4-(-4-methoxybenzoyl)-5-(-4-methoxyphenyl)-2,3-dihydro-2,3-furandione, its Synthesis, Thermolysis and Diels-Alder Reactions with Schiff Bases: Experimental Data and Calculations

EMIN SARIPINAR*, YAHYA GÜZEL, ZÜLBIYE ÖNAL,
ILHAN ÖZER ILHAN AND YUNUS AKÇAMUR.
Department of Chemistry, Arts and Sciences Faculty,
Erciyes University 38039 Kayseri-TURKEY

(Received 15th June, 1999, revised 3rd July, 2000)

Summary: *p,p'*-Dimethoxydibenzoylmethane **1** combines with oxalyl chloride **2** to yield novel furan-2,3-dione **3**. Thermal transformation is supposed to occur by the ring opening of the **3** followed by the intermediate *p,p'*-dimethoxydibenzoylketene **IN1** cyclization resulting in the γ-pyrone **IN3**. The reaction of **3** with Schiff bases under thermolysis conditions leads to 1,3 oxazinones **5,6**. The reaction pathways include formal [4+2] cycloaddition processes, obviously. Electronic structures of reactants, transition states, intermediates and final products of the reaction are calculated by the AM1 method. Transition states was further confirmed by vibrational analysis (computation of force constants analytically) and characterised by the corresponding imaginary vibration modes and frequencies.

Introduction

Recently, reactions of cyclic oxalyl compounds have been reported to give substituted heterocyclic compounds [1]. The 4-arylcarbonyl-5-aryl-2,3-dioxo-2,3-dihydrofuranes were obtained starting from 1-3-dicarbonyl compounds with oxalyl halides [1d]. The reactions of substituted 2,3-furandiones with various dienophiles [2] or nucleophiles [3] in different solvents and at various temperatures have been studied, too. A convenient method for the synthesis, and the mechanism of reactions and calculations on the interaction of 2,3-dioxo-2,3-dihydrofuranes with several semicarbazones, ureas and their thio-anologs have been reported recently [4]. The last few years have witnessed the development of a powerful new methodology for the synthesis of substituted aromatic

---

*To whom all correspondence should be addressed.

systems and heterocyclic compounds, proceeding through putative ketene intermediates [5]. Thermal decomposition of the 2,3-dioxo-2,3-dihydrofurans leads to the formation of reactive α-oxoketenes (acylketenes) intermediates [6]. These ketenes are particularly reactive and cannot normally be isolated under usual reaction conditions. Several examples have been detected by low-temperature IR Spectroscopy at 77°K or in Ar matrix at ca. 12°K. Sterically hindered dipivaloylketene is reported to be stable in CCl_4, at 20°C for several months [7]. α-Oxoketenes are highly reactive molecules which can be trapped by nucleophiles to give β-ketocarbocylic acid derivatives [8] or alternatively undergo cycloaddition reactions [9]. In the absence of nucleophiles or suitable dienophiles dimerization of α-oxoketenes takes place as a special case of [4+2] cyloadditions [9b,10]. This interest in ketene chemistry is also demonstrated by recent efforts to extend the MM2 and MM3 force fields to these types of molecules [11]. The general reactivity of ketenes has been reviewed recently, and a few *ab initio* and semiempirical (AM1 and PM3) calculations on a series of differently substituted *α*-oxoketenes, especially substituent effects on their stability as well as reactivity, have been published [12].

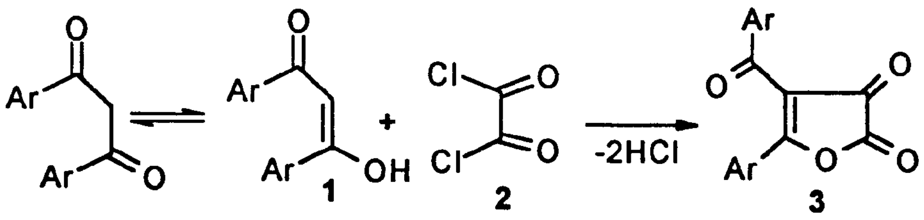
In this paper, the synthesis and characterization of the compound **3** obtained from the reaction between *p,p'*-dimethoxydibenzoylmethane **1** and oxalyl chloride **2** are presented, our findings during the course of synthesizing **3**, too, as well as further investigations of its thermal decomposition and reactivity with *Schiff* bases at high temperatures.

To study the mechanism of the reaction all calculations were carried out by means of semiempirical AM1 methods [13] with full geometry optimisation for reactants, products and intermediates. Transition structures, located with saddle calculations, were refined by minimizing the scalar gradient of energy with respect to the geometry and characterized as saddle points by diagonalizing the hessian (force constant) matrix and establishing the presence of one and only one negative force constant. The AM1 calculations were carried out with the help of MOPAC 7 program package [14]. Model compounds with aryl and phenyl groups substituted by hydrogen atoms were used in the theoretical calculations.

Results and Discussion

Reaction of the 1,3-dicarbonyl compound (1,3-di(*4*-methoxyphenyl)-1,3-propanedione) **1** with oxalyl chloride **2** yields namely 4-(*4*-methoxybenzoyl)-5-(*4*-methoxyphenyl)-2,3-dihydro-2,3-furandione **3**. The structure of **3** is confirmed by analytical, IR and NMR spectroscopic data which agree with those found for the similar substituted 2,3-dihydro-2,3-furandione [1] (see Scheme 1). The formation of **3** is supported by the results of spectroscopic measurements in particular in presence of three carbonyl bonds (IR: 1810, 1720, 1645 cm^{-1}; ^{13}C-NMR: 187.81, 176.46, 154.53 ppm). The results of measurements are given in the section of experimental tail. To clarify some steps of 2,3-furandione **3** reactions with *Schiff* base and thermolysis, theoretical calculations have been done for initials, transition states, intermediates and products of the reactions. The results of the calculations (the formation entalpies ΔH_f, in kcal mol^{-1}; dipole moments μ, in debye; the highest molecular orbital energies $-E_{HOMO}$, in eV and imaginary frequencies, $\bar{\nu}$ in icm^{-1}) are given in table 1.

