Photochemistry of heterocycles
IX.* Preparation and photochemistry of substituted 7-(X-phenyl)--9,10-dioxa-8-azatricyclo[4,3,0,$1^{2,5}$]-7-decene derivatives

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Preparation and photolysis of isoxazolines fused with oxabicyclic heterocyclic ring have been described. The title compounds *VIb*—*VIi* were prepared by 1,3-dipolar cycloaddition of substituted benzenenitrile oxides. When X was 4-OCH_3, 4-CH_3, 4-F, 4-Cl, and 3-Cl, irradiation at $\lambda = 253.7$ nm brought about a selective photo-rearrangement under the formation of 3-aryl-4-formyl-8-oxa-2-azabicyclo[3,2,1]-3-octene derivatives in good yields. The bromo substituted derivatives gave on irradiation polymeric materials only, the nitro derivative was photostable. Quantum yields in photoreactions varied from 0.005 to 0.081, the values obtained with *p*-derivatives were higher than those obtained with *m*-derivatives. The benzo derivative *VIII* ($\Phi = 0.58$) afforded polymeric materials only.

Описано получение и фотолиз изоксазолинов, конденсированных с оксабициклическим гетероциклом. Заглавные соединения *VIb*—*VIi* были получены посредством 1,3-диполярного циклоприсоединения замещенных бензонитрилоксидов. При X = 4-OCH_3, 4-CH_3, 4-F, 4-Cl и 3-Cl облучение при $\lambda = 253{,}7$ нм вызывало селективную фото-перегруппировку с образованием производных 3-арил-4-формил-8-окса-2-азабицикло[3,2,1]-3-октена с хорошими выходами. Бромзамещенные производные при облучении давали только полимерные продукты, а нитропроизводное было фотоустойчиво. Квантовый выход в реакциях варьировался от 0,005 до 0,081, причем величины, получаемые с *пара*-производными были выше, чем величины, достигаемые с *мета*-производными. Бензопроизводное *VIII* ($\Phi = 0{,}58$) давало только полимерные продукты.

Recently, increased attention has been devoted to photochemistry of isoxazoline derivatives [1—14]. The biradical, formed by fission of the N—O bond in the primary photochemical step, is further stabilized in dependence on the structure of the skeleton [6]. Owing to this, several products are formed nonselectively, *e.g.*

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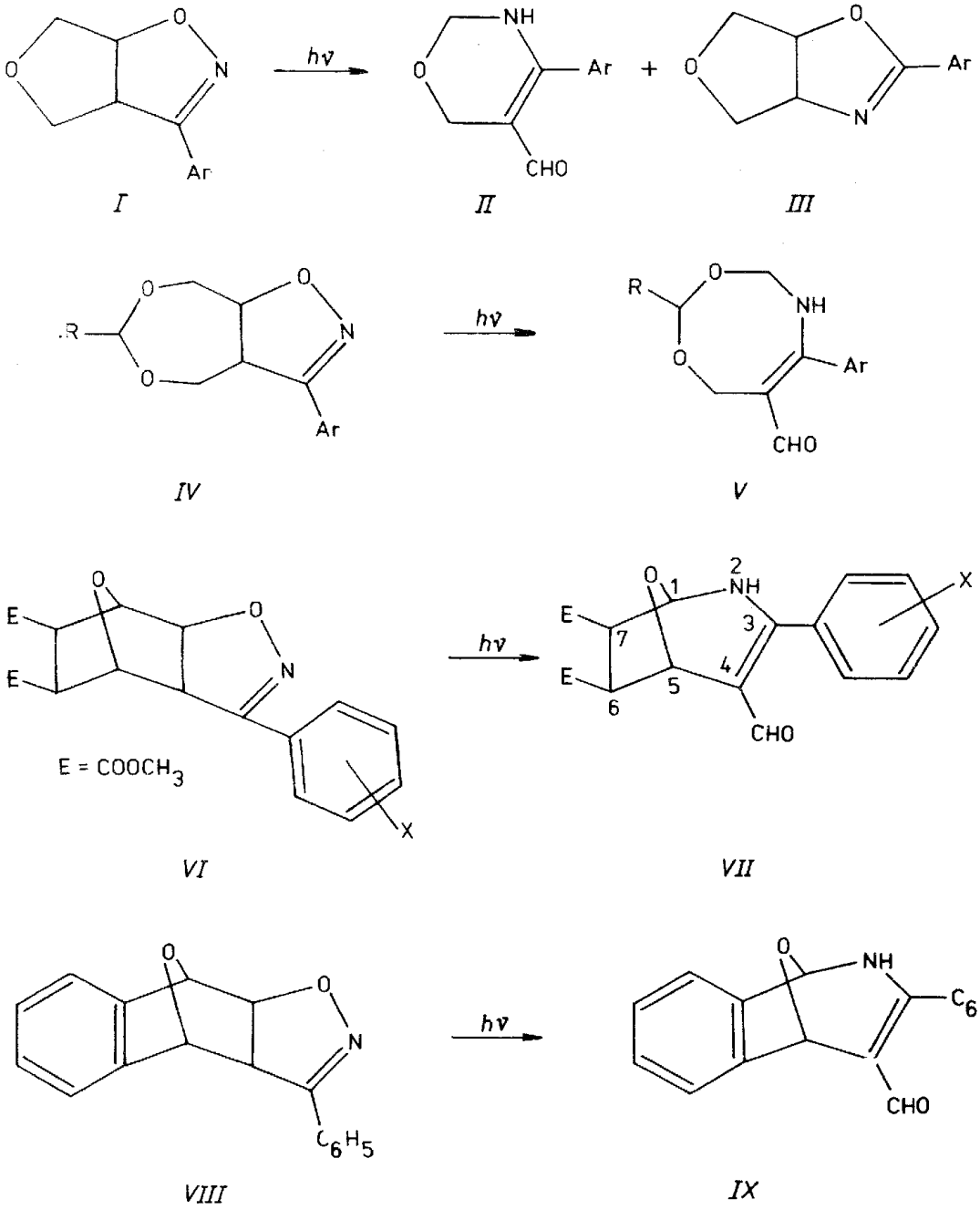
oxazolines [1—6, 8], β-aminochalcones [1—3, 6, 8], 1,3-oxazepines [6], cyclic enamine aldehydes [6, 7], [2+2] cycloadducts on the C=N bond [8, 9], and products of abstraction with hydrogen donors [9]. In our previous works [10—14], dealing with the effect of the hetero atom on fragmentation of the primarily formed biradical, we found that by introduction of an oxygen atom into the β-position with regard to the isoxazoline oxygen an unambiguous photo-rearrangement proceeded, e.g. *I* → *II* [10, 11] and *IV* → *V* [12, 13] (Scheme 1). With the derivative *I* we found an unexpected effect both of the bound substituent and the solvent on the selectivity of photo-rearrangement [14]. The aim of the present work was to study the substituent effect on photochemical reactions of further fused isoxazolines (*VIb*—*VIi*).

