SUBSTITUTED 4(5H)-OXAZOLONES AND THEIR SALTS.

3.* SYNTHESIS OF 4(5H)-OXAZOLONIUM SALTS FROM AMIDES OF 2,4-DIHYDROXY-3,3-DIMETHYLBUTANOIC ACID

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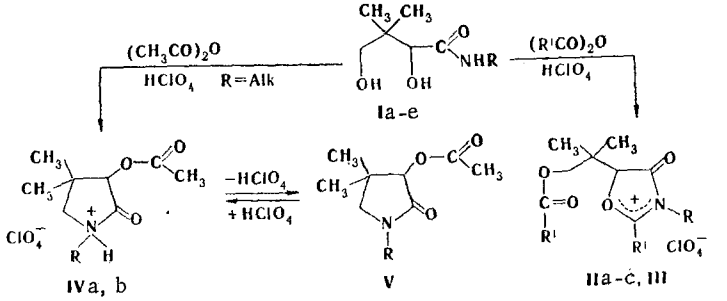
2-Alkyl-substituted 4(5H)-oxazolonium salts were synthesized by the reaction of amides of 2,4-dihydroxy-3,3-dimethylbutanoic (pantoic) acid with aliphatic carboxylic acid anhydrides in the presence of an equimolar amount of perchloric acid. The hydrolysis of these salts was realized. Various acyl derivatives of pantoic acid amides were obtained, and the possibility of their cyclization to give 4(5H)-oxazolonium salts under the influence of condensing reagents was demonstrated. The mechanism of the heterocyclization of pantoic acid amides is discussed on the basis of these results.

Syntheses of 4(5H)-oxazolonium salts by bromocyclization of N-acylamides of cinnamic and maleic acids [2] and by the reaction of monobromoacetyl chlorides and bromides with carboxylic acid amides [3, 4] have been published. A significant expansion of the preparative possibilities in the chemistry of 4(5H)-oxazolonium salts was provided by methods for their synthesis by the reaction of amides [5-7] or nitriles [8, 9] of α-hydroxy carboxylic acids with aliphatic acid anhydrides in the presence of an equimolar amount of perchloric acid.

We have investigated the synthesis of 4(5H)-oxazolonium salts based on 2,4-dihydroxy-3,3-dimethylbutanoic (pantoic) acid amides (Ia-e). Pantoic acid amides are used as inhibitors of the growth of microorganisms [10, 11] and can be readily obtained by aminolysis of pantolactone [10-13], which is an intermediate in the synthesis of vitamin B_3. In addition, these compounds have proved to be interesting subjects of investigation from a synthetic point of view, since under the influence of acylating reagents in the presence of perchloric acid one should expect dual reactivity for them with the formation of not only a 4(5H)-oxazolonium ring [7] but also 1,3-dioxanium salts [14].

Zelikman and co-workers [14] were unable to obtain 2-alkyl-1,3-dioxanium perchlorates by the action of 70% perchloric acid on a cooled (to −5°C) mixture of amide Ia-e and an aliphatic carboxylic acid anhydride. A colorless oil, which did not crystallize even upon prolonged standing in the cold, precipitated. 2-Alkyl-5-(2-methyl-1-acyloxy-2-propyl)-



Ia R=H; b R=CH_3; c R=*n*-C_4H_9; d R=*iso*-C_4H_9; e R=CH_2—C_6H_5; II R=H; [a] R^1=CH_3; b R^1=C_2H_5; c R^1=C_3H_7; III R=R^1=CH_3; IV [a] R=CH_3; [b] R=*n*-C_4H_9; V R=CH_3

*See [1] for communication 2.