Thermolysis of 3 (ΔH_f = -99.32 kcal mol^{-1}) at 170-175°C leads to the formation of IN1 (ΔH_f = -



Ar =p-CH_3O-C_6H_4-

Scheme 1

Table 1: Calculated heat of formation (Δhf, kcal mol^{-1}), dipole moments, (μ, debye), HOMO orbital energies ($-E_{mHOMO}$, eV) and imaginary frequencies ($\bar{\nu}$, icm^{-1}) for the transition states (TS), intermediates (IN) and products (3-5) of cycloaddition pathways (a-e).

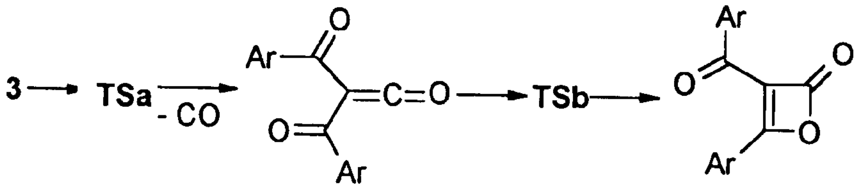
Compounds	ΔH_f kcal mol^{-1}	μ debye	E_{HOMO}, ev	‾ icm^{-1}
3	-99.32	1.28	11.13	-
Tsa	-71.88	2.54	10.15	402.18
IN1	-72.88	2.92	10.56	-
CO	-5.68	0.06	13.31	
TSb	-29.42	0.57	10.40	572.44
IN2	-31.22	1.15	10.80	
TSc	-131.84	4.31	9.75	352.53
IN3	-162.58	3.43	11.08	
TSd	-103.97	6.75	10.08	658.69
4	-99.65	2.41	10.67	
CO_2	-79.83	0.00	13.21	
S1	18.69	1.87	10.55	
TSe	-44.79	5.10	9.61	422.55
5	-85.33	4.54	10.24	

Table 2: Selected structural data for transition states (TSa and TSb) and intermediates (IN1 and IN2)

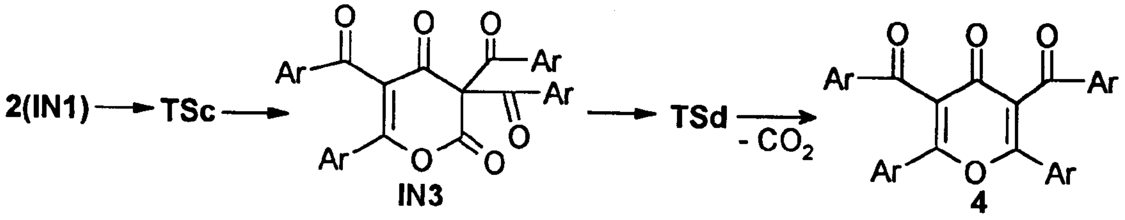
Bond lengths (Å)	3	TSa	IN1+CO	Bond lengths	TSb	IN2
O1-C2	1.4266	**2.1666**	3.0800	C3-C4	1.4537	1.4941
C2-C3	1.5312	**1.8791**	3.1700	C4-C5	1.4044	1.3799
C3-C4	1.4747	1.3675	1.3358	C5-O1	1.3421	1.4013
C4-C5	1.3709	1.4437	1.4634	C6-C4	1.4325	1.4373
C5-O1	1.3832	1.2644	1.2321	O8-C3	1.2357	1.2344
C6-C4	1.4543	1.4614	1.4674	C7-C6	1.1887	1.2018
C7-C6	1.2331	1.2339	1.2331	C3-O1	**1.6772**	1.4842
O8-C3	1.2200	1.1999	1.1786			
O9-C2	1.2118	1.1639	1.1698			
C3-O1	2.3097	**2.8753**	2.8859			
Bond angles				**Bond angles**		
O1-C2-C3	107.42	103.97	109.72	O1-C5-C4	100.19	97.15
C4-C3-C2	103.35	90.11	55.02	C5-C4-C3	91.16	86.81
O1-C5-C4	113.49	123.56	122.85	C6-C4-C3	131.39	138.82
C6-C4-C3	108.44	123.11	120.63	O7-C6-C4	123.38	123.87
O7-C6-C4	123.62	118.07	118.41	08-C3-C4	**160.03**	149.79
					Torsion angle	
08-C3-C4	131.33	**150.73**	179.65		C6-C4-C3-O1	179.99
O9-C2-C3	137.21	172.85	137.21		O7-C6-C4-C3	179.99
C5-O1-C2	107.49	99.52	124.82		O8-C3-C4-O1	-179.98
O9-C2-01	115.18	96.99	113.07			
Torsionangle						
O1-C2-C3-C4	-0.02	-0.01				
C2-C3-C4-C5	0.04	0.01	-			
C6-C4-C3-C2	179.99	-179.99	-			
O7-C6-C4-C3	179.97	-179.98	-			
O8-C3-C4-C5-	179.99	179.99	-			
O9-C2-C3-C4	179.98	179.90	-			
O1-C5-C4-C3	-	-	178.88			
O8-C3-C4-C5	-	-	-0.01			
C6-C4-C5-O1	-	-	-1.27			
O7-C6-C4-C5	-	-	-179.84			