Isoxazolines were synthesized by 1,3-dipolar cycloaddition of substituted benzenenitrile oxides to 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene (*XIII*) both by classical method [15] through hydroximoyl chlorides (method *A*, Scheme 1, derivatives *VId*—*VIi*) and by the method generating nitrile oxides by treatment of the substituted benzaldoximes with sodium hypochlorite under catalysis of triethylamine [16] (method *B*, derivatives *VIb*, *VIc*). The corresponding cycloadducts, 3,4-dimethoxycarbonyl-7-(X-phenyl)-9,10-dioxa-8-azatricyclo[4,3,0,$1^{2,5}$]--7-decenes (*VIb*—*VIi*), were formed in very good yields (56—91 %). All cycloadducts were assigned the *exo* structure (with regard to the oxygen bridge) on the basis of zero values of coupling constants J_{1-2} and J_{5-6}. Both bridged protons 2-H and 5-H absorbed as singlets at different fields due to bent structure of the tricyclic system, e.g. for the compound *VIb* (4-OCH_3) $\delta = 4.93$ ppm (2-H) and $\delta = 4.83$ ppm (5-H). The higher chemical shift was assigned to 2-H proton in all cases due to the effect of the adjacent isoxazoline oxygen. In the case of *endo*-1,3-dipolar cycloaddition the protons mentioned above should have appeared in the ^{1}H NMR spectrum as doublets with coupling constants $J = \sim 5$ Hz.The isoxazoline protons 1-H and 6-H appeared in the spectrum as doublets at $\delta = \sim 5.00$ ppm and $\delta = \sim 3.90$ ppm, respectively, with the coupling constant $J_{1-6} = 9.0$ Hz confirming thus the *cis*-stereospecificity of 1,3-dipolar cycloaddition. The chemical shift for the C(=N) atom $\delta = 153.09$—154.41 ppm in the ^{13}C NMR spectrum was characteristic of the isoxazoline derivatives [11] and depended negligibly on the bound substituent X. The chemical shift values in the ^{13}C NMR spectra were for the bridged carbon atoms different due to the bent structure mentioned already, e.g. with *VIb* the doublets for C-2 and C-5 appeared at $\delta = 84.27$ ppm and $\delta = 79.72$ ppm, for C-1 and C-6 at $\delta = 85.56$ ppm and $\delta = 58.41$ ppm, and for C-3 and C-4 at $\delta = 50.15$ ppm and $\delta = 46.45$ ppm. All spectral data obtained with the derivatives *VIb*—*VIj* were in accordance with those of the unsubstituted derivative *VIa*, the properties of which were described in [11].

As follows from the UV spectra of the prepared adducts, it is reasonable to have the radiation wavelength below 300 nm. The source of the mentioned radiation



