REACTION OF ENAMINOCARBONYL COMPOUNDS WITH NITROACETIC ESTER

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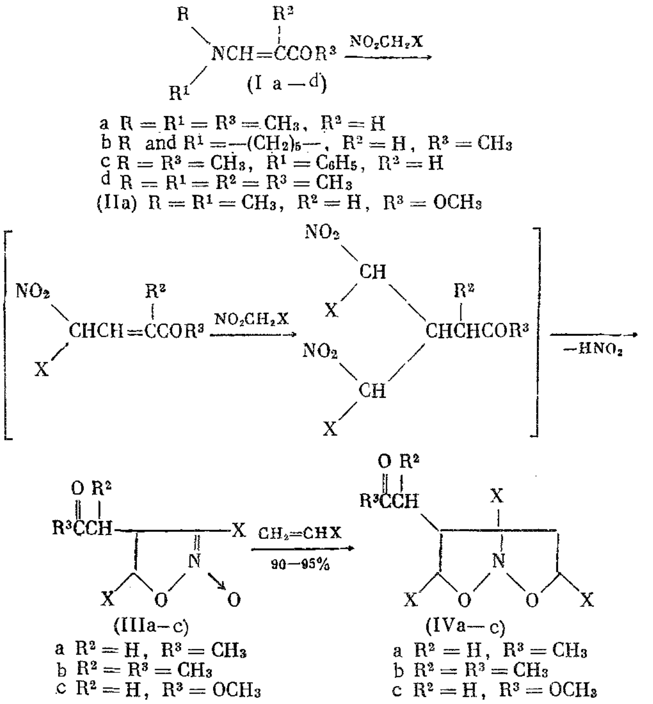
As a continuation of studying unsaturated aminocarbonyl compounds [1, 2], we were the first to study the reactions of various enaminocarbonyl compounds (ketones, aldehydes, esters, etc.) with nitroacetic ester (NAE).

It proved that cyclic nitronic esters or isoxazoline N-oxides (III) (always X = $COOCH_3$) are formed when β-dialkylaminovinyl ketones (Ia-d) and β-dialkylaminoacrylic acid esters (II) are heated with NAE in alcohol at 60-65°C.



(I a—d)

a $R = R^1 = R^3 = CH_3$, $R^2 = H$
b R and $R^1 = -(CH_2)_5-$, $R^2 = H$, $R^3 = CH_3$
c $R = R^3 = CH_3$, $R^1 = C_6H_5$, $R^2 = H$
d $R = R^1 = R^2 = R^3 = CH_3$
(IIa) $R = R^1 = CH_3$, $R^2 = H$, $R^3 = OCH_3$

(IIIa-c)
a $R^2 = H$, $R^3 = CH_3$
b $R^2 = R^3 = CH_3$
c $R^2 = H$, $R^3 = OCH_3$

(IVa—c)
a $R^2 = H$, $R^3 = CH_3$
b $R^2 = R^3 = CH_3$
c $R^2 = H$, $R^3 = OCH_3$

The structure of (IIIa-c) unequivocally follows from the elemental analysis, UV, IR, and mass spectral data (Table 1), as well as the NMR spectral data (Table 2), and is confirmed by the following chemical reactions: liberation of iodine from KI in CH_3COOH solution, and 1,3-dipolar cycloaddition to olefins [3, 4], which leads to the formation of isoxazolizidine derivatives (IV), the structure of which is in agreement with the physicochemical data (Tables 2 and 3). The formation of the N-oxides (III) from ketones and esters can be explained by the above given scheme. The first step of the reaction is apparently nucleophilic replacement of the amino group by the NAE anion, analogous to the reaction with cyanoacetic ester, which was studied by us previously [2]. The subsequent addition of a second NAE molecule by the Michael reaction

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 845-853, April, 1974. Original article submitted October 22, 1973.

