Photochemistry of heterocycles
XIV.* Heteroatom and substituent effect on the photochemistry of condensed isoxazolines

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Photochemistry of isoxazolines, fused with 2,3-dihydrofuran, 2,3-dihydropyran, 2,3- and 2,5-dihydrothiophene as well as 1,3-dithiep-5-ene has been described. Sulfur stabilized by N—O bond cleavage formed primary biradical better than oxygen; heteroatoms in β-position relative to isoxazoline oxygen were more effective stabilizers than those in α-position. Primary photoproducts of sulfur-containing species as well as those having oxygen in α-position were photolabile. Biphenyl-substituted condensed isoxazolines were photostable ($\Phi < 0.001$). Irradiation of 3-phenyl-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole in the presence of $Fe(CO)_5$ produced 3-benzoyl-4-hydroxy- and 4-methoxytetrahydrofuran. Cycloadducts were prepared by 1,3-dipolar cycloaddition of nitrile oxide to the corresponding heterocycles.

Описаны фотохимические реакции изоксазолинов, конденсированных с 2,3-дигидрофураном, 2,3-дигидропираном, 2,3- и 2,5-дигидротиофеном, а также с 1,3-дитиеп-5-еном. Сера, стабилизированная вследствие распада связи N—O, образовывала первичные бирадикалы легче, чем кислород; гетероатомы в β-положении по отношению к кислороду изоксазолина являются более эффективными стабилизаторами, чем гетероатомы в α-положении. Первичные продукты фотореакций серусодержащих соединений, а также соединений с кислородом в α-положении были фотолабильны. Бифенильные производные конденсированных изоксазолинов были фотостабильны ($\Phi < 0,001$). Облучение 3-фенил-3a,4,6,6a-тетрагидрофуро[3,4-*d*]изоксазола в присутствии $Fe(CO)_5$ вело к образованию 3-бензоил-4-гидрокси- и 4-метокситетрагид-

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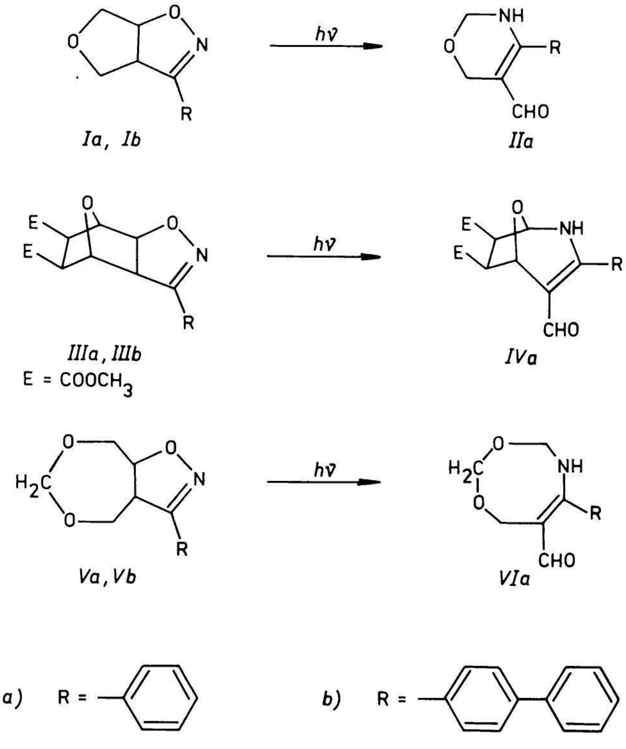
* For Part XIII see Ref. [17].

рофурана. Были получены циклоаддукты посредством 1,3-диполярного циклоприсоединения нитрилоксидов к соответствующим гетероциклам.

Photochemistry of isoxazolines has been intensively studied during the recent decade [1—9]. The first step in most cases was recognized to be the homolytic N—O bond cleavage. Further fate of the thus formed biradical depends on its structure. Consequently, the irradiation results in nonselective formation of oxazolines, β-aminocarbonyl compounds, cyclic enamino aldehydes, 1,3-oxazepines, [2+2] cycloadducts on the C=N bond as well as the corresponding nitriles [1—9]. In our previous papers [10—19] we have described a surprisingly straightforward photorearrangement of 3-(X-phenyl)-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazoles (*Ia*) to 4-X-phenyl-5-formyl-2,3-dihydro-6*H*-1,3-oxazines (*IIa*) [10, 11]. Analogically, *IIIa* rearranged upon irradiation to *IVa* [10, 11, 18] and $Va \xrightarrow{h\nu} VIa$ [12—14] (Scheme 1). Exclusive formation of cyclic enamino



