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Conjugated *Schiff* Bases. 15[1]. Substituent Effect on the Cycloaddition of Heterocumulenes to Some 1-Oxa-4-azabutadienes

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The substituent effect on the cycloaddition of aryl isocyanates to some 1-oxa-4-azabutadienes has been investigated. It has been found that electron-withdrawing groups located in the aryl isocyanate ring distinctly increase the rate of the cycloaddition. The importance of isocyanate nitrogen unshared electrons has been considered. Rate constants and activation parameters have been discussed with respect to the mechanism.

(Keywords: 1,3-Cycloaddition; 1,3-Heterodienes; Substituent effects)

Konjugierte Schiff-Basen, 15. Mitt.: Substituenteneffekte bei der Cycloaddition einiger Heterocumulene mit 1-Oxa-4-azabutadienen

Der Substituenteneffekt bei der Cycloaddition von Arylisocyanaten an einige 1-Oxa-4-azabutadiene wurde untersucht. Es wurde festgestellt, daß e-anziehende Gruppen am Aryl-isocyanat-Ring deutlich die Geschwindigkeit der Cycloaddition erhöhen. Geschwindigkeitskonstanten und Aktivierungsparameter werden im Hinblick auf den Reaktionsmechanismus diskutiert.

Introduction

Recently it has been reported[1–3] that 1-oxa-4-azabutadienes represented by 2-monoanils of some vicinal dicarbonyl compounds are prone to react with aryl isocyanates after the 1,3-dipolar cycloaddition mode

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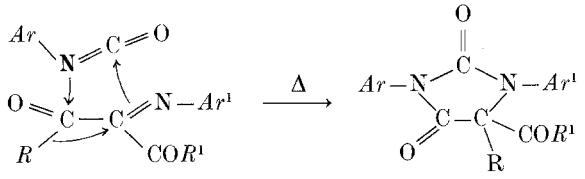
yielding five-membered heterocycles. The proper cycloaddition is combined with simultaneous 1,2-migration of a substituent attached to carbon C2 of the 1-oxa-4-azabutadiene moiety:

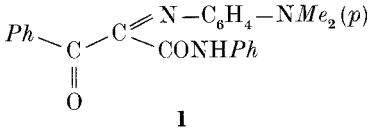


1, **2** **3**

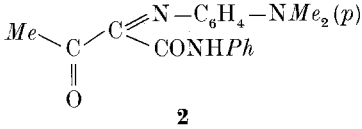
This reaction has been considered as a synchroneous concerted process in which unshared electrons of the aryl isocyanate nitrogen atom played the important role. In order to confirm such a concept the effect of substituents on this cycloaddition has now been investigated.

Results and Discussion

Two of 1-oxa-4-azabutadienes were chosen as model compounds: 2-*N*,*N*-dimethylaminoanil of *β*-phenyl-*α*,*β*-diketopropionic acid anilide (**1**) and 2-*N*,*N*-dimethylaminoanil of *α*,*β*-diketobutyric acid anilide (**2**).



1

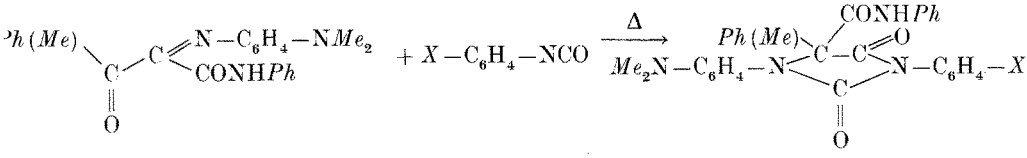


2

This choice was imposed by the characteristic spectral properties of these compounds which showed intense absorptions in the visible region (422 and 430 nm; ε_{max} *Et*OH, 9 600 and 20 800, respectively) originated from the $n \rightarrow \pi^*$ transitions within the dimethylaminoanil fragment[4]. This made it very easy to follow the progress of the cycloaddition reaction with aryl isocyanates in which **1** or **2** vanished. The 1-oxa-4-azabutadienes were reacted with several *para*-substituted aryl isocyanates. The products of all these reactions were found to be exclusively 1,3,5,5-tetrasubstituted imidazolidine-2,4-diones (**3**).

