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# IMIDAZOLES IN THE HETARYLATION REACTION

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UDC 547.78.751'785.5

Indoles and pyrrole were subjected to hetarylation with imidazole and benzimidazole in the presence of aliphatic, aromatic, and heteroaromatic carboxylic acid chlorides. The resulting N,N'-diacylimidazolinyl- and N,N'-diacylbenzimidazolinylindoles were converted to 2-(3'-indolyl)-1,3-diacylimidazolium and N,N'-diacylbenzimidazolium salts by the action of trityl perchlorate.

Until recently the direct hetarylation of nucleophilic organic compounds was possible only by means of N-heteroaromatic anion radicals [1] or N-acylpyridinium [2] or N-alkoxypyridinium [3] and benzopyridinium salts in situ. The behavior of azoles in these reactions has not been studied systematically, although the presence of a "pyridine" nitrogen atom in the ring and the ability to form N-acyl salts on reaction with acylating agents [4] have made it possible to consider the possibility of the use of these heterocycles also in hetarylation reactions [2].

The reaction of benzimidazole with nucleophiles in the presence of acylating agents was studied by Gerngross in 1913 [5]. Bergman [6], who obtained hetarylation products rather than acylation products in attempts to acylate indole with N-acetylimidazole, also recently reported the possibility of using azoles in the hetarylation reaction. Independently of him and almost simultaneously, in a continuation of our system studies of the behavior of N-heteroaromatic systems in the hetarylation reaction in the presence of acyl halides, we also observed the possibility of the use of imidazole, benzimidazole, and perimidine in it [7]. However, up until now the conditions for hetarylation by N-acyl salts of imidazoles and the physical constants of the resulting compounds have not been indicated in the literature, including the communications mentioned above [6, 7]. Rigorous proof of their structures has also been lacking. In the present communication we examine in detail the hetarylation of indoles by N-acylimidazolium and benzimidazolium salts in situ.*

We obtained N,N'-diacylimidazolinyl- and N,N'-diacylbenzimidazolinylindoles (II) (Table 1) by reaction of imidazole and benzimidazole with indoles in the presence of aliphatic, aromatic, and heterocyclic carboxylic acid chlorides. Indoles II are evidently formed as a result of attack on the indole ring by the intermediately formed N,N'-diacylimidazolium and benzimidazolium cations (I) via the following scheme:

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*We will separately report the possibilities of the use of other azoles and perimidine in this reaction.

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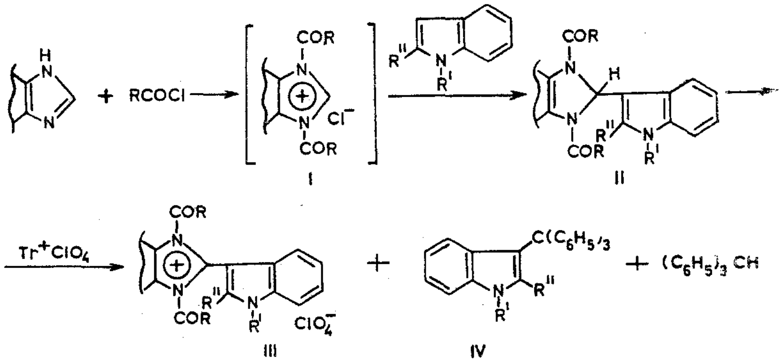
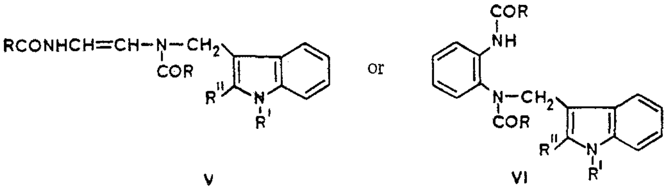
Donetsk State University, Donetsk 340055. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 238-247, February, 1977. Original article submitted December 30, 1975; revision submitted May 13, 1976.



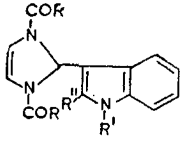
The formation of salts of the I type as intermediates is confirmed by the fact that II are also obtained under similar conditions when imidazole is replaced by N-acylimidazole. N,N'-Diacylimidazolium salts I cannot be isolated because of their extremely low stabilities. However, we obtained salts of this type (Table 2) stabilized by an indole fragment in the 2 position of the imidazolium cation III by the action of triphenylmethyl perchlorate on imidazolinylindole II. In this case diphenyl(3-indolyl)methanes (IV), which we obtained by an independent method, are formed as side products.