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TABLE 1. 4(5H)-Oxazolonium Salts

Compound	mp, °C	IR spectrum,[a] ν, cm⁻¹				Found, %				Empirical formula	Calculated, %				Yield, %
		C=O	O—C=O	O=C=N	C=O	C	H	Cl	N		C	H	Cl	N	
IIa	142[b]	1830	1740	1600, 1520	1240	38,20	5,10	11,80	4,40	$C_{10}H_{16}ClNO_8$	39,29	5,14	11,30	4,46	85
IIb	130[b]	1830	1740	1600, 1515	1240	41,90	5,80	10,00	4,10	$C_{12}H_{20}ClNO_8$	42,17	5,90	10,38	4,10	62
IIc	98—99[b]	1830	1740	1600, 1515	1240	45,30	6,50	10,00	3,80	$C_{14}H_{24}ClNO_8$	45,47	6,54	9,58	3,79	51
III	165 b	1840	1740	1610, 1510	1250	40,60	5,70	11,00	4,30	$C_{11}H_{18}ClNO_8$	40,32	5,53	10,82	4,27	26
IX	144[c]	1840	1740	1610, 1510	1250	23,50	3,20	38,00	2,50	$C_{11}H_{18}Cl_6NO_4Sb$	23,48	3,22	37,80	2,49	88

[a]An intense band of stretching vibrations of the perchlorate anion at 1100 cm^{-1} is present in the IR spectra of all of the perchlorates. [b]From glacial acetic acid. [c]From methylene chloride—ether.

4(5H)-oxazolonium perchlorates (IIa-c) (Table 1) were obtained from amide Ia when this reaction mixture was heated to the boiling point. A mixture of two substances, viz., III and IVa, is formed from N-methylamide Ib in acetic anhydride. Owing to their different solubilities in chloroform, they were isolated in pure form. Only perchlorate IVb was obtained from the N-butylamide.

Compounds IVa, b are colorless crystalline substances that are soluble in water, ethanol, chloroform, and benzene. Their IR spectra contain two intense bands of two oxo groups, viz., a ring oxo group (1780 cm^{-1}) and an ester oxo group (1740 cm^{-1}). Perchlorate IVa is deprotonated in the reaction with water to give butyrolactam V. The latter is converted to perchlorate IVa when it is dissolved in a 2 N solution of $HClO_4$ in glacial acetic acid. Lactam V is a colorless oil that is readily soluble in both water and polar organic solvents.

The formation of IVa, b in the course of the synthesis under the conditions in [5-7] indicates that pantoic acid amides, like γ-hydroxy amides, are inclined to undergo dehydration with cyclization to the corresponding butyrolactams V. The larger the volume of the substituent attached to the nitrogen atom of the amide group, the more favorable, evidently, the formation of a lactam and the less likely the production of a 4(5H)-oxazolonium salt. We therefore were unable to synthesize 4(5H)-oxazolonium perchlorates on the basis of N-alkyl-substituted amides Ic-e or by the reaction of amide Ib with propionic and butyric anhydrides. The decrease in the yields of 4(5H)-oxazolonium perchlorates in the order IIa > IIb > IIc > III indicates hindering of the formation of a 4(5H)-oxazolonium ring as the volume of the R and R^1 substituents increases.

Salts IIa-c and III are colorless crystalline substances. Their IR spectra contain clearly distinguishable bands of two oxo groups, viz., a ring oxo group (1830-1840 cm^{-1}) and an ester oxo group (1740 cm^{-1}). The anomalously high frequency of the $\nu_{C=O}$ bands of close analogs, viz., 2-alkyl-N-acyloxazolonium salts ($\nu_{C=O}$ 1725-1750 cm^{-1}) [15], is due to the strain of the five-membered ring [8]. The $O{=}\overset{+}{C}{-}N$ fragment is manifested by two bands of skeletal vibrations at 1510-1520 and 1600-1610 cm^{-1}. The band at 1240-1250 cm^{-1}, which is due to the stretching vibrations of the C—O bond of an ester group, is very characteristic. The absorption of the stretching vibrations of the ClO_4^- anion is observed at 1100 cm^{-1}.

