AN UNUSUAL EFFECT OF EXO–ENDO CONFIGURATION ON THE QUANTUM YIELD Φ OF PHOTOCHEMICAL REARRANGEMENT OF 4-R-SUBSTITUTED 8-PHENYL-3,5,10-TRIOXA-9-AZABICYCLO-[5,3,0]-8-DECENES*

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The dependence has been found of the quantum yield Φ of photochemical rearrangement of the title compounds (where R means ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, 2-furyl, 2-thienyl) on the exo (*I*) or endo (*II*) arrangement of the R substituent. The endo derivatives exhibit higher Φ values (0·020—0·041) than the exo derivatives (0·007—0·019). The photochemical rearrangement gives the derivatives of 2-R-6-phenyl-7-formyl-2,4,5,8-tetrahydro-1,3-dioxa-5-azocine as the single products in good yields. The 2-furyl derivative gives polymeric products. The title compounds have been prepared by 1,3-dipolar cycloaddition of benzenenitriloxide to the respective substituted 1,3-dioxep-5-enes.

Our previous papers showed that photochemical rearrangements of isoxazolines, which are known[1–9] to be usually non-selective, proceed unusually selectively to give the heterocyclic enaminoaldehydes, if a structural element is introduced which enables a fragmentation of the primary biradical[10–15]. Measurements of quantum yields of the transformation of 4-R-substituted 8-phenyl-3,5,10-trioxa-9-azabicyclo[5,3,0]--8-decenes (*I* and *II*) into 2-R-6-phenyl-7-formyl-2,4,5,8-tetrahydro-1,3-dioxa-5-azocines (*III*), where R stands for methyl or phenyl, revealed[13] unequal Φ values for the endo derivatives (*IIb*, *IIc*) and the corresponding exo derivatives** (*Ib*, *Ic*). As such phenomena of dependence of a photochemical reaction on exo–endo stereochemical arrangement of a substituent have been little known yet, the aim of the present paper is preparation of a larger series of the derivatives *I* and *II* for verification of the dependence found.

The model isoxazoline compounds were prepared by 1,3-dipolar cycloaddition of benzenenitriloxide to 2-R-substituted 1,3-dioxep-5-enes (*IV*). For the R substituent

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** Which were uncorrectly denoted as endo derivatives in our previous papers[12,13,15].

we chose, besides methyl and phenyl described in ref.[13], also ethyl, propyl, isopropyl, butyl, tert-butyl, 2-furyl, and 2-thienyl. In all the cases the reaction produced the diastereoisomeric pair of exo adduct *I* and endo adduct *II*. Surprisingly, the *I* : *II* ratio does not increase with increasing size of the substituent (Table I) but, on the contrary, the portion of endo derivative *II* increases in the series Me < Et < Pr < < tert-Bu. In the case of the isopropyl derivative the endo derivative *IIf* already represents the main reaction product. From the 2-furyl and 2-thienyl derivatives of *IV*, the two products *I* and *II* are formed in equal amounts. The mentioned anomaly can be explained by the finding[16] that the 1,3-dioxep-5-ene system represents a dynamic equilibrium between the chair (C_s) and twist form (C_2) of *IV*. The chair form portion increases with increasing size of the R substituent (8, 15, and 55% for R = H, Me, and tert-Bu, respectively). The highest yields of the 1,3-dipolar cycloaddition were obtained just in the cases of the isopropyl derivative (*If* + *IIf* 84%) and tert-butyl derivative (*Ii* + *IIi* 95%). With the heterocyclic R substituents the predominant reaction is dimerization of benzenenitriloxide. The exo and endo derivatives *I*, *II* could be separated by column chromatography. From the butyl and isobutyl derivatives the exo adducts *Ig* and *Ih* are only formed. The endo derivatives *IIg* and *IIh* were not found. It seems likely that a long linear chain with possible rotation prevents the approach of the 1,3-dipole from the endo side. The assignment of exo and endo

TABLE I

The photolysis quantum yields (methanol) and UV spectral data of the compounds prepared

R	exo		endo	
	Φ	λ_{max} (log ε) nm	Φ	λ_{max} (log ε) nm
Me[a]	0·024	261 (3·00)	0·041	265 (2·97)
Et	0·016	258 (2·99)	0·033	263 (3·06)
Pr	0·014	258 (3·03)	0·041	263 (3·03)
iso-Pr	0·015	257 (3·00)	0·029	265 (2·89)[c]
Bu	0·016	258 (2·99)		
iso-Bu	0·019	268 (3·03)		
tert-Bu	0·014	256 (3·00)	0·027	265 (2·95)
C_6H_5[a]	0·008	260 (2·99)	0·026	266 (3·03)
2-Furyl	0·005	260 (3·00)	0·007	265 (3·03)
2-Tienyl	0·007	260 (3·00)[d]	0·020	264 (3·05)[e]

