

DERIVATIVES OF TETRAHYDRO-2H-PYRIDINE FROM PHOTO-REARRANGED CYCLOADDUCTS OF NITRILE OXIDES*

Lubor FIŠERA^a, Vladimír ONDRUŠ^a and Hans-Joachim TIMPE^b

^a Department of Organic Chemistry,

Slovak Institute of Technology, 812 37 Bratislava, Czechoslovakia and

^b Department of Photochemistry,

Technical University, Merseburg 42, G.D.R.

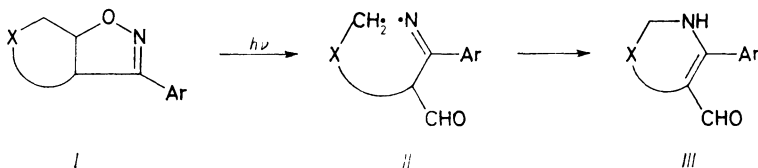
Received March 9, 1989

Accepted May 29, 1989

Dedicated to Professor P. Kristian on the occasion of his 60th birthday.

1,3-Dipolar cycloaddition of methoxycarbonylnitrile, furannitrile and substituted benzene nitrile oxides ($X = 4\text{-CH}_3, 4\text{-OCH}_3, 3\text{-OCH}_3, 4\text{-Cl}, 3\text{-Cl}, 2,4\text{-diCl}, 4\text{-F}$) to dimethyl 7-(diphenylmethylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (*XII*) led exclusively to *exo* cycloadducts *IV*, which, on irradiation with a low-pressure mercury lamp afforded the required 4-substituted derivatives of dimethyl 2,2-diphenyl-5-formyl-3-azabicyclo[4.3.0]nona-4,9-diene-7,8-dicarboxylate (*XI*) as sole products. Selectivity of the photorearrangement of isoxazolines *IV* to enaminoaldehydes *XI* is due to a stabilization of the biradical *VII* by the overlap of the radical-electron with π -electrons of the $\text{C}=\text{C}$ double bond and by two benzene rings. Quantum yields of the photorearrangement, established from the deficit of the starting *IV*, were found to be greater than those for the analogous oxabicyclic derivatives *XVI*. The reaction mechanism is proposed and the dependence on various solvents is pointed out; this reaction sequence, viz. the 1,3-dipolar cycloaddition followed by a photochemical rearrangement provides a new method for obtaining derivatives of tetrahydro-2H-pyridine from the well available cyclopentadiene.

Isoxazolines are suitable synthons for preparing β -hydroxyketones, β -hydroxynitriles, γ -aminoalcohols, and α,β -unsaturated carbonyl compounds¹. In contrast to the non-selective course of the majority of photochemical reactions with isoxazolines², we found a structural type of fused isoxazoline *I* allowing an extraordinarily unequi-



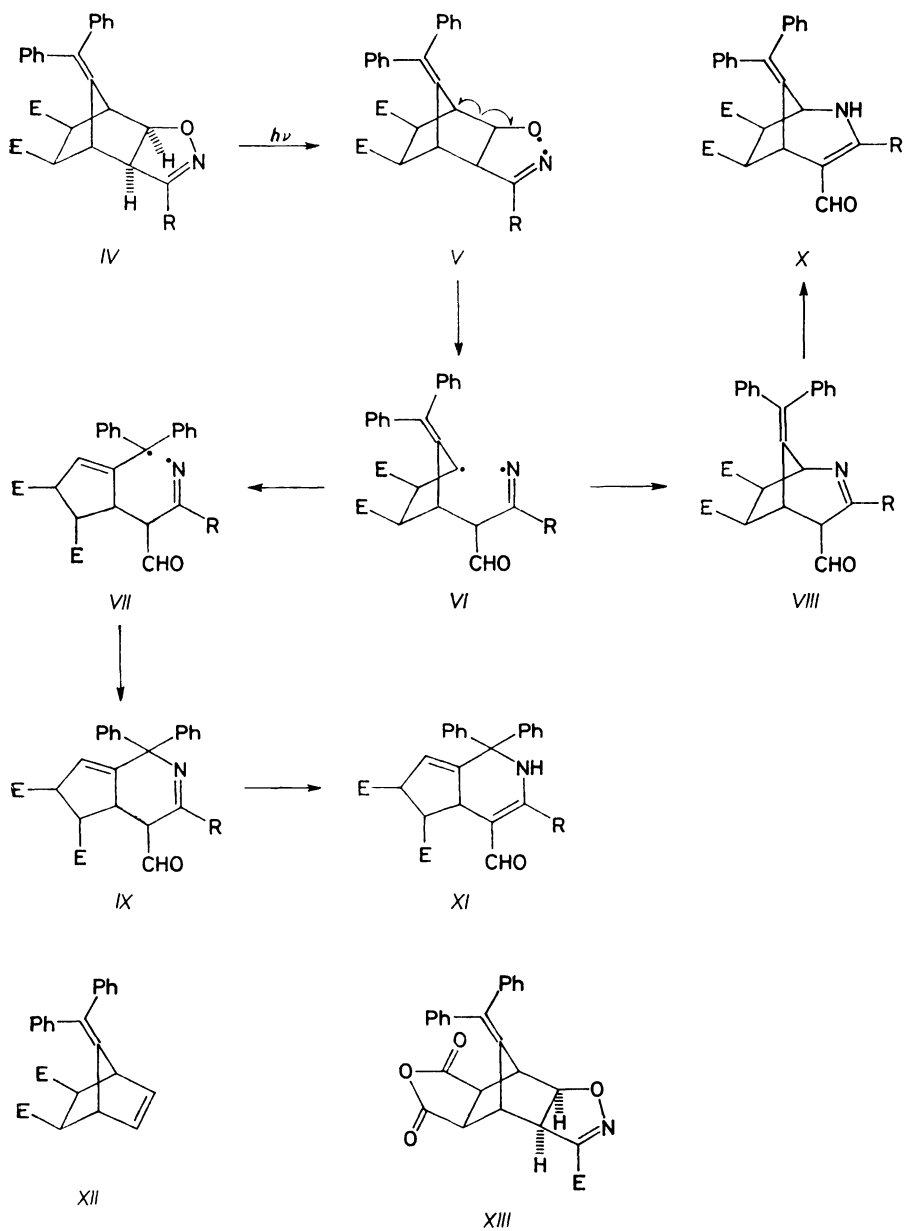
* Part XXV in the series Photochemistry of Heterocycles; Part XXIV: Chem. Papers, in press.

