Synthesis and Thermolysis of the 2,3-dihydro-1*H*-pyrole-2,3-diones, Pseudopericyclic Reactions of Formyl(*N*-phenylimidoyl)ketene: Experimental Data and PM3 Calculations.

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The reactions of the 2,3-dihydro-1*H*-furan-2,3-dione **1** with *Schiff* bases **2a-f** at 60-70°C furnish the corresponding 2,3-dihydro-1*H*-pyrole-2,3-diones **3a-f**. The heating of **3a-d** afforded the corresponding 4-methoxybenzoyl(*N*-arylimidoyl)ketenes **4a-d** as intermediates which undergo a very facile cyclization to quinoline-4-ones **5a-d**. According to our PM3 calculations, fragmentation of 4-formyl-2,3-dihydro-1*H*-pyrole-2,3-dione and 1,4-cyclization of formyl(*N*-phenylimidoyl)ketene **IN1** to azetin-2-one **IN2** and oxetone **IN3** are pseudopericyclic reactions with two orbital connections, proceed *via* planar transition structures. Due to to the possibility of *syn* and *anti* conformations of the imine phenyl, there are eight **E/Z-**isomers of **IN1**. In addition, we have also calculated reaction mechanism of formation of quinoline-4-ones by the PM3 method.

Introduction.

The oxa-1,3-diene moiety in 4-acyl substituted hetero-cylic 2,3-diones, *e.g*., 2,3-dihydro-1*H*-furan-2,3-diones or 2,3-dihydro-1*H*-pyrole-2,3-diones add various isocyanides [1], isocyanates [2], carbodiimides [3], ketenimines [4], diphenylketene [5], imines [6], and alkenes [7], *via* [2+2], [4+1], or [4+2] cycloaddition processes affording novel mono- and bicyclic systems. The primary formed cycloadducts are not stable and undergo unusual furan-dione rearrangements, made evident by [17]O-labeling experiments [8]. The effect of substitiuent on the site selectivity (C=C vs C=N) in the [4+2] cycloaddition between ketene imines with heterodienes (acroliens or 4-acyl-2,3-dihydro-1*H*-furan-2,3-diones) was treated by semiempirical molecular orbital AM1, density functional calculations using Becke's three-parameter hybrid (B3LYP/6-31G*) and *ab initio* method [9]. *N*-Phenylimino-2,3-dihydro-1*H*-furan-2,3-diones, obtainable *e.g*. by reactions of 4-acyl-2,3-dihydro-1*H*-furan-2,3-diones with tosylsulfinylamines or arylalkylcarbodiimides or imines, thermally rearrange to 4-acyl-2,3-dihydro-1*H*-pyrole-2,3-diones [3a,6b,8b]. Semiempirical molecular orbital calculations were used to rationalize this behavior [10]. Thermal decarbonylation of 4-acyl-2,3-dihydro-1*H*-pyrole-2,3-diones leads to the formation of highly reactive acyl(*N*-arylimidoyl)ketenes. The acyl(*N*-arylimidoyl)-ketenes cyclize very easily to quinolones [11]. Imidoyl-ketenes are also generated by flash vacuum thermolysis of Meldrum's acid [11b,g,h], triazole derivatives [11e,f,g] and the elimination of alcohols from enamine ester [12]. These reactions proceed readily at temperatures ranging from 160 to 185 °C in static systems or above 300 °C under fvp conditions [11b,d,e]. Imidoylketenes are closely related to formylketene; the substituents in both possess a π-bond in conjugation with the ketene as well as an in-plane lone pair. Although substituted imidoylketenes have been less widely studied than α-oxoketenes [13], they undergo a rich variety of reactions.

In this paper, the synthesis and characterization of the 2,3-dihydro-1*H*-pyrole-2,3-diones derivatives **3a-f** obtained from the reactions between various imine deriva-tives **2a-f** and 2,3-dihydro-1*H*-furan-2,3-diones **1** are pres-ented, our findings during the course of synthesizing **3a-d**, too, as well as further investigations of its thermal decomposition and cyclization to quinolones **5a-d** at high temperatures. To study the mechanism of the reaction all calculations were carried out by means of semiempirical PM3 method [14] with full geometry optimisation for reactants, products and intermediates. The PM3 calcula-tions were carried out using the SPARTAN program pack-age [15]. Transition structures have been located using the linear synchronous transition method contained within Spartan. Vibrational mode analyses were systematically carried out to confirm that on a potential energy surface all optimized geometries correspond to a local minimum that has no imaginary frequency mode or a saddle point that has only one imaginary frequency mode. Model com-pounds with aryl and phenyl groups substituted by hydro-gen atoms were used in the theoretical calculations. The results of the calculations (the formation entalpies ΔH_f, in kcalmol^{-1}; dipole moments μ, in debye; the highest and lowest molecular orbital energies E_{HOMO} and E_{LUMO}, in eV and lowest or imaginary frequencies, in cm^{-1}) are given in Table 1.

Results and Discussion.

Treatment of the yellow 4-(-4-methoxybenzoyl)-5-(-4-methoxyphenyl)-2,3-dihydro-2,3-furandione **1** with *Schiff* bases **2a-f** at 60-70 °C furnishes the corresponding red coloured 2,3-dihydro-1*H*-pyrole-2,3-diones **3a-f**. The reaction equation is shown in Scheme 1. The structures of **3a-f** were confirmed by elemental analysis, IR, ^{1}H and [13]C

Table 1

Relative energies, dipole moments, HOMO and LUMO orbital energies and imaginary frequencies for the reactants **R**, transition states **TS**, intermediates **IN** and products **P**.

Compounds	ΔH_{rel} kcalmol^{-1}	μ Debye	E_{HOMO} eV	E_{LUMO} eV	ν cm^{-1}
R1	-43,30	3.87	-10.56	-1.42	49.83
CO	-15.91	0.18	-13.03	1.00	2306.00
TS1	-13.88	0.80	-9.12	-0.46	*365.25i*
IN1-ZZ$_{(anti)}$	0	2.08	-9.30	-0.31	34.09
IN1-EZ$_{(anti)}$	2.31	2.17	-9.19	-0.48	31.82
IN1-ZZ$_{(syn)}$	2,62	0.86	-9.25	-0.56	30.54
IN1-ZE$_{(anti)}$	3,29	3.53	-9.30	-0.31	33.19
IN1-ZE$_{(syn)}$	3.76	1.11	-9.21	-0.56	33.57
IN1-EZ$_{(syn)}$	5.43	3.72	-9.16	-0.74	27.39
IN1-EE$_{(syn)}$	9.75	3.92	-8.88	-0.61	*49.88i*
IN1-EE$_{(anti)}$	11,53	3.58	-8.72	-0.73	*27.46i*
TS2	20.25	4.76	-8.60	-1.01	*340.93i*
IN2$_{(pyramidal)}$	15.74	4.75	-9.05	-1.12	44.32
IN2$_{(planar)}$	17.75	4.95	-8.74	-1.09	*161.41i*
TS3	34.94	3.68	-8.96	-0.82	*519.11i*
IN3	33.51	4.48	-9.27	-0.97	36.92
TS4	27.42	4.09	-9.25	-0.57	*835.56i*
IN4	2.00	4.08	-9.48	-1.74	48.20
TS5	34.09	4.09	-9.54	-1.67	*1600.44i*
P1	-28.22	5.64	-8.93	-0.73	41.88
P2	-26.97	5.13	-9.35	-1.12	57.13
P3	-31.26	0.69	-9.20	-1.08	83.37

nmr data. Product 3a was obtained by reacting 1 with *N*-benzylidene aniline **2a** in 83 % yield. In the ir spectra of compound **3a**, the C=O absorption bands were found at about 1750, 1710 and 1640 cm^{-1}, typical of pyrrole-2,3-diones [3a]. The basic structure of **3a** is strongly supported by ^{13}C nmr found at 187.79 (t, j = 3.7 Hz, ArCO), 179.28 (s, C$_3$ = O), 162.30 (s, C$_2$ = O), 172.02 (s, C-5), 113.91 (s, C-4), 55.85(OCH$_3$) and 55.68 ppm (OCH$_3$). ^{1}H nmr signals were found at δ = 7.97-6.74 (m, Ar-H) and δ =

3.84, 3.69 (two s, 2OCH$_3$) ppm. The reaction of 1 with *N,N*'-bis(benzylidene)ethane-1,2-diamine **2e** and *N,N*'-bis(benzylidene)benzene-1,4-diamine **2f** at 60 °C furnishes the corresponding red coloured 1,2-bis[4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydro-1*H*-pyrrole-2,3-dione-1yl]ethane **3e** and 1,4-bis[4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydro-1*H*-pyrrole-2,3-dione-1-yl]benzene **3f**, respectively (see Experimental). The reaction equations are shown in Scheme 1.

