Synthesis of Novel 4,5-Diazafluoren-9-one Derivatives and Theoretical Study of 3+2 Cycloaddition Reactions

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Some novel salts of 4,5-diazafluoren-9-one N-monosubstituted have been obtained by using Kröhnke method. The ability of 9-oxo-4,5-diazafluorenium phenacylides (as 1,3-dipoles) to react with activated symmetric dipolarophiles to give new heterocyclic compounds is presented. The new heterocyclic system of 10,10c-diazacyclopenta[*c*]fluoren-6-one is illustrated by a series of derivatives. The cycloaddition reaction proceeds, according to the semiempirical study, *via* a concerted nonsynchronous mechanism.

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Introduction.

There are many recent references in the literature related to the 3+2 cycloaddition reaction of cycloimmonium ylides to activated symmetrical or non-symmetrical olefins and alkynes [1-6]. These reactions are very interesting due to the possibility of preparing cycloadducts, which are difficult to obtain otherwise. The capacity of 4,5-diazafluoren-9-one derivatives to form metal complexes is well known [7-8]. Also, in our previous paper we reported the synthesis of new similar derivatives of 1,10-phenanthroline, which present some interesting semiconductor, phytotoxic or antimicrobial and antifungical properties [9-12]. These were the main reasons we decided to prepare new 9-oxo-4,5-diazafluorenium salts and then, corresponding novel cycloadducts with dimethyl acetylenedicarboxylate (DMAD) by 3+2 dipolar cycloadditions. The practical data were supported by some theoretical study regarding the mechanism of 3+2 dipolar cycloaddition reactions.

Results and Discussions.

In the first part of our research we have synthesized the 4,5-diazafluoren-9-one **1** by oxidation of 1,10-phenanthroline with alkaline potassium permanganate according to literature data [13]. Then, using an adaptation of the Kröhnke method, we prepared five new 4,5-diazafluorenium-9-one salts by treating the 4,5-diazafluoren-9-one **1** with 2-bromo-4'-X-acetophenones (Figure 1) in warm anhydrous acetone [14-15]. The novel *N*-[(4'-X-benzoyl)methyl]-9-oxo-4,5-diazafluorenium bromides **3a-e** were characterized by chemical and spectral analyses.

Good yields and high purity of new monoquaternary salts were obtained by using a small excess of halide derivative and a small amount of solvent in the reaction pathway. This change in the reaction conditions permits rapid formation of salt crystals, thus avoiding the possible secondary reactions. The ir spectra for synthesized compounds **3a-e** showed absorption bands in the range of 1725-1735 cm^{-1} for ketonic carbonyl group 9 and 1684-1705 cm^{-1} for ketonic carbonyl group 11.

In the ^1H nmr spectrum of salts **3a-e** the most important signals are those of the 3–H and 10-H atoms. The 3-H atoms appear at δ=9.16-9.24 ppm due to deshielding effect induced by positive nitrogen atom while aliphatic 10-H atoms are much deshielded due to the ketonic group and positive nitrogen atom neighborhood.

In the next step, the obtained quaternary salts **3a-e** were used in 3+2 dipolar cycloaddition reactions with DMAD. Thus, salts **3a-e** were suspended in ethanol and an aqueous solution of 0.2 *N* sodium hydroxide (NaOH) was added drop wise to form *in situ* ylides **4a-e** which rapidly react with the DMAD. In this reaction, ylides **4a-e**, generated *in situ*, are characterized by a zwitterionic structure and, therefore, can be dipole 1,3 reagents in the 3+2 dipolar cycloaddition reactions to give the 10,10c-diazacyclopenta[*c*]fluoren-6-one derivatives **6a-e** (Figure 2) [16-17].

