SYNTHESIS OF 2-ARYLAZOBENZIMIDAZOLES ON THE BASIS OF AROMATIC HYDROCARBONS

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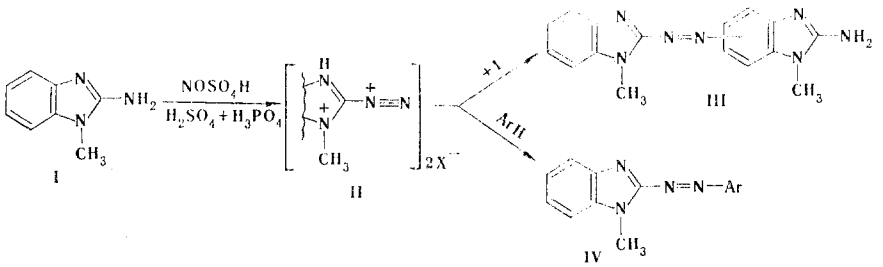
Conditions that exclude "self-coupling" in the reaction of benzimidazole-2-diazonium salts with the simplest aromatic hydrocarbons were selected. The synthesis of 3'-tolyl- and 2'-6'-xylylazobenzimidazoles, which are isolated along with the expected isomers in diazo coupling with toluene and m-xylene, was also realized by an alternative pathway from the corresponding p-aminophenylazobenzimidazoles. The reaction of benzimidazole-2-diazonium salts with primary aromatic amines, which is complicated in the benzimidazole series by side reactions, was studied. The structures of the newly synthesized compounds were confirmed by spectral methods.

We have recently shown [1] that the quaternary salts of the products of diazo coupling of benzene and its homologs with benzimidazole-2-diazonium salts readily undergo arylamination, which leads to deeply colored and previously difficult-to-obtain azo compounds. The diazo coupling of the simplest aromatic hydrocarbons is thus not only of theoretical interest [2] but also has practical significance as one of the steps in the synthesis of cationic dyes. In this connection we set out to replace the diazo component used in [3, 4] by the more accessible 2-aminobenzimidazoles (I) with free 5 and 6 positions, for which side "self-coupling" [5], which leads to the conversion of amine I to azo compound III under the conditions in [3, 4], should have been excluded. Inasmuch as amine I is capable of diazo coupling only with the most active diazonium salt II, which contains a doubly charged cation, one might have expected that the concentration of active diazonium salt II would decrease as the percentage of sulfuric acid in the reaction mixture is decreased and that "self-coupling" processes would be suppressed.

In fact, virtually no "self-coupling" occurs in the diazotization of amine I in concentrated H_3PO_4, but diazo coupling with the simplest homologs of benzene gives unsatisfactory results. We found that the optimum medium for the synthesis of 2-arylazobenzimidazoles (IVa-h) is a mixture of sulfuric and phosphoric acids in a ratio of 1:5. The diazotization of amine I with nitrosyl sulfate in the presence of the corresponding arene gives azo compounds IVa-h in rather high yields under these conditions (Table 1), while "self-coupling" products III are formed as impurities (up to 4%).



IV a Ar = 2′-tolyl; b Ar = 4′-tolyl; c Ar = 3′-tolyl; d Ar = 2′,4′-xylyl; e Ar = 2′,6′-xylyl; f Ar = 2′,5′-xylyl; g Ar = duryl; h Ar = 1′-naphthyl

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TABLE 1. Yields and Spectral Characteristics of the 2-Arylbenzimidazoles (IV, VI)