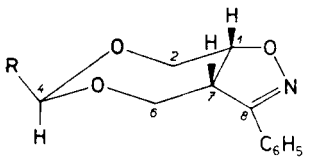
[a] For R = H it is Φ = 0·016 in methanol and 0·026 in acetonitrile, λ_{max} = 260 nm (log ε = 2·97); [b] the values measured in acetonitrile[2,13]; [c] another band at 240 nm (log ε = 2·98); [d] 248 nm (log ε = 3·10); [e] 236 nm (log ε = 3·12).

structure was carried out as in ref.[13] on the basis of different chemical shift values (due to the bent structure of the bicyclic adducts) of triplets of $C_{(2)}$ and $C_{(6)}$ carbon atoms in the ^{13}C NMR spectra. The exo adducts *Ib–Ik*, having equatorial arrangement of the 4-R substituent, exhibit the mentioned signals in the regions of 67·96 to 70·90 ppm ($C_{(2)}$) and 63·15–66·90 ($C_{(6)}$), *i.e.* at the δ values almost equal to those of the unsubstituted derivative *Ia* (ref.[13]). The endo derivatives *IIb–IIk* show the γ effect in their ^{13}C NMR spectra, the respective triplets being shifted by 3–4 ppm to higher field due to the effect of the axial 4-R substituent, and the δ values of $C_{(2)}$ and $C_{(6)}$ are approximately the same. Moreover, the endo derivatives exhibit higher δ values of the isoxazoline 1-H and 4-H atoms in their ^1H NMR spectra and also, in all the cases, higher values of the longest-wave absorption maximum in their UV spectra ($\Delta\lambda$ = 4–9 nm). The effect of R substituents on the chemical shift values in the ^{13}C NMR spectra is interesting. Besides the effect already mentioned (the values of $C_{(2)}$ and $C_{(6)}$ triplets) the most distinct difference in the δ values is observed for the $C_{(4)}$ carbon atom, the values for the exo and endo derivatives being different in this case, too. Higher δ values of $C_{(4)}$ atom of the alkylated and arylated derivatives are found with the endo and exo isomers, respectively. The effect of exo–endo arrangement makes itself felt also in the δ values of $C_{(7)}$ isoxazoline carbon atom, whereas the δ values of $C_{(1)}$ and $C_{(8)}$ isoxazoline carbon atoms are practically constant.

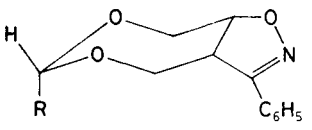
The preparative photoreactions were realized with the use of monochromatic radiation with λ_{max} = 253·7 nm. The photolyses of the methanolic solutions always (except for *Ij* and *IIj*) gave the rearrangement products of 2-R-6-phenyl-7-formyl-2,4,5,8-tetrahydro-1,3-dioxa-5-azocine (*IIIc–IIIi, IIIk*). Their structure was proved, as in the case of the derivatives *IIIb, IIIc* (ref.[13]), on the basis of the presence of aldehydic proton in the ^1H NMR spectrum (8·83–8·92 ppm), doublet of CHO in the ^{13}C NMR spectrum (190·48–190·70 ppm), singlets of carbon atoms of the double bond of the enaminoaldehydic structural unit at 162·17–162·95 ppm ($C_{(7)}$) and at 113·20–113·63 ppm ($C_{(6)}$) as well as on the basis of their bathochromic shift of the longest-wave absorption maximum (λ_{max} 298–300 nm) in the UV spectrum, as compared with the starting derivatives *I* and *II*, which proves the presence of NH—C=C—CHO and C_6H_5—C=C—CHO chromophores, respectively.

The triplets due to $C_{(4)}$ and $C_{(8)}$ carbon atoms are found in the regions of 73·94 to 74·08 ppm and 66·20–67·24 ppm, respectively. In the ^1H NMR spectrum the multiplet signal of aromatic protons of the starting derivatives *I* and *II* is simplified to a distinct singlet of the rearrangement products. The geminal protons 4-H_A and 4-H_B are found in the spectra as distinct doublets about 5·50 and 4·16 ppm with the coupling constant J_{AB} = 15.0 Hz in contrast to the geminal protons 8-H_2 which make themselves felt as a complex multiplet in the region of 4·1–5·1 ppm. In deuterated dimethyl sulphoxide, however, the above-mentioned signals form apparent singlets (*e.g.* 4·86 and 4·95 ppm for *IIId*). The photochemical reactions were carried out until disappearance of the starting derivative *I* or *II* (proved by TLC), so that