The PMR spectrum of salt IIa confirms the presence of a carbonium ion at the meso carbon atom of the heteroring. Evidence for this is provided by the singlet (3.08 ppm) of the 2-CH_3 group and the signal (5.52 ppm) of a proton attached to the chiral C_5 atom, which are shifted significantly to weak field. The chiral character of the C_5 atom leads to anisochronicity of the gem-dimethyl grouping, while the methylene protons in the α position relative to the C_5 atom are isochronic and give a singlet at 4.27 ppm.

We investigated the reaction of 4(5H)-oxazolonium salts with water. The corresponding diacyl derivatives (VIa, b) of pantoic acid amides were obtained from salts IIa and III in

TABLE 2. Acyl Derivatives of Pantoic Acid Amides

Compound	bp, °C (pressure, Pa)	n_D^{20}	R_f[a]	IR spectrum, ν, cm^{-1}				Found, %			Empirical formula	Calc., %			Yield, %
				C=O ether	C=O amide	C—N	C—O	C	H	N		C	H	N	
VIa	84[b]	—	0,27	1740	1690	1610	1230	51,90	7,35	6,00	$C_{10}H_{17}NO_5$	51,94	7,41	6,05	78[c]
VIb	179 (1066)	1,4570	0,44	1730	1640	1550	1240	53,90	7,75	5,60	$C_{11}H_{19}NO_5$	53,86	7,81	7,51	88[c]
VIc	181 (666)	1,4638	0,42	1730	1640	1520	1240	58,50	9,10	4,83	$C_{14}H_{25}NO_5$	58,51	9,12	4,87	75
VII	—	1,4540	0,72	1750	1730—1720	—	1350	53,74	7,72	5,70	$C_{11}H_{19}NO_5$	53,87	7,81	5,71	76
VIII	87—88[d]	—	—	1760—1740	1710	1520	1240 1260	52,80	6,92	5,10	$C_{12}H_{19}NO_6$	52,74	7,00	5,12	65

[a]Silufol and benzene—ethanol (20:2) with development by iodine vapors. [b]From ether; this is the melting point. [c]This compound was obtained by hydrolysis of the corresponding 4(5H)-oxazolonium perchlorate IIa. [d]From benzene—hexane; this is the melting point.

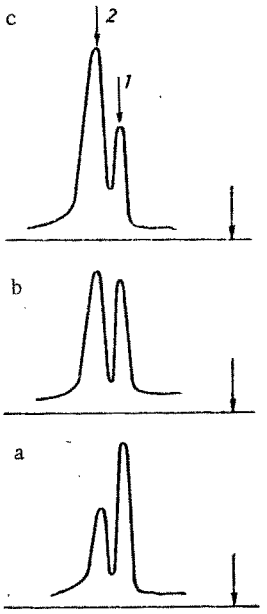
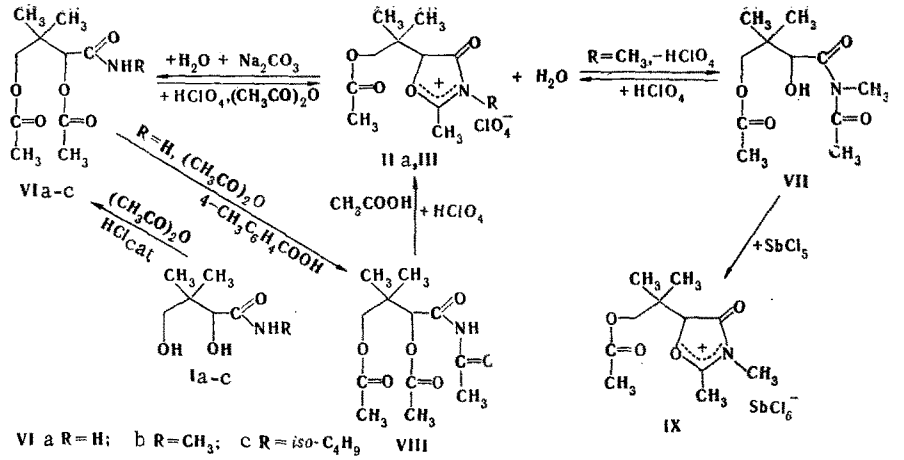


