PREPARATION AND PHOTOCHEMISTRY OF FUROISOXAZOLINES. AN EXTRAORDINARILY UNAMBIGUOUS PHOTO-INDUCED REARRANGEMENT*

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Preparation and photolysis of furoisoxazoline derivatives is described. The respective compounds *IVa, II* and *VI* were obtained by a 1,3-dipolar cycloaddition of benzenenitrile oxide to 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene, 2,5-dihydrofuran and furan; *IVb* was synthesized from benzoylnitrile oxide. The biradical primarily formed by photolysis was stabilized with respect to the arrangement of the heteroatom and the isoxazoline chromophore. The new 1,3-oxazine derivatives *III* and *V* were obtained in high yields as single products. The quantum yield of photoreaction of *II, IVa* and *XXVII* was found to be 0·04, 0·26 and 0·07, respectively. Were the stabilization of the radical by conjugation with the lone electron pair of oxygen impossible, oxazoline *VII* should be formed. Photolysis of the benzoyl derivative *IVb* had an anomalous course and yielded the β-aminochalcone *Xb*.

The majority of 2-isoxazoline derivatives undergoes first of all a cleavage of the N—O bond due to irradiation[1-7]. This reaction is characterized by formation of 3-oxazolines[1-5], β-aminochalcones[1-5], 1,3-oxazepines[6], and cyclic enamine-aldehydes[7]. The effect of a heteroatom on the photolysis of isoxazoline has not been reported as yet. This series of papers[8] concerns the preparation and photolysis of isoxazolines with a fused oxygen-containing heterocycle in order to investigate the influence of a heteroatom.

Isoxazolines were obtained by a 1,3-dipolar cycloaddition of benzenenitrile oxide to an oxygen-containing heterocycle possessing a multiple bond. The monoadduct 3-phenyldihydrofuro[3,2-*d*]-isoxazoline (*VI*) and bisadduct *VIII* were prepared from benzenenitrile oxide and furan according to[9], the synthesis of 3-phenyltetrahydro[3,4-*d*]-isoxazoline (*II*), ref.[10] was modified by using triethylamine. The ^{1}H NMR spectrum of *II* revealed a doublet at 5·41 ppm ($J_{3a,6a}$ = 4·0 Hz) ascribable to the bridged 6a-H proton and two singlets associated with 4-H_A and 6-H_B protons.

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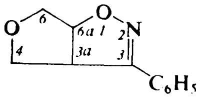
The doublet in the ^{13}C NMR spectrum of a higher chemical shift value at 86·28 ppm was attributed to the $C_{(6a)}$ atom due to an oxygen atom shielding, that at 53·79 to the $C_{(3a)}$ atom. The bent structure of the bicyclic system *II* resulted in different chemical shift values of triplets $C_{(6)}$ (79·26 ppm) and $C_{(4)}$ (71·73 ppm). Derivatives *IVa* and *IVb* were prepared by cycloaddition to 5,6-dimethoxycarbonyl-7-oxabicyclo-[2,2,1]-2-heptene. The mentioned oxanobornene derivative was chosen for both its high reactivity in 1,3-dipolar cycloadditions[11], and formation of strained dihydrofuran skeleton the nature of which can direct the photochemical reaction[6]. The cycloaddition itself proceeded smoothly at room temperature in dioxane in which both the starting compounds and the dimers of benzenenitrile oxide (by-products) are well soluble in contrast to commercially used ether. The originating *IVa* could be isolated sufficiently pure without any chromatographic separation by mere concentration. The adduct *IVa* was assigned the *exo*-structure on the basis of coupling constants $J_{3a,4} = J_{7,7a} = 0$. Both signals of the bridge protons 4-H and 7-H appeared as a singlet at 4·9 ppm. For an *endo*-addition the proper coupling constants should be $\sim$5 Hz. The signals of isoxazoline protons 3a-H and 7a-H occurred as doublets at 5·08 and 3·98 ppm, respectively, with a coupling constant $J_{3a,7a} = 9{\cdot}0$ Hz thus evidencing the *cis*-stereoselectivity of the concerted 1,3-dipolar cycloaddition. The structure of *IVa* was unequivocally backed by the ^{13}C NMR spectrum. The signal of C(=N) atom at 153·9 ppm was typical of isoxazoline derivatives. The correct assignment of three doublets at 85·89, 84·20 and 79·65 ppm for carbon atoms adjacent to the oxygen atom is quite complicated; nevertheless, both bridge $C_{(4)}$ and $C_{(7)}$ atoms should have approximately the same chemical shift values, as apparent from the ^{1}H NMR spectrum. The mass spectrum of *IVa* displayed an intense peak of molecular radical ion, whilst fragments of 1,3-dipolar cycloreversion were absent.

