# SOLVENT AND SUBSTITUENT EFFECTS ON REARRANGEMENT OF 4-(4-X-PHENYL)-2,7-DIOXA-3-AZABICYCLO[3,3,0]OCT-3-ENES

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*Dedicated to Prof. R. Huisgen on the occasion of his 65th birthday.*

Preparation of the title compounds *V* is described. They give, on irradiation, the 2,3-dihydro-6*H*-1,3-oxazine derivatives *VI* as the main products besides the tetrahydrofuro[3,4-*d*]oxazoline derivatives *VII*. The *VI* to *VII* product ratio depends on the substituent bound to the aromatic residue. Polar solvents favour formation of the *VI* derivatives in the order Cl > H > $CH_3$. In non-polar solvents the proportion of *VII* is increased. The quantum yields of the photoreaction vary within the limits from 0·006 to 0·04 (H > F > Cl > $CH_3$ > $OCH_3$).

In the last few years greater attention has been paid to photochemistry of isoxazoline derivatives, even though this field is less investigated than photochemistry of isoxazoles[1]. The first studies[2-10] found the primary photochemical step to consist in splitting of N—O bond with formation of a biradical which is further stabilized in various ways depending on the structure of substituents at the $C_{(4)}$ and $C_{(5)}$ positions. It was found that their $\pi - \pi^*$ singlet excited state leads to formation of oxazolines, β-aminocarbonyl compounds, cyclic enaminoaldehydes, oxazepines, [2 + 2] cycloadducts, azirine derivatives, and benzonitriles[9,10]. We are interested in preparation of heterocyclic compounds using photochemistry of isoxazolines condensed to a heterocyclic system. In our previous works[11-14] it was found that introduction (into β position with respect to the isoxazoline oxygen atom) of a structural element which can stabilize the biradical formed by resonance results in enhanced selectivity of the photorearrangement giving new heterocyclic systems. In this way we prepared 2,3-dihydro-6*H*-1,3-oxazine derivatives[11,12] (*I* → *II* and *Va* → *VIa*) and 2,4,5,8-tetrahydro-1,3-dioxa-5-azocine derivatives[13,14] (*III* → *IV*). The aim of this work was to determine the solvent and substituent effects on selectivity of the photorearrangement of tetrahydrofuroisoxazolines.

For the model structures we chose 4-(4-X-phenylsubstituted)-2,7-dioxa-3-azabicyclo[3,3,0]oct-3-enes, where X means $CH_3$ (*Vb*), $CH_3O$ (*Vc*), Cl (*Vd*), and F

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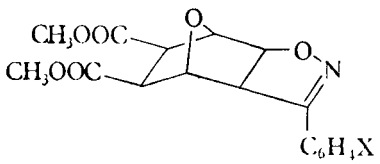
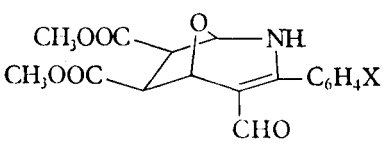
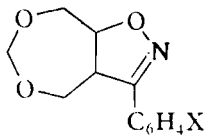
(*Ve*). The isoxazolines *Vb*–*Ve* were prepared in good yields by 1,3-dipolar cycloadditions of benzenenitriloxides (formed *in situ* by action of sodium hypochlorite and triethylamine (as catalyst) on the respective substituted benzaldoximes[15]) to 2,5-dihydrofurane. The $^1$H NMR spectrum of *Vb* shows the signal of the bridge-head proton 1-H at 5·37 ppm which is due to the shielding effects of the adjacent oxygen atom. The signal of the other bridge-head proton 5-H is found in a multiplet at a higher field along with the triplets due to 6-$H_2$ and 8-$H_2$ in the region of 3·71–4·40 ppm. Such structure assignment to *Vb* also corresponds to the signals of the carbon systems in $^{13}$C NMR spectrum: the doublets at 86·06 and 53·99 ppm were assigned to the bridge-head carbon atoms $C_{(1)}$ and $C_{(5)}$ on the basis of the above-mentioned effect of oxygen atom. Signals of triplets of $C_{(8)}$ and $C_{(6)}$ atoms are found at 76·40 and 71·86 ppm, respectively. Their different values are due to the bent structure of 2,7-dioxa-3-azabicyclic system. The higher $\delta$ value was assigned to the $C_{(8)}$ triplet with respect to the greater effect of the isoxazoline oxygen atom. The *Vc*–*Ve* structures were assigned in analogous way. The values of $^1$H and $^{13}$C NMR spectra indicate that the substituent present has almost no effect on the chemical shifts except for those of the aromatic residue (as compared with the non-substituted derivative *Va*)[12].