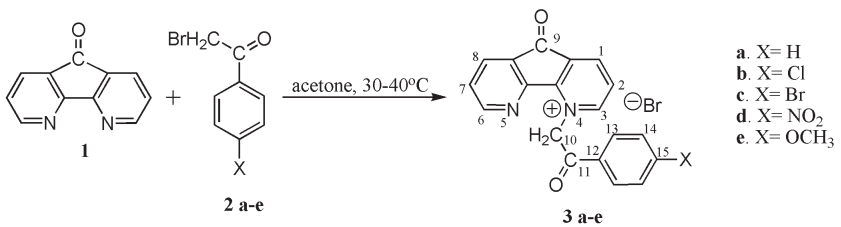


Figure 1. Reaction between 4,5-diazafluoren-9-one and 2-bromo-4'-X-acetophenones

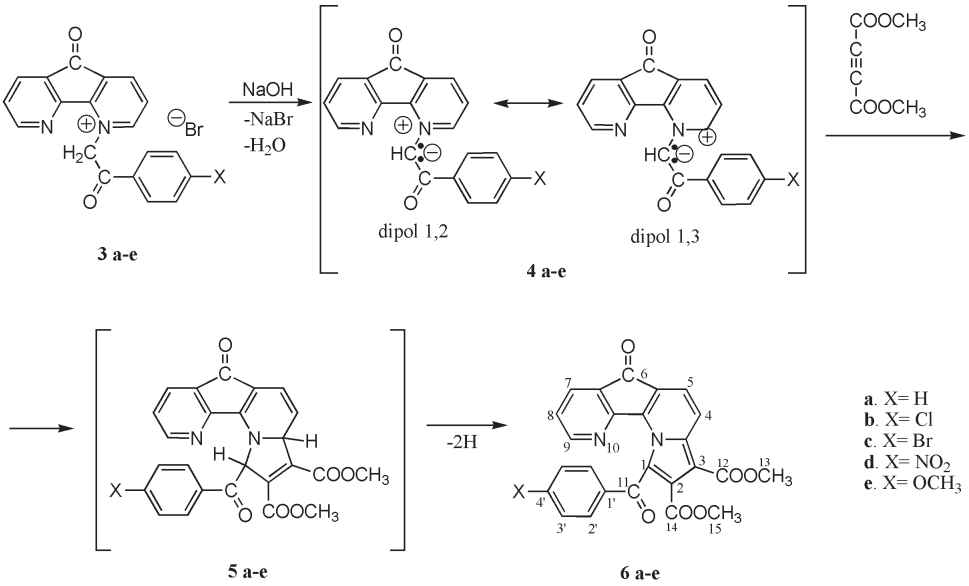


Figure 2. Reaction between in situ generated cycloimmonium ylides and DMAD

The reaction with DMAD occurs as a normal 3+2 dipolar cycloaddition leading in first instance to the non-isolating hydrogenated cycloadducts **5a-e**, which *via* an oxidative dehydrogenation lead to the more stable aromatized cycloadducts **6a-e** (Figure 2).

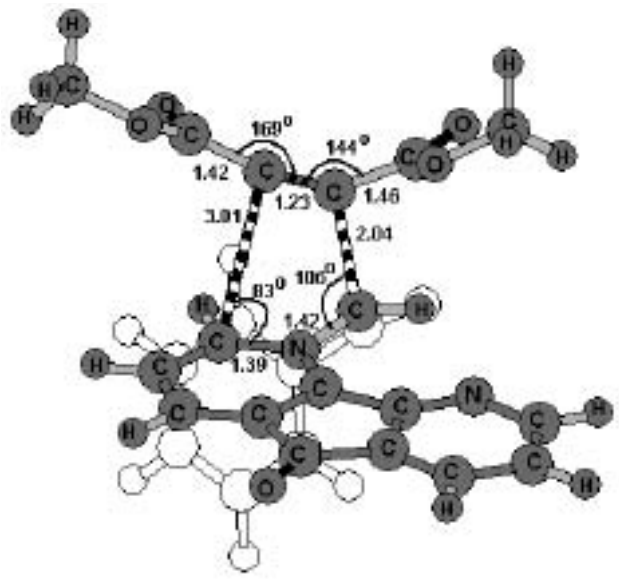
The structures of compounds **6a-e** were also proved by elemental and spectral methods. In ir spectra of all adducts posses a strong absorption band between 1725 cm^{-1} and 1728 cm^{-1} for ketonic carbonyl group 6 and esteric carbonyl group 14. The esteric carbonyl groups 12 absorb in the range of 1691-1693 cm^{-1} and the ketonic carbonyl groups 11 between 1644 cm^{-1} and 1664 cm^{-1}. The structures of compounds **6a-e** were also investigated by ^1H nmr spectroscopy. Two singlet signals corresponding to methyl protons appear at δ=3.91-3.93 ppm for the 13-H protons and at δ=3.43-3.50 ppm for the 15-H protons. The resonance at weak fields (δ=8.47-8.51 ppm) of 4-H protons is caused by interaction with the neighboring methoxycarbonyl group. Supplementary evidence was given by two-dimensional experiments 2D-COSY and 2D-HETCOR experiments for compound **6d**. All the remaining signals in ^1H nmr and ir for the compound **3a-e** and **6a-e** were in accordance with the proposed structure.