Cycloaddition of benzoyl nitrile oxide *Ib* to 5,6-dimethoxycarbonyl-7-oxabicyclo-[2,2,1]-2-heptene yielded the adduct *IVb*, the spectral data of which were consistent with the *exo*-structure as in *IVa*. The replacement of benzoyl group for phenyl did not result in changes in chemical shift data of the corresponding oxabicyclic ring protons; protons 4-H and 7-H appeared as singlets. The chemical shift value of C(=N) was downfield shifted (156·90 ppm) when compared with that of *IVa* (153·90); likewise, the molecular radical ion peak of *IVb* was far less intense and the mass spectrum also lacked fragments of 1,3-dipolar cycloreversion.

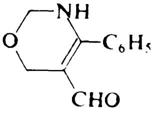
Cycloaddition of benzenenitrile oxide to the adduct of furan to maleic anhydride afforded the monoadduct *IX*. Its photochemical reactions could not be investigated for its very low solubility. The structure of *IX* could be deduced from the process of preparation, from the mass spectrum showing a 1 : 1 adduct, and from its IR (KBr) spectrum indicative of C=O bond vibrations in the anhydride moiety (1 765 and 1 710 cm^{-1}) and of the C=N one (1 590 cm^{-1}).

$R-C\equiv\overset{(+)}{N}-\overset{(-)}{O}$

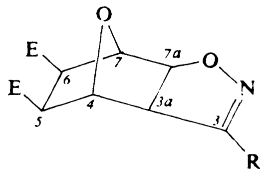
Ia, R = C_6H_5
Ib, R = C_6H_5CO



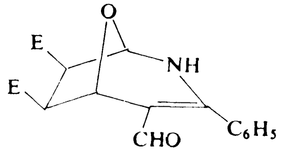
II



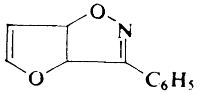
III



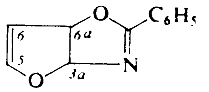
IVa,b, E = $COOCH_3$



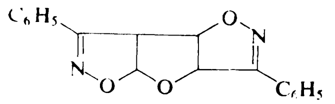
V



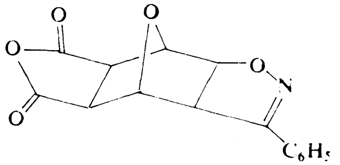
VI



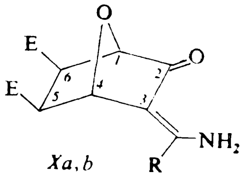
VII



VIII



IX

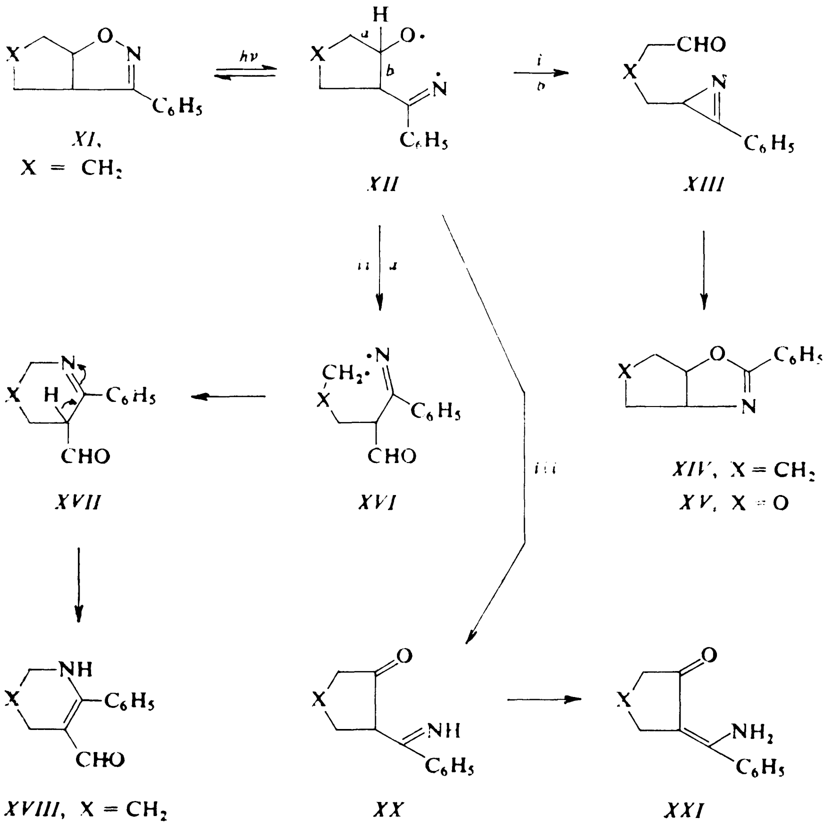


Xa,b

Attempts to dehydrogenate *IVa* aiming to obtain the corresponding isoxazoles failed. Active manganese(IV) oxide (reflux in benzene), or *o*-bromcanile in benzene (100–110°C, 20 h) effective with other isoxazolines did not react.

