

## Photochemical Reactions of Regioisomeric 2,2-Dimethyl-5,5-diphenyl- and 5,5-Dimethyl-2,2-diphenyl-Substituted Diazo Ketones of a Tetrahydrofuran Series

by Ludmila L. Rodina<sup>a</sup>), Sergey A. Malashikhin<sup>a</sup>)<sup>b</sup>1), Olesya S. Galkina<sup>a</sup>)<sup>2</sup>), and Valerij A. Nikolaev<sup>a</sup>)\*

<sup>a</sup>) Department of Organic Chemistry, Saint-Petersburg State University, University prosp. 26, RU-198504 Saint-Petersburg, Russia

(phone: +7-812-3231068; fax: +7-812-4286939; e-mail: vnikola@vn6646.spb.edu)

<sup>b</sup>) Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

---

The principal direction of conventional photolysis of the regioisomeric 2,2-dimethyl-5,5-diphenyl- and 5,5-dimethyl-2,2-diphenyl-substituted 4-diazodihydrofuran-3(2*H*)-ones **1a** and **1b**, respectively, is the *Wolff* rearrangement, while other photochemical processes, which are giving rise to the formation of C–H-insertion, 1,2-alkyl- or -aryl-shifts, as well as H-atom-abstraction products occur to a much lower degree (*Schemes 2* and *3*). The ratio of similar reaction products from both regioisomers **1a** and **1b** is essentially independent of their structure, and a substantial effect of the relative position of the Ph and diazo group to each other on the yield of C–H-insertion products does not occur. Based on stereochemical considerations, the *Wolff* rearrangement of diazodihydrofuran-3(2*H*)-ones apparently proceeds in a concerted manner, whereas the appearance in the reaction mixture of 1,2-shift and H-atom-abstraction products points to the parallel generation during photolysis of singlet and triplet carbenes (*Schemes 4* and *5*).

---

**1. Introduction.** – Direct photolysis of cyclic diazocarbonyl compounds usually proceeds with elimination of N<sub>2</sub> and formation of the *Wolff* rearrangement products (for reviews, see [1–6]). Thus, light-induced decomposition of diazo ketones **A** with 2,2,5,5-tetraalkyl substituents at the heterocycle (R = Me, Et, and others) by short-wavelength UV light ( $\lambda > 210$  nm) in dioxane solution, as a rule, gives rise to oxetanecarboxylic acids **B** or their derivatives (*Scheme 1*) in yields of up to 90–95% [7].

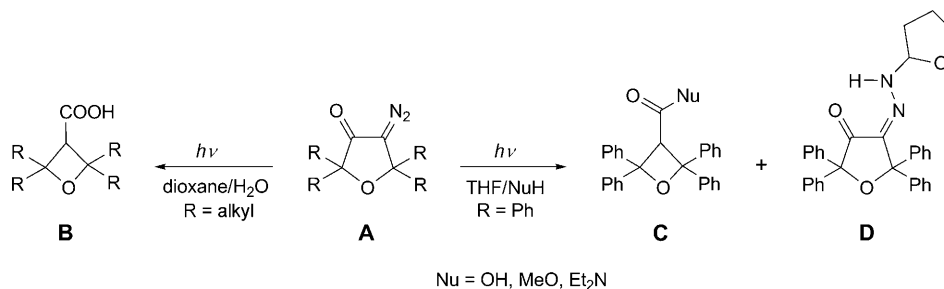
On the other hand, it was recently established [8] that photolysis of tetraphenyl-substituted diazo ketone **A** (R = Ph) in THF solution, besides ordinary *Wolff*-rearrangement products **C**, furnished the adduct **D** of diazo ketone **A** with THF (*Scheme 1*). The latter can be considered as the product of the insertion of the terminal N-atom of the diazo group into the H–C(2) bond of THF. The revealed transformation of tetraphenyl-substituted diazo ketone **A** is apparently the first example of the photolysis of diazo ketones which proceeds with the retention of both N-atoms of the diazo group in the reaction products [9][10].

---

1) Part of the Diploma Thesis of S.A.M., Saint-Petersburg State University, 2005.

2) Part of the Bachelor research of O.S.G., Saint-Petersburg State University, 2009.

Scheme 1



Having in mind the difference in the structure of the above-mentioned diazo ketones **A** (R = Me or Ph), one could assume that the pivotal effect on the appearance of a new direction during photolysis of diazo ketone **A** (R = Ph) is due to the presence of two Ph substituents in the  $\alpha,\alpha$ -position to the diazo group. In this connection, the main goal of the current research was to compare the photochemistry of the regioisomeric 2,2-dimethyl-5,5-diphenyl- and 5,5-dimethyl-2,2-diphenyl-substituted diazo ketones **1a** and **1b** with alternative location of the Ph substituents relative to the diazo group.



It was anticipated that 4-diazodihydro-2,2-dimethyl-5,5-diphenylfuran-3(2H)-one (**1a**), by analogy with the tetraphenyl-substituted diazo ketone **A** (R = Ph) will give rise to the formation of the C–H-insertion products (along with the *Wolff* rearrangement) [8], whereas 4-diazodihydro-5,5-dimethyl-2,2-diphenylfuran-3(2H)-one (**1b**), with the diazo group adjacent to the  $\alpha,\alpha$ -methyl groups, should be photolyzed similarly to the tetramethyl-substituted diazo ketone **A** (R = Me) [7], *i.e.*, **1b** will produce solely the *Wolff* rearrangement products.