vocal course of photorearrangement³⁻⁹. Selectivity of the photochemical reaction $I \rightarrow III$ is due to the stabilizing effect of the heteroatom X on the biradical II formed after a primary cleavage of the N—O bond, thereby suppressing other fragmentation reactions of the biradical intermediate II . So far, our attention has been pointed toward compounds in which X was oxygen³⁻⁹, sulfur¹⁰ and nitrogen¹¹, where overlapping of p -electrons of the respective heteroatom with the radical electron caused the stabilization of II . A possible stabilization of the biradical II by π -electrons of the C=C double bond opening the route to preparation of cyclic enaminoaldehydes of type III was exemplified by rearrangement of $IVh \rightarrow XIh$ (Scheme 1) in our short communication¹²; the ring of the above-mentioned enaminoaldehydes is extended by one member when compared with the starting heterocycles.

This paper is aimed to investigate the influence of a substituent in position 5 on the direction of photorearrangement and to generalize the utilization of the tandem reaction 1,3-dipolar cycloaddition—photochemical rearrangement as a new synthetic approach to compounds related to tetrahydro-2H-pyridine from cyclopentadiene, which is a common by-product when processing the C-5 fraction.

The starting isoxazolines IV were prepared from cyclopentadiene via fulvene \rightarrow maleic anhydride \rightarrow Diels–Alder adduct \rightarrow methanolysis to XII followed by a 1,3-dipolar cycloaddition. Crucial point of the synthesis of dimethyl 7-(diphenylmethylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (XII) is the methanolysis of the cycloadduct of diphenylfulvene to maleic anhydride — 7-(diphenylmethylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic anhydride. A cycloreversion was observed when applying the original procedure¹³ and only pure maleic anhydride was obtained from the reaction mixture. Advantageous was found the modification based upon a short heating of the reaction components to 60–70°C followed by standing at room temperature for 48 h. 5-Substituted derivatives of dimethyl 10-(diphenylmethylene)-3-oxa-4-azabicyclo[5.2.1.0.^{2,6}]deca-4-ene-8,9-dicarboxylate (IV) were prepared by a 1,3-dipolar cycloaddition of substituted benzenenitrile oxides (X = 4-CH₃, 4-OCH₃, 3-OCH₃, 4-Cl, 3-Cl, 2,4-diCl, 4-F), furannitrile and methoxycarbonylnitrile oxides in 33–87% yields (Table I). The corresponding aromatic nitrile oxides were generated from benzaldoximes on treatment with sodium hypochlorite under catalysis of triethylamine. Methoxycarbonylnitrile and furannitrile oxides were obtained via the triethylamine method from methyl chloroximidoacetate and 2-furanhydroximic acid chloride, respectively. Both methods afforded compounds IV , the unreacted starting material XII and dimers of nitrile oxides¹⁴.