TABLE 1. Isoxazoline N-Oxides[a]

Compound	Yield, %	T. mp, °C	UV spectrum (in EtOH)		IR spectrum, ν, cm^{-1} (with KBr)		Mol. wt		Empirical formula	Found, %				Calculated, %			
			λ_{max}	ε	$C{=}N{\rightarrow}O$	CH_3CO, $COOCH_3$, $COOC_2H_5$	found by mass spectrometry	calculated		C	H	N	OCH_3	C	H	N	OCH_3
(IIIa)[b]	40	95—96	270 217 sh	9100 2130	1630	1710, 1740	259	259	$C_{10}H_{13}NO_7$	46,31	5,16	5,38	23,94	46,4	5,02	5,4	23,95
(IIIb)[c]	42	98—100	270	9660	1628	1715, 1740, 1745			$C_{11}H_{15}NO_7$	48,35	5,68	5,35		48,35	5,53	5,13	
(IIIc)	40	71—72	270 213 sh	9000 2870	1632	1725, 1740, 1760			$C_{10}H_{13}NO_8$	43,59	4,68	5,26	33,82	43,64	4,76	5,09	33,8
(IIIe)	30	155—156	270	10300	1640	1750 br. b. [d]			$C_{10}H_{14}N_2O_7$	43,84	5,18	10,63		43,80	5,15	10,22	
(IIIf)[e]	32	66—67	269	10100	1625	1716, 1745			$C_{12}H_{17}NO_7$	50,27	5,97	5,11		50,17	5,97	4,88	
(VIb)	50	142—143	269 240 sh	7200 3500	1631 1610 sh[f]	1740, 1760	328	328	$C_{12}H_{12}N_2O_9$	43,87	3,68	8,68	28,91	43,91	3,69	8,54	28,38
(VIb)	—	124—125	264	9900	1625 1640[f]	1722, 1740, 1755			$C_{13}H_{14}N_2O_9$	45,61	4,17	8,35		45,62	4,12	8,19	

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[a] All of the N-oxides give one spot on Silufol (UV-254), system: acetone-hexane, 2 : 3, $R_f \sim 0.45$, detection of the spots in UV light.

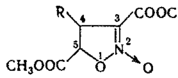
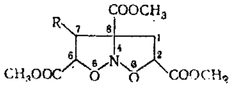
[b] Mp of 2,4-DNPH 185-187°.

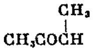
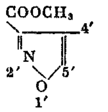
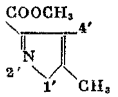
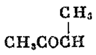
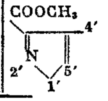
[c] Infrared spectrum taken in Nujol.

[d] The IR spectrum in $CHCl_3$ contains additional bands at 1680 cm^{-1} (I amide) and 1545 cm^{-1} (II amide); as KBr pellet at 3300 cm^{-1} (stretching vibrations of NH).

[e] Obtained from (Ia) and $NO_2CH_2COOC_2H_5$ in C_2H_5OH.

[f] The bands belong to the stretching vibrations of the double bonds of the isoxazole ring.

TABLE 2. NMR Spectra of Isoxazoline N-Oxides  and Isoxazolizidines 

Compound	R	Chemical shifts, δ, ppm											Spin-spin coupling constants, Hz								Solvent
		R											isoxazoline N-oxides					isoxazolizidines			
		CH_3CO	CH_2	CH	CH_3	CH_3OCO	H_4	H_5	H_1	H_6	H_7	H_2	$J_{4,5}$	$J_{4,5'}$	$J_{CH_3, CH}$	J_{CH_2, H_4}	J_{CH, H_4}	$J_{1,2}$	J_{1H}[a]	$J_{6,7}$	
(IIIa)	CH_3COCH_2	2,15	2,98			3,78	4,05	4,69					3,5			5					$CDCl_3$
(IIIb)	 $CH_3COCH(CH_3)$	2,13		3,2	1,18	3,77	3,94	4,85					3,5		7		5				$CDCl_3$
(IIIc)	CH_3OCOCH_2		2,88			3,58; 3,72[b]	4,05	5,0					3,5			6,5					CD_3COCD_3
(IIId)	$CH_3NHCOCH_2$[c]		2,69		2,64	3,75; 3,7	4,05	5,0					3,0			5,5					CD_3OD+CD_3COCD
(VIa)				8,59		3,7; 3,8; 3,94	5,31	4,86					4	0,6							$CDCl_3$
(VIb)					2,42	3,68; 3,8; 3,9	5,28	4,9					5								$CDCl_3$
(IVa)[d]	CH_3COCH_2	2,08	e			3,66; 3,68[b]			e	4,56	e	4,97						6 8		8	CD_3COCD_3
(IVb)	 $CH_3COCH(CH_3)$	2,1		f	1,17[g]	3,70; 3,75[b]			f	4,51	f	4,98						8		7	$CDCl_3$
(VIII)				8,6		3,44; 3,73[b], 3,97			3,07	4,8	4,8	5,1						8	5		$CDCl_3$

[a] Geminal J constant.

