 7.36 (*d*, *J* = 1.9, 1 arom. H); 7.48 (*d*, *J* = 8.7, 1 arom. H); 7.56 (*d*, *J* = 1.5, H–C(3)). Anal. calc. for $C_{16}H_{16}Cl_2N_2O_3$ (355.22): C 54.10, H 4.54, N 7.89; found: C 54.34, H 4.65, N 7.74.

Data of Minor Isomer **11e**: Yield 0.176 g (10%). M.p. 124–126° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*s*, 1 Me–C(7)); 1.28 (*s*, 1 Me–C(7)); 2.42 (*d*, *J* = 16.0, 1 H–C(6)); 2.97 (*d*, *J* = 16.0, 1 H–C(6)); 3.85

(*s*, MeOOC–C(2)); 5.74 (*d*, *J* = 1.6, H–C(1)); 5.98 (*d*, *J* = 1.6, H–C(2)); 7.32 (*dd*, *J* = 1.9, 8.2, 1 arom. H); 7.37 (*d*, *J* = 1.9, 1 arom. H); 7.81 (*d*, *J* = 8.7, 1 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 20.5; 25.8; 50.2, 53.1; 61.0; 64.3; 122.3; 128.3; 129.4; 131.0; 131.1; 132.7; 134.6; 137.6; 159.5; 166.8. Anal. calc. for $C_{16}H_{16}Cl_2N_2O_3$ (355.22): C 54.10, H 4.54, N 7.89; found: C 54.27, H 4.69, N 7.84.

*Methyl 1-(2,6-Dichlorophenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10f**). From **6f** (xylene, 7 h): 1.510 g (85%). M.p. 145–147° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, 1 Me–C(7)); 1.34 (*s*, 1 Me–C(7)); 2.40 (*d*, *J* = 15.8, 1 H–C(6)); 2.84 (*d*, *J* = 15.8, 1 H–C(6)); 3.62 (*s*, MeOOC–C(2)); 6.47 (*d*, *J* = 1.7, H–C(1)); 7.16 (*dd*, *J* = 8.3, 7.9, 1 arom. H); 7.31 (*dd*, *J* = 8.3, 1.1, 1 arom. H); 7.32 (*dd*, *J* = 7.9, 1.1, 1 arom. H); 7.53 (*d*, *J* = 1.7, H–C(3)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 19.6; 25.0; 49.9; 52.0; 61.9; 65.2; 114.5; 128.6; 129.7; 131.1; 131.2; 134.9; 135.9; 137.4; 164.1; 166.4. Anal. calc. for $C_{16}H_{16}Cl_2N_2O_3$ (355.22): C 54.10, H 4.54, N 7.89; found: C 54.02, H 4.63, N 7.85.

*Methyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(2,4,6-trimethylphenyl)-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10g**). From **6g** (PhMe, 8 h): 1.443 g (88%). M.p. 135–136° (Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, 1 Me–C(7)); 1.30 (*s*, 1 Me–C(7)); 2.24 (*s*, 1 arom. Me); 2.40 (*d*, *J* = 15.4, 1 H–C(6)); 2.42 (*s*, 1 arom. Me); 2.47 (*s*, 1 arom. Me); 2.81 (*d*, *J* = 15.4, 1 H–C(6)); 3.60 (*s*, MeOOC–C(2)); 6.00 (*d*, *J* = 1.9, H–C(1)); 6.80 (br. *s*, 2 arom. H); 7.46 (*d*, *J* = 1.9, H–C(3)). Anal. calc. for $C_{19}H_{24}N_2O_3$ (328.41): C 69.49, H 7.37, N 8.53; found: C 69.81, H 7.34, N 8.72.

*Methyl 6,7-Dihydro-7,7-dimethyl-5-oxo-1-(2,4,6-trimethoxyphenyl)-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10h**). From **6h** (PhMe, 3 h): 1.204 g (64%). M.p. 162–165° (PhMe). ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.16 (*s*, 1 Me–C(7)); 1.28 (*s*, 1 Me–C(7)); 2.32 (*d*, *J* = 15.6, 1 H–C(6)); 2.84 (*d*, *J* = 15.6, 1 H–C(6)); 3.61 (*s*, MeOOC–C(2)); 3.79 (br. *s*, 1 arom. MeO); 6.06 (*d*, *J* = 1.8, H–C(1)); 6.13 (*s*, 2 arom. H); 7.43 (*d*, *J* = 1.8, H–C(3)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 19.4; 24.8; 50.1; 51.6; 55.5; 55.6; 56.4; 65.2; 91.3; 92.7; 110.3; 118.1; 129.2; 161.3; 164.8; 166.8. Anal. calc. for $C_{19}H_{24}N_2O_6$ (376.41): C 60.63, H 6.43; N 7.44; found: C 60.50, H 6.78, N 7.64.