**2. Results and Discussion.** – 2.1. *Synthesis and UV Spectra of the Diazodihydrofuran-3(2H)-ones 1a and 1b.* Diazo ketones **1a** and **1b** were prepared in accordance with the previously elaborated scheme and protocols [7][11]; their structures as regioisomeric dimethyl-diphenyl-substituted diazodihydrofuran-3(2H)-ones were established by spectroscopic methods and X-ray crystal-structure analysis [11]. The preliminary tests for thermal stability have shown that both diazo ketones are quite persistent on heating up to 100° and above in the molten state or in toluene and dioxane solutions [12].

The electronic spectra of diazo ketones **1a** and **1b** in solutions are characterized by two major absorption bands, a strong one in the region  $\lambda$  252–257 nm, and a weaker one at 305–307 nm (*Table*). The position of these absorbance bands is virtually independent from the polarity of the solvents used, and thus does not allow a confident

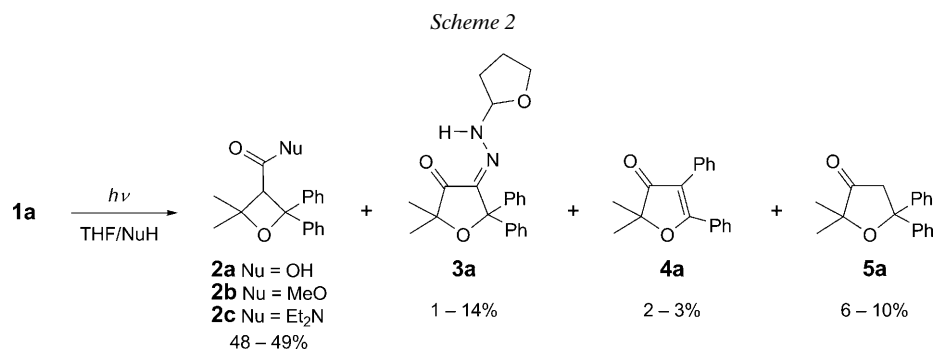
assignment to the relevant transitions. However, by analogy with other diazocarbonyl compounds [13–16], these absorptions can be evidently attributed to  $\pi-\pi^*$  and  $n-\pi^*$  electronic transitions, respectively (see also [17]).

Table. UV Spectra of the Diazofuranidones **1a** and **1b**.  $\lambda_{\max}$  in nm.

	$\lambda_{\max}$ (log $\epsilon$ )		
	hexane	THF	MeOH
<b>1a</b>	252 (4.22), 306 (2.99)	253 (4.18), 305 (3.30) <sup>a</sup>	255 (4.02), 306 (3.03)
<b>1b</b>	255 (4.40), 307 (3.17)	256 (4.79), 305 (3.76)	257 (4.15), 306 (3.27)

<sup>a</sup>) Inflection point at the absorption curve.

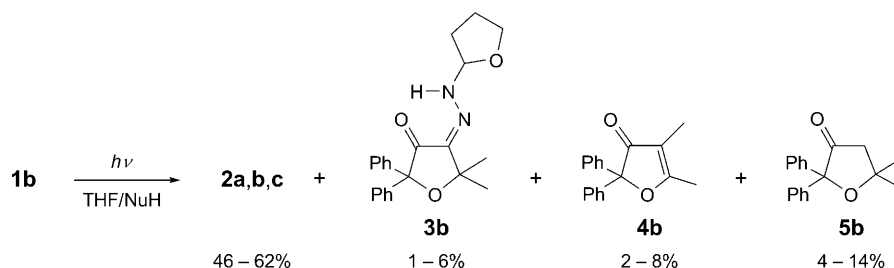
2.2. Photochemical Transformations of Diazo Ketones **1a** and **1b**. Conventional photolysis of diazo ketone **1a** or **1b** was performed in solution of freshly distilled THF, containing a nucleophilic reagent NuH (= H<sub>2</sub>O, MeOH, or Me<sub>2</sub>NH) to trap the intermediate ketene (Schemes 2 and 3). Irradiation was carried out in a quartz vessel with UV light of a medium-pressure Hg lamp ( $\lambda > 210$  nm) under an O<sub>2</sub>-free atmosphere until complete disappearance of **1a** or **1b** in the reaction mixture (by TLC; normally 1.5–2 h). After removal of the solvent and nucleophile by distillation *in vacuo*, the residue was recrystallized or/and subjected to chromatography (silica gel), and the crude reaction mixture or the isolated compounds were analyzed by spectroscopic methods (see *Exper. Part*). After photolysis of diazo ketone **1a**, four major products were isolated, namely oxetanecarboxylic acid **2a** (or its methyl ester **2b** or amide **2c**), hydrazone **3a** (the C–H-insertion product), unsaturated ketone **4a**, and monoketone **5a** (Scheme 2)<sup>3</sup>. The UV irradiation of the regioisomeric diazo ketone **1b** gave, under the same reaction conditions, the four similar reaction products **2a,b,c**, **3b**, **4b**, and **5b** (Scheme 3).



The structures of the obtained compounds **2a,b,c**, **3a,b**, **4a,b**, and **5a,b** were established by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy as well as by IR and MS data. In the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of oxetanecarboxylic acid **2a** and its derivatives **2b** and **2c**, the

<sup>3</sup>) Usually, the reaction mixtures of diazo ketones **1a** and **1b** also contained minor amounts of other compounds with unknown structure.

Scheme 3



position of the  $^1\text{H}$  and  $^{13}\text{C}$  signals of H–C(3) in the quite narrow regions  $\delta(\text{H})$  4.2–4.4 and  $\delta(\text{C})$  56.1–58.2, respectively, as well as the  $\delta(\text{C})$  80.8 and 83.8 of C(2) and C(4) of the oxetane ring, are most characteristic.