The heating of 2,3-dihydro-1*H*-pyrole-2,3-diones **3a-d** under thermolytic conditions afforded the corresponding 1*H*-quinolin-4-one derivatives **5a-d** in moderate to acceptable yields (40-52 %), obviously obtained as a result of thermolysis of the primary formed 4-methoxybenzoyl(*N*-arylimidoyl)ketenes **4a-d** generated immediately undergoes a 6π electrocyclic ring closure to afford the quinoline derivative **5** during warm-up. The reaction equation is shown in Scheme 2. This case is well known from other *N*-aryl-imidoylketenes [2c], irrespective from which precursor they were generated and independent of the thermolytic or pyrolytic reaction conditions employed [11a]. In the ir spectra of compound **5a**, the N-H and C=O absorption bands were found to be at about 3360, 1670, and 1630 cm^{-1}, respectively (see Experimental). ^{1}H nmr signals about **5a** were found at δ = 12.01 (s, NH or OH), 8.14-6.94 (m, Ar-H) and δ = 3.81, 3.76 (two s, 2xOCH$_3$) ppm. In particular from the ^{13}C nmr spectrum of **5a**, important structural information can be obtained. δ Values of 195.96 and 176.84 ppm for the carbon atoms at ArCO and C-4 are in good accordance with those of very close analogues having identical 1*H*-quinolin-4-one ring systems [2b,c,3a]. Elemental analysis data and more information about the **5a-d** spectra were given in the Experimental section.

Scheme 1
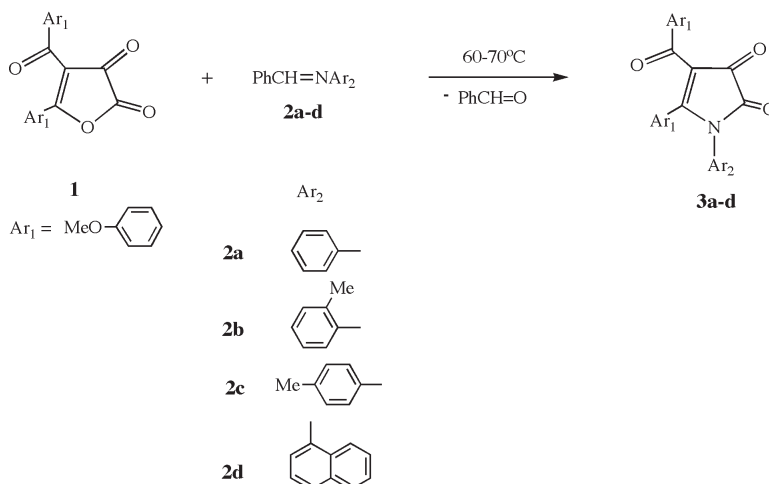
The reaction mechanism for selected model structures, formation of formyl(*N*-phenylimidoyl)ketene **IN1**, its conformational structures and *N*-phenylacylazetion **IN2** and *N*-phenylimodyloxetone **IN3** equilibrium have been resulted by PM3 calculations. A comprehensive theoretical study of the electrocyclization of **IN1-ZZ$_{(anti)}$** was conducted. The study included a conformational analyis of the reactants, locating transition structures and optimizing closed products. The spatial dispositions of atoms for the reactant **R**, intermediates **IN**, transition states **TS** and products **P** are shown in Figures 1-4. To ease the consideration of changes in the systems, the same numbering of atoms is kept for reactants, transition states, intermediate and final products of the reactions.

Thermolysis of **R1** leads to the formation of **IN1** as an intermediate (see Figure 1). As seen from Table 1, the molecule CO disconnection is realized through a transitional state **TS1** with the value of ΔH_{rel} equal to –13.88 kcal.mol^{-1}. The characteristic structural variations for the reacting molecules are given in the Table 2. The calculated transition structure **TS1** for the decarbonylation of **R1** is shown in Figure 1. The **TS1** is formed when the atom C2 moves to the distance of 2.099 and 2.475 Å from the atoms N1 and C3, respectively. **TS1** is an asynchronous transition structure and the reaction is concerted. The C2-C3 bond breaking to a greater degree in **TS1**, rather than the amide N1-C2 bond; because amides are stabilized and α-dicarboyl compounds are destabilized. Because of unsaturated carbonyl structure of pyrrole-2,3-dion, nitrogen gives its lone pair easily to C5 rather then to C2. Bond orders of C5-N1, N1-C2 and C2-C3 at the **R1** are 1.145, 0.958 and 0.829, respectively. However, the nearly linear O7-C3-C4 geometry (168.28°) suggests that it is more appropriate to consider the reverse reaction, the interaction of CO with formyl(*N*-phenylimidoyl)ketene, in which donation of the CO lone pair to the in-plane ketene LUMO is the dominant interaction, and leads to the nearly linear geometry.

In a recent series of publications, Birney *at al*. has reported a number of examples for thermal pseudopericyclic reactions that include cycloadditions, sigmatropic rearrangements and electrocyclizations. Such pseudopericyclic reactions are typically characterized by planar (or

Atom Charges	R1	TS1	IN-ZZ$_{(anti)}$
N1	0.077	-0.188	-0.120
C2	0.195	0.110	
C3	0.325	0.514	0.484
C4	-0.432	-0.476	-0.471
C5	0.049	0.092	0.056
O6	-0.246	-0.166	
07	-0.239	-0.136	-0.105
C8	0.365	0.370	0.377
O9	-0.335	-.332	-0.357
Bond Lengths			
N1-C2	1.462	2.099	
C2-C3	1.553	2.475	
C4-C3	1.482	1.350	1.345
C5-C4	1.363	1.446	1.454
C5-N1	1.418	1.304	1.295
O7-C3	1.202	1.162	1.158
Bond Angles			
C3-C2-N1	105.49	77.68	
C6-C2-C3	129.73	171.51	
O7-C3-C4	130.73	168.29	179.52
C5-N1-C2	108.25	114.07	
Torsion Angles			
N1-C2-C3-C4	-0.21	-13.25	
C2-C3-C4-C5	0.06	12.56	
O6-C2-C3-C4	177.94	-167.10	
C5-N1-C10-C11	-179.98	-129.25	