The structures of **3** were confirmed by spectroscopic evidences. Thus, ir spectra showed sharp bands in carbonyl stretching vibration region, at approximately 1 775, 1 715, and 1 690 cm^{-1} ascribed to 2-CO, 4-CO, and amide CO groups, respectively[1, 5, 6]. ^1H nmr spectra of the compounds **3f** to **3j** revealed three

proton singulets of the methyl group substituted imidazolidinedione ring at approximately 1.9 ppm. ^{13}C nmr spectra exhibited singulets of carbonyl carbons at about 170, 160, and 154 ppm for 2-CO, 4-CO, and amide CO respectively. Quaternary ring carbons produced signals at 77 ppm for **3a** to **3e**, which were shifted upfield in the case of the hydantoins derived from **2** to approximately 69.5 ppm. Methyl groups attached to the ring were found as quartets at 20 ppm with coupling constants of about 130 Hz.



3

3		*X*	Yield %	
Ph	*Me*		*Ph*	*Me*
a	**f**	O*Me*	52	58
b	**g**	*Me*	59	68
c	**h**	H	80[3]	68[1]
d	**i**	Cl	75	75
e	**j**	NO_2	78	76

Cycloaddition reactions were carried out in dry xylene or toluene. As expected, all of them were second order processes (first order with respect to both aryl isocyanate and 1-oxa-4-azabutadiene as well). Rate constants were evaluated from the slope of the best linear second-order dependence[7]. They are listed in Table **1**.

Table 1. *Rate constants for the cycloaddition reactions*

	1 + *X*-C_6H_4—NCO + **2**			
	$10^6 k$ ($dcm^3 mol^{-1} s^{-1}$)			
X	80 ± 0.5 °C	110 ± 0.5 °C	80 ± 0.5 °C	110 ± 0.5 °C
O*Me*	56.2 ± 1.7	251.0 ± 4.1	151.2 ± 5.6	302.4 ± 2.1
Me	79.4 ± 1.4	347.2 ± 2.9	195.2 ± 6.3	500.8 ± 7.2
H	91.9 ± 1.3	551.1 ± 6.6	268.9 ± 2.4	1 162.4 ± 8.5
Cl	257.3 ± 9.0	1 290.0 ± 11.0	1 350.0 ± 39.0	3 890.0 ± 88.0
NO_2	1 660.0 ± 2.3	7 940.0 ± 87.0	15 900.0 ± 442.0	63 100.0 ± 576.0

Strong effect of substituents on the cycloaddition of aryl isocyanates to 1-oxa-4-azabutadienes proved its atypical mechanism involving participation of unshared electrons of the isocyanate nitrogen atom. Electron-withdrawing substituents located in the aryl ring of the aryl

isocyanate caused a rapid increase of the cycloaddition rate, more than 60 times in the case of **2**. Electron-releasing groups distincltly decrease the reaction rate. It seems reasonable to consider substituent effects on the heterocumulene moiety[8]. Electron accepting groups favourize polarization of the carbon nitrogen double bond (a) whereas donors affect the carbon oxygen double bond (b):

$$\underset{\text{(a)}}{\leftarrow {}^{-}\mathrm{N}-\mathrm{C}^{+}{=}\mathrm{O} \leftrightarrow -\mathrm{N}=\mathrm{C}=\mathrm{O} \leftrightarrow \rightarrow \mathrm{N}=\mathrm{C}^{+}-\mathrm{O}^{-} \leftrightarrow \rightarrow {}^{+}\mathrm{N}\equiv\mathrm{C}-\mathrm{O}^{-}} \quad \underset{\text{(b)}}{}$$

Such polarization as (a) means a greater role of the p_x and p_y orbitals participating mainly in the nitrogen n orbital, in the HOMO of aryl isocyanate. Hence an increase of the reaction rate due to the substituent effect expresses also the importance of the n orbital in the reaction mechanism. The effect of substituents on the cycloaddition of aryl isocyanates to 1-oxa-4-azabutadienes proved to be very regular and the *Hammett*-type relationship[9] $[\lg(k_x/k_H) = \rho\sigma]$ was fulfilled showing correlation coefficients of 0.99. The values for ρ were found to be $\rho_{(1)}^{80} = 1.42$, $\rho_{(2)}^{80} = 1.44$, $\rho_{(1)}^{110} = 1.99$, and $\rho_{(2)}^{110} = 2.21$; the substituent parameters σ are given in ref. [9].

