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Transformations of S-substituted 5,7-dimethyl-4a,5a-diphenyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-2-ones under treatment of 1,2-benzoquinones and photochemical properties of reaction products

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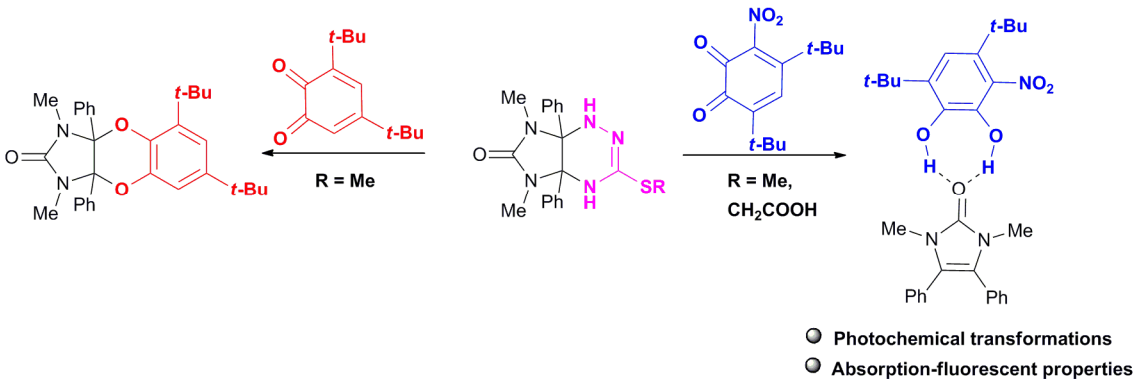

- Photochemical transformations
- Absorption-fluorescent properties

Transformations of S-substituted 5,7-dimethyl-4a,5a-diphenyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-2-ones under treatment of 1,2-benzoquinones and photochemical properties of reaction products

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For the first time 5,7-di-*tert*-butyl-1,3-dimethyl-3a,9a-diphenyl-3,3a-dihydro-1*H*-benzo[5,6][1,4]dioxino[2,3-*d*]imidazol-2(9a*H*)-one **13** and complex **9** of 4,6-di-*tert*-butyl-3-nitrobenzene-1,2-diol with 1,3-dimethyl-4,5-diphenyl-1*H*-imidazol-2(3*H*)-one **10a** were prepared by the reactions of 3-alkylthio-5,7-dimethyl-4a,7a-diphenyl-4a,5,7,7a-tetrahydro-1*H*-imidazo[4,5-e]-1,2,4-triazin-6(4*H*)-ones with 3,5-di-*tert*-butyl-1,2-benzoquinone **1** and 4,6-di-*tert*-butyl-3-nitro-1,2-benzoquinone **2**, respectively. Photochemical transformations of compounds **9** and **10a** as well as products of its photooxygenation involving singlet oxygen under UV irradiation: urea **16**, isomeric 1,3-dimethyl-4,5-diphenylimidazolidin-2-ones **17** and **17`**, and compound **18** were studied by the spectral-kinetic method. Data on the absorption and fluorescence properties of synthesized compounds and their photoproducts were obtained.

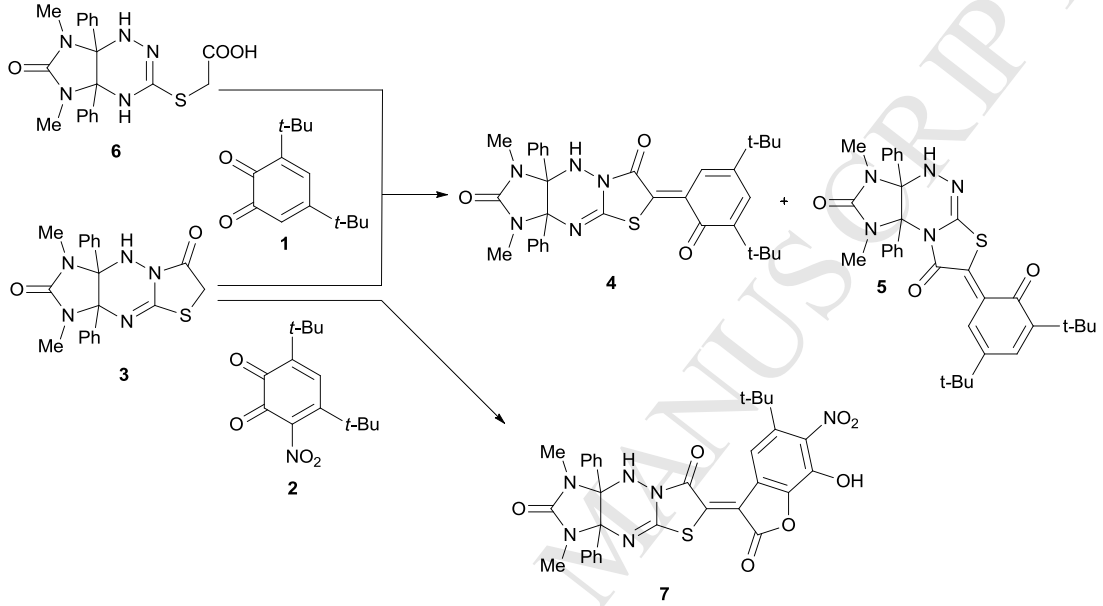
Keywords

1,2-benzoquinones, S-substituted 5,7-dimethyl-4a,5a-diphenyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-2-ones; photochemical transformations; 5,7-di-*tert*-butyl-1,3-dimethyl-3a,9a-diphenyl-3,3a-dihydro-1*H*-benzo[5,6][1,4]dioxino[2,3-*d*]imidazol-2(9a*H*)-one; 1,3-dimethyl-4,5-diphenyl-1,3-dihydro-2*H*-imidazol-2-one

Introduction

It is known that the reactivity of spatially hindered quinoid compounds is quite diverse and depends on their structure. Reactions of sterically hindered 1,2-benzoquinones with heterocycles containing a reactive methylene group at the ring or in a substituent do not stop at in nucleophilic addition products as they are unstable and readily undergo various further reactions.[1-3] For example, we have recently found that 3,5-di-*tert*-butyl-1,2-benzoquinone (benzoquinone) **1** and

4,6-di-*tert*-butyl-3-nitro-1,2-benzoquinone (nitrobenzoquinone) **2** react with imidazothiazolotriazine **3** in different ways (Scheme 1).[1,2] Benzoquinone **1** is subjected to aldol-crotonic condensation with compound **3** to give adduct **4**, which rearranges to isomer **5** under the reaction conditions.[1] Similar transformations occur in the reaction of benzoquinone **1** with (imidazotriazin-3-ylthio)acetic acid **6.** However, in the reaction with nitrobenzoquinone **2**, nucleophilic 1,4-addition of the methylene-active group of compound **3** initiates a cascade process resulted in an unusual polyheterocyclic compound **7**.[2]



Scheme 1 Condensation of benzoquinone **1** and nitrobenzoquinone **2** with tricyclic structure **3**.

In this work we have studied the reactions of 1,2-benzoquinones **1** and **2** with S-substituted 5,7-dimethyl-4a,7a-diphenyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-2-ones ((imidazotriazin-3-ylthio)acetic acid **6** and 3-methylthioimidazotriazine **8**) which lead to tricyclic product containing annulated imidazolidine, dioxane and benzene moieties and complex **9** comprising 1,3-dimethyl-4,5-diphenyl-1,3-dihydro-2*H*-imidazol-2-one (imidazolinone) and 4,6-di-*tert*-butyl-3-nitrobenzene-1,2-diol. The photochemical transformations and absorption-fluorescent properties of imidazolinone alone and in the complex **9,** as well as compounds synthesized from imidazolinone by photooxygenation involving singlet oxygen under UV irradiation were investigated by a spectral-kinetic method for the first time.