almost planar) transition states and low activation energy [12,16]. Decarbonylation of 2,3-dihydro-1*H*-furan-2,3-diones or 2,3-dihydro-1*H*-pyrole-2,3-diones are pseudopericyclic reactions that proceed *via* planar transition structure [17]. For decarbonylation of 4-acyl-2,3-dihydro-1*H*-pyrole-2,3-dione **R1**, a pseudopericyclic orbital topology is possible, with two orbital disconnections, *i.e*. two atoms where orthogonal sets of orbitals meet, but do not overlap. Because no electrons are exchanged between the in-plane and out-of plane orbitals, the transition state for **R1** is orbital symmetry allowed when the CO departs in the plane of the molecule. The near planarity of **TS1** and the short C=O bond predict that the carbon monoxide product should be formed rotationally and vibrationally cold. Furthermore, the pseudopericyclic orbital topology of this reaction, combined with favorable interactions between electrophilic and nucleophilic centers, results in barriers substantially lower than would be expected for pericyclic decarbonylation analogous. This nearly planar transition structure is in contrast to other pericyclic reactions, where the transition states are usually nonplanar so as to maximize orbital overlap [17a]. Two views of the structures of **R1**, **TS1** and **IN1** are shown in Figure 1. 4-Acyl-2,3-dihydro-1*H*-pyrole-2,3-dione groups of the two structures, **R1** and **TS1,** are remarkably similar, as can be
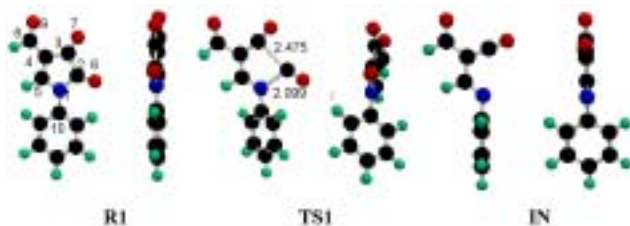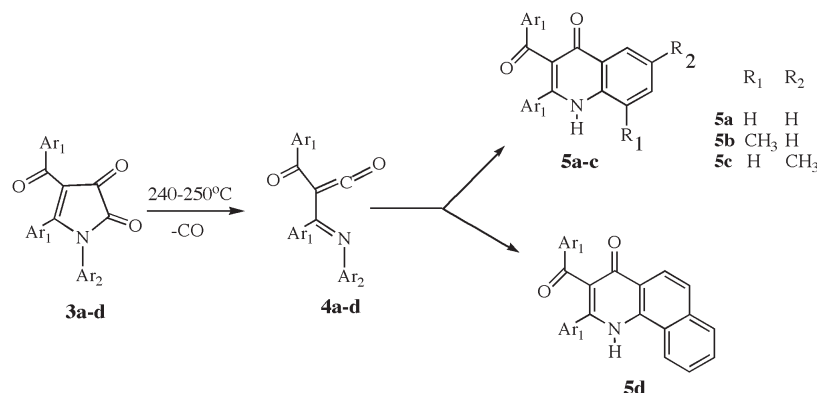

Figure 1: Atom numbering scheme and structures for **R1, TS1** and **IN**. Two side views, rotated by approximately 90º, are given.

Scheme 2

seen most clearly in the side views. All of the atoms are nearly in the same plane at **R1**, with the exception of phenyl groups at **TS1**. Torsion angle C5-N1-C10-C11 of **R1** and **TS1** are –179.98 and –129.25° respectively. Charge of N1 at the **R1** is partial positive. As a result of the rehybridization of N1 from sp^3 toward sp^2, there is an increase in negative charge from 0.077 au, to -0.120 au (at **IN1-ZZ$_{(anti)}$**) (see Table 2). Calculated charge densities of isomers of formyl(*N*-phenylimidoyl)ketenes **IN1** show the highest positive charge on C3 (q=0.484-0.385au), so that nucleophilic attack is expected to occur at C3. The molecular structures of **IN1** has now been refined and distinguished by short C3-C4 and C3-O7 bond lengths of about 1.345 and 1.158 Å, respectively, involving the sp-hybridized carbon. The bond angles of O7-C3-C4 for **R1 TS1** and **IN1-ZZ$_{(anti)}$** are calculated as 130.73° 168.29° and 179.52°, respectively. The atom C3 conversion from sp^2-hybridized state of **R1** to the linear sp-hybridized state leads to **IN1** being planer.

In general, oxoketenes are mixtures of **Z** and **E** isomers. Both experimental and theoretical methods were employed to study the conformational behaviour of oxo-ketene molecules [16b,18]. The conformational stability and the size of the rotational barrier of the oxo-ketenes were found to be greatly influenced by the extent of the interaction between the CO and both the C=C=O group and the substituent plays the major role in determining the direction of the conformational equilibrium in these molecules [19]. *Ab initio* calculations on a series of differently substituted imodoyl-ketenes were used to investigate **E/Z**-isomerism and rotational barriers in these molecules [20].

The preferred conformation of planar systems with sp^2 carbon atoms can result partly from stereoelectronic effects and steric repulsion. In the usual conformation of formylketenes or imidoylketenes, the C=O or C=N- lone pair is **Z** to the C=C=O groups, and can interact with the π_{C4C3O7} orbital. The electron-affinity of the π_{C3O7} orbital of the ketene is the highest one, in comparison to the other

classes of the carbonyl compound. The **E** conformers of formylketene or imodylketenes are calculated to be less stable than the **Z** conformer, presumably because of dipole-dipole interactions. D. M. Birney calculated four conformers of imidoylketene, due to the possibility of *syn* and *anti* conformations of the imine hydrogen [20]. According to our PM3 calculations, formyl(*N*-phenylimidoyl)ketenes **IN1** are mixtures of **E** and **Z** isomers. Due to to the possibility of *syn* and *anti* conformations of the imine phenyl, there are in fact eight isomers of **IN1**. Conformational structures of **IN1** are shown in Figure 2. Carbonyl, imino and ketene groups are planar, except for phenyl group. The relative energies of the conformation isomers of **IN1** are shown in Table 1. According to these data, **IN1-ZZ$_{(anti)}$** conformation should be slightly more stable than the other conformations. Steric and electronic congestion between the C8=O9 and C5=N1 groups in the **IN1-EE** isomer forms of formyl(*N*-phenylimidoyl)ketene has been suggested as the origin of the conformational prefence for **IN1-ZZ$_{(anti)}$**. **IN1-EE$_{(syn)}$** and **IN1-EE$_{(anti)}$**
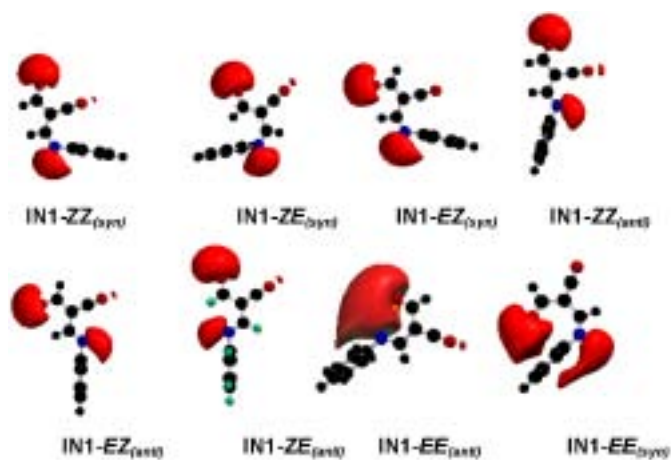
Figure 2: Views of calculated geometries of intermediates, **IN1**.

conformations of **IN1** are unstable in energy. Relative energy of **IN1-EE(syn)** and **IN1-EE(anti)** are 9.75, 11.53 kcal.mol^{-1}, respectively. Electron density is distributed between the carbonyl and imino groups in **IN1-EE(syn)** and **IN1-EE(anti)** (see Figure 2). These structures represent the transition state on the potential energy surface. The imaginary frequencies of **IN1-EE(syn)** and **IN1-EE(anti)** are 49.88 and 27.46 icm[-1] respectively. Steric hindrance would also be expected to play a role in the conformational preference of **IN1-EE**, although electronic factors may also be important. The most dramatic distortions are seen in the C8-C4-C5 angles. In **IN1-EE(anti)**, this angle is 10.24° wider than in **IN1-ZZ(anti)** in order to accommadate the two electron withdrawing groups (C=O, C=N) and steric hindrance between the imino phenyl and carbonyl groups (C=O). The C8-C4-C5 angle in **IN-EE(anti)** is 3.04, bigger then that in **IN1-EE(syn)**. The C4-C5-N1 angle in **IN1-EE(anti)** is 133.81°, which is larger than the **IN1-EE(syn)**, 121.61°. An alternative model, which offers a more consistent explanation of the stability of the **IN1-EZ** or **IN1-ZE** forms, except for **IN1-EE** conformations, is based on the electrostatic interactions of the array of atomic charges. The central carbon, C3, of the formyl(*N*-phenylimidoyl)-ketene **IN1** functionality bears a partial positive charge (0.484-0.385 au) and the carbonyl oxygen (-0.363- -0.289 au) and imino nitrogen (-0.088 - -0.120au) bear a partial negative charge. The **Z** conformations bring these charges into close proximity and, thus, should be stabilized by the electrostatic attraction between these three centers. Due to partial negative charge effect between the C8=O9 and C5=N1 groups at **IN1-EE(anti)** atom charges enforce a lesser degree of charge separation (see Figure 2). The charge of C3 at **IN1-EE(syn)** and **IN1-EE(anti)** is 0.398 and 0.385 au, respectively. Since electronic interactions of the nucleophylic imine nitrogen with electrophylic ketene carbon C3 is more than carbonyl oxygen lone pair with C3, **IN1-EZ(anti)** conformer is lower energy than IN-**ZE(anti)** and IN1-**ZE(syn)**, thus, more stable than the corresponding, and as there is no interaction between the lone pairs of O8 and N1 with C3 in **IN1-EZ(syn)**, this conformation is less stable than **IN1-ZE(syn)**.