Scheme 1

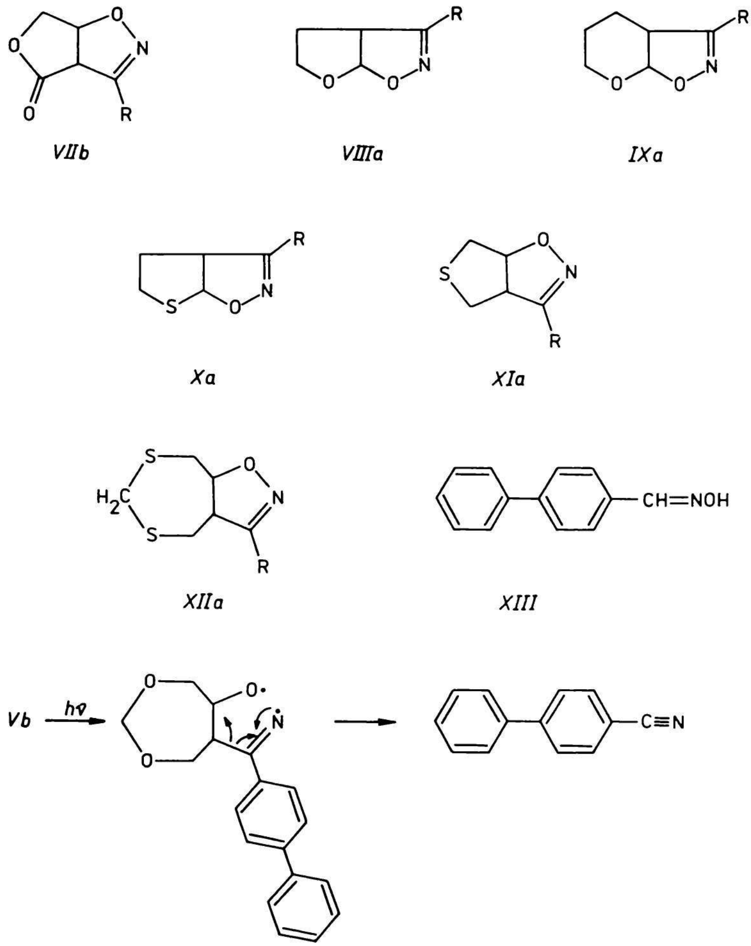
aldehydes *II, IV, VI* has been ascribed to the stabilizing effect of a heteroatom in β-position on the oxygen radical. Now we present the study of the stabilizing effect of heteroatoms in various positions, influence of biphenyl as a substituent at isoxazoline ring as well as the role of iron pentacarbonyl in the rearrangement.

Condensed isoxazolines substituted by biphenyl (*Ib, IIIb, Vb,* and *VIIb*) were prepared by 1,3-dipolar cycloaddition of the corresponding nitrile oxides to 2,5-dihydrofuran, 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene, 1,3-di-oxep-5-ene, and 5*H*-furan-2-one, respectively. In all cases nitrile oxide was generated *in situ* from 4-biphenylcarbaldehyde oxime and sodium hypochlorite, catalyzed by triethylamine [20].

NMR spectrum of 3-(4-biphenyl)-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ib*), prepared in 44 % yield, showed a doublet of doublets at $\delta = 5.37$ ppm ($J_{3a,6a} = 9.0$ Hz), belonging to H-6a. Signals of other protons (H_2-6, H_2-4, H-3a) were multiplets at $\delta = 3.65$—4.40 ppm. ^{13}C NMR signals of the bridgehead carbons C-6a, C-3a were found at $\delta = 85.89$ ppm and 52.83 ppm; the higher value belonging to the more deshielded carbon close to the oxygen of the isoxazoline ring. More distant C-6 ($\delta = 75.36$ ppm) and C-4 ($\delta = 71.15$ ppm) "feel" the influence of oxygen much less, the small difference in their chemical shifts being due to the bent structure of the bicyclic skeleton.

Spectral data of 3-(4-biphenyl)-4-oxo-3a,4,6,6a-tetrahydrofuro[3,4-*d*] isoxazole (*VIIb*) (Scheme 2), prepared in 39 % yield, showed signals in the same sequence as *Ib*, the presence of carbonyl group asserts itself in higher δ values. Thus doublet of doublets of the bridgehead protons H-6a having coupling constant $J_{3a,6a} = 9.0$ Hz was found at $\delta = 5.64$ ppm (excluding the head to head orientation of the cycloadduct), doublet of H-3a at $\delta = 5.09$ ppm, multiplet at $\delta = 4.60$—4.81 ppm of H_2-6 protons.

In the NMR spectrum of 8-(4-biphenyl)-3,5,10-trioxa-9-azabicyclo[5,3,0]dec-8-ene (*Vb*), prepared in 43 % yield, a doublet at $\delta = 4.92$ ppm ($J_{1,7} = 8.0$ Hz) belonging to H-1 proton could be identified in the overlapping multiplets. Triplet at $\delta = 97.77$ ppm in ^{13}C NMR spectrum has been assigned to C-4 carbon, triplet at $\delta = 69.74$ ppm and 67.11 ppm to C-2 and C-6, respectively. Higher δ values for C-2 as compared to C-6, as well as that of C-1 ($\delta = 82.79$ ppm) as compared to C-7 ($\delta = 51.25$ ppm) can be accounted for by the same reasoning as in case of *Ib*. Based on zero coupling constants $J_{1,2}$ and $J_{5,6}$ in the NMR spectrum of *IIIb*, *exo* cycloaddition must have taken place, for an *endo* adduct coupling constants on the order of 5 Hz would have been expected. The suggested structure was further supported by doublets in ^{13}C NMR spectrum, belonging to C-1, C-2, C-5, and C-6, located at $\delta = 85.36$ ppm, 83.84 ppm, 79.45 ppm, and 51.55 ppm, respectively. 3-Phenyl-3a,4,5,6a-tetrahydrofuro[2,3-*d*]isoxazole (*VIIIa*) was prepared by 1,3-dipolar cycloaddition of benzonitrile oxide, generated from benzhydroximoyl chloride by classical procedure using triethylamine, to 2,3-dihydrofuran in 76 % yield. Preparation of *VIIIa* in 40 % yield was described in [21], with NaOH used as the base, giving m.p. = 77 °C, without spectral data. In our hands the adduct melted at 100 °C, its head to head structure was unambiguously established by ^{1}H and ^{13}C NMR spectra as well as by mass spectra (see Experimental). NMR spectra are very similar to those of the corresponding adduct of 9-anthracenenitrile oxide to 2,3-dihydrofuran and 2,3-dihydropyran