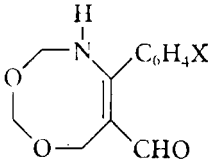

*I*



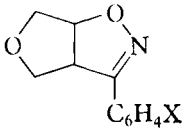

*II*



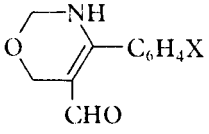

*III*



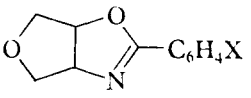

*IV*




*V*




*VI*




*VII*

The time changes of UV spectrum observed during irradiation of *Vb* (in acetonitrile) with monochromatic radiation of 253·7 nm wavelength are given in Fig. 1. The irradiation of adduct *Vb* in benzene solution on preparative scale gave two rearrangement products: *VIb* (43%) and *VIIb* (14%). On the basis of analogy to the product *VIa* (ref.[12]) and spectral data, the derivative *VIb* was assigned the structure of 4-(4-methylphenyl)-5-formyl-2,3-dihydro-6*H*-1,3-oxazine. The UV spectrum of *VIb* shows a bathochromic shift as compared with that of *Vb*, which is due to the presence of the NH—C=C—CHO or Ar—C=C—CHO chromophores ($\lambda_{max}$ 311 nm). The $^1$H and $^{13}$C NMR spectra indicate the presence of aldehydic groups, the singlet at 9·06 ppm and the doublet at 187·44 ppm, as well as the presence of singlets at 158·98 and 112·07 ppm for the double bond C=C. A broad band of NH group is found at 5·36 ppm, the triplets due to $C_{(2)}$ and $C_{(6)}$ are found at 73·94 and 64·64 ppm, respectively. On the contrary, $^1$H NMR spectrum of *VIIb* does not much differ from that of *Vb*. A significant downfield shift is observed in the case of the bridge-head 5-H proton from the region of 3·71–4·40 (for *Vb*) to 4·83 ppm (for *VIIb*). The UV spectrum showed a hypsochromic shift from 265 to 247 nm. The $^{13}$C NMR spectrum contains a distinct singlet at low field with the value of 164·7 ppm, which indicates that the C=N double bond was maintained in the molecule. In comparison with the starting compound *Vb*, a marked shift of the $C_{(5)}$ doublet can be observed from 53·99 to 72·44 ppm, which can only be explained by a reorganization involving a change in position of the N atom in the molecule. This conclusion is also confirmed by the values of the methylene triplets of $C_{(6)}$ and $C_{(8)}$ which have almost the same values (74·71 and 74·39 ppm) in contrast to the starting *Vb* ($C_{(6)}$ at 71·86

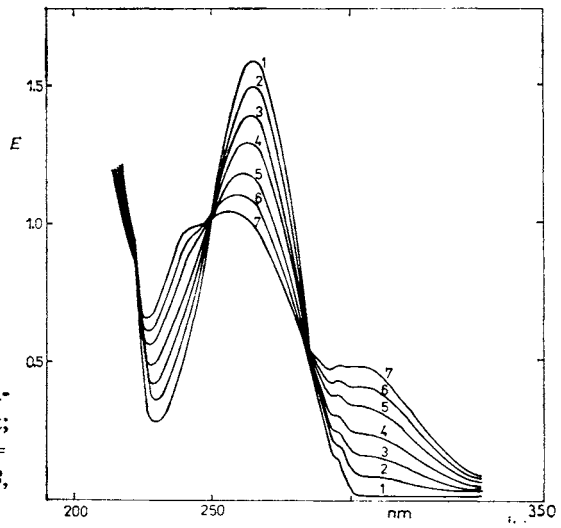



FIG. 1

Photoreaction of *Vb* in acetonitrile on irradiation using 253·7 nm monochromatic light; absorbance, $E$, $c = 10^{-3}$ mol $l^{-1}$, $d_{cuvette}$ = = 0·001 m, $v$ = 15 ml, for 0 *1*, 15 *2*, 30 *3*, 45 *4*, 60 *5*, 75 *6*, and 90 *7* min

ppm and $C_{(8)}$ at 76·40 ppm). Out of the possible structures for the rearrangement product the only corresponding one is 3-(4-methylphenyl)-2,7-dioxa-4-azabicyclo-[3,3,0]oct-3-ene (*VIIb*).

The irradiation of adduct *Vc* in benzene again gave two rearrangement products: 4-(4-methoxyphenyl)-5-formyl-2,3-dihydro-6*H*-1,3-oxazine (*VIc*, 50%) and 3-(4--methoxyphenyl)-2,7-dioxa-4-azabicyclo[3,3,0]oct-3-ene (*VIIc*, 25%). The irradiation in cyclohexane gave the ratio of 3 : 1 in favour of *VIc*. The photolysis of *Vd* also gave the two rearrangement products: 4-(4-chlorophenyl)-5-formyl-2,3-dihydro--6*H*-1,3-oxazine (*VId*, 33%) and 3-(4-chlorophenyl)-2,7-dioxa-4-azabicyclo[3,3,0]-oct-3-ene (*VIId*, 16·8%). The irradiation of the *p*-fluoro derivative *Ve* in benzene gave the derivatives *VIe* and *VIIe* in the ratio of 3 : 2, in cyclohexane the ratio being 1 : 1. Structures of the products were assigned as in the case of *VIb* and *VIIb*. The ratio of the rearrangement products depends on substituent in the aromatic nucleus and on solvent (benzene, cyclohexane). Mukai and coworkers[10] found an only negligible effect of substituent on distribution of photolysis products from 3-arylisoxazolines. A significant feature of the photolysis of *V* is the formation of two products (*VI* and *VII*), as compared with exclusive formation of cyclic enaminoaldehydes *II* and *IV* from the equally substituted derivatives *I* and *III*, respectively. From the isobestic points at 248 and 286 nm (Fig. 1) and from analysis of the photoproducts at the beginning and at the end of the photoreaction it follows that there exists no mutual interconversion between *VI* and *VII*.

