PREPARATION AND PHOTOCHEMISTRY OF 3-METHOXYCARBONYL SUBSTITUTED CONDENSED ISOXAZOLINES*

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The 1,3-dipolar cycloaddition of methoxy- and ethoxycarbonylnitriloxide to 2,3- and 2,5-dihydrofuran, 2,3-dihydropyrane, 7-oxabicyclo[2,2,1]-2-heptene, and 1,3-dioxep-5-ene derivatives is described. The condensed isoxazolines *Ia*, *IIIa*, *Va*, *Vb* are rearranged on irradiation to give the methoxycarbonyl substituted enaminoaldehydes *IIa*, *IVa*, *VIa*, *VIb*, respectively. The photolysis of *VIIc*, *VIIIa*, *VIIIc* is connected with destruction. The quantum yields of the photorearrangement are higher than those of the phenyl substituted derivatives but lower than those of the corresponding cyano derivatives. The enaminoaldehydes *IIa* and *VIa* have been used for preparation of new heterocyclic pyridazino[4,5-*d*]oxazine (*IX*) and pyridazino[7,8-*d*]-2,4,6-dioxazocine (*X*) systems, respectively.

Our earlier works revealed[1-7] that the new synthesis principle found, which consists in the 1,3-dipolar cycloaddition of nitriloxides to n-membered heterocycles containing an oxygen atom at the β position and in subsequent photorearrangement producing (n + 1)-membered hetrocycles (*I* → *II*, *III* → *IV*, *V* → *VI*), could find broader applications if a reactive functional group were introduced instead of the aryl R^1. In the previous communication[8] we dealt with the preparation and photochemistry of 3-cyano substituted (R^1 = CN) condensed isoxazolines. The successful results of this work initiated an investigation of photochemistry of condensed isoxazolines containing an alkoxycarbonyl group, because in this case a formation of reactive 1,4-dicarbonyl system could be expected. As far as we know, only the photochemistry of the isoxazoline derivatives with an aryl chromophore[9-12] was described.

The reaction of methoxycarbonylnitriloxide $CH_3OCOC{\equiv}\overset{(+)}{N}\!-\!\overset{(-)}{O}$ with suitable dipolarophiles as *e.g.* 2,3- and 2,5-dihydrofuran, 2,3-dihydropyrane, 5,6-bis(methoxycarbonyl)-7-oxabicyclo[2,2,1]-2-heptene, 2*H*,4*H*,7*H*-1,3-dioxepine, and 2-phenyl-2*H*,4*H*,7*H*-1,3-dioxepine gave the corresponding isoxazolines *Ia*, *IIIa*, *Va*–*Vc*, *VIIa*, and *VIIIa* containing the methoxycarbonyl group (yields 40–60%). The ethoxycarbonyl derivatives *VIIc* and *VIIIc* were prepared in a similar way. The

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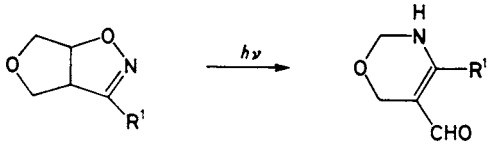
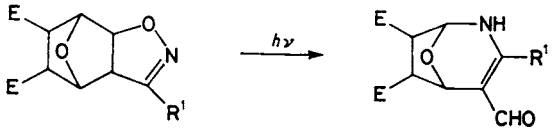
said cycloaddition to the heterocyclic dipolarophiles is distinctly accompanied also by the dimerization of methoxycarbonylnitriloxide (yield 30–50%). The lower yields of isoxazolines are rather surprising, because the electron-acceptor character of the

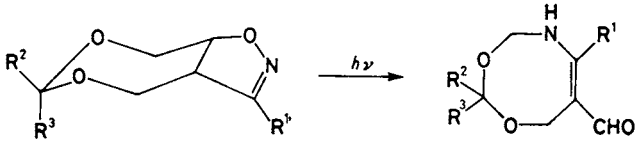


I *II*



III *IV*

$E = COOCH_3$



V *VI*

VII *VIII*

In formulae *I–IV, VII, VIII*: *a*, $R^1 = COOCH_3$ *b*, $R^1 = C_6H_5$ *c*, $R^1 = COOC_2H_5$