Scheme 2

[22], obviating their detailed analysis. Quite analogically, 2,3-dihydrothiophene produced in cycloadditions only one head to head isomer — 3-phenyl-3a,4,5,6a-tetrahydrothieno[2,3-*d*]isoxazole (*Xa*). Both 2,3-dihydrofuran and 2,3-

-dihydrothiophene, when acting as dipolarophiles, behave like an enol ether and thioenol ether, respectively, having greater atomic orbital coefficient in HOMO at β-carbon atom [23]. Taking into account that donor heterocycles react in cycloadditions with their HOMO's [24, 25], the LUMO of benzonitrile oxide having the greatest value of atomic orbital coefficient at the terminal carbon [23], the formation of head to head adducts of the type *VIIIa*, *IXa* or *Xa* is to be expected. Due to their low dipolarofilicity both 2,3- and 2,5-dihydrothiophenes give in 1,3-dipolar cycloadditions very low yields, the main product being dimers of benzonitrile oxide.

Repeating the cycloaddition procedure with 2,3-dihydropyran as dipolarophile gave cycloadduct *IXa* in quite unsatisfactory yield. Varying the reaction conditions (temperature and solvent) did not rise the yield. The only workable procedure proved to be the reaction of solid benzonitrile oxide, prepared by low-temperature evaporation, with excess 2,3-dihydropyran without solvent.

As can be seen from electronic spectra of the prepared isoxazolines, they should be irradiated by the light with $\lambda < 300$ nm. We used a low-pressure Hg lamp in an onion type reaction vessel. Samples were dissolved in acetonitrile, due to low solubility of biphenyl derivatives in less polar solvents.

In contrast to analogical phenyl-substituted isoxazolines, ($\Phi \sim 0.04$—0.20) biphenyl-substituted derivatives were photostable, the measured quantum yields were lower than 0.001. The reason may be the dissipation of excitation energy by benzene ring rotation in biphenyl. On prolonged irradiation ($t > 40$ h) gradual dwindling of the starting material with concomitant tar formation was observed, the only isolable product (in 8—10 % yield) having been white crystalline, sublimable compound with molecular peak at $m/z = 197$, identified as amide of the 4-biphenylcarboxylic acid. The amide can be seen to arise from the corresponding nitrile during the work-up. Thus instead of the expected photorearrangement *I→II, III→IV* or *V→VI*, biphenyl derivatives undergo on prolonged irradiation fragmentation to nitriles (Scheme 2), a minor product in case of phenyl-substituted analogues (yield ~ 1—2 %) [10, 11].

Next we have investigated the irradiation of condensed isoxazolines, having an oxygen or sulfur in α-position relative to the oxygen of isoxazoline ring, represented by derivatives *VIIIa*, *IXa*, *Xa*, *XIa*, *XIIa*, in order to compare their behaviour with those, having the heteroatom in β-position [10—18]. Experiments showed that derivatives with α-positioned oxygen or sulfur atom behave unlike their β-analogues. Thus irradiation of *VIIIa* failed to produce an isolable product, although many attempts were made to find the suitable solvent (methanol, acetone, acetonitrile, benzene, 2-propanol were tried) or utilize a trapping agent for the tentative nitrile ylide intermediate, formed during the irradiation (*e.g.* acetylenedicarboxylic acid dimethyl ester, trifluoroacetic acid methyl ester). Monitoring of the reaction by means of UV, TLC, and LC revealed the early formation (after ~ 30 s) of an extremely photolabile product, decaying into many secondary products (15—17 peaks on LC). Cycloadducts *IXa—XIIa* likewise furnished only polymeric material. UV monitoring of the irradiation of *Xa* and *XIa* showed at concentrations 10^{-3} mol cm^{-3} in acetonitrile probable formation of enamino aldehydes, indicated by the appearance of bands with $\lambda = 310$ nm (Figs. 1 and 2), found in the case of *Ia*, *IIIa*, and *Va* as well. Quantum yields (Φ) were 0.25 for *XIa* and 0.024 for *Xa*. An oxygen analogue *Ia* had $\Phi = 0.08$ [11]. Based on these quantitative data, sulfur appears to exert biradical stabilizing influence superior to that of oxygen, the same being true for the sulfur in β-position.

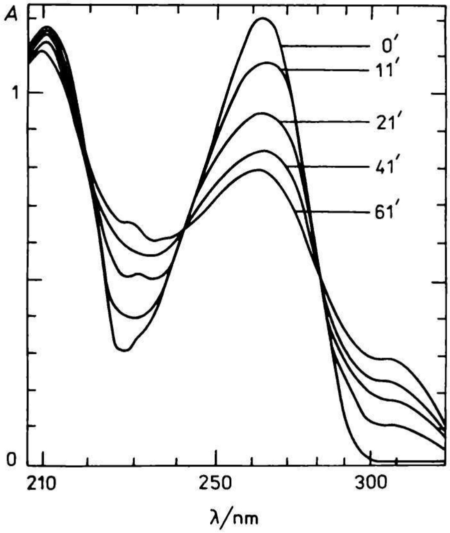


Fig. 1. Spectral changes during the irradiation of *Xa* in acetonitrile, $\lambda_{max} = 253.7$ nm, $c = 1 \times 10^{-3}$ mol cm^{-3}, measured in 1 cm cuvette, time in min.

Moreover, primary photoproducts of sulfur containing derivatives as well as those, having oxygen in α-position are photolabile. This finding accounts for the resulting mixture of photoproducts.