I II III

IV V

VI VII

VIII IX

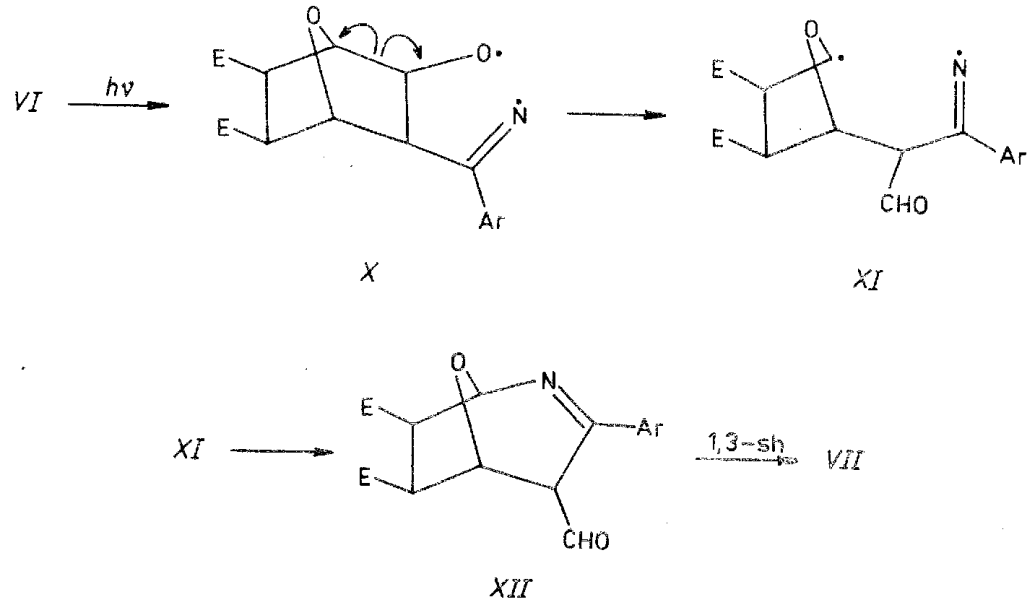
X

a	H	*d*	4-F	*g*	4-Br
b	4-OCH_3	e	4-Cl	*h*	3-Br
c	4-CH_3	*f*	3-Cl	*i*	3-NO_2

Scheme 1

was a low-pressure lamp with radiation wavelength $\lambda = 253.7$ nm. The reaction was conducted in a reactor with quartz finger until the starting derivative *VI* was not provable anymore by thin-layer chromatography. Photolysis of the acetonitrile solution of *VIe* afforded the compound *VIIe* in 74 % yield. The mass spectrum of this product indicated that it was a rearrangement derivative. On the basis of accordance of the following spectral data with those of the unsubstituted compound *VIIa* [11] it was assigned the structure of the cyclic enamine aldehyde, *i.e.* 3-(4-chlorophenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2-azabicyclo[3,2,1]-3-octene (*VIIe*). In the ^{1}H NMR spectrum of *VIIe* a distinct singlet appeared at low field $\delta = 8.97$ ppm. The position and intensity of this signal did not change with temperature or addition of heavy water. This signal belonged to aldehyde proton as indicated also by the presence of a doublet at $\delta = 185.88$ ppm in the ^{13}C NMR spectrum assigned to the aldehyde carbon. The structure of the cyclic enamine aldehyde was proved by bathochromic shift of the long-wave maximum at $\lambda = 269$ nm for *VIe* and $\lambda = 312$ nm for *VIIe* in the UV spectra, caused by the presence of the chromophores NH—C=C—CHO and C_6H_5—C=C—CHO, respectively. The ^{1}H NMR spectrum revealed further doublets at $\delta = 6.27$ ppm (NH) and $\delta = 5.91$ ppm (1-H) as well as a singlet $\delta = 5.49$ ppm of the bridge 5-H proton. The structure suggested for the cyclic enamine aldehyde *VIIe* was perfectly proved by the presence of the singlets at $\delta = 155.80$ ppm and $\delta = 116.69$ ppm belonging to C-4 and C-3 of the C=C bond. The doublets of the bridged carbon atoms C-1 and C-5 were observed at $\delta = 84.92$ ppm and $\delta = 76.27$ ppm. By irradiation of the derivatives *VIb*, *VIc*, *VId*, and *VIf* analogous rearrangement derivatives were obtained as single products, *i.e.* *VIIb* (4-OCH_3) in 34 %, *VIIc* (4-CH_3) 67 %, *VIId* (4-F) 59 %, and *VIIf* (3-Cl) in 24 % yield. Their structures were proved similarly as in the case of *VIIe*. The compound *VIIf* was obtained as a colourless oil with increased amount of polymeric materials. Irradiation of *p*-bromo (*VIg*) and *m*-bromo (*VIh*) derivatives resulted in polymeric materials only. In these cases probably photochemical substitution Br→H occurred and the leaking hydrogen bromide brought about polymerization of the forming photoproducts. The increasing facility of photosubstitution of halogens with hydrogen in the sequence F, Cl, Br and *p*, *m*, *o*, known from the literature [17], is in agreement with our results. The *m*-nitro derivative (*VIi*) was under the given conditions photostable in accordance with the literature data [8]. The same results were obtained about the substitution effect on photo-rearrangement in the series *IV*→*V* [13].