The mechanism of dipolar cycloadditions has been the subject of large discussions [18-19]. There are only two alternatives to be considered: a synchronous two-bond mechanism or a nonsynchronous cycloadditon. Useful information has been provided by theoretical study (*ab initio* calculation) for the dipolar cycloaddition of fulminic acid to acetylene to form isoxazole [20-21].

The structure calculated for the transition state indicated a synchronous mechanism, the lengths of the two forming bonds being almost identical (C-C, 2.20 Å; C-O, 2.24 Å). In mean time, the force constant for the C-C bond (3.0 mdyn/Å) is shown to be strong whereas the C-O bond (0.3 mdyn/ Å) is shown to be weak, corresponding to bond strength of at most a few kcal/mol. This indicates that first, C-O bond formation begins, and then formation of the C-C bond follows, thus the apparent equality of bond lengths is a misleading coincidence and the mechanism of bond formation is nonsynchronous.

In the light of presented data, we carried out PM3/AMSOL semi empirical calculations for the 3+2

Scheme 1



The transition state structure of reaction between 4,5-diazafluorenium-9-one ylides and DMAD (lengths are in Å).

cycloaddition reaction of ylides **4a-e**, generated *in situ*, with DMAD (Scheme 1) [22].

The structure calculated for the transition state [the force constants: C_1-C_2, 1.28 mdyn/Å, C_{3a}-C_3, 0.06 mdyn/Å (see Scheme 1); transition state energy -58.60 kcal/mol; vibration imaginary frequency of transition state, -510.06 cm^{-1}, activation energy ΔE= 16.47 Kcal/mol showed a concerted nonsynchronous mechanism. First, a nucleophilic attack of ylidic carbon took place, followed by immediate formation of the next C-C bond, the mechanism being similar to isoxazole formation.

Conclusions.

Five novel *N*-[(4'-X-benzoyl)methyl]-9-oxo-4,5-diazafluorenium salts have been synthesized with good yields using an adaptation of Kröhnkes method. The structures of obtained salts were proved by chemical and spectral analyses. Also, reaction of 4,5-diazafluorenium-9-one ylides, generated *in situ*, with activated symmetrical alkynes (DMAD) occurs as a 3+2 dipolar cycloaddition leading to new five 10,10c-diazacyclopenta[*c*]fluoren-6-one derivatives. The theoretical study of 3+2 dipolar cycloaddition reaction, which uses PM3/AMSOL semiempirical calculations were carried out in order to support experimental data for the mechanism. Thus, cycloaddition reaction proceeds, according to the semiempirical study, *via* a concerted nonsynchronous mechanism. Studies of biological and physical (optical and electrical) properties of the synthesized compounds as well as theoretical and experimental studies of other cycloaddition reactions are in progress and will be published in the near future.

EXPERIMENTAL

The ir spectra were recorded on a FT-IR spectrometer in KBr. The ^{1}H nmr spectra were run on a BRUKER-300 spectrometer and were recorded in ppm downfield from an internal standard TMS in DMSO-d_6 for compounds **3a-e** and in $CDCl_3$ for compounds **6a-e**. The coupling constants are given in Hz. Melting points were measured on a MEL-TEMP capillary apparatus and are uncorrected.

The structure calculated for transition state was optimized by the PM3/AMSOL (SM5.4P) computational method including the solvent effect on an INTEL P4 1.7 GHz personal computer.

General Procedure for Preparation of Compounds **3a-e**.

A solution of anhydrous 4,5-diazafluoren-9-one (1 mmol, 0.18 g) and 2-bromo-4'-X-acetophenone (1.1 mmol, 0.19 g **2a**, 0.23 g **2b**, 0.28 g **2c**, 0.24 g **2d**, 0.23 g **2e**) in anhydrous acetone (7 mL) was magnetically stirred for 3-4 hours at 40-50 °C. The resulting pale yellow precipitate was removed by filtration and then washed with acetone. All products were recrystallized from ethanol-acetone (4:1, v/v).