The cycloadditions were found to follow the isokinetic dependence which pointed to the fact that they proceeded via the same mechanism[7]: $\lg k_{(1)}^{110} = 1.00232 \lg k_{(1)}^{80} + 0.6987$ ($r = 0.9957$), $\lg k_{(2)}^{110} = 1.0877 \lg k_{(2)}^{80} + 0.7586$ ($r = 0.9918$).

Table 2. *Activation parameters for the cycloaddition reactions*

	$\Delta H^{\neq}$ (kJ mol^{-1})		$\Delta S^{\neq}$ (J mol^{-1} deg^{-1})	
X	**1**	**2**	**1**	**2**
O*Me*	46.6 ± 1.6	24.7 ± 3.0	−204.9 ± 4.6	−258.1 ± 8.1
Me	48.0 ± 0.9	28.5 ± 3.7	−197.6 ± 2.4	−244.7 ± 10.2
H	64.2 ± 0.7	51.9 ± 0.4	−150.4 ± 1.9	−176.2 ± 1.2
Cl	53.6 ± 1.3	41.5 ± 1.8	−171.1 ± 3.6	−192.5 ± 4.9
NO_2	53.1 ± 0.9	48.9 ± 0.9	−157.6 ± 2.3	−159.4 ± 2.3

The isokinetic temperatures evaluated from these relations were equal to 10·16 °K and 186.6 °K for **1** and **2**, respectively. These are the temperatures of which the reactions of **1** and **2** proceed with the same rate.

The activation parameters calculated according to the *Eyring* equation[10] are given in Table 2.

The activation enthalpy reflecting changes of potential and oscillation energies[11] was found to be relatively great for the cycloaddition employing phenyl isocyanate. This can be partly ascribed to weaker solvation effects and perhaps to steric effects as well. On the other hand substituent migration from C2 to C3 of the 1-oxa-4-azabutadiene moiety might be the dominant contribution to the activation energy. It seems to be supported by only slightly variable values of $\Delta H^{\neq}$ found for the reaction of **1** connected with bulky phenyl group migration. In contrast, values of $\Delta H^{\neq}$ ascribed to the cycloaddition of **2** were much more differentiated. Electron-withdrawing substituents caused a two-fold increase of the activation enthalpy compared with that estimated for electron-releasing groups. The activation entropy indicated the structure of the transition state similar to that of the cyclic end-products[12]. The lower values of $\Delta S^{\neq}$ characterizing the reaction employing aryl isocyanates containing electrondonating groups could suggest a more rigid, bicyclic-type structure for the transition state than in the other cases.

Finally it may be concluded that cycloaddition of aryl isocyanates to 1-oxa-4-azabutadienes is strongly affected by substituents located in the aryl ring indicating the important role of the isocyanate nitrogen unshared electrons and supporting the proposed mechanism.

Experimental

Ir spectra were recorded on a Perkin-Elmer 257 spectrophotometer, using KBr pellets. ^{1}H nmr spectra were determined on an Hitachi Perkin-Elmer R 24 B spectrometer, in $CDCl_3$ or *DMSO-d_6* with *TMS* as internal standard. ^{13}C Nmr spectra were recorded on a Varian XL-100 or NICOLET spectrometers, in $CDCl_3$ or *DMSO*. Coupling constants J_{CH} of aryl ring carbons varied from 158 to 164 Hz. Mass spectra were recorded on a Micromas 3 D 8 spectrometer using diret inlet, electron voltage 70 eV, accelerating voltage 8 kV, Sample Inlet Temp, 100 to 150 °C. Fragmentation patterns for the reported type of hydantoins were published previously[18]. Uv spectra were determined on a Varian Cary 210 automatic spectrophotometer, in ethanol, using 1 cm silica transmission cells. C, H, N-values agree very well with the molecular formulas given.

1-Oxa-4-azabutadienes **1** and **2** were synthesized using the method described in Ref.[13–15], based on a base promoted condensation of nitrosoarenes with compounds containing active methylene groups. Aryl isocyanates were prepared by *Curtius* rearrangement[16] of the corresponding acyl azides.