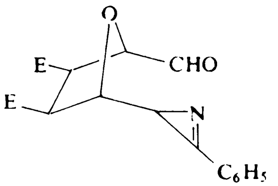
Photochemical investigations of isoxazolines showed that the N—O bond primarily undergoes splitting to furnish the biradical *XII* (Scheme 1), which subjects to various reaction changes depending on the possible stabilization of the biradical due to structural variations of the starting components. The analogous derivative *XI*, ($X = CH_2$) afforded product *XIV* by a cleavage of bond *b*; the azirine derivative *XIII* formed *via i* gave through a photochemical opening a nitrile ylide. The latter was added by a 1,3-dipolar cycloaddition to C=O to give oxazoline *XIV*. Cleavage of bond *a via ii* afforded tetrahydropyridine *XVII*, which became stabilized by a hydrogen transfer to tetrahydropyridine *XVIII*. Schmidt and coworkers[3] described formation of derivative *XIV* in a low yield by photochemical reaction of *XI*; these results, however, were corrected by the finding[7] that *XIV* was isolated in a 32% yield in addition to *XVIII*, obtained in a 13% yield. The latter was ascribed the structure *XXI*, which can originate *via iii*.

As showed the UV spectra of adducts prepared, the favourable irradiation wavelength is below 300 nm. Photolysis of the benzene solution of *IVa* afforded crystals having the molecular radical ion peak at *m/z* 331, which is the same as that of the starting material and thereby indicating a product of rearrangement. Taking the hitherto known findings shown in Scheme 1 into consideration, one can presume formation of products *XXII*, *XXIII*, *Xa*, and *V*.

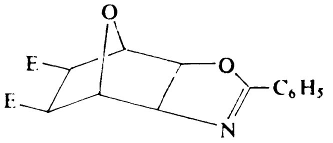


Scheme 1

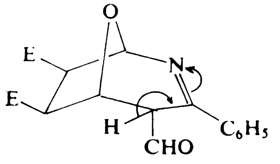
The ^1H NMR spectrum of the isolate displayed a noticeable singlet at δ 9·03 ppm, which did not change its position and intensity either by temperature or after addition of heavy water. Consequently, this has to be an aldehyde proton so that the isoxazoline *XXIII* and compound *Xa* can be excluded. The IR spectrum showed stretching vibrations of methoxycarbonyl group at 1 749 cm^{-1} and of an NH group at 3 405 cm^{-1}, whilst the absorption typical of an azirine ring at 1 730 – 1 750 cm^{-1} was absent. This means that structures *XXII* and *XXIV* are also excluded and therefore, we ascribed the product structure of 6,7-dimethoxycarbonyl-4-formyl-8-oxa-3-phenyl-2-azabicyclo[3,2,1]-3-octene (*V*). The proposed assignment *V* was backed by stretching vibrations of an α,β-unsaturated system at 1 632 cm^{-1} (C=O), and



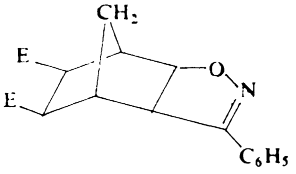
XXII



XXIII



XXIV



XXVII

1 588 cm^{-1} (C=C), and by a bathochromic shift in the UV spectrum from 264 nm (*IVa*) to 309 nm. The ^1H NMR spectrum revealed signals of signglets due to bridged 1-H and 5-H protons at 5·95 and 5·55 ppm, respectively. The ^{13}C NMR spectrum evidenced the suggested structure *V*: the off-resonance technique allowed to assign singlets at 170·50 ppm to C=O of the methoxycarbonyl group and at 157·60 and 115·50 ppm to carbons of the enamine grouping. Signal of the doublet at 186·1 ppm proved the presence of an aldehyde, that at 84·8 and 58·54 ppm belonged to two bridged carbon atoms.

Formation of *V* could be rationalized by an initial α-cleavage of the O—N bond of *IVa* giving rise to biradical *XII*, stabilized *via ii* (Scheme 1) to biradical *XVI*, which is more advantageous for overlapping the $—OCH_2^{\bullet}$ radical by *p*-electrons of oxygen. Compound *XXIV*, resulting from recombination, was stabilized by a hydrogen transfer to *V*, as evidenced by monitoring the reaction mixture by UV spectrum. The UV spectrum of photolyzed *IVa* at a low concentration ($5 . 10^{-5}$ mol l^{-1}) and at 254 nm (ref.[14]) showed the presence of isosbestic points at 247 and 284 nm indicating a photochemical reaction of the A→B type (Fig. 1); similarly, the ED digrams were found to be linear. Quantitative measurements of the *IVa*→*V* rearrangement were photochemically investigated. Considering *IVa* rearranges quantitatively to *V* at a monochromatic irradiation of $\lambda = 254$ nm (this being highly probably due to the presence of isosbestic points) the quantum yield can easily be determined from the concentration decrease of *IVa* (ref.[14]). The quantum yield of photolysis of *IVa*→*V* was 0·26 ± 0·02. The reaction proceeds either in the presence or in the absence of oxygen. These facts and the finding that this reaction takes place also in benzene allowed us to presume a singlet mechanism in accordance with[6].