The structures of cycloadducts IV and $XIII$ were deduced from the ¹H and ¹³C NMR spectra (Tables II and III). The 1,3-dipolar cycloaddition to XII can theoretically give rise to two isomers, namely *exo*- and *endo*-adducts with *cis*-arrangement of bridge hydrogens. Spatial arrangement of the final cycloadducts IV and $XIII$ was adduced as *exo-cis* on the basis of multiplicities of the ¹H NMR signals as follows:



In formulae IV–XIII: Ph = C₆H₅; E = COOCH₃

a, R = 4-CH₃C₆H₄ b, R = 4-CH₃OC₆H₄ c, R = 3-CH₃OC₆H₄ d, R = 4-ClC₆H₄,
 e, R = 3-ClC₆H₄ f, R = 2,4-Cl₂C₆H₃ g, R = 4-FC₆H₄ h, R = H i, R = 2-furyl,
 j, R = COOCH₃

SCHEME 1

in the spectrum of *IV* two multiplets at δ 4.97–5.40 and δ 4.05–4.73 were observed, which were attributed to H-2 and H-6 bridge hydrogens. Were an *endo* arrangement be involved, the coupling constants $J(1,2)$ and $J(6,7)$ should appear as doublet-doublets. The coupling constant $J(2,6)$ 5–10 Hz provides an evidence for *cis*-arrangement of H-2 and H-6 bridge hydrogens. On the other hand, multiplicities of *trans-exo* and *trans-endo* isomers (*trans* arrangement of H-2 and H-6) have to appear as singlet-doublet and doublet-singlet, respectively. So far, all known 1,3-dipolar cycloadditions of nitrile oxides are concerted reactions, i.e. they are *cis*-stereospecific¹⁴. The proposed structure *IV* is also backed by the chemical shift values of ¹³C NMR spectra (Table III). Cycloaddition to the adduct of diphenylfulvene to maleic anhydride forming 10-(diphenylmethylene)-3-oxa-4-azabicyclo-

TABLE I
Characteristic data for fused substituted dihydroisoxazoles *IV* and *XIII*

Compound	Formula (M.w.)	M.p., °C (Yield, %)	Calculated/Found			λ_{\max} , nm (log <i>e</i>)
			% C	% H	% N	
<i>IVa</i>	C ₃₂ H ₂₉ NO ₅ (507.6)	232 (40)	75.72	5.76	2.76	253 (4.31)
			75.43	5.84	3.03	
<i>IVb</i>	C ₃₂ H ₂₉ NO ₆ (523.6)	200–202 (77)	73.41	5.58	2.68	252 (3.27)
			72.99	5.51	2.90	
<i>IVc</i>	C ₃₂ H ₂₉ NO ₆ (523.6)	206–207 (57)	73.41	5.58	2.68	253 (3.31)
			73.08	5.77	2.49	
<i>IVd</i>	C ₃₁ H ₂₆ ClNO ₅ (527.9)	222–223 (87)	70.53	4.96	2.65	253 (3.18)
			70.88	5.00	2.61	
<i>IVe</i>	C ₃₁ H ₂₆ ClNO ₅ (527.9)	186–188 (53)	70.53	4.96	2.65	249 (3.32)
			70.69	5.21	2.83	
<i>IVf</i>	C ₃₁ H ₂₅ Cl ₂ NO ₅ (562.4)	184–186 (64)	66.20	4.48	2.49	248 (3.30)
			66.29	4.70	2.60	
<i>IVg</i>	C ₃₁ H ₂₆ FNO ₅ (511.5)	274–277 (50)	72.79	5.12	2.73	249 (3.30)
			72.39	5.01	2.96	
<i>IVi</i>	C ₂₉ H ₂₅ NO ₆ (483.5)	162–163 (33)	72.04	5.21	2.90	246 (3.24)
			72.09	5.33	2.81	
<i>IVj</i>	C ₂₇ H ₂₅ NO ₇ (475.5)	220–222 (51)	68.20	5.30	2.95	248 (3.01)
			68.24	5.63	3.17	
<i>XIII</i>	C ₂₅ H ₁₉ NO ₆ (429.4)	145–147 (75)	69.92	4.46	3.26	248 (3.04)
			70.28	4.71	3.33	

[5.2.1.0^{2,6}]deka-4-ene-8,9-dicarboxylic anhydride (*XIII*) was found to proceed analogously.

For photochemical reactions of isoxazolines *IV* monochromatic radiation $\lambda = 254$ nm was chosen on the basis of their absorption maximum in the UV region at $\lambda = 246-253$ nm; suitable solvents were shown to be acetonitrile and methanol. Provided the photolysis of *IV* be not selective², the oxazoline *XIV* has to be expected in addition to the 3-aminocarbonyl compound *XV* and two cyclic enaminoaldehydes *X* and *XI*. The structures of compounds *XIa-XIj*, prepared by irradiation of *IV*,

TABLE II

¹H NMR chemical shift data of 5-substituted dimethyl 10-(diphenylmethylene)-3-oxa-4-azatri-cyclo[5.2.1.0^{2,6}]deka-4-ene-8,9-dicarboxylates *IV* and *XIII*