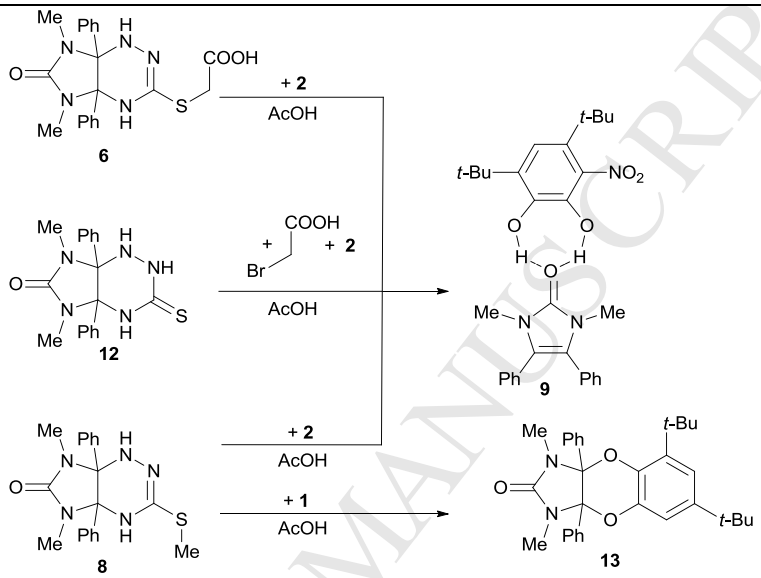
Results and discussion

Synthesis

Since acid **6** has not been used in the interaction with nitrobenzoquinone **2** we studied this reaction both under conditions of aldol-crotonic condensation of compound **3** with benzoquinone

1 (60 °C, 5 h, AcOH)[1] and under conditions of mentioned above polyheterocycle **7** formation (7 days at 20 °C, AcOH)[2] (Table 1, entries 2 and 7, respectively). However, we obtained complex **9** consisting of known 1,3-dimethyl-4,5-diphenyl-1,3-dihydro-2*H*-imidazol-2-one (imidazolinone) **10a**[4-7] and 4,6-di-*tert*-butyl-3-nitrobenzene-1,2-diol **11**[8] instead of expected polycycle **7** or analogues of compounds **4** and **5**. The structure of cocrystal **9** was confirmed by X-ray single crystal analysis (see X-Ray structural investigation).

Table 1 Synthesis of complex **9** and compound **13**.



Entries	Reagents	T, °C	Reaction time	Product (Yield, %)
1	**6**, **2**	60	2 h	**9** (38%)
2	**6**, **2**	60	5 h	**9** (30%)
3	**6**, **2**	70*	2 h*	**9** (40%)
4	**6**, **2**	70	5 h	**9** (26%)
5	**6**, **2**	20**	2 d**	**9** (70%)
6	**6**, **2**	20	5 d	**9** (52%)
7	**6**, **2**	20	7 d	**9** (35%)
8	**8**, **2**	70*	2 h*	**9** (74%)
9	**8**, **2**	20**	2 d**	**9** (95%)
10	**12**, **2**, $BrCH_2COOH$	70*	2 h*	**9** (18%)
11	**12**, **2**, $BrCH_2COOH$	20**	2 d**	**9** (32%)
12	**8**, **1**	70*	2 h*	**13** (25%)

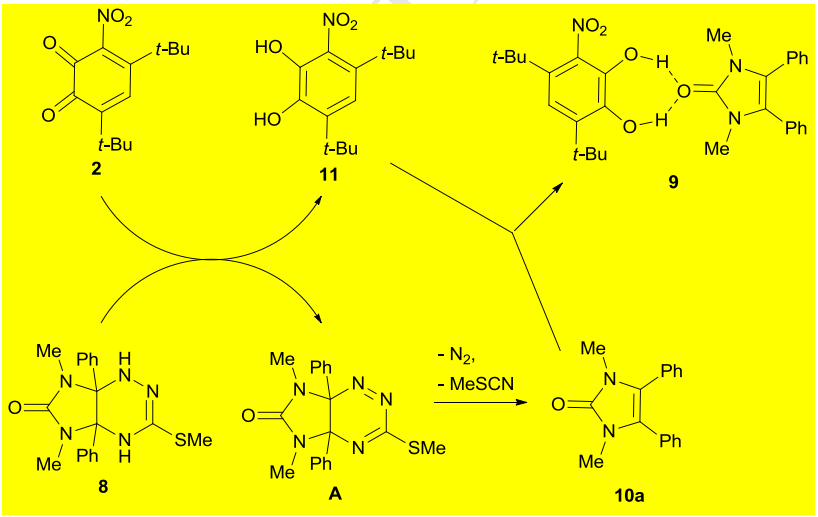
* - Conditions **A**: Solution of **2** (0.53 g, 2 mmol) and **6** (0.82 g , 2 mmol) in 10 mL of AcOH was heated at 70 ºC and stirred for 2 h.

** - Conditions **B**: Solution of **2** (0.53 g, 2 mmol) and **8** (0.73 g, 2 mmol) in 10 ml of AcOH was stirred at 20 ºC for 2 days.

The yield of complex **9** was 30-35%. We varied conditions of the experiment: keeping the reaction mixture for 2-5 h at 60 °C or 70 °C or for 2-7 days at 20 °C. However, the main product of the reaction was only complex **9** the highest yields of which (40% and 70%) were obtained upon keeping reagents **2** and **6** at 70 °C for 2 h (conditions **A**) and for 2 days at 20 °C (conditions **B**), respectively.

Interesting, that nitrobenzoquinone **2** reacts with 3-methylthioimidazotriazine **8** in a similar manner. Complex **9** is formed in 74% and 95% yields on keeping the reaction mixture under conditions **A** and **B**, respectively. The presence of a substituent at the sulfur atom is a prerequisite since imidazotriazine **12** does not react with nitrobenzoquinone **2**. However, complex **9** is formed in 18% (conditions A) and 32% yield (conditions B) under three-component condensation conditions upon addition of bromoacetic acid as an alkylating reagent to a mixture of compounds **12** and **2**.

The study of the reaction of benzoquinone **1** with 3-methylthioimidazotriazine **8** (Scheme 2, conditions **A**) gave other result. 5,7-Di-*tert*-butyl-1,3-dimethyl-3a,9a-diphenyl-3,3a-dihydro-1*H*-benzo[5,6][1,4]dioxino[2,3-*d*]imidazol-2(9a*H*)-one **13** was the main reaction product. The structure of compound **13** was confirmed by ^{1}H and ^{13}C NMR spectra and high resolution mass spectra. We assumed that compound **13** could be the product of the hetero-Diels-Alder reaction of imidazolinone **10a** formed under reaction conditions and benzoquinone **1**. However, previously prepared imidazolinone **10a** and benzoquinone **1** do not react under conditions **A** and were isolated unchanged. Based on the results obtained we proposed the following path of the formation of complex **9** and compound **13** depicted in Schemes 2 and 3, respectively.

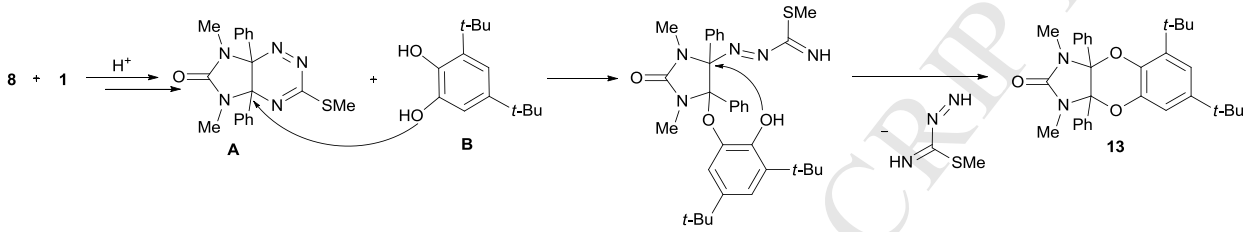


Scheme 2 Pathway of complex **9** formation

Probably, redox reaction of nitrobenzoquinone **2** with methylthioimidazotriazine **8** leads to 4,6-di-*tert*-butyl-3-nitrobenzene-1,2-diol **11** and 5,7-dimethyl-3-methylthio-4a,7a-diphenyl-