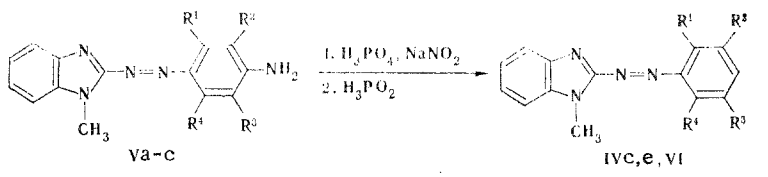
Compound	PMR spectrum, ppm (CCl_4)				IR spectrum, cm^{-1}		Yield, %
	o-CH_3	other CH_3	>N—CH_3	Ar (H)	680-900 cm^{-1} region	other intense bands	
IVa	2,77 (3H)	—	3,82	7,87—7,20 (6H)	760, 785	1155, 1330, 1450, 1490	34
IVb	—	2,30 (3H)	4,00	8,04—7,14 (8H)	750, 830	1160, 1325, 1350, 1400, 1460, 1490	35
IVc	—	2,31 (3H)	3,97	7,75—7,17 (8H)	685, 720, 740 805	1335, 1460, 1500	2
IVd	2,69 (3H)	2,25 (3H)	3,82	7,63—6,72 (7H)	745, 840, 870	1125, 1150, 1335, 1460, 1595	73
IVe	2,52 (6H)	—	3,97	7,78—7,10 (7H)	750, 760, 785	1155, 1330, 1460, 1490	5
IVf	2,73 (3H)	2,30 (3H)	4,01	7,79—7,15 (7H)	755, 830	930, 1160, 1330, 1455, 1485, 1500	84
IVg	2,18 (12H)		3,92	7,78—6,90 (5H)	750, 880	975, 1025, 1170, 1260, 1350, 1400, 1450, 1490, 1520	70
IVh	—	—	4,02	7,90—7,12 (10H)	745, 770, 805	1330, 1450, 1490	65
VI	—	2,28 (6H)	3,85	7,42—6,92 (7H)	685, 750, 805	1120, 1330, 1450, 1500, 1605	46

The "milder" character of the reaction medium as compared with the conditions in [3, 4] made it possible to obtain azo compound IVh on the basis of naphthalene, which in a mixture with a close ratio of sulfuric and phosphoric acids itself reacts with nitrosyl sulfate. However, virtually no diazo coupling occurs with benzene under the modified conditions, and this makes it possible to conclude that the 5 and 6 positions of protonated amine I and the unsubstituted benzene ring have comparable activities.

The ratios of the isomers formed in the diazo coupling of toluene and m-xylene are close to those previously obtained in a medium with a high percentage of sulfuric acid [4] (Table 1). This provides a basis for the assumption that dication II remains the electrophilic particle under the modified conditions; the II concentration is insufficient for diazo coupling with benzene and "self-coupling" at appreciable rates, but this decrease in the concentration has little effect on the rates of the reactions with homologs of benzene.

The structures of all of the IVa-h are confirmed by spectral data. The weak-field shift of the signal of the proton of the methyl group in the arene ring indicates its ortho orientation with respect to the azo group; only the o-methyl groups of 2',3',5',6'-tetramethyl-substituted IVg constitute an exception. In the IR spectra the characteristic bands that correspond to the type of substitution of the benzene ring are observed at 675-900 cm^{-1}; the absorption at 745-760 cm^{-1}, which is common to all IV, corresponds to the 1,2-disubstituted benzene ring of the benzimidazole part of the molecule. The two absorption bands (779 and 805 cm^{-1}) in the case of naphthylazo compound IVh indicate the formation of an α-naphthyl-substituted compound [7].

In a number of cases (IVc,e) the structures of the azo compounds were proved by alternative synthesis from p-aminophenylazo-substutited benzimidazoles Va,b, respectively, by elimination of the amino group. This method was also used to obtain 3',5'-xylylazo-substituted VI, which is necessary for the subsequent study of the amination of 2-arylbenzimidazolium salts, from azo compound Vc.



Va-c IVc,e, VI

V a $R^1=R^3=R^4=H$, $R^2=CH_3$; b $R^1=R^4=CH_3$, $R^2=R^3=H$; c $R^2=R^3=CH_3$, $R^1=R^4=H$;
VI $R^2=R^3=CH_3$, $R^1=R^4=H$

The presence in azo compounds IVc,e and VI of a free para position relative to the azo group makes it possible to use them in the synthesis of cationic dyes (cf.[1]). The low

TABLE 2. Characteristics of the 2-Aminophenylazobenzimidazoles (V, VII, VIII)