In formulae *V, VI*: *a*, $R^1 = COOCH_3$; $R^2 = R^3 = H$ *b*, $R^1 = COOCH_3$; $R^2 = H$; $R^3 = C_6H_5$ *c*, $R^1 = COOCH_3$; $R^2 = C_6H_5$; $R^3 = H$ *d*, $R^1 = C_6H_5$; $R^2 = R^3 = H$ *e*, $R^1 = C_6H_5$; $R^2 = H$; $R^3 = C_6H_5$ *f*, $R^1 = C_6H_5$; $R^2 = C_6H_5$; $R^3 = H$

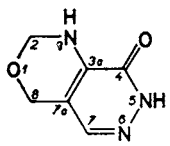
group chosen should decrease the LUMO energy of the corresponding nitriloxide and thus favour the dominant frontier orbital interaction LU(1,3-dipole)–HO-

(heterocycle) in the transition state. The available papers dealing with the 1,3-dipolar cycloadditions of nitriloxides to heterocyclic compounds[13-17] showed just the fact that these reactions are governed by the above-mentioned dominant frontier orbital interaction. This presumption is also confirmed by the fact that some dipolarophiles used by us and containing a carbonyl group, as *e.g.* maleic anhydride, 1,4-benzoquinone, and 2(5*H*)-furanone, do not react at all by the 1,3-dipolar cycloaddition. In this case always the nitriloxide dimer was only isolated. Obviously, for the dominant frontier orbital interaction LU(nitriloxide)–HO(heterocycle) the methoxycarbonyl group increases the reactivity of nitriloxide in its 1,3-cycloaddition with a heterocycle but, at the same time, increaes the rate of its dimerization. No other products are formed beside the dimerization and cycloaddition products. The methoxycarbonylnitriloxide used was generated *in situ* by addition of triethylamine to methyl chlorimidatoacetate in ether[18]. The structure of the condensed isoxazolines prepared was determined from the ^{1}H and ^{13}C NMR data on the basis of analogy with the corresponding phenyl derivatives *Ib*, *IIIb*, *Vb*, *VIIb*, *VIIIb* (refs[1-7]). The *exo*-*Vd* and *endo*-*Vc* derivative formed in the reaction with 2-phenyl-2*H*,4*H*,7*H*-1,3-dioxepine (their ratio is 7 : 3 as in the cases of the cycloadditions with benzenenitriloxide[3] or cyanonitriloxide[8]) were obtained in pure state by column chromatography. The structure of the two diastereoisomers *Vc* and *Vb* was assigned in analogous way as that used in the case of the aryl derivatives[2,3]. With the non-symmetrical dipolarophiles, 2,3-dihydrofuran and 2,3-dihydropyrane, the regioisomers head-to-head *VIIa* and *VIIIa* are only formed. As characteristical of the structures mentioned we can give especially the signals with the chemical shifts for the doublet adjacent to isoxazoline oxygen within the limits of δ 4·72–5·41 (symmetric dipolarophiles) and δ 6·00 (non-symmetric dipolarophiles). The isoxazoline structure is further confirmed by the presence of the singlet of methoxycarbonyl group at δ 3·86–3·90. In contrast to the 3-cyanosubstituted derivatives, the ^{13}C NMR spectra of the isoxazolines prepared exhibit easily distinguishable C=N carbon atom signals of isoxazoline ring.

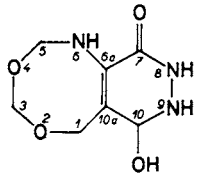
The photochemical reactions of isoxazolines were carried out in acetonitrile or methanol with application of monochromatic radiation (λ_{max} 254 nm) as in our earlier works[1-8]. From the results obtained it can be concluded that in the case of 3-methoxycarbonylsubstituted isoxazolines *Ia*, *IIIa*, *Va*–*Vc*, too, the free electron pair of oxygen atom at the α position with respect to one of the radical centres exerts a stabilizing effect, which results in formation of the heterocyclic enaminoaldehydes *IIa*, *IVa*, *VIa*, and *VIc*. The ^{1}H NMR spectra of all the enaminoaldehydes contain a singlet characteristical of an aldehydic proton in the region of δ 9·0–10·5 whose presence is also confirmed by the doublet at δ 186–188 in the ^{13}C NMR spectra. The photorearrangement of the diastereomers *Vb* and *Vc* gives the same products (*VIb* ≡ *VIc*). The structures of the enaminoaldehydes prepared, *viz.* *IIa* (69%), *IVa* (33%), *VIa* (65%), and *VIb* (68%) were proved by comparison of the spectral