Kinetic measurements

Solutions of **1** and **2** were prepared in concentrations approximately 10^{-3} *M* using analytically pure xylene as a solvent. Solutions of aryl isocyanates were obtained in the same concentration by thermal decomposition of the corresponding acyl azide in xylene (concentrations were checked spectrophotometrically). Samples of equimolar ammounts of both reactants (10 ml) were placed into a

paraffin oil bath equipped with submersible thermostat E1N (VEB MLW production) maintaining a temperature range of 0.2 °C. Test samples (0.2 ml) were taken from the above mentioned samples in given intervals in order to determine the progress of cycloaddition by spectrophotometric measurements of the intensity of the longwave absorption characterizing **1** and **2**. Test samples were diluted 1 : 50 with ethanol to stop the cycloaddition by quenching the aryl isocyanates (urethane formation) and to achieve the proper concentration necessary for spectroscopic measurements; a VSU-2P (Zeiss, Jena) spectrophotometer was used. The reaction order was calculated using a graphic method based on a choice of the best linear dependence. Rate constants were evaluated from the slope of this linear relationship[17] ($r \geqslant 0.995$).

Synthesis of 1,3,5,5-tetrasubstituted hydantoins

1 g of the 1-oxa-4-azabutadiene and the molar equivalent amount of an aryl isocyanate were refluxed for 2 to 4 h in 30 ml of dry toluene. The reaction mixture was cooled to room temperature and 10 ml of *n*-hexane were added. The crude crystalline product was filtered off, washed with *n*-hexane and purified by "flash chromatography" on a column filled with alumina (Brockmann, 90, II/III activity) using a 1 : 1 mixture of *n*-hexane and dichloromethane as eluent. Analitically pure compounds were obtained after crystallization from ethanol. Yields: 52 to 80%.

1-(4'-N,N-Dimethylaminophenyl)-3-(4'-methoxyphenyl)-5-phenyl-5-phenylamidoimidazolidin-2,4-dione (**3 a**)

M.p., 235–236 °C; $C_{31}H_{28}N_4O_4$ (520.23). Ir (cm^{-1}): 3 385, s, NH; 2 835, w, OCH_3, 2 800, w, N—CH_3; 1 775, s, 2 CO; 1 715, s, 4 CO; 1 695, s, CO amide; 1 355, 1 415, 1 442, s, CH_3 def.; 818, 760, 690, s, ring subst. ^{1}H nmr (ppm): 8.35, s, 1 H; 7.55–6.55, m, 18 H; 3.70, s, 3 H; 2.95, s, 6 H; ^{13}C nmr (ppm): 170.9, s, C2; 163.0, s, C4; 77.1, s, C5; aryl at N1: 150.5, s, C4; 127.0, d, C2, C6; 112.2, d, C3, C5; 119.4, s, C1; 40.3, q, N—CH_3, J_{CH} = 130.7 Hz; aryl at N3: 131.2, s, C1; 127.3, d, C2, C6; 113.6, d, C3, C5; 159.0, s, C4; 55.2, q, OCH_3, J_{CH} = 150.3 Hz; phenylamido at C5: 154,6, s, CO; 136.8, s, C1; 119.9, d, C2, C6; 128.9, d, C3, C5; 124.8, d, C4; phenyl at C5: 134.8, s, C1, 129.8, d, C2, C6; 128.5, d, C3, C5; 129.1, d, C4. Ms (*m/z*, %): M^+, 520, 14.0; $M+1$, 5.0; *M-Ph*NCO, 401, 100; 400, 9.2; 224, 29.8; 223, 5.5; 211, 15.7; 210, 22.8; 196, 11.6; Me_2NPhNCO$^{+\cdot}$, 162, 35.5; 161, 13.4; *Me*O*Ph*NCO$^{+\cdot}$, 149, 1.5; 134, 2.7; 133, 2.4; 121, 41.0; Me_2NPh^+, 120, 6.3; *Ph*NCO$^{+\cdot}$, 119, 53.9; *Me*O*Ph*$^+$, 107, 1.7; 92, 5.5; 91, 23.5; Ph^+, 77, 10.5; 64, 16.8; Uv (λ nm, ε_{max}): 208, 34 500; 253, 29 300; 267, 22 500.