Compound	δ , ppm/ <i>J</i> , Hz				
	H-2	H-1, H-7, H-8, H-9	H-6	COOCH ₃	H-arom
<i>IVa</i> ^a	4.97 (5.0)	3.15-3.63 m	4.63 (5.0)	3.73	6.80-7.31 7.65-7.75
<i>IVb</i> ^b	4.95 (8.0)	3.15-3.60 m	4.63 (8.0)	3.75	6.85-7.33 7.75-7.85
<i>IVc</i> ^c	4.97 (5.0)	3.10-3.50 m	4.57 (5.0)	3.67	6.80-7.35
<i>IVd</i>	5.05 (10.0)	2.75-3.45 m	4.63 (10.0)	3.73	6.75-7.35 7.90-8.20
<i>IVe</i>	5.00 (8.0)	3.08-3.55 m	4.57 (8.0)	3.73	6.83-7.35 7.53-7.67
<i>IVf</i>	5.20 (5.0)	3.50-3.60 m	4.73 (5.0)	3.63	6.88-7.27
<i>IVg</i>	4.95 (8.0)	3.00-3.55 m	4.60 (8.0)	3.70	6.87-7.27 7.67-7.85
<i>IVi</i> ^d	5.00 (8.0)	2.87-3.30 m	4.20 (8.0)	3.57	6.75-7.25 7.75-7.78
<i>IVj</i>	5.40 (5.0)	3.25-3.45 m	4.10 (5.0)	3.65 3.63	6.93-7.23
<i>XIII</i>	5.35 (4.0)	2.93-3.25 m	4.05 (5.0)	3.60	6.75-7.23

^a 2.37 s (CH₃); ^b 3.85 s (OCH₃); ^c 3.77 s (OCH₃); ^d 6.63 d (H-3', *J*(3', 4') = 3.5); 6.50 dd (H-4', *J*(4', 5') = 1.2).

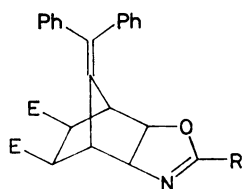
were deduced from their NMR data (Tables V, VI) as 4-substituted dimethyl 2,2-diphenyl-5-formyl-3-azabicyclo[4.3.0]nona-4,9-diene-7,8-dicarboxylates. The presence of an aldehyde group was evidenced by the δ values 8.77–9.75 (singlet) and 185.05–188.17 (doublet) in their respective ^1H and ^{13}C NMR spectra, thereby excluding structures *XIV* and *XV*. Structure of the aldehyde *X*, which can be deduced by analogy³⁻⁹ from the photochemical reactions with fused isoxazolines having oxygen in β -position (*I*) should exhibit in the ^1H NMR spectrum doublet at $\delta \sim 5$. The structure of aldehyde *XI* was proved by the occurrence of a multiplet of the olefinic

TABLE III
 ^{13}C NMR chemical shifts of *IV* and *XIII*

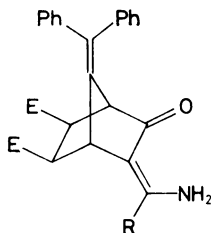
Compd.	δ , ppm						
	C-2	C-1	C-9, C-8	C-7	C-6	C-5	CH ₃
<i>IVa</i> ^a	83.31	47.62	44.22	43.46	52.12	157.19	51.71
<i>IVb</i> ^b	82.96	47.89	44.23	43.47	52.19	156.79	55.15 51.78
<i>IVc</i> ^c	83.37	47.39	44.34	43.52	51.80	157.37	55.40 52.19
<i>IVd</i> ^d	84.36	47.68	44.08	44.08	52.30	157.65	51.65
<i>IVe</i> ^e	83.55	47.21	44.17	43.53	52.18	156.44	51.83
<i>IVf</i> ^f	82.37	47.57	43.99	43.65	52.29	156.56	52.01
<i>IVg</i> ^g	83.35	47.33	44.16	43.58	52.94	156.44	51.72
<i>IVi</i> ⁱ	81.86	46.64	44.36	43.13	52.08	151.88	51.67
<i>IVj</i> ^j	85.00	46.88	44.35	43.85	52.41	151.99	52.00 51.71
<i>XIII</i> ^k	85.88	48.96	46.45	45.75	52.36	152.29	52.19