data with those of the corresponding phenyl[1-7] and cyano derivatives[8]. In analogy, we also presume the same mechanism of their formation.

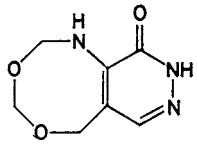
Table I presents the results of measurements of the rearrangement quantum yields which were obtained from the concentration decrease of the starting isoxazolines up to max. 20% conversion. The quantum yield does not depend on the presence or absence of oxygen, the reaction proceeds identically in benzene, and it is not sensitized with acetophenone or acetone, which – in accordance with refs[9-12] – indicates the singlet mechanism. According to expectations, the Φ values are higher in acetonitrile than in methanol, *e.g.* 0·079 and 0·058, respectively, for *Ia* → *IIa*, which agrees with our previous results[1-7]. Except the derivative *IIIa*, the methoxycarbonyl derivatives have higher Φ values than the corresponding phenyl derivatives (Table I) but lower values than the cyano derivatives[8]. In the case of the phenyl and cyano derivatives we found a surprising dependence of Φ on the stereochemistry: the *endo* derivatives *V* showed higher values than the corresponding *exo* derivatives. The said dependence is not so distinct for the methoxycarbonyl derivatives, the quantum yields lying almost within the experimental error (Φ = 0·042 and 0·039 for the *endo* derivative *Vc* and the *exo* derivative *Vd*, respectively).



IX



X



XI

The irradiation of the isoxazolines *VIIa* and *VIIIa* containing an oxygen atom at α position with regard to the isoxazoline oxygen atom gave also only polymeric products in accordance with the phenyl and cyano derivatives[19].

TABLE I

The photorearrangement quantum yields Φ (methanol)

Compound	*Ia*[a]	*Ib*	*IIIa*	*IIIb*	*Va*	*Vb*	*Vc*	*Vd*	*Ve*	*Vf*
Φ[b]	0·058	0·04	0·10	0·13	0·061	0·042	0·039	0·016	0·026	0·008

[a] In acetonitrile 0·079; [b] the values measured from the decrease of the starting components.

The rearrangement products of *IIa* and *VIa* containing a 1,4-dicarbonyl grouping were further used for a synthesis of condensed derivatives of pyridazine. According to expectation, the reaction of *IIa* with hydrazine in methanol gave 2,3-dihydro--1,3-oxazine-4-one (*IX*). The suggested structure *IX* is especially confirmed by the presence of a singlet at high values of δ 7·39 for the H-8 proton and of the corresponding doublet of C-8 at δ 135·41. The other δ values in ^{1}H and ^{13}C NMR spectra indicate the retention of the dihydroxazine skeleton. The reaction of *VIa* with hydrazine took a surprising course: Instead of the expected pyridazine derivative *XI* it gave its precursor – 10-hydroxy-1,3,5,6,7,8-hexahydro-8,9-pyridazino[7,8-*d*]--2,4,6-dioxazocine-7-one (*X*) which represents a new condensed system. The structure of *X* is proved by the absence of the singlet at low field $\sim\delta$ 7·5 and of the corresponding doublet at $\sim\delta$ 135 for H-10 and C-10, respectively; instead, the ^{1}H NMR spectrum exhibits a signal in the region of δ 4·12–4·95 hidden in a multiplet for 5 protons, and the ^{13}C NMR spectrum exhibits a corresponding doublet at δ 83·79 (C-10). Again the other signals confirm retention of the dioxazocine skeleton. The same anomaly, *i.e.* that in the cyclization reactions of a system condensed with a larger ring the reaction is stopped with formation of the hydroxy derivative, was also observed in the reactions of furolactones with hydrazines[20].

