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Stabilization of (*N*-methyleneamino)imidoylketenes: synthesis of dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazines

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Abstract—Thermolysis of substituted methyl 1-methyleneamino-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates **2a**,**b** led to substituted dimethyl 3,9-dioxo-1,5,7,11-tetrahydro-1*H*,7*H*-dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazine-1,7-dicarboxylates **4a**,**b** and methyl 2,5-dihydro-5-oxo-1*H*-pyrazole-3-carboxylates **5a**,**b** as minor products. The structure of compound **4a** was determined by X-ray crystallography. The proposed mechanism of this conversion includes generation of (*N*-methyleneamino)imidoylketenes **6a**,**b** and its intramolecular transformation to azomethine imines—5-oxo-2,5-dihydropyrazole-1-methylium-2-ides **7a**,**b**, which undergo dimerization in head-to-tail manner yielding products **4a**,**b** and partially hydrolyse to compounds **5a**,**b**.

1. Introduction

The chemistry of imidoylketenes was being extensively investigated during the last few decades from preparative, mechanistic and theoretical points of view.[1] Furthermore, these highly reactive molecules are of considerable current interest because of their wide use as building blocks in organic chemistry. The thermal cheletropic extrusion of CO from pyrrol-2,3(1*H*)-diones is the convenient method for the generation of these ketenes. The variation of substituents in the pyrrole ring leads to the generation of new imidoylketenes and widens their potential for the new types of transformation. As we and other authors have shown in the previous works, imidoylketenes can be involved into various types of intramolecular cyclization,[1,2] dimerization[3] and interaction with nucleophiles[4] and dienophiles.[5]

We report herein the synthesis and thermolysis of new pyrrole-2,3(1*H*)-diones—methyl 3-acyl-1-diphenylmethyleneamino-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates (**2a**,**b**) (Scheme 1). We also describe a new and unusual type of stabilisation of (*N*-methyleneamino)imidoylketenes[6] to produce the novel tetrazine derivatives, namely dimethyl 2,8-diacyl-3,9-dioxo-5,5,11,11-tetraphenyl-1,5,7,11-tetrahydro-1*H*,7*H*-dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazine-1,7-dicarboxylates (**4a**,**b**), whose structure was defined by X-ray crystallography (Fig. 1).

2. Results and discussion

Reaction of primary β-enaminoketones with oxalyl chloride is the most common method of the pyrrole-2,3(1*H*)-diones[7] synthesis. The corresponding methyl 3-acyl-1-diphenylmethyleneamino-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates (**2a**,**b**) were obtained from methyl ethers of 4-acyl-2-diphenylmethylenehydrazino-4-oxo-2-butenoic acids[8] (**1a**,**b**) and oxalyl chloride in 80, 60% yield (Scheme 1). The spectroscopic data of pyrrole-2,3(1*H*)-diones **2a**,**b** are in good agreement with the other similar systems.[6,7,9]

Unfortunately, the quantitative isolation and further application of the deep red coloured pyrrole-2,3(1*H*)-diones **2a**,**b** appeared to be difficult since they are highly sensitive to moisture and easily hydrolyse to afford light yellow methyl 3-acyl-1-diphenylmethyleneamino-2,4-dihydroxy-2,5-dihydro-5-oxo-1*H*-pyrrole-2-carboxylates (**3a**,**b**), whose structure was confirmed by X-ray crystallography.[10]

We have noticed that the deep red solution of pyrrole-2,3(1*H*)-diones **2a**,**b** became deep blue at heating, this colour gradually disappeared after cooling and some colourless products were formed. The preparative thermolysis of **2a**,**b** (130–140 °C, *p*-xylene) resulted in substituted dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazines **4a**,**b** as the main products (80, 67%, respectively) and pyrazoles **5a**,**b** (15, 25%, respectively) as the by-products (Scheme 1). The structure of **4a** was defined by X-ray analysis. The structure of **5a**,**b** was established by elemental analysis, IR and ^{1}H NMR spectroscopic data.