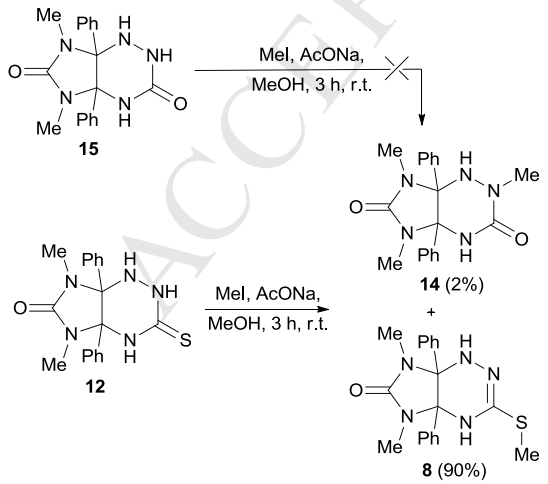
7,7a-dihydro-4a*H*-imidazo[4,5-*e*]-1,2,4-triazin-6(5*H*)-one (**A**). The latter undergoes opening of the triazine ring to give imidazolinone **10a**, methylthiocyanate and nitrogen molecule (Scheme 2).

Benzoquinone **1** is reduced into 3,5-di-*tert*-butylbenzene-1,2-diol **B** analogously to nitrobenzoquinone **2**. Apparently, pyrocatechol **B** as more nucleophilic agent than its nitroanalogue **11** react with intermediate **A** to give the substitution product **13** (Scheme 3).



Scheme 3 Pathway of compound **13** formation

A synthesis of hitherto unreported methylthioimidazotriazine **8** was performed in 90% yield by S-methylation of imidazotriazine **12** with methyl iodide under standard methylation conditions (Scheme 4).[9] Furthermore, the N-methylation product **14**, in which the sulfur atom is replaced by an oxygen atom, was isolated in 2% yield (Scheme 4). X-Ray single crystal diffraction was used to confirm the structure of the hitherto unknown compound **14** (see X-Ray structural investigation). It is interesting that imidazotriazine **15** do not undergo alkylation with MeI in the same conditions. Only starting compound **15** is isolated from reaction mixture.



Scheme 4 Synthesis of methylimidazotriazines **8** and **14**.

Spectral-kinetic and photochemical study

We have found that solutions of complex **9** in CD_3CN, $CDCl_3$ and DMSO-d_6 manifest fluorescent properties. This phenomenon can be explained by the presence of compound **10a** in complex **9**. Previously compound **10a** was characterized only by the maximum of the absorption band.[6] To confirm that the fluorescent properties of complex **9** belong to imidazolinone **10a**, we were the first to study the photochemical transformations of complex **9** and imidazolinone **10a** (Fig.1-3, Table 1).

It has been found by the spectral-kinetic method that complex **9** in MeCN is characterized by an absorption band with two maxima at 279 and 304 nm (Fig. 1, curve 1; Table 2) and a fluorescence band with a maximum at 420 nm (Fig. 1, curve 5, Table 2), which belongs to this particular compound, as follows from the match between the absorption and fluorescence excitation spectra (Fig. 1, curve 6).

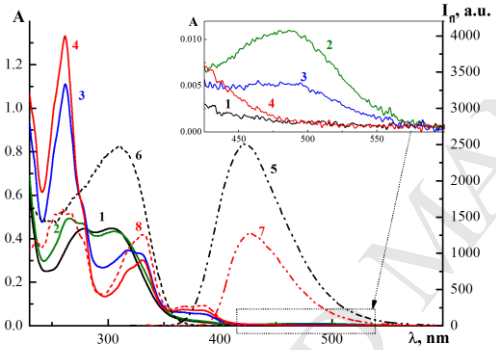


Fig 1 Absorption spectra (curves 1-4) (solid), fluorescence excitation spectra measured at a wavelength of 428 nm (curves 6,8) (short dash) and fluorescence spectra with excitation with a wavelength of 312 nm (curve 5) and 331 nm (curve 7) (dash dot dot) of complex **9** in MeCN before irradiation (curves 1,5,6), in the beginning (curves 2,3) and after UV irradiation (curves 4,7,8). The working solution concentration is C = $4x10^{-5}$ M. The cell thickness is 10 mm. The inset demonstrates a magnified part of the absorption spectra in the spectral region of 420-540 nm.

Table 2 Spectral, fluorescent and kinetic characteristics of the samples synthesized

Sample	Solvent	λ^0, nm	ε, $M^{-1}.cm^{-1}$	λ^{30}, nm (ΔD^{30})	λ_{flu}, nm	I^0_{flu}, a.u.	I^{30}_{flu}, a.u.	λ^{30}_{flu}, nm (I^{30}_{sh},a.u.)
9	MeCN	279 304	11175 11200	262(1.3), 330(0.3), 367(<0,1), 383(<0,1)	420	2500	1200	427(1280)
	C_6H_{14}	316	2700	262(0,2), 322(<0,1), 336(0,1), 375(<0,1), 393(<0,1)	412	380	320	399(400), 421(360)

10a	MeCN	304	13825	261(1,4), 330(0,2), 382(<0,1)	425	2750	590	425
18	MeCN	261 330 384	72000 16900 3100	261(2,4) 330(0,5) 384(0,1)	417	2070	1895	417
Смесь **17+17'**	MeCN	258	618	258(0,3) 329(<0,1)	313 423	32 68	30 133	313 423
17*	MeCN	257	425	-	315	28	27	315
17**	MeCN	257	350	-	313	23	22	313
16	MeCN	236	18975	-	0	0	0	0

Note: λ^0 and λ^{30} are the wavelengths of the absorption bands before and after irradiation for 30 min, respectively; ΔD^{30} is the optical density change at the absorption band maximum upon UV irradiation for 30 min; ε is the molar extinction coefficient at the absorption band maximum of the original form; λ_{flu} and λ^{30}_{flu} are the wavelengths of the fluorescence band maxima before and after UV irradiation for 30 min, respectively; I^0_{flu}, I^{30}_{flu} and I^{30}_{sh} are the fluorescence intensities at the band maximum before and after UV irradiation for 30 min, without and with a shift of the fluorescence band maximum, respectively.
* - the major isomer isolated from the (**17** + **17`**) mixture.
** - isomer **17** synthesized by the known procedure.[10]

Under UV irradiation, complex **9** undergoes irreversible photochemical transformations that manifest themselves as changes in the absorption spectra (Fig. 1, curves 2-4) and fluorescence spectra (Fig. 1, curve 7). The final photoproduct is characterized by a few absorption bands located in the short-wave (at 262 and 330 nm) and long-wave (at 390 nm) regions of the UV spectral range. In this case an intermediate short-living photoproduct **10`a** appears. It absorbs in the visible region of the spectrum with a maximum at 487 nm (Fig. 1, inset; Table 3). It disappears during UV irradiation of the solution, as indicated by the photo-induced spectral changes (Fig. 1, inset), as well as in the dark (Table 3). The nature of these changes will be the subject of our further studies.

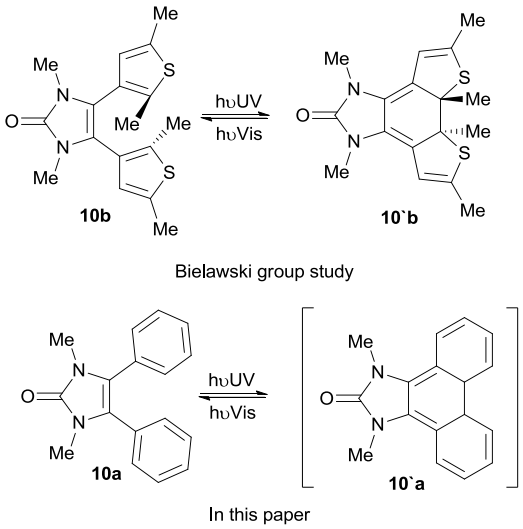
Table 3 Spectral-kinetic properties of the short-living photoinduced absorption band of samples **9** and **10a** in acetonitrile.