[b] The integral intensity corresponds to 6 protons.

[c] The position of the CH_3NHCO groups was not established.

[d] Data for the isomer with mp 113-115°.

[e] 2.6 - 3.1 ppm region (superimposition of signals).

[f] 2.6 - 3.6 ppm region (superimposition of signals).

[g] Unresolved multiplet due to virtual coupling.

TABLE 3. Isoxazolizidines

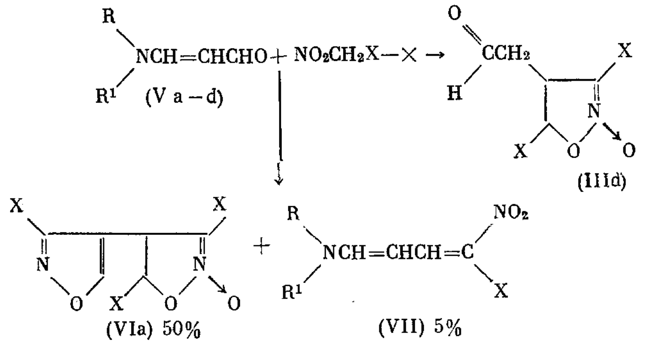
Compound	Yield, %	T_{mp}, °C	UV spectrum, ν, cm^{-1} (in $CHCl_3$)		IR spectrum, ν, cm^{-1} (in $CHCl_3$)		Empirical formula	Found, %			Calculated, %		
			λ_{max},	ε	CH_3CO, $COOCH_3$	C=N C=C		C	H	N	C	H	N
(IVa)*	95	113–115	<220		1745 br. in.†		$C_{14}H_{19}NO_9$	48,64	5,62	4,01	48,69	5,55	4,06
(IVb)	92	105–107	<220		1720 sh 1745		$C_{15}H_{21}NO_9$	50,04	5,89	3,94	50,13	5,89	3,90
(IVC)	90	Oil	<220		1740 br. in.		$C_{14}H_{19}NO_{10}$	46,82	5,32	3,90	46,54	5,30	3,88
(VIII)	94	108–110	238	2220	1745	1590	$C_{16}H_{18}N_2O_{11}$	46,25	4,44	6,69	46,40	4,34	6,76

* Based on the NMR spectral and TLC data, (IVa) is a mixture of two steric isomers; one isomer with mp 113-115° was isolated from $CHCl_3$ solution.

† br. in) broad intense.

leads to 1,3-dinitropropanes, which are converted to isoxazoline N-oxides. The conversion of certain 1,3-dinitropropanes to isoxazoline N-oxides under the influence of bases is known [5].

Initially it could be expected that the reaction of β-dialkylaminoacroleins (V) with NAE will proceed in a similar manner and lead to the corresponding N-oxide (IIId), which contains a CH_2CHO group in the 4 position.

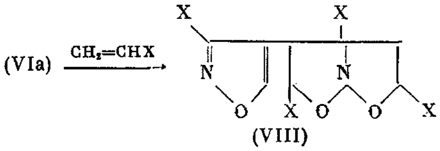


(Va) $R = R^1 = CH_3$; (Vb) $R = R^1 = C_2H_5$;
(Vc) R and $R^1 = -(CH_2)_5-$; (Vd) R = H; $R^1 = C_4H_9$

A crystalline product with mp 142-143°C was obtained in 50% yield as the result of the reaction of aldehyde (Va), which, based on the data of TLC under conditions analogous to those used for N-oxides (IIIa-c), is a pure compound. However, the empirical formula $C_{12}H_{12}N_2O_9$ follows from its elemental analysis and molecular weight, determined by mass spectrometry, which does not correspond to (IIId). The data of the UV and IR spectra (λ_{max} 268 nm, ν1631 cm^{-1} $C=N\rightarrow O$) of this compound, and also its ability to displace iodine from KI in CH_3COOH solution, show that the obtained product is an isoxazoline N-oxide.