Keywords: Pyrrole-2,3(1*H*)-diones; (*N*-Methyleneamino)imidoylketenes; Azomethine imines; Dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazines.
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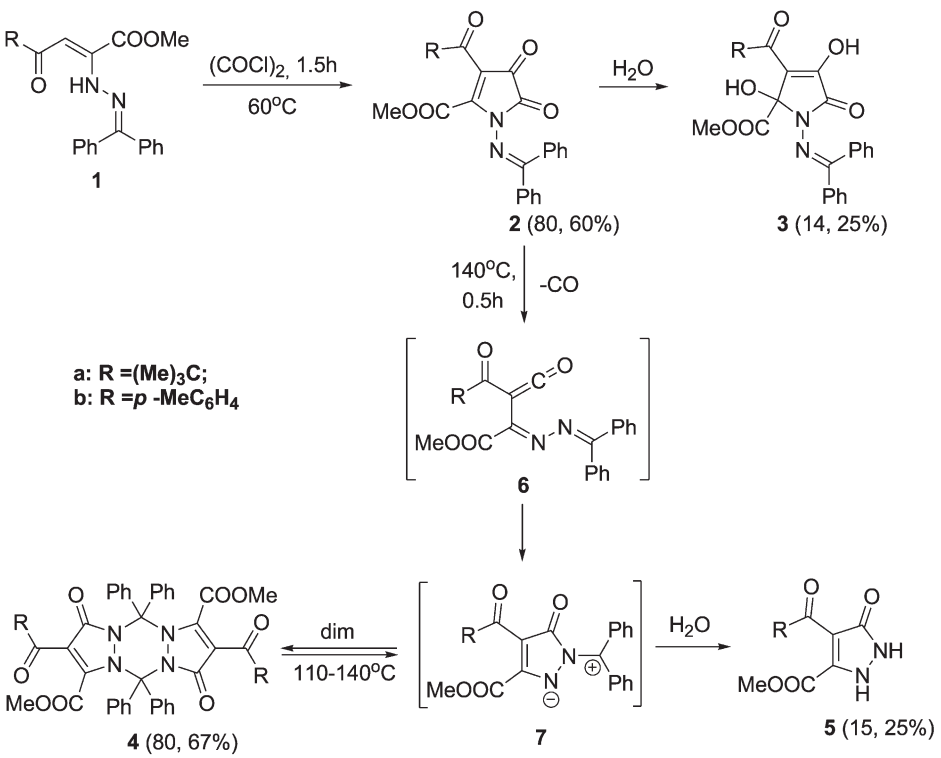

Scheme 1. Synthesis and thermolysis of 1-diphenylmethilenamino-2,3-dihydropyrrole-2,3-dione **2a**,**b**.

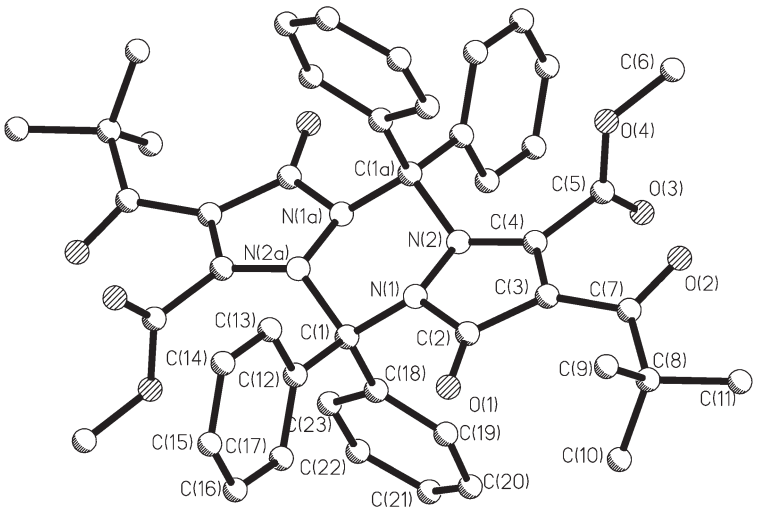

Figure 1. Perspective view of the structure of **4a**, showing the crystallographic labeling.

Crystals of **4a** suitable for X-ray analysis were obtained from a toluene solution. Figure 1 shows a perspective view of the structure, which crystallizes in the monoclinic space group $P2_1/c$. The molecule in the crystal lies in the centre of the symmetry. The tetrazine has a chair-conformation. The inflexion along N1···N2a line is 48.5° and the deviation of the C1 from the plane of four nitrogen atoms is 0.7 Å. The nitrogen atoms have a pyramidal structure. The sums of the valence angles around N1 and N2 are 347.5 and 348.6°, respectively. The pyrazole cycle with local double bond is planar. The C3–C4 distance in the five-membered ring is 1.368(4) Å, that corresponds to the C=C double bond length in the pyrazoles.[11] The plane of the methoxycarbonyl group at the C4 has an orthogonal position with respect to the pyrazole ring, and the plane of the pivaloyl fragment at the C3 an angle 14.7°. The torsion angle O2–C7–C3–C4 is 12.2°. Hydrogen bonds and other shortened intermolecular contacts were not found. The values of all bonds lengths in this molecule are in nice agreement with the other known data.[11]