Sample	λ, нм	D_{max}	τ, с
9	487	0.011	60
10a	480	0.017	80

Note: λ is the wavelength of the absorption band maximum of the short-living photoproduct; D_{max} is the maximum optical density at the absorption band maximum of the short-living photoproduct; τ is the life time of the short-living photoinduced absorption band.

Based on the data obtained by the Bieławski group[11] during the studies of the photochemical properties of compound **10b,** we could assume a structure of short-living photo-induced intermediate **10`a** (Scheme 5). Analogous product **10'b** obtained under UV irradiation

of the compound **10b** solution in acetonitrile was characterized with absorption maximum at 476 nm.



Scheme 5 A known product **10'b** obtained under UV irradiation of the compound **10b** (Bielawski group study) and proposed structure of the short-living photoinduced intermediate **10`a**.

Similar photochemical transformations of complex **9** are also observed in C_6H_{14}. Unlike the spectra in polar acetonitrile, both absorption spectra and the fluorescence spectra of the final photoproduct manifest an electronic vibrational structure in non-polar hexane (Fig. 2).

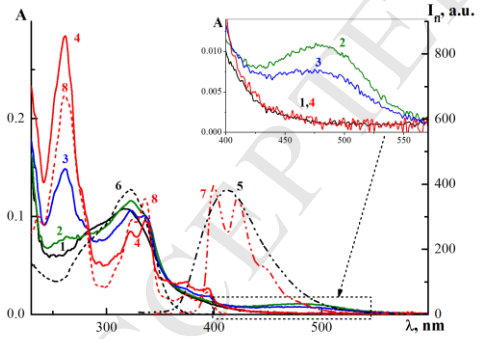


Fig. 2 Absorption spectra (curves 1-4) (solid), fluorescence excitation spectra measured at a wavelength of 412 nm (curve 6) and 421 nm (curve 8) (short dash), and fluorescence spectra with excitation by light with a wavelength of 323 nm (curve 5) and 336 nm (curve 7) (dash dot dot) of complex **9** in hexane before (curves 1,5,6), at the beginning (curves 2,3), and after UV irradiation (curves 4,7,8). The working solution concentration is $C = 4x10^{-5}$ M. The cell thickness is 10 mm. The inset shows a magnified part of the absorption spectra.

Comparison of the photoinduced spectral changes of samples **9** (Fig. 1) and **10a** (Fig. 3) in MeCN indicate that the photochemical transformations of these compounds, including those

with involvement of the short-living intermediate photoproduct that absorbs in the visible region, are identical (Table 2).

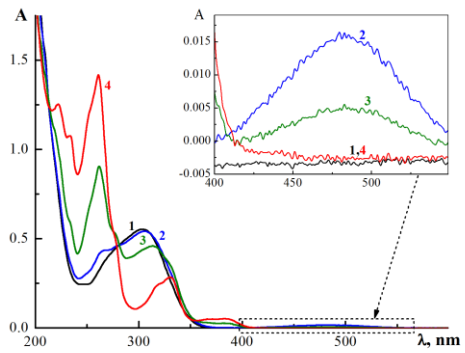


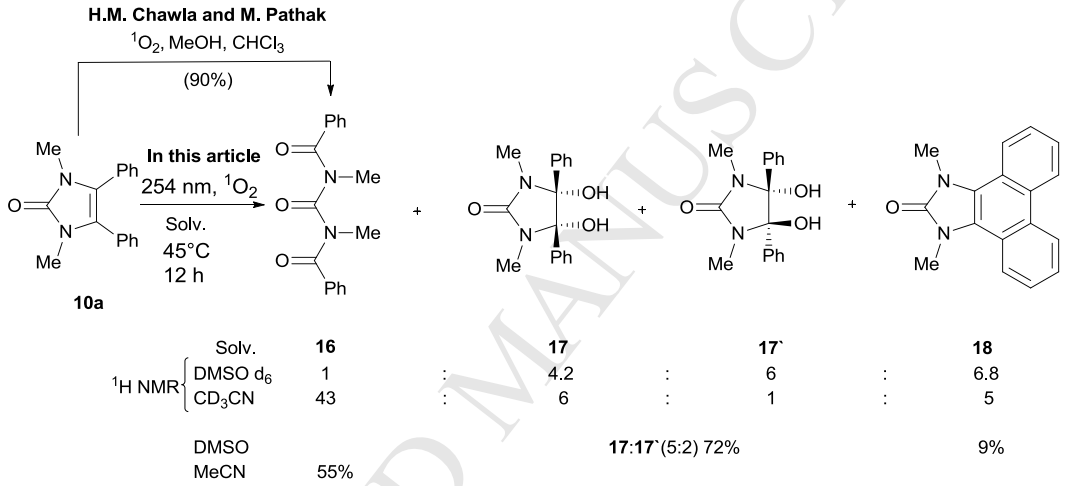
Fig. 3 Absorption spectra (curves 1-4) of a solution of compound **10a** in MeCN before (curve 1), in the beginning (curves 2,3) and after UV irradiation (curve 4). The working solution concentration is C = $2x10^{-4}$ M. The cell thickness is 2 mm. The inset shows a magnified part of the absorption spectra.

The reversibility of the photoinduced transformations of compounds **10a** and **10'a** is confirmed by the results of kinetic studies according to which the short-serving photoconductive photoproduct **10'a** undergoes reversible conversion to compound **10a** both in the dark and under the action of visible light (Fig ... S).

To establish the structure of products of irreversible photochemical transformations of compound **10a** we synthesized these products and studied their photochemical properties. Previously H.M. Chawla and M. Pathak[5] investigated dye sensitized photooxigenation of imidazolidine-2-ones and showed that the oxidation of imidazolinone **10a** with singlet oxygen generated by UV irradiation in the presence of methylene blue gave 1,3-dibenzoyl-1,3-dimethylurea **16** (Scheme 6). We found that not only urea **16** is a product of oxidation of compound **10a** with singlet oxygen generated from the oxygen in the air by UV irradiation. The other products of this reaction are mesoform (4*S*,5*R*)-4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidin-2-one **17**,[10] racemic (4*R*,5*R*)-4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidin-2-one **17`**[10] and 1,3-dimethyl-1*H*-phenanthro[9,10-*d*]imidazol-2(3*H*)-one **18**. The formation of compounds **17**, **17`** and **18** under the action of singlet oxygen generated by UV irradiation was not reported before. These processes do not occur without access of oxygen.

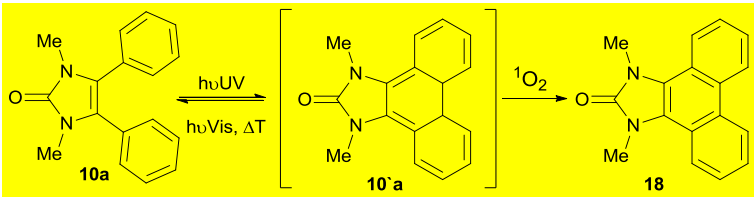
We noted that after UV irradiation of solution of compounds **10a** for 12 h in NMR ampoules (DMSO-d_6 or CD_3CN) the signal of 2 Me (6 H) is disappeared and the ratio of products **16**-**18** changed depending on the solvent used. The ratio of compounds **16** : **17**+**17`** : **18** was determined by integral intensity of signals of Me groups in ^{1}H NMR spectra. In DMSO-d_6 the singlet of 2 Me (6 H) of urea **16** is located at 2.94 ppm; the singlet of 4 Me (12 H) of isomers **17**

and **17`** is located at 2.61 ppm; the singlet of 2 Me (6 H) of hitherto unknown compound **18** is located at 3.84 ppm. The ratio of compounds **17** : **17`** was determined by integral intensity of signals of Ph group protons. For compounds **17** and **17`**, multiplets of Ph group protons are located at 6.85-7.07 ppm (for **17**) and 7.15-7.39 ppm (for **17`**). Therefore, the ratio of compounds **16** : **17** : **17`** : **18** is 1 : 4.2 : 6 : 6.8. In $CD_3CN$ the ratio of compounds **16** : **17** : **17`** : **18** is 43 : 6 : 1 : 5. To prepare compounds **16**,**17+17`** and **18**, the oxidation of 1 g of compound **10** in DMSO or MeCN was carried out. A mixture of isomeric diols **17** : **17`** (5 : 2, 0.85 g, 72%) and compound **18** (0.09 g, 9%) was obtained when using DMSO. Urea **16** (0.31 g, 55%) was synthesized in MeCN.