A detailed study was carried out of the solvent effect on the photoreaction course of the isoxazolines having electron-acceptor (Cl, *Vd*) and -donor ($CH_3$, *Vb*) substituent in the phenyl residue. The time dependence of the product distribution in various solvents was followed by means of high-pressure liquid chromatography (Tables I and II and Fig. 2).

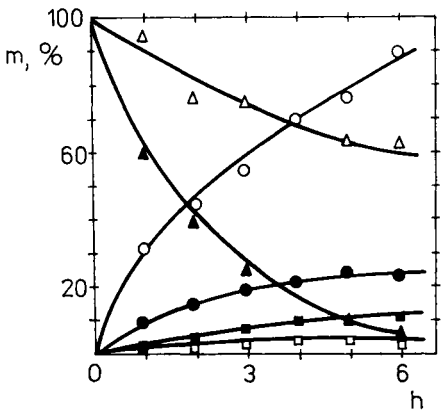



FIG. 2

Dependence of the product distribution from compound *Vd* on the solvent and irradiation time. Symbols ●, ▲ and ■ show the amount of *Vd*, *VId*, *VIId* respectively in the photolysis of *Vd* in benzene, while ○, △ and □ represent the amount of *Vd*, *VId*, *VIId*, in the photolysis of *Vd* in methanol

The rearrangement product *VId* is decomposed on further irradiation in acetonitrile, ether, tetrahydrofuran, and cyclohexane. The oxazoline derivative *VIId* needs much longer irradiation for its decomposition which agrees with well-known photostability of oxazoline derivatives[1]. In the case of irradiation of derivative *Vd* we can observe a distinct trend of preferred formation of *VId* in polar solvents and increase of the proportion of the oxazoline derivative *VIId* in non-polar solvents.

The mixture obtained by irradiation of the methyl derivative *Vb* shows (in com-

TABLE I

Dependence of the product distribution (%) from *Vb* and *Vd* on the solvent and irradiation time

| Solvent | Compound | Time | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 h | 2 h | 3 h | 4 h | 5 h | 6 h |
| Benzene | *Vb* | 72·4 | — | 51·7 | 42·9 | 40·3 | 24·4[a] |
| | *VIb* | 17·9 | — | 36·6 | 45·5 | 43·28 | 42·77 |
| | *VIIb* | 3·59 | — | 8·03 | 10·5 | 12·7 | 11·2 |
| Cyclohexane | *Vb* | 19·4 | 9·4 | 5·3 | 2·6 | 1·9 | 1·7 |
| | *VIb* | 41·2 | 19·7 | 11·6 | 7·6 | 6·7 | 6·1 |
| | *VIIb* | 23·4 | 25·0 | 24·7 | 23·3 | 22·6 | 20·8 |
| Methanol | *Vb* | 78·5 | 30·4 | 17·2 | 11·8 | 8·7 | 5·7 |
| | *VIb* | 25·1 | 32·4 | 37·7 | 40·0 | 41·2 | 43·5 |
| | *VIIb* | 15·8 | 20·5 | 20·0 | 19·0 | 19·4 | 16·1 |
| Ether | *Vb* | 16·5 | 3·8 | 2·0 | 1·5 | 1·5 | — |
| | *VIb* | 54·8 | 49·5 | 48·1 | 46·0 | 44·3 | — |
| | *VIIb* | 32·0 | 30·4 | 30·0 | 29·5 | 29·3 | — |
| Cyclohexane | *Vd* | 10·4 | 3·97 | 2·69 | 1·55 | 1·5 | 1·0 |
| | *VId* | 65·8 | 33·83 | 23·3 | 18·02 | 12·86 | 8·44 |
| | *VIId* | 23·5 | 26·5 | 23·55 | 11·02 | 9·0 | 7·28 |
| Ether | *Vd* | 50·5 | 28·2 | 20·8 | 19·3 | 17·8 | 11·7 |
| | *VId* | 48·2 | 71·7 | 63·4 | 58·3 | 51·6 | 49·9 |
| | *VIId* | 1·3 | 2·8 | 3·3 | 7·7 | 5·4 | 4·0 |
| Tetrahydrofuran | *Vd* | 54·3 | 32·0 | 16·0 | 11·3 | 5·8 | 6·5 |
| | *VId* | 33·7 | 44·5 | 49·5 | 47·6 | 42·7 | 39·9 |
| | *VIId* | 11·2 | 13·5 | 14·7 | 13·0 | 10·4 | 9·4 |
| Acetonitrile | *Vd* | 55·2 | 25·5 | 22·3 | 9·07 | 7·1 | 6·1 |
| | *VId* | 34·5 | 22·95 | 13·1 | 11·2 | 11·9 | 8·5 |
| | *VIId* | 8·1 | 8·95 | 11·9 | 11·1 | 10·5 | 8·8 |

[a] 9 h.