General Procedure for Preparation of Compounds **6a-e**.

The cycloimmonium salt **3a-e** (1 mmol, 0.38 g **3a**, 0.41 g **3b**, 0.46 g **3c**, 0.42 g **3d**, 0.41 g **3e**) and dimethyl acetylenedicarboxylate (1.1 mmol, 1.56 g) were dissolved in 10 mL ethanol and stirred together at room temperature. Then a 0.2 *N* aqueous NaOH solution was added drop wise over 2 hours (magnetic stirring). At the beginning, the solution became dark brown in color due to the formation of ylides and then, the red product began to crystallize. The adduct was collected by filtration to give a crystalline powder which was washed with 10 mL ethanol. The product was recrystallized from ethanol-chloroform (2:1, v/v).

N-(Benzoylmethyl)-9-oxo-4,5-diazafluorenium Bromide (**3a**).

This compound was obtained as khaki crystals (0.28 g). Yield 75%, mp 170-172 °C; ir: CH 3015, 2990, CO 1735,1689, CC, CN 1591, 1560, 1445; ^{1}H nmr: δ 7.08 (s, 2H, 10-H); 7.73 (m, 3H, 14-H and 15-H); 7.78 (dd, 1H, 7-H, J = 7.2, 4,9 Hz); 8.14 (dd, 2H, 13-H, J = 7.5, 1.3 Hz); 8.38 (m, 2H, 2-H and 8-H); 8.78 (dd, 1H, 6-H, J = 4.9, 1.2 Hz); 9.01 (dd, 1H, 1-H, J = 7.3, 1.1 Hz); 9.24 (dd, 1H, 3-H, J = 6.0, 1.1 Hz).

Anal. Calcd. for $C_{19}H_{13}BrN_2O_2$: C, 59.86; H, 3.44; N, 7.35. Found: C, 59.89; H, 3.48; N, 7.29.

N-[(4'-Chlorobenzoyl)methyl]-9-oxo-4,5-diazafluorenium Bromide (**3b)**.

This compound was obtained as yellow crystals (0.33 g). Yields 80%, mp 207-209 °C; ir: CH 3031, 2980, CO 1725, 1684, CC, CN 1591, 1560; ^{1}H nmr: δ 7.03 (s, 2H, 10-H); 7.78 (dd, 1H, 7-H, J = 7.7, 4.3 Hz); 8.07 (d, 2H, 14-H, J = 8.5 Hz); 8.17 (d, 2H, 13-H, J = 8.5 Hz); 8.39 (dd, 1H, 2-H, J = 7.3, 5,8 Hz); 8.48 (dd, 1H, 8-H, J = 7.7, 1.2 Hz); 8.78 (dd, 1H, 6-H, J = 4.3, 1.2 Hz); 9.00 (dd, 1H, 1-H, J = 7.3, 1.1 Hz); 9.17 (dd, 1H, 3-H, J = 5.8, 1.1 Hz).

Anal. Calcd. for $C_{19}H_{12}BrClN_2O_2$: C, 54.90; H, 2.91; N, 6.74. Found: C, 54.84; H, 2.95; N, 6.72.

N-[(4'-Bromobenzoyl)methyl]-9-oxo-4,5-diazafluorenium Bromide (**3c**).

This compound was obtained as yellow crystals (0.39 g). Yield 85%, mp 222-224 °C; ir: CH 3019, 2980, CO 1728, 1684, CC, CN 1629, 1564: ^{1}H nmr: δ 7.05 (s, 2H, 10-H); 7.75 (dd, 1H, 7-H, J = 7.0, 4.9 Hz); 7.92 (d, 2H, 14-H, J = 7.8 Hz); 8.09 (d, 2H, 13-H, J = 7.8 Hz); 8.39 (m, 2H, 8-H, 2-H); 8.78 (dd, 1H, 6-H, J = 4.9, 1.2 Hz); 9.01 (dd, 1H, 1-H, J = 7.3, 1.1 Hz); 9.22 (dd, 1H, 3-H, J = 5.4, 1.1 Hz).