Fig. 1. Gas-liquid chromatography (GLC) of the compounds obtained in the hydrolysis of perchlorate III when the reaction is carried out for 1 min (a), 10 min (b), and 30 min (c): 1) imide VIII; 2) amide VIb (the absolute retention times are 3.1 and 3.8 min, respectively).

aqueous sodium bicarbonate solution (pH $\geqslant$ 7) (Table 2). In the absence of sodium bicarbonate nucleophilic attack by the water molecule may be directed to the 2 and 5 positions of the heteroring. A mixture of the corresponding diacyl derivative of the amide (VIb) and imide VII was obtained in the reaction of salt III with water. We proved the simultaneous formation of VIb and VII by means of thin-layer chromatography (TLC) and gas—liquid chromatography (GLC), and their subsequent separation was carried out by column chromatography. It should be noted that the yield of diacyl derivative VIb increases with the time of the reaction of salt III with water (Fig. 1); this may be associated with the existence of an equilibrium between III and VII under the given reaction conditions.

Diacyl derivatives VIa, b in a 2 N solution of $HClO_4$ in acetic acid do not form perchlorates IIa and III; VIa undergoes decomposition with the liberation of ammonium perchlorate. Salt formation takes place only when the reaction mixture is heated to the boiling point in the presence of an equimolar amount of acetic anhydride. We were unable to synthesize the corresponding 4(5H)-oxazolonium perchlorate on the basis of N-butylamide VIc, which was obtained by acylation of amide Id with acetic anhydride in the presence of catalytic amounts of hydrochloric acid.



In contrast to amides VIa-c, imide VII undergoes cyclization to give perchlorate III in 70% aqueous or 2 N acetic acid solutions of $HClO_4$, as well as hexachloroantimonate IX (Table 1) in a solution of antimony pentachloride in methylene chloride. Salt IX is readily converted to corresponding perchlorate III in a 2 N acetic acid solution of $HClO_4$. Imide VIII, which we obtained by acylation of diacyl derivative VIa in the presence of p-toluenesulfonic acid [19], like imide VII, under the influence of $HClO_4$ undergoes cyclization to perchlorate IIa. These facts indicate the low probability of the direct cyclization of diacyl derivatives of pantoic acid amides to give 4(5H)-oxazolonium salts via the method in [5, 6]. The decisive factor in the formation of 4(5H)-oxazolonium salts is apparently the acylation of the amide group. The use of less active propionic and butyric anhydrides therefore complicates the synthesis of salts IIb, c (Table 1) and does not lead to the formation of the 4(5H)-oxazolonium cation in the case of N-alkylamides Ib-e, since the latter are evidently more difficult to acylate under the conditions indicated in [5, 6].

Thus the previously advanced assumption of the direct cyclization of O-acyl derivatives of amides of α-hydroxy carboxylic acids in the synthesis of 4(5H)-oxazolonium salts [7-9] was not confirmed in our studies.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the crystalline substances and thin layers of the liquid compounds were recorded with Specord and UR-20 spectrometers. The PMR spectra were recorded with Varian HA-100 D and C-60 HL spectrometers with tetramethylsilane as the internal standard. Analysis of VII and VIb by GLC was carried out with a Tsvet-6A chromatograph with a flame-ionization detector under isothermal conditions with a 3-m long column with a diameter of 3 mm; the stationary phase was 5% SE-30 on Chromaton N-AW DMCS (0.250-0.315 mm particles) at a vaporizer temperature of 315°C, the ribbon rate was 600 mm/h, and the volume of the injected sample η = 0.4 μl.