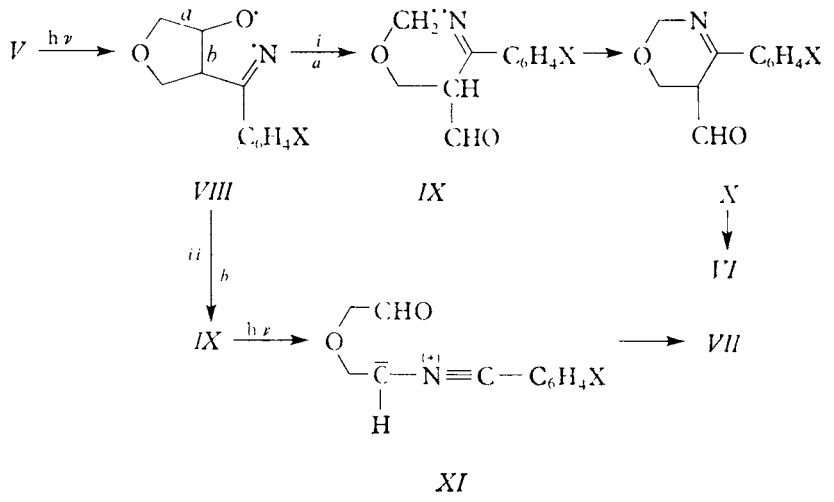
parison with *Vd*) an increased amount of *VIIb*, but *VIb* is the main product in this case, too. The effect of solvent polarity on the ratio of the products *VIb* and *VIIb* is not so marked.

Our previous communications[10,11] gave the formation of 4-phenyl-5-formyl--2,3-dihydro-6*H*-1,3-oxazine (*VIa*) as the only product of photolysis of the non--substituted derivative *Va*. Although the *VI* : *VII* ratio also depends on the X substituent in the aromatic nucleus, the exclusive formation of *VIa* seems illogical. Therefore, we submitted the photolysis of *Va* to a repeated, more detailed study using a radiation source of higher efficiency. Cyclohexane was used as the solvent, because it is possible to expect the highest amount of the derivative *VIIa* in this solvent. The reaction conditions were chosen in such way that the longer irradiation period might support decomposition of *VIa* (4·5 h; in acetonitrile it was 1 h). The experiment really gave, besides *VIa* (7%), also 14% tetrahydrofuro[3,4-*d*]oxazole *VIIa*. In the originally used solvent[11,12] acetonitrile the *VIa* to *VIIa* ratio was 12·5 : 1 after six hours,

TABLE II

Dependence of the product distribution (%) from *Va* on the solvent and the irradiation time

| Solvent | Compound | Time | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 h | 2 h | 3 h | 4 h | 5 h | 6 h |
| Benzene | *Va* | 74·3 | 52·6 | 43·8 | 38·4 | 31·9 | 30·8 |
| | *VIa* | 21·8 | 31·9 | 39·1 | 39·3 | 41·6 | 43·9 |
| | *VIIa* | 3·5 | 4·2 | 5·8 | 6·4 | 6·7 | 7·4 |
| Cyclohexane | *Va* | 42·2 | 16·4 | 5·0 | 4·0 | 2·7 | 2·2 |
| | *VIa* | 14·6 | 10·5 | 12·6 | 11·1 | 9·9 | 6·4 |
| | *VIIa* | 11·8 | 11·3 | 13·3 | 11·2 | 11·2 | 10·9 |
| Ether | *Va* | 52·1 | 18·0 | 11·0 | 2·7 | 2·1 | 1·6 |
| | *VIa* | 29·1 | 44·9 | 56·7 | 57·6 | 47·0 | 43·7 |
| | *VIIa* | 9·0 | 12·9 | 14·9 | 14·9 | 14·9 | 12·3 |
| Acetonitrile | *Va* | 78·8 | 67·5 | 53·1 | 43·9 | 32·0 | 26·9 |
| | *VIa* | 13·3 | 25·9 | 30·6 | 35·3 | 47·4 | 47·7 |
| | *VIIa* | 2·1 | 2·9 | 3·0 | 3·7 | 3·4 | 3·8 |
| Methanol | *Va* | 63·4 | 42·5 | 29·4 | 5·9 | 4·8 | 4·2 |
| | *VIa* | 7·5 | 16·6 | 22·8 | 32·0 | 32·3 | 32·2 |
| | *VIIa* | 7·2 | 11·6 | 13·1 | 12·7 | 12·7 | 10·5 |
| 2-Propanol | *Va* | 47·7 | 26·7 | 8·2 | 5·9 | — | — |
| | *VIa* | 25·5 | 33·1 | 46·2 | 48·0 | 49·6 | 49·7 |
| | *VIIa* | 5·1 | 6·4 | 7·2 | 8·7 | 7·4 | 6·9 |