Birney and coworkers have previously shown that the relative energies of oxo-ketenes conformers do not correlate with the dipole moments [6b,18d]. In the case of formyl(*N*-phenylimidoyl)ketenes the same result has been obtanined by using PM3 calculations methods. For example, **IN1-ZZ(syn)** has the lowest dipole moment (0.86D), but the third highest relative energy (2.62 kcal.mol^{-1}) as compared to **IN1-ZZ(anti)**.

We have studied the ring-closure of the formyl(*N*-phenylimidoyl)ketenes **IN1-EZ(anti)** to cyclic *N*-phenylacylazetion **IN2** and *N*-phenylimodyloxetone **IN3** (see Figure 3). Energetic aspects obtained for the two cyclizations are collected in Table 1. Involvement of the lone pair of nitrogen or oxygen atom is expected to facilitate the interaction between the vacant carbon p orbital of the ketene LUMO and lone pair electrons of nitrogen or oxygen atom, but azetin-2-one and oxetone-2-one cycles are unstable [16b,17b,18a,c,21]. Azetin-2-ones are rather elusive compounds requiring sterically protecting groups such as adamantyl or *tert*-butyl for stabilization under ordinary reaction conditions [11c]. Alajarin *et al*. have carried out *ab initio* calculations showing that the energy barrier for the ring closure of *N*-formylimidoylketene to *N*-formylazetone is 23.24 kcal.mol^{-1}, being an endotermic process [21c].

Bond orders of N1-C3 and O9-C3 at **IN1-ZZ(anti)** structure are 0.038 and 0.027 respectively. Electronic repulsion between O9 and C3 is weaker than that between N1 and C3. Ring-closure of the formyl(*N*-phenylimidoyl)ketenes, the **IN1-ZZ(anti)**, to cyclic azetin-2-one **IN2** and oxetone-2-on **IN3** is computed to be higher in energy than that of **IN1-ZZ(anti)**. We located the transition states **TS2** and **TS3** for this isomer. The barriers for these are comparable, 20.25 kcal.mol^{-1} for **TS2** and 34.94 kcal.mol^{-1} for **TS3**. There is a good match between the nucleophilic imine nitrogen and electrophlic ketene carbon of **IN-ZZ(anti)** isomer, which favors the reaction than between oxygen and C3. Also, resonance in amides is stronger than in esters, thus lactam **TS2** and **IN2** is stabilized more than **TS3** and **IN3**. At **TS2**, the distance of C3-N1, which can be considered as the reaction coordinate, reaches 1.831 Å. This is
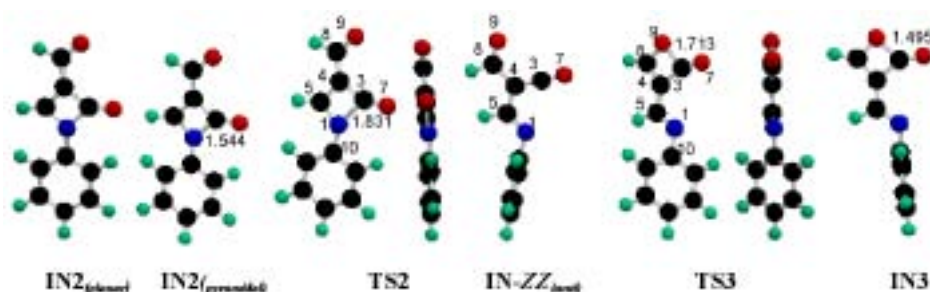

Figure 3: Atom-numbering scheme and structures for **TS2**, **TS3**, **IN2** and **IN3**.. Two side views, rotated by approximately 90°, are given for **TS2** and **TS3**.

very close to the value 1.544 Å in the ring **IN2** (see Table 3). Our calculations show that the formation energy of **IN1-ZZ**$_{(anti)}$ lies 15.74 kcal.mol^{-1} below that of its cyclic isomer **IN2**$_{(pyramidal)}$ and it undergoes ring-closure with an energy barrier of 20.25 kcal.mol^{-1}. The azetin-2-ones, **IN2**, possesses the additional feature that resonance of the carbonyl groups leads to formally anti-aromatic structure. This suggests that the ring **IN2** is thermodynamically less stable than open forms of **IN1**. Regarding the structural features of azetone-2-one **IN2**, the pyramidal geometry of the nitrogen atom is remarkable. The degree of pyramidalization can be measured by the sum of the bond angles at the nitrogen atom, which is 339.35°. The planar structure of **IN2** is characterized as a transition structure for nitrogen inversion. There is only one imaginary vibrational frequency in the transition state, ν = 161.41 icm^{-1}. The analysis of the hessian eigenvector associated with this frequency indicates that the bond is bending rather than stretching. The sum of the bond angle at the nitrogen atom in the planar **IN2** structure is 359.99°, which is showing an almost planar geometry. This value is nearly equal to the corresponding value of *N*-formylazeton [21c]. The inversion energy barrier from pyramidal **IN2** to planar structure of **IN2** is 2.01 kcal.mol^{-1}. The value for unsubstituted azetidin-2-one has been found to be 5.8 kcal.mol^{-1} by Nguyen [18a]. The angle O7-C3-C4 in pyramidal structure **IN2** is lower than the planar structure **IN2** (142.77:144.28). A transition structure **TS3** for the electro-

cyclization of *IN-ZZ*$_{(anti)}$ to generate **IN3** was also located. The geometry of **TS3** is remarkably similar to the ring closing transition state **TS2** described above. The frequency analysis confirmed both structures **IN3** and **IN2**$_{(pyramidal)}$ as minima, isomer **IN2**$_{(pyramidal)}$ being the most stable one by 15.74 kcal.mol^{-1}.

In the case of electrocyclic reactions the 1,4-cyclization of **IN1-ZZ**$_{(anti)}$ to both **IN2** and **IN3** were found to be proceed in a pseudopericyclic manner, by in plane attack of the lone-pair of electrons on the imine nitrogen or carbonyl oxygen to the electrophilic ketene carbon, respectively. The most prominent feature of **TS2** and **TS3** are complete planarity (N1-C3-C4-C5=0.00° and C3-C4-O8-C9 = -0.18°), conforming the pseudopericyclic nature of this ring closure reaction. The **IN2** cyclization requires an *Z*$_{(anti)}$ configuration of the imine group as in **IN1-ZZ**$_{(anti)}$ so that the lone pair of electrons on the imine nitrogen is oriented toward the ketene functionality. Note that for this cyclization mode no rotation of the imine group is required which therefore can be designated as a "*nonrotatory*" cyclization. The N1-C3 bond distance changes, but the N1-C3-C4-C5 system remains essentially planar. Our calculations show that, **TS2** and **TS3** are associated with a concerted process whose primary changes in bonding compass a cyclic array of atoms, where nonbonding and bonding atomic orbitals interchange their roles. The geometric and electronic features of both transition structures, **TS2** and **TS3**, do not correspond to those expected for a conrotatory mecha-

Table 3

Selected structural data and Mulliken charges for **IN-ZZ**$_{(anti)}$, **IN2**$_{(pyramidal)}$, **IN3**, **TS2** and **TS3**.