The  $^1\text{H}$ -NMR data of the C–H-insertion products **3a,b** point to the formation of a rather strong intramolecular H-bond  $\text{C}=\text{O} \cdots \text{H}-\text{N}$ , which gives rise to the displacement of the N–H signal to  $\delta(\text{H})$  11.4–11.6 [18][19].

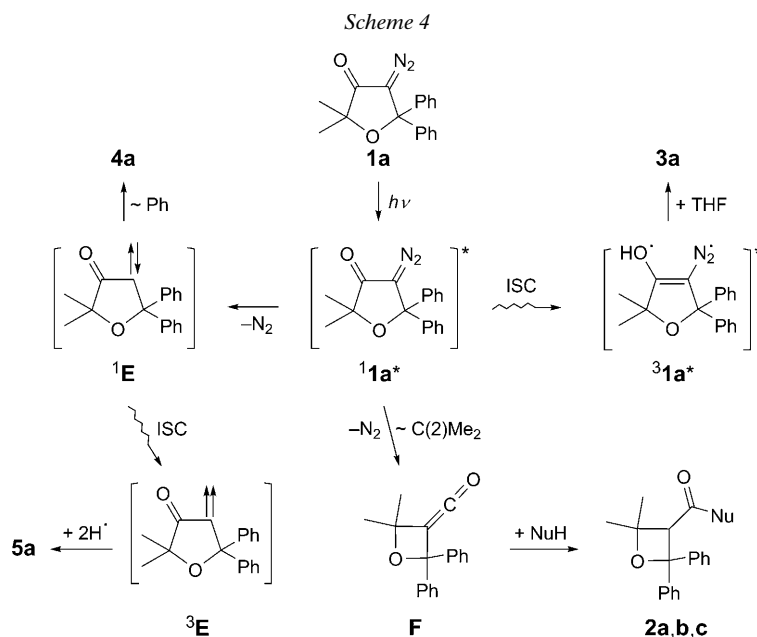
In the  $^{13}\text{C}$ -NMR spectra of the unsaturated ketones **4a** and **4b**, only one signal of a tertiary C-atom C(2) is observed at  $\delta(\text{C})$  87.0 and 91.3, respectively, and at lower field appear the signals of the olefinic C(4) and C(5) at  $\delta(\text{C})$  113.4 and 110.2, and 178.3 and 183.9, respectively, besides the usual aromatic C-signals. The position of the C=C bond in the heterocyclic vinyl ketone **4b** was in addition confirmed by the COLOC experiments. In the IR spectra of **4a** and **4b**, the absorption bands  $\tilde{\nu}_{\text{C}=\text{O}}$  are observed at 1680 and 1640  $\text{cm}^{-1}$ , respectively, that is also typical for unsaturated conjugated ketones [20].

The product analysis shows that the main direction of the photochemical reactions of both regioisomeric diazo ketones **1a,b** is the Wolff rearrangement (with yields up to 62%), whereas other photochemical processes, which give rise to the formation of the insertion products **3a,b**, vinyl ketones **4a,b**, and monoketones **5a,b**, proceed to a smaller extent (up to 10–14%). Furthermore, it is evident that the efficiency of all photoreactions observed is little affected by the structure of the regioisomers **1a,b** (Schemes 2 and 3).

As for the ratio of C–H-insertion products **3a,b**, it turned out that the yields of **3a,b** under the same reaction conditions were little affected by the structure of the starting diazo ketones **1a,b** (the yields of hydrazones **3a,b** were 3–6% (with  $\text{H}_2\text{O}$ ), 6–14% (with MeOH), and 0.5–1% (with  $\text{Me}_2\text{NH}$ )). Thus, it may be concluded that the assumption of the pivotal effect of the  $\alpha,\alpha$ -phenyl groups on the yield of C–H-insertion products (as was observed previously with tetraphenyl-substituted diazodihydrofuran-3(2H)-one [8]) did not get essential support from these experimental data.

**2.3. Pathways of Photochemical Transformations of Diazo Ketones 1a and 1b.** Based on the obtained results and known literature data [1–6][9][10][21–25], we propose the following explanations for the observed photochemical transformations of the regioisomeric diazo ketones **1**, as exemplified by the diazodihydrofuran-3(2H)-one **1a** (Scheme 4). Irradiation of diazo ketone **1a** by UV light results in the excitation of **1a** to one of the singlet excited states  $^1\mathbf{1a}^*$ , which can basically undergo subsequent chemical transformations with the elimination of  $\text{N}_2$  or retention of both diazo group N-atoms in

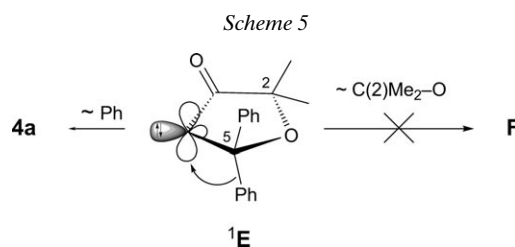
the structure of reaction products. Elimination of the  $\text{N}_2$  molecule from  ${}^1\mathbf{1a}^*$  leads to either a singlet  $\alpha$ -oxocarbene  ${}^1\mathbf{E}$  or – in the case of the concerted *Wolff* rearrangement – directly to the formation of ketene  $\mathbf{F}$  (Scheme 4). The succeeding reaction of  $\mathbf{F}$  with a nucleophile  $\text{NuH}$  ( $= \text{H}_2\text{O}$ ,  $\text{MeOH}$ , or  $\text{Me}_2\text{NH}$ ) produces oxetanecarboxylic acid  $\mathbf{2a}$  or its derivatives  $\mathbf{2b,c}$ .