^a C=O, aromatic and vinyl shifts: 171.81, 171.41, 140.70, 139.88, 138.58, 129.35, 128.82, 128.12^a, 127.71, 127.30, 126.89, 127.07; ^b C=O, aromatic and vinyl shifts: 171.95, 171.48, 160.77, 140.78, 140.41, 138.60, 136.02, 129.35, 128.83, 128.53, 128.12, 127.77, 127.31, 126.96, 121.57, 114.14; ^c C=O, aromatic and vinyl shifts: 171.83, 171.47, 159.1, 140.76, 140.41, 138.56, 136.20, 130.14, 129.76, 129.35, 128.88, 128.18, 127.83, 127.36, 127.01, 119.65, 116.71, 111.22; ^d C=O, aromatic and vinyl shifts: 171.88, 171.34, 149.65, 140.58, 135.14, 129.47, 128.59, 128.06, 127.54, 126.95, 123.97, 122.39, 120.98; ^e C=O, aromatic and vinyl shifts: 171.74, 171.35, 140.64, 140.17, 138.28, 136.31, 134.62, 130.70, 129.93, 129.76, 129.29, 128.71, 128.12, 127.42, 127.07, 126.83, 125.02; ^f C=O, aromatic and vinyl shifts: 171.65, 171.12, 140.94, 140.23, 138.54, 135.85, 133.38, 132.16, 130.11, 129.88, 129.06, 128.18, 128.06, 127.60, 127.42, 126.89, 126.48; ^g C=O, aromatic and vinyl shifts: 171.94, 140.76, 138.36, 135.20, 129.53, 129.35, 129.12, 128.76, 128.18, 127.83, 127.07, 116.30, 115.43, 103.96; ⁱ C=O, aromatic, furyl and vinyl shifts: 171.42, 171.01, 145.27, 143.93, 148.84, 140.12, 138.55, 134.45, 128.90, 127.78, 127.25, 126.90, 112.54, 111.11; ^j C=O, aromatic and vinyl shifts: 171.53, 170.83, 160.77, 140.99, 139.76, 138.24, 136.33, 129.29, 128.71, 128.28, 127.64, 127.36; ^k C=O aromatic and vinyl shifts: 176.16, 175.97, 160.60, 141.41, 140.29, 138.83, 135.26, 129.41, 128.94, 128.01, 127.19, 127.01.

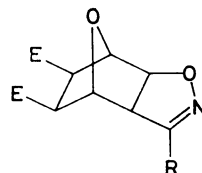
proton H-9 at δ 5.25 – 5.64 and a singlet of C-2 at δ 66.00 – 67.12, which is inconsistent with the structure X. The UV spectra revealed, in accordance with our previous



XIV



XV



XVI

TABLE IV

Characteristic data for dimethyl 2,2-diphenyl-5-formyl-3-azabicyclo[4.3.0]nona-4,9-diene-7,8-dicarboxylates XI

Compound	Formula (M.w.)	M.p., °C (Yield, %)	Calculated/Found			λ_{max} , nm (log ϵ)	
			% C	% H	% N		
XIa	C ₃₂ H ₂₉ NO ₅ (507.6)	245 (50)	75.72	5.76	2.76	312	244
			75.31	5.91	2.88	(3.12)	(3.07)
XIb	C ₃₂ H ₂₉ NO ₆ (523.6)	248–250 (73)	73.41	5.28	2.68	313	253
			73.66	5.44	2.57	(3.18)	(3.14)
XIc	C ₃₂ H ₂₉ NO ₆ (523.6)	239–241 (51)	73.41	5.58	2.68	311	
			73.72	5.41	2.89	(3.16)	
XI d	C ₃₁ H ₂₆ ClNO ₅ (528.0)	251 (70)	70.53	4.96	2.65	310	240
			70.71	5.00	2.54	(3.14)	(3.14)
XI e	C ₃₁ H ₂₆ ClNO ₅ (528.0)	247–249 (48)	70.53	4.96	2.65	311	
			70.78	4.87	2.79	(3.06)	
XI f	C ₃₁ H ₂₅ Cl ₂ NO ₅ (563.5)	247–248 (54)	66.20	4.48	2.49	308	
			66.33	4.77	2.41	(3.35)	
XI g	C ₃₁ H ₂₆ FNO ₅ (511.5)	248–251 (21)	72.79	5.12	2.73	311	
			73.05	4.99	2.62	(3.04)	
XI i	C ₂₉ H ₂₅ NO ₆ (483.5)	186–188 (33)	72.04	5.21	2.90	322 ^a	248
			72.41	5.17	2.82	(3.24)	(3.00)
XI j	C ₂₇ H ₂₅ NO ₇ (475.5)	oil ^b (34)	68.20	5.30	2.95	314	
			68.01	5.17	2.99	(2.63)	

^a 279 (2.98); ^b 90–95°C/1 Pa.

papers³⁻⁹ the long-wave absorption maximum at λ 310 nm, corresponding to chromophores $\text{NH}-\text{C}=\text{C}-\text{CHO}$ or $\text{Ar}-\text{C}=\text{C}-\text{CHO}$. Moreover, this grouping was also corroborated by the presence of two singlets at δ 110 (C-4) and 156–161 (C-5).

A detailed attention has been paid to the effect of the substituent in position 5 on rearrangement of isoxazolines *IV*. From X-phenylsubstituted derivatives (X = = 4- CH_3 , 4- OCH_3 , 3- OCH_3 , 3-Cl, 2,4-diCl and 4-F as well as R = methoxycarbonyl) enaminoaldehydes *XI* were the only photorearrangement products. Surprisingly enough, also the photochemical reaction with 2-furyl substituted derivative *IVi* was successful forming the enaminoaldehyde *XIi*, since irradiation at $\lambda = 254$ nm of isoxazolines substituted by a 2-furyl residue led to undefinable polymers¹⁵ as yet. The ¹H NMR spectrum of *XIi* showed signals at δ 7.62 (H-5'), 6.63 (H-4') and 6.80 (H-3') characteristic of the furan ring. 2-Substituted derivatives of furan undergo very easily a photoisomerization to cyclopropenylcarbonyl or 3-substituted derivatives of furan¹⁶.