72.88 kcal mol^{-1}) as an intermediate. As seen from table 1 the molecule CO disconnection is realized through a transitional state **TSa** (Ar = H) with the value of ΔH_f equal to -71.88 kcal mol^{-1} The characteristic structural variations for the reacting molecules are given in the table 2. The TSa is formed when the atom C2 moves to the distance of 1.8791Å and 2.1666Å from the atoms C3 and O1, respectively. The difference in the energy of the **3** and the sum of the **IN1** and **CO** is equal to 20.76 kcal mol^{-1}. At a separation of 3.0800Å for O1-C2 and 3.1700Å for C2-C3 bonds, ΔH_f of the molecular complex (**IN1**+CO) is 0.08 kcal mol^{-1} above that of the sum of the separated molecules. Molecular orbital calculated charge densities of α-oxoketene **IN1** show the highest positive charge on C3 (q=0.39 eV), so that electrophilic attack is expected to occur at C3. The molecular structure of **IN1** has now been refined and distinguished by short C3-C4 and C3-O8 bond lengths of 1.3358Å and 1.1786Å, respectively, involving the sp-hybridized carbon. The transition for molecule **IN1** causes a bond angle increase for O8-C3-C4 equal to 179.65, and the atom C3 conversion from sp^2-hybridized state to the linear sp-hybridized state. Molecule obtained **IN1** is planar, and the torsion angle O8-C3-C4-C5 is equal to -0.01. Ring-closure of the α-oxoketen **IN1** to cyclic oxetone **IN2** (see scheme II) is computed to be higher in energy than **IN1**. The cyclization of **IN1** takes place through the transition structure **TSb**. At this point, the distance of C3-O1, which can be considered as the reaction coordinate, reaches 1.6772Å This is very close to the value 1.4842Å in the ring **IN2** (see table 2). Our calculations show that the formation energy of **IN1** lies -41.66 kcal mol^{-1} below that of its cyclic isomer **IN2** and it undergoes ring-closure with an energy barrier of -43.46 kcal mol^{-1}. The oxetone **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**.

In the absence of nucleophiles or suitable dienophiles, dimerization of acylketenes takes place as a special case of [4+2] cycloadditions [15]. Generally, in these reactions the acylketene **IN1**, dimerized to the 3-acyl-α-pyrone derivative **IN3** under ordinary reaction conditions in a process involving a [4+2] cycloaddition of one ketene molecule to the C=C double bond of another, gives pyranone **4** as final stable compound on CO_2 extrusion (see Scheme 3). The basic structure of **4** is strongly supported by its ^{13}C-NMR spectrum (^{13}C-NMR: 192.18, 176.58, 164.69, 123.76 ppm). The dimerization proceeds via a single transition state by approach of the two acylketene molecules being occured rather unsymmetrically. The formation of the O1-C2 bond is much more pronounced than is the formation of the C3-C4 bond. Difference in the bond lengths of forming σ-bond at the transition state is enormously big, about 2.0114Å. The saddle point TSc is located at a O1-C2 length of 1.7209Å and a C3-C4 length of 3.7323Å; thus the O1-C2 bond has been formed to a greater extent than C3-C4 bond. This shows that the reaction pathway is asynchronous and the formation of the O1-C2 and C3-C4 is not simultaneous. The Table 1 indicates that intermediate **IN3** is located below the level of the reactants. The energies of **IN1** and **IN3** were calculated to be 2.(-72.88 kcal mol^{-1}) and -162.58 kcal mol^{-1}, respectively. The energy difference between 2(**IN1**) and **IN3** is -16.82 kcal mol^{-1}, this



Scheme 2



Scheme 3

step is exothermic. At the transition state TSc, molecular planes of the two acylketene molecules approach at an angle of 70.02 and the six heavy atoms are not coplanar. The next step of the reaction is the molecule CO_2 disconnection. Reorganisation of bonds during the formation of 4 can be traced from bond distances given in Table 3. When the reaction proceeds towards the saddle point TSd, C6-O1 and C3-C2 bond lengths increase while that of C6-O13 decreases. The transition state TSd is located at O1-C6 length of 1.8689Å and a C2-C3 length of 1.7106Å. C6-O13 distance at TSd is 1.4323Å. The bond angles, O14-C2-O1, for TSc, IN3, TSd and 4 are 100.79, 112.03, 131.59 and 180.00, respectively.

The reaction of **3** with benzylidenaniline **S1** and N,N'-dibenzyliden-*p*-phenylendiamine **S2** under thermolysis (170-175°C) conditions leads via the diacylketene **IN1** to the formation of the Diels-Alder adducts; the 1,3-oxazinone **5** and bis-1,3-oxazinone **6**, respectively (see Scheme 4). From spectroscopic data (see experimental tail) in particular from the

Table 3: Selected structural data for transition states(TSc, TSd and TSe), intermediate (IN3) and final products (4 and 5).