Product *V* was obtained in a relatively high yield: 57% in benzene, 63% in acetonitrile. Separation on a preparative-scale thin-layer chromatography also afforded the unreacted starting *IVa* and a polymeric residue. The photolysis lasted 4 h; at a total conversion the yield of V after 5 h was 75% in acetonitrile. Further irradiation resulted in a concentration decrease of the product of rearrangement.

The analogous photolysis of *II* was highly selective as with *IVa*. 3-Formyl-4-phenyl-2,3-dihydro-6*H*-1,3-oxazine (*III*), obtained a 53% yield in benzene, or 68% in acetonitrile, was the single rearrangement product in addition to the unreacted *II* (30%). Structure *III* was ascribed on the basis of spectral evidence showing the fragment NH—C=C—CHO ($\tilde{\nu}$(NH) 3 422 cm^{-1}, $\tilde{\nu}$(C=O) 1 626 cm^{-1}, (C=C) 1 594 cm, λ_{max} 310 nm). The ^1H- and ^{13}C NMR spectra revealed the presence of an aldehyde group (8·87 ppm, s, and 187·30 ppm, d) and a C=C double bond (159·18 and 111·81 ppm). The analogy between the structures *III* and *V*, the presence of equal isosbestic points at 246 and 283 nm (Fig. 2) and the linearity of ED-digrams let us propose the mechanism of formation. Even here, decisive was the greater stability of biradical *XVI* due to possible stabilization of —$OCH_2^{\bullet}$ by delocalization with the lone electron pair of oxygen atom. 1,3-Oxazine *XVII* formed by recombination of this radical became stabilized by a 1,3-sigmatropic hydrogen transfer to *III*.

The quantum yield of photolysis of *II*→*III* was found to be $\Phi = 0{\cdot}04$; the difference $\Phi = 0{\cdot}26$, when compared with that of *IVa*→*V* was influenced by strain factors in tricyclic derivative *IVa*. A similar influence of factors was observed[6]

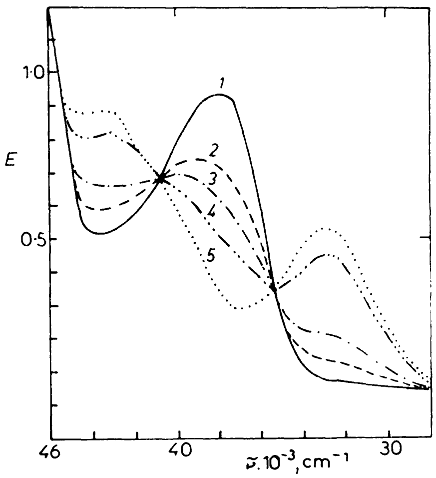


Fig. 1

UV Spectrum of photolyzed *IVa* at low concentration and 254 nm

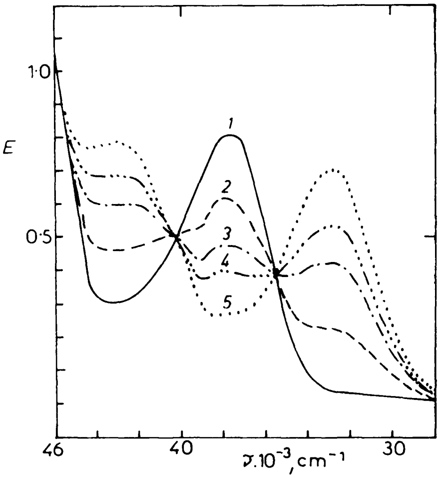
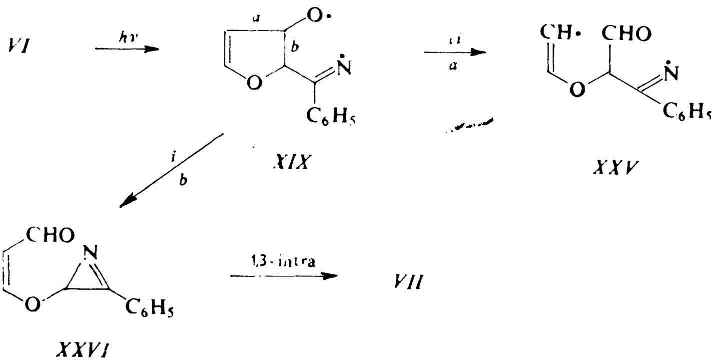