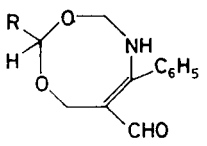
subsequent photochemical reactions of the derivative *III* might be prevented which would lead to polymeric materials. Therefore, methanol was chosen as the solvent for the photolysis, the enaminoaldehydes being least labile therein (see ref.[14]). Both diastereoisomers *I* and *II* give the same rearrangement product *III*, which was explained in the previous paper[13]. Also formation of the derivatives *IIId*–*IIIi* and *IIIk* is presumed to proceed by the same mechanism as that of *IIIa*–*IIIc* (ref.[13]). The 2-furyl derivatives *Ij* or *IIj* gave on irradiation (under the same conditions as above) polymeric materials only. Presumably in this case the photochemical reaction prefers the furane ring.



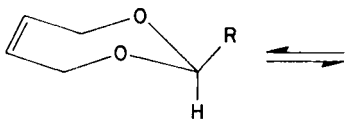
I



II



III



C_S *IV* C_2

In formulae *I*–*IV*: *a*, R = H; *b*, R = C_6H_5; *c*, R = CH_3; *d*, R = C_2H_5; *e*, R = $CH_3CH_2CH_2$; *f*, R = $(CH_3)_2CH$; *g*, R = $CH_3(CH_2)_3$; *h*, R = $(CH_3)_2CHCH_2$; *i*, R = $(CH_3)_3C$; *j*, R = 2-furyl; *k*, R = 2-thienyl.

Table I gives the results of measurements of quantum yields of the photorearrangements *I* → *III* and *II* → *III*. In all the cases the endo derivatives *II*, having higher λ_{max} values, exhibit also higher values of quantum yields than the corresponding exo derivatives *I*. With the alkyl-containing exo derivatives the quantum yield Φ changes but slightly, being in the region from 0·014 to 0·019 and corresponding to that of the unsubstituted derivative *Ia* (Φ = 0·016). The aryl-containing exo derivatives exhibit lower Φ values: 0·008 and 0·007 for the phenyl and 2-thienyl derivatives, respectively. With the endo derivatives *II* the substituents have greater effect on the efficiency of the photorearrangement, and the quantum yields are higher (in the regions of 0·027–0·041 and 0·020–0·026 for the alkyl and aryl derivatives, respectively). The Φ values found from the decrease of the starting compound for the 2-furyl derivatives are very low, but – as already mentioned – in this case the photoreaction is of another type. Our previous report[13] gives two potential expla-

nations in the case of the methyl and phenyl derivatives: a possible effect of additional absorption maxima of the endo derivatives as compared with the corresponding exo derivatives or a loss of 1,3-diaxial strain in the endo derivatives. The first explanation was not confirmed, because in the series prepared the 2-isopropyl derivative only has an additional absorption maximum (at 240 nm). Hence there remains the above-mentioned loss of the 1,3-diaxial interactions in the endo derivatives *II* as a possible explanation of their higher Φ values. Moreover, the 1,3-diaxial interactions presumably lead to the twist-type conformation for the endo derivatives, which enables through-space interactions between *n* electrons of 5-O oxygen atom and π electrons of C=N group and causes the above-mentioned differences between the UV spectra of the exo and endo derivatives.

The UV spectra also exhibit an unexpected difference between the corresponding exo and endo derivatives. In all the cases the endo compounds absorb at higher wavelengths ($\Delta\lambda = 4-9$ nm), $\Delta\lambda$ being larger for the derivatives with bulkier R substituents.

EXPERIMENTAL

The melting points are not corrected. The ^{1}H NMR spectra were measured with a Tesla BS 487 C apparatus, the ^{13}C NMR spectra with a JEOL apparatus in deuteriochloroform (if not otherwise stated), using tetramethylsilane as the internal standard. The UV spectra were measured with a Perkin–Elmer 323 apparatus in temperated cells in methanol. The ε values are given in $m^2\ mol^{-1}$. The 2-substituted 1,3-dioxep-5-enes (*IV*) were prepared by the reaction of the corresponding aldehyde with commercial *cis*-2-butene-1,4-diol in the presence of *p*-toluenesulphonic acid as a catalyst[17], the chloride of benzenehydroximic acid was prepared by chlorination of benzaldoxime in chloroform according to ref.[18].

The photochemical reactions were realized with the use of a low-pressure discharge lamp Toshiba GL-15 (15 W) in a quartz burner. The photoreactions were carried out in a temperated 300 ml reactor[19] with forced circulation of the irradiated solution (methanol) at 15°C. The reaction course was followed by TLC on Silufol plates. The measurement of quantum-chemical yields (in methanol) at the wavelength of 253·7 nm was described in refs[11,20].