Formation of the substituted *VII* can be explained by analogous mechanism as in the case of the unsubstituted derivative *VIIa* (Scheme 2). The biradical *X*, formed by primary fission of the N—O bond, is further fragmented to the biradical *XI* which affords 3-aryl-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2-azabicyclo[3,2,1]-3-octene (*XII*). The derivative *XII* on subsequent 1,3-sigmatropic re-



Scheme 2

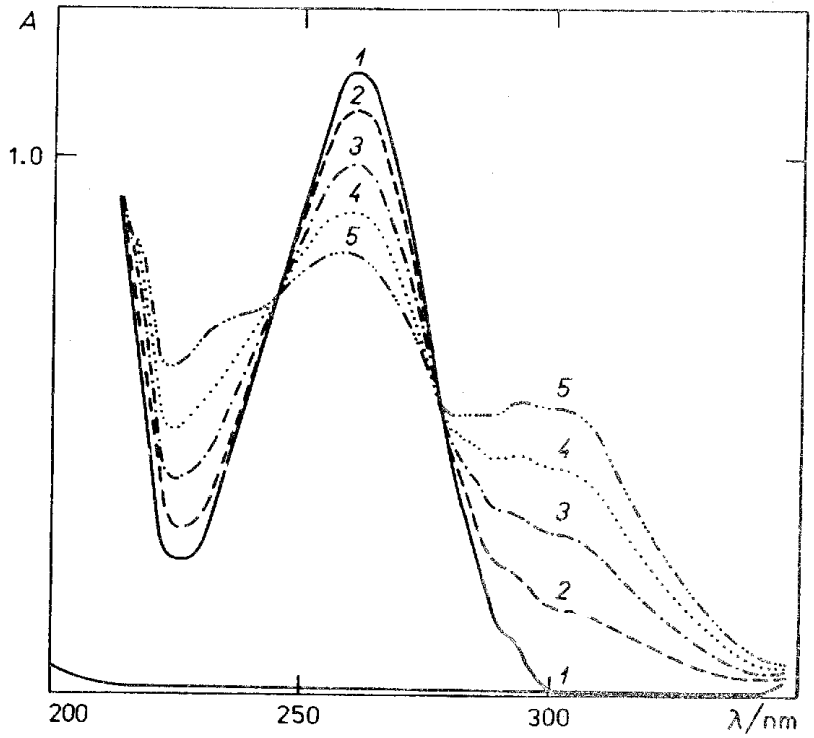


Fig. 1. Photoreaction of *VId* in acetonitrile brought about by irradiation with monochromatic radiation of $\lambda = 253.7$ nm; $c = 10^{-3}$ mol dm^{-3}, cell thickness 0.001 m, volume 15 cm^3. Curves *1*—*5* are for t/min: 0, 4, 8, 12, and 16.

arrangement gives the derivative *VII*. The UV spectra, recorded during photolysis of *VIb*—*VIf* at low concentration ($c = 5 \times 10^{-5}$ mol dm^{-3}) with radiation of $\lambda =$ 253.7 nm [18], revealed the presence of isosbestic points (for *VId* at $\lambda = 244$ nm and $\lambda = 277$ nm, Fig. 1) indicating a photochemical reaction of the A→B type; the

ED diagrams were found to be linear as well. The photoreactions proceeded similarly both in the presence and absence of oxygen and in benzene. Therefore, we assumed in agreement with the literature [1—14] that a singlet mechanism was involved. With *p*- and *m*-bromo derivatives the same mechanism was suggested, however, in this case the above-mentioned successive photoreactions proceeded. Photolysis of these derivatives at low concentrations ($c = 5 \times 10^{-5}$ mol dm^{-3}), monitored by the UV spectra, revealed the formation of absorption bands at $\lambda = 310$ nm (*p*-Br) and $\lambda = 305$ nm (*m*-Br) which pointed to the rearrangement product *VII*. However, on further irradiation these bands vanished. In the presence of diazabicyclooctane as a trap for hydrogen bromide distinct absorption bands with $\lambda_{max} = 310$ nm for *VIIg* and $\lambda_{max} = 305$ nm for *VIIh* were observed, which on further irradiation vanished as well.

Quantitative measurement of the *VI* → *VII* rearrangement was performed spectrophotometrically. Assuming that at monochromatic radiation $\lambda = 253.7$ nm *VI* is totally converted into *VII*, which is highly probable as evidenced by the presence of isosbestic points, the quantum yields can be easily established from the concentration decrease of *VI* [18]. The quantum yield obtained from the increase of the rearrangement product (up to 20 % conversion) is the same as Φ obtained by the method mentioned above. The quantum yields of photolysis Φ varied from 0.005 to 0.13 (Table 1). The highest value was obtained with the unsubstituted derivative *VIa*, in the case of the derivatives substituted with halogens Φ decreased in the order $\Phi(F) > \Phi(Cl) > \Phi(Br)$ and $\Phi(p\text{-halogen}) > \Phi(m\text{-halogen})$. In agreement with the literature, the results obtained could not be correlated with any known constant of the substituent. *Mukai et al.* correlated Φ with excitation energies E_s of isoxazolines [8]. The same substituent effect on the quantum yield Φ was observed in the series *IV* → *V* [13] and *I* → *II* [14].

Table 1

Quantum yields Φ of the conversion *VI* → *VII*

Derivative	*VIa*	*VIb*	*VIc*	*VId*	*VIe*	*VIf*	*VIg*	*VIh*
Φ	0.13	0.022	0.056	0.081	0.04	0.015	0.01	0.005

The highest quantum yield $\Phi = 0.58$, found so far in our studies of photochemistry of fused isoxazolines, was obtained on photolysis of the benzo derivative *VIII*, the preparation of which was described in [19]. The strong blue fluorescence observed in the first stage of irradiation vanished within some time and polymeric materials were formed. Changing the reaction conditions, decreasing the conversion, and irradiation in the presence of an inert gas did not result in higher yields. In each case green polymorphous materials were the only products. Their ^{1}H NMR

spectra displayed aromatic protons only and molecular peaks were absent in their mass spectra. The rearrangement derivative *IX* probably underwent rapid photochemical decomposition.