The migration of the Ph group (or Me with  $\mathbf{1b}$ ) at the vacant p-orbital of the singlet  $\alpha$ -oxocarbene  ${}^1\mathbf{E}$  furnishes the unsaturated ketone  $\mathbf{4a}$  (or  $\mathbf{4b}$ ) (Scheme 5), which is a typical product of 1,2-nucleophilic rearrangements of singlet carbenes [1][5][22][26]. Apparently, the conformation of carbene  ${}^1\mathbf{E}$  with the Ph–C(5) bond (or Me–C(5) for  $\mathbf{1b}$ ) of the migrating group located essentially parallel to the vacant carbene p-orbital strongly favors this migration, as it has been already suggested before in the case of other cyclic diazo ketones [1][2][27]. The acyl group C(2)–C=O, on the other hand, is aligned in the plane of the occupied  $\sigma$ -orbital of  ${}^1\mathbf{E}$ , which is orthogonal to the vacant p-orbital. In this situation, the migration of the C(2) atom of the acyl group with its electrons on the occupied  $\sigma$ -orbital of the singlet carbene  ${}^1\mathbf{E}$  is hardly probable [28], and thus the *Wolff* rearrangement with the formation of ketene  $\mathbf{F}$  via the oxocarbene pathway seems unlikely (Scheme 5).

Partial intersystem crossing (ISC) of the singlet carbene  ${}^1\mathbf{E}$  leads to the triplet  $\alpha$ -oxocarbene  ${}^3\mathbf{E}$ , which is formally a biradical. The latter reacts with the solvent to give products typical for a triplet carbene reduction ('double H-atom abstraction') [9][21][22], *i.e.*, monoketones  $\mathbf{5a}$  (or  $\mathbf{5b}$ ) (Scheme 4).

And lastly, unusual for diazocarbonyl compounds, the photochemical reaction with the retention of both N-atoms in the reaction products is probably initiated by a partial interconversion of the singlet diazo compound  ${}^1\mathbf{1a}^*$  into a triplet one,  ${}^3\mathbf{1a}^*$ . The latter,



being essentially a biradical species, reacts with one of the H–C(2) bonds of THF by, ordinary for radicals, an ‘abstraction–recombination’ mechanism, and as the final product of this reaction, triplet intermediate  $^3\mathbf{1a}^*$  gives the C–H-insertion product, *i.e.*, hydrazone  $\mathbf{3a}$  (or  $\mathbf{3b}$ ) (Scheme 4)<sup>4</sup>.

2.4. *Conclusions.* Thus, the main direction of the photolysis of the regioisomeric diazo ketones  $\mathbf{1a}$  and  $\mathbf{1b}$  is the *Wolff* rearrangement, while competitive photochemical processes, which give rise to the formation of C–H-insertion products  $\mathbf{3a,b}$ , 1,2-shift products  $\mathbf{4a,b}$ , as well as reduction products  $\mathbf{5a,b}$  occur to a much lower degree. The ratio of similar reaction products from both regioisomers is essentially independent of their structure. The *Wolff* rearrangement of the isomeric diazodihydrofuran-3(2*H*)-ones  $\mathbf{1a,b}$  apparently proceeds as a concerted process, whereas the appearance of the 1,2-shift and reduction products in the reaction mixture indicates that during photolysis, a parallel formation of singlet and triplet carbenes occurs.

This comparison study of the photolysis of regioisomeric diazodihydrofuran-3(2*H*)-ones did not reveal a pronounced effect of the relative location of the Ph and diazo group to each other on the efficiency of the interaction of the excited diazo ketones with tetrahydrofuran, *i.e.*, on the stabilization of their excited states and, consequently, on the increasing of their lifetimes, which is necessary for accomplishing the bimolecular interactions.

Further studies focused on the elucidation of the genuine reasons of the significant difference in the photochemical behavior of tetramethyl- and tetraphenyl-substituted 3-diazodihydrofuran-3(2*H*)-ones are currently in progress.

#### Experimental Part

1. *General.* All reagents and solvents were used after recrystallization or distillation unless otherwise specified. TLC Monitoring: *Silufol-UV/VIS* 254 plates (Czechia); detection by UV light and  $\text{I}_2$ . Column chromatography (CC): neutral silica gel ( $\text{SiO}_2$ ; *Merck* 70–230 mesh or *Chemapol L 40/100*); eluting solvent optimized by TLC. M.p.: *Boetius* micro-melting-point apparatus; uncorrected. UV Spectra: *Specord M-40* in the range 200–500 nm; cell thickness 1.0 cm; concentration of solns.  $3 \cdot 10^{-4}$ – $6 \cdot 10^{-3}$  mol  $\text{l}^{-1}$ . IR Spectra: *Perkin-Elmer-Spectrum-One* (FT-IR) spectrophotometer or *Specord-IR-75* instrument; in KBr; in  $\text{cm}^{-1}$ .  $^1\text{H}$ - (300 MHz) and  $^{13}\text{C}$ -NMR ( $^1\text{H}$ -decoupled; 75.5 MHz) Spectra: *Bruker-AV-300* instrument; in  $\text{CDCl}_3$ ;  $\delta$  in ppm ( $\text{Me}_4\text{Si} = 0$  ppm), coupling constants  $J$  in Hz. CI-MS ( $\text{NH}_3$ ):

<sup>4</sup>) However, one cannot rule out an alternative possibility for the appearance of the triplet diazo compound  $^3\mathbf{1}^*$  in the reaction mixture, for example, *via* sensitization of the initial diazo ketone  $\mathbf{1}$  by one of the reaction products in the triplet excited state, followed by an insertion reaction of the formed  $^3\mathbf{1}^*$  with THF.