Compound	mp, °C (benzene)	PMR spectrum, ppm			IR spectrum, cm^{-1}		Found, %			Empirical formula	Calc., %			Yield, %
		CH_3	$N-CH_3$	NH_2	νNH_2	other intense bands	C	H	N		C	H	N	
Va	182—183	2,08 (3H-*m*)	4,07	6,43	3130, 3310, 3475	1235, 1320, 1595, 1635	67,7	5,5	26,7	$C_{15}H_{15}N_5$	67,9	5,7	26,4	9
VIIa	252—253	2,10 (3H-*m*)	3,92	5,87	3180, 3300, 3370	1255, 1355, 1385, 1495, 1575, 1625	67,6	5,7	26,5	$C_{15}H_{15}N_5$	67,9	5,7	26,4	13
Vb	197*—198	2,60 (6H-*o*)	4,02	6,40	3180, 3310, 3370	1250, 1320, 1600, 1635	68,8	6,1	25,0	$C_{16}H_{17}N_5$	68,8	6,1	25,1	12
VIIb	226—227	2,54 (3H-*o*), 2,18 (3H-*p*)	3,93	5,84	3160, 3280, 3355	1225, 1340, 1540, 1580, 1625	68,9	6,2	25,1	$C_{16}H_{17}N_5$	68,8	6,1	25,1	3
VIIc	208*—209	2,02, 2,12 (6H-*m*)	3,87	5,80	3185, 3310, 3340	1235, 1265, 1330, 1495, 1635	68,8	6,1	24,8	$C_{16}H_{17}N_5$	68,8	6,1	25,1	15
VIII	204—205	2,62 (3H-*o*), 2,10 (3H-*p*)	4,02	6,42	3150, 3300, 3480	1265, 1315, 1490, 1585, 1620, 1645	69,0	6,1	25,0	$C_{16}H_{17}N_5$	68,8	6,1	25,1	6
Vc	207—208	2,10 (6H-*m*)	3,97	4,07	3215, 3330, 3470	1570, 1610, 1630, 1645	69,3	6,1	24,8	$C_{16}H_{17}N_5$	68,8	6,1	25,1	16

*From benzene with petroleum ether.

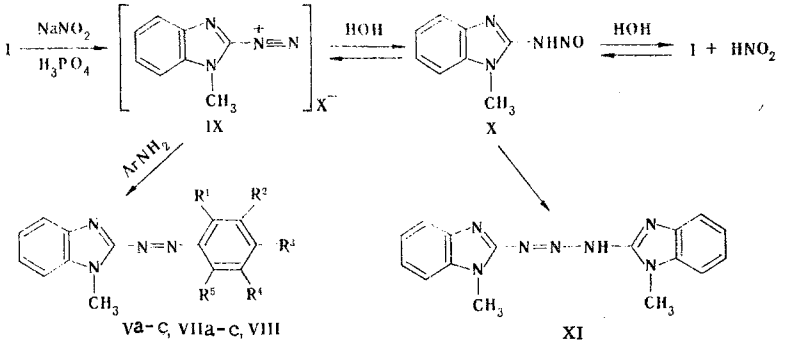
TABLE 3. 2-Arylazobenzimidazoles (IV, VI)

Compound	mp, °C (from petroleum ether)	Found, %			Empirical formula	Calc., %		
		C	H	N		C	H	N
IVa	179—180	72,2	6,0	22,7	$C_{15}H_{14}N_4$	72,0	5,6	22,4
IVb	140—141	72,3	5,4	22,1	$C_{15}H_{14}N_4$	72,0	5,6	22,4
IVc	147—148	71,7	5,3	22,6	$C_{15}H_{14}N_4$	72,0	5,6	22,4
IVd	128—129	72,9	6,3	21,0	$C_{16}H_{16}N_4$	72,7	6,1	21,2
IVe	125—126*	73,1	5,8	21,3	$C_{16}H_{16}N_4$	72,7	6,1	21,2
IVf	144—145	72,5	6,2	21,5	$C_{16}H_{16}N_4$	72,7	6,1	21,2
IVg	148—149	74,1	7,0	19,6	$C_{18}H_{20}N_4$	74,0	6,8	19,2
IVh	147—148	74,8	4,8	19,1	$C_{18}H_{14}N_4$	75,5	4,9	19,6
VI	116—117*	72,4	5,8	21,4	$C_{16}H_{16}N_4$	72,7	6,1	21,2

*From hexane.

accessibility of IVc,e and VI through direct diazo coupling with arenes and the possibility of realization of their synthesis by the alternative route indicated above compelled us to make a more detailed study of the diazo coupling of benzimidazole-2-diazonium salts with primary aromatic amines.