We propose the following mechanism of pyrrole-2,3(1*H*)-diones **2a**,**b** conversion into dipyrazolo[1,2-*a*;1′,2′-*d*]-[1,2,4,5]tetrazines **4a**,**b** and pyrazoles **5a**,**b**. The thermal cheletropic extrusion of CO from **2a**,**b** affords the new (*N*-methyleneamino)imidoylketenes **6a**,**b**, which unexpectedly intermolecular cyclized into azomethine imines—4-acyl-3-methoxycarbonyl-5-oxo-2,5-dihydropyrazole-1-(diphenylmethylium)-2-ides **7a**,**b**. These intermediates undergo dimerization in head-to-tail manner yielding

products **4a**,**b**, while azomethine imines **7a**,**b** are partially hydrolysed under action of water traces in a solvent with ejection of benzophenone molecule to produce the compounds **5a**,**b**.

On the other hand, the dimerization of azomethine imines **7a**,**b** is a reversible process, in our opinion. The colourless solutions of dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazines **4a**,**b** in completely anhydrous inert solvents (such as *p*-xylene, toluene) become deep blue at heating (110–140 °C) and again colourless after cooling. Moreover, the analogous process is observed in mass spectrum of **4a**, where intense peak of the azomethine imine **7a** (*m*/*z* 390) is present.

An additional proof for the suggested mechanism is the dimerization of stable pyrazolidin-3-ones—azomethine imines, giving the centrally symmetric dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazine-1,7-diones and mirror-symmetric dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazine-1,9-diones early reported by Dorn and co-workers.[12]

3. Conclusion

In summary, the results showed that the thermolysis of methyl 3-acyl-1-diphenylmethyleneamino-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates **2a**,**b** led to unexpected products **4a**,**b** and **5a**,**b**. We propose the mechanism of this conversion, including (*N*-methyleneamino)imidoylketenes **6a**,**b** generation, its further cyclization to azomethine imines **7a**,**b**, which dimerize into final compounds **4a**,**b**. A novel pathway of imidoylketenes stabilization via their preliminary cyclization to azomethine imines is an unusual process and it has never been observed before. Furthermore, the pyrazoles **5a**,**b** formation by hydrolysis of **7a**,**b** indirectly confirms the suggested mechanism.

The insertion of methyleneamino moiety to the nitrogen atom of pyrrole-2,3-diones has allowed us not only to obtain an attractive heterocyclic system and to expand the synthetic opportunities of five-membered 2,3-dioxoheterocycles, but also to offer a new synthetic way to arduous unsaturated azomethine imines formation through the intramolecular cyclization of (*N*-methyleneamino)imidoylketenes. Saturated azomethine imines have been prepared by catalytic nucleophilic addition of substituted pyrazolidin-3-ones to various aldehydes and ketones, as reported by Dorn,[12] Stanovnik,[13] Sharpless[14] and co-workers.

4. Experimental

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ solutions with HMDS as the internal standard on a Bruker AM-300 (300 MHz) and a Bruker DPX 400 (400 MHz) spectrometers. The IR spectra were recorded in Nujol mulls on a UR-20 spectrometer. The mass spectrum was recorded on a MX-1310 spectrometer (70 eV). The melting points are uncorrected. Reactions were monitored by TLC on Silufol UV-254 plates. Solvents were dried according to standard protocols.

X-ray crystallography. The unit cell parameters were measured on a four-circle automatic detector KM-4 (KUMA DIFRACTION) with χ-geometry (graphite monochromatised Cu K_α radiation, $\omega-2\theta$ scan mode, $2\theta \leq 80.5°$). The total number of data collected was 4249 [4119 of it were independent with *R*(int.) 0.081]. No correction for absorption was applied ($\mu=0.724\ mm^{-1}$). The structure was determined by a direct method by program SIR92[15] with the subsequent series of calculations of electronic density maps. The hydrogen atoms positions were calculated from geometrical terms. The final anisotropic specification LSM was completed by program SHELXL-97[16] at $R_1=0.0519$, $wR_2=0.1346$ on 1629 reflections with $I \geq 2\sigma(I)$ and $R_1=0.1721$; $wR_2=0.1911$ on all 4119 reflections, GOF=1.002.