SCHEME 1

in benzene it was 5·9 : 1, in cyclohexane it is approximately 1 : 1. In this case, too, the more polar solvent favours the formation of the cyclic enaminoaldehyde *VIa*. This trend increases in the order $CH_3 < H < Cl$. Mechanism of the photoreaction of *V* is given in Scheme 1. The main product *VI* is formed by isomerization of 2,5--dihydro-6*H*-1,3-oxazine *XII* resulting from recombination of the biradical *XI*. The formation of *XI* is explained as in the case of formation of *VIa* (ref.[12]) by the pathway *i* (splitting of the bond *a*). This pathway is favoured by resonance stabilization of the radical by *p* electrons of the oxygen atom. The intermediate *X* formed by the primary splitting of N—O bond is presumed to be the precursor of both the products *VI* and *VII*. The formation of oxazolines *VII* can be explained by the reaction course already described[1] (the pathway *ii*, splitting of the bond *b*), *via* the azirine derivative which gives the nitrile-ylide *XIII* by the photochemically alowed disrotational ring opening. The last step consists in thermal intramolecular 1,3-dipolar cycloaddition giving *VII*. Two findings obtained are noteworthy. In the case of the isoelectronical equally substituted derivatives *I* (which differ from *V* by strain) and *III* (which differ by magnitude of the ring), the cyclic enaminoaldehydes *II* and *IV* were only formed. In these cases the dominant factor was the resonance stabilization of the radical type *XI* (the reaction pathway *i*) by *p* electrons of oxygen atom. One of the products can be presumed to be formed from the singlet state $S_1$, the other resulting from the higher singlet state $S_2$ (upper-state photoreaction). The solvent polarity and substituent effects affect the energy difference between $S_2$ and $S_1$ and, hence, also the *VI* : *VII* product ratio. Available literature data[10], however, are consistent with the $S_1$ state being preferred. Another explanation considers the

primary photochemical process to be the same for both the derivatives, the solvent polarity affecting the reaction pathways *i* and *ii* (Scheme 1). The stronger is the electron-acceptor effect of the substituent bound to the aromatic nucleus (Cl > H > > $CH_3$), the more polar character is observed with the biradical *XI* and the higher is its stabilization in a polar solvent.

We also determined the quantum yields $\Phi$ of the photoreactions of the derivatives *V* from the concentration decrease of the starting derivative: they decrease in the order H > F > Cl > $CH_3$ > $CH_3O$ ($\Phi$ = 0·04 for *Va*, 0·016 for *Vb*, 0·0063 for *Vc*, 0·017 for *Vd*, and 0·028 for *Ve*). The quantum yield has the same value whether the measurement is carried out in the presence or in the absence of oxygen, which (along with the benzene sensibilization) confirms the photoreaction course from the singlet state.

## EXPERIMENTAL

The melting points were not corrected. The $^1$H NMR spectra were measured with a Tesla BS 487C apparatus, and the $^{13}$C NMR spectra were measured with a JEOL apparatus, using tetramethylsilane as the internal standard. The UV spectra were measured with a Perkin Elmer 323 apparatus in thermostated cells in methanol. The $\varepsilon$ values are given in $m^2\ mol^{-1}$. The photochemical reactions were realized with application of a low-pressure discharge lamp Toshiba GL-15 (15 W) in a quartz burner. The reactions proceeded in a thermostated 300 ml reactor[17] with forced circulation of the irradiated solution at 15°C. The reaction course was followed by TLC (Silufol) and HPLC. The solvent and substituent effects on the product distribution were followed by analysis of the reaction mixtures by liquid chromatography using a Spectra Physic apparatus. In order to check these analyses, we irradiated 0·0025 mol of the compounds *Va*— *Ve* in the corresponding solvent for 7 h. The sample was concentrated in vacuum (in the case of benzene or ether) or, without concentrating it, diluted with the mobile phase used (methanol–water 7 : 3) and separated on a column Separon Six C18 5 μm, flow rate 0·5 ml $min^{-1}$, pressure 10 MPa, indication at 250 nm. The results were evaluated by means of calibration measurements. The quantum yields were determined at the wavelength of 253·7 nm using the apparatus described in ref.[16]. Concentration of compounds *Vb*— *Ve* was followed by the extinction decrease at their maxima (about 265 nm). After finishing the photochemical reactions, the reaction mixtures were concentrated in vacuum and separated by column chromatography (silica gel, hexane-ethyl acetate 1 : 3).

### 4-(4-X-Phenyl)-2,7-dioxa-3-azabicyclo[3,3,0]oct-3-enes

A solution of 21 mmol substituted benzaldoxime in 10 ml dichloromethane was added to a mixture of 5 ml 2,5-dihydrofurane, 0·2 g (1·98 mmol) triethylamine, 20 ml 11% sodium hypochlorite (*i.e.* 2·5 g (34 mmol) NaClO), and 15 ml dichloromethane during 15 min with stirring and cooling at 0°C. After 3 h stirring the layers were separated, the aqueous layer was extracted with 3× 20 ml dichloromethane, the combined organic portions were dried over magnesium sulphate and concentrated, and the product obtained was recrystallized. The following substances were prepared in this way.