Useful hints of the lability of some derivatives have been gained from the study of their mass spectra, indicating possible fragmentation routes. Compound *Xa* displayed in its mass spectrum an ion with $m/z = 158$, resulting from the loss of $\cdot SCH_3$ group from the molecular peak, accompanied by metastable peak. Loss of $OH^\cdot$ was observed in the mass spectrum of *VIIIa*, whereas *IXa* suffered cycloreversion in mass spectrometer, as evidenced by ion with $m/z = 119$, belonging to benzonitrile oxide and with $m/z = 84$ of 2,3-dihydropyran.

One of the current trends in organic synthesis is the utilization of products of 1,3-dipolar cycloadditions as synthetic equivalents [26]. Among the most popular are isoxazolines [27], used for the preparation of γ-amino alcohols [28], α,β- and β,γ-unsaturated oximes [29], β-hydroxycarbonyl [30] as well as β-hydroxycarboxylic acid derivatives [31]. *Nitta et al.* [32, 33] found that irradiation of 3,5-disubstituted isoxazolines in methanol in the presence of iron pentacarbonyl follows a different course; cleavage of N—O bond and C-4—C-5 bond brings about the formation of an aldehydic and a ketonic fragments (*XVI* and *XVII*) (Scheme 3). A complex of isoxazoline/Fe(CO)$_4$ was responsible for this. 3-Substituted isoxazolines ($R^3 = H$) gave β-hydroxy and β-methoxy ketones (*XVIII*). Inspired by the example and in an attempt to give our photochemical studies a synthetic turn, we have studied the photochemistry of 3-phenyl-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ia*) in the presence of Fe(CO)$_5$ in dry methanol.

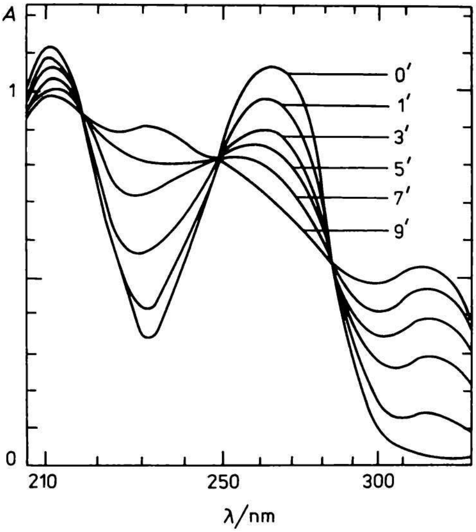
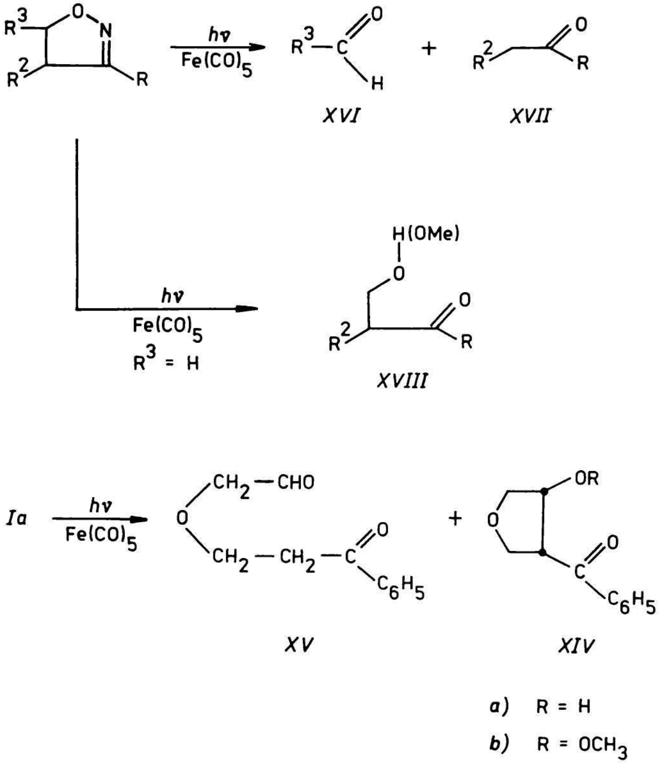


Fig. 2. Spectral changes during the irradiation of *XIa*, condition as in the case of *Xa*.

Irradiation in absence of Fe(CO)$_5$ in a Simax glass vessel, passing only light with $\lambda > 310$ nm, failed to initiate any photochemical reaction. One to twofold excess of iron pentacarbonyl, though absorbing the incident light still resulted only in the recovery of the starting material. Fivefold excess of Fe(CO)$_5$ was necessary to start the photoreaction, furnishing two products as colourless viscous oils. Analogy with the previously published studies supplied the first structural clues, namely compound of the type *XIVa*, *XIVb*, and *XV*. The latter could immediately be excluded, since NMR spectrum failed to show a typical singlet of an aldehydic proton at $\delta = 9.5$ ppm. Both products displayed a two-group aromatic multiplet, indicative of a benzoyl group at δ = 7.9—8.1 ppm and 7.3—7.7 ppm, respectively. Another multiplet at $\delta = 3.78$—4.40 ppm could be taken for the signal of the tetrahydrofuran ring, preserved in the molecule. The structure of 3-benzoyl-4-hydroxytetrahydrofuran was suggested at last for *XIVa*, further supported by bands in IR spectrum at $\tilde{\nu} = 3616$ and 3591 cm^{-1}, lacking in the spectrum of the other product. The NMR spectrum of the latter showed a methoxy group singlet at $\delta = 3.35$ ppm, clinching the final structure assignment as 3-benzoyl-4-methoxytetrahydrofuran (*XIVb*).