Pantoic acid amides Ia-e were obtained by the methods in [10, 11, 13]. The 2 N solution of $HClO_4$ in glacial acetic acid was prepared by the method in [20].

2-Methyl-5-(2-methyl-1-acetoxy-2-propyl)-4(5H)-oxazolonium Perchlorate (IIa). A) A 3-ml (0.03 mole) sample of 70% $HClO_4$ was added dropwise to a cooled (to 0°C) mixture of 4.2 g (0.03 mole) of amide Ia and 18 ml of acetic anhydride, after which the mixture was heated to the boiling point, cooled to room temperature, and diluted with ether. The precipitated crystals were removed by filtration and washed successively with glacial acetic acid and ether to give 8 g of snow-white crystals of IIa. PMR spectrum (in CF_3COOH at 27-29°C): 1.36 [strong s, $(CH_3)_2$], 2.28 (s, $OCOCH_3$), 3.08 (s, 2-CH_3), 4.27 (s, CH_2), and 5.52 ppm (s, 5-CH). Compounds IIb, c were synthesized similarly. Data on salts IIa-c are presented in Table 1.

B) A 5-ml sample of a 2 N solution of $HClO_4$ in glacial acetic acid was added dropwise with stirring to a cooled (to 0°C) solution of 2.3 g (0.01 mole) of amide VIa in 4 ml of acetic anhydride, after which the mixture was heated to the boiling point, cooled, and diluted with ether. The liberated oil was crystallized from 3 ml of chloroform with the addition of ether to give 2.5 g (80%) of product. Perchlorate III was similarly obtained in 30% yield from amide VIb.

C) A 2.73-g (0.01 mole) sample of imide VIII was dissolved in 5 ml of a 2 N solution of $HClO_4$ in glacial acetic acid, and the solution was maintained at 80°C with stirring for 15 min. It was then diluted with ether, and the liberated oil was separated by decantation and dissolved in 3 ml of chloroform. The chloroform solution was treated with ether until snow-white crystals of salt IIa began to precipitate. Workup gave 2.3 g (73%) of product. Perchlorate III was similarly obtained from imide VII without heating.

2,3-Dimethyl-5-(2-methyl-1-acetoxy-2-propyl)-4(5H)-oxazolonium Perchlorate (III). A) A 3-ml (0.03 mole) sample of 70% $HClO_4$ was added dropwise to a cooled (to 0°C) mixture of 4.83 g (0.03 mole) of amide Ib and 18 ml of acetic anhydride, after which the mixture was heated to the boiling point and maintained at that temperature for 1 min. It was then cooled to 20°C and treated with ether to precipitate crystals, which were removed by filtration and washed with ether. The crystalline product was refluxed in 20 ml of chloroform, and 2.6 g of snow-white crystals of III, data on which are presented in Table 1, was obtained from the hot suspension by filtration and subsequent washing with ether.

B) A 2.45-g (0.01 mole) sample of imide VII was dissolved in 1 ml of 70% $HClO_4$, and the precipitated crystals of salt III were removed by filtration and washed with ether to give 2.6 g (80%) of product.

C) A 2.8-g (0.005 mole) sample of hexachloroantimonate IX was dissolved in 2.5 ml of a 2 N solution of $HClO_4$ in glacial acetic acid, and the solution was heated to the boiling point. It was then cooled and diluted with ether, and the precipitated crystals of salt III were removed by filtration and washed with ether to give the product in 98% yield.

2,3-Dimethyl-5-(2-methyl-1-acetoxy-2-propyl)-4(5H)-oxazolonium Hexachloroantimonate (IX). A 0.65-ml (0.005 mole) sample of $SbCl_5$ was added slowly dropwise to a cooled (to 0°C) solution of 1.22 g (0.005 mole) of imide VII in 5 ml of methylene chloride. After 15-20 min, the precipitated colorless crystals were removed by filtration to give 2 g of salt IX (Table 1).