1-(4'-N,N-Dimethylaminophenyl)-3-(4'-methylphenyl)-5-phenyl-5-phenylamido-imidazolidin-2,4-dione (**3 b**)

M.p. 233–234 °C; $C_{31}H_{28}N_4O_3$ (504.23). Ir (cm^{-1}): 3 385, s, NH; 2 920, 2 900, w, CH_3; 2 810, w, N—CH_3; 1 775, s, 2 CO; 1 715, s, 4 CO; 1 695, s, CO amide; 1 442, 1 410, 1 358, s, CH_3 def.; 825, 756, 690, s, ring subst. ^{1}H nmr (ppm): 8.33, s, 1 H; 7.50–6.58, m, 18 H; 2.98, s, 6 H; 2.25, s, 3 H. ^{13}C nmr (ppm): 170.9, s, C2; 162.9, s, C4; 76.2, s, C5; aryl at N1: 150.5, s, C4; 127.2, d, C2, C6; 112.0, d, C3, C5; 119.4, s, C1; 40.3, q, N—CH_3, J_{CH} = 133.5 Hz; aryl at N3: 137.7, s, C1; 128.9, d, C2, C6; 129.1, d, C3, C5; 132.2, d, C4; 21.0, q, CH_3, J = 125.8 Hz; phenylamido at C5: 154.4, s, CO; 136.8, s, C1; 119.9, d, C2, C6; 128.9, d, C3, C5; 124.8, d, C4; phenyl at C5: 134.9, s, C1; 128.9, d, C2, C6; 128.1, d, C3, C5; 129.1, d, C4. Ms (*m/z*, %): M^+, 504, 25.2; $M^+ + 1$, 9.2; *M-Ph*NCO, 385, 22.7; 384, 14.8; 224, 7.2; 223, 1.9;

195, 9.6; 194, 52.7; $Me_2NPhNCO^{+\cdot}$, 162, 17.4; 161, 13.0; 134, 1.9; 133, 2.0; 121, 100; Me_2NPh^+, 120, 10.8; $PhNCO^{+\cdot}$, 119, 10.0; $C_7H_7^+$, 91, 28.5; Ph^+, 77, 8.4; 65, 10.8; Uv (λ nm, ε_{max}): 207, 28 900; 267, 32 700.

1-(4'-N,N-Dimethylaminophenyl)-3,5-diphenyl-5-phenylamido-imidazolidin-2,4-dione (**3 c**)

M.p. 194–195 °C; Ref. [3]; ^{13}C nmr (ppm): 170.9, s, C2; 163.1, s, C4; 77.0, s, C5; aryl at N1: 150.4, s, C4; 126.7, d, C2, C6; 112, 3, d, C3, C5; 119.6, s, C1; 40.4, q, N—CH_3, J_{CH} = 132.7 Hz; aryl at N3: 134.6, s, C1; 125.9, d, C2, C6; 127.0, d, C3, C5; 129.1, d, C4; phenylamide at C5: 154.7, s, CO; 136.6, s, C1; 119.8, d, C2, C6; 128.8, d, C3, C5; 124.9, d, C4; phenyl at C5: 134.8, s, C1; 129.8, d, C2, C6; 129.2, d, C3, C5; 128.1, d, C4.

1-(4'-N,N-Dimethylaminophenyl)-3-(4'-chlorophenyl)-5-phenyl-5-phenylamido-imidazolidin-2,4-dione (**3 d**)

M.p. 238–239 °C; $C_{30}H_{25}N_4O_3Cl$ (524.88). Ir (cm^{-1}): 3 385, s, NH; 2 810, w, N—CH_3; 1 775, s, 2 CO; 1 712, s, 4 CO; 1 695, s, CO amide; 1 442, 1 408, 1 365, s, CH_3 def.; 808, 730, 695, s, ring subst. ^{1}H nmr (ppm): 8.40, s, 1 H; 7.50–6.60, m, 18 H; 2.98, s, 6 H; ^{13}C nmr (ppm): 170.7, s, C2; 162.6, s, C4; 76.1, s, C5; aryl at N1: 150.5, s, C4; 127.0, d, C2, C6; 112.2, d, C3, C5; 119.2, s, C1; 40.3, q, N—CH_3, J_{CH} = 135.0 Hz; aryl at N3: 133.7, s, C1; 128.8, d, C2, C6; 130.7, d, C3, C5; 133.6, s, C4; phenylamido at C5: 154.3, s, CO; 136.6, s, C1; 119.9, d, C2, C6; 129.0, d, C3, C5; 125.0, d, C4; phenyl at C5: 134.6, s, C1; 130.1, d, C2, C6; 128.4, C3, C5; 129.6, d, C4. Ms (*m/z*, %): M^+, 524, 46.2; $M+1$, 170, $M+2$, 18.4; *M-Ph*NCO, 405, 94.0; 407, 34.2; 404, 16.0; 224, 30.6; 223, 6.9; 214, 47.5; 216, 16.3; $Me_2NPhNCO^{+\cdot}$, 162, 60.5; 161, 31.2; 146, 5.8; 126, 9.7; 121, 100.0; Me_2NPh^+, 120, 12.4; $PhNCO^{+\cdot}$, 119, 38.2; $ClPh^+$, 111, 15.5; 113, 5.5; 91, 17.7; 84, 9.8; Ph^+, 77, 13.4; Uv (λ nm, ε_{max}): 207, 39 100, 266, 22 800.