From an analysis of all of the presented data (see Table 1) and the NMR data (see Table 2) it follows that this compound is 3,5-dicarbomethoxy-4-(3'-carbomethoxyisoxazol-4'-yl)isoxazoline (VIa). The following assignment of the lines in the NMR spectrum was made for (VIa): the three singlets of equal intensity (3H each) at 3.7, 3.8, and 3.94 ppm belong to the protons of the $COOCH_3$ groups at C_3, C_5, and $C_{3'}$; the doublet with $\delta = 4.86$ ppm (1H), $J_{4,5} = 4$, belongs to the proton at C_3; the quadruplet with $\delta = 5.31$ ppm (1H), $J_{4,5} = 4$ and $J_{4,5'} = 0.6$ Hz, belongs to the proton at C_4; the doublet at 8.59 ppm (1H), $J_{5',4} = 0.6$ Hz, belongs to the proton at $C_{5'}$ of the isoxazole ring. Based on the data given in [6], the signal of the proton at C_5 in the isoxazole is found at 8.51 ppm.

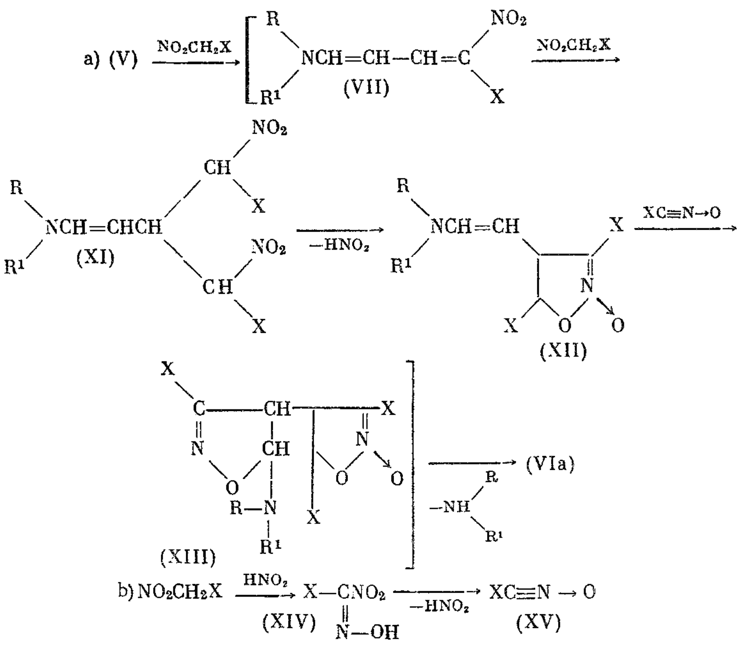
N-Oxide (VIa) readily enters into the 1,3-dipolar cycloaddition reaction with methyl acrylate to give the isoxazolizidine derivative (VIII), the structure of which is found to be in agreement with the elemental analysis and spectral data (see Tables 2 and 3). The absorption in the UV spectrum (λ_{max} 238 nm) and the band at 1590 cm^{-1} in the IR spectrum belong to the isoxazole ring [7, 8].



(VIII)

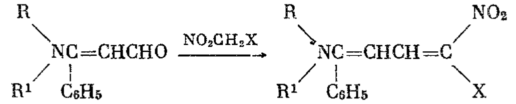
The β-dialkylaminoacroleins (Va-c), and also the β-monoalkylaminoacrolein (Vd), react with NAE to give N-oxide (VIa), independent of the character of the R and R^1 substituents on the nitrogen. It should be mentioned that the reaction products contain 5% of the methyl ester of the 5-dialkylamino-2-nitro-2,4-pentadienoic acid (VII). By means of special experiments it was shown that N-oxide (VIa) is also formed in 45% yield by the reaction of the authentic (VII, $R = R^1 = CH_3$) [9] with NAE.

The formation of N-oxide (VIa) from aldehydes (Va-d) can be depicted by the scheme:



According to [10], 1,3-dinitropropanes are formed when NAE is reacted with certain aldehydes in the presence of amines in alcohol, which are converted to isoxazoline N-oxides. A similar transformation apparently also occurs in the case of the β-dialkylaminoacrolein (V), which leads first to the formation of N-oxide (XII) via diene (VII). Then N-oxide (XII) reacts as a 1,3-dipolarophile, analogous to enamines [11], with nitrile oxide (XV), the presence of which can be explained by scheme b), taking into account the case with which nitrolic acids (XIV), as well as nitrile oxides, are formed from them [12].