Experimental

^{1}H NMR spectra of the synthesized derivatives were recorded with a Tesla BS 487 C spectrometer at 80 MHz. ^{13}C NMR spectra were measured with a Jeol apparatus using tetramethylsilane as internal standard. UV spectra were measured in acetonitrile solution with a Perkin—Elmer spectrophotometer, the ε values are expressed in $m^2 mol^{-1}$. Mass spectra of the synthesized derivatives were recorded on an MS 902S spectrometer with direct inlet system at ionizing energy 70 eV.

Low-pressure lamp Toshiba GL-15 (15 W) in quartz vessel was used for photochemical reactions. The reactions were conducted in a tempered 300-cm^3 reactor [20] with forced circulation of the irradiated solution at 25 °C. The reaction course was checked by thin-layer chromatography on silufol plates and by simultaneous spectroscopic measurements of the photochemical mixtures in the UV region with a Specord UV VIS (Zeiss, Jena) spectrometer. Melting points were obtained on a Kofler block.

Measurement of quantum-chemical yields: The solvents were purified by standard methods. The quantum yields at the wavelength of $\lambda = 253.7$ nm were measured with the equipment described in [18]. Concentrations of the compounds *VIb—VIh* were followed from the decrease of extinction of the long-wave maximum at $\lambda \approx 264$ nm. Measurements were performed at $c = 5 \times 10^{-5}$ mol dm^{-3} in acetonitrile up to maximum 20 % conversion; cell thickness for photolysis was 2 cm.

5,6-Dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene (*XIII*) was prepared according to [21].

Method A

To the solution of benzenehydroximoyl chloride (10 mmol) and dipolarophile *XIII* (10 mmol) in dry ether (40 cm^3) triethylamine (13 mmol) in dry ether was added within 1 h at cooling and stirring so that the temperature was 0—5 °C. After stirring at room temperature overnight, the precipitated triethylammonium chloride was filtered off, the supernatant was evaporated *in vacuo* and worked up by trituration from a suitable solvent or by chromatographic separation on a column or silica gel plates (20 cm × 20 cm) of 2 mm thickness.

Method B

To the mixture of the dipolarophile *XIII* (21 mmol), triethylamine (0.2 g; 1.98 mmol), 11 % sodium hypochlorite (20 cm^3, 2.5 g; 34 mmol), and dichloromethane (15 cm^3) the solution of substituted benzaldoxime (21 mmol) in dichloromethane (10 cm^3), cooled to 0 °C, was added with stirring during 15 min. After stirring for 3 h the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 30 cm^3), the combined organic

layers were dried (magnesium sulfate), evaporated *in vacuo*, and worked up similarly as in the method *A*.

3,4-Dimethoxycarbonyl-7-(4-methoxyphenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIb)

The compound prepared by the method *B*, obtained in 56 % yield by trituration from ether, m.p. 156—157 °C. For $C_{18}H_{19}NO_7$ (M_r = 361.34) w_i(calculated): 59.83 % C, 5.30 % H, 3.88 % N; w_i(found): 60.01 % C, 5.24 % H, 4.06 % N. UV spectrum, λ_{max}/nm (log {ε}): 274 (3.24). ^{1}H NMR, $\delta(C^2HCl_3)$/ppm: 6.86—6.97 and 7.55—7.65 (m, 4H, H_{arom}), 5.05 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 4.93 (s, 1H, 2-H), 4.83 (s, 1H, 5-H), 3.95 (d, 1H, 6-H), 3.84 (s, 3H, OCH_3), 3.66 and 3.68 (s, s, 6H, 2 × $COOCH_3$), 3.28 (d, $J_{3,4}$ = 10 Hz, 1H, 3-H), 3.03 (d, 1H, 4-H). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 170.29 (s, C=O), 153.85 (s, C=N), 161.13, 128.32, 120.59, 114.35 (C_{arom}), 85.56 (d, C-1), 84.27 (d, C-2), 79.72 (d, C-5), 58.41 (d, C-6), 55.35 (q, OCH_3), 52.36 (q, $COOCH_3$), 50.15 (d, C-3), 46.45 (d, C-4).

3,4-Dimethoxycarbonyl-7-(4-methylphenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIc)

The compound prepared by the method *B*, obtained in 76 % yield by column chromatography (silica gel), eluent cyclohexane—ethyl acetate (volume ratio = 1:3), m.p. 175—177 °C. For $C_{18}H_{19}NO_6$ (M_r = 345.34) w_i(calculated): 62.60 % C, 5.55 % H, 4.06 % N; w_i(found): 62.77 % C, 5.41 % H, 4.13 % N. UV spectrum, λ_{max}/nm (log {ε}): 265 (3.12). ^{1}H NMR, $\delta(C^2HCl_3)$/ppm: 7.48—7.58 and 7.72—7.82 (m, 4H, H_{arom}), 5.01 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 4.96 (s, 1H, 2-H), 4.83 (s, 1H, 5-H), 3.96 (d, 1H, 6-H), 3.66 and 3.63 (s, s, 6H, 2 × $COOCH_3$), 3.21 (d, J = 9.0 Hz, 1H, 3-H), 3.02 (d, 1H, 4-H). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 171.91 (s, C=O), 154.31 (s, C=N), 140.08, 138.45, 129.62, 125.89 (C_{arom}), 85.69 (d, C-1), 84.59 (d, C-2), 79.91 (d, C-5), 58.21 (d, C-6), 52.17 (q, $COOCH_3$), 49.63 (d, C-3), 47.36 (d, C-4), 21.37 (q, CH_3).