Finnigan-MAT-90 instrument; in  $m/z$  (rel. %). Elemental analyses were performed at the Department of Organic Chemistry, StPSU, and at the Institute of Organic Chemistry, University of Zürich.

2. *Regioisomeric Diazodihydrofuran-3(2H)-ons 1a and 1b*. 2.1. *4-Diazodihydro-2,2-dimethyl-5,5-diphenylfuran-3(2H)-one (1a)* was prepared by a diazo-transfer reaction [4][29] from dihydro-2,2-dimethyl-5,5-diphenylfuran-3(2H)-one [30] and 2,4,6-tris(isopropyl)benzenesulfonyl azide [31] according to [11]. Yield 66%. M.p. 92–93° [11]<sup>5)</sup>.

2.2. *4-Diazodihydro-5,5-dimethyl-2,2-diphenylfuran-3(2H)-one (1b)* was obtained from 5,5-dimethyl-2,2-diphenylfuran-3,4(2H,5H)-dione 4-hydrazone [11]. Yield 86%. M.p. 116–117° [11]<sup>5)</sup>.

3. *Photolysis of 4-Diazofuran-3(2H)-ons 1a and 1b: General Procedure (G. P.)*. Irradiation of diazo ketone **1a** or **1b** was carried out in a small (25 ml) quartz device with a Hanau S-81 medium-pressure mercury lamp (100–130 W) without any monocromatization of UV light (*i.e.*, with  $\lambda > 210$  nm) [8]. The soln. of **1a** or **1b** (1 g, 3.4 mmol) and a corresponding nucleophile (34 mmol) in freshly distilled THF (20 ml) was irradiated by UV light at 20–25° until complete consumption of **1** (TLC monitoring; usually 1.5–2 h). The solvent and nucleophile were removed at 25–35° *in vacuo* (initially at 10–15, then at 1–0.5 Torr). The reaction products were isolated from the solid residue by recrystallization or/and CC (light petroleum ether (40–65°)/Et<sub>2</sub>O in different ratio).

3.1. *Photochemical Reactions of 1a*. 3.1.1. *In the Presence of H<sub>2</sub>O*. A soln. of **1a** (1 g; 3.4 mmol) in THF (20 ml) and H<sub>2</sub>O (0.6 g, 34 mmol) was irradiated for 2 h according to the *G. P.* To separate the main portion of **2a**, the solid mixture was recrystallized from petroleum ether. The residue from the mother liquid was subjected to CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 50:1 → 10:1): 0.48 g (overall yield 49%, including preliminary crystallization) of **2a**, 0.078 g (6%) of **3a**, 0.018 g (2%) of **4a**, and 0.056 g (6%) of **5a**.

3.1.2. *In the Presence of MeOH*. Irradiation of **1a** (1 g, 3.4 mmol) in THF (20 ml) and MeOH (1.1 g, 34 mmol) according to the *G. P.* for 2 h, followed by CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 100:1 → 5:1) provided 0.49 g (49%) of **2b**, 0.172 g (14%) of **3a**, 0.027 g (3%) of **4a**, and 0.094 g (10.5%) of **5a**.

3.1.3. *In the Presence of Me<sub>2</sub>NH*. Irradiation of **1a** (1 g, 3.4 mmol) in THF (20 ml) and Me<sub>2</sub>NH (1.5 g, 34 mmol) for 2 h according to the *G. P.* followed by usual workup and CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 50:1 → 1:1) provided 0.50 g (48%) of **2c**, 0.0012 g (1%) of **3a**, 0.027 g (3%) of **4a**, and 0.09 g (10%) of **5a**.

3.2. *Photochemical Reactions of 1b*. 3.2.1. *In the Presence of H<sub>2</sub>O*. A soln. of **1b** (1 g, 3.4 mmol) in THF (20 ml) and H<sub>2</sub>O (0.6 g, 34 mmol) was irradiated for 2 h according to the *G. P.* The main portion of **2a** was separated by recrystallization from petroleum ether, and the residue from the mother liquid was subjected to CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 6:1 → 3:1): 0.59 g (overall yield 62%, including preliminary crystallization) of **2a**, 0.03 g (2%) of **3b**, 0.02 g (2%) of **4b**, and 0.04 g (4%) of **5b**.

3.2.2. *In the Presence of MeOH*. Irradiation of **1b** (1 g, 3.4 mmol) in THF (20 ml) and MeOH (1.1 g, 34 mmol) for 2 h according to the *G. P.* followed by CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 100:1 → 5:1) provided 0.46 g (46%) of **2b**, 0.07 g (6%) of **3b**, 0.06 g (7%) of **4b**, and 0.05 g (5.5%) of **5b**.

3.2.3. *In the Presence of Me<sub>2</sub>NH*. Irradiation of **1b** (1 g, 3.4 mmol) in THF (20 ml) and Me<sub>2</sub>NH (1.5 g, 34 mmol) for 2 h according to the *G. P.* followed by usual workup and CC (SiO<sub>2</sub>, petroleum ether/Et<sub>2</sub>O 20:1 → 1:1) provided 0.54 g (51%) of **2c**, 0.006 g (0.5%) of **3b**, 0.07 g (8%) of **4b**, and 0.18 g (14%) of **5b**.