Scheme 6 Photooxygenation of imidazolinone **10a**

Apparently, the unexpected formation of compound **18** under the UV irradiation can be explained by the formation of a short-living intermediate **10 `a**, which is then oxidized by singlet oxygen (Scheme 7).



Scheme 7 The proposed mechanism of the formation of compound **18**.

Comparative absorption-fluorescent studies of samples **9** and **10a** have shown that compound **18** is the final photoproduct (Fig. 4, Table 1).

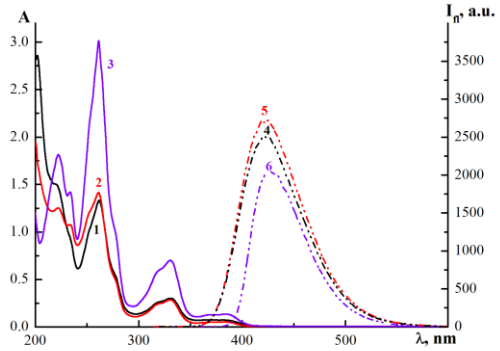


Fig. 4 Absorption spectra (curves 1-3) (solid) and fluorescence spectra upon excitation with light with a wavelength of 312 nm (curve 4), 310 nm (curve 5) and 331 nm (curve 6) (dash dot dot) of compound **18** (curves 3,6) and of the photoproducts of samples **9** (curves 1,4) and **10a** (curves 2,5) in MeCN.

In turn, the compound **18** undergoes irreversible transformations into a photoproduct absorbing in the spectral field 400-450 nm (Fig. 5). This is evidenced by a decrease in the intensity of the absorption and fluorescence bands of the compound **18** and the appearance of absorption bands (Fig. 5, curves 5, 6) and fluorescence (Fig. 5, curves 7.8) of the photoproduct.

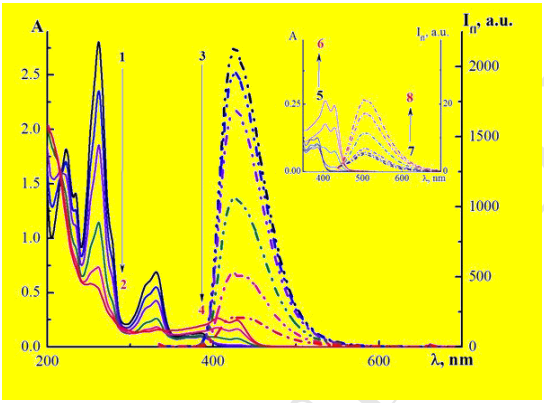


Fig. 5 Absorption spectra (curves 1,2,5,6), fluorescence spectra (3,4,7,8) upon excitation with light with a wavelength 331 nm (3,4) and 429 nm (7,8) of compound **18** in MeCN before irradiation (curves 1,3,5,7), upon an increase in exposure under UV light (curve 2,4,6,8). The working solution concentration is C = $4x10^{-5}$ M. The cell thickness is 10 mm.

Photoinduced spectrum changes were also observed for the isomer mixture **17**+**17`**(ratio 100 : 6.8) in MeCN (Fig. 6). The mixture of compounds **17**+**17`** in MeCN is characterized by an absorption spectrum with a maximum at 258 nm and a shoulder around 300-350 nm, as well as a fluorescence spectrum with maxima at 320 and 422 nm. After UV irradiation, a new band with a maximum at 335 nm appears in the absorption spectrum, while the intensity of the fluorescence band increases. One can see from Fig. 6 that UV irradiation resulted not only in absorption spectrum changes but also in photoinduced changes in the fluorescence excitation spectra and an

increase in fluorescence intensity at 423 nm. The intensity of the second short-wave fluorescence band remained invariable.

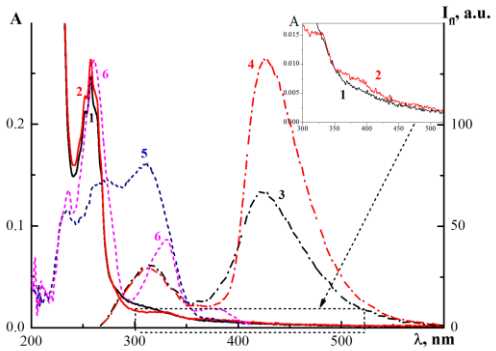


Fig. 6 Absorption spectra (curves 1,2) (solid), fluorescence excitation spectra measured at a wavelength of 424 nm (curves 5,6) (short dash) and fluorescence spectra with excitation by light with a wavelength of 258 nm (curve 3) and 261 nm (curve 4) (dash dot) for a mixture of compounds **17**+**17`** (ratio 100 : 6.8) in MeCN before (curves 1,3,5) and after UV irradiation (curves 2,4,6). The working solution concentration is C = $4x10^{-4}$ M. The cell thickness is 10 mm. The inset shows a magnified part of the absorption spectra.

Isomer **17** isolated from the mixture and synthesized by a reported procedure[10] is characterized by only one absorption band with a maximum at 258 nm and only one fluorescence band at 315 nm (Fig. 7). The fluorescence excitation spectrum indicates that the observed fluorescence is due only to the compound that absorbs at 258 nm, *i.e.*, isomer **17** in the **17**+**17`** mixture is photochemically stable, since the absorption and fluorescence spectra remain almost unchanged under UV irradiation. The photochemical transformations of this mixture are due to the second component, **17`**. However, the observed photochemical transformations with photoinduced changes in the absorption and fluorescence spectra cannot be due to the formation of a photoproduct with urea **17** structure (Table 1). Like in the case of compounds **9** and **10a**, insignificant changes were observed only in the visible spectral range (Fig. 7, inset).

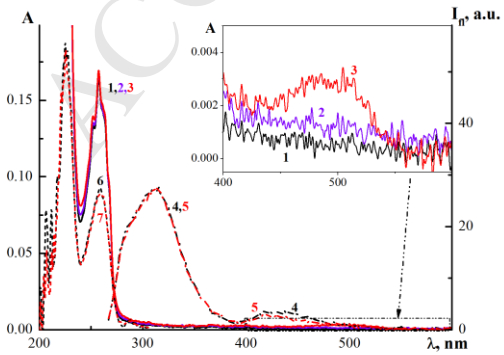


Fig. 7 Absorption spectra (curves 1,2,3) (solid), fluorescence excitation spectra measured at a wavelength of 315 nm (curves 6,7) (short dash), and fluorescence spectra with excitation with a

wavelength of 258 nm (curves 4,5) (dash dot) of isolated compound **17** in MeCN before (curves 1,4,6) and in 30 min (curve 2) or 60 min (curves 3,5,7) of UV irradiation. The working solution concentration is C = $4x10^{-4}$ M. The cell thickness is 10 mm.

X-Ray structural investigation

Molecules **14**, **16** and cocrystal **9** were studied by X-ray diffraction. Experimental details and crystallographic data are provided in Supporting Information.