In contrast to the unsubstituted aldehydes (Va-c), the β-phenyl-β-dialkylaminoacroleins (IX) when reacted with NAE form the esters of the 5-dialkylamino-5-phenyl-2-nitro-2,4-pentadienoic acid (X) in 46% yield, which are identical with the nitro esters (X) that were obtained by us previously from the acetals (IX) [9].



$$RR^1NC(C_6H_5){=}CHCHO \xrightarrow{NO_2CH_2X} RR^1NC(C_6H_5){=}CHCH{=}C(NO_2)X$$

IXa) $R = R^1 = C_2H_5$; (IXb) $R = R^1 = CH_3$ (Xa) $R = R^1 = C_2H_5$; (Xb) $R = R^1 = CH_3$

Despite the fact that the unsubstituted and substituted N-dialkylaminoacroleins (V) and (IX) lead to completely different products (VIa) and (X), their transformations are based on the reaction involving the CHO group. The reactions of β-aminoacroleins with NAE, discovered by us, show that the CO group in enaminocarbonyl compounds can be quite active. A high activity of the CO group in dienic δ-aminoketo esters was already observed previously [1].

A study was made of the reaction of NAE with enaminocarbonyl compounds that contain either a primary or a secondary NH_2 group. Here it proved that N-oxides of the (IIIe) type, in which one of the carbomethoxy groups is replaced by an amide group,* are also formed from the esters of the β-monoalkylaminoacrylic acids.

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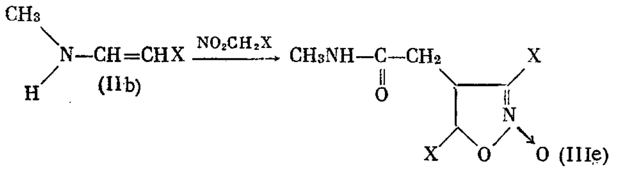
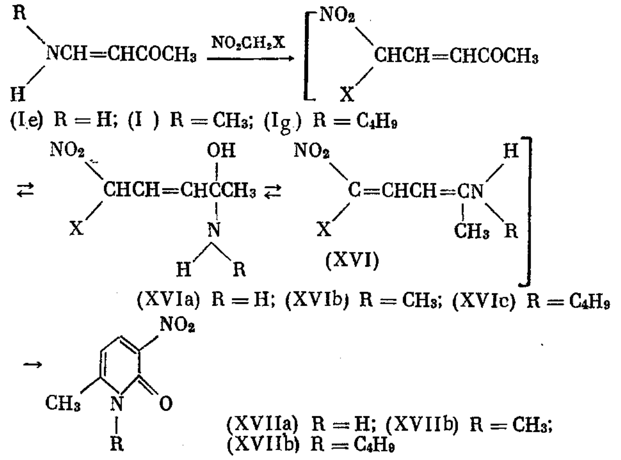
*The position of the amide group was not established.


(IIb) (IIIe)

However, ketones (Ie, If), in contrast to the β-dialkylaminovinyl ketones (Ia-d), react with NAE to give 3-nitro-6-methylpyridones (XVIIa) and (XVIIb) in respective yields of 30 and 70%, the structure of which was confirmed by comparison with authentic specimens.

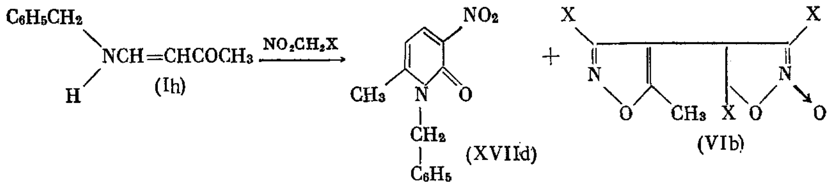

(Ie) R = H; (I) R = CH_3; (Ig) R = C_4H_9

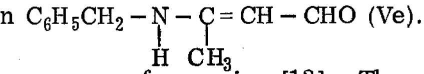
(XVI)

(XVIa) R = H; (XVIb) R = CH_3; (XVIc) R = C_4H_9

(XVIIa) R = H; (XVIIb) R = CH_3; (XVIIb) R = C_4H_9

Diene (XVIc) was isolated in the case of ketone (Ig), which cyclized to pyridone (XVIIc) when heated in alcohol, analogous to the previously described cyclization [1]. Pyridones (XVIIa) and (XVIIb) are also formed as the result of the intramolecular cyclization of the corresponding dienes (XVIa, b). Together with with pyridone (XVIId), a small amount of N-oxide (VIb) was isolated in the reaction of ketone (Ih) with NAE.