The photochemistry of the 4-chloro derivative *IVd* was interesting in that it furnished not only the expected *XId* (70%), but also *XIh* (12%, ref.¹²). The last-mentioned photochemical reaction $\text{Ar}-\text{Cl} \rightarrow \text{Ar}-\text{H}$, replacing halogen in *IVd* for hydrogen in *XId* from the solvent¹⁷. The interesting result was observed when irradiating 5-methoxycarbonyl substituted derivatives *IVj* and *XIII* in methanol; both afforded

TABLE V

¹H NMR chemical shift data for dimethyl 2,2-diphenyl-5-formyl-3-azabicyclo[4.3.0]nona-4,9-diene-7,8-dicarboxylates *XI*

Compound	δ , ppm					
	H-6, H-7, H-8	H-9	NH	CHO	COOH ₃	H-arom
<i>XIa</i> ^a	3.60–4.31 m	5.37 m	5.40	8.85	3.66	7.06–7.45
<i>XIb</i> ^b	3.90–4.25 m	5.25 m	5.53	8.77	3.63	6.85–7.40
<i>XIc</i> ^c	3.93–4.33 m	5.40 m	5.55	8.93	3.70	6.94–7.46
<i>XId</i>	3.84–4.22 m	5.43 m	5.57	8.78	3.59	7.21–7.49
<i>XIe</i>	3.77–4.28 m	5.55 m	5.67	8.77	3.67	7.03–7.55
<i>XIf</i>	3.80–4.24 m	5.45 m	5.59	8.78	3.60	7.01–7.59
<i>XIg</i>	3.81–4.24 m	5.46 m	5.52	8.81	3.70	6.83–7.79
					3.72	
<i>XIi</i> ^d	3.85–4.25 m	5.60 m	5.85	9.40	3.68	7.03–7.40
<i>XIj</i>	4.07–4.25 m	5.64 m	6.20	9.75	3.63	7.00–7.35
					3.83	

^a 2.40 s (CH_3); ^b 3.00 s (OCH_3); ^c 3.93 s (OCH_3); ^d 7.62 d (H-5'), 6.80 d (H-3', $J(3',4') = 3.5$), 6.57 dd (H-4', $J(4',5') = 1.3$).

TABLE VI
¹³C NMR chemical shifts of XI

Compound	δ, ppm									
	C-2	C-4	C-5	C-6	C-7	C-8	CHO	COO	CH ₃	
<i>XIa^a</i>	66-81	110-69	161-18	43-12	51-25	53-94	188-15	172-11 172-00	51-95	21-41
<i>XIb^b</i>	66-29	110-57	160-87	43-73	51-25	53-98	188-16	172-70 172-00	51-78	55-49
<i>XIc^c</i>	66-89	110-59	159-64	43-08	51-17	53-93	188-09	172-80 171-90	51-71	55-36
<i>XId^d</i>	67-04	110-64	156-20	42-94	50-91	53-72	187-00	172-79 171-86	53-45	
<i>XIe^e</i>	66-00	109-11	160-25	42-60	50-79	52-78	185-05	171-77 171-54	51-61	
<i>XIf^f</i>	67-12	110-91	156-85	42-62	51-13	53-80	186-92	172-49 171-79	51-84	
<i>XIg^g</i>	66-95	111-37	161-92	43-59	51-78	54-02	187-84	171-92 171-43	51-68	
<i>XIj^j</i>	66-92	111-11	159-84	43-15	54-07	55-36	188-17	172-70 171-92	51-84	51-20

^a Aromatic, C-1 and C-9 shifts: 145-85, 143-04, 141-12, 131-40, 129-41, 128-89, 128-30, 128-13, 127-30, 125-60; ^b aromatic, C-1 and C-9 shifts: 161-65, 146-03, 143-04, 141-05, 130-93, 128-89, 128-36, 128-13, 127-31, 125-55, 114-14; ^c aromatic, C-1 and C-9 shifts: 160-71, 145-79, 142-97, 142-31, 135-61, 129-85, 128-67, 128-29, 128-11, 127-27, 125-77, 121-58; ^d aromatic, C-1 and C-9 shifts: 144-95, 143-73, 142-97, 141-68, 136-59, 134-26, 132-56, 131-55, 129-79, 128-91, 128-50, 128-26, 127-44, 127-10; ^e aromatic, C-1 and C-9 shifts: 145-09, 143-05, 142-17, 135-32, 132-69, 130-00, 129-18, 128-72, 127-72, 126-20; ^f aromatic, C-1 and C-9 shifts: 145-02, 143-79, 143-07, 141-77, 140-88, 136-71, 134-10, 132-61, 131-95, 131-70, 130-21, 128-97, 128-32, 127-93, 127-15; ^g aromatic, C-1 and C-9 shifts: 165-24, 142-94, 141-04, 140-77, 138-39, 136-27, 131-32, 129-23, 128-95, 128-75, 128-17, 127-81, 127-33, 125-91, 125-28; ^j aromatic, C-1 and C-9 shifts: 160-62, 145-80, 143-20, 141-25, 135-03, 129-95, 128-90, 128-83, 127-35, 125-92, 121-63, 115-91, 115-92.