Preparation of 4-R-Substituted 8-Phenyl-3,5,10-trioxa-9-azabicyclo[5,3,0]-8-decenes

During 1 h, a solution of 2·8 ml (26 mmol) triethylamine in 20 ml dry ether was added to a solution of 20 mmol benzenehydroximic acid chloride and 20 mmol respective 1,3-dioxep-5-ene in 40 ml dry ether with stirring and cooling at 0–5°C. The mixture was stirred at room temperature overnight, and the separated triethylamine hydrochloride was filtered off and washed with 30 ml dry ether. The combined ethereal solutions were concentrated in vacuum, and the evaporation residue was submitted to column chromatography (100 g silica gel, 40–100 μ; chloroform as the eluent) to give the respective isoxazolines *I* and *II*. The first fractions of eluate contain benzenenitriloxide dimer (yield 2–66%). In all the cases the endo derivatives *I* have higher R_F values than the exo derivatives *II*.

Endo-4-ethyl-8-phenyl-3,5,10-trioxa-9-azabicyclo[5,3,0]-*8-decene* (IId): yield 8%, m.p. 56°C. For $C_{14}H_{17}NO_3$ (247·3) calculated: 67·99% C, 6·93% H, 5·66% N; found: 68·17%C, 7·04% H,

5·61% N. ^{1}H NMR spectrum: 7·33—7·72 (m, 5 H, aromatic H), 5·03 (M, 1 H, 1-H), 4·57 (t, J = 6·0 Hz, 1 H, 4-H), 3·61—4·41 (m, 5 H, 2-H_2, 6-H_2, 7-H), 1·46—1·82 (m, 2 H, CH_2), 0·90 (t, J = 6·0 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 157·24 (s, $C_{(8)}$), 130·33, 128·97, 128·58, 126·89 (aromatic C), 109·22 (d, $C_{(4)}$), 83·49 (d, $C_{(1)}$), 65·88 (t, $C_{(2)}$), 65·42 (t, $C_{(6)}$), 52·37 (d, $C_{(7)}$), 27·29 (t, CH_2), 8·84 (q, CH_3).

Exo-4-*ethyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Id): yield 32%, m.p. 137—140°C. For $C_{14}H_{17}NO_3$ (247·3) calculated: 67·99%C, 6·93% H, 5·66% N; found: 68·14% C, 6·82% H, 5·47% N. ^{1}H NMR spectrum: 7·29—7·71 (m, 5 H, aromatic H), 4·81 (dd, $J_{1,7}$ = 11·0 Hz, 1 H, 1-H), 4·42 (t, J = 5·5 Hz, 1 H, 4-H), 3·66—4·53 (m, 5 H, 2-H_2, 6-H_2, 7-H), 1·41—1·75 (m, 2 H, CH_2), 0·85 (t, J = 6·0 Hz, 3 H, CH_3).

Endo-4-*propyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (IIe): yield 11%, m.p. 52 to 55°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94% C, 7·33% H, 5·36% N; found: 69·03% C, 7·27% H, 5·45% N. ^{1}H NMR spectrum: 7·32—7·73 (m, 5 H, aromatic H), 5·00 (m, 1 H, 1-H), 4·77 (t, J = 5·5 Hz, 1 H, 4-H), 3·75—4·66 (m, 5 H, 2-H_2, 6-H_2, 7-H), 1·25—1·68 (m, 4 H, CH_2), 0·93 (t, J = 6·0 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 157·13 (s, $C_{(8)}$), 130·25, 128·88, 128·49, 126·80, 126·35 (aromatic C), 107·91 (d, $C_{(4)}$), 83·43 (d, $C_{(1)}$), 65·83 (t, $C_{(3)}$), 65·32 (t, $C_{(6)}$), 52·33 (d, $C_{(7)}$), 36·10, 17·85, 13·82 (propyl C).

Exo-4-*propyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,8]-8-*decene* (Ie): yield 39%, m.p. 78—81°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94% C, 7·33% H, 5·36% N; found: 68·83% C, 7·21% H, 5·39% N. ^{1}H NMR spectrum: 7·36—7·71 (m, 5 H, aromatic H), 4·81 (dd, $J_{1,7}$ = 11·0 Hz, 1 H, 1-H), 4·36 (t, J = 6·0 Hz, 1 H, 4-H), 3·52—4·52 (m, 5 H, 2-H_2, 6-H_2, 7-H), 1·10—1·71 (m, 4 H, CH_2), 0·83 (t, J = 6·0 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 157·58 (s, $C_{(8)}$), 129·86, 128·75, 126·87 (aromatic C), 107·13 (d, $C_{(4)}$), 84·43 (d, $C_{(1)}$), 68·24 (t, $C_{(2)}$), 63·43 (t, $C_{(6)}$), 51·68 (d, $C_{(7)}$), 36·23, 17·72, 13·76 (propyl C).