4-(4-*Methylphenyl*)-2,7-*dioxa*-3-*azabicyclo*[3,3,0]*oct*-3-*ene* (Vb): yield 44% after recrystallization from dichloromethane and hexane, m.p. 115—117°C. For $C_{12}H_{13}NO_2$ (203·2) calculated: 70·91% C, 6·45% H, 6·89% N; found: 70·65% C, 6·20% H, 6·81% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$):

265 nm (3·19). $^1$H NMR spectrum: 7·17—7·60 (m, 4 H, aromatic H), 5·37 (d,d, $J_{1-5}$ = 9 Hz, 1 H, 1-H), 3·71—4·40 (m, 5 H, 6-$H_2$, 8-$H_2$, 5-H), 2·40 (s, 3 H, $CH_3$). $^{13}$C NMR spectrum: 140·40, 129·62, 126·82 (aromatic C), 86·08 (d, $C_{(1)}$), 76·40 (t, $C_{(8)}$), 71.86 (t, $C_{(6)}$), 53·99 (d, $C_{(5)}$), 21·44 (q, $CH_3$).

4-(4-*Methoxyphenyl*)-2,7-*dioxa*-3-*azabicyclo*[3,3,0]*oct*-3-*ene* (Vc): yield 78%, m.p. 95—97°C. For $C_{12}H_{13}NO_3$ (219·2) calculated: 65·74% C, 5·98% H, 6·39% N; found: 65·60% C, 5·92% H, 6·28% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 265 nm (3·16). $^1$H NMR spectrum: 6·83—7·60 (m, 4 H, aromatic H), 5·29 (d,d, $J_{1-5}$ = 9·0 Hz, 1 H, 1-H), 3·62—4·32 (m, 5 H, 6-$H_2$, 8-$H_2$, 5-H), 3·81 (s, 3 H, $OCH_3$). $^{13}$C NMR spectrum: 156·26 (s, $C_{(4)}$), 128·45, 121·17, 114·35 (aromatic C), 85·95 (d, $C_{(1)}$), 76·47 (t, $C_{(8)}$), 71·86 (t, $C_{(6)}$), 55·42 (d, $C_{(5)}$), 54·12 (q, $OCH_3$).

4-(4-*Chlorophenyl*)-2,7-*dioxa*-3-*azabicyclo*[3,3,0]*oct*-3-*ene* (Vd): yield 73%, m.p. 134—135°C. For $C_{11}H_{10}ClNO_2$ (223·6) calculated: 59·07% C, 4·47% H, 6·26% N; found: 59·23% C, 4·54% H, 6·10% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 267 nm (3·10). $^1$H NMR spectrum: 7·30—7·62 (m, 4 H, aromatic H), 5·37 (d,d, $J_{1-5}$ = 9·0 Hz, 1-H), 3·66—4·37 (m, 5 H, 6-$H_2$, 8-$H_2$, 5-H). $^{13}$C NMR spectrum: 155·74 (s, $C_{(4)}$), 136·18, 129·23, 128·12 (aromatic C), 86·54 (d, $C_{(1)}$), 76·40 (t, $C_{(8)}$), 71·66 (t, $C_{(6)}$), 53·66 (d, $C_{(5)}$).

4-(4-*Fluorophenyl*)-2,7-*dioxa*-3-*azabicyclo*[3,3,0]*oct*-3-*ene* (Ve): yield 65%, m.p. 89—90°C. For $C_{11}H_{10}FNO_2$ (207·2) calculated: 63·77% C, 4·83% H, 6·76% N; found: 63·99% C, 4·94% H, 6·53% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 262 nm (3·06). $^1$H NMR spectrum: 6·98—7·72 (m, 4 H, aromatic H), 5·38 (d,d, $J_{1-5}$ = 9·0 Hz, 1 H, 1-H), 3·67—4·37 (m, 5 H, 6-$H_2$, 8-$H_2$, 5-H). $^{13}$C NMR spectrum: 172·11 (s, $C_{(4)}$), 137·54, 129·10, 128·51, 116·88, 115·39 (aromatic C), 86·41 (d, $C_{(1)}$), 76·40 (t, $C_{(8)}$), 71·66 (t, $C_{(6)}$), 53·86 (d, $C_{(5)}$).