3,4-Dimethoxycarbonyl-7-(4-fluorophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VId)

The compound prepared by the method *A*, obtained in 77 % yield by trituration from dry ether, m.p. 204—205 °C. For $C_{17}H_{16}FNO_6$ (M_r = 349.31) w_i(calculated): 58.45 % C, 4.62 % H, 4.01 % N; w_i(found): 58.36 % C, 4.90 % H, 4.14 % N. UV spectrum, λ_{max}/nm (log {ε}): 264 (3.06). ^{1}H NMR, $\delta(C^2HCl_3)$/ppm: 7.00—7.76 (m, 4H, H_{arom}), 5.12 (s, 1H, 2-H), 4.98 (s, 1H, 5-H), 4.92 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 3.93 (d, 1H, 6-H), 3.70 and 3.67 (s, s, 6H, 2 × $COOCH_3$), 3.18 (d, J = 9.0 Hz, 1H, 3-H), 3.02 (d, 1H, 4-H). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 170.23 (s, C=O), 153.09 (s, C=N), 129.10, 128.51, 116.95, 115.52 (C_{arom}), 86.02 (d, C-1), 84.33 (d, C-2), 79.59 (d, C-5), 58.28 (d, C-6), 52.49 (q, $COOCH_3$), 50.28 (d, C-3), 46.58 (d, C-4).

3,4-Dimethoxycarbonyl-7-(4-chlorophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIe)

The compound prepared by the method *A*, the reaction accomplished in dioxan, obtained in 68 % yield by trituration from dry ether, m.p. 231—232 °C. For $C_{17}H_{16}ClNO_6$ (M_r = 365.76) w_i(calculated): 55.82 % C, 4.41 % H, 3.83 % N; w_i(found): 55.71 % C, 4.44 % H, 3.97 % N. UV spectrum, λ_{max}/nm (log {ε}): 269 (3.18). Mass spectrum, *m/z* 365 ($M^{+\cdot}$), base peak 59 ($\dot{C}OOCH_3$). ^{1}H NMR, δ(C^2H_3CN)/ppm: 7.58—7.70 and 7.30—7.41 (m, 4H, H_{arom}), 4.87 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 4.86 (s, 1H, 2-H), 4.76 (s, 1H, 5-H), 3.97 (d, 1H, 6-H), 3.53 (s, 6H, 2 × $COOCH_3$), 3.25 (d, J = 9.0 Hz, 1H, 3-H), 3.02 (d, 1H, 4-H), ^{13}C NMR, δ(C^2HCl_3)/ppm: 170.23 (s, C=O), 153.46 (s, C=N), 136.44, 129.36, 128.06, 126.76 (C_{arom}), 86.21 (d, C-1), 84.33 (d, C-2), 79.59 (d, C-5), 58.08 (d, C-6), 52.56 (q, $COOCH_3$), 50.28 (d, C-3), 46.58 (d, C-4).

3,4-Dimethoxycarbonyl-7-(3-chlorophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIf)

The compound prepared by the method *A*, worked up as in the case of *VIe*, obtained in 54 % yield, m.p. 218—219 °C. For $C_{17}H_{16}ClNO_6$ (M_r = 365.76) w_i(calculated): 55.82 % C, 4.41 % H, 3.83 % N; w_i(found): 55.99 % C, 4.29 % H, 3.66 % N. UV spectrum, λ_{max}/nm (log {ε}): 267 (3.05). Mass spectrum, *m/z*: 365 ($M^{+\cdot}$), base peak 59 ($\dot{C}OOCH_3$). ^{1}H NMR, δ(C^2H_3CN)/ppm: 7.37—7.77 (m, 4H, H_{arom}), 4.96 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 4.95 (s, 1H, 2-H), 4.85 (s, 1H, 5-H), 4.05 (d, 1H, 6-H), 3.61 (s, 6H, 2 × $COOCH_3$), 3.32 (d, J = 9.0 Hz, 1H, 3-H), 3.27 (d, 1H, 4-H).

3,4-Dimethoxycarbonyl-7-(4-bromophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIg)

The compound prepared by the method *A*, the reaction conducted in dioxan, the obtained solid was sucked, washed with water to remove triethylammonium chloride, yield 86 %, m.p. 234—236 °C. For $C_{17}H_{16}BrNO_6$ (M_r = 410.19) w_i(calculated): 49.78 % C, 3.90 % H, 3.41 % N; w_i(found): 49.99 % C, 4.12 % H, 3.38 % N. UV spectrum, λ_{max}/nm (log {ε}): 270 (3.11). ^{1}H NMR, δ/ppm (deuterated dimethyl sulfoxide): 7.73 (s, 4H, H_{arom}), 5.06 (d, $J_{1,6}$ = 9.0 Hz, 1H, 1-H), 4.91 (s, 1H, 2-H), 4.78 (s, 1H, 5-H), 4.23 (d, 1H, 6-H), 3.60 (s, 6H, 2 × $COOCH_3$), 3.10—3.87 (m, 2H, 3-H and 4-H).