The geometry of molecule **14** in crystal (Fig. 8) is very close to that in similar imidazotriazines.[12-14] The conformation of five-membered heterocyclic ring is close to an envelope with deviation of atom C(1) by 0.176 Å, whereas the conformation of six-membered ring is a distorted boat with atoms N(1) and N(3) deviating from the average plane C(1)-C(2)-N(2)-C(3) by 0.345 and 0.590 Å, respectively. Nitrogen atoms N(1), N(2), N(3) and N(5) are piramidalized with sum of CNN, CNC and CNH angles equal to 352.92, 357.18, 324.15 and 355.31°, respectively. The mutual disposition of the phenyl substituents is a cisoid one with the torsion angle C(5)C(1)C(3)C(11) of 8.71(15)° that lead to a shortened intramolecular contact C(5)···C(11) [2.858(2) Å]. Molecules of **14** in crystal are connected in centrosymmetric homodimers *via* N(1)–H(1N)···O(1) bonds [N···O 2.8886(15) Å; NHO 172.5(18)°], which in turn are assembled into infinite chains *via* N(3)–H(3N)···O(2) bonds [N···O 2.9100(16) Å; NHO 156.3(16)°].

Compound **16** crystallizes in C2/c space group, the molecule is symmetric with atoms O(1) and C(1) located on a twofold axis. Atom N(1) is perfectly planar with sum of angles equal to 360°. The torsion O(1)-C(1)···C(2)-O(2) equal to 78.66(16)° lead to a screwed conformation of the central molecular fragment.

Crystal **9** was obtained by crystallization from glacial acetic acid. Despite the absence of optical centers, the structure crystallizes in the chiral space group $P2_12_12_1$. The structure **9** contains both molecules **10a** and **11** in ratio 1:1 and is therefore an example of a binary molecular complex, or a co-crystal in modern terminology. The molecules are connected with each other *via* a bifurcated hydrogen bond of medium strength with slightly different distances O(1)···O(2) and O(1)···O(3) [2.654(3) and 2.706(3) Å] and angles OHO close to 180° [179(4)º and 173(4)º with atom H normalized to 0.993 Å] (Fig. 9). Geometry of the component **10a** is almost unaffected by cocrystallization, bond lengths and angles don't actually differ from those observed in the crystal of the pure compound (CSD refcode PEDLAN).[7] The most significant difference is the elongation of the C=O bond of the carbonyl group due to the formation of two H-bonds (from 1.2358(16) to 1.259(3) Å). The NO_2 group in **11** is rotated by 78.4° relative to the plane of the cycle due to steric effects which is typical for ortho-substituted phenols, the

distances between atom O(2) and atoms of NO_2 group are shortened [2.588(3), 2.888(4) and 3.226(3) Å for N(3)···O(2), O(4)···O(2) and O(5)···O(2), respectively]. Intermolecular interactions in co-crystal **9** other than H-bonds are non-directional and are represented by numerous C–H···O, C–H···π and H···H contacts. Molecules form alternating layers in the direction of the crystallographic *c* axis.

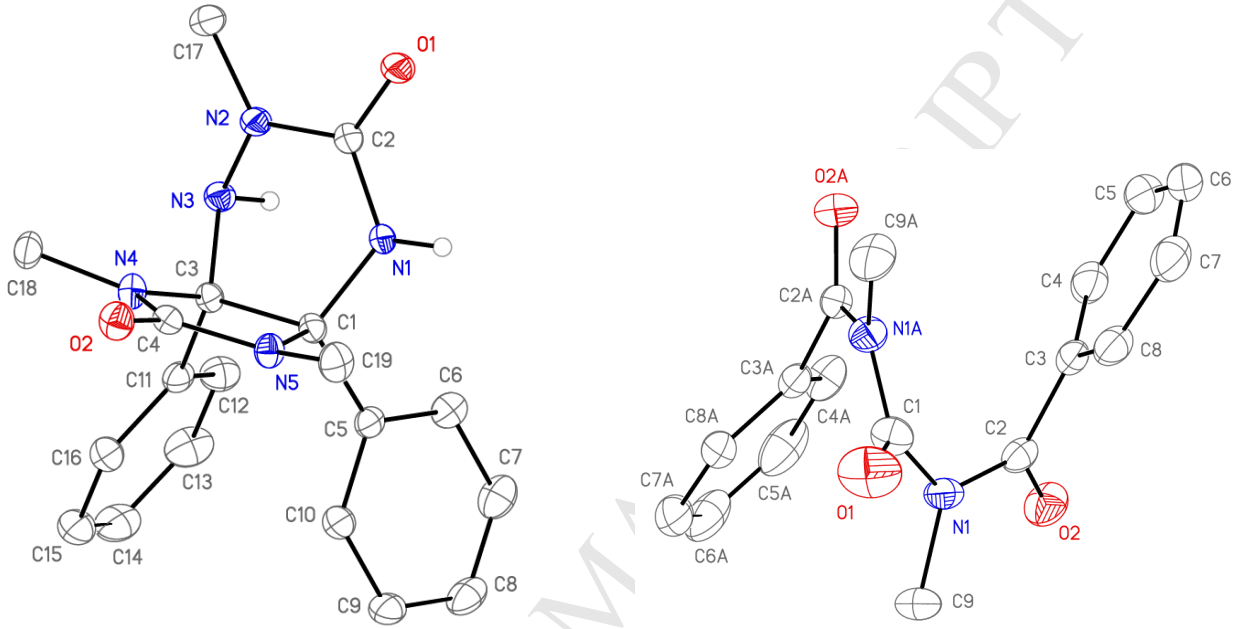


Fig. 8 General view of molecules **14** (left) and **16** (right) in crystal in thermal ellipsoid representation (p=50%). Hydrogen atoms connected to carbon atoms are omitted for clarity.

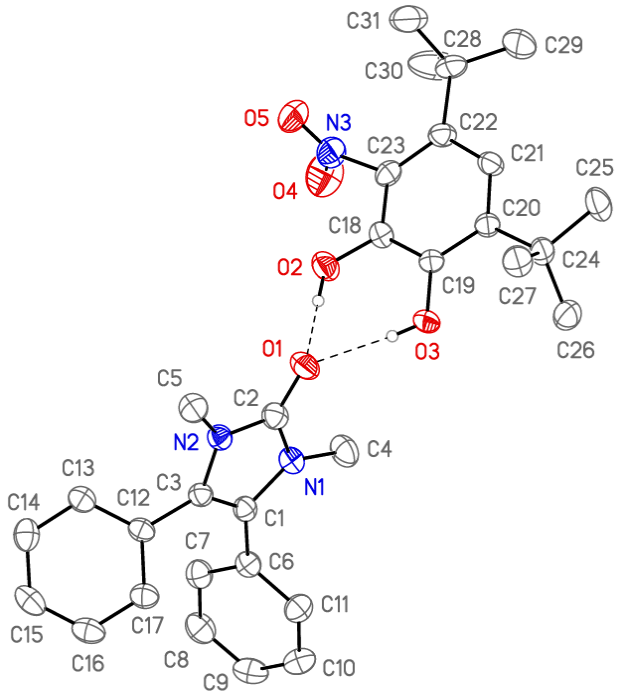


Fig. 9 General view of cocrystal **9** in thermal ellipsoid representation (p=50%). Hydrogen atoms connected to carbon atoms are omitted for clarity.

Conclusion

The novel transformations of 3-alkylthio-5,7-dimethyl-4a,7a-diphenyl-4a,5,7,7a-tetrahydro-1*H*-imidazo[4,5-e]-1,2,4-triazin-6(4*H*)-ones **6** and **8** under treatment of sterically hindered 1,2-benzoquinones **(**3,5-di-*tert*-butyl-1,2-benzoquinone **1** and 4,6-di-*tert*-butyl-3-nitro-1,2-benzoquinone **2)** were studied and 5,7-di-*tert*-butyl-1,3-dimethyl-3a,9a-diphenyl-3,3a-dihydro-1*H*-benzo[5,6][1,4]dioxino[2,3-*d*]imidazol-2(9a*H*)-one **13** and complex **9** of 4,6-di-*tert*-butyl-3-nitrobenzene-1,2-diol with 1,3-dimethyl-4,5-diphenyl-1*H*-imidazol-2(3*H*)-one **10a** were prepared. Novel products of photooxygenation of imidazolinone **10a** involving singlet oxygen under UV irradiation, i.e. isomeric 1,3-dimethyl-4,5-diphenylimidazolidin-2-ones **17, 17`**, and compound **18**, were found. Photochemical transformations of compounds **9**,**10a**,**16-18** were investigated by the spectral-kinetic method for the first time. Data on the absorption and fluorescence properties of synthesized compounds and their photoproducts were obtained. It was also showed that compounds **17** and **17`** exhibit different photochemical properties. Major isomer **17** is photochemically stable while minor isomer **17'** is photochemically unstable compound. Pathway for the formation of compounds **13** and **9** and for the photochemical transformations of compound **10a** involving singlet oxygen were proposed.