Bond lengths (Å)	TSc	In3	TSd	4	Bond lengths	TSe	5
O1-C2	**1.7209**	1.3949	**1.2785**	1.2103	O1-C2	**2.6230**	1.4499
C2-C3	**1.3711**	1.5048	**1.7106**	3.8307	C2-N3	1.2736	1.4316
C3-C4	**3.7323**	1.5343	1.5446	1.4707	N3-C4	**1.9899**	1.3897
C4-C5	1.3486	1.4670	1.4489	1.4707	C4-C5	1.3664	1.4779
C5-C6	1.4367	1.3543	1.3892	1.3564	C5-C6	1.4472	1.3580
C6-O1	**1.2667**	1.3639	1.8689	3.1119	C6-O1	1.2400	1.3579
C7-C5	1.4738	1.4746	1.4568	1.4728	C7-C5	1.4638	1.4648
O8-C7	1.2310	1.2283	1.2303	1.2332	O8-C7	1.2347	1.2348
O9-C4	1.1719	1.2277	1.2256	1.2383	O9-C4	1.1960	1.2444
C10-C3	1.4594	1.5311	1.4981	1.4728	H10-N3	0.9944	0.9923
O11-C10	1.2351	1.2239	1.2294	1.2332	**Bond angles**		
C12-C3	1.4457	1.5314	1.4361	1.3564	O1-C2-N3	84.32	115.89
O13-C12	1.2451	1.2244	1.3251	1.3727	C2-N3-C4	125.48	122.33
C6-O13	**2.3895**	3.4995	**1.4323**	1.3727	N3-C4-C5	107.14	115.84
C6-O11	5.5835	5.2023	4.6872	4.9980	C4-C5-C6	127.45	119.61
C2-O14	1.2029	1.2236	1.2136	1.2103	C4-C5-C7	115.37	117.89
Bond angles					O8-C7-C5	123.39	122.73
O1-C2-C3	108.06	120.16	110.72		O9-C4-C5	**151.19**	124.30
C2-C3-C4	50.29	111.49	101.05		H10-N3-C2	120.36	117.92
C3-C4-C5	82.50	114.10	110.09	113.58	**Torsion angle**		
C4-C5-C6	124.04	119.99	116.94	120.77	O1-C2-N3-C4	**53.11**	**22.54**
C4-C5-C7	118.54	119.66	122.67	118.20	C2-N3-C4-C5	-78.66	-7.17
O8-C7-C5	123.25	123.25	124.78	122.67	N3-C2-O1-C6	-12.73	-24.86
O9-C4-C5	177.45	115.16	129.32	123.21	N3-C4-C5-C6	31.31	-6.26
C10-C3-C2	117.26	108.29	117.18		C2-N3-C4-O9	104.13	175.20
O11-C10-C3	123.11	122.09	121.42	122.67	C6-C5-C4-O9	-154.36	171.25
C12-C3-C2	124.43	110.96	100.34		H10-N3-C2-O1	-121.63	-160.46
O13-C12-C3	124.62	122.54	117.69	123.76	C7-C5-C4-O9	23.89	-6.32
O14-C2-C3	151.15	127.81	116.61				
C4-C3-C12	120.76						
C10-C3-C12				121.03			
Torsion angle							
O1-C2-C3-C4	75.74	30.40	70.02				
C2-C3-C4-C5	-94.50	36.14	-60.97				
C3-C4-C5-C6	34.96	23.30	-4.04	-0.04			
C3-C4-C5-C7	-144.20	-157.01	169.37	179.96			
C4-C5-C7-O8	-3.07	16.18	10.08	-179.99			
O9-C4-C3-C2	85.96	143.81	117.32				
C10-C3-C2-O1	-163.06	150.57	-168.71				
O11-C10-C3-C2	-179.98	146.35	111.60				
C12-C3-C2-O1	15.60	-89.22	-44.94				
O13-C12-C3-C2	9.53	24.89	58.78				
O14-C2-C3-O1	178.21	179.10	-177.26				
C5-C4-C3-C12				0.04			
C4-C3-C12-O13				0.01			
O11-C10-C3-C12				-0.01			
C10-C3-C12-O13				-179.99			