Anal. Calcd. for $C_{19}H_{12}Br_2N_2O_2$: C, 49.60; H, 2.63; N, 6.09. Found: C, 49.64; H, 2.70; N, 6.03.

N-[(4'-Nitrobenzoyl)methyl]-9-oxo-4,5-diazafluorenium Bromides (**3d**).

This compound was obtained as white-yellow crystals (0.36 g). Yield 85%, mp 204-207 °C; ir: CH 3034, 2980, CO 1735, 1705, NO_2 1520, 1347, CC CN 1600, 1440. ^{1}H nmr: δ 7.07 (s, 2H, 10-H) 7.74 (dd, 1H, 7-H, J = 7.5, 5.1 Hz); 8.36 (dd, 1H, 2-H, J = 7.5, 6.0 Hz); 8.38 (dd, 1H, 8-H, J = 7.5, 1.2 Hz); 8.40 (d, 2H, 13-H, J = 8.7 Hz); 8.52 (d, 2H, 14-H, J = 8.7 Hz); 8.73 (dd, 1H, 6-H, J = 5.1, 1.2 Hz); 9.02 (dd, 1H, 1-H, J = 7.5, 1.1 Hz); 9.16 (dd, 1H, 3-H J = 6.0, 1.1 Hz).

Anal. Calcd. for $C_{19}H_{12}BrN_3O_4$: C, 53.54; H, 2.84; N, 9.86. Found: C, 53.59; H, 2.90; N, 9.84.

N-[(4'-Methoxybenzoyl)methyl]-9-oxo-4,5-diazafluorenium Bromide (**3e**).

This compound was obtained as yellow crystals (0.30 g). Yield 75%, mp 192-193 °C; ir: CH 3011, 2970, CO 1733, 1687, CC,

CN 1595, 1435, COC 1241, 1169. ^{1}H nmr: δ 3.91 (s, 3H, OCH3); 7.00 (s, 2H, 10-H); 7.20 (d, 2H, 14-H, J = 8.4 Hz); 7.73 (dd, 1H, 7-H, J =7.2, 4.8 Hz); 8.09 (d, 2H, 13-H, J = 8.4); 8.34 (dd, 1H, 2-H J = 7.5, 6.0 Hz); 8.39 (dd, 1H, 8-H, J = 7.2, 1.2 Hz); 8.79 (dd, 1H, 6-H, J = 4.8, 1.2 Hz); 9.00 (dd, 1H, 1-H, J = 7.5, 1.1 Hz); 9.18 (dd, 1H, 3-H, J = 6.0, 1.1 Hz).

Anal. Calcd. for $C_{20}H_{15}BrN_2O_3$: C, 58.41; H, 3.68; N, 6.81. Found: C, 58.49; H, 3.74; N, 6.78.

1-Benzoyl-2,3-dimethoxycarbonyl-10,10c-diazacyclopenta[*c*]-fluoren-6-one (**6a**).

This compound was obtained as red crystalline powder (0.23 g). Yield 54%, mp 299-301 °C; ir: CH 3050, 2950, CO 1725, 1691, 1657, CC, CN 1620, 1576, 1487, 1390, COC 1232, 1168, 1084. ^{1}H nmr: δ 3.43 (s, 3H, 15-H); 3.92 (s, 3H, 13-H); 7.11 (dd, 1H, 8-H, J = 7.2, 4.8 Hz); 7.51 (dd, 2H, 3'-H, J =7.1, 7.2 Hz); 7.55 (dd, 1H, 4'-H, J = 7.2, 1.3 Hz); 7.68 (d, 1H, 5-H, J = 9.1 Hz); 7.81 (dd, 1H, 7-H, J = 7.2, 1.2 Hz); 7.99 (dd, 2H, 2'-H J = 7.1, 1.3 Hz); 8.20 (dd, 1H, 9-H, J = 4.8, 1.2 Hz); 8.49 (d, 1H, 4-H, J = 9.1 Hz).

Anal. Calcd. for $C_{25}H_{16}N_2O_6$: C, 68.18; H, 3.66; N, 6.36. Found C, 68.22; H, 3.71; N, 6.34.

1-(*p*-Chlorobenzoyl)-2,3-dimethoxycarbonyl-10,10c-diazacyclopenta[*c*]fluoren-6-one (**6b**).