1-(4'-N,N-Dimethylaminophenyl)-3-(4'-nitrophenyl)-5-phenyl-5-phenylamido-imidazolidin-2,4-dione (**3 e**)

M.p. 211–212 °C; $C_{30}H_{25}N_5O_5$ (533.21). Ir (cm^{-1}): 3 380, s, NH; 2 800, N—CH_3; 1 775, s, 2 CO; 1 715, s, 4 CO; 1 692, s, CO amide; 1 520, 1 358, s, NO_2; 1 442, 1 412, m, CH_3 def.; 808, 752, 689, s, ring subst.; ^{1}H nmr (ppm): 8.65, s, 1 H; 7.35, q_{AB}, J_{HH} = 11 Hz, $\Delta\nu$ = 76 Hz, 4 H; 7.55–7.10, m, 14 H; 2.99, s, 6 H; ^{13}C nmr (ppm): 170.4, s, C2; 161.8, s, C4; 77.1, s, C5; aryl at N1: 150.6, s, C4; 127.0, d, C2, C6; 112.2, d, C3, C5; 118.6, s, C1; 40.3, q, N—CH_3, J_{CH} = 133.5 Hz; aryl at N3: 141.8, s, C1; 123.7, d, C2, C6; 130.4, d, C3, C5; 145.7, s, C4; phenylamide at C5: 153.9, s, CO; 136.3, s, C1; 120.0, d, C2, C6; 129.0, d, C3, C5; 125.3, d, C4; phenyl at C5: 134.5, s, C1; 129.8, d, C2, C6; 127.9, d, C3, C5; 127.6, d, C4. Ms (*m/z*, %): M^+, 535, —; *M-Ph*NCO, 416, 35.2; 224, 13.8; $Me_2NPhNCO^{+\cdot}$, 162, 26.8; 161, 11.2; 121, 3.2; Me_2NPh^+, 120, 8.5; $PhNCO^{+\cdot}$, 119, 100; 91, 73.8; 90, 7.1; 86, 13.0; 84, 20.8; Ph^+, 77, 6.0. Uv (λ nm, ε_{max}): 208, 28 300; 219, 14 600; 267, 20 100; 305, 9 800.

1-(4'-N,N-dimethylaminophenyl)-3-(4'-methoxyphenyl)-5-methyl-5-phenylamido-imidazolidin-2,4-dione (**3 f**)

M.p. 234–235 °C; $C_{26}H_{26}N_4O_4$ (458.21). Ir (cm^{-1}): 3 380, s, NH; 2 930, 2 900, w, CH_3; 2 830, w, OCH_3; 2 800, w, N—CH_3; 1 780, s, 2 CO; 1 710, s, 4 CO; 1 695, s, CO amide; 1 365, 1 410, 1 440, s, m, CH_3 def.; 810, 692, 765, s, ring subst. ^{1}H nmr