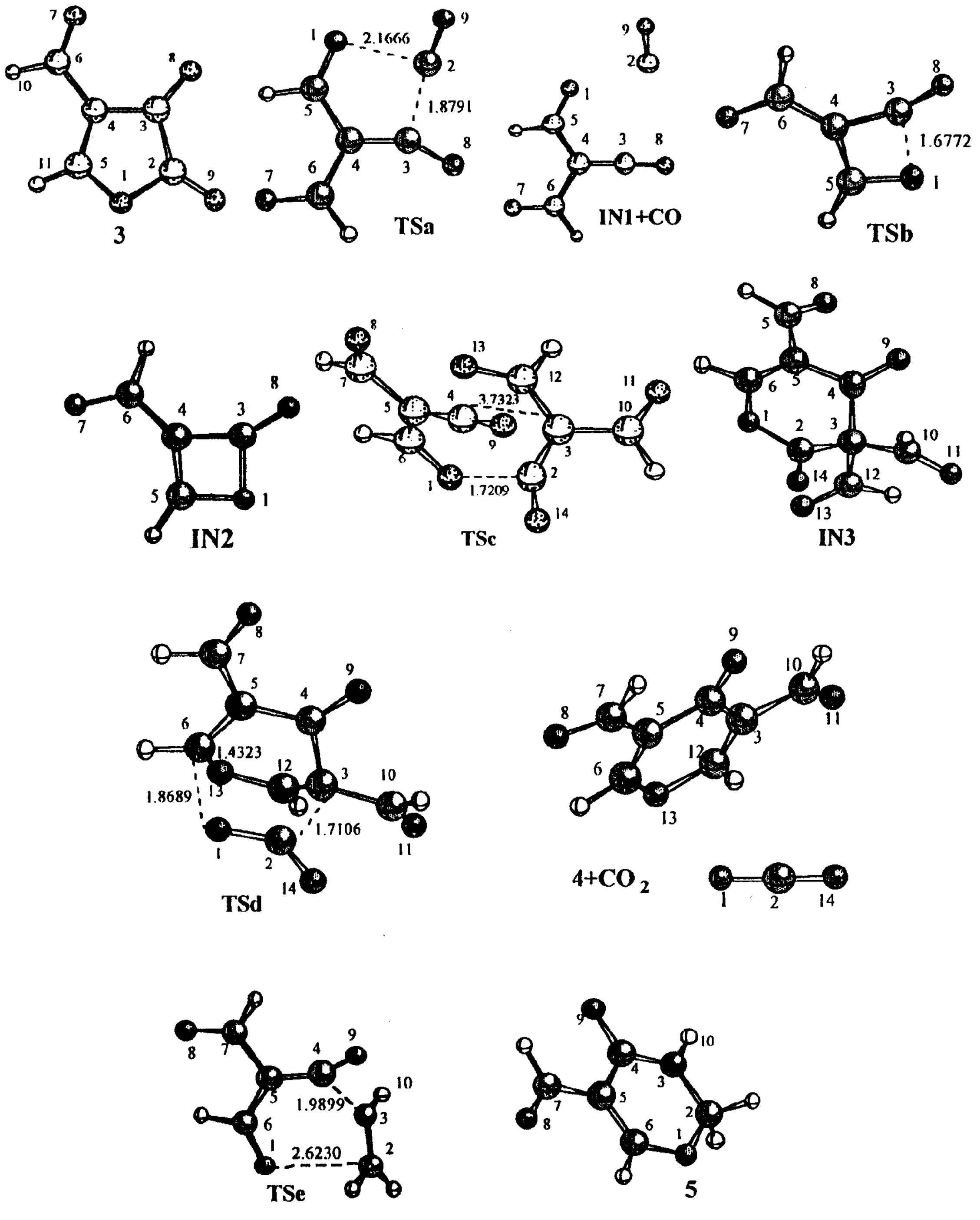
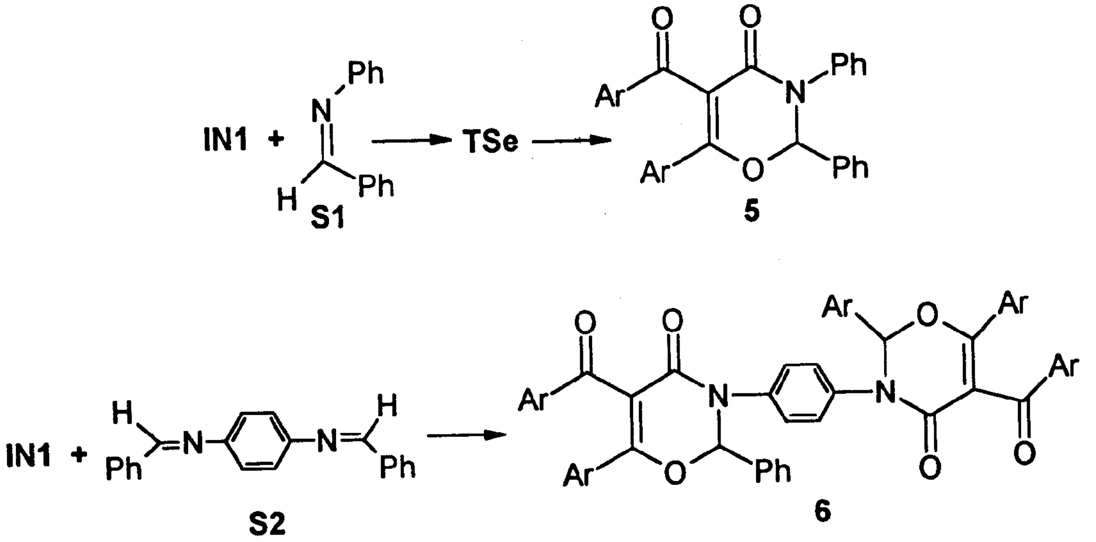


Fig. 1: Atom-numbering scheme and structures of transition states (TSa, TSb, TSc, TSd and TSe), intermediate (IN1, IN2 and IN3) and products (3,4 and 5) (for structural data see table1-3).



Scheme 4

^{1}H-NMR spectrum of 5 and 6, important structural information can be obtained. Chemical shift values of 6.82 and 6.47 ppm for the protons at C2 are in good accordance with those of very close anologs having identical 2H-1,3-oxazin-4-one ring systems [6c, 7b, 16]. The reaction equations are shown in scheme 4. The atomic numbering of transition state TSe and product 5 are given in Figure 1. The calculated equilibrim structures of TSe and 5 are given in Table 3, from which it can be realized that in the TSe the bonds lengths O1-C2 and C4-N3 lengths are 2.6230Å and 1.9899Å, respectively. All said above means that the reaction is an asynchronous concerted reaction at a retro-Diels-Alder reaction with an activation energy of 9.40 kcal mol^{-1}. At the transition state TSe, molecular planes of the two reactants approach at an angle of 53.11 and the six heavy atoms are not coplanar. This situation can be explained by means of electrostatic interaction. The net charges of nitrogen N3 and carbon C2 in methylenimine S1 are -0.23 and -0.12 respectively, while those of the centre carbon C3 and oxygen O1 in α-oxoketen IN1 are 0.39 and -0.29, respectively. Obviously, the approach of N3 to C4 is more favourable than that of O1 to C2.