2,4-Diacetoxy-3,3-dimethylbutanoic Acid Amide (VIa) [18]. An 18.8-g (0.06 mole) sample of salt IIa was dissolved in 8 ml of water, and 10 g of sodium carbonate was added. After gas evolution ceased, the mixture was extracted with chloroform, and the extract was dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated, and the residual viscous oil was distilled *in vacuo* to give 10.8 g of VIa as a colorless oil, which crystallized in ether. Amide VIb was similarly obtained from perchlorate III. Data on VIa, b are presented in Table 2.

2,4-Diacetoxy-3,3-dimethylbutanoic Acid N-Isobutylamide (VIc). A four-necked flask equipped with a stirrer, a reflux condenser, and a thermometer was charged with 21 ml of acetic anhydride, and 0.5 ml of concentrated HCl was added. The reaction mixture was heated to 50°C with stirring, and 12.2 g (0.06 mole) of amide Id was added gradually, during which the temperature was raised to 80°C; stirring was continued at this temperature for another 15 min. The acetic acid and residual acetic anhydride were then removed by vacuum distillation, and the residual viscous oil was distilled *in vacuo* to give 12.9 g of VIc (Table 2). Amides VIa, b were similarly synthesized in 5 and 68% yields, respectively [17].

2-Hydroxy-3,3-dimethyl-4-acetoxybutanoic Acid N-Acetyl-N'-Methylamide (VII). A 3.27-g (0.01 mole) sample of perchlorate III was suspended in 30 ml of chloroform, 6 g of anhydrous sodium carbonate was added, and 1 ml of water was then added dropwise with vigorous stirring. Filtration and evaporation at reduced pressure and a bath temperature no higher than 70°C gave 2.4 g of a colorless viscous oil, which was dissolved in ethanol–benzene (0.5:20) and passed through a column filled with silica gel to give 1.8 g (76%) of imide VII as a colorless viscous oil (Table 2).

2,4-Diacetoxy-3,3-dimethylbutanoic Acid N-Acetylamide (VIII). A mixture of 11.56 g (0.05 mole) of amide VIa, 10 ml of acetic anhydride, and 1 g of p-toluenesulfonic acid was heated at 100°C for 1 h, after which the volatile components were distilled *in vacuo* at a

bath temperature no higher than 100°C. The residual oil was treated with water, and the aqueous mixture was extracted with ether. The extract was washed with 5% KOH solution and water and dried over anhydrous Na_2SO_4. The oil that remained after evaporation of the ether was crystallized from benzene–hexane to give 8.9 g of colorless crystals of VIII (Table 2). PMR spectrum (in $CDCl_3$, 26°C): 1.10 [s, $(CH_3)_2$]; 2.06, 2.15 (strong s, two $OCOCH_3$); 2.45 (s, $NCOCH_3$); 3.95 (q, CH_2); 4.95 (s, CH); 8.90 ppm (s, NH).

N-Methyl-3-acetoxy-4,4-dimethyl-2-pyrrolidonium Perchlorate (IVa). A) This reaction was carried out initially as described for the synthesis of perchlorate III (method A). The chloroform mother liquor obtained after filtration of the crystals of salt III was diluted with ether, and the precipitated crystals of IVa were removed by filtration. The precipitated oil from the previously obtained ethyl acetate mother liquor was separated by decantation and dissolved in chloroform. After cooling to 0°C, ether was added, and the precipitated crystals of IVa were removed by filtration to give 4.2 g (49%) of a product with mp 124-125°C (from chloroform–ether). IR spectrum: 1780 (C=O); 1740 (O–C=O; 1220 (C–O); 3180, 3280 (N–H); 1100 cm^{-1} (ClO_4^-). Found: C 38.22; H 5.75; Cl 11.93; N 4.86%. $C_9H_{16}ClNO_7$. Calculated: C 37.83; H 6.65; Cl 12.41; N 4.90%.