This compound was obtained as red crystalline powder (0.26 g). Yield 64%, mp 305-307 °C; ir: CH 3080, 2950, CO 1727, 1691, 1654, CC, CN 1620, 1590, 1487, 1393, COC 1233, 1166, 1088. ^{1}H nmr: δ 3.50 (s, 3H, 15-H); 3.93 (s, 3H, 13-H); 7.12 (dd, 1H, 8-H, J = 7.3, 5.3 Hz); 7.49 (d, 2H, $H_{3'}$, J = 8.4 Hz); 7.69 (d, 1H, 5-H, J = 9.1 Hz); 7.82 (dd, 1H, 7-H, J = 7.3, 1.2 Hz); 7.93 (d, 2H, $H_{2'}$, J = 8.4 Hz); 8.18 (dd, 1H, 9-H, J = 5.3, 1.2 Hz); 8.49 (d, 1H, 4-H J = 9.1 Hz).

Anal. Calcd. for $C_{25}H_{15}ClN_2O_6$: C, 63.23; H, 3.18; N, 5.90. Found C, 63.28; H, 3.25; N, 5.87.

1-(*p*-Bromobenzoyl)-2,3-dimethoxycarbonyl-10,10c-diazacyclopenta[*c*]fluoren-6-one (**6c**).

This compound was obtained as red crystalline powder (0.27 g). Yield 60%, mp 282-284 °C; ir: CH 3080, 2950, CO 1727, 1691, 1654, CC, CN 1620, 1581, 1486, 1393, COC 1233, 1166, 1086. ^{1}H nmr: δ 3.50 (s, 3H, 15-H); 3.92 (s, 3H, 13-H); 7.11 (dd, 1H, 8-H, J = 7.2, 5.5 Hz); 7.65 (d, 2H, 3'-H, J = 8.0 Hz); 7.70 (d, 1H, 5-H, J = 8.9 Hz); 7.83 (dd, 1H, 7-H, J = 7.2, 1.1 Hz); 7.86 (d, 2H, 2'-H, J = 8.0 Hz); 8.18 (dd, 1H, 9-H, J = 5.5, 1.1 Hz); 8.51 (d, 1H, 4-H, J = 8.9 Hz).

Anal. Calcd. for $C_{25}H_{15}BrN_2O_6$: C, 57.82; H, 2.91; N, 5.39. Found C, 57.87; H, 2.96; N, 5.34.

1-(*p*-Nitrobenzoyl)-2,3-dimethoxycarbonyl-10,10c-diazacyclopenta[*c*]fluoren-6-one (**6d**).

This compound was obtained as red crystalline powder (0.27 g). Yield 65%, mp 268-270 °C; ir: CH 3090, 2950, CO 1728, 1693, 1664, NO_2 1528, 1347, CC, CN 1611, 1580, 1486, COC 1392, 1234, 1160, 1087. ^{1}H nmr: δ 3.50 (s, 3H, 15-H); 3.93 (s, 3H, 13-H); 7.14 (dd, 1H, 8-H, J = 7.0, 5.4); 7.72 (d, 1H, 5-H, J = 8.9 Hz); 7.84 (dd, 1H, 7-H, J = 7.0, 1.2 Hz); 8.13 (d, 2H, 2'-H, J = 8.4 Hz); 8.15 (dd, 1H, 9-H, J = 5.4, 1.2 Hz); 8.35 (d, 2H, 3'-H, J = 8.4 Hz); 8.51 (d, 1H, 4-H, J = 8.9 Hz). ^{13}C nmr: δ 51,93 (1C, 13-C); 52,55 (1C, 15-C); 120,09 (2C, 3-C, 4-C); 121,15 (1C, 5a-C); 123,71 (3C, 8-C, 5-C, 1-C); 124,06 (1C, 2-C); 124,56 (2C, 3'-C, 5'-C); 127,49 (1C, 6a-C); 129,86 (3C, 7-C, 1'-C, 10b-C); 130,80 (2C, 2'-C, 6'-C); 139,10 (1C, 3a-C); 142,46 (1C, 4'-C); 149,57 (1C, 9-C), 151,05 (1C, 10a- C), 157,66 (1C, 11-C), 162,16 (1C, 12-C); 164,08 (1C, 14-C), 187,00 (1C, 6-C).