Experimental

Solvents were dried by refluxing with the appropriate drying agent and distilled before use. Melting points (m.p) were determined on the Electrothermal 9200 apparatus and uncorrected. Elemental analysis was performed with the Carlo Erba Elemental Analyzer, 1108. IR spectra were recorded on a Shimadzu 435 V-04 apparatus, using potassium bromide tablets. The ^{1}H and ^{13}C-NMR spectra were obtained on a Gemini-Varian 200 instrument. The chemical shifts are reported in ppm from tetramethylsilane and given in δ units.

p,p'-*Dimethoxydibenzoylmethane (1):*

To a solution of NaOH (40.0 g) in a mixture of ethyl alcohol (600 ml) and water (600 ml) were added *p*-metoxyacetophenon (85.3 ml) dropwise with stirring at -10°C. *p*-metoxybenzaldehyde (70.0 ml) was poured into the mixture at once and stirred about -10°C for 6 hours and kept in a fridge for a night. The product was filtered from cooled mixture, washed with cold ethyl alcohol solution and dried to yield 118.0g (%77) of pure 1,3-di(4-metoxyphenyl)-2-propen-1-one. To a solution of pure 1,3-di(4-metoxyphenyl)-2-propen-1-one (83.0 g) in carbontetrachloride (1000 ml) was added bromine (50.0 g) dropwise with stirring at -10°C for 1 hour. The residue was filtered and washed in cold and hot alcohols, respectively, and dried to yield 118.0g (%90). To a solution of 2,3-dibromo-1,3-di(4-metoxy phenyl)-1-propanone (60.0 g) in methanol (100 ml) was added NaOCH$_3$, which was formed by dissolving small pieces of natrium (7.0 g) in dry methanol (80 ml), stirred 1 hour at 50-55°C. After the solution being cooled to the room temparature, concentrated HCl was added and the degree of pH was kept around 1. The mixture was kept in a fridge for two hours, filtered, washed with water, crystallised from methanol and dried in order to give of pure *p,p'*-Dimethoxydibenzoylmethane 1 (1,3-di(4-metoxy phenyl)-1,3-propanedione), yield 23.0g (%70), m.p.118°C.

4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl) furan-2,3-dione (3).

3.0 g. (10.6 mmoles) of *p,p'*-Dimethoxydibenzoylmethane **1** was dissolved in 100 ml of dry diethyl ether, 1ml (11.7 mmoles) of oxalylchloride **2** added and the mixture kept at room temperature for 48 hrs. The liquid phase was pipetted from the yellow crystals. It was washed with dry diethyl ether for several times ; yield 2.4 g (%67), m.p. 155°C. IR (KBr): $\bar{\nu}$=1810 cm^{-1} (C2=O); 1720 (C3=O); 1645 (Ar-C=O); 1600 (C=C). ^{1}H-NMR ($CDCl_3$): δ=3.87 (3H, CH_3O); 3.88 (3H, CH_3O); 6.92 (2H, Ar-H); 6.94 (2H, Ar-H); 6.97 (2Ar-H); 7.90 (2H, Ar-H); ^{13}C-NMR ($CDCl_3$): δ=187.81 (C6); 176.46 (C3); 175.84 (C5); 154.53 (C2); 118.2 (C4); 166.62-114.74 (Aromatic C); 56.35 (CH_3O); 56.11 (CH_3O). Found C 67.62; H 4.13. Calc. for $C_{19}H_{14}O_6$: C 67.45; H 4.17.

3,5-Di(4-methoxybenzoyl)-2,6-di(4-methoxyphenyl)-4H-4-pyranone (4).

0.50 g. (1.48 mmoles) of **3** are heated to 170-175°C for 15 minutes. After cooling to room temperature the residue is treated with dry diethyl ether. After suction, the 0.32 g of white solid was obtained and recrystallized from butanol, yield 0.19 g (%45). m.p. 248°C. IR (KBr): $\bar{\nu}$=1660cm^{-1} (C4=O); 1630 (Ar-C=O); 1600 (C=C). ^{1}H-NMR ($CDCl_3$): δ=3.80 (6H, 2CH_3O); 3.84 (6H, 2CH_3O); 6.85-7.96 (m, 16H, Ar-H). ^{13}C-NMR ($CDCl_3$): δ=192.18 (t, j=4.1 Hz, Ar-C7=O); 176.58 (s, C4); 164.69 (t, j=2.6 Hz, C2); 123.76 (s, C3); 114.56-162.55 (Aromatic C); 55.99 (CH_3O); 55:88 (CH_3O). Found: C 73.06, H 5.02. Calc. for $C_{35}H_{28}O_8$: C 72.91; H 4.89.

5-(4-methoxybenzoyl)-6-(4-methoxyphenyl)-2,3-diphenyl-3,4-dihydro-2H-1,3-Oxazin-4-one (5).

0.25 g (0.74 mmoles) **3** and 0.13 (0.74 mmoles) benzylidenaniline **S1** are heated to 170-175°C for 15 minutes without any solvent. After cooling to room temperature, the residue is washed with anhydrous cyclohexan and petroleum benzene for several times, yield 0.24 g (%66). m.p. 125°C. IR (KBr): $\bar{\nu}$=1685 cm^{-1} (C4=O); 1650 (C7=O); 1600 (C=C); 1360 (C-N); 1255 (C-O-C). ^{1}H-NMR: δ=3.76 (6H, 2CH_3O); 6.95 (s, 1H, C2); 6.56-7.99 (m, 18H, Ar-H). ^{13}C-NMR ($CDCl_3$): δ=192.85 (t, j=4.0 Hz, Ar-C7=O); 165.39 (s, C4=O); 164.26 (t, j=2.8 Hz, C6); 162.59-115.34 (Aromatic C); 114.51 (s, C5); 92.40 (d, j=111.4 Hz, C2); 57.46 (CH_3O); 57.29 (CH_3O). Found: C 75.71; H 5.01; N 2.91. Calc.for $C_{31}H_{25}O_5N$: C 75.75; H 5.12; N 2.97.

Bis-[5-(4-methoxybenzoyl)-6-(4-methoxyphenyl)-4-oxo-2-phenyl-2,3-dihydro-4H-1,3-Oxazin-3-YL)]-1,4-phenylene (6).