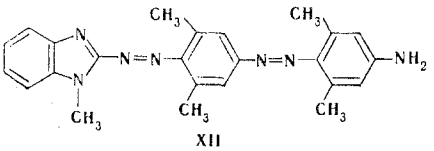
We found that, in contrast to many known samples [8, 9], this reaction in the benzimidazole series proceeds in an extremely complex manner to give, as a rule, mixtures of isomeric azo compounds in low yields (Table 2). The use of a relatively concentrated solution of phosphoric acid (∿35%) as the medium gives better results, although the low concentration of the free amine in these solutions is the reason for the formation of bisazo compounds and, in the case of 2,4-xylidine, m-amino-substituted VIII.



VIIa $R^1=NH_2$, $R^2=CH_3$, $R^3=R^4=R^5=H$; b $R^1=NH_2$, $R^2=R^4=H$, $R^3=R^5=CH_3$; c $R^1=NH_2$, $R^2=R^4=CH_3$, $R^3=R^5=H$; VIII $R^1=R^4=H$, $R^2=NH_2$, $R^3=R^5=CH_3$

Isomeric azo compounds V, VII, and VIII were separated by chromatography, and their identification was based on certain regularities in their IR and PMR spectra, which make it possible to distinguish o-substituted VII from the p (or m)-amino isomers V and VIII (Table 2). Thus in the PMR spectra the signal of the protons of the amino group in the ortho position relative to the azo bridge is shifted almost 0.6 ppm to strong field as compared with the p- or m-amino group. Compound Vc, in which the amino group is shielded by two methyl groups, constitutes an exception. The high-frequency νNH_2 band in the IR spectra of o-amino-substituted VII is shifted 40-100 cm^{-1} to the low-frequency region as compared with the analogous band of the para or meta isomers. The structure of amino azo compound VIIb was also confirmed by its deamination to the known IVd, the structure of which was proved by reductive cleavage.

Diazo coupling in more dilute solutions of phosphoric acid (dilution of the diazonium solution by a factor of more than two) gives a difficult-to-separate multicomponent mixture, from which, in addition to desired products V, VII, and VIII (in an overall yield of less than 10%), one can isolate up to 20% starting amine I, symmetrical triazene XI, and a number of other colored compounds such as the bisazo compound with structure XII.



XII

One of the possible explanations for the unusual character of diazo coupling with primary amines consists in the peculiarity of the state of the diazo equilibrium in the 2-diazobenzimidazole series. The most stable diazo form here is primary N-nitrosamine X [10], which surpasses in this respect the quite stable nitrosamines of other azoles [11]. The denitrosation of X, which ensures the possibility of transdiazotization of the arylamino group, and the known ease of conversion of nitrosamine X to symmetrical triazene XI [12, 13] are in good agreement with the observed pattern.

The complexity of the preparation of aminoarylazobenzimidazoles V, VII, and VIII make the alternative method of synthesis on the basis of aromatic hydrocarbons unpromising in a preparative respect. On the other hand, direct diazo coupling with homologs of benzene under the proposed conditions opens up the possibility of the preparation of compounds that are of interest in a practical respect.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Tesla-467°C spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. Chromatography was carried out on activity II aluminum oxide in a benzene—CCl_4—ethyl acetate system (1:2:0.2).

General Method for the Preparation of 2-Arylazobenzimidazoles IV by Direct Diazo Coupling with Arenes. A 10-mmole (1.47 g) sample of amine I was dissolved in 25 ml of concentrated H_3PO_4, the solution was cooled to −5°C, 5.5 ml of a solution of nitrosyl sulfate in concentrated H_2SO_4 (obtained by the method in [14]) was added, and 30 mmole of the arene was then added with vigorous stirring. Stirring was continued as the temperature was raised to room temperature. After 5 h from the start of the reaction, the mixture was poured into ice water, and the aqueous mixture was neutralized to pH 8-9 with sodium carbonate solution and extracted with benzene (three 15-ml portions). The extract was separated into its components as described for IVa-e. The purity of the substances was monitored by thin-layer chromatography (TLC) with development with iodine. The yields and characteristics of IV are presented in Tables 1 and 3.