(Ih) (XVIId) (VIb)

A signal with δ 9.25 ppm was detected in the NMR spectrum of the reaction mass, which can be assigned to the aldehyde proton in  $C_6H_5CH_2-\underset{H}{N}-\underset{CH_3}{C}=CH-CHO$ (Ve). Compound (Ve) is apparently formed by the isomerization of (Ih) in the presence of an amine [13]. The presence of (Ve) makes it possible to explain the formation of (VIb) in the same manner as that of (VIa) from (Va).

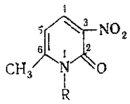
EXPERIMENTAL

The NMR spectra (δ, ppm) were taken on a DA-60-1L instrument, using HMDS as the internal standard. The NMR spectra of (XVIIa-d) are given in Table 4).

N-Oxides (IIa, b, c, e, f) and (VIa). A mixture of 1 mole of the appropriate enaminocarbonyl compound and 2 moles of NAE in an equal volume of absolute methanol was heated at 60°C for 3 h. The crystalline N-oxides were isolated by cooling the reaction mixture, and were purified by recrystallization from methanol. The yields, constants, and spectral data are given in Tables 1 and 2. Based on the TLC and UV spectral data, the mother liquor from the separation of (VIa) contains 5% of (VII). Compound (VIa) was also obtained in 45% yield by heating 1 mole of (VII) [9] with 1.5 moles of NAE in MeOH for 3 h at 60°C.

Isoxazolizidines (IVa, b, c) and (VIII). A solution of 0.35 g of the isoxazoline N-oxide in 18 ml of methyl acrylate was kept at ~20°C for from 7 to 20 days. The completion of reaction was checked by the UV spectrum, by the disappearance of absorption at λ_{max} 269 nm, or by the IR spectrum, by the disappearance of absorption at 1628-1632 cm^{-1}. The methyl acrylate was vacuum-distilled, while the residue was recrystallized from either MeOH or $CHCl_3$. The yields, constants, and spectral data are given in Tables 2 and 3.

TABLE 4. NMR Spectra of 2-Pyridones



Compound	R	Chemical shifts, δ, ppm						Solvent
		CH_3 C_6	H_5*	H_4	N–CH_3	N–CH_2	C_6H_5	
(XVIIa)	H	2,27	6,16	8,29				DMSO + CD_3OD
(XVIIb)	CH_3	2,42	6,08	8,05	3,55			$CDCl_3$
(XVIIc)	C_4H_9	2,52	6,18	8,08	—	4,03		CD_3COCD_3
(XVIId)	$CH_2C_6H_5$	2,34	6,13	8,21		5,34	7,16	$CDCl_3$

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* $J_{4,5} = 8$ Hz.

Methyl Ester of 5-Diethylamino-5-phenyl-2-nitro-2,4-pentadienoic Acid (Xa). A mixture of 0.9 g of (IXa) and 1 g of NAE in 3 ml of absolute MeOH was refluxed for 5 h. Here the intensity of the absorption at λ_{max} 313 nm decreases in the UV spectrum [starting (IXa)], and absorption with λ_{max} 435 nm appears and increases. After cooling, we isolated 0.62 g (46%) of (Xa) with mp 105-106° (from MeOH). λ_{max} in EtOH, nm: 250 (ε 6600), 310 (ε 8700), 435 (ε 41,500). Compound (Xa) does not depress the mixed melting point with an authentic specimen [9], and their UV, IR, and NMR spectra are also identical.

Methyl Ester of 5-Dimethylamino-5-phenyl-2-nitro-2,4-pentadienoic Acid (Xb). Using the above described method, from (IXb) and NAE we obtained (Xb) with mp 134-134.5°C (from MeOH). λ_{max} in EtOH, nm: 255 (ε 7040), 310 (ε 8750), 440 (ε 43,500). Found: C 60.98; H 5.84; N 10.14%. $C_{14}H_{16}N_2O_4$. Calculated: C 60.86; H 5.84; N 10.14%.