EXPERIMENTAL

The melting points were not corrected. The ^{1}H NMR spectra were measured with a Tesla 487 C (80 MHz) apparatus and the ^{13}C NMR spectra with a JEOL JX = 60 apparatus in deuteriochloroform (if not otherwise stated) with 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 mass spectra were measured with an AEI MS 902 S apparatus with direct inlet system, the ionization energy of 70 eV, trapping current of 100 μA. The IR spectra were measured with a Specord IR-60 apparatus in chloroform. Methyl and ethyl chloroximidoacetates were prepared according to ref.[18].

The preparative-scale photochemical reactions were performed with a low-pressure Toshiba GL-15 (15 W) discharge lamp in a temperated quartz reactor of 300 ml volume with forced circulation of the irradiated solution at 15°C. The course of the photoreactions was followed by means of TLC (Silufol plates) or UV spectroscopy. The photoreactions were carried out until consumption of the starting isoxazolines. The determination of quantum yields is described elsewhere[4].

General Procedure of Preparation of 3-Alkoxycarbonylsubstituted Isoxazolines

A solution of 0·01 mol alkyl chloroximidoacetate in 20 ml dry ether was added drop by drop at room temperature to a solution of 0·01 to 0·05 mol dipolarophile and 0·01 mol triethylamine in 20 ml dry ether with stirring during 5 h. Then the reaction mixture was stirred for another 1 h at room temperature. The separated triethylamine hydrochloride was filtered off and the filtrate was concentrated under reduced pressure and submitted to column chromatography (silica gel, chloroform) to give the corresponding isoxazolines. The first fractions contain the dimer of methoxy- or ethoxycarbonylformonitriloxide[18] which is formed in the yields of 30 to 50%.

3-*Methoxycarbonyl*-3a,4,6,6a-*tetrahydrofuro*[3,4-*d*]*isoxazole* (Ia) was prepared from 2,5-dihydrofuran in the yield of 42%, m.p. 43–45°C. For $C_7H_9NO_4$ (171·1) calculated: 49·12% C, 5·30% H, 8·18% N; found: 49·31% C, 5·22% H, 8·06% N. ^{1}H NMR: 5·41 dd, 1 H (H-6a, J(3a, 6a) = 9; J(6, 6a) = 4); 4·37–3·95 m, 3 H (H-3a, 2× H-6); 3·87 s, 3 H (CH_3); 3·87–3·55 m, 2 H (2× H-4). ^{13}C NMR: 160·81 s (C=O); 151·45 s (C=N); 88·62 d (C-6a); 75·82 t (C-6); 71·73 t (C-4); 52·82 q (CH_3); 52·63 d (C-3a). IR spectrum: 1 693 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 242 nm (2·74). Mass spectrum, m/z: 171 ($M^{\ddagger}$).

3,4,7-*Tris*(*methoxycarbonyl*)-9,10-*dioxa*-8-*azatricyclo*[4,3,0,$1^{2,5}$]-7-*decene* (IIIa) was prepared from 5,6-bis(methoxycarbonyl)-7-oxabicyclo[2,2,1]-2-heptene, yield 57%, m.p. 135–137°C. For $C_{13}H_{15}NO_8$ (313·3) calculated: 49·84% C, 4·83% H, 4·47% N; found: 50·07% C, 5·04% H, 4·33% N. ^{1}H NMR: 5·14–4·92 m, 3 H (H-1, H-2, H-5); 3·90 s, 3 H (OCH_3); 3·90–3·81 m, 1 H (H-6); 3·70 s, 6 H (2× OCH_3); 3·10–3·01 m, 2 H (H-3, H-4). ^{13}C NMR: 169·97 s (2× C=O); 160·68 s (C=O); 149·31 s (C=N); 87·97 d (C-1); 83·95 d (C-2); 79·98 d (C-5); 56·98 d (C-6); 53·02 q (OCH_3); 52·50 q (2× OCH_3); 50·03 d (C-3); 46·46 d (C-4). IR spectrum: 1 690 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 246 nm (2·69).