Scheme 3

The formation of *β*-hydroxy- and *β*-methoxycarbonyl compounds was observed by *Nitta et al.* [32, 33] only in the case of C-5-substituted derivatives. Since *Ia* represents a 3,4,5-trisubstituted isoxazoline, one would expect the cleavage of C-4—C-5 bond to give *XV*. Due to the special circumstances, the actual reaction pathway remains a moot point, since *XIVa* can be shown to arise from *XV*, making *XIVa* the ultimate product of both routes. *XIVa* has been prepared by an alternative method, giving higher yields and better selectivity — the reduction of *Ia* on RaNi in water—methanol mixture with small addition of H_3BO_3 [34] — disqualifying the photoreaction in the presence of $Fe(CO)_5$ as a prospective synthetic method.

Experimental

All melting points are uncorrected. The mass spectra were obtained with an AEI MS 902 S high-resolution mass spectrometer at an ionizing voltage of 70 eV and an ionizing current of 100 μA. NMR spectra were recorded on a Tesla BS 487 C (proton) and Jeol XF-100 (carbon) in deuteriochloroform with tetramethylsilane as an internal standard, unless otherwise stated. Ultraviolet absorption spectra were measured with a Perkin—Elmer model 323 in methanol, the absorption coefficients reported in $m^2 mol^{-1}$. Infrared spectra were obtained as chloroform solutions on a Unicam SP 100 spectrophotometer.

LC analysis was performed with a modular system consisting of MMC micropump, injection valve with 10 mm^3 loop VALCO, variable UV detector SP 8400 coupled to line recorder TZ 4100. Irradiation experiments were carried out in a forced circulation 300 cm^3 reactor with quartz sleeved low-pressure Hg lamp Toshiba GL-15 as light source [35] at 15 °C. The progress of reaction was checked by TLC and UV spectra measurements. Irradiation of *VIIIa*, *Xa*, and *XIa* was monitored by LC. Experiments with $Fe(CO)_5$ were performed with medium-pressure Hg lamp RVK 125 (Tesla) as light source, in a Simax glass vessel, stirred with magnetic stirrer at 25 °C. Quantum yields measurements were performed as described in [36].

Isoxazolines Ib, IIIb, Vb, VIIb

To the stirred mixture of dipolarophile (21 mmol), triethylamine (0.2 g; 1.98 mmol), 11 % aqueous solution of sodium hypochlorite (20 cm^3; 2.5 g; 34 mmol) and dichloromethane (15 cm^3) at 0 °C was during 15 min added a solution of 4-phenylbenzaldehyde oxime (*XIII*) (21 mmol) in dichloromethane (20 cm^3). Stirring was continued overnight, organic layer separated and concentrated *in vacuo*.

3-(4-Biphenyl)-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ib*) prepared from 2,5-dihydrofuran (fivefold excess), obtained by column chromatography on silica gel with hexane—ethyl acetate as eluant (volume ratio = 1 : 3) in 44 % yield, m.p. = 162—163 °C. For $C_{17}H_{15}NO_2$ ($M_r = 265.17$) w_i(calc.): 76.95 % C, 5.71 % H, 5.27 % N; w_i(found): 76.70 % C, 5.98 % H, 5.27 % N. UV spectrum, λ_{max}/nm (log {ε}): 290 (3.32). Mass spectrum: $m/z = 265$ ($M^{+\cdot}$, base peak). ^1H NMR spectrum, δ/ppm: 7.34—7.70 (m, 9H, H_{arom}), 5.37 (d, d, d, 1H, $J_{3a,6a} = 9.0$ Hz, H-6a), 3.65—4.40 (m, 5H, H_2-4, H_2-6, H-3a). ^{13}C NMR spectrum (d-DMSO), δ/ppm: 156.27 (s, C=N), 128.71, 127.60 127.08, 126.84, 126.37 (aromatic carbons), 85.89 (d, C-6a), 75.36 (t, C-6), 71.15 (t, C-4), 52.83 (d, C-3a).

3,4-Dimethoxycarbonyl-7-(4-biphenyl)-9,10-dioxa-8-azatricyclo[4,3,0,$1^{2,5}$]dec-7-ene (*IIIb*) prepared from 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]hept-2-ene, obtained by trituration of the dry residue by dry ether, yield = 58 %, m.p. = 233—235 °C. For $C_{23}H_{21}NO_6$ ($M_r = 407.23$) w_i(calc.): 67.83 % C, 5.15 % H, 3.43 % N; w_i(found): 67.82 % C, 5.20 % H, 3.70 % N. Mass spectrum: m/z = 407 ($M^{+\cdot}$), 179 ($C_6H_5C_6H_4—\dot{C}{\equiv}N$, base peak). ^1H NMR spectrum (d-DMSO), δ/ppm: 7.35—7.75 (m, 9H, H_{arom}), 4.95 (d, 1H, $J_{1,6}$ = 8.0 Hz, H-1), 4.82 (s, 1H, H-2), 4.73 (s, 1H, H-5), 4.19 (d, 1H, H-6), 3.50 (s, 6H, 2 × $COOCH_3$), 3.25—3.35 (d, d, 2H, H-3a, H-4). ^{13}C NMR (d-DMSO),

δ/ppm: 170.37 (s, C=O), 154.11 (s, C=N), 128.77, 127.72, 127.14, 126.96, 126.49 (aromatic carbons), 85.36 (d, C-1), 83.84 (d, C-2), 79.45 (d, C-5), 56.75 (q, $COOCH_3$), 51.55 (d, C-6), 49.15 (d, C-3), 45.58 (d, C-4).