Atom charges	IN1-ZZ$_{(anti)}$	TS2	IN2$_{(pyramidal)}$	TS3	IN3
N1	-0.120	-0.153	-0.054	-0.085	-0.029
C3	0.484	0.532	0.404	0.526	0.452
C4	-0.471	-0.531	-0.429	-0.404	-0.298
C5	0.056	0.130	0.070	0.038	0.012
07	-0.105	-0.186	-0.224	-0.178	-0.223
C8	0.377	0.338	0.373	0.275	0.149
O9	0.377	0.338	0.373	0.275	0.149
Bond Lengths					
N1-C3	2.782	1.831	1.544	3.065	3.153
C4-C3	1.345	1.458	1.504	1.464	1.508
C5-C4	1.454	1.409	1.363	1.433	1.437
C5-N1	1.295	1.360	1.458	1.296	1.292
O7-C3	1.158	1.169	1.189	1.169	1.185
C8-O9	1.214	1.215	1.209	1.331	1.402
C3-O9	2.827	3.058	3.171	1.713	1.495
Bond Angle					
N1-C3-C4		79.87	85.72		
C8-O9-C3				84.19	87.57
N1-C5-C4	119.77	98.18	94.71	119.55	119.50
O7-C3-C4	179.52	157.36	142.77	157.75	148.81
C8-C4-C5	119.77	131.73	133.92	134.91	136.03
Torsion Angle					
C3-C4-C8-C9	0.00	-0.19	13.20	-0.18	0.00
N1-C3-C4-C5	0.00	0.00	-4.33	-2.62	0.02

nism. The bond angles, O7-C3-C4, for **IN1-ZZ**$_{(anti)}$, **TS2**, **IN2**, **TS3**, and **IN3** are 179.52, 157,36, 142.77, 157.75°, and 148.81°, respectively.

A transition structure **TS4** for the electrocyclization of **IN1-ZZ**$_{(syn)}$ to generate **IN4** was also located (see Figure 4). The energy barrier for the ring closure from **IN1-ZZ**$_{(syn)}$ to **IN4** is 24.80 kcal.mol^{-1}. Table 4 shows the main distances, bond angles and torsion angles for each of the optimized geometries. Molecular orbital calculated charge densities of formyl(*N*-phenylimidoyl)ketene **IN1-ZZ**$_{(syn)}$ show the highest positive charge on C3 (q=0.454 au), so that nucleophilic attack of negative C11 (-0.123 au) is expected to occur at C3. The most important factor governing the PyC11 orbital (or PyC12) of the phenyl group is electron donation from this group into the ketene C3 atom (PyC3), which has a large coefficient at the central ketene C atom to which the attack takes place, resulting in the pyramidalization of C11. The value of valence angle of C10-C11-H13 at **TS4** is 116.03° and at **IN4** is close to that of bonds in sp^3 hybridized carbon (105.95°). It can be clearly seen that there is a loss of the phenyl nodal plane and a partial loss of aromaticity in phenyl both in structures **TS4** and **IN4**. When the **IN1-ZZ**$_{(syn)}$ is being transformed into its transition state, **TS4**, the C3-C11 bond length decreases. One of the major outcomes of this strong interaction of C3 with phenyl is that the carbon atom C11 of benzene which is closest to the C3 atom becomes highly nucleophilic at **TS4**. This is clearly demonstrated in Table 4 where in the partial charges of selected atoms are given (-0.315 au for C11 and 0.493 au for C3). The torsion angle of N1-C10-C11-H13 (48.01°) clearly shows that the atoms are not coplanar.

The small computed energy of **IN4** confirms our hypothesis that the donor-acceptor interaction between the π electrons of phenyl groups and the vacant carbon p orbital of the ketene LUMO is the key factor in stabilizing the **IN4** (ΔH_{rel}=2.00 kcal.mol^{-1}). The electrocyclization reaction of

Table 4
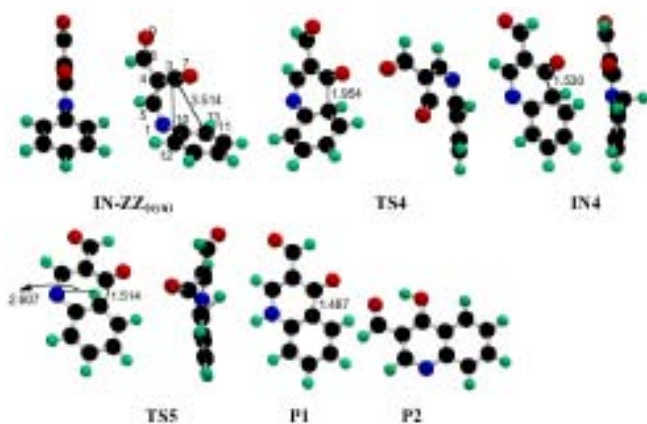
Selected structural data and Mulliken charges for **IN-ZZ**$_{(syn)}$, **IN4**, **TS4**, **TS5** and **P1**.

Atom Charges	IN-ZZ$_{(syn)}$	TS4	IN4	TS5	P1
N1	-0.088	-0.215	-0.127	-0.144	0.224
C3	0.454	0.493	0.349	0.392	0.349
C10	-0.053	0.150	0.053	0.071	-0.069
C11	-0.123	-0.315	-0.109	-0.251	-0.174
H13	0.114	0.194	0.122	0.232	0.074
Bond Lengths					
C5-N1	1.288	1.332	1.409	1.349	1.386
N1-C10	1.428	1.380	1.311	1.372	1.421
C10-C11	1.400	1.432	1.504	1.444	1.404
C11-H13	1.096	1.112	1.126	1.447	3.315
N1-H13	2.685	2.761	2.965	2.607	0.993
C3-C11	3.514	1.914	1.530	1.514	1.487
O7-H13	4.080	2.794	2.889	2.808	5.060
Bond Angles					
C10-C11-H13	120.70	116.03	105.95	100.54	
C4-C3-C11	92.41	107.43	115.08	115.73	115.65
O7-C3-C4	177.69	142.59	122.90	129.62	122.68
Torsion Angles					
C5-N1-C10-C11	-93.82	-32.46	-5.58	5.93	8.82
N1-C10-C11-H13	80.75	48.01	23.64	29.18	2.59
C11-C3-C4-C5	20.28	6.15	17.07	55.26	
C10-C11-C3-C4	-59.90	-34.40	-27.94	-55.80	-1.41
N1-C10-C11-C13	5.42	-90.62	-46.61	-45.44	

IN-ZZ$_{(syn)}$ to **P1** are normal pericyclic reactions. The **IN4** is a true minimal energy structure (all positive vibrational frequencies), while **TS4** and **TS5** each have one imaginary frequency. The hydrogen migration in the transition state **TS5** is supported by the analysis of motion along the imaginary vibrational mode. This mode's frequency is very large, 1600.44 cm^{-1}, and the corresponding reduced mass of 0.983 amu is very close to that of the hydrogen atom. The structure of the transition state **TS5** corresponds to the H13 atom inserting into the C5=N1 bond and involves primarily hydrogen migration from C11. The reacting atoms approach cause the C11-H13 bond length to increase and C5=N1 double bond to be weaken. The transition state **TS5** is characterized by the presence of a four membered cycle. For **TS5**, the bond distances N1-C10, C10-C11 and C11-H13 are 1.372, 1.444 and 1.447 Å, respectively (see Table 4). Bond length of H13 to N1 and O7 at the TS5 are 2.607 and 2.808 Å, respectively. As H13 lies directly over the π cloud of the ring, H13 shifts on to N1 not on to O7. The calculated heat of formation of enol structure **P2** were compared with that of keto structure **P1**, which is slightly more stable than the enol form **P2**.