8-*Methoxycarbonyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Va) was prepared from *2H*, *4H*,*7H*-1,3-dioxepine, yield 45%, m.p. 79–81°C. For $C_8H_{11}NO_5$ (201·2) calculated: 47·76% C, 5·51% H, 6·96% N; found: 47·93% C, 5·55% H, 7·09% N. ^{1}H NMR: 5·10–4·82 m, 2 H (2× H-4); 4·72–4·25 m, 3 H (H-1, H_A-2, H_A-6); 3·95–3·70 m, 3 H (H-7, H_B-2, H_B-6); 3·90 s, 3 H (OCH_3). ^{13}C NMR: 160·87 s (C=O); 150·87 s (C=N); 99·15 t (C-4); 85·39 d (C-1); 70·43 t (C-2); 67·18 t (C-6); 52·63 q (OCH_3); 51·20 d (C-7). IR spectrum: 1 700 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 249 nm (2·70).

Endo-4-*phenyl*-8-*methoxycarbonyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Vb), yield 11%, m.p. 75–76°C. For $C_{14}H_{15}NO_5$ (277·5) calculated: 60·64% C, 5·45% H, 5·05% N; found: 60·48% C, 5·73% H, 5·21% N. ^{1}H NMR: 7·53–7·28 m, 5 H (aromatic H); 5·75 s, 1 H (H-4); 5·17–4·89 m, 1 H (H-1); 4·45–3·71 m, 5 H (2× H-2, 2× H-6, H-7); 3·85 s, 3 H (OCH_3). UV spectrum, λ_{max} (log ε): 252 nm (2·60).

Exo-4-*phenyl*-8-*methoxycarbonyl*-3,5,10-*trioxa*-9-*azabicyclo*[5,3,0]-8-*decene* (Vc), yield 26%, m.p. 118–120°C. For $C_{14}H_{15}NO_5$ (277·3) calculated: 60·64% C, 5·45% H, 5·05% N; found: 60·39% C, 5·31% H, 5·07% N. ^{1}H NMR: 7·50–7·23 m, 5 H (aromatic H); 5·36 s, 1 H (H-4); 5·09–4·38 m, 3 H (H-1, H_A-2, H_A-6); 4·12–3·64 m, 3 H (H_B-2, H_B-6, H-7); 3·86 s, 3 H (OCH_3). ^{13}C NMR: 160·94 s (C=O); 151·06 s (C=N); 138·26, 128·78, 126·18 (aromatic C); 106·95 d (C-4); 85·37 d (C-1); 69·00 t (C-2); 65·10 t (C-6); 52·63 q (OCH_3); 51·97 d (C-7). UV spectrum, λ_{max} (log ε): 251 nm (2·73).

7-*Methoxycarbonyl*-2,9-*dioxa*-8-*azabicyclo*[4,3,0]-7-*nonene* (VIIIa) was prepared from 2,3-dihydropyrane, yield 43%, m.p. 35°C. For $C_8H_{11}NO_4$ (185·2) calculated: 51·88% C, 5·99% H, 7·56% N; found: 52·05% C, 6·21% H, 7·33% N. ^{1}H NMR: 6·00 d, 1 H (H-1, J(1, 6) = 8·0); 3·94 s, 3 H (OCH_3); 3·85–3·65 m, 2 H (2× H-3); 3·50–3·25 m, 1 H (H-6); 2·18–1·56 m, 4 H (2× H-4, 2× H-5). ^{13}C NMR: 160·41 s (C=O); 154·31 s (C=N); 104·08 d (C-1); 62·04 t (C-3); 52·88 q (OCH_3); 42·17 d (C-6); 19·30 t (C-4); 17·61 t (C-5).

3-*Ethoxycarbonyl*-3a,4,5,6a-*tetrahydrofuro*[3,2-*d*]*furan* (VIIc) was prepared from 2,3-dihydrofuran, yield 51%, a viscous oil. For $C_8H_{11}NO_4$ (185·2) calculated: 51·88% C, 5·99% H, 7·56% N; found: 52·03% C, 6·09% H, 7·30% N. ^{1}H NMR: 6·34 d, 1 H (H-6a, J(3a, 6a) = 6·0); 4·37 q, 2 H (O–CH_2); 4·25–3·87 m, 2 H (2× H-5); 3·77–3·40 m, 1 H (H-3a); 2·42–2·15 m, 2 H (2× H-4), 1·40 t, 3 H (CH_3).