0.31 g (1.48 mmoles) **3** and 0.13 (0.74 mmoles) N,N'-dibenzyliden-4-phenylendiamine **S2** are heated to 170-175°C for 15 minutes without any solvent. After cooling to room temperature, the residue is washed with anhydrous diethyl ether for several times, yield 0.26 g (%63). m.p. 135 °C. IR (KBr): $\bar{\nu}$=1686 cm^{-1} (C4=O); 1646 (C7=O); 1600 (C=C); 1350 (C-N); 1250 (C-O-C). ^{1}H-NMR ($CDCl_3$): δ=3.66-3.84 (12H, 4CH_3O); 6.97 (s, 2H); 6.74-7.97 (m, 30H, Ar-H). ^{13}C-NMR ($CDCl_3$) : δ=191.16 (C7, C7'); 163.88 (C4, C4'); 162.77 (Ar-C6); 113.67-161.23 (Aromatic C); 112, 89 (s, C5); 89.83 (d, C2, j=108.4 Hz); 56.00 (CH_3O). Found: C 73.89; H 4.88; N 3.04. Calc. for $C_{56}H_{44}O_{10}N_2$: C 74.33; H 4.90; N 3.10.

Conclusion

The following conclusions may be drawn from the above discussions. The reaction between *p,p'*-dimethoxydibenzoylmethane and oxalyl chloride yields the novel furan-2,3-dione compound which passes to reactive *p,p'*-dimethoxydibenzoylketene with the thermal decomposition. At the first stage after diacylketene is formed it gives [4+2] cycloaddition reaction leading to the 3-acyl-α-pyrone derivative **IN3** in the absence of dienophile or nucleophile. At the next stage CO_2 extrusion and γ-pyrone derivative formation takes place. The reaction of furandione with *Schiff* bases under thermolysis conditions afforded the corresponding 1,3-oxazine derivatives and in moderate acceptable yield. AM1 studies indicate that the dimerization of diacylketene and cycloaddition of ketene with *Schiff* bases take place in a concerted but asynchronous manner.

Acknowledgements

The authors wish to express their gratitude to Prof.Dr. G. Kollenz and Dr. Saban Patat for helpful and encouraging discussions. This project was financially supported by the Science and Technical Research Council of Türkiye (TÜBITAK, project no :TBAG-AY/118), Research Center of Erciyes University and Arçelik Company

References

1. (a) E. Ziegler, M. Eder, C. Belegratis and E. Prewedourakis, *Monatsh. Chem.*, **98**, 2249 (1967).
   (b) E. Ziegler, G. Kollenz and H. Igel, *Monatsh. Chem.*, **102**, 1769 (1971).
   (c) G. Kollenz, C.O. Kappe and H.A. el Nabey, *Heterocycles*, **32**(4), 669 (1991).
   (d) R.W. Saalfrank, T. Lutz, B. Hörner, J. Gündel, K. Peters and H.G. von Schnering, *Chem. Ber.*, **124**, 2289 (1991).
2. (a) Y. Akçamur, G. Penn, E.Ziegler, H. Sterk, G. Kollenz, K. Peters and H.G. von Schnering, *Monatsh. Chem.*, **117**, 231 (1986).
   (b) Y. Akçamur and G. Kollenz, *Org. Prep. Proc. Int.*, **19**, 52 (1987).
   (c) E. Terpetschnig, W. Ott, G. Kollenz, K. Peters and H.G. von Schnering, *Monatsh. Chem.*, **119**, 367 (1988).
   (d) G. Kollenz, G. Penn, G. Dolenz, Y. Akçamur, K. Peters, E.M. Peters and H.G. von Schnering, *Chem. Ber.*, **117**, 1299 (1984).
   (e) G. Kollenz, G. Penn, W. Ott, K. Peters, E.M. Peters and H.G. von Schnering, *ibid*, **117**, 1310 (1984).
   (f) G. Kollenz, W. Ott, E. Ziegler, E.M. Peters, K. Peters, H.G. von Schnering, V. Formacek and H. Quast, *Liebigs Ann Chem.*, 1137 (1984).
   (g) G. Kollenz, G. Penn, W. Ott, K. Peters, E.M. Peters and H.G. von Schnering, *Heterocyclic*, **26**, 625 (1987).
   (h) G. Kollenz, H. Sterk and G. Hutter, *J.Org Chem.*, **56**, 235 (1991).
   (I) E. Terpetschnig, G. Penn, G. Kollenz, K. Peters, E.M. Peters and H.G. von Schnering, *Tetrahedron*, **47**, 3045 (1991).
3. (a) G. Kollenz, E. Ziegler, W. Ott and H. Igel, *Z. Naturforsch*, **31b**, 1511 (1976).
   (b) W. Ott, E.. Ziegler and G. Kollenz, *Synthesis*, **7**, 477 (1976).
   (c) Y. Akçamur, A. Sener, A.M. Ipekoglu and G. Kollenz, *J. Heterocyclic Chem.*, **34**, 221 (1997).
4. (a) Y. Akçamur, B. Altural, E. Saripinar, G. Kollenz, C.O. Kappe, E.M. Peters and H.G. von Schnering, *J. Heterocyclic Chem.*, **25**; 1419 (1988).
   (b) B. Altural, Y. Akçamur, E. Saripinar, I. Yildirim and G. Kollenz, *Monatsh. Chem.*, **120**, 1015 (1989).
   (c) I. Yildirim, E. Saripinar, Y. Güzel, S. Patat and Y. Akçamur, *J. Mol. Struct.*, **334**, 165 (1995).
   (d) E. Saripinar, I. Yildirim, Y. Güzel and Y. Akçamur, *Monatsh. Chem.*, **127**, 505 (1996).
   (e) I. Yildirim, M. Tezcan, Y. Güzel, E. Saripinar and Y. Akçamur, *Tr. J. Chem.*, **20**, 27 (1996).
5. (a) D.L. Boger, *Tetrahedron*, **39**, 2869 (1983).
   (b) A.G. Birchler, F. Liu and L.S. Liebeskind, *J.Org. Chem.*, **59**, 7737 (1994).
   (c) J.A. Hyatt, P.L. Feldman and R.J. Clemens, *J.Org.Chem.*, **49**, 5105 (1984).
   (d) D.W. Emerson, R.L. Titus and R.M. Gonzales, *J.Org. Chem.*, **56**, 5301 (1991).
   (e) B. Freiermuth and C. Wentrup, *J.Org. Chem.*, **56**, 2286 (1991).
6. (a) G. Kollenz, H. Igel and E. Ziegler, *Motatsch. Chem.*, **103**, 450 (1972).
   (b) E. Ziegler, G. Kollenz, G. Kriwetz and W. Ott, *Liebig's Ann. Chem.*, **12**, 1751 (1977).
   (c) E. Ziegler, G. Kollenz and W. Ott, *Synthesis*, **11**, 679 (1973).
7. (a) Y.S. Andreichikov, G. Kollenz, C.O. Kappe, R.L. Toung and C. Wentrup, *Acta Chem. Scand.*, **46**, 683 (1992).
   (b) C.O. Kappe, G. Farber, C. Wentrup and G. Kollenz, *J.Org. Chem.*, **57**, 7078 (1992).
   (c) T. Mosandl and C. Wentrup, *J. Org. Chem.*, **58**, 747 (1993).
   (d) C.O. Kappe, R.A. Evans, C.H.L. Kennard