(ppm): 8.40, s, 1 H; 7.50–6.50, m, 13 H; 3.72, s, 3 H; 2.88, s, 6 H; 1.75, s, 3 H. ^{13}C nmr (ppm): 170.5, s, C2; 163.7, s, C4; 69.5, s, C5; aryl at N1: 150.2, s, C4; 126.8, d, C2, C6; 111.8, d, C3, C5; 119.2, s, C1; 40.2, q, N—CH_3, J_{CH} = 130.9 Hz; aryl at N3: 159.1, s, C1; 127.4, d, C2, C6; 113.4, d, C3, C5; 131.2, s, C4; 55.2, q, OCH_3, J_{CH} = 150.7 Hz; phenylamido at C5: 154.2, s, CO; 136.5, s, C1; 120.5, d, C2, C6; 128.9, d, C3, C5; 124.9, d, C4; methyl at C5: 20.6, q, J_{CH} = 117.6 Hz. Ms (*m/z*, %): M^+, 458, 46.5; $M+1$, 13.8; *M-Ph*NCO, 339, 14.7; 338, 19.6; 296, 7.1; $Me_2NPhNCO^{+\cdot}$, 162, 26.4; 161, 18.3; *MeOPh*NCO$^{+\cdot}$, 149, 9.8; 121, 100; Me_2NPh^+, 120, 12.3; *Ph*NCO$^{+\cdot}$, 119, 7.2; *MeOPh*$^+$, 107, 13.4; 106, 11.3; 92, 12.5; Ph^+, 77, 11.1. Uv (λ nm, ε_{max}): 207, 24 200; 236, 13 300; 263, 20 200.

1-(4′-N,N-Dimethylaminophenyl)-3-(4′-methylphenyl)-5-methyl-5-phenylamido-imidazolidin-2,4-dione (**3 g**)

M.p. 209–210 °C; $C_{26}H_{26}N_4O_3$ (442.21). Ir (cm^{-1}): 3 310, s, NH; 2 930, 2 920, w, CH_3; 2 820, w, N—CH_3; 1 778, s, 2 CO; 1 715, s, 4 CO; 1 670, s, CO amide; 1 365, 1 410, 1 445, s, m, CH_3 def.; 810, 755, 700, s, ring subst. ^{1}H nmr (ppm): 8.40, s, 1 H; 7.55–7.00, m, 13 H; 2.95, s, 6 H; 2.35, s, 3 H; 1.83, s, 3 H; ^{13}C nmr (ppm): 170.5, s, C2; 163.9, s, C4; 69.8, s, C5; aryl at N1: 150.1, s, C4; 126.7, d, C2, C6; 111.9, d, C3, C5; 119.2, s, C1; 40.1, q, N—CH_3; J_{CH} = 133.7; aryl at N3: 137.0, s, C1; 126.0, d, C2, C6; 129.6, d, C3, C5; 132.0, s, C4; 20.8, q, CH_3, J_{CH} = 124.2 Hz; phenylamido at C5: 154.7, s, CO; 136.7, s, C1; 120.5, d, C2, C6; 128.7, d, C3, C5; 124.8, d, C4; methyl at C5: 19.9, q, J_{CH} = 131.3 Hz. Ms (*m/z*, %): M^+, 442, 49.3; $M+1$, 15.0; *M-Ph*NCO, 323, 11.6; 322, 21.8; 280, 6.2; $Me_2NPhNCO^{+\cdot}$, 162, 22.7; 161, 15.1; *Tol*NCO$^{+\cdot}$, 133, 11.1; 132, 87.7; 121, 100; Me_2NPh^+, 120, 10.4; *Ph*NCO$^{+\cdot}$, 119, 6.5; $C_7H_7^+$, 91, 35.8; Ph^+, 77, 7.1; 65, 9.2. Uv (λ mn, ε_{max}): 208, 28 100; 262, 25 100.

1-(4′-N,N-Dimethylaminophenyl)-3-phenyl-5-methyl-5-phenylamido-imidazolidin-2,4-dione (**3 h**)

M.p. 202–203 °C; Ref. [1]; ^{13}C nmr (ppm): 170.4, s, C2; 163.8, s, C4; 69.8, s, C5; aryl at N1: 150.1, s, C4; 126.7, d, C2, C6; 111.9, d, C3, C5; 119.1, s, C1; 40.1, q, N—CH_3, J_{CH} = 135.5 Hz; aryl at N3: 134.8, s, C1; 125.8, d, C2, C6; 129.1, d, C3, C5; 127.1, d, C4; phenylamido at C5: 154.7, CO; 136.7, s, C1; 120.5, d, C2, C6; 128.8, d, C3, C5; 124.9, d, C4; methyl at C5: 19.9, q, J_{CH} = 117.6 Hz.