3,4-Dimethoxycarbonyl-7-(3-bromophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIh)

The compound prepared by the method *A*, the reaction carried out similarly as in the case of *VIg*, yield 87 %, m.p. 228—229 °C. For $C_{17}H_{16}BrNO_6$ (M_r = 410.19) w_i(calculated): 49.78 % C, 3.90 % H, 3.41 % N; w_i(found): 49.57 % C, 4.01 % H, 3.69 % N. UV spectrum, λ_{max}/nm (log {ε}): 267 (3.06). Mass spectrum, *m/z*: 408, 410 ($M^{+\cdot}$), base peak 59 ($\dot{C}OOCH_3$). ^{1}H NMR, δ/ppm (deuterated dimethyl sulfoxide): 7.47—8.02 (m, 4H, H_{arom}),

5.08 (d, $J_{1,6}=9.0$ Hz, 1H, 1-H), 4.92 (s, 1H, 2-H), 4.78 (s, 1H, 5-H), 4.25 (d, 1H, 6-H), 3.58 (s, 3H, $COOCH_3$), 3.47 (s, 3H, $COOCH_3$), 3.15 (d, $J=10$ Hz, 1H, 3-H), 3.00 (d, 1H, 4-H).

3,4-Dimethoxycarbonyl-7-(3-nitrophenyl)-9,10-dioxa-8-aza-tricyclo[4,3,0,1^{2,5}]-7-decene (VIi)

The compound prepared by the method *A*, the reaction carried out similarly as in the case of *VIg*, yield 91 %, m.p. 208—209 °C. For $C_{17}H_{16}N_2O_8$ ($M_r=376.18$) w_i(calculated): 54.28 % C, 4.25 % H, 7.44 % N; w_i(found): 54.36 % C, 4.21 % H, 7.61 % N. ^{1}H NMR, $\delta(C^2H_3CN)$/ppm: 7.56—8.50 (m, 4H, H_{arom}), 5.03 (d, $J_{1,6}=8.0$ Hz, 1H, 1-H), 4.97 (s, 1H, 2-H), 4.87 (s, 1H, 5-H), 4.16 (d, 1H, 6-H), 3.62 and 3.60 (s, s, 6H, 2 × $COOCH_3$), 3.36 (d, $J=10.0$ Hz, 1H, 3-H), 3.16 (d, 1H, 4-H).

Photochemical reaction of VI

The solution prepared from the respective derivative (3 mmol) in acetonitrile (250 cm^3) was irradiated under the foregoing conditions until the starting compound was identifiable on TLC plates (silufol, cyclohexane—ethyl acetate at volume ratio = 1 : 3). Then the reaction mixture was evaporated *in vacuo* and worked up by trituration from a suitable solvent or by chromatographic separation.

3-(4-Methoxyphenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2--azabicyclo[3,2,1]-3-octene (VIIb)

The compound prepared from *VIb*, irradiation 6 h, worked up by separation on a column of silica gel, eluent hexane—ethyl acetate (volume ratio = 1 : 3), yield 34 %, m.p. 76—78 °C. For $C_{18}H_{17}NO_7$ ($M_r=361.34$) w_i(calculated): 59.83 % C, 5.30 % H, 3.88 % N; w_i(found): 59.67 % C, 5.22 % H, 3.96 % N. UV spectrum, λ_{max}/nm (log {ε}): 245 (2.83), 313 (3.06). ^{1}H NMR, $\delta(C^2HCl_3)$/ppm: 9.16 (s, 1H, CHO), 7.31—7.42 and 6.88—7.00 (m, 4H, H_{arom}), 5.93 (m, 1H, 1-H), 5.57 (s, 1H, 5-H), 3.86 (s, 3H, OCH_3), 3.73 (s, 6H, $COOCH_3$), 3.58—3.83 (m, 2H, 6-H and 7-H). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 186.47 (d, CHO), 170.49 (s, $COOCH_3$), 162.30 (s, C-4), 156.97, 131.24, 123.97, 114.22 (C_{arom}), 115.91 (s, C-3), 84.98 (d, C-1), 76.53 (d, C-5), 58.47 (d, C-7), 55.48 (d, C-6), 52.36 (q, q, $COOCH_3$ and OCH_3).