EXPERIMENTAL

Solvents were dried by refluxing the appropriate drying agent and distilled before use. Melting points were determined on the Electrothermal 9200 apparatus and are uncorrected.

Figure 4: Atom-numbering scheme and structures for **IN-ZZ**$_{(syn)}$, **IN4), TS4, TS5, P1, P2** and **P3**.. Two side views, rotated by approximately 90º, are given for **IN-ZZ**$_{(syn)}$, **TS4, IN4** and.**TS5**.

Microanalyses were performed on a Carlo Erba Elemental Analyser Model 1108; the results agreed favourably with the calculated values. IR spectra were recorded on a Shimadzu Model 435 V-04 spectrometer, using potassium bromide discs. ^{1}H and ^{13}C NMR spectra were recorded on Varian 4200 Gemini spectrometer. The chemical shifts are reported in ppm from tetramethylsilane and given in δ units. All experiments were followed by tlc using DC Alufolien kieselgel 60 F$_{254}$ Merck and with a Model Camag tlc lamp (254/366 nm).

Synthesis of the 2,3-Dihydro-1H-pyrole-2,3-diones (3a).

General Procedures.

Appropriate amounts of 4-(-4-methoxybenzoyl)-5-(-4-methoxyphenyl)-2,3-dihydro-1H-2,3-furandione **1** and the corresponding *Schiff* bases **2a-f** were mixed and allowed to react for 48-96 h at 60-70 °C in an oven. The red crude product formed was triturated with dry ether, collected by filtration and recrystallized from a suitable solvent and dried on P$_2$O$_5$.

4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-phenyl-2,3-dihydro-1H-pyrrole-2,3-dione (3a).

1 g (2.96 mmol) of **1** and 0.54 g (2.96 mmol) N-benzylidene aniline **2a** yield 1.02 g (83 %) of **3a** (reaction time and temperature 48 h, 60 °C), mp 182 °C (xylene); ir (KBr): ν=1750, 1710, 1640 (C=O), 1600-1480 (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1300 (C-N), 1240, 1060 cm^{-1} (C-O-C ν$_{as}$, ν$_s$); ^{1}H nmr (DMSO-d$_6$): δ=7.97-6.74 (m, 13H, Ar-H), 3.84 (s, 3H, OCH$_3$), 3.69 ppm (s, 3H, OCH$_3$); ^{13}C nmr (DMSO-d$_6$): δ=187.79 (t, *j*=3.7 Hz, ArCO), 179.28 (s, C$_3$=O), 172.02 (s, C-5), 163.69 (s, C-10), 163.12 (s, C-17), 162.30 (s, C$_2$=O), 158.45 (s, C-21), 113.91 (s, C-4), 136.08-112.67 (m, aromatic C's), 55.85, 55.68 (two s, 2 x OCH$_3$).

Anal. Calcd. for C$_{25}$H$_{19}$NO$_5$: C, 72.63; H, 4.63; N, 3.39. Found: C, 72.90; H, 4.65; N, 3.33.

4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(2-methylphenyl)-2,3-dihydro-1H-pyrrole-2,3-dione (3b).

1 g (2.96 mmol) of **1** and 0.58 g (2.96 mmol) N-(benzylidene)-2-methylaniline **2b** afford 1.07 g (85 %) of **3b** (reaction time and temperature 48 h, 65-70 °C), mp 232-233°C (xylene); ir (KBr): ν=1750, 1710, 1640 (C=O), 1605-1480 cm^{-1} (C⋯C and C⋯N, aromatic rings); ^{1}H nmr (CDCl$_3$): δ=7.88-6.66 (m, 12H, Ar-H), 3.86 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 2.25 ppm (s, 3H, CH$_3$); ^{13}C nmr (CDCl$_3$): δ=189.46 (t, *j*=3.8 Hz, ArCO), 180.58 (s, C$_3$=O), 175.29 (t, *j*=4.3 Hz, C-5), 166.07 (s, C-10), 165.27 (s, C-17), 160.01 (s, C$_2$=O), 134.80 (s, C-21), 115.76 (s, C-4), 138.35-114.65 (m, Aromatic C's), 57.49, 57.38 (s, 2 x OCH$_3$), 20.13 (s, CH$_3$).

Anal. Calcd. for C$_{26}$H$_{21}$NO$_5$: C, 73.06; H, 4.95; N, 3.28. Found: C, 72.95; H, 4.88; N, 3.49.

4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(4-methylphenyl)-2,3-dihydro-1H-pyrrole-2,3-dione (3c).

1 g (2.96 mmol) of **1** and 0.58 g (2.96 mmol) N-(benzylidene)-4-methylaniline **2c** yield 1.05 g (83 %) of 3c (reaction time and temperature 48h, 60 °C), mp 180 °C (toluene); ir (KBr): ν=1755, 1705, 1640 (C=O), 1600-1460 cm^{-1} (C⋯C and C⋯N, aromatic rings); ^{1}H nmr (CDCl$_3$): δ=7.84-6.66 (m, 12H, Ar-H), 3.83 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 2.32 (s, 3H, CH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ=189.46 (t, *j*=4.0 Hz, ArCO), 180.54 (s, C$_3$=O), 174.65 (t, *j*=4.4 Hz, C-5), 166.02 (s, C-10), 165.16 (s, C-17), 160.23 (s, C$_2$=O), 115.73 (s, C-4), 140.40-114.82 (m, aromatic C's), 57.49, 57.41 (two s, 2 x OCH$_3$), 23.09 (s, CH$_3$).

Anal. Calcd. for C$_{26}$H$_{21}$NO$_5$: C, 73.06; H, 4.95; N, 3.28. Found: C, 73.25; H, 4.86; N, 3.30.

4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-1-(1-naphtyl)-2,3-dihydro-1H-pyrrole-2,3-dione (3d).

1 g (2.96 mmol) of **1** and 0.68 g (2.96 mmol) N-(benzylidene)naphthalen-1-amine benzylidene-1-naphtyl amine **2d** yield 0.96 g (70 %) of **9d** (reaction time and temperature 48h, 65-70 °C), mp 209-210 °C (toluene); ir (KBr): ν=1760, 1710, 1640 (C=O), 1600-1460 cm^{-1} (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1300 (C-N), 1240, 1080 cm^{-1} (C-O-C ν$_{as}$, ν$_s$); ^{1}H nmr (CDCl$_3$): δ=7.94-6.53 (m, 15H, Ar-H), 3.87 (s, 3H, -OCH$_3$), 3.65 (s, 3H, OCH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ=189.51 (t, *j*=4.2 Hz, ArCO), 180.56 (s, C$_3$=O), 175.87 (t, *j*=3.5 Hz, C-5), 166.11 (s, C-10), 165.25 (s, C-17), 160.64 (s, C$_2$=O), 115.61 (s, C-4), 136.34-115.14 (m, aromatic C's), 57.50, 57.30 (two s, *j* = 145.7 Hz, 2 x OCH$_3$).

Anal. Calcd. for C$_{29}$H$_{21}$NO$_5$: C, 75.15; H, 4.57; N, 3.02. Found: C, 75.16; H, 4.31; N, 3.04.

1,2-Bis[4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrole-2,3-dione-1-yl]ethane (3e).