B) A 1.85-g (0.01 mole) sample of butyrolactam V was dissolved in 5 ml of a 2 N solution of $HClO_4$ in glacial acetic acid, and the solution was diluted with ether. The precipitated oil was separated by decantation and dissolved in chloroform, and ether was added to precipitate crystals of salt IVa (98%).

N-n-Butyl-3-acetoxy-4,4-dimethyl-2-pyrrolidonium Perchlorate (IVb). A 12-g (0.06 mole) sample of amide Ic was dissolved in 40 ml of acetic anhydride, the solution was cooled to 0°C, and 6 ml (0.06 mole) of 70% $HClO_4$ was added. The reaction mixture was then heated to 80°C with constant stirring for 5 h. It was then cooled and diluted with ether, and the precipitated oil was separated by decantation and dissolved in 10 ml of benzene. The addition of ether in the cold precipitated colorless crystals of salt IVb, which were removed by filtration and washed with ether to give 7.5 g (38%) of a product with mp 94°C (from benzene–hexane). IR spectrum: 1780, 1740 (C=O); 1220 (C–O); 3180, 3280 (N–H); 1100 cm^{-1} (ClO_4^-). Found: C 44.20; H 6.38; Cl 10.15; N 4.20%. $C_{12}H_{22}ClNO_7$. Calculated: C 43.97; H 6.77; Cl 10.82; N 4.27%.

N-Methyl-3-acetoxy-4,4-dimethyl-2-pyrrolidone (V). A 5.7-g (0.02 mole) sample of perchlorate IVa was suspended in 30 ml of chloroform, 10 g of anhydrous sodium carbonate was added, and 2 ml of water was then added slowly dropwise with vigorous stirring. After filtration, the mother liquor was dried over anhydrous Na_2SO_4, and the solvent was evaporated at reduced pressure. The residual viscous oil was distilled at 105°C (666 Pa) to give 2.7 g (72%) of butyrolactam V as a colorless oil with n_D^{20} 1.4556, d^{20} 1.083 g/cm_3, and R_f 0.38 [Silufol, benzene–ethanol (20:0.5), development with iodine vapors]. IR spectrum: 1755 (C=O), 1740 (C=O), and 1240 cm^{-1} (C–O). Found: C 58.40; H 7.85; N 7.55%. $C_9H_{15}NO_3$. Calculated: C 58.36; H 8.15; N 7.56%.

LITERATURE CITED

1. V. G. Kul'nevich, T. P. Kosulina, and F.-U. Lyubke, Khim. Geterotsikl. Soedin., No. 1, 30 (1980).
2. I. V. Smolanka, S. M. Khripak, and V. I. Staninets, Ukr. Khim. Zh., 30, 950 (1964).
3. I. V. Smolanka, S. M. Khripak, and V. I. Staninets, Ukr. Khim. Zh., 30, 265 (1964).
4. I. V. Smolanka, S. M. Khripak, and V. I. Staninets, Ukr. Khim. Zh., 30, 618 (1964).
5. T. P. Kosulina, Z. I. Zelikman, and V. G. Kul'nevich, Zh. Org. Khim., 12, 1134 (1976).
6. T. P. Kosulina, Z. I. Zelikman, and V. G. Kul'nevich, USSR Inventor's Certificate No. 537598; Byull. Izobret., No. 3, 235 (1979).
7. G. N. Dorofeenko, V. D. Karpenko, Yu. I. Ryabukhin, Khim. Geterotsikl. Soedin., No. 5, 702 (1977).
8. G. N. Dorofeenko, V. D. Karpenko, and Yu. I. Ryabukhin, Zh. Org. Khim., 14, 1905 (1978).
9. A. T. Balaban, A. Bota, G. N. Dorofeenko, V. D. Karpenko, and Yu. I. Ryabukhin, Tetrahedron, 34, 2035 (1978).
10. W. Shive and E. Snell, J. Biol. Chem., 160, 287 (1945).
11. J. D. Fissekis, C. G. Skinner, and W. Shive, J. Med. Chem., 2, 47 (1960).
12. V. M. Berezovskii, The Chemistry of Vitamins [in Russian], The Food Industry, Moscow (1973), p. 60.
13. S. G. Tishchenko, V. P. Chekhun, and S. R. Gavrilov, USSR Inventor's Certificate No. 360340; Byull. Izobret., No. 49, 66 (1972).