*Methyl 1-(2,6-Dimethoxyphenyl)-6,7-dihydro-7,7-dimethyl-5-oxo-1*H,5H-*pyrazolo[1,2-*a*]pyrazole-2-carboxylate* (**10i**). From **6i** (toluene, 4 h): 1.386 g (80%). M.p. 159–162° (heptane). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*s*, 1 Me–C(7)); 1.29 (*s*, 1 Me–C(7)); 2.33 (*d*, *J* = 15.5, 1 H–C(6)); 2.85 (*d*, *J* = 15.8, 1 H–C(6)); 3.60 (*s*, MeOOC–C(2)); 3.81 (br. *s*, 1 arom. Me); 6.16 (*d*, *J* = 1.9, H–C(1)); 6.56 (*d*, *J* = 8.3, H–C(3′), H–C(5′)); 7.21 (*t*, *J* = 8.4, H–C(4′)); 7.46 (*d*, *J* = 1.9, H–C(3)). Anal. calc. for $C_{18}H_{22}N_2O_5$ (346.39): C 62.42, H 6.40, N 8.09; found: C 62.65, H 6.42, N 8.17.

X-Ray Structure Determination of Compounds **6f** *and* **10g**. The crystallographic data are presented in the *Table*. The pictures of the molecular structures of compounds **6f** and **10g** are shown in *Figs. 1* and *2*. Both structures were solved by direct methods with the SIR92 [15] program. The positions of H-atoms were obtained from difference *Fourier* maps. We employed full-matrix least-squares refinement on F_o with anisotropic temperature factors for all non-H atoms. For compound **10g**, H-atoms were refined isotropically; for compound **6f**, the positions of H-atoms were refined with fixed displacement parameters of atoms of attachment. For compound **10g**, the correction for secondary extinction [16] was applied with $g = 2.5(9) \cdot 10^4$. The Xtal3.4 [17] system of crystallographic programs was used for the correlation and reduction of data, structure refinement, and interpretation. ORTEPII [18] and ORTEPIII [19][20] programs were used to produce molecular graphics. Further details of crystal structures of compounds **6f** and **10g** can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk), quoting the deposition numbers CCDC 145358 and CCDC 145359, resp.

Table 1. *Crystallographic Data for Compounds* **6f** *and* **10g**

	6f	**10g**
Crystal data		
Chemical formula	$C_{12}H_{12}Cl_2N_2O$	$C_{19}H_{24}N_2O_3$
M_r	271.15	328.4
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	11.630(1)	8.315(1)
b [Å]	8.343(1)	10.077(1)
c [Å]	13.069(1)	11.634(1)
α [°]	90.00	74.43(1)
β [°]	96.49(1)	82.65(1)
γ [°]	90.00	72.72(1)
V [Å^3]	1260.0(1)	895.4(2)
Z	4	2
Calc. density D_x [Mg m^{-3}]	1.429	1.218
Radiation type	MoK_α	MoK_α
Wavelength (λ)	0.71069	0.71069
No. of refl. for cell parameters	75	100
θ range [°]	8.9–15.9	8.26–17.87
μ [mm^{-1}]	0.4994	0.0772
Temperature [K]	293(1)	293(1)
Crystal shape	prism	prism
Crystal size [mm]	$0.95 \times 0.53 \times 0.39$	$0.56 \times 0.45 \times 0.28$
Crystal color	colorless	yellow
Data collection		
Diffractometer	*Enraf Nonius CAD-4*	*Enraf Nonius CAD-4*
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	none	none
No. of measured refl.	12127	8683
No. of independent refl.	3020	4298
No. of observed refl.	2630	3204
Criterion of observed refl.	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
R_{int}	0.0244	0.0067
θ_{max} [°]	28	28
No. of standard refl.	3	3
Frequency of standard refl.	every 333.3 min of scan time	every 333.3 min of scan time
Intensity decay [%]	−0.05	−0.58
Refinement		
R	0.041	0.040
wR	0.036	0.047
No. of contributing refl.	2630	3806
No. of parameters	190	314
$(\Delta/\sigma)_{max}$	0.004	0.008
$\Delta\rho_{max}$	0.274	0.259
$\Delta\rho_{min}$	−0.668	−0.182

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