the same product *XIj*. It is our belief that the anhydride *XIII* underwent methanolysis due to irradiation yielding *IVj*, which rearranged to *XIj*. An analogous photochemical methanolysis was encountered with isoxazolines fused to the phenyl-maleinimide skeleton¹¹.

Table VII lists the quantum yields of rearrangements in methanol obtained by measuring the concentration decrease of the starting derivatives up to 20% conversion. The quantum yields do not depend on the presence or absence of oxygen. The wavelength values of isosbestic points varied between 279 and 294 nm. On the basis of the above-mentioned facts as well as the linear course of ED diagrams¹⁸ (photo-reaction of type $A \rightarrow B$), the impossibility to sensitize the reaction $IV \rightarrow XI$ by acetone or acetophenone, and in agreement with² a singlet mechanism can be presumed. The series of reactions $IV \rightarrow V \rightarrow VI \rightarrow VIII \rightarrow X$ would fit the mechanism of rearrangement of isoxazolines containing oxygen in β -position to the isoxazoline oxygen, which was studied in detail in our preceding communications³⁻⁹. The unequivocal course of the photorearrangement $IV \rightarrow XI$ is due to a greater stability of the biradical *VII* in comparison with *VI*, because in this case the radical electron is stabilized not only by an overlap with π -electrons of the C=C double bond, but also with that of π -electrons of two benzene rings. Recombination to a non-conjugated aldehyde *IX* followed by a 1,3-H shift is analogous to that of the oxygen-containing derivatives $I \rightarrow III$ (refs³⁻⁹).

The quantum yield values in methanol (Table VII) are higher than those for the corresponding fused isoxazolines *XVI* having the diphenylmethylene bridging substituted by oxygen²⁰.

Stabilization of the biradical due to an allylic overlap and an electronic effect of benzene rings attached to an exocyclic double bond (*VI*, *VII*) is more effective than that due to *p*-electrons of the oxygen atom in *II* ($X = O$). The photoreaction in methanol is evidently so fast that even the furyl derivative *IVi* afforded cyclic enaminoldehyde *XIi* on irradiation, although a photoreaction of the furan itself was originally anticipated.

TABLE VII

The photorearrangement quantum yields Φ (methanol)

Compound	<i>IVa</i> ^a	<i>IVb</i> ^b	<i>IVc</i>	<i>IVd</i>	<i>IVe</i>	<i>IVf</i>	<i>IVg</i>	<i>IVh</i>	<i>IVi</i>	<i>IVj</i>
Φ^c	0.28	0.09	0.10	0.28	0.35	0.38	0.17	0.10 ^d	0.13	0.14

^a In acetonitrile 0.18; ^b in acetonitrile 0.05; ^c the values measured from the deficit of the starting components; ^d ref.¹².

The photorearrangement was investigated in various solvents. Thus, in acetonitrile the same products were obtained as in methanol; the values were lower in acetonitrile (derivatives *I*, $X = O$ revealed higher values³⁻⁹). No isobestic points were observed when monitoring the reaction with UV spectrometry; in other words, the reaction afforded a stable intermediate²⁰ (probably *IX*). The photochemical reaction in acetonitrile proceeded accordingly via $IV \rightarrow IX \rightarrow XI$, the last stage, the 1,3-shift of hydrogen in methanol is faster than in acetonitrile. A like effect was observed by photorearrangement in methanol giving 1,3-dioxa-5-azocine derivatives^{4,5}. The photochemical rearrangement in hexane proceeded differently, the UV spectra did not show isobestic points and the products were undefinable polymers. The photorearrangement of *IV* in cyclohexane did not take place at all. The results are rather surprising, because Mukai and coworkers^{2,21} did find the highest values for photorearrangements of isoxazolines in cyclohexane. The photorearrangement of *IV* in solvents of decreasing polarity proceeded increasingly worse.

EXPERIMENTAL

The melting points are uncorrected, the ¹H and ¹³C NMR spectra were recorded with the respective Tesla 487 C (Czechoslovakia), Jeol JX-100 and Varian VXR-300 spectrometers, hexadeuteriodimethyl sulfoxide being the solvent and tetramethylsilane the internal reference. The UV spectra of methanolic solutions were recorded with an M-40 (Zeiss, Jena) spectrophotometer in tempered cells, the ϵ values refer to $\text{m}^2\text{mol}^{-1}$. The reaction course and purity of products were monitored by thin-layer chromatography using Alufol sheets and UV light (254 nm), or iodine vapours for visualization.