8-(4-Biphenyl)-3,5,10-trioxa-9-azabicyclo[5,3,0]dec-8-ene (*Vb*) prepared from 1,3-dioxep-5-ene, obtained by trituration of the dry residue with dry ether, yield = 43 %, m.p. = 171—173 °C. For $C_{18}H_{17}NO_3$ ($M_r = 295.35$) w_i(calc.): 73.19 % C, 5.81 % H, 7.74 % N; w_i(found): 73.15 % C, 5.83 % H, 5.00 % N. UV spectrum, λ_{max}/nm (log {ε}): 285 (3.31). Mass spectrum: $m/z = 295$ ($M^{+\cdot}$), 179 ($C_6H_5—C_6H_4—\dot{C}{\equiv}N$, base peak). ^{1}H NMR spectrum, δ/ppm: 7.40—7.80 (m, 9H, H_{arom}), 4.92 (d, 1H, $J_{1,7} = 8.0$ Hz, H-1), 3.87—4.96 (m, 7H, H_2-2, H_2-4, H_2-6, H-7). ^{13}C NMR spectrum (d-DMSO), δ/ppm: 156.33 (s, C=N), 128.71, 127.90, 127.54, 127.14, 126.73, 126.37 (aromatic carbons), 97.77 (t, C-4), 82.79 (d, C-1), 69.74 (t, C-2), 67.11 (t, C-6), 51.25 (d, C-7).

3-(4-Biphenyl)-4-oxo-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*VIIb*) prepared from 5*H*-furan-2-one, obtained by column chromatography of the dry residue (silica gel, hexane—ethyl acetate (volume ratio = 1:3)) in 39 % yield, m.p. = 155—157 °C. For $C_{17}H_{13}NO_3$ ($M_r = 279.30$) w_i(calc.): 73.10 % C, 4.70 % H, 5.01 % N; w_i(found): 73.31 % C, 4.90 % H, 5.12 % N. UV spectrum, λ_{max}/nm (log {ε}): 291 (2.90). Mass spectrum: $m/z = 279$ ($M^{+\bullet}$, base peak). ^{1}H NMR spectrum (d-DMSO), δ/ppm: 7.38—7.96 (m, 9H, H_{arom}), 5.64 (d, d, d, 1H, $J_{3a,6a} = 9.0$ Hz, H-6a), 5.90 (d, 1H, H-3a), 4.60—4.81 (m, 2H, H_2-6). ^{13}C NMR (d-DMSO), δ/ppm: 172.06 (s, C=O), 157.52 (s, C=N), 129.86, 129.08, 128.43, 127.00, 126.35, 125.96 (aromatic carbons), 83.76 (d, C-6a), 73.37 (t, C-6), 53.63 (d, C-3a).

3-Phenyl-3a,4,5,6a-tetrahydrofuro[2,3-d]isoxazole (VIIIa)

To the stirred solution of benzhydroximoyl chloride (1 g; 64 mmol) in dry ether (150 cm^3), kept at (−5) — (−10) °C was dropwise added a solution of triethylamine (10 cm^3; 72 mmol) in dry ether (50 cm^3). Stirring and cooling was continued for another 10 min, precipitated triethylammonium chloride was removed. To the cooled filtrate 2,3-dihydrofuran was gradually added (4.5 g; 64 mmol). The reaction mixture was left to stand overnight, then concentrated to yield *VIIIa*, purified by crystallization from ether. Yield = 9.1 g (76 %), m.p. = 100 °C, Ref. [21] gives m.p. = 77 °C and 40 % yield. For $C_{11}H_{11}NO_2$ ($M_r = 189.21$) w_i(calc.): 69.82 % C, 5.86 % H, 7.40 % N; w_i(found): 70.03 % C, 5.77 % H, 7.44 % N. UV spectrum, λ_{max}/nm (log {ε}): 262 (2.71). Mass spectrum: $m/z = 189$ ($M^{+\cdot}$). ^{1}H NMR spectrum, δ/ppm: 7.30—7.82 (m, 5H, H_{arom}), 6.30 (d, 1H, $J_{3a,6a} = 6.0$ Hz, H-6a), 4.11 (m, 2H, H_2-5), 3.65 (m, 1H, H-3a), 2.02—2.45 (m, 2H, H_2-4). ^{13}C NMR spectrum, δ/ppm: 157.49 (s, C=N), 109.21 (d, C-6a), 66.46 (t, C-5), 51.52 (d, C-3a), 30.47 (t, C-4).

7-Phenyl-2,9-dioxa-8-azabicyclo[4,3,0]non-7-ene (IXa)

To the stirred solution of benzhydroximoyl chloride (2.5 g; 16 mmol) in dry ether (50 cm^3), kept at −5 to −10 °C, was during 15 min added a solution of triethylamine (2.5 cm^3, 18 mmol) in ether (25 cm^3). After additional 15 min of stirring the triethylammonium salt was removed and filtrate concentrated at low temperature ($\theta < -5$ °C) using a rotary vacuum evaporator. Thus obtained pure crystalline benzonitrile oxide was then reacted with pure 2,3-dihydropyran (15 cm^3; 178 mmol), the slow addition of which was followed by overnight standing and distilling off the excess pyran. Derivative *IXa* was obtained by column chromatography on silica gel with 4:1 volume mixture of hexane and ethyl acetate as eluant. Yield = 0.7 g (22 %), m.p. = 86 °C, identical with Ref. [37]. UV spectrum, λ_{max}/nm (log {ε}): 265 (2.90). Mass spectrum: $m/z = 203$ ($M^{+\cdot}$). ^{1}H NMR spectrum, δ/ppm: 7.35—7.75 (m, 5H, H_{arom}), 5.98 (d, 1H, $J_{1,6} = 8.0$ Hz, H-1), 3.42—4.00 (m, 3H, H-6, H_2-3), 1.85—2.12 (m, 2H, H_2-4), 1.40—1.75 (m, 2H, H_2-5). ^{13}C NMR spectrum, δ/ppm: 160.54 (s, C=N), 130.20, 128.84, 126.82 (aromatic carbons), 102.33 (d, C-1), 59.44 (t, C-3), 53.01 (d, C-6), 19.43 (t, C-4), 18.90 (t, C-5).