Anal. Calcd. for $C_{25}H_{15}N_3O_8$: C, 61.86; H, 3.11; N, 8.66. Found: C, 61.89; H, 3.16; N, 8.60.

1-(*p*-Methoxybenzoyl)-2,3-dimethoxycarbonyl-10,10c-diazacyclopenta[*c*]fluoren-6-one (**6e**).

This compound was obtained as red crystalline powder (0.23 g). Yield 58%, mp 276-278 °C; ir: CH 3060, 2950, CO 1725, 1693, 1644, CC, CN 1599, 1574, 1488, 1388, COC 1230, 1159, 1086, 1024. ^{1}H nmr: δ 3.50 (s, 3H, 15-H); 3.91 (s, 3H, OCH_3); 3.92 (s, 3H, 13-H); 6.98 (d, 2H, 3'-H, J = 8.7 Hz); 7.09 (dd, 1H, 8-H, J = 7.2, 5.3 Hz); 7.65 (d, 1H, 5-H, J = 9.1 Hz); 7.80 (dd, 1H, 7-H, J =7.2, 1.2 Hz); 7.96 (d, 2H, 2'-H, J =8.7); 8.18 (dd, 1H, 9-H, J = 5.3, 1.2 Hz); 8.47 (d, 1H, 4-H, J = 9.1 Hz).

REFE RENCES AND NOTES

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[1] I. Druta, M. Andrei and P. Aburel, *Tetrahedron*, **54**, 2107 (1998).

[2] I. Druta, R. Dinica, E. Bacu and I. Humelnicu, *Tetrahedron*, **54**, 10811 (1998).

[3] I. Druta, M. Andrei, C. Ganj and P. Aburel, *Tetrahedron*, **55**, 13063 (1999).

[4] R. Dinica, I. Druta and C. Pettinari, *Synlett*, **7**, 1013 (2000).

[5] I. Mangalagiu, G. Mangalagiu, C. Deleanu, G. Drochioiu, M. Petrovanu, *Tetrahedron*, **59**, 111 (2003).

[6] R. Danac, A. Rotaru, G. Drochioiu and I. Druta, *J. Heterocyclic Chem*., **40**, 283 (2003).

[7] W. Zhiyong, X. Duanjun, W. Jingyun and C. Michael, *Acta Crystallographica*, **C58(7)**, 374 (2002).

[8] Z. Guangchang and H. Issifu, *Tetrahedron Lett*., **44**, 4617 (2003).

[9] L. Leontie, I. Druta, R. Alupoae and G. I. Rusu, *Material Science and Engineering*, **B100**, 252 (2003).

[10] I. Druta, R. Danac and G. Drochioiu, *Ann. Sci. Univ. 'Al.I.Cuza' Iasi*, **9**, 143 (2001).

[11] I. Druta, C. Cuciac, R. Danac, E. Avram, A. Rotaru and G. Drochioiu, *Pakistan Journal of Applied Science*, **2**, 145 (2002).

[12] I. Druta, R. Danac, M. Ungureanu, G. Grosu and G. Drochioiu, *Ann. Pharm. Fr*. **60**, 348 (2002).

[13] I. Eckhard and L. A. Summers, *Aust. J. Chem*. **26**, 2727 (1973).

[14] F. Kronhke, *Angew. Chem*., ***65***, 605 (1953).

[15] F. Kronhke, *Angew. Chem. Int. Edn*., ***2***, 225 (1963).

[16] I. Zugravescu and M. Petrovanu, N-Ylides-Chemistry, McGraw Hill, London, 1976.

[17] A. Padwa, 1,3-Dipolar Cycloaddition Chemistry, John Wiley & Sons, New York, 1984.

[18] R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976).

[19] R. A. Firestone, *J. Org. Chem.*, **37**, 218 (1972).

[20] M. J. S. Dewar, *J. Am. Chem. Soc*., **106**, 209 (1984).

[21] A. Komornicki, J. D. Goddard and H. F. Schaefer, *J. Am. Chem. Soc*., **102**, 1763 (1980).

[22] C. J. Cramer and D. G. Truhlar, *Chem. Rev*., **99**, 2161, (1999).