3-(4-Methylphenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2--azabicyclo[3,2,1]-3-octene (VIIc)

The compound obtained from *VIc*, irradiation 3 h, worked up as in the case of *VIIb*, yield 67 %, m.p. 154—155 °C. For $C_{18}H_{19}NO_6$ ($M_r=345.34$) w_i(calculated): 62.60 % C, 5.55 % H, 4.06 % N; w_i(found): 62.83 % C, 5.11 % H, 4.12 % N. UV spectrum, λ_{max}/nm (log {ε}): 244 (3.07), 312 (3.15). ^{1}H NMR, $\delta(C^2HCl_3)$/ppm: 8.96 (s, 1H, CHO), 7.31

(s, 4H, H_{arom}), 5.72 (m, 1H, 1-H), 5.40 (s, 1H, 5-H), 3.55—3.75 (m, 2H, 6-H and 7-H), 3.63 (s, 6H, 2 × $COOCH_3$), 2.38 (s, 3H, CH_3). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 186.34 (d, CHO), 170.41 (s, $COOCH_3$), 157.23 (s, C=N), 141.90, 129.62, 129.42 (C_{arom}), 84.58 (d, C-1), 76.40 (d, C-5), 58.47 (d, C-7), 55.48 (d, C-6), 52.36 (q, $COOCH_3$), 21.37 (q, CH_3).

3-(4-Fluorophenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2--azabicyclo[3,2,1]-3-octene (VIId)

The compound prepared from *VId*, irradiation 1.5 h, obtained after evaporation of the reaction mixture by trituration from dry ether, yield 59 %, m.p. 60—62 °C. For $C_{17}H_{16}FNO_6$ (M_r = 349.31) w_i(calculated): 58.45 % C, 4.62 % H, 4.01 % N; w_i(found): 58.54 % C, 4.73 % H, 3.96 % N. UV spectrum, λ_{max}/nm (log {ε}): 239 (3.21), 307 (3.15). ^1H NMR, $\delta(C^2HCl_3)$/ppm: 9.02 (s, 1H, CHO), 7.00—7.50 (m, 4H, H_{arom}), 5.93 (broad singlet, 1H, 1-H), 5.53 (s, 1H, 5-H), 3.70 (s, 6H, 2 × $COOCH_3$), 3.60—3.82 (m, 2H, 6-H and 7-H). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 186.21 (d, CHO), 170.35 (s, $COOCH_3$), 156.13 (s, C=N), 132.08, 131.50, 116.88 (C_{arom}), 115.45 (s, C-3), 84.98 (d, C-1), 76.40 (d, C-5), 58.47 (d, C-7), 55.42 (d, C-6), 52.49 (q, $COOCH_3$).

3-(4-Chlorophenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2--azabicyclo[3,2,1]-3-octene (VIIe)

The compound prepared from *VIe*, irradiation 3 h, obtained as *VIIb*, yield 74 %, m.p. 199—201 °C. For $C_{17}H_{16}ClNO_6$ (M_r = 365.76) w_i(calculated): 55.82 % C, 4.41 % H, 3.83 % N; w_i(found): 55.94 % C, 4.72 % H, 3.89 % N. UV spectrum, λ_{max}/nm (log {ε}): 246 (3.11), 312 (3.10). Mass spectrum, *m/z*: 365 ($M^{+\cdot}$), base peak 31 ($\dot{O}CH_3$). ^1H NMR, $\delta(C^2HCl_3)$/ppm: 8.97 (s, 1H, CHO), 7.37 (s, 4H, H_{arom}), 6.27 (d, J = 4.0 Hz, 1H, NH), 5.91 (d, 1H, 1-H), 5.49 (s, 1H, 5-H), 3.66 (s, 8H, 2 × $COOCH_3$, 6-H and 7-H). ^1H NMR, δ/ppm (deuterated acetone): 8.99 (s, 1H, CHO), 7.50 (s, 4H, H_{arom}), 6.12 (d, 1H, NH), 5.82 (d, 1H, 1-H), 5.41 (s, 1H, 5-H), 3.75 (m, 2H, 6-H, 7-H), 3.61 (s, 6H, 2 × $COOCH_3$). ^{13}C NMR, $\delta(C^2HCl_3)$/ppm: 185.88 (d, CHO), 170.29 (s, $COOCH_3$), 155.80 (s, C-4), 137.74, 130.92, 130.20, 129.10 (C_{arom}), 116.69 (s, C-3), 84.92 (d, C-1), 76.27 (d, C-5), 58.47 (d, C-7), 55.48 (d, C-6), 52.36 (q, $COOCH_3$).

3-(3-Chlorophenyl)-4-formyl-6,7-dimethoxycarbonyl-8-oxa-2--azabicyclo[3,2,1]-3-octene (VIIf)

The compound prepared from *VIf*, irradiation 8 h, worked up as in the case of *VIIb*, yield 24 %, colourless oil. For $C_{17}H_{16}ClNO_6$ (M_r = 365.76) w_i(calculated): 55.82 % C, 4.41 % H, 3.83 % N; w_i(found): 55.74 % C, 4.14 % H, 3.97 % N. UV spectrum, λ_{max}/nm (log {ε}): 243 (3.01), 309 (3.06). ^1H NMR, $\delta(C^2H_3CN)$/ppm: 8.95 (s, 1H, CHO), 7.32—7.51 (m, 4H, H_{arom}), 5.73 (s, 1H, 1-H), 5.38 (s, 1H, 5-H), 3.63 (s, 6H, 2 × $COOCH_3$), 3.40—3.86 (m, 2H, 6-H and 7-H).

Irradiation of the compounds *VIg*, *VIh*, and *VIII* resulted in polymeric materials, on irradiation of *VIi* for 6 h the unreacted *VIi* was recovered practically quantitatively.

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