Fig. 2

UV Spectrum of the analogy between the structures *III* and *V* in photolysis of isoxazolines fused to cyclopropane or cyclopentane rings. The influence of a heteroatom upon photolysis of isoxazolines was evidenced for derivative *XXVII* differing from *IVa* ($\Phi = 0{\cdot}26$) by replacement of the oxygen bridge for a methylene one. The above-mentioned stabilization by a lone electron pair is no more possible in this case, and the quantum yield $\Phi = 0{\cdot}07$ proved our consideration[13]. The 2,3-dihydro-6*H*-1,3-oxazine system prepared is rare; known are its oxo derivatives and isomeric 5,6-dihydro-4*H*-1,3-oxazines and 3,4-dihydro-2*H*-1,3-oxazines[12].

Photolysis of adduct *VI* led to the expected rearrangement product-2-phenyldihydro[4,3-*d*]-oxazole (*VII*). Its origination can be rationalized by an O—N bond cleavage to afford the biradical *XIX*, which becomes stabilized by fission of bond *b* (path *i*, Scheme 2), giving azirine *XXVI*. The latter yielded nitrile-ylide by a known



Scheme 2

process *via* electrocyclic cleavage; this product furnished the oxazoline *VII* by an intramolecular 1,3-dipolar cycloaddition. Due to unfavourable energy conditions the bond *a* cleavage did not take place in the primarily formed boradical *XIX* (path *ii*), since the biradical *XXV* would contain a radical localized at the sp^2 carbon. The UV spectra of *VI* and *VII* are in accord with the presented interpretation of rearrangement. Structure *VII* was adduced from the ^{1}H NMR spectral data of *VI* and *VII*, because they are close to each other. Photochemical treatment of the bisadduct *VIII* afforded unidentified compounds only; their UV spectrum indicated a loss of heterocyclic chromophore, the ^{1}H NMR spectrum showed signals of aromatic ring protons only; proton signals of tetrahydrofuran ring, indicating a total decomposition of bisadduct *VIII* were absent.

Photolysis of *IVb*, the benzoyl analogue of *IVa* had an unexpected course: not even a trace amount of the benzoyl analogue *V* could be found after photolysis. When photolysis of *IVb* was carried out at a low conversion, a product was obtained the long-wave UV absorption band of which was bathochromically shifted by 41 nm relative to *IVb*. Its mass spectrum indicated a product of rearrangement the IR spectrum showed stretching vibrations of a strained cyclic ketone at 1 755 cm^{-1} and a C=C—C=O grouping at 1 635 cm^{-1}. The ^1H NMR spectrum lacked the signal of an aldehyde proton, what means that structures *XXIV* and *V* containing a benzoyl group are excluded; two singlets at 5·67 and 6·26 ppm were attributed to protons in the neighbourhood of the oxygen atom, that at 3·70 ppm to a methoxycarbonyl group. The product of rearrangeemnt, isolated in addition to the unreacted *IVb* in a 20% yield was assigned the structure of enamine *Xb*. Its formation can be explained by a hydrogen transfer from the initially originated biradical *XII via iii*. The imine radical *XII*, having the benzoyl group replaced for a phenyl one. has likely a greater electrophility due to a conjugation with the electron-withdrawing benzoyl group. The reaction was finished by a 1,3-sigmatropic hydrogen transfer from derivative *XX* to furnish *Xb*.

Product *Xb* was not formed when the photolysis of *IVb* was carried out up to total conversion. Mass spectrum showed that a total decomposition occurred. Isolated were: benzoic acid, resulting probably from hydrolysis and decarbonylation of benzoylnitrile, and benzoylnitrile itself. Photolysis to a 60% conversion was characterized by diminuation of the absorption band of *IVb*, whilst a little change at 315 nm indicated the formation of the product of rearrangement *Xb*. Photolysis to a 16% conversion after which the reaction mixture was left to stand for 14 h afforded a product having the UV spectrum diagnostic of *Xb*. This fact entitled us to presume that the hydrogen transfer from *XX* to *Xb* is a dark reaction. Surprisingly enough, no reaction was observed when *IVb* was irradiated at λ = 330 and 313 nm (ref.[14]), although *IVb* has a weak $n \rightarrow \pi$ band associated with the carbonyl group in this region.

The reaction mixtures after photolysis were also investigated by gas chromatography in order to determine the amount of benzonitrile accompanying the photolysis of isoxazolines[6]. The yield of benzonitrile, when photolysing *IVa* in benzene, was 1·6%, that of *VI* and *VIII* 0·6, whilst no benzonitrile was found when photolysing *IVa* and *II* in acetonitrile.