1 g (2.96 mmol) of **1** and 0.35 g (1.48 mmol) N,N'-bis(benzylidene)ethane-1,2-diamine 1,2-dibenzylidene ethylenediamine 2e yield 1.66 g (80 %) of **9e** (reaction time and temperature 96h, 60 °C), mp 148-150 °C (chloroform/n-hexane); ir (KBr): ν=1750, 1720, 1700, 1650, 1640 (C=O groups), 1600-1480 (C⋯C and C⋯N, aromatic rings), 1370 (O-CH$_3$), 1320 (C-N), 1250, 1040 cm^{-1} (C-O-C ν$_{as}$, ν$_s$); ^{1}H nmr (CDCl$_3$): δ=7.75-6.55 (m, 16H, Ar-H), 3.80-3.77 (12H, 4 x OCH$_3$), 3.70-3.55 (4H, NCH$_2$CH$_2$N) ppm; ^{13}C nmr (CDCl$_3$): δ = 188.67 (t, *j*=3.8 Hz, 2 x ArCO), 180.62 (s, C-3 and C-3'), 175.03 (t, *j*=4.4 Hz, C-5 and C-5'), 165.98 (d, C-10 and C-10'), 165.06 (s, C-17 and C-17'), 160.92 (s, C-2 and C-2'), 120.63 (s, C-4 and C-4'), 134.02-115.00 (m, aromatic C's), 57.44, 57.17 (two d, *j* = 145.7 Hz, 4 x OCH$_3$), 41.77 (s, -CH$_2$CH$_2$-).

Anal. Calcd. for C$_{40}$H$_{32}$N$_2$O$_{10}$: C, 68.57; H, 4.60; N, 4.00. Found: C, 68.27; H, 4.45; N, 4.21.

1,4-Bis[4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrole-2,3-dione-1-yl]benzene (3f).

1 g (2.96 mmol) of **1** and 0.42 g (1.48 mmol) N,N'-bis(benzylidene)benzene-1,4-diamine **2f** yield 1.77 g (80 %) of **9f** (reaction time and temperature 96 h, 60 °C), mp 152 °C (chloroform/n-hexane); ir (KBr): ν=1770, 1720, 1700, 1650, 1640 (C=O groups), 1600-1480 (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1310 (C-N), 1250, 1050 cm^{-1} (C-O-C ν$_{as}$, ν$_s$); ^{1}H nmr (CDCl$_3$): δ=8.01-6.60 (m, 20H, Ar-H), 3.83-3.62 (b, 12H, 4 x OCH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ=189.39 (t, *j*=4.2 Hz, 2 x ArCO), 180.34 (s, C-3 and C-3'), 173.42 (t, *j*=4.5 Hz, C-5 and C-5'), 166.47 (d, C-10 and C-10'), 165.39 (s, C-17 and C-17'), 160.11 (s, C-2 and C-2'), 120.77 (s, C-4 and C-4'), 135.05-115.05 (m, aromatic C's), 57.48, 57.20 (two d, *j* = 145.7 Hz, 4xOCH$_3$).

Anal. Calcd. for C$_{44}$H$_{32}$N$_2$O$_{10}$: C, 70.58; H, 4.31; N, 3.74. Found: C, 70.31; H, 4.58; N, 4.01.

Thermolysis of the 2,3-Dihydro-1H-pyrole-2,3-diones 3a-d and Synthesis of the 1H-Quinolin-4-ones (5a-d).

General Procedures.

Approximately 10 min. heating on an oil-bath of 2,3-dihydro-1H-pyrole-2,3-diones **3a-d** (1 g, equivalent mol) at 240-

250 °C led to a crude product, which was treated with ether and recrystallized from *n*-butanol and left to dry on P_2O_5 to give **5a-d** (40-52 %).

3-(4-methoxybenzoyl)-2-(4-methoxyphenyl)quinolin-4(1*H*)-one (**5a**).

This compound was obtained by the general procedure as white solid, mp 262 °C, yield 0.42 g (45%); ir (KBr): ν=3360 (b, N-H), 1670, 1630 (C=O), 1600-1450 (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1300 cm^{-1} (C-N); ^{1}H nmr (DMSO-d$_6$): δ = 12.01 (br s, 1H, NH), 8.14-6.94 (m, 12H, Ar-H), 3.81, 3.76 (6H, 2 x OCH$_3$); ^{13}C nmr (DMSO-d$_6$): δ=195.96 (t, *j*=3.8 Hz, ArCO), 176.84 (d, *j*=2 Hz, C-4), 164.83 (s, C-15), 162.31 (s, C-22), 150.47 (t, *j*=4.1 Hz, C-2), 141.74 (s, C-8a), 127.71 (s, C-4a), 133.96-115.71 (m, aromatic C's), 115.60 (s, C-3), 57.26, 57.10 (s, *j*=145.7 Hz, 2 x OCH$_3$).

Anal. Calcd. for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 74.63; H, 4.97; N, 3.48.

3-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-8-methylquinolin-4(1*H*)-one (**5b**).

This compound was obtained by the general procedure as white solid, mp 233 °C, yield 0.49 g (52%); ir (KBr): ν=3350 (b, N-H), 1680, 1635 (C=O), 1600-1450 (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1300 cm^{-1} (C-N); ^{1}H nmr (CDCl$_3$): δ=8.56-6.62 (m, 11H, Ar-H), 3.80, 3.67 (6H, 2 x OCH$_3$), 2.47 (s, 3H, CH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ = 196.17 (t, *j*=4 Hz, ArCO), 178.38 (d, *j*=2.1 Hz, C-4), 165.42 (s, C-15), 163.06 (s, C-22), 150.49 (t, *j*=3.6 Hz, C-2), 140.06 (s, C-8a), 127.22 (s, C-4a), 135.22-116.36 (m, aromatic C's), 115.62 (s, C-3), 57.36, 57.22 (s, *j*=145 Hz, 2 x OCH$_3$), 18.64 (s, CH$_3$).

Anal. Calcd. for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 74.93; H, 5.29; N, 3.50.

3-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-6-methylquinolin-4(1*H*)-one (**5c**).

This compound was obtained by the general procedure as light yellow solid, mp 141 °C, yield 0.37 g (40%); ir (KBr): ν=3350 (b, N-H), 1680, 1635 (C=O), 1600-1460 (C⋯C and C⋯N, aromatic rings), 1360 (O-CH$_3$), 1300 cm^{-1} (C-N); ^{1}H nmr (CDCl$_3$): δ=11.62 (br s, 1H, NH), 7.68-6.38 (m, 11H, Ar-H), 3.74, 3.46 (m, 6H, 2 x OCH$_3$), 2.30 (s, 3H, CH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ = 197.34 (t, *j*=4.2 Hz, ArCO), 178.08 (d, C-4), 165.32 (s, C-15), 162.58 (s, C-22), 151.55 (t, *j*=3.5 Hz, C-2), 140.15 (s, C-8a), 127.75 (s, C-4a), 135.53-115.67 (m, aromatic C's), 115.50 (s, C-3), 57.31, 56.88 (two s, 2 x OCH$_3$), 23.08 (s, CH$_3$).

Anal. Calcd. for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 75.04; H, 5.36; N, 3.49.

3-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)benzo[*h*]quinolin-4(1*H*)-one (**5d**).

This compound was obtained by the general procedure as white solid, mp 141 °C, yield 0.44 g (47%); ir (KBr): ν=3300 (b, N-H), 1670, 1630 (C=O), 1600-1450 (C⋯C and C⋯N, aromatic rings), 1350 (O-CH$_3$), 1300 cm^{-1} (C-N); ^{1}H nmr (CDCl$_3$): δ=10.51 (br s, 1H, NH), 8.58-6.46 (m, 14H, Ar-H), 3.76, 3.35 (two s, 6H, 2 x OCH$_3$) ppm; ^{13}C nmr (CDCl$_3$): δ=196.20 (t, *j*=3.8 Hz, ArCO), 177.92 (d, C-4), 165.31 (s, C-15), 162.53 (s, C-22), 150.42 (t, *j*=3.6 Hz, C-2), 138.83 (s, C-8a), 127.70 (s, C-4a), 136.97-115.72 (m, aromatic C's), 115.46 (s, C-3), 57.30, 56.77 (two s, 2 x OCH$_3$).

Anal. Calcd. for $C_{28}H_{21}NO_4$: C, 77.23; H, 4.86; N, 3.22. Found: C, 76.98; H, 4.73; N, 3.20.