Crystallographic data (excluding structural factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC No 229731. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.1.1. Methyl 1-diphenylmethyleneamino-3-pivaloyl-4,5-dihydro-4,5-dioxo-1*H*-pyrrole-2-carboxylate (2a). A solution of oxalyl chloride (0.25 mL, 28 mmol) in dry chloroform (1 mL) was added to a solution of **1a**[8] (1.00 g, 27 mmol) in dry chloroform (3 mL). The reaction mixture was heated for 1.5 h, solvent (2 mL) was evaporated and resulting solution was cooled. The solid was filtered off gave the title compound **2a** (0.92 g, 80%) as a deep red crystals, mp 138–140 °C; [Found: C, 68.97; H, 5.21; N, 6.72. $C_{24}H_{22}N_2O_5$ requires C, 68.89; H, 5.30; N, 6.69%]; ν_{max} 1760 (O–C=O, C^2=O); 1740 (C^3=O); 1680 (C^4–C=O); δ_H (400 MHz, $CDCl_3$) 7.10–7.62 (10H, m, 2Ph); 3.86 (3H, s, OMe); 1.05 (9H, s, Me_3C).

4.1.2. Methyl 1-diphenylmethyleneamino-2,4-dihydroxy-3-pivaloyl-2,5-dihydro-5-oxo-1*H*-pyrrole-2-carboxylate (3a). The residue solution after synthesis compound **2a** was allowed to contact with air moisture for 24 h. The solid was filtered off and recrystallized from chloroform–hexane (1:1) to give the title compound **3a** (0.17 g, 14%) as a light yellow crystals, mp 149–150 °C; [Found: C, 66.15; H, 5.12; N, 6.47. $C_{24}H_{24}N_2O_6$ requires C, 66.05; H, 5.22; N, 6.42%]; ν_{max} 3480, 3210 (OH); 1740 (O–C=O, C^2=O); 1680 (C^4–C=O); δ_H (300 MHz, DMSO-d_6) 7.12–7.84 (11H, m, 2Ph+C^5–O*H*); 3.84 (3H, s, OMe); 1.20 (9H, s, Me_3C).

4.1.3. Methyl 1-diphenylmethyleneamino-3-*p*-toluoyl-4,5-dihydro-4,5-dioxo-1*H*-pyrrole-2-carboxylate (2b). This compound was prepared from **1b**[8] (1.00 g, 25 mmol) and oxalyl chloride (0.22 mL, 26 mmol), according to above described method for **2a**. Yield compound **2b** (0.71 g, 60%) as a deep red crystals, mp 144–146 °C; [Found: C, 71.83; H, 4.35; N, 6.24. $C_{27}H_{20}N_2O_5$ requires C, 71.67; H, 4.46; N, 6.19%]; ν_{max} 1740 (O–C=O, C^2=O); 1725 (C^3=O); 1630 (C^4–C=O); δ_H (400 MHz, $CDCl_3$)

7.00–7.79 (14H, m, 2Ph+C_6H_4); 3.80 (3H, s, OMe); 2.29 (3H, s, Me).

4.1.4. Methyl 1-diphenylmethyleneamino-2,4-dihydroxy-3-*p*-toluoyl-2,5-dihydro-5-oxo-1*H*-pyrrole-2-carboxylate (3b). This compound was prepared according to above described method for **3a**. Purification crude precipitate from chloroform–hexane (1:1) to give compound **3b** (0.31 g, 25%) as a light yellow crystals, mp 164–166 °C; [Found: C, 68.98; H, 4.65; N, 6.00. $C_{27}H_{22}N_2O_6$ requires C, 68.93; H, 4.71; N, 5.95%]; ν_{max} 3395, 3150 (OH); 1760 (O–C=O, C^2=O); 1620 (C^4–C=O); δ_H (300 MHz, DMSO-d_6) 7.22–7.81 (15H, m, 2Ph+C_6H_4+C^5–O*H*); 3.87 (3H, s, OMe); 2.42 (3H, s, Me).