EXPERIMENTAL

Melting points are uncorrected. The mass spectra were measured with an MS 902 (AEI Manchester) apparatus at an ionization energy 70 eV. The ^1H NMR spectra of deuteriochloroform solutions were recorded on a Tesla BS 487 C instrument operating at 80 MHz, the ^{13}C NMR spectra on a Jeol spectrometer operating at 25·05 MHz using tetramethylsilane as an internal reference. The UV spectra of methanolic solutions were taken with a Specord UV-VIS (Zeiss, Jena) apparatus in temperated cells, the IR spectra of chloroform solutions with a Unicam SP spectrophotometer. 2,5-Dihydrofuran was prepared by dehydratation of *cis*-2-butenediol[15], 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene (*XXVIII*) by methanolysis of the furan-maleic anhydride adduct, 3-phenyl-3a,6a-dihydrofuro[3,2-*d*]-isoxazole (*VI*) and the bis-adduct *VIII* by cycloaddition of benzenenitrile oxide to furan according to[9], and benzoylnitrile oxide according to[16]. The content of benzonitrile in reaction mixtures was estimated with a Hewlett-

-Packard gas chromatograph equipped with a stainless steel column (2 mm i.d., 1·8 m) packed with 10% OV-17 over Chromosorb AVA DMCS (0·15—0·20 mm grain size), carrier gas nitrogen (45 ml min^{-1}), inlet temperature 200°C.

Quartz glass protected, water-cooled, high-pressure UV-lamp Tesla RVK 125 was employed for photochemical reactions carried out in an argone atmosphere at 25°C in a vessel equipped with a magnetic stirrer. The reaction course was monitored by thin-layer chromatography on Silufol sheets (Kavalier, Czechoslovakia). Products of photolysis as $\lambda = 254$ nm were also monitored by a concurrent measurement of UV spectra in acetonitrile[14].

Measurement of quantum-chemical yields: Solvents were purified by standard methods; the quantum yields at 254 nm were measured in an apparatus described in[14]. The respective concentrations of *II*, *IVa* and *XXVII* were estimated from the extinction decrease of their long-wave maximum at $\lambda = 264$ nm. Measured were 5 . 10 mol l^{-1} solutions in acetonitrile up to a 20% conversion; the cell length for UV spectrum and photolysis was 0·2 and 2 cm, respectively.

Reaction of *I* with 5,6-Dimethoxycarbonyl-7-oxybicyclo[2,2,1]-2-heptene (*XXVIII*)

Triethylamine (1·3 g, 13 mmol) was added during 1 h to a mixture of *XXVIII* (2·12 g, 10 mmol) and benzenehydroximic acid chloride (1·6 g, 10 mmol) in dioxane (10 ml) at 15°C. The mixture was stirred at an ambient temperature overnight, the separated triethylammonium chloride was filtered off, the filtrate was concentrated to a half of its volume under diminished pressure and crystallized from dichloromethane. Yield 1·1 g (33%) of *IVa*, m.p. 192—194°C. For $C_{17}H_{17}NO_6$ (331·3) calculated: 61·63% C, 5·17% H, 4·23% N; found: 61·69% C, 5·31% H, 4·47% N. IR spectrum (KBr), cm^{-1}: 1 742 ($COOCH_3$) and 1 605 (C=N); UV spectrum, λ_{max}, nm (log ε): 264 (4·12). Mass spectrum, *m/z*: 331 ($M^{+\bullet}$) base peak, 59 $(COOCH_3)^{\bullet}$. ^1H NMR spectrum, ppm: 7·37—7·75 (m, 5 H, H_{arom}), 5·08 (d, $J_{3a,7a}$ = 9·0 Hz, 1 H, 7a-H), 4·90 (s, 2 H, 4-H), 7-H), 3·98 (d, 1 H, 3a-H), 3·72 and 3·70 (s, 6 H, 2 × $COOCH_3$), 3·31 (m, 2 H, 5-H and 6-H), ^{13}C NMR spectrum, ppm: 170·35 (s, $COOCH_3$), 153·9 (s, C=N), 130·33, 129·03, 128·15 and 126·82 (C_{arom}), 85·89 (d), 84·20 (d) and 79·65 (d), ($C_{(7a)}$, $C_{(7)}$, $C_{(4)}$), 58·21 (d, $C_{(3a)}$), 52·49 (d) and 50·28 ($C_{(6)}$ and $C_{(5)}$).