Separation of Isomeric 2-(2'-Tolylazo)- and 2-(4'-Tolylazo)-1-methylbenzimidazoles (IVa, b). The mixture (1.9 g) of azo compounds obtained by diazo coupling with toluene was dissolved in 15 ml of boiling CCl_4, an equal volume of petroleum ether was added to the hot solution, and the mixture was allowed to stand for 2-3 h. The precipitate was recrystallized from CCl_4—petroleum ether (2:1) to give 0.45 g of p-isomer IVb (R_f 0.53). The mother liquors were diluted to twice their original volume with petroleum ether, and the precipitated IVb (0.12 g) was recrystallized from CCl_4—petroleum ether until it had a constant melting point. The residue remaining after removal of the solvents from the mother liquors by distillation was chromatographed with a column (l = 45 cm, d = 4.5 cm) with collection of the first fraction containing o-isomer IVa (20-25 ml) with R_f 0.74. The eluate was then collected in 2-ml fractions with simultaneous monitoring by TLC in the same solvent system. Pure p-isomer IVb was eluted with chloroform; the intermediate fraction (0.045 g) contained primarily m-isomer IVc with R_f 0.61 (Table 1). The yield of o-isomer IVa was 0.85 g, while the yield of p-isomer IVb was 0.87 g.

Separation of Isomeric 2-(2'-4'-Xylylazo)- and 2-(2',6'-Xylylazo)-1-methylbenzimidazoles IVd,e). The mixture (2.2 g) of isomers obtained by diazo coupling with m-xylene was passed through a chromatographic column (l = 50 cm, d = 3.5 cm) in the CCl_4—benzene—ethyl acetate system (5:2:0.4). The forerunning slightly colored impurities were eluted, and the aluminum oxide column was pushed out and cut in half. Extraction of the upper part (~2/3 of the colored column) with acetone gave 1.25 g of virtually pure 2',4' isomer IVd with R_f 0.68; a spot of this product on the thin-layer chromatogram was colored green in iodine. The mixture of isomers extracted from the lower third of the colored column was crystallized three times from petroleum ether to give 0.27 g of pure IVd. The petroleum ether was removed from the mother liquors by distillation, the residue was dissolved in 9 ml of CCl_4, and the solution

was chromatographed in a thin layer of aluminum oxide (eight to nine 16 by 25 cm plates). The upper one fourth of the area of the colored zone was separated, and the substance was extracted and crystallized from hexane to give 0.06 g of the pure 2',6' isomer IVe with R_f 0.73. Workup of the lower (~1/3 in area) part gave 0.17 g of IVd. The combined intermediate zone and hexane mother liquor was reseparated in a thin layer to give 0.06 g of IVe and 0.24 g of slightly impure 2',4' isomer IVd.

The azo compounds obtained on the basis of p-xylene (IVf), durene (IVg), and naphthalene (IVh) (in the latter two cases the hydrocarbons were subjected to diazo coupling after prior dissolving in chlorobenzene) were purified to remove the more poorly forerunning impurities by chromatography in the usual solvent system. Their characteristics are presented in Tables 1 and 3.

Preparation of 2-Arylazobenzimidazoles from p-Amino Azo Compounds. A 1.5-mmole sample of azo compound Va-c was dissolved in 10 ml of concentrated H_3PO_4, the solution was cooled to −7°C, and 2.3 mmole (1.6 g) of sodium nitrite was added with stirring. After 0.5 h, 3 ml of a 50% solution of hypophosphorous acid was added, and the mixture was stirred for 2-3 h and allowed to stand at 0-3°C for 24 h. The mixture was then maintained at 18-20°C for 3-4 h, after which it was poured into 50 ml of water. The aqueous mixture was made alkaline to pH 8-9 with sodium carbonate and extracted with chloroform (three 10-ml portions). The desired product was isolated by chromatography in the usual solvent system. No melting-point depressions were observed for mixtures of the 3'-tolylazo- and 2',6'-xylylazo-substituted azo compounds IVc,e obtained in 40 and 41% yields, respectively, from Va,b with the substance isolated from the reaction of the azo compounds with toluene and m-xylene. 2',5'-Xylylazobenzimidazole VI was formed in 46% yield from p-aminophenylazo-substituted Vc (Tables 1 and 3).