Experimental section

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM300 (300.13 MHz and 75.5 MHz, respectively) and Bruker DRX500 (500.13 MHz and 125.76 MHz, respectively) spectrometers using DMSO-d_6 as solvent. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

The spectrophotometric and kinetic measurements were performed on spectrophotometer «CARY 50bio» (Varian) in 2- or 10-mm thick quartz cells. Luminescent characteristics were measured on the spectrofluorimeter «Cary Eclipse» (Varian) in 10-mm thick fluorimetric quartz cell. The voltage on the fluorimeter photomultiplier was E=600 V. The slit width of the monochromator was 5 nm when spectra of fluorescence and fluorescence excitation were measured. Photochemical transformations were carried out using xenon lamp included in an LC-4 radiation unit (Hamamatsu) at a medium radiation power through colour glass filter UFS-1 (~51.2 W/m^2 in the 235-400 nm range). Solutions of samples **9**,**10a**,**16-18** were prepared in MeCN (99.8%, anhydrous, «Sigma-Aldrich») and C_6H_{14} («Reakhim»). The solution concentrations were C=4 x 10^{-5} M and C=2 x 10^{-4} M. The solutions were treated in an ultrasonic bath «Sapphire» for 10 min.

The oxidation reactions were carried out by using UV lamp VL-6.C (254 nm). Progress of the oxidation reaction (Scheme 4) was monitored using TLC sheets "Silufol UV254". The solvent system was $CHCl_3$:MeCN – 5:1.

Melting points were determined in open glass capillaries on a Gallenkamp (Sanyo) melting point apparatus.

Starting compounds **1,2** were synthesized according to the known procedures.[8,15] 3,5-Di-*tert*-butyl-1,2-benzoquinone **1** was prepared from pyrocatechol, *tert*- butyl alcohol and $NaNO_2$.[15] 3-Nitro-4,6-di-*tert*-butyl-benzoquinone-1,2 **2** was obtained under treatment of 2,4,6-tri-*tert*-butylphenol with 60% nitric acid.[8] (Imidazotriazin-3-ylthio)acetic acid **6** was prepared by the reaction of bromoacetic acid with imidazotriazine **12** in ethanol.[16] Syntheses of imidazotriazines **12** and **15** were carried out *via* an α-ureidoalkylation of thiosemicarbazide or semicarbazide with 1,3-dimethyl-4,5-dihydroxy-4,5-diphenylimidazolidin-2-one **17**,[12,13] obtained by the reaction of benzil with 1,3-dimethylurea.[10]

Melting points and ^{1}H NMR spectral data of compounds **1**,[15] **2**,[8] **6**,[16] **10a**,[6] **12**,[12] **15**,[13] **16**,[5] **17** and **17+17`**[10] are consistent with literature values.

Compound (**10**): white solid; m.p. 186-189 °C (185-187 °C)[6]; ^{1}H NMR (DMSO-d_6), δ: 3.09 (s, 6 H, Me), 7.20 – 7.43 (s, 10 H, Ph).

Reactions of compounds **6**, **8** and **12** with benzoquinones **1** and **2** were performed in AcOH. Photooxygenation of imidazolinone **10a** was carried out in DMSO and MeCN.

Synthesis of 5,7-dimethyl-3-methylthio-4a,7a-diphenyl-4a,5,7,7a-tetrahydro-1*H*-imidazo[4,5-*e*]-1,2,4-triazin-6(4*H*)-one (**8**) **and 2,5,7-trimethyl-4a,7a-diphenyltetrahydro-1*H*-imidazo[4,5-*e*]-1,2,4-triazine-3,6(2*H*,4*H*)-dione** (**14**). Iodomethane (1 mL, 0.012 mol) was added dropwise to a suspension of 5,7-dimethyl-4a,7a-diphenyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-6-one (**12**) (2.1 g, 0.006 mol) and AcONa (0.5 g, 0.006 mol) in methanol (20 mL). Reaction mixture was stirred at 20 °C for 3 h. Suspension dissolved, then a new precipitate was formed. The precipitate was filtered off, washed with methanol and dried to give compound **8**. The filtrate obtained after isolation of compounds **8** was left at room temperature until the crystals of the product **14** were precipitated. They were collected by filtration and dried in air.

Compound (**8**): Yield: 2 g, 91%; white solid; m.p. 252-254 °C (MeOH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.62 (s, 3H, SMe), 2.64 (s, 6H, NMe), 6.81, 6.84 (both s, 1H, Ph), 7.12-7.17 (m, 8H, Ph), 8.06, 10.34 (both br.s, 1H, NH). ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ 14.3 (SMe), 25.6, 26.2 (NMe), 83.6, 83.7 (Ph-*C*-*C*-Ph), 126.6, 127.7, 128.0, 128.67, 128.71 (CH(Ph)), 133.2, 133.9 (C(Ph)), 157.7, 158.3 (C=O, C=N). HRMS-ESI (*m/z*): calcd for $C_{19}H_{22}N_5OS$ $[M+H]^+$: 368.1540, found 368.1531.

Compound (**14**): Yield: 42 mg, 2%; colorless crystals; m.p. 274-276 °C (MeOH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.57 (s, 3H, NMe), 2.62 (s, 3H, NMe), 2.97 (s, 3H, NMe), 6.83 (s, 1H, HN-N), 7.01 (br. s, 10H, 2Ph), 7.77 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ 25.6, 26.2,

35.3 (NMe), 83.4, 85.4 (Ph-*C*-*C*-Ph), 126.5, 127.4, 127.4, 127.5, 127.8 (CH(Ph)), 135.6, 137.1 (C(Ph)), 158.8, 160.2 (C=O). HRMS-ESI (*m/z*): calcd for $C_{19}H_{21}N_5OS$ $[M+H]^+$: 368.1540, found 368.1533.

Synthesis of complex (**9**).

Method A: Solution of **2** (0.53 g, 2 mmol) and **6** (0.82 g , 2 mmol) in 10 mL of AcOH was heated at 70 ºC and stirred for 2 h. Then reaction mixture was cooled to room temperature. The precipitate **9** formed was filtered off, washed with AcOH and H_2O and dried in air.

Method B: Solution of **2** (0.53 g, 2 mmol) and **8** (0.73 g, 2 mmol) in 10 ml of AcOH was stirred at 20 ºC for 2 days. The precipitate **9** formed was filtered off, washed with AcOH and H_2O (100 mL) and dried in air. Yield: 0.78 g, 74% (method 1), 1.01 g, 95% (method 2); white solid; m.p. 210-213° C (AcOH); ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.26 (s, 9H, Bu^t(4)), 1.35 (s, 9H, Bu^t(6)), 3.10 (s, 6H, NMe), 6.88 (s, 1H, C(5)H), 7.23-7.37 (m, 10H, Ph), 8.72 (s, 1H, OH(1)), 9.22 (s, 1H, OH(2)). ^{13}C NMR (DMSO-d_6, 75.5 MHz): δ 28.6 (NMe), 29.3, 30.7 (Me(Bu^t)), 34.9, 35.0 (C(Bu^t)), 116.0, 120.5, 128.0, 128.6, 128.9, 129.5, 130.0, 137.8, 138.3, 141.4, 144.2 (C(Ar), C=C), 153.0 (C=O). IR (KBr), ν, cm^{-1}: 3252 (OH), 2955, 1639 (C=O), 1605, 1577, 1527, 1493, 1478, 1403, 1371, 1307, 1237. Anal. calcd. for $C_{31}H_{37}N_3O_5$: C, 70.03; H, 7.01; N, 7.90; found: C, 70.12; H, 7.04; N, 7.85.