REFERENCES AND NOTES

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　[1a]　G. Kollenz, W. Ott, E. Ziegler, K. Peters, H.G. von Schnering, H. Quast, *Liebigs Ann. Chem.*, 1801 (1980); [b] G. Kollenz, W. Ott, E. Ziegler, K. Peters, H.G. Schnering, V. Formacek, H. Quast, *Liebigs Ann. Chem*., 1137 (1984).
　[2a]　K. Peters, G. Kollenz, *Chem . Ber*., **114,** 1206 (1981); [b] G. Kollenz, G. Penn, Dollenz, Y. Akçamur, K. Peters, E-M. Peters, and H. G. von Schnering, *Chem. Ber,* **117**, 1299 (1984); [c] H. A. El-Nabi, Abd, G. Kollenz, *Monatsh Chem.*, **128,** 381 (1997).
　[3a]　G. Kollenz, G. Penn, W. Ott, K. Peters, E-M. Peters and H.G. von Schnering, *Chem. Ber*., **117**, 1310 (1984); [b] W. Heilmayer, C. O. Kappe, H. Sterk, G. Kollenz, K. Peters, E- M. Peters, H.G. von Schnering and L. Walz, *Chem. Ber,* **126**, 2061 (1993).
　[4]　G. Kollenz, G. Penn, W. Ott, K. Peters, E-M. Peters and H.G. von Schnering, *Heterocycles*, **26**, 625 (1987).
　[5]　E. Terpetsching, G. Penn, G. Kollenz, K. Peters, E-M. Peters and H.G. von Schnering, *Tetrahedron,* **47**, 3045 (1991).
　[6a]　W. Ott, *Synthesis*, 478 (1976); [b] W. Ott, E. Terpetsching, H. Sterk and G. Kollenz, *Synthesis,* 176 (1987).
　[7]　G. Kollenz, E. Terpetsching, H. Sterk, K. Peters and E-M. Peters, *Tetrahedron*, **55**, 2973 (1999).
　[8a]　G. Kollenz, H. Sterk and G. Hutter, *J. Org. Chem.*, **56**, 235 (1991); [b] W. Heilmayer, H. Sterk and G. Kollenz, *Tetrahedron*, **54**, 8025 (1998).
　[9a]　W.M. F. Fabian, *Acta Chim. Hung*., 129, 347 (1992); [b] W. M. F. Fabian and G. Kollenz, *J. Chem. Soc. Perkin Trans 2*, 515 (1995); [c] W. M. F. Fabian and G. Kollenz, *J. Org. Chem.* **62**, 8497 (1997); [d] K. Bowden, W. M. F. Fabian and G. Kollenz, *J. Chem. Soc., Perkin Trans. 2*, 547 (1997); [e] W. M. F. Fabian and G. Kollenz, *J. Mol. Struct. (theochem)*, **187**, 199 (1989).
　[10]　[http://www-ang.kfunigraz.ac.at/fabian/echet98/index.htm].
　[11a]　C. O. Kappe, G. Kollenz and C. Wentrup, *J. Chem. Soc., Chem. Commun*., 485 (1992); [b] C. O. Kappe, G. Kollenz, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun.,* 487 (1992); [c] C. O. Kappe, G. Kollenz, R. K. P. Netsch, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun*., 488 (1992); [d] B. Fullon, H. A. A. El-Nabi, G. Kollenz and C. Wentrup, *Tetrahedron Lett.,* 36, 6547 (1995); [e] B. E. Fullon and C. Wentrup, *J. Org. Chem.,* **61**, 1363 (1996); [f] V. V. R. Rao, B. E. Fulloon, P. V. Bernhardt, R. Koch and C. Wentrup, *J. Org. Chem.,* **63**, 5779 (1998); [g] R. V. V. Rao and C. Wentrup, *J. Chem. Soc., Perkin Trans. 1*, 2583 (1998); [h] C. Wentrup, V. V. Rammana Rao, W. Frank, B. E. Fulloon, D. W. j. Moloney and T. Mosandl, *J. Org. Chem*., **64**, 3608 (1999).
　[12]　D. M. Birney, X. Xu, S. Ham, and X. Huang, *J. Org. Chem*., **62**, 7114 (1997).
　[13a]　C. Wentrup, W. Heilmayer and G. Kollenz, *Synthesis*, 1219 (1994); [b] T. T. Tidwell, Ketenes. John Wiley and Sons. New York. p 665 (1995); [c] E. Sarıpınar, İ. Ö. İlhan and Y. Akcamur, *Heterocycles*, **57**, 1445 (2002).
　[14]　J. J. P. Stewart, *J. Comp. Chem*., **10**, 209 (1989).
　[15]　PC Spartan Pro, Wavefunction, Inc.; Irvine, California, (1999).

[16a]   P. E. Wagenseller, D. M. Birney, and D. Roy, *J. Org. Chem.*, **60**, 2853 (1995); [b] D. M. Birney, *J. Org. Chem.*, **61**, 243 (1996); [c] S. Ham, and D. M. Birney, *Tetrahedron Lett.*, **38**, 5925 (1997); [d] W. M. F. Fabian, V. A. Bakulev, and C. O. Kappe, *J. Org. Chem.*, **63**, 5801 (1998); [e] D. M. Birney, X. Xu, and S. Ham, Angew. *Chem. Int. Ed.*, **38**, 189 (1999); [f] W. Shumway, S. Ham, J. Moer, B. R. Whittlesey, and D M. Birney, *J. Org. Chem.*, **65**, 7731 (2000); [g] D. M. Birney, *J. Am. Chem. Soc.*, **122**, 10917 (2000); [h] W.M. F. Fabian, C. O. Kappe, and V. A. Bakulev, *J. Org. Chem.*, **65**, 47 (2000); [i] W. W. Shumway, N. K. Dalley, and D. M. Birney, *J. Org. Chem.*, **66**, 5832 (2001); [j] C. Zhou, and D. M. Birney, *J. Am. Chem. Soc.,* 124, 5231 (2002).

[17a]   Birney, D. M.; S. Ham, G.R. Unruh, *J. Am. Chem. Soc.,* 119, 4509 (1997); [b] E. Sarıpınar, Y. Güzel, Z. Önal, İ. Ö. İlhan and Y. Akçamur, *J. Chem. Soc. Pak.,* **22**, 308 (2000).

[18a]   M. T. Nguyen, T. Ha and R. A. M. O'. Ferrall*, J. Org, Chem.,*

55, 3251 (1990); [b] R. L. Toung and C. Wentrup, *Tetrahedron Lett.*, **48**, 7641 (1992); [c] M. Birney, and P. E. Wagenseller, *J. Am. Chem. Soc.*, **116**, 6262 (1994); [d] D. M. Birney, *J. Org. Chem.*, **59**, 2557 (1994); [e] M. W. Wong and C. Wentrup, *J. Org. Chem.*, **59**, 5279 (1994); [f] R. Janoschek, W. M. F. Fabian, G. Kollenz and C. O. Kappe, *J. Comput. Chem.*, **15**, 132 (1994); [g] H. Bibas, M. W. Wong, and C. Wentrup, *J. Am. Chem., Soc.*, **117**, 9582 (1995); [h] C. O. Kappe, M. W. Wong, and C. Wentrup, *J. Org. Chem.,* **60**, 1686 (1995).

[19a]   A. A. Al-Saadi and H. M. Badawi, *J. Mol. Struct. (theochem)*, **582**, 11 (2002); [b]   H. M. Badawi, A.Al-Saadi and W. Förner, *Spectrochimica Acta Part A.* **58**, 33 (2002).

[20]   S. Ham, and D. M. Birney*, J. Org. Chem.*, **61**, 3962 (1996).

[21a]   R. A. Olofson, D.S. Morrison and A. Banerji, *J. Org. Chem.*, **49**, 2653 (1984); [b] W.-J. Ding and D.-C. Fang*, J. Mol. Struct. (theochem),* **468**, 119 (1999); [c] M. Alajarin, P. Sanchez-Andrada, F. P. Cossio, A. Arreta, and B. Leceai, *J. Org. Chem.,* **66**, 8470 (2001).