Diazo Coupling with Primary Aromatic Amines. A 10-mmole (1.47 g) sample of amine I, dissolved in 20 ml of 85-90% H_3PO_4, was diazotized with a saturated solution of 12 mmole (0.83 g) of sodium nitrite at −10°C, after which stirring was continued for 30 min as the temperature was raised to 2-5°C. The resulting viscous mass was poured rapidly with stirring and cooling into a solution of 15 mmole of the aromatic amine in 4-5 ml of dilute H_3PO_4. After 1 h, an equal volume of water was added to the reaction mixture, and the mixture was stirred for another 4 h and allowed to stand in a refrigerator for 24 h. It was then neutralized to pH 8-9 with sodium carbonate solution and extracted with chloroform (three 10-ml portions). The extract was chromatographed in a benzene—CCl_4—ethyl acetate system (6:8:1). The first brownish-red fraction, which corresponds to o-amino-substituted compound VII, was collected and rechromatographed in a benzene—chloroform system (1:3). After separation of the ortho isomer with the first column, the adsorbent column was pushed out, cut into zones with respect to color, and eluted with acetone; the yellow substance at the start was eluted with hot alcohol. After purification from ethanol, the latter had mp 213-215°C and did not depress the melting point of genuine 1,3-bis(1'-methyl-2'-benzimidazolyl)-triazene [13]. The yield after purification was 10%. The brown-orange fractions of the first and second columns, which emerged after VIIa-c and contained p-isomers Va-c, were combined, the solvent was removed by distillation, and the residue was crystallized from benzene. In the reaction with 2,4-xylidine the fraction corresponding to the p-amino-substituted compound, which, however, was less intensely colored, contained primarily the meta isomer. Data on V, VII, and VIII are presented in Table 2.

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SYNTHESIS AND REACTIVITIES OF IMIDAZOLIN-2-ONE 3-OXIDES

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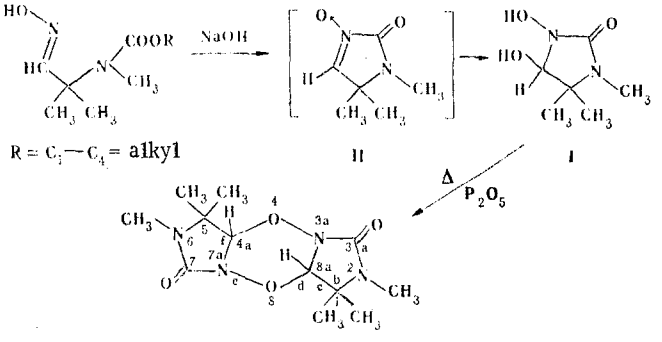
3'717'642.07:543.422'51

The cyclization of 3-[N-methyl-N-(ethoxycarbonyl)amino]-3-methyl-2-butanone oxime in an alkaline medium leads to 1-hydroxy-2,2'-dioxo-3,4,4,3',4'-hexamethylimidazolidine-spiro-5,6'-perhydroimidazo[2,3-c]-isoxazole, whereas the cyclization of 3-[N-(ethoxycarbonyl)amino]-3-methyl-2-butanone oxime leads to 2-oxo-4,5,5-trimethyl-Δ^3-imidazoline 3-oxide. The latter is converted to 1-hydroxyl-2,2'-dioxo-4,4,4',4'-tetramethylimidazolidine-spiro-5,6'-perhydroimidazo[2,3-c]isoxazole upon refluxing in water. 1,4,5,5-Tetramethyl-3-methoxy-4-hydroxyimidazolidin-2-one was synthesized by methylation of the compounds obtained by means of dimethyl sulfate. A scheme for the reactions is proposed.

We have previously shown [1] that 2-[N-methyl-N-(alkoxycarbonyl)amino]-2-methylpropanaldoximes undergo cyclization to 3,4-dihydroxy-1,5,5-trimethylimidazolidin-2-one (I), which is evidently the product of addition of water to the intermediately formed 1,5,5-trimethyl-2-oxo-Δ^3-imidazolin 3-oxide (II). However, an attempt to obtain N-oxide II by treatment of dihydroxy derivative I with phosphrus pentoxide led to the isolation of 1,1,2,5,5,6-hexamethyl-3,7-dioxo-4,8,2,3a,6,7a-dioxatetraazacyclopenta[f]hexahydroindan — the product of dimerization of two molecules of II [1].



We examined the cyclization of 3-[N-methyl-N-(ethoxycarbonyl)amino]-3-methyl-2-butanone (IIIa) under alkaline conditions and found that it also does not lead to N-oxide IVa. However, according to the results of elementary analysis and the mass-spectrometric data, the product of this reaction (Va) has empirical formula $C_{14}H_{24}N_4O_4$. The presence in the mass spectrum of, in addition to a molecular-ion peak with m/z 312, an intense peak with m/z 156 (the mass of imidazolin-2-one N-oxide IVa) makes it possible to assume that dimerization of the intermediately formed IVa also occurs in this case.

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