7-Ethoxycarbonyl-2,9-dioxa-8-azabicyclo[4,3,0]-*7-nonene* (VIIIc) was prepared from 2,3-dihydropyrane, yield 41%, a viscous oil. For $C_9H_{13}NO_4$ (199·2) calculated: 54·26% C, 6·58% H, 7·03% N; found: 54·49% C, 6·21% H, 7·43% N. ^{1}H NMR: 6·01 d, 1 H (H-1, $J(1, 6) = 8·0$); 4·36 q, 2 H (O—CH_2); 3·85—3·65 m, 2 H (2× H-3); 3·50—3·27 m, 1 H (H-6); 2·31—1·57 m, 4 H (2× H-4, 2× H-5); 1·40 t, 3 H (CH_3). ^{13}C NMR: 160·41 s (C=O); 154·31 s (C-7); 104·09 d (C-1); 62·04 t (C-3); 59·19 t (O—CH_2); 42·17 d (C-6); 19·29 t (C-4); 17·61 t (C-5); 14·10 q (CH_3).

Photorearrangement of Isoxazolines

A solution of the respective isoxazoline (3 mmol) in 300 ml acetonitrile was irradiated until complete consumption of the starting derivative (TLC). The solution was concentrated under reduced pressure and the rearrangement product was obtained from the evaporation residue by means of column chromatography (silica gel, chloroform).

4-Methoxycarbonyl-5-formyl-2,3-dihydro(6*H*)-*1,3-oxazine* (IIa) was prepared from *Ia*, the irradiation time 60 min, yield 69%, m.p. 118—120°C. For $C_7H_9NO_4$ (171·1) calculated: 49·15% C, 5·30% H, 8·18% N; found: 48·99% C, 5·17% H, 8·10% N. ^{1}H NMR: 10·08 s, 1 H (CHO); 6·18 bs: 1 H (NH); 4·77—4·67 m, 2 H (2× H-2); 4·55 s, 2 H (2× H-6); 3·94 s, 3 H (OCH_3). ^{13}C NMR, 186·73 d (CHO); 160·94 s (C=O); 141·58 s (C-4); 114·74 s (C-5); 72·51 t (C-2); 62·96 t (C-6); 52·30 q (OCH_3). IR spectrum: 3 350 cm^{-1} (NH), 1 710 cm^{-1} (C=O), 1 599 cm^{-1} (C=C). Mass spectrum, *m/z*: 171 (M^+). UV spectrum, λ_{max} (log ε): 325 nm (2·51), 222 nm (2·09).

2-Formyl-3,6,7-tris(*methoxycarbonyl*)-*8-oxa-4-azabicyclo*[3,2,1]-*2-octene* (IVa) was prepared from *IIIa*, the irradiation time 45 min, yield 33%, a viscous oil. For $C_{13}H_{15}NO_8$ (313·3) calculated: 49·84% C, 4·83% H, 4·47% N; found: 49·81% C, 4·98% H, 4·27% N. ^{1}H NMR: 10·50 s, 1 H (CHO); 6·66—6·58 m, 1 H (H-1); 5·93—5·85 m, 1 H (H-5); 5·58 bs, 1 H (NH); 3·90 s, 3 H (OCH_3); 3·70 s, 3 H (OCH_3); 3·67 s, 3 H (OCH_3); 3·90—3·25 m, 2 H (H-6, H-7). ^{13}C NMR: 186·79 s (CHO); 169·70 s (2× C=O); 161·71 s (C=O); 158·99 s (C-3); 119·74 s (C-2); 84·79 d (C-5); 75·69 d (C-1); 58·61 d (C-6); 56·85 d (C-7); 53·34 q (OCH_3); 52·37 q (2× OCH_3). UV spectrum, λ_{max} (log ε): 330 nm (2·71).