Photochemical Reaction of *Vb*

Irradiation of a solution of 0·45 g (2·2 mmol) *Vb* in 300 ml benzene for 6 h gave 0·1 g (22%) unreacted *Vb* and 0·05 g (14% with respect to the reacted *Vb*) 3-(4-methylphenyl)-2,7-dioxa--4-azabicyclo[3,3,0]oct-3-ene (*VIIb*), m.p. 118—120°C. For $C_{12}H_{13}NO_2$ (203·2) calculated: 70·91% C, 6·45% H, 6·89% N; found: 70·67% C, 6·38% H, 6·72% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 247 nm (3·03). $^1$H NMR spectrum: 7·14—7·85 (m, 4 H, aromatic H), 5·17 (d,d $J_{1-5}$ = 7·0 Hz, 1 H, 1-H), 4·83 (m, 1 H, 5-H), 3·52—4·30 (m, 6-$H_2$, 8-$H_2$), 2·37 (s, $CH_3$). $^{13}$C NMR spectrum: 164·70 (s, $C_{(3)}$), 141·83, 129·03, 128·32, 124·42, 113·11 (aromatic C), 83·10 (d, $C_{(1)}$), 74·65 and 74·33 (t,t, $C_{(6)}$ and $C_{(8)}$), 72·44 (d, $C_{(5)}$), 21·50 (q, $CH_3$). Moreover, we obtained 0·15 g (43% with respect to the reacted *Vb*) 4-(4-methylphenyl)-5-formyl-2,3-dihydro-5*H*-1,3-oxazine(*VIb*), m.p. 130—133°C. For $C_{12}H_{13}NO_2$ (203·2) calculated: 70·91% C, 6·45% H, 6·89% N; found: 70·84% C, 6·30% H, 6·90% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 242 nm (2·92), 311 nm (3·00). $^1$H NMR spectrum: 9·06 (s, 1 H, CHO), 7·16—7·40 (m, 4 H, aromatic H), 5·36 (bd, 1 H, NH), 4·58—4·77 (m, 4 H, 2-$H_2$, 6-$H_2$), 2·40 (s, 3 H, $CH_3$). $^{13}$C NMR spectrum: 187·44 (s, CHO), 158·98 (s, $C_{(5)}$), 141·51, 130·20, 129·75, 129·42 (aromatic C), 112·07 (s, $C_{(4)}$), 73·94 (t, $C_{(2)}$), 64·64 (t, $C_{(6)}$), 21·44 (q, $CH_3$). The irradiation in cyclohexane for 11 h gave 0·2 g (44%) oil, 0·05 g (11%) *VIb*, and 0·2 g (44%) *VIIb*.

Photochemical Reaction of *Vc*

Irradiation of a solution of 1 g (4·56 mmol) *Vc* in 300 ml benzene for 400 min and subsequent treatment gave 0·1 g (10%) oil fraction, 0·6 g (60%) unreacted *Vc*, and 0·1 g (25% with respect to the reacted *Vc*) 3-(4-methoxyphenyl)-2,7-dioxa-4-azabicyclo[3,3,0]oct-3-ene (*VIIc*), m.p. 84—86°C. For $C_{12}H_{13}NO_3$ (219·2) calculated: 65·74% C, 5·98% H, 6·39% N; found: 65·44% C,

5·94% H, 6·73% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 261 nm (3·09). $^1$H NMR spectrum: 6·83—7·92 (m, 4 H, aromatic H), 5·16 (d,d, $J_{1-5}$ = 7·0 Hz, 1 H, 1-H), 4·83 (m, 1 H, 5-H), 3·35—4·30 (m, 4 H, 6-$H_2$, 8-$H_2$), 3·80 (s, 3 H, $OCH_3$). $^{13}$C NMR spectrum: 162·23 (s, $C_{(3)}$), 130·14, 129·29, 119·68, 113·70 (aromatic C), 83·16 (d, $C_{(1)}$), 74·71 and 74·39 (t,t, $C_{(6)}$ and $C_{(8)}$), 72·38 (d, $C_{(5)}$), 55·35 (q, $OCH_3$). Moreover, we obtained 0·2 g (50% with respect to the reacted *Vc*) 4-(4-methoxyphenyl)-5-formyl-2,3-dihydro-6*H*-1,3-oxazine (*VIc*), m.p. 114—116°C. For $C_{12}H_{13}NO_3$ (219·2) calculated: 65·74% C, 5·98% H, 6·39% N; found: 65·91% C, 6·04% H, 6·21 % N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 275 nm (3·25). $^1$H NMR spectrum: 9·10 (s, CHO), 6·87—7·46 (m, 4 H, aromatic H), 5·43 (br. NH), 4·60—4·78 (m, 4 H, 2-$H_2$, 6-$H_2$), 3·86 (s, 3 H, $OCH_3$). The irradiation of 0·5 *Vc* in cyclohexane for 7 h gave 0·1 g (20%) *VIc* and 0·04 g (8%) *VIIc*.