*2,2-Dimethyl-4,4-diphenyloxetane-3-carboxylic Acid (2a)*: Colorless solid. M.p. 185.5–186.5°. *R<sub>f</sub>* (petroleum ether/Et<sub>2</sub>O 5:1) 0.15. <sup>1</sup>H-NMR: 1.44 (*s*, Me); 1.61 (*s*, Me); 4.23 (*s*, CH); 7.09–7.50 (*m*, 10 arom. H). <sup>13</sup>C-NMR: 25.9 (Me); 32.5 (Me); 58.2 (CH); 80.8 (Me<sub>2</sub>C); 83.9 (Ph<sub>2</sub>C); 125.2, 126.5, 127.4, 127.5, 128.1, 128.7 (6 arom. CH); 142.9, 148.2 (2 arom. C); 174.6 (C=O). CI-MS: 282 (5.6, *M*<sup>+</sup>), 183 (69), 182 (100), 178 (5.6), 83 (12), 77 (47.5). Anal. calc. for C<sub>18</sub>H<sub>17</sub>O<sub>3</sub> (282.33): C 76.87, H 6.05; found: C 76.47, H 6.36.

*2,2-Dimethyl-4,4-diphenyloxetane-3-carboxylic Acid Methyl Ester (2b)*: Colorless solid. *R<sub>f</sub>* (petroleum ether/Et<sub>2</sub>O 10:1) 0.27. IR: 3200w, 3000w, 2955w, 2935w, 1740vs, 1710m, 1480m, 1440s, 1430s, 1365s, 1390w, 1222s, 1180m, 1150s, 1122s, 1450m, 990s, 960m, 865m, 730s. <sup>1</sup>H-NMR: 1.42 (*s*, Me); 1.66 (*s*, Me); 3.48 (*s*, MeO); 4.22 (*s*, CH); 7.10–7.51 (*m*, 10 arom. H). <sup>13</sup>C-NMR: 26.1 (Me); 32.6 (Me); 51.7 (MeO);

<sup>5)</sup> In [11], incorrect melting points of diazo ketones **1a** and **1b** were given.

58.2 (CH); 80.8 (Me<sub>2</sub>C); 83.8 (Ph<sub>2</sub>C); 125.4, 126.5, 127.4, 127.5, 128.2, 128.7 (6 arom. CH); 143.4, 148.4 (2 arom. C); 169.5 (C=O). Anal. calc. for C<sub>19</sub>H<sub>19</sub>O<sub>3</sub> (296.36): C 77.29, H 6.44; found: C 77.24, H 6.77.

*N,N*,2,2-Tetramethyl-4,4-diphenyloxetane-3-carboxamide (**2c**): Colorless solid. M.p. 117.5–119°. *R*<sub>f</sub> (petroleum ether/Et<sub>2</sub>O 3:1) 0.1. IR: 3040w, 3000w, 2940w, 2900w, 1650vs, 1480m, 1440m, 1370s, 1310w, 1250w, 990m, 720m, 690s. <sup>1</sup>H-NMR: 1.52 (s, Me); 1.54 (s, Me); 2.86 (s, MeN); 2.94 (s, MeN); 4.37 (s, CH); 7.16–7.49 (m, 10 arom. H). <sup>13</sup>C-NMR: 25.5 (Me); 31.6 (Me); 35.5, 37.4 (Me<sub>2</sub>N); 50.1 (CH); 80.9 (Me<sub>2</sub>C); 83.9 (Ph<sub>2</sub>C); 125.6, 126.1, 126.6, 127.1, 127.4, 128.2 (6 arom. CH); 143.2, 148.1 (2 arom. C); 168.1 (C=O). Anal. calc. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> (309.40): C 77.92, H 7.14, N 4.55; found: C 77.78, H 7.23, N 4.48.

2,2-Dimethyl-5,5-diphenylfuran-3,4(2H,5H)-dione 4-[2-(Tetrahydrofuran-2-yl)hydrazone] (**3a**): Colorless solid. M.p. 108–109°. *R*<sub>f</sub> (petroleum ether/Et<sub>2</sub>O 10:1) 0.16. <sup>1</sup>H-NMR: 1.26 (s, Me); 1.34 (s, Me); 1.81–2.25 (m, CH<sub>2</sub>CH<sub>2</sub>); 3.81–3.89 (m, CH<sub>2</sub>O); 5.37–5.43 (m, CHN); 7.19–7.49 (m, 10 arom. H); 11.60 (d, *J* = 6.5, NH). <sup>13</sup>C-NMR: 25.0 (CH<sub>2</sub>); 25.24, 25.27 (2 Me); 30.17 (CH<sub>2</sub>); 67.9 (CH<sub>2</sub>O); 80.7 (Me<sub>2</sub>C); 82.9 (Ph<sub>2</sub>C); 90.7 (CHN); 126.8, 126.9, 127.1, 127.1, 127.8, 127.9 (6 arom. CH); 135.2 (C=N); 145.5, 145.7 (2 arom. C); 200.2 (C=O). Anal. calc. for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub> (364.44): C 72.53, H 6.59, N 7.69; found: C 72.70, H 6.68, N 7.59.