The preparative reactions were carried out at 25°C in a quartz reactor (300 ml) with a forced circulation of the solution irradiated by Toshiba GL-15 (15 W) incandescent lamp. Measurement of the quantum yields was already described⁵.

Dimethyl 7-(diphenylmethylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (XII) was synthesized according to the modified method¹³ by methanolysis of 7-(diphenylmethylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic anhydride (*XIV*) (the cycloadduct of diphenylfulvene to maleic anhydride).

Isoxazolines *IVa*—*IVi*

Sodium hypochlorite²² (8 ml, 12%) was added to a stirred solution of the respective benzaldoxime (10 mmol), triethylamine (0.15 ml) and the dipolarophile *XII* (10 mmol) in dichloromethane at 20°C for 30 min. The mixture was stirred at an ambient temperature overnight and extracted with dichloromethane (3 × 15 ml). The combined extracts were dried with magnesium sulfate, the solvent was evaporated under reduced pressure, the residue was triturated with a suitable solvent or separated by chromatography on a silica gel column (chloroform), and purified by crystallization.

Isoxazolines *IVj* and *XIII*

Methyl chloroximidoacetate (10 mmol) in ether (30 ml) was added to a stirred solution of triethylamine (13 mmol) and the dipolarophile *XII* or *XIV* (10 mmol) in ether (30 ml) at 0–5°C within 5 h. The mixture was stirred at room temperature overnight, the separated triethylammonium

chloride was filtered off, removed by dissolving in water, the organic material was evaporated under diminished pressure and the residue was worked up as with isoxazolines *IVa–IVi*.

Photorearrangement of Isoxazolines

A solution of the respective isoxazoline (3 mmol) in 300 ml of acetonitrile was irradiated until the starting derivative was completely consumed (TLC). The solution was evaporated under reduced pressure and the rearranged product was purified by column chromatography (silica gel, chloroform).

REFERENCES

1. Kozikowski A. P.: *Acc. Chem. Res.* **17**, 410 (1984).
2. Mukai T., Kumagai T., Seshimoto O.: *Pure Appl. Chem.* **49**, 287 (1977).
3. Fišera L., Laudar S., Timpe H.-J., Zálupský P., Štibrányi L.: *Collect. Czech. Chem. Commun.* **49**, 1193 (1984).
4. Fišera L., Štibrányi L., Mátušová A., Oremus V., Timpe H.-J.: *Tetrahedron Lett.* **1984**, 2731.
5. Fišera L., Oremus V., Timpe H.-J., Štibrányi L., Zálupský P.: *Collect. Czech. Chem. Commun.* **51**, 2158 (1986).
6. Fišera L., Konopíková M., Štibrányi L., Timpe H.-J.: *Collect. Czech. Chem. Commun.* **50**, 1971 (1985).
7. Fišera L., Oravec P., Štibrányi L., Kozhina N. D., Badovskaya L. A.: *Synthesis* **1986**, 565.
8. Oremus V., Fišera L., Štibrányi L.: *Collect. Czech. Chem. Commun.* **52**, 1773 (1987).
9. Oremus V., Fišera L., Timpe H.-J.: *Collect. Czech. Chem. Commun.* **52**, 2953 (1987).
10. Fišera L., Štibrányi L., Mátušová A., Oravkin J.: *Chem. Papers* **40**, 693 (1986).
11. Fišera L., Konopíková M., Timpe H.-J.: *Chem. Papers* **41**, 95 (1987).
12. Zálupský P., Fišera L., Timpe H.-J.: *Z. Chem.* **26**, 441 (1986).
13. Thiele J.: *Ber. Dtsch. Chem. Ges.* **33a**, 671 (1900).
14. Caramella P. in: *1,3-Dipolar Cycladdition Chemistry* (A. Padwa, Ed.), p. 291. Wiley, New York 1984.
15. Jedlovská E., Fišera L., Kováč J.: *Chem. Papers* **42**, 823 (1988).
16. Padwa A. in: *Molecular Rearrangements* (P. de Mayo, Ed.), p. 501. Wiley, New York 1980.
17. Becker H. G. O.: *Einführung in die Photochemie*. VEB Deutscher Verlag der Wissenschaften, Berlin 1983.
18. Fišera L., Kozhina N. D., Oravec P., Timpe H.-J., Štibrányi L., Badovskaya L. A.: *Collect. Czech. Chem. Commun.* **51**, 2167 (1986).
19. Fišera B., Oravkin J.: *Chem. Zvesti* **39**, 783 (1985).
20. Timpe H.-J., Dietrich R., Böckelmann J., Friedl J., Bögel H., Hanke G.: *Collect. Czech. Chem. Commun.* **46**, 219 (1981).
21. Kumagi T., Shimizu K., Kawamura Y., Mukai T.: *Tetrahedron* **37**, 3365 (1981).
22. Lee G. A.: *Synthesis* **1982**, 508.

Translated by Z. Votický.