1-(4′-N,N-Dimethylaminophenyl)-3-(4′-chlorophenyl)-5-methyl-5-phenylamido-imidazolidin-2,4-dione (**3 i**)

M.p. 216–217 °C; $C_{25}H_{23}N_4O_3Cl$ (462.64). Ir (cm^{-1}): 3 382, s, NH; 2 940, 2 920, w, CH_3; 2 805, w, N—CH_3; 1 782, s, 2 CO; 1 712, s, 4 CO; 1 685, s, CO amide; 1 440, 1 408, 1 368, s, CH_3 def.; 808, 760, 690, s, ring subst. ^{1}H nmr (ppm): 8.33, s, 1 H; 7.35–6.90, m, 11 H; 6.75, q_{AB}, J_{HH} = 9 Hz, Δv = 18 Hz; 2.85, s, 6 H; 1.71, s, 3 H. ^{13}C nmr (ppm): 170.6, s, C2; 163.8, s, C4; 69.6, s, C5; aryl at N1: 150.3, s, C4; 126.8, d, C2, C6; 112.0, d, C3, C5; 118.9, s, C1; 40.2, q, N—CH_3, J_{CH} = 133.3 Hz; aryl at N3: 133.4, s, C1; 127.9, d, C2, C6; 129.9, d, C3, C5; 133.1, s, C4; phenylamido at C5: 154.5, s, CO; 136.6, s, C1; 120.4, d, C2, C6; 128.9, d, C3, C5; 125.1, d, C4; methyl at C5: 20.8, q, J_{CH} = 130.9 Hz. Ms (*m/z*, %): M^+, 462, 33.7; $M+1$, 9.9; $M+2$, 12.0; 344, 4.4; 343, 7.9; $Me_2PhNCO^{+\cdot}$, 162, 25.0; 161, 16.2; Cl*Ph*NCO$^{+\cdot}$, 152, 38.9; 154, 19.2; 121, 100; Me_2Ph^+, 120, 10.8; *Ph*NCO$^{+\cdot}$, 119, 6.9; ClPh^+, 111, 16.6; 113, 5.2; Ph^+, 77, 8.1. Uv (λ nm, ε_{max}): 207, 24 500; 251, 29 000; 261, 31 300.

1-(4'-N,N-Dimethylaminophenyl)-3-(4'-nitrophenyl)-5-methyl-5-phenylamido-imidazolidin-2,4-dione (**3j**)

M.p. 212–213 °C; $C_{25}H_{23}N_5O_5$ (473.19). Ir (cm^{-1}): 3330, s, NH; 2940, 2910, w, CH_3; 2820, w, N—CH_3; 1775, s, 2 CO; 1710, s, 4 CO; 1690, s, CO amide; 1520, 1330, s, NO_2; 1440, 1408, 1360, s, CH_3 def., 855, 755, 692, s, ring subst. ^{1}H nmr (ppm): 8.35, s, 1 H; 7.42, q_{AB}, $J_{HH} = 9$ Hz, $\Delta v = 8.6$ Hz, 4 H; 7.80–7.10, m, 9 H; 2.99, s, 6 H; 2.00, s, 3 H; ^{13}C nmr (ppm): 169.3, s, C2; 163.7, s, C4; 69.8, s, C5; aryl at N1: 150.4, s, C4; 127.9, d, C2, C6; 111.8, d, C3, C5; 119.5, s, C1; 40.0, q, N—CH_3; $J_{CH} = 135.7$ Hz; aryl at N3: 141.8, s, C1; 128.7, d, C2, C6; 121.6, d, C3, C5; 143.7, s, C4; phenylamido at C5: 153.9, s, CO; 137.8, s, C1; 121.6, d, C2, C6; 128.0, d, C3, C5; 125.0, d, C4; methyl at C5: 18.6, q, $J_{CH} = 129.8$ Hz. Ms (*m/z*, %): M^+, 473, 38.1; $M+1$, 11.4; 354, 14.2; $O_2NPhNCO^{+\cdot}$, 164, 4.8; 163, 43.9; $Me_2NPhNCO^{+\cdot}$, 162, 36.8; 161, 17.8; O_2NPh^+, 122, 8.8; 121, 100; Me_2NPh^+, 120, 11.0; $PhNCO^{+\cdot}$, 119, 15.4; 117, 28.2; 91, 7.4; 83, 6.5; Ph^+, 77, 9.8, 76, 10.9. Uv (λ nm, ε_{max}): 206, 32800; 263, 23400; 299, 14800.

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