3-Phenyl-3a,4,5,6a-tetrahydrothieno[2,3-*d*]isoxazole (*Xa*) was prepared by the procedure described for *VIIIa*, in 15 % yield, m.p. = 102 °C, purified on a silica gel column with 4:1 volume mixture of cyclohexane—ethyl acetate as eluant. For $C_{11}H_{11}NOS$ (M_r = = 205.21) w_i(calc.): 64.38 % C, 5.40 % H, 6.83 % N; w_i(found): 64.39 % C, 5.61 % H, 7.01 % N. UV spectrum, λ_{max}/nm (log {ε}): 270 (2.83). Mass spectrum: $m/z = 205$ ($M^{+\cdot}$). ^{1}H NMR spectrum, δ/ppm: 7.32—7.73 (m, 5H, H_{arom}), 6.43 (d, 1H, $J_{3a,6a} = 8.0$ Hz, H-6a), 4.55 (m, 2H, H-3a, H_A-5), 2.12—2.91 (m, 3H, H_B-5, H_2-4). ^{13}C NMR spectrum, δ/ppm: 158.07 (s, C=N), 130.14, 128.84, 127.02, 124.81 (aromatic carbons), 94.07 (d, C-6a), 56.26 (d, C-3a), 36.16 (t, C-5), 31.18 (t, C-4).

3-Phenyl-3a,4,6,6a-tetrahydrothieno[3,4-*d*]isoxazole (*XIa*) prepared from 2,5-dihydrothiophene by the procedure already described for *Xa*, in 13 % yield, m.p. = 82 °C. For $C_{11}H_{11}NOS$ (M_r = 205.21) w_i(calc.): 64.38 % C, 5.40 % H, 6.83 % N; w_i(found): 64.14 % C, 5.45 % H, 6.71 % N. UV spectrum, λ_{max}/nm (log {ε}: 270 (2.85). Mass spectrum: $m/z = 205$ ($M^{+\cdot}$). ^{1}H NMR spectrum, δ/ppm: 7.28—7.68 (m, 5H, H_{arom}), 5.50 (d, d, d, 1H, $J_{3a,6a} = 7.0$ Hz, H-6a), 4.45 (d, d, d, 1H, H-3a), 2.88—3.41 (m, H-4, H_2-4, H_2-6). ^{13}C NMR spectrum, δ/ppm: 156.90 (s, C=N), 130.07, 128.84, 126.95, 124.29 (aromatic carbons), 88.75 (d, C-6a), 56.20 (d, C-3a), 41.51 (t, C-6), 37.03 (t, C-4).

8-Phenyl-10-oxa-3,5-dithia-9-azabicyclo[5,3,0]dec-8-ene (*XIIa*) prepared by the procedure described for *VIIIa*, in 17 % yield, m.p. = 84—86 °C, purified by column chromatography on silica gel with 3 : 1 volume mixture of hexane—ethyl acetate as eluant. For $C_{12}H_{13}NOS_2$ (M_r = 251.23) w_i(calc.): 57.37 % C, 5.22 % H, 5.58 % N; w_i(found): 57.53 % C, 5.41 % H, 5.56 % N. UV spectrum, λ_{max}/nm (log {ε}): 234 (3.38), 276 (2.83). Mass spectrum: $m/z = 251$ ($M^{+\cdot}$). ^{1}H NMR spectrum, δ/ppm: 7.25—7.75 (m, 5H, H_{arom}), 5.47 (m, 1H, H-1), 4.12—4.41 (m, 1H, H-7), 3.21 (s, 2H, H_2-4), 2.63—3.75 (m, H-4, H_2-2, H_2-6). ^{13}C NMR spectrum, δ/ppm: 156.19 (s, C=N), 130.99, 130.47, 129.04, 128,26, 127.48, 127,09 (aromatic carbons), 86.29 (d, C-1), 55.75 (d, C-7), 39,63 (t, C-4), 33.14 (t, C-2), 28.85 (t, C-6).

Photochemical reaction of Ia in the presence of iron pentacarbonyl

The solution of isoxazoline *Ia* (3 mmol) and iron pentacarbonyl (2.93 g; 15 mmol) in dry methanol (250 cm^3) was irradiated under conditions already specified (medium-pressure Hg lamp, $\lambda > 310$ nm) under nitrogen atmosphere. After 21/2 h irradiation time the reaction mixture was filtered, concentrated *in vacuo* and worked up on a silice gel column with 1 : 2 volume mixture of hexane—ethyl acetate as eluant. The chromatography furnished two products:

a) 3-Benzoyl-4-hydroxytetrahydrofuran (*XIVa*), yield = 26 %, as colourless viscous oil. For $C_{11}H_{12}O_3$ ($M_r = 192.21$) w_i(calc.): 68.73 % C, 6.29 % H; w_i(found): 69.02 % C, 6.44 % H. Infrared spectrum (chloroform), $\tilde{\nu}/\mathrm{cm}^{-1}$: 1684 ν(CO), 3591, 3616, 3300 ν(OH). ^{1}H NMR spectrum, δ/ppm: 7.92—8.02 (m, 2H, H_{arom}), 7.30—7.66 (m, 3H, H_{arom}), 4.65 (m, 1H, H-4), 3.78—4.40 (m, 5H, H_2-2, H-3, H_2-5).

b) 3-Benzoyl-4-methoxytetrahydrofuran (*XIVb*), yield = 20 %, colourless viscous oil. For $C_{12}H_{14}O_3$ ($M_r = 206.23$). w_i(calc.): 69.88 % C, 6.84 % H; w_i(found): 69.57 % C, 7.05 % H. Infrared spectrum (chloroform), $\tilde{\nu}/\mathrm{cm}^{-1}$: 1685 ν(CO). ^{1}H NMR spectrum, δ/ppm: 7.96—8.08 (m, 2H, H_{arom}), 7.36—7.67 (m, 3H, H_{arom}), 4.30 (m, 1H, H-4), 3.83—4.15 (m, 5H, H_2-2, H-3, H_2-5), 3.35 (s, 3H, OCH_3).