Photochemical Reaction of *Vd*

Irradiation of 0·45 g (2 mmol) *Vd* dissolved in 300 ml benzene (9 h) and subsequent treatment gave 0·15 g (33%) oil, 0·15 g (33%) unreacted *Vd*, and 0·05 g (16·8% with respect to the reacted *Vd*) 3-(4-chlorophenyl)-2,7-dioxa-4-azabicyclo[3,3,0]oct-3-ene (*VIId*), m.p. 146—147°C. For $C_{11}H_{10}ClNO_2$ (223·6) calculated: 59·07% C, 4·47% H, 6·26% N; found: 59·16% C, 4·38% H, 6·12% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 250 nm (3·04). $^1$H NMR spectrum: 7·22—7·88 (m, 4 H, aromatic H), 5·18 (d,d, $J_{1-5}$ = 7·0 Hz, 1 H, 1-H), 4·83 (m, 1 H, 5-H), 3·51—4·28 (m, 4 H, 6-$H_2$, 8-$H_2$). $^{13}$C NMR spectrum: 163·86 (s, $C_{(3)}$), 137·80, 129·81, 128·71, 125·72 (aromatic C), 83·55 (d, $C_{(1)}$), 74·65 and 74·26 (t,t, $C_{(6)}$ and $C_{(8)}$), 72·57 (d, $C_{(5)}$). Furthermore, we obtained 0·09 g (33% with respect to the reacted *Vd*) 4-(4-chlorophenyl)-5-formyl-2,3-dihydro-6*H*-1,3-oxazine (*VId*), m.p. 141—143°C. For $C_{11}H_{10}ClNO_2$ (223·6) calculated: 59·07% C, 4·47% H, 6·26% N; found: 59·25% C, 4·54% H, 5·99% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 244 nm (2·98), 310 nm (2·91). $^1$H NMR spectrum: 8·95 (s, 1 H, CHO), 7·28—7·60 (m, 4 H, aromatic H), 6·08 (br, NH), 4·55 (m, 4 H, 2-$H_2$, 6-$H_2$). $^{13}$C NMR spectrum: 187·12 (d, CHO), 131·04, 129·10, 128·12 (aromatic C), 113·18 (s, $C_{(4)}$), 74·07 (t, $C_{(2)}$),64·58 (t, $C_{(6)}$).

Photochemical Reaction of *Ve*

Irradiation of a solution of 0·3 g (1·45 mmol) *Ve* in 300 ml acetonitrile for 5 h and subsequent treatment gave 0·1 g (33%) 3-(4-fluorophenyl)-2,7-dioxa-4-azabicyclo[3,3,0]oct-3-ene (*VIIe*), m.p. 126—128°C. For $C_{11}H_{10}FNO_2$ (207·2) calculated: 63·77% C, 4·83% H, 6·76% N; found: 63·99% C, 4·81% H, 6·74% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 238 nm (2·96). $^1$H NMR spectrum: 6·99—7·90 (m, 4 H, aromatic H), 5·22 (m, 1 H, 1-H), 4·80 (m, 1 H, 5-H), 3·61—4·30 (m, 4 H, 6-$H_2$, 8-$H_2$). $^{13}$C NMR spectrum: 130·98, 130·40, 121·30, 116·23, 114·80 (aromatic C), 83·49 (d, $C_{(1)}$), 74·26 (t, $C_{(6)}$ and $C_{(8)}$), 72·57 (d, $C_{(5)}$). Furthermore, we obtained 0·14 g (45%) 4-(4-fluorophenyl)-5-formyl-2,3-dihydro-6*H*-1,3-oxazine (*VIe*), m.p. 167—169°C. For $C_{11}H_{10}$-.$FNO_2$ (207·2) calculated: 63·77% C, 4·83% H, 6·76% N; found: 64·02% C, 5·01% H, 6·57% N. UV spectrum, $\lambda_{max}$ (log $\varepsilon$): 237 nm (2·98), 309 nm (3·16). $^1$H NMR spectrum: 9·05 (s, 1 H, CHO), 7·00—7·55 (m, 4 H, aromatic H), 5·27 (br, NH), 4·58—4·78 (m, 4 H, 2-$H_2$, 6-$H_2$). $^{13}$C NMR spectrum: 187·18 (d, CHO), 132·08, 131·50, 116·69 (aromatic C), 115·26 (s, $C_{(4)}$), 74·07 (t, $C_{(2)}$), 64·58 (t, $C_{(6)}$). The irradiation in benzene (5 h) gave 0·1 g (33%) non-reacted *Ve*, 0·09 g (45% with respect to the reacted *Ve*) *VIe*, and 0·06 g (30% with respect to the reacted *Ve*) *VIIe*. In cyclohexane (6·5 h) we obtained *Ve* (40%), *VIe* (33% with respect to the reacted *Ve*), and *VIIe* (33%).

Photochemical Reaction of *Va*

Irradiation of a solution of 0·7 g (3·7 mmol) *Va* in 300 ml cyclohexane for 4·5 h gave 0·05 g (7·2%) *VIa* (refs[10,11]) and 0·1 g (14%) 3-phenyl-2,7-dioxa-4-azabicyclo [3,3,0] oct-3-ene (*VIIa*),

m.p. 86–88°C. For $C_{11}H_{11}NO_2$ (189·2) calculated: 69·82% C, 5·86% H, 7·40% N; found: 70·03% C, 5·72% H, 6·98% N. $^1$H NMR spectrum: 7·36–8·00 (m, 5 H, aromatic H), 5·20 (d,d, $J_{1-5}$ = 7·0 Hz, 1 H, 1-H), 4·86 (d,d, 1 H, 5-H), 3·53–4·31 (m, 4 H, 6-$H_2$, 8-$H_2$).

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