Endo-4-*isopropyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (IIf): yield 46%, m.p. 115—118°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94% C, 7·33% H, 5·36% N; found: 68·87% C, 7·49% H, 5·28% N. ^{1}H NMR spectrum: 7·35—7·75 (m, 5 H, aromatic H), 4·93 (m, 1 H, 1-H), 3·63 4·42 (m, 6 H, 2-H_2, 6-H_2, 7-H), 1·81 (m, 1 H, CH), 0·91 (d, 6 H, CH_3).

Exo-4-*isopropyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (If): yield 38%, m.p. 87 to 90°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94% C, 7·33% N, 5·36% N; found: 68·74% C, 7·14% H, 5·51% N. ^{1}H NMR spectrum: 7·32—7·67 (m, 5 H, aromatic H), 4·80 (dd, $J_{1,7}$ = 11 Hz, 1 H, 1-H), 4·31 (d, J = 3·0 Hz, 1 H, 4-H), 3·65—4·51 (m, 5 H, 2-H_2, 6-H_2, 7-H), 1·73 (m, 1 H, CH), 0·80 and 0·88 (dd, CH_3, CH_3). ^{13}C NMR spectrum: 157·62 (s, $C_{(8)}$), 129·88, 129·23, 128·77, 126·95 (aromatic C), 111·29 (d, $C_{(4)}$), 83·36 (d, $C_{(1)}$), 69·00 (t, $C_{(2)}$), 63·86 (t, $C_{(6)}$), 51·84 (d, $C_{(7)}$), 32·29, 17·41 (isopropyl C).

Exo-4-*butyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Ig): yield 21%, m.p. 66—69°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 70·02% C, 7·48% H, 5·21% N. ^{1}H NMR spectrum: 7·30—7·75 (m, 5 H, aromatic H), 4·80 (d, $J_{1,7}$ = 11·0 Hz, 1 H, 1-H), 3·52—4·55 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H), 1·27—1·72 (m, 6 H, CH_2), 0·85 (t, 3 H, CH_3). ^{13}C NMR spectrum: 157·56 (s, $C_{(8)}$), 129·81, 128·71, 126·82 (aromatic C), 107·21 (d, $C_{(4)}$), 83·36 (d, $C_{(1)}$), 68·09 (t, $C_{(2)}$), 63·22 (t, $C_{(6)}$), 51·52 (d, $C_{(7)}$), 33·78, 26·50, 22·28, 13·83 (butyl C).

Exo-4-*isobutyl*-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Ih): yield 23%, m.p. 80 to 82°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 69·87% C, 7·53% H, 5·08% N. ^{1}H NMR spectrum: 7·33—7·72 (m, 5 H, aromatic H), 4·81 (dd, $J_{1,7}$ = = 11·0 Hz, 1 H, 1-H), 3·66—4·63 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H), 1·36—1·75 (m, 3 H, CH, CH_2), 0·85 (d, J = 6·0 Hz, 6 H, 2 × CH_3). ^{13}C NMR spectrum: 157·63 (s, $C_{(8)}$), 129·88, 128·71,

126·89 (aromatic C), 106·10 (d, $C_{(4)}$), 83·42 (d, $C_{(1)}$), 67·96 (t, $C_{(2)}$), 63·15 (t, $C_{(6)}$), 51·59 (d, $C_{(7)}$), 42·62, 24·10, 22·34, 13·84 (isobutyl C).

Endo-4-*tert*-butyl-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (IIi): yield 41%, m.p. 78–82°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 70·07% C, 7·63% H, 5·24% N. ^{1}H NMR spectrum: 7·35–7·72 (m, 5 H, aromatic H), 4·95–5·27 (m, 1 H, 1-H), 3·61–4·53 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H), 0·90 (s, 9 H, CH_3). ^{13}C NMR spectrum: 157·30 (s, $C_{(8)}$), 126·82–130·86 (aromatic C), 116·40 (d, $C_{(4)}$), 82·97 (d, $C_{(1)}$), 69·19 (t, $C_{(2)}$), 67·75 (t, $C_{(6)}$), 53·41 (d, $C_{(7)}$), 34·54 (s, C), 24·95 (q, CH_3).