6-Methoxycarbonyl-7-formyl-2,4,5,8-tetrahydro-1,3-diox-5-azocine (VIa) was prepared from *Va*, the irradiation time 120 min, yield 65%, m.p. 128—130°C. For $C_8H_{11}NO_5$ (201·2) calculated: 47·76% C, 5·51% H, 6·96% N; found: 50·01% C, 5·63% H, 7·05% N. ^{1}H NMR: 9·62 s, 1 H (CHO); 6·12 bs, 1 H (NH); 4·87—4·66 m, 4 H (2× H-2, 2× H-8); 4·02—3·75 m, 2 H (2× H-4); 3·90 s, 3 H (OCH_3). ^{13}C NMR (hexadeuteriodimethyl sulphoxide): 188·16 d (CHO); 166·53 s (C=O); 153·40 s (C-8); 112·59 s (C-7); 96·22 t (C-4); 75·82 t (C-2); 64·19 t (C-6), 53·42 q (OCH_3). UV spectrum, λ_{max} (log ε): 327 nm (2·61).

2-Phenyl-6-methoxycarbonyl-7-formyl-2,4,5,8-tetrahydro-1,3-dioxa-5-azocine (VIb) was prepared from *Vc* or *Vd*, the irradiation time 120 min, yield 68%, m.p. 64—66°C. For $C_{14}H_{15}NO_5$ (277·3) calculated: 60·64% C, 5·45% H, 5·05% N; found: 60·69% C, 5·21% H, 5·17% N. ^{1}H NMR (hexadeuterioacetone): 10·05 s, 1 H (CHO); 8·17—7·25 m, 5 H (aromatic H); 5·75—3·25 m, 6 H (2× H-2, H-4, 2× H-6, H-7); 3·77 s, 3 H (OCH_3).

Reaction of Enaminoaldehydes *IIa* and *VIa* with Hydrazine

A solution of 6 mmol hydrazine hydrate in 1 ml methanol was added drop by drop to a solution of 5 mmol corresponding enaminoaldehyde in 10 ml methanol with stirring. The reaction mixture was stirred overnight and then concentrated under reduced pressure. The evaporation residue was submitted to column chromatography (silica gel, chloroform–methanol 99 : 1 to 95 : 5).

2,3-*Dihydro*(8*H*)-5,6-*pyridazino*[4,5-*d*]-1,3-*oxazine*-4-*one* (IX) was prepared from *IIa*, yield 40%, m.p. 186—188°C. For $C_6H_7N_3O_2$ (153·1) calculated: 47·05% C, 4·61% H, 27·44% N; found: 47·14% C, 4·52% H, 27·14% N. ^{1}H NMR (hexadeuteriodimethyl sulphoxide): 7·39 s, 1 H(H-7); 7·11 b, 2 H (2× NH); 4·64 d, 2 H (2× H-2, $J(2, 3) = 3·0$); 4·50 s, 2 H (2× H-8). ^{13}C NMR (hexadeuteriodimethyl sulphoxide): 155·68 s (C=O); 137·87 s (C-3a); 135·41 d (C-7); 111·62 s (C-7a); 73·55 t (C-2); 63·28 t (C-8). Mass spectrum, *m/z*: 153 ($M^{\ddagger}$).

10-*Hydroxy*-1,3,5,6,7,8-*hexahydro*-8,9-*pyridazino*[7,8-*d*]-2,4,6-*dioxazocine*-7-*one* (XII) was prepared from *VIa*, yield 75%, m.p. above 300°C with decomposition. For $C_7H_{11}N_3O_3$ (185·2) calculated: 45·40% C, 5·99% H, 22·69% N; found: 45·61% C, 6·13% H, 22·57% N. ^{1}H NMR (hexadeuteriodimethyl sulphoxide): 6·40—5·90 m, 2 H (NH, OH); 4·95—4·12 m, 5 H (2× NH, 2× H-3, H-10); 4·52 s 2 H (H-5); 4·10 s, 2 H (H-1). ^{13}C NMR (hexadeuteriodimethyl sulphoxide): 165·12 s (C=O); 133·25 s (C-6a); 111·03 s (C-10a); 95·26 t (C-3); 83·79 d (C-10); 75·83 t (C-5); 64·80 t (C-1). Mass spectrum, *m/z*: 185 ($M^{\ddagger}$), 167 ($M^{\ddagger} - 18$).

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