3-Nitro-6-methyl-2-pyridone (XVIIa). A mixture of 0.5 g of (Ie) and 1.6 g of NAE in 1.5 ml of absolute MeOH was heated at 60°C for 1 h. After cooling, we isolated (XVIIa) with mp 227-227.5°C (from MeOH). λ_{max} in EtOH 375 nm. The obtained (XVIIa) does not depress the mixed melting point with an authentic specimen, which was obtained by the nitration of 6-methyl-2-pyridone [14] as described in [15].

3-Nitro-1,6-dimethyl-2-pyridone (XVIIb). A mixture of 0.5 g of (If) and 0.6 ml of NAE in 1 ml of absolute MeOH was either allowed to stand for a day at ~20°C, or it was heated at 60°C for 3 h. After cooling, we isolated 0.6 g of (XVIIb) with mp 133-133.5°C (from MeOH). λ_{max} in EtOH, nm: 266 (ε 1990), 371 (ε 8950). Found: C 49.54; H 4.61; N 16.91%. $C_7H_8N_2O_3$. Calculated: C 50.00; H 4.8; N 16.68%. Compound (XVIIb) does not depress the mixed melting point with an authentic specimen, which was obtained by the methylation of (XVIIa) as described in [16].

Methyl Ester of 5-Butylamino-2-nitro-2,4-hexadienoic Acid (XVIc). A mixture of 1 g of (Ig) and 1 g of NAE in 1 ml of absolute MeOH was allowed to stand for a day. Here the absorption at λ_{max} 313 nm in the UV spectrum of the reaction mass disappears (starting Ig), and absorption appears at λ_{max} 430 nm. After evaporation we obtained 2 g of a red oil, which was chromatographed on SiO_2. Elution with a 3 : 2 hexane – acetone mixture gave (XVI) with mp 112-113°C. λ_{max} in EtOH, nm: 248 (ε 5400), 312 (ε 7860), 430 (ε 31,200). Found: C 55.02; H 7.64; N 11.58%. $C_{11}H_{18}N_2O_4$. Calculated: C 54.53; H 7.49; N 11.56%. NMR spectrum (with $CDCl_3$, δ, ppm): 2.32 ($CH_3C=C$), 3.74 (OCH_3), 6.64 (4CH), 8.21 (3 CH), 3.36 (NCN_2), 0.83-1.5 ($CH_2CH_2CH_3$), $J_{3,4} = 13.5$ Hz.

3-Nitro-6-methyl-1-butyl-2-pyridone (XVIIc). A solution of 50 mg of (XVIc) in 0.5 ml of absolute MeOH was heated at 60°C for 4 h. The checking was done either by the UV spectrum (decrease in the absorption at λ_{max} 430 and appearance of absorption at 378 nm), or by TLC on Silufol (2 : 3 acetone – hexane) (disappearance of a bright yellow spot with R_f 0.45 and appearance of a spot with R_f 0.55, which is dark violet in UV light). After evaporation we obtained (XVIIc) with mp 51-53°C (from MeOH). λ_{max} in EtOH, nm: 268 (ε 1400), 378 (ε 8800). Found: C 57.08; H 6.78; N 13.11%. $C_{10}H_{14}N_2O_3$. Calculated: C 57.13; H 6.71; N 13.33%.

3-Nitro-6-methyl-1-benzyl-2-pyridone (XVIId) and N-Oxide (VIb). A mixture of 0.5 g of (Ih) and 0.5 ml of NAE in 1 ml of MeOH was heated at 60°C for 6 h. The aldehyde proton at 9.25 ppm was detected in the NMR spectrum of the reaction mass after heating for 3 h. After evaporation in vacuo, the residue was chromatographed on SiO_2 (1 : 4 acetone – hexane). We isolated 0.1 g of (XVIId) with mp 102-104°C. λ_{max} in EtOH, nm: 259 (ε 2060), 375 (ε 8700). Found: C 63.86; H 5.07; N 11.64%. $C_{13}H_{12}N_2O_3$. Calculated: C 63.92; H 4.95; N 11.47%. In addition, 60 mg of (VIb) was isolated (the data are given in Tables 1 and 2).

CONCLUSIONS

1. A study was made of the reaction of enaminocarbonyl compounds (ketones, aldehydes, and esters) with nitroacetic ester.

2. Some new methods were proposed for the synthesis of substituted isoxazoline and 3-nitro-2-pyridone N-oxides.

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