Reaction of *IVb* with *XXVIII*

The same procedure was applied starting from *XIX* (2·1 g, 10 mmol), benzenehydroximic acid chloride (1·9 g, 10 mmol), dioxane (40 ml), and triethylamine (1·2 g, 12 mmol). The distillation residue was triturated with chloroform and filtered off. Yield 1·8 g (50%) *IVb*, m.p. 164—167°C (acetonitrile). For $C_{18}H_{17}NO_7$ (359·3) calculated: 60·16% C, 4·77% H, 3·90% N; found: 60·23% C, 4·71% H, 3·86% N. IR spectrum (KBr), cm^{-1}: 1 750 ($COOCH_3$), 1 665 (C=O), 1 605 (C=N) and 1 590 (C=C). UV spectrum λ_{max}, nm (log ε): 274 (3·94). Mass spectrum, *m/z*: 359 (M^{+}.), base peak, 41. ^1H NMR spectrum, ppm: 7·25—8·15 (m, 5 H, H_{arom}), 5·19 (s, 1 H, 7-H), 5·11 (s, 1 H, 4-H), 4·94 (d, $J_{3a,7a}$ = 8·0 Hz, 1 H, 7a-H), 3·98 (d, 1 H, 3a-H), 3·71 (s, 6 H, 2 × × $COOCH_3$), 3·10 (m, 2 H, 5-H, and 6-H). ^{13}C NMR spectrum, ppm: 187·2 (C=O), 171·5 ($COOCH_3$), 156·90 (C=N), 134·55, 130·99, 129·35 (C_{arom}), 88·28 (d), 85·00 (d), and 81·26 (d), ($C_{(7a)}$, $C_{(7)}$ and $C_{(4)}$), 58·32 (d, $C_{(3a)}$), 52·65 and 50·66 ($C_{(5)}$ and $C_{(6)}$).

Reaction of *Ia* with the Furan-to-Maleic Anhydride Adduct

The adduct (3 g, 18 mmol), benzenehydroximic acid chloride (2·8 g, 18 mmol), chloroform (40 ml), and triethylamine (1·9, 19 mmol) afforded *IX* (3·3 g, 63%), m.p. 225—230°C. For $C_{19}H_{11}NO_5$ (333·3) calculated: 68·47% C, 3·33% H, 4·20% N; found: 68·61% C, 3·51% H, 4·55% N.

Reaction of *Ia* with 2,5-Dihydrofuran

The mixture consisting of hydroximic acid (3·3 g, 21 mmol), 2·5-dihydrofuran (1 g, 14 mmol) and dioxane (30 ml) was kept at 15°C for 30 min after addition of triethylamine (2·2 g, 22 mmol) and then at 50°C for 2 h. The work-up and separation on a silica gel column (eluent cyclohexane–ethyl acetate 7 : 3) yielded *II* (1·2 g, 45%), m.p. 62—63°C, m.p. 64°C (ref.[9]). ^{1}H NMR spectrum, ppm: 7·40—7·60 (m, 5 H, H_{arom}), 5·31 and 5·27 (s, s, 2 H, 4-H_A and 6-H_A), 5·41 (d, $J_{3a,6a}$ = 4·0 Hz, 1 H, 6_a-H), 3·65—4·35 (m, 3 H, 3a-H, 3-H_B and 6-H_B). ^{13}C NMR spectrum, ppm: 156·71 (s, C=N), 130·07, 128·90 and 126·82 (C_{arom}), 86·28 (d, ($C_{(6a)}$), 79·26 (t, $C_{(6)}$), 71·73 (t, $C_{(4)}$), 53·79 (d, $C_{(3a)}$). UV spectrum, λ_{max}, nm (log ε): 264 (4·12).

Photochemical Treatment of *II*

A benzene solution (10 ml) of *II* (0·4 g, 2·1 mmol) was irradiated for 6 h under the above-mentioned conditions. The vacuum-concentrated oily solution was chromatographed over a silica gel column cyclohexane–ethyl acetate 1 : 2 being the eluent. Yield 0·12 g (30%) of the unreacted *II* and 0·15 g of *III* (53% per reacted *II*). Photolysis in acetonitrile gave *III* in a 68% yield; m.p. 118—120°C C (ethyl acetate). For $C_{11}H_{11}NO_2$ (189·2) calculated: 69·82% C, 5·86% H, 7·40% N; found: 70·01% C, 5·71% H, 6·98% N. IR spectrum (cm^{-1}): 3 422 (NH), 1 626 (C=O), 1 606, 1 594 (C=C), UV spectrum λ_{max}, nm (log ε): 310 (4·12), 238 (4·08). Mass spectrum, *m/z*: 189 ($M^{+\bullet}$, base peak). ^{1}H NMR spectrum, ppm: 8·87 (s, 1 H, CHO), 7·40 (s, 5 H, H_{arom}), 4·73 (d, $J_{CH,NH}$ = 4·0 Hz, 2 H, 2-H), 4·35 (s, 2 H, 6-H); ^{13}C NMR spectrum, ppm: 187·30 (d, CHO), 159·18 (s, $C_{(5)}$), 130·98, 129·81, 128·64 and 128·38 (C_{arom}), 111·81 (s, $C_{(4)}$), 83·23 (t, $C_{(2)}$) and 64·58 (t, $C_{(6)}$).