We proved the structures of N,N'-diacylimidazolinyl- and N,N'-diacylbenzimidazolinylindoles II by PMR, IR, and mass spectroscopy. In particular, the absence in the IR spectra of IIa, e, h, m ($R' = CH_3$) of an absorption band of an NH group at 3200-3500 $cm^{-1}$ constitutes evidence for the addition of two acyl residues to the nitrogen heteroatoms of the imidazoline ring and excludes structures with an open imidazole ring of the V or VI type, in which there is a free NH group.

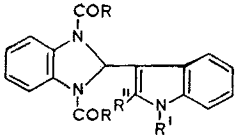


The position of the $\nu_{CO}$ carbonyl band (1650-1660 $cm^{-1}$) also indicates the presence of an amide rather than a ketone grouping. We made the assignment of the remaining bands, which confirm the structures of the compounds obtained, on the basis of a study of the IR spectra of the compounds in various solvents. For the complete assignment of the absorption bands of the C = O and C – N groups we used the possibility of the formation of hydrogen bonds of compounds of this type with a polar solvent. It is known that a shift in $\nu_{CO}$ of 10-40 $cm^{-1}$ to the lower-frequency region occurs in the spectra of both primary and secondary amides during the formation of hydrogen bonds, while $\nu_{C-N}$ is lowered by the same value to the high-frequency region [8]. The spectra of all of the compounds in solvents with different polarities – carbon tetrachloride, chloroform, n-butylalcohol, and tetrahydrofuran (THF) – were recorded. It was found that a shift of 20-30 $cm^{-1}$ (from 1670-1690 to 1650-1660 $cm^{-1}$) of the absorption band of the C = O group to the low-frequency region occurs when the more polar chloroform is used, and an additional shift of 10-20 $cm^{-1}$ (to 1630-1650 $cm^{-1}$) of $\nu_{CO}$ occurred on passing from chloroform to n-butyl alcohol. Correspondingly, the $\nu_{CN}$ band is shifted 15-30 $cm^{-1}$ (from 1380 to 1410 $cm^{-1}$) to the higher-frequency region on passing from $CCl_4$ to chloroform. The highest frequencies of the carbonyl group and the lowest frequencies of the C – N bond were observed in dilute $CCl_4$ solutions; this is due to the absence of intramolecular and intermolecular hydrogen bonds and of hydrogen bonds with the solvent. The same frequencies of the C = O and CN groups were also observed in the spectrum of a concentrated solution in THF, and this is also explained by the absence of intra- and intermolecular hydrogen bonds owing to the fact that the N–H group of the indole ring is tied up completely by a hydrogen bond with the solvent. The band of $C_4 = C_5$ stretching vibrations (1610-1620 $cm^{-1}$) of the imidazoline ring was identified from the absence of a solvent effect on the frequency of its absorption and also by comparison with the IR spectrum of a genuine sample, which does not contain this band. This band is absent in the spectra of benzimidazoline derivatives. The PMR spectra of imidazoline derivatives IIa-c contains singlets of methyl groups of acetyl residues at δ 2.10 ppm. The signals of the $H_2$, $H_4$, and $H_5$ protons of the imidazoline ring and the indole protons forms a complex multiplet at δ 6.9-8.5 ppm, from which the $H_2$ singlet of the imidazoline fragment at δ 6.9 ppm and indole N–H bonds at 12.05 ppm can be isolated. The PMR spectra of benzimidazole derivatives II*l*-o also confirm their structures. Thus the signal characteristic for the protons of the N-methylene group is not observed in the PMR spectrum of II*l*, and this would constitute evidence in favor of the open form (VI) of the synthesized compounds. We assigned the two singlets with chemical shifts δ 2.20 and 6.00 ppm to the resonance of the protons of two methyl

TABLE 1. 1,3-Diacyl-2-(3'-indolyl)-1,2-dihydroimidazoles (IIa-k) and Benzimidazoles (II*l*-n)