2,2-Dimethyl-4,5-diphenylfuran-3(2H)-one (**4a**): Colorless solid. *R*<sub>f</sub> (petroleum ether/Et<sub>2</sub>O 10:1) 0.23. IR: 3020w, 3010w, 2970w, 2910w, 1680vs, 1600s, 1440m, 1370vs, 1230s, 1040s, 900m, 690vs. <sup>1</sup>H-NMR: 1.56 (s, 2 Me); 7.29–7.65 (m, 10 arom. H). <sup>13</sup>C-NMR: 23.4 (2 Me); 87.0 (Me<sub>2</sub>C); 113.4 (C(4)); 127.6, 128.03, 128.07, 128.4, 128.6, 129.6, 130.1, 131.8, (8 arom. C); 178.5 (C(5)); 205.4 (C=O). CI-MS: 264 (69, *M*<sup>+</sup>), 263 (20), 178 (100), 105 (18), 77 (16). Anal. calc. for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> (264.32): C 81.82, H 6.06; found: C 81.77, H 6.05.

Dihydro-2,2-dimethyl-5,5-diphenylfuran-3(2H)-one (**5a**): Colorless solid. M.p. 63–65°. *R*<sub>f</sub> (petroleum ether/Et<sub>2</sub>O 10:1) 0.38. <sup>1</sup>H-NMR: 1.21 (s, 2 Me); 3.32 (s, CH<sub>2</sub>); 7.20–7.42 (m, 10 arom. H). <sup>13</sup>C-NMR: 25.3 (2 Me); 48.1 (CH<sub>2</sub>); 81.4, 82.7 (Me<sub>2</sub>C, Ph<sub>2</sub>C); 126.0, 127.4, 128.3 (6 arom. CH); 146.1 (2 arom. C); 200.2 (C=O).

5,5-Dimethyl-2,2-diphenylfuran-3,4(2H,5H)-dione 4-[2-(Tetrahydrofuran-2-yl)hydrazone] (**3b**): Colorless solid. M.p. 79–80°. *R*<sub>f</sub> (petroleum ether/BuOMe 8:1) 0.22. <sup>1</sup>H-NMR: 1.45 (s, Me); 1.46 (s, Me); 1.89–2.33 (m, CH<sub>2</sub>CH<sub>2</sub>); 3.80–3.94 (m, CH<sub>2</sub>O); 5.39 (d, *J* = 6.5, CHN); 7.20–7.54 (m, 10 arom. H); 11.41 (d, *J* = 6.8, NH). CI-MS: 364 (9, *M*<sup>+</sup>), 183 (93), 182 (74), 105 (100), 84 (76), 77 (63).

4,5-Dimethyl-2,2-diphenylfuran-3(2H)-one (**4b**): Colorless solid. M.p. 110–110.5°. *R*<sub>f</sub> (petroleum ether/BuOMe 8:1) 0.27. IR: 3020w, 3005w, 2935w, 2900w, 2840w, 1930w, 1860w, 1700s, 1640vs, 1480m, 1440m, 1400s, 1340m, 1210s, 1080m, 980m, 690s, 660m, 610m. <sup>1</sup>H-NMR: 1.71 (s, Me); 2.32 (s, Me); 7.22–7.51 (m, 10 arom. H). <sup>13</sup>C-NMR: 6.30 (Me); 15.5 (Me); 91.3 (Ph<sub>2</sub>C); 110.2 (C(4)); 126.9, 128.6, 128.8, 139.1 (8 arom. C); 183.9 (C(5)); 203.1 (C=O). CI-MS: 264 (82, *M*<sup>+</sup>), 235 (72), 221 (100), 182 (87), 166 (50), 115 (13), 105 (52.6), 77 (28.9), 54 (21.1). Anal. calc. for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> (264.32): C 81.82, H 6.06; found: C 81.53, H 5.99.

Dihydro-5,5-dimethyl-2,2-diphenylfuran-3(2H)-one (**5b**): Colorless solid. M.p. 79–80°. *R*<sub>f</sub> (petroleum ether/BuOMe 8:1) 0.51. <sup>1</sup>H-NMR: 1.44 (s, 2 Me); 2.61 (s, CH<sub>2</sub>); 7.20–7.62 (m, 10 arom. H). <sup>13</sup>C-NMR: 29.7 (2 Me); 49.3 (CH<sub>2</sub>); 77.7, 86.8 (Me<sub>2</sub>C, Ph<sub>2</sub>C); 126.1, 127.4, 128.2, 128.3, 130.0, 132.4 (6 arom. CH); 137.6, 142.3 (2 arom. C); 196.7 (C=O). CI-MS: 266 (4.9, *M*<sup>+</sup>), 183 (47.3), 182 (31.6), 165 (4.9), 105 (100), 77 (44.7), 56 (7.0), 51 (19.6). Anal. calc. for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> (266.33): C 81.20, H 6.77; found: C 81.09, H 6.78.

## REFERENCES

- [1] W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2193.
- [2] H. Zollinger, 'Diazo Chemistry II. Aliphatic, Inorganic and Organometallic Compounds', Wiley-VCH, Weinheim, 1998.
- [3] G. B. Gill, in 'Comprehensive Organic Synthesis', Eds. B. V. Trost, I. Fleming, and G. Pattenden, Pergamon, Oxford, 1991, Vol. 3, p. 887.
- [4] M. Regitz, G. Maas, 'Diazo Compounds. Properties and Synthesis', Academic Press, New York, 1986.
- [5] H. Meier, K. P. Zeller, *Angew. Chem., Int. Ed.* **1975**, *14*, 32.
- [6] L. L. Rodina, I. K. Korobitsina, *Russ. Chem. Rev. (Engl. Transl.)* **1967**, *36*, 260.