Exo-4-*tert*-butyl-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Ii): yield 54%, m.p. 123 to 126°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 69·92% C, 7·53% H, 5·32% N. ^{1}H NMR spectrum: 7·33–7·66 (m, 5 H, aromatic H), 4·84 (dd, $J_{1,7}$ = = 11·0 Hz, 1 H, 1-H), 3·67–4·55 (m, 5 H, 2-H_2, 6-H_2, 7-H), 3·93 (s, 1 H, 4-H), 0·84 (s, 9 H, CH_3). ^{13}C NMR spectrum: 157·30 (s, $C_{(8)}$), 129·62, 128·71, 127·02 (aromatic C), 113·83 (d, $C_{(4)}$), 82·97 (d, $C_{(1)}$), 70·62 (t, $C_{(2)}$), 65·17 (t, $C_{(6)}$), 52·43 (d, $C_{(7)}$), 35·67 (s, C), 25·01 (q, CH_3).

Endo-4-(2-*furyl*)-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (IIj): yield 18%, m.p. 107 to 110°C. For $C_{16}H_{15}NO_4$ (285·3) calculated: 67·36% C, 5·30% H, 4·91% N; found: 67·12% C, 5·41% H, 4·99% N. ^{1}H NMR spectrum: 7·35–7·80 (m, 6 H, aromatic H, 5-H furane), 6·46 (m, 2 H, 3-H and 4-H furane), 4·95 (m, 1 H, 1-H), 3·86–4·43 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide): 157·78 (s, $C_{(8)}$), 150·44, 142·97, 110·25, 108·04 (furane C), 130·25, 128·95, 128·43, 126·74 (aromatic C), 97·45 (d, $C_{(4)}$), 83·50 (d, $C_{(1)}$), 63·95 (t, $C_{(2)}$), 62·00 (t, $C_{(6)}$), 49·99 (d, $C_{(7)}$).

Exo-4-(2-*furyl*)-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Ij): yield 18%, m.p. 148 to 150°C. For $C_{16}H_{15}NO_4$ (285·3) calculated: 67·36% C, 5·30% H, 4·91% N; found: 67·57% C, 5·15% H, 5·04% N. ^{1}H NMR spectrum: 7·28–7·72 (m, 6 H, aromatic H, 5-H furane), 6·41 (d, $J_{3,4}$ = 3·5 Hz, 1 H, 3-H furane), 6·30 (dd, 1 H, 4-H furane), 4·82 (dd, $J_{1,7}$ = 8·0 Hz, 1 H, 1-H), 3·72–4·52 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide): 157·16 (s, $C_{(8)}$), 151·06, 142·55, 110·19, 107·13 (furane C), 129·81, 128·90, 126·82 (aromatic C), 100·05 (d, $C_{(4)}$), 82·84 (d. $C_{(1)}$), 68·93 (t, $C_{(2)}$), 65·55 (t, $C_{(6)}$), 51·00 (d, $C_{(7)}$).

Endo-4-(2-*thienyl*)-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (IIk): yield 23%, m.p. 117–119°C. For $C_{16}H_{15}NO_3S$ (301·3) calculated: 63·79% C, 4·98% H, 4·65% N; found: 63·85% C, 5·03% H, 4·57% N. ^{1}H NMR spectrum (hexadeuteriodimethyl sulphoxide): 6·92–7·75 (m, 8 H, aromatic H, thiophene), 4·94 (d, $J_{1,7}$ = 11·0 Hz, 1 H, 1-H), 4·00–4·48 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide): 157·62 (s, $C_{(8)}$), 141·05, 130·21, 128·97, 128·38, 128·12, 126·76, 126·24, 125·39 (aromatic C, thiophene), 100·32 (d, $C_{(4)}$), 83·23 (d, $C_{(1)}$), 64·19 (t, $C_{(2)}$), 62·37 (t, $C_{(6)}$), 50·09 (d, $C_{(7)}$).

Exo-4-(2-*thienyl*)-8-*phenyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-decene (Ik): yield 20%, m.p. 156–159°C. For $C_{16}H_{15}NO_3S$ (301·3) calculated: 63·79% C, 4·98% H, 4·65% N; found: 64·02% C, 5·12% H, 4·61% N. ^{1}H NMR spectrum: 6·86–7·95 (m, 8 H, aromatic H, thiophene), 4·91 (m, 1 H, 1-H), 3·75–4·57 (m, 6 H, 2-H_2, 6-H_2, 4-H, 7-H). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide): 157·06 (s, $C_{(8)}$), 141·74, 129.73, 128·82, 126·80, 126·48, 125·89, 124·98 (aromatic C, thiophene), 102·46 (d, $C_{(4)}$), 82·72 (d, $C_{(1)}$), 69·15 (t, $C_{(2)}$), 65·71 (t, $C_{(6)}$), 51·10 (d, $C_{(7)}$).