and C. Wentrup, *J. Am. Chem. Soc.*, **113**, 4234 (1991).

8. (a) H. Meier, H. Wengenroth, W. Lauer and W. Vogt, *Chem.Ber.*, **121**, 1643 (1988).
   (b) R.L. Toung and C. Wentrup, *Tetrahedron Letters*, **48**, 7641 (1992).
   (c) H Meier, H. Wengenroth, W.Lauer and V. Krause, *Tetrahedron Letters*, **30**, 5253 (1989).
   (d) H. Meier, W. Lauer and V. Krause, *Chem.Ber.*, **119**, 3382 (1986).
   (e) W.M.F. Fabian, G. Kollenz, Y. Akçamur, T.R. Kök, M. Tezcan, M. Akkurt. and W. Hiller, *Monatsch. Chem.*, **123**, 265 (1992).
   (f) I. Yildirim and I.Ö. Ilhan, *J.Heterocyclic Chem.*, **34**, 1047 (1997).
9. (a) G. Kollenz, E. Ziegler and W. Ott, *Org. Prep.Proc. Int.*, 5(6), 261 (1973).
   (b) G. Kollenz, E. Ziegler, W. Ott and G. Kriwetz, *Naturforschg*, **32B**, 701 (1977).
   (c) E. Ziegler, G. Kollenz, G. Kriwetz and W. Ott, *Liebigs Ann. Chem.*, **12**, 1751 (1977).
   (d) G. Kollenz, H. Igel and E. Ziegler, *Motatsch. Chem.*, **103**, 450 (1972).
   (e) E. Ziegler, G. Kollenz and W. Ott, *Synthesis*, **11**, 679 (1973).
10. (a) C. Wentrup, H-W. Winter, G. Gross, K-P. Netch, G. Kollenz, W. Ott and A.G. Biederman, *Angew. Chem. Int. Ed. Engt.*, **23**(10), 800 (1984).
    (b) C.O. Kappe, G. Farber, C. Wentrup and G. Kollenz, *J.Org. Chem.*, **57**, 7078 (1993).
11. E.L. Steward and P. Bowen, *J. Comput. Chem.*, **13**, 1125 (1992).
12. (a) W.M.F. Fabian and G. Kollenz, *J. Mol. Struct.*, **313**, 219 (1994).
    (b) M.W. Wong and C. Wentrup, *J. Org. Chem.*, **59**, 5279 (1994).
    (c) R. Janoschek, W.M.F. Fabian, G. Kollenz and C.O. Kappe, *J. Comput. Chem.*, **15**, 132 (1994).
    (d) L. Gong, M.A. Allister and T.T. Tidwell, *J.Am. Chem. Soc.*, **113**, 6021 (1991).
    (e) D.M. Birney, *J. Org. Chem.*, **59**, 2557 (1994).
    (f) F.P. Cossio, J.M. Ugalde, X. Lopez, B. Lecea and C. Palomo, *J. Am. Chem. Soc.*, **115***(3)*, 995 (1993).
    (g) S. Hamabe, T. Minato, Y.Osamura, *J. Chem. Soc., Chem. Commun.*, 450 (1993).
    (h) D. Fang and X. Fu, Inter. *J. of Quantum Chem.*, **43**, 677 (1992).
    (i) M.W. Wong and C. Wentrup, *J. Org. Chem.*, **59**, 5279 (1994).
    (j) D.M. Birney, *J.Org. Chem.*, **59**, 2557 (1994).
13. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
14. J.J.P. Stewart, MOPAC, Version 7.00, QCPE Program No. 455.
15. R.J. Clemens and J.A. Hyatt, *J.Org.Chem.*, **50**, 2431 (1985).
16. H.A. Abd El-Nabi and G. Kollenz, *Monatsh. Chem.*, **128**, 381 (1997).