- [7] I. K. Korobitsina, L. L. Rodina, *Zh. Org. Khim.* **1965**, *1*, 932 (*Chem. Abstr.* **1965**, *63*, 6939a); I. K. Korobitsina, L. L. Rodina, V. G. Shuvalova, *Zh. Org. Khim.* **1968**, *4*, 2016 (*Chem. Abstr.* **1969**, *70*, 28725j).
- [8] L. L. Rodina, V. L. Mishchenko, S. A. Malashikhin, M. Platz, V. A. Nikolaev, *Russ. J. Org. Chem.* **2003**, *39*, 1530.
- [9] W. Ando, 'Photochemistry of Diazonium and Diazo Groups', in 'The Chemistry of Diazonium and Diazo Groups', Ed. S. Patai, J. Wiley & Sons, Chichester–Toronto, 1978, Vol. 1, p. 366.
- [10] T. C. Celius, Y. Wang, J. P. Toscano, 'Photochemical Reactivity of  $\alpha$ -Diazocarbonyl Compounds', in 'CRC Handbook of Organic Photochemistry and Photobiology', 2nd edn., Eds. W. Hoorspool and F. Lenci, CRC Press, Boca Raton – New York, 2004, Sect. 90, pp. 1–16.
- [11] S. A. Malashikhin, A. Linden, H. Heimgartner, L. L. Rodina, V. A. Nikolaev, *Helv. Chim. Acta* **2008**, *91*, 1662.
- [12] N. A. Malashikhina, O. S. Galkina, S. A. Malashikhin, Thesis of the International Conference 'Chemistry of the Compounds with Multiple Carbon-Carbon Bonds', Saint-Petersburg, June 16–19, 2008, Book of Abstracts, p. 204.
- [13] S. Sorriso, 'Structural Chemistry', in 'The Chemistry of Diazonium and Diazo Groups', Ed. S. Patai, J. Wiley & Sons, Chichester–Toronto, 1978, Vol. 1, p. 113.
- [14] I. K. Korobitsina, O. P. Studzinsky, *Russ. Chem. Rev. (Engl. Transl.)* **1970**, *39*, 1754; V. A. Nikolaev, I. K. Korobitsina, *Zh. Org. Khim.* **1976**, *12*, 1244 (*Chem. Abstr.* **1976**, *85*, 158795c).
- [15] A. L. Fridman, T. S. Ismagilova, V. S. Zalesov, S. S. Novikov, *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 722.
- [16] I. G. Csizmadia, S. A. Houlden, O. Meresz, P. Yates, *Tetrahedron* **1969**, *25*, 2121.
- [17] A. Bogdanova, V. V. Popik, *J. Am. Chem. Soc.* **2003**, *125*, 1457; A. Bogdanova, V. V. Popik, *J. Am. Chem. Soc.* **2003**, *125*, 14158.
- [18] G. A. Jeffrey, 'An Introduction to Hydrogen Bonding', Oxford University Press, N. Y., 1997; C. G. Pimentel, A. L. McClellan, 'The Hydrogen Bond', Freeman, San Francisco, 1960.
- [19] G. R. Desiraju, T. Steiner, 'The Weak Hydrogen Bond in Structural Chemistry and Biology', Oxford University Press, Oxford, 1999.
- [20] I. J. Bellami, 'The Infra-Red Spectra of Complex Molecules', J. Wiley & Sons, London, 1963.
- [21] M. Jones, R. A. Moss, 'Carbenes', Wiley, New York, 1973; W. Kirmse, 'Carbene Chemistry', Academic Press, New York–London, 1964.
- [22] J. P. Toscano, *Adv. Carbene Chem.* **1998**, *2*, 215; W. Kirmse, *Adv. Carbene Chem.* **1994**, *1*, 39; G. B. Schuster, *Adv. Phys. Org. Chem.* **1986**, *23*, 311.
- [23] M. S. Platz, 'Observing Invisible Carbenes By Trapping Them with Pyridine', in 'Carbene Chemistry', Ed. G. Bertrand, Marcel Dekker Inc., New York, 2002, p. 27; J. E. Jackson, M. S. Platz, *Adv. Carbene Chem.* **1994**, *1*, 89.
- [24] J. Wang, G. Burdzinski, J. Kubicki, M. S. Platz, *J. Am. Chem. Soc.* **2008**, *130*, 11195; G. T. Burdzinski, J. Wang, T. L. Gustafson, M. S. Platz, *J. Am. Chem. Soc.* **2008**, *130*, 3746, and refs. cit. therein.
- [25] T. T. Tidwell, 'Ketenes', J. Wiley & Sons, New York–Singapore, 1995.
- [26] A. Nickon, F. Huang, R. Wiglein, *J. Am. Chem. Soc.* **1974**, *96*, 5264; J. A. Altman, J. G. Chizmadia, P. Yates, *J. Am. Chem. Soc.* **1975**, *97*, 5217.
- [27] V. A. Nikolaev, V. V. Popik, *Tetrahedron Lett.* **1992**, *33*, 4483.
- [28] R. J. McMahon, O. L. Chapman, R. A. Hayes, T. C. Hess, H.-P. Krimmer, *J. Am. Chem. Soc.* **1985**, *107*, 7597.
- [29] M. P. Doyle, M. A. McKervey, T. Ye, 'Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: from Cyclopropanes to Ylides', J. Wiley & Sons, New York, 1998.
- [30] Yu. S. Zal'kind, E. D. Venus-Danilova, V. I. Ryabtseva, *Zh. Obshch. Khim.* **1950**, *20*, 2222 (*Chem. Abstr.* **1951**, *45*, 41391).
- [31] 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. A. Paquette, Wiley, New York, 1995, Vol. 7, p. 5174.

Received March 9, 2009