Photochemical Reactions of the Isoxazolines Prepared

A solution of 1·3 mmol isoxazoline *I* or *II* in 300 ml methanol was irradiated until the starting derivative was non-detectable by TLC (Silufol, cyclohexane–ethyl acetate 1 : 3). The reaction mixture was concentrated in vacuum (the bath temperature below 30°C), and the rearrangement

product *III* was obtained by trituration of the evaporation residue with dry ether or by column chromatography.

2-*Ethyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIId) was obtained from *Id* by 4 h irradiation, yield 48%, m.p. 177–181°C. For $C_{14}H_{17}NO_3$ (247·3) calculated: 67·99% C, 6·93% H, 5·66% N; found: 67·77% C, 7·04% H, 5·52% N. UV spectrum, λ_{max} (log ε): 236 nm (2·93) and 299 nm (3·06). ^{1}H NMR spectrum: 8·87 (s, 1 H, CHO), 7·41 (s, 5 H, aromatic H), 6·07 (broad s, 1 H, NH), 5·51 (d, $J_{AB} \doteq$ 15 Hz, 1 H, 4-H_A), 4·62–5·15 (m, 2 H, 8-H_2), 4·27 (t, J = 5·5 Hz, 1 H, 2-H), 4·17 (d, 1 H, 4-H_B), 1·72 (m, 2 H, CH_2), 0·97 (t, J = 6·5 Hz, 3 H, CH_3). ^{1}H-NMR spectrum (hexadeuteriodimethyl sulphoxide): 8·72 (s, 1 H, CHO), 7·97 (broad s, 1 H, NH), 7·47 (s, 5 H, aromatic H), 5·23 (d, J_{AB} = 15 Hz, 1 H, 4-H_A), 4·86 and 4·95 (apparent singlets, 2 H, 8-H_2), 4·51 (t, J = 5·5 Hz, 1 H, 2-H), 4·26 (d, 1 H, 4-H_B), 1·60 (m, 2 H, CH_2), 0·91 (t, J = 6·5 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 190·7 (d, CHO), 162·4 (s, $C_{(7)}$), 136·6, 130·6, 128·6 (aromatic C), 113·4 (s, $C_{(6)}$), 107·9 (d, $C_{(2)}$), 74·0 (t, $C_{(4)}$), 66·2 (t, $C_{(8)}$), 28·3 and 9·3 (ethyl C). The irradiation of endo derivative *IId* for 2 h gave *IIId* in the yield of 85%.

2-*Propyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIIe) was obtained from *Ie* by 4·5 h irradiation, yield 55%, m.p. 178–180°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94%C, 7·33% H, 5·36% N; found: 69·15% C, 7·31% H, 5·52% N. UV spectrum, λ_{max} (log ε): 235 nm (3·03) and 298 nm (3·16). ^{1}H NMR spectrum: 8·92 (s, 1 H, CHO), 7·43 (s, 5 H, aromatic H), 5·53 (d, J_{AB} = 15 Hz, 1 H, 4-H_A), 4·72–5·17 (m, 3 H, 8-H_2, NH), 4·55 (t, J = 5·5 Hz, 1-H, 2-H), 1·22–1·75 (m, 4 H, CH_2), 0·93 (t, J = 7·0 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 190·62 (d, CHO), 162·17 (s, $C_{(7)}$), 136·50, 130·53, 128·51 (aromatic C), 113·37 (s, $C_{(6)}$), 106·62 (d, $C_{(2)}$), 73·94 (t, $C_{(4)}$), 66·20 (t, $C_{(8)}$), 36·97, 18·19, 13·83 (propyl C). The irradiation of endo derivative *IIe* for 3 h gave *IIIe* in the yield of 61%.

2-*Isopropyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIIf) was obtained from *If* by 3·5 h irradiation and column chromatography (silica gel; hexane–ethyl acetate 1 : 2), yield 50%, m.p. 190–193°C. For $C_{15}H_{19}NO_3$ (261·3) calculated: 68·94% C, 7·33% H, 5·36% N; found: 70·21% C, 7·17% H, 5·49% N. UV spectrum, λ_{max} (log ε): 235 nm (3·07) and 299 nm (3·21). ^{1}H NMR spectrum: 8·87 (s, 1 H, CHO), 7·42 (s, 5 H, aromatic H), 5·50 (d, J_{AB} = 15 Hz, 1 H, 4-H_A), 4·17–5·13 (m, 4 H, 8-H_2, 2-H, NH), 4·16 (d, 1 H, 4-H_B) 1·88 (m, 1 H, CH), 0·97 (d, J = 5·0 Hz, 6 H, 2 × CH_3). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide): 188·29 (d, CHO), 162·95 (s, $C_{(7)}$), 136·31, 129·94, 128·25 (aromatic C), 111·10 (s, $C_{(6)}$), 108·37 (d, $C_{(2)}$), 73·29 (t, $C_{(4)}$), 64·19 (t, $C_{(8)}$), 32·35 and 17·80 (isopropyl C).