4.1.5. Dimethyl 2,8-dipivaloyl-5,5,11,11-tetraphenyl-1,5,7,11-tetrahydro-3,9-dioxo-1*H*,7*H*-dipyrazolo[1,2-*a*;1′,2′-*d*][1,2,4,5]tetrazine-1,7-dicarboxylate (4a). A solution of **2a** (1.00 g, 24 mmol) in dry *p*-xylene (6 mL) was held at 138–140 °C for 0.5 h and then cooled. The solid was isolated by filtration and then recrystallized from acetone to give title compound **4a** (0.75 g, 80%) as a colourless crystals, mp 223–224 °C; [Found: C, 70.93; H, 5.51; N, 7.22. $C_{46}H_{44}N_4O_8$ requires C, 70.75; H, 5.68; N, 7.17%]; ν_{max} 1760 (O–C=O); 1730, 1700 (N–$C^{1(7)}$=O); 1670 ($C^{2(8)}$–C=O); δ_H (400 MHz, DMSO-d_6) 7.10–7.54 (20H, m, 4Ph); 3.13 (6H, s, 2OMe); 1.07 (18H, s, 2Me_3C); δ_C (100.6 MHz, DMSO-d_6) 203.7, 163.2, 160.5, 155.3, 130.6, 129.7, 126.6, 120.6, 114.7, 88.1, 56.8, 44.5, 26.7; MS (*m*/*z*, %): 390 ($M/2^+$, 20), 333 ($M/2^+-Me_3C$, 100).

4.1.6. Methyl 4-pivaloyl-2,5-dihydro-1*H*-pyrazole-3-carboxylate (5a). The residue solution after synthesis compound **4a** was allowed to contact with air moisture for 0.5 h. The precipitate was filtered off and recrystallized from toluene to give the title compound **5a** (0.08 g, 15%) as a colourless solid, mp 201–203 °C; [Found: C, 53.14; H, 6.18; N, 12.40. $C_{10}H_{14}N_2O_4$ requires C, 53.09; H, 6.24; N, 12.38%]; ν_{max} 3250 (NH); 1760 (O–C=O); 1720 (N–C=O); 1670 (C^4–C=O); δ_H (400 MHz, DMSO-d_6) 13.52 (1H, br s, N*H*); 10.15 (1H, br s, N*H*); 3.81 (3H, s, OMe); 1.20 (9H, s, Me_3C); δ_C (100.6 MHz, DMSO-d_6) 203.9, 163.5, 158.8, 157.2, 113.9, 51.6, 44.9, 26.6.

4.1.7. Dimethyl 5,5,11,11-tetraphenyl-2,8-ditoluoyl-1,5,7,11-tetrahydro-3,9-dioxo-1*H*,7*H*-dipyrazolo[1,2-*a*;1′,2′-*d*]-[1,2,4,5]tetrazin-1,7-dicarboxylate (4b). This compound was prepared from **2b** (1.00 g, 22 mmol) according to above described method for **4a**. Purification crude precipitate from ether to give compound **4b** (0.57 g, 67%) as colourless crystals, mp 207–209 °C. [Found: C, 72.93; H, 4.73; N, 6.84. $C_{50}H_{40}N_4O_8$ requires C, 72.80; H, 4.89; N, 6.79%]; ν_{max} 1760 (O–C=O); 1690 (N–$C^{1(7)}$=O); 1650 ($C^{2(8)}$–C=O); 1600 (C=C); δ_H (400 MHz, DMSO-d_6) 7.03–7.74 (28H, m, 4Ph+2C_6H_4); 3.45 (6H, s, 2 OMe); 2.35 (6H, s, 2Me); δ_C (100.6 MHz, DMSO-d_6) 187.8, 160.8, 158.7, 152.3, 141.9, 137.0, 132.1, 129.7, 129.5, 128.4, 127.4, 118.6, 113.3, 86.1, 54.1, 21.1.

4.1.8. Methyl 4-*p*-toluoyl-2,5-dihydro-1*H*-pyrazole-3-carboxylate (5b). This compound was prepared according to above described method for **5a**. Purification crude precipitate from toluene to give compound **5b** (0.14 g, 25%) as a colourless solid, mp 210–212 °C; [Found: C, 59.89; H, 4.63; N, 10.80. $C_{13}H_{12}N_2O_4$ requires C, 60.00; H, 4.65; N, 10.76%]; ν_{max} 3250 (NH); 1770 (O–C=O); 1670 (N–C=O); 1620 (C^4–C=O); δ_H (300 MHz, DMSO-d_6) 13.20 (1H, br s, N*H*); 10.35 (1H, br s, N*H*); 7.60 (2H, d, *J*=8.0 Hz, C_6H_4); 7.26 (2H, d, *J*=8.0 Hz, C_6H_4); 3.60 (3H, s, OMe); 2.40 (3H, s, Me).

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