Synthesis of 5,7-di-*tert*-butyl-1,3-dimethyl-3a,9a-diphenyl-3,3a-dihydro-1*H*-benzo[5,6][1,4]dioxino[2,3-*d*]imidazol-2(9a*H*)-one (**13**). Solution of **1** (0.44 g, 2 mmol) and **8** (0.73 g, 2 mmol) in 10 ml of AcOH was heated at 70 ºC and stirred for 2 h. After cooling to room temperature H_2O (100 mL) was added. The precipitate formed was filtered off, washed with H_2O (100 mL) and dried in air. The precipitate was dissolved in a minimum amount of $CHCl_3$. The solution in chloroform was dried over anhydrous Na_2SO_4 for 4 h and passed through a chromatographic column with SiO_2 (eluent $CHCl_3$). Colorless fraction (R_f = 0.6) was collected and the solvent was removed in vacuo. Compound **13** was obtained.

Compound (**13**): Yield: 0.24 g, 25%; white solid, m.p. 239-241 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (s, 9H, Bu^t(5)), 1.44 (s, 9H, Bu^t(7)), 2.78 (s, 3H, MeN), 2.86 (s, 3H, MeN), 6.96 (d, J = 2.3 Hz, 1H, CH), 7.03-7.15 (m, 11H, 2Ph+CH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.9, 27.6 (NMe), 30.5, 31.5 (Me(Bu^t)), 34.6, 35.1 (C(Bu^t)), 96.0, 97.3 (Ph-*C*-*C*-Ph), 113.0, 118.2, 127.4, 127.7, 127.9, 128.4, 128.5, 135.41, 135.45, 137.5, 139.9, 141.4, 144.5 (C(Ar)), 159.2 (C=O). HRMS-ESI (*m/z*): calcd for $C_{31}H_{36}N_2O_3Na$ $[M+Na]^+$: 507.2624, found 507.2618.

Synthesis of N,N'-carbonylbis(N-methylbenzamide) (**16**). The solution of 1,3-dimethyl-4,5-diphenyl-1*H*-imidazol-2(3*H*)-one **10a** (0.50 g, 0.0019 mol) in MeCN (35 mL) was irradiated UV for 12 h at 45°C. Then the reaction mixture was evaporated to solid and $CHCl_3$ (10 mL) were

added to the reaction mixture. Formed precipitate of **17 : 17`** (100 : 6.8; 0.05 g) was filtered off. The filtrate was evaporated and crude product **16** was purified by column chromatography $CHCl_3$:MeCN – 5:1. Yield: 0.31 g, 55 %; colorless crystals; m.p. 149-150 °C (149 °C)[5]; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.94 (s, 6H, Me), 7.38 (d, J = 7.4 Hz, 2H, Ph), 7.50 (t, J = 7.5 Hz, 2H, Ph), 7.60 (t, J = 7.3 Hz, 2H, Ph).

Synthesis of 4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidin-2-ones (**17+17`**) **and 1,3-dimethyl-1*H*-phenanthro[9,10-*d*]imidazol-2(3*H*)-one** (**18**). The suspension of 1,3-dimethyl-4,5-diphenyl-1*H*-imidazol-2(3*H*)-one **10a** (1.00 g, 0.00379 mol) in DMSO (15 mL) was irradiated UV for 12 h at 45°C. Then the H_2O (30 mL) and $CHCl_3$ (20 mL) were added to the reaction mixture. Formed precipitate (0.85 g) of (**17+17`**) was filtered off. The organic layer was separated from filtrate and evaporated to beige solid. Compound **18** was separated from beige solid by column chromatography $CHCl_3$:MeCN – 5:1.

Sample 17+17`**. Yield: 0.85 g, 72 % (**17** : **17` - 5 : 2); white solid; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.60 (s, 12H, Me(**17**+**17`**)), 5.97 (s, 2H, OH(**17`**)), 6.56 (s, 2H, OH(**17**)), 6.85 – 6.96 (m, 4H, Ph(**17**)),6.98 – 7.07 (m, 6H, Ph(**17**)),7.15 – 7.24 (m, 4H, Ph(**17`**)),7.29 – 7.38 (m, 6H, Ph(**17`**)).

Compound 18. Yield: 0.09 g, 9 %; yellow needles; m.p. 248-250 °C, ^{1}H NMR (DMSO-d_6, 500 MHz): δ 3.84 (s, 6H, Me), 7.59 (t, J = 7.5 Hz, 2H, CH), 7.67 (t, J = 7.5 Hz, 2H, CH), 8.43 (d, J = 8.3 Hz, 2H, CH), 8.88 (d, J = 8.3 Hz, 2H, CH). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 31.33, 120.28, 120.77, 121.53, 124.01, 124.44, 126.97, 127.05, 154.94. IC 1685 (C=O). HRMS-ESI (m/z): calcd for $C_{17}H_{14}N_2ONa$ $[M + Na]^+$: 285.0998, found: 285.0999.

X-ray diffraction analysis. Data collection for sample **16** was performed on a Bruker APEX DUO diffractometer, equipped with Apex II CCD detector, and for samples **9** and **14** on a Bruker SMART 1000 diffractometer, equipped with Bruker SMART 1000 CCD detector (both operating with graphite-monochromated MoKα radiation, λ=0.71073 Å). Frames were integrated using the Bruker SAINT software package[17] by a narrow-frame algorithm. A semiempirical absorption correction was applied with the SADABS[18] program using the intensity data of equivalent reflections. The structures were solved with direct methods and refined by the full-matrix least-squares technique against F^2_{hkl} in anisotropic approximation with SHELX[19] software package. Hydrogen atoms of NH groups in **14** and OH groups in **9** were found from difference Fourier synthesis and refined isotropically. All other hydrogen atoms were placed in calculated positions and refined in riding model with $U_{iso}(H) = 1.5U_{eq}(C_m)$ and $1.2U_{eq}(C_i)$, where $U_{eq}(C_m)$ and $U_{eq}(C_i)$ are respectively the equivalent thermal parameters of the methyl carbon and other

carbon atoms to which corresponding H atoms are bonded. Detailed crystallographic information is given in Table 3. Crystallographic data have been deposited to the Cambridge Crystallographic Data Centre, CCDC numbers 1574578-1574580; copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 3 Crystallographic data for crystals **9**, **14** and **16**.

	9	**14**	**16**
Empirical formula	$C_{31}H_{37}N_3O_5$	$C_{19}H_{21}N_5O_2$	$C_{17}H_{16}N_2O_3$
Formula weight	531.63	351.41	296.32
T, K	100	100	120
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	C2/c
Z / Z'	4 / 1	4 / 1	4 / 0.5
a, Å	9.860(2)	16.4618(16)	13.9890(15)
b, Å	10.524(2)	6.9012(7)	7.3378(8)
c, Å	26.911(5)	15.7448(16)	16.1193(18)
α, °	90	90	90
β, °	90	105.334(2)	115.478(2)
γ, °	90	90	90
V, Å^3	2792.5(10)	1725.0(3)	1493.7(3)
d_{calc}, g cm^{-3}	1.265	1.353	1.318
μ, cm^{-1}	0.86	0.92	0.92
F(000)	1136	744	624
$2\theta_{max}$, °	60	60	61
Refls collected	31880	15669	9931
Independent refls [Rint]	7985 [0.0383]	4959 [0.0279]	2292 [0.0431]
Observed refls [I>2σ(I)]	5692	3647	1708
R1	0.0570	0.0503	0.0466
wR2	0.1430	0.1243	0.1211
Goodness-of-fit on F^2	0.949	1.035	1.035
Residual density, e Å^{-3} (d_{min}/d_{max})	-0.205/0.415	-0.276/0.389	-0.190/0.361

Acknowledgment

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X-ray diffraction data were collected at the Center for molecular composition studies of INEOS RAS. High resolution mass spectra were recorded in the Department of Structural Studies of N.D. Zelinsky Institute of Organic Chemistry, Moscow.

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