The irradiation of endo derivative *IIf* for 3 h gave *IIIf* in the yield of 57%.

2-*Butyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIIg) was obtained from *Ig* by 4 h irradiation, yield 83%, m.p. 185–187°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 69·92% C, 7·57% H, 5·28% N. UV spectrum, λ_{max} (log ε): 235 nm (3·05) and 299 nm (3·21). ^{1}H NMR spectrum: 8·91 (s, 1 H, CHO), 7·43 (s, 5 H, aromatic H), 5·53 (d, J_{AB} = 15 Hz, 1 H, 4-H_A), 4·58–5·13 (m, 3 H, 8-H_2, NH), 4·52 (t, J = 5·0 Hz, 1 H, 2-H), 4·16 (d, 1 H, 4-H_B), 1·25–1·72 (m, 6 H, CH_2), 0·90 (t, J = 5·5 Hz, 3 H, CH_3). ^{13}C NMR spectrum: 190·63 (d, CHO), 162·17 (s, $C_{(7)}$), 136·31, 130·53, 128·51 (aromatic C), 113·37 (s, $C_{(6)}$), 106·87 (d, $C_{(2)}$), 73·94 (t, $C_{(4)}$), 66·20 (t, $C_{(8)}$), 34·69, 27·02, 22·41, 14·03 (butyl C).

The irradiation of endo derivative *IIg* for 2 h gave *IIIg* in the yield of 74%.

2-*Isobutyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIIh) was obtained from *Ih* by 3 h irradiation and column chromatography (silica gel, hexane–ethyl acetate 1 : 2), yield 30%, m.p. 187–189°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·67% H, 5·09% N; found: 69·87% C, 7·61% H, 5·33% N. UV spectrum, λ_{max} (log ε): 235 nm (2·92) and 289 nm (3·13). ^{1}H NMR spectrum: 8·83 (s, 1 H, CHO), 7·38 (s, 5 H, aromatic H). 5·47 (d, $J_{AB} \approx$ 15 Hz, 1 H,

4-H_A), 4·68—5·12 (m, 3 H, 8-H_2, NH), 4·56 (t, J = 5·5 Hz, 1 H, 2-H), 4·15 (d, 1 H, 4-H_B), 1·33—2·00 (m, 3 H, CH, CH_2), 0·92 (d, J = 6·0 Hz, 6 H, 2 × CH_3). ^{13}C NMR spectrum: 190·48 (d, CHO), 162·28 (s, $C_{(7)}$), 136·48, 130·46, 128·47 (aromatic C), 113·20 (s, $C_{(6)}$), 105·77 (d, $C_{(2)}$), 73·94 (t, $C_{(4)}$), 66·22 (t, $C_{(8)}$), 43·58, 24·57, 22·81 and 22·52 (isobutyl C).

2-*tert.Butyl*-6-*phenyl*-7-*formyl*-2,4,5,8-*tetrahydro*-1,3-*dioxa*-5-*azocine* (IIIi) was obtained from *Ii* by 5 h irradiation, yield 73%, m.p. 174—176°C. For $C_{16}H_{21}NO_3$ (275·3) calculated: 69·79% C, 7·69% H, 5·09% N; found: 69·71% C, 7·81% H, 5·24% N. UV spectrum, λ_{max} (log ε): 236 nm. (3·04) and 300 nm (3·14). ^{1}H NMR spectrum: 8·89 (s, 1 H, CHO), 7·42 (s, 5 H, aromatic H), 5·51 (d, J_{AB} = 15 Hz, 1 H, 4-H_A), 4·56—5·13 (m, 3 H, 8-H_2, NH), 4·17 (d, 1 H, 4-H_B), 4·12 (s, 1 H, 2-H), 0·97 (s, 9 H, CH_3). ^{13}C NMR spectrum: 190·62 (d, CHO), 162·17 (s, $C_{(7)}$), 136·70, 130·53, 128·45 (aromatic C), 113·63 (s, $C_{(6)}$), 112·79 (d, $C_{(2)}$), 74·07 (t, $C_{(4)}$), 67·24 (t, $C_{(8)}$), 35·47 (s, C), 25·14 (q, CH_3).

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