14. Z. I. Zelikman, T. P. Kosulina, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 2, 169 (1976).
15. D. A. Tomalia and J. N. Paige, J. Org. Chem., 38, 422 (1973).
16. C. U. Pittman, S. P. McManus, and J. W. Larsen, Chem. Rev., 72, 357 (1972).
17. N. V. Dormidontova, M. I. Ustavshchikov, and M. I. Farberov, Zh. Prikl. Khim., 42, 921 (1969).
18. S. A. Harris, G. A. Boyack, and K. Folkers, J. Am. Chem. Soc., 63, 2662 (1941).
19. E. N. Muzinov, E. N. Zil'berman, S. M. Danov, R. V. Efremov, and R. A. Navolokina, Khim. Élementoorg. Soedin., No. 4, 72 (1976).
20. I. Denesh, Titration in Nonaqueous Media [Russian translation], Mir, Moscow (1971), p. 144.

DERIVATIVES OF DIAZIRINE-3,3-DICARBOXYLIC ACID*

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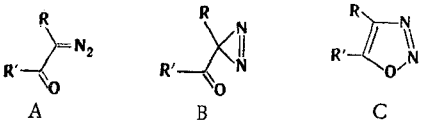
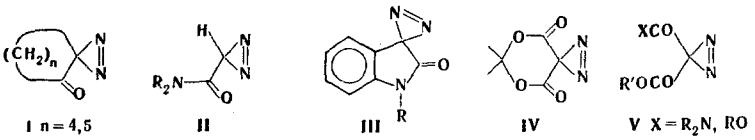
The amidation and alkaline hydrolysis of diazirine-3,3-dicarboxylic acid esters, which proceed with retention of the diazirine ring, were studied. The higher stability of diazirine-3,3-dicarboxylic acid esters as compared with their spirocyclic analogs is explained by the conformational lability of the C=O groups. The UV and mass spectra of the diazirines are discussed.

The synthesis and properties of α-diazo carbonyl compounds A have been studied extensively [2], while their valence isomers, viz., diazirines B, are represented by only a few examples.† These representatives are α-cyclodiazo ketones I, which were obtained by oxidation of the corresponding alcohols [4, 5], and products of photoisomerization of linear α-diazo carbonyl compounds, viz., cyclodiazoacetic acid amides II [6, 7], 3-cyclodiazo-2,3-dihydroindol-2-ones III [8], and isopropylidene cyclodiazomalonate (IV) [9].





However, the photochemical synthesis of diazirines is not of preparative value, since the yields in this case are 20-30% [6, 7, 9], and attempts to realize the photocyclization of the diester and amidoester of diazomalonic acid were unsuccessful; this was explained by the spontaneous retrotransformation of diazirines V because of the steric effect of two carbonyl substituents [6, 7], in analogy with 3,3-diphenyldiazirine [10].

We have previously shown that cyclodiazomalonic esters (diazirine-3,3-dicarboxylic acid esters) VIIa, b are readily obtained from O-tosyloximes VIa, b and alkoxyamines or by oxidation of diaziridine-3,3-dicarboxylic acid ester VIII [1, 11]:

*See [1] for our preliminary communication.
†A third valence isomer, viz., 1,2,3-oxadiazole C, has been found only in the gas phase by FES in the case of o-quinone diazide [3].

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