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References

1. Giezendanner, H., Rozenkranz, H.-J., and Schmid, H., *Helv. Chim. Acta 56,* 2588 (1973).
2. Claus, P., Jürgen, H., Heimgartner, H., Jackson, B., and Schmid, H., *Helv. Chim. Acta 57,* 2173 (1974).
3. Matsuura, T. and Ito, Y., *Tetrahedron Lett. 1973,* 2283.
4. Ito, Y. and Matsuura, T., *Tetrahedron 31,* 1373 (1975).
5. Kumagai, T., Kawamura, A., and Mukai, T., *Tetrahedron Lett. 1983,* 2279.
6. Seshimoto, O., Kumagai, T., Shimizu, K., and Mukai, T., *Chem. Lett. 1977,* 1195.
7. Kumagai, T., Kawamura, Y., and Mukai, T., *Chem. Lett. 1983,* 1357.
8. Mukai, T., Kumagai, T., and Seshimoto, O., *Pure Appl. Chem. 49,* 287 (1977).
9. Kumagai, T., Shimizu, K., Kawamura, Y., and Mukai, T., *Tetrahedron 37,* 3365 (1981).
10. Fišera, Ľ., Laudár, S., and Timpe, H.-J., *Z. Chem. 23,* 148 (1983).
11. Fišera, Ľ., Laudár, S., Timpe, H.-J., Zálupský, P., and Štibrányi, L., *Collect. Czechoslov. Chem. Commun. 49,* 1193 (1984).
12. Fišera, Ľ., Štibrányi, L., Máťušová, A., Oremus, V., and Timpe, H.-J., *Tetrahedron Lett. 1984,* 2731.
13. Fišera, Ľ., Oremus, V., Štibrányi, L., Timpe, H.-J., and Máťušová, A., *Collect. Czechoslov. Chem. Commun. 50,* 1982 (1985).
14. Fišera, Ľ., Oremus, V., Timpe, H.-J., Štibrányi, L., and Zálupský, P., *Collect. Czechoslov. Chem. Commun.*, in press.
15. Fišera, Ľ., Konopíková, M., Štibrányi, L., and Timpe, H.-J., *Collect. Czechoslov. Chem. Commun. 50,* 1971 (1985).
16. Fišera, Ľ., Oravec, P., Štibrányi, L., Kožina, N. D., and Badovskaya, L. A., *Synthesis,* in press.
17. Fišera, Ľ., Kožina, N. D., Oravec, P., Timpe, H.-J., Štibrányi, L., and Badovskaya, L. A., *Collect. Czechoslov. Chem. Commun.*, in press.
18. Fišera, Ľ. and Oravkin, J., *Chem. Papers 39,* 783 (1985).
19. Fišera, Ľ., Kožina, N. D., Badovskaya, L. A., and Štibrányi, L., *Chem. Papers 40,* 685 (1986).
20. Lee, G. A., *Synthesis 1982,* 508.

21. Paulet, R. and Tchelitcheff, S., *Bull. Soc. Chim. Fr. 1962*, 2215.
22. Fišera, Ľ., Štibrányi, L., and Oremus, V., *Chem. Zvesti 38*, 557 (1984).
23. Carramella, P., Cellerino, G., Corsico Coda, A., Gambaa Invernizzi, A., Grünanger, P., Houk, K. N., and Marinone Albini, F., *J. Org. Chem. 41*, 3343 (1976).
24. Fišera, Ľ., *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. R. 32*, 390 (1983).
25. Fišera, Ľ., Kováč, J., Patúš, J., and Mesko, P., *Chem. Zvesti 37*, 819 (1983).
26. *1,3-Dipolar Cycloaddition Chemistry.* (Padwa, A., Editor.) Wiley, New York, 1984.
27. Kozikowski, A. P., *Accounts Chem. Res. 17*, 410 (1984).
28. Jäger, V. and Schwab, W., *Tetrahedron Lett. 1978*, 3129.
29. Grund, H. and Jäger, V., *Justus Liebigs Ann. Chem. 1980*, 80.
30. Curran, D. P., *J. Amer. Chem. Soc. 105*, 5826 (1983).
31. Andersen, S. H., Sharma, K. K., and Torsell, K. B. G., *Tetrahedron 39*, 223 (1983).
32. Nitta, M. and Kobayashi, T., *Chem. Lett. 1983*, 51.
33. Nitta, M. and Kobayashi, T., *Tetrahedron Lett. 1982*, 3925.
34. Fišera, Ľ., Štibrányi, L., and Závacká, A., *Chem. Papers*, in press.
35. Štibrányi, L., *Czech. Appl.* 7366 (1983).
36. Timpe, H.-J., Dietrich, R., Böckelmann, J., Friedel, I., Bögel, H., and Hanke, G., *Collect. Czechoslov. Chem. Commun. 46*, 219 (1981).
37. Adachi, J. and Kano, H., *Chem. Pharm. Bull.* (Tokyo) *16*, 117 (1968).

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