Photochemical Treatment of *IVa*

A solution of *IVa* (0·4 g, 1·2 mmol) in benzene (100 ml) was irradiated for 4 h and the oil obtained by removal of the solvent under reduced pressure was triturated with methanol (6 ml). Crystallization from acetone gave *V* (0·2 g, 57% per reacted *IVa*), m.p. 188—190°C. For $C_{17}H_{17}NO_6$ (331·3) calculated: 61·63% C, 5·17% H, 4·23% N; found: 61·81% C, 5·31% H, 4·33% N. IR spectrum, cm^{-1}: 3 405 (NH), 1 749 ($COOCH_3$), 1 632 (C=O) and 1 588 (C=C). UV spectrum, λ_{max}, nm (log ε): 309 (4·15), 238 (4·02). Mass spectrum, *m/z*: 331 ($M^{+\bullet}$), 187 (base peak). ^{1}H NMR spectrum, ppm: 9·03 (s, 1 H, CHO), 7·43 (s, 5 H, H_{arom}), 5·95 (s, 1 H, 1-H), 5·55 (s, 1 H, 5-H), 3·71 (s, 6 H, 2 × $COOCH_3$), 3·63 (s, 2 H, 6-H a 7-H); ($C^2H_3O^2H$): 8·86 (s, 1 H, CHO), 7·31—7·60 (m, 5 H, H_{arom}), 5·80 (s, 1 H, 1-H), 5·50 (s, 1 H, 5-H), 3·76 (s, 2 H, 6 H, and 7-H) and 3·68 (s, 6 H, 2 × $COOCH_3$). ^{13}C NMR spectrum, ppm: 186 (d, CHO), 170·50 (s, $COOCH_3$), 157·60 (s, $C_{(4)}$), 131·76, 131·30, 129·70 and 128·60 (C_{arom}), 115·50 (s, $C_{(3)}$), 84·81 (d, $C_{(1)}$), 58·54 (d, $C_{(5)}$), 55·70 and 52·40 (d, $C_{(6)}$ and $C_{(7)}$). Separation of the filtrate by preparative thin-layer chromatography (silica gel, cyclohexane–ethyl acetate) gave 0·05 g of the unreacted *IVa* and a little amount of polymeric substances left on the start. This reaction in acetonitrile furnished *V* in a 63% yield, and at a total conversion (320 min) the yield was 75%.

Photochemical Reaction of *VI*

The solution of *VI* (0·2 g, 1 mmol) in benzene (80 ml) was irradiated for 4·5 h, concentrated under diminsihed pressure, and the residue, chromatographed on a silica gel column (cyclohexane–ethyl acetate 1 : 2), afforded an oil from which impurities were distilled off at 75°C bath temperature and 270 Pa. Yield of oily *VII* 0·05 g (25%). For $C_{10}H_9NO_2$ (175·2) calculated: 68·56% C, 5·18% H, 8·00% N; found: 68·71% C, 5·16% H, 7·85% N. UV spectrum, λ_{max}, nm: 264. ^{1}H NMR spectrum, ppm: 7·27–7·82 (m, 5 H, H_{arom}), 6·57 (d, $J_{5,6}$ = 1·5 Hz, 5-H), 6·19 (d, $J_{3a,6a}$ = 9·0 Hz, 3a-H), 5·94 (d, d, $J_{6a,6}$ = 1 Hz, 6a-H), 5·30 (d, d, 1 H, 6-H).

Photochemical Treatment of *IVb*

The solution of *IVb* (0·5 g, 1·4 mmol) in acetonitrile (20 ml) was irradiated for 1 h, concentrated *in vacuo* and the residue, separated by a preparative thin-layer chromatography (silica gel, cyclohexane–ethyl acetate 1 : 2), furnished *Xb* (0·1 g, 34% per the reacted *IVb*) and 0·2 g (40%) of unreacted *IVb*, m.p. 114–116°C (ethyl acetate). For $C_{18}H_{17}NO_7$ (359·3) calculated: 60·16% C, 4·77% H, 3·90% N; found: 60·31% C, 5·01% H, 4·12% N. IR spectrum (KBr), cm^{-1}: 1 755 (C=O) and 1 635 (C=C). UV spectrum λ_{max}, nm (log ε): 315 (3·61), 264 (4·11). Mass spectrum, *m/z*: 359 ($M^{+\bullet}$). ^1H NMR spectrum, ppm: 7·35–7·40 (m, 5 H, H_{arom}), 5·67 (s, 1 H, 1-H), 5·26 (s, 1 H, 4-H), 3·82 (s, 2 H, 5-H and 6-H), 3·70 (s, 6 H, 2 × $COOCH_3$).

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