II a-k



II *l*-o

| Compound | R | R′ | R″ | mp, °C[a] | $R_f$ | Found, % | | | Empirical formula | Calculated, % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | | C | H | N | |
| IIa | $CH_3$ | $CH_3$ | H | 165—166 | 0,36 | 67,7 | 6,0 | 14,9 | $C_{16}H_{17}N_3O_2$ | 67,9 | 6,0 | 14,8 | 7 |
| IIb | $CH_3$ | H | $CH_3$ | 229—230 | 0,30 | 67,8 | 6,3 | 14,5 | $C_{16}H_{17}N_3O_2$ | 67,9 | 6,0 | 14,8 | 50 |
| IIc | $CH_3$ | H | H | 214—215 | 0,23 | 66,6 | 5,7 | 15,3 | $C_{15}H_{15}N_3O_2$ | 66,9 | 5,6 | 15,7 | 22,5 |
| IId | $C_6H_5$ | H | H | 195—196 | 0,35 | 76,1 | 5,4 | 10,9 | $C_{25}H_{19}N_3O_2$ | 75,9 | 5,1 | 10,6 | 36 |
| IIe | $C_6H_5$ | $CH_3$ | H | 201—202[b] | 0,64 | 76,6 | 5,3 | 10,6 | $C_{26}H_{21}N_3O_2$ | 76,6 | 5,2 | 10,3 | 15 |
| IIf | $C_6H_5$ | H | $CH_3$ | 237—238 | 0,47 | 76,8 | 5,3 | 10,1 | $C_{26}H_{21}N_3O_2$ | 76,6 | 5,2 | 10,3 | 95 |
| IIg | $CHBrCH(CH_3)_2$[c] | H | H | 139—140[b] | 0,31 | 49,1 | 5,2 | 8,3 | $C_{21}H_{25}N_3O_2Br_2$ | 49,3 | 4,9 | 8,2 | 48 |
| IIh | $CHBrCH(CH_3)_2$[d] | $CH_3$ | H | 204—205 | 0,79 | 50,6 | 5,2 | 8,3 | $C_{22}H_{27}N_3O_2Br_2$ | 50,3 | 5,1 | 8,0 | 23 |
| IIi | $CHBrCH(CH_3)_2$[e] | H | $CH_3$ | 178—180 | 0,46 | 50,5 | 5,4 | 7,9 | $C_{22}H_{27}N_3O_2Br_2$ | 50,3 | 5,1 | 8,0 | 68 |
| IIj | 2-Thienyl[f] | H | H | 230—231 | 0,31 | 61,9 | 4,0 | 15,4 | $C_{21}H_{15}N_3O_2$ | 62,2 | 3,7 | 15,8 | 25 |
| IIk | 5-Benzyl-2-furyl | H | H | 144—145 | 0,35 | 75,6 | 5,2 | 7,4 | $C_{35}H_{27}N_3O_4$ | 75,9 | 4,9 | 7,6 | 58 |
| II*l* | $CH_3$ | H | H | 241—242 | 0,19[g] | 71,2 | 6,1 | 12,8 | $C_{19}H_{19}N_3O_2$ | 71,0 | 5,9 | 13,1 | 37,5 |
| IIm | $CH_3$ | $CH_3$ | H | 197—198 | 0,60 | 72,0 | 5,5 | 12,6 | $C_{20}H_{19}N_3O_2$ | 72,1 | 5,7 | 12,6 | 24 |
| IIn | $CH_3$ | H | $CH_3$ | 244—245 | 0,42 | 72,3 | 5,9 | 12,3 | $C_{20}H_{19}N_3O_2$ | 72,1 | 5,7 | 12,6 | 70 |
| IIo | $C_6H_5$ | H | H | 211—212 | 0,25 | 78,6 | 4,8 | 9,4 | $C_{29}H_{21}N_3O_2$ | 78,5 | 4,7 | 9,5 | 22,5 |

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[a] From butanol.

[b] From ethanol.

[c] Found: Br 31.0%. Calculated: Br 31.3%.

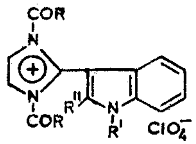
[d] Found: Br 30.3%. Calculated: Br 30.5%.

[e] Found: Br 30.2%. Calculated: Br 30.5%.

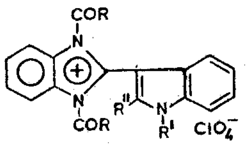
[f] Found: S 20.6%. Calculated: S 20.9%.

[g] In a chloroform–benzene–hexane system (30 : 6 : 1).

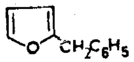
TABLE 2. 1,3-Diacyl-2(3'-indolyl)imidazolium and 1,3-Diacyl-2-(3'-indolyl)benzimidazolium Salts



III a-e



III f-h

| Compound | R | R′ | R″ | mp, °C[a] | $\nu_{CO}$, cm$^{-1}$ | Found, % | | | | Empirical formula | Calculated, % | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | Cl | | C | H | N | Cl | |
| IIIa | $C_6H_5$ | H | H | 160—161 | 1757 | 61,0 | 4,1 | 8,8 | 6,8 | $C_{25}H_{18}N_3O_6Cl$ | 61,0 | 3,7 | 8,2 | 7,2 | 61,2 |
| IIIb | $C_6H_6$ | $CH_3$ | H | 145—146 | 1740 | 61,5 | 4,3 | 8,7 | 7,3 | $C_{26}H_{20}N_3O_6Cl$ | 71,7 | 4,0 | 8,3 | 7,0 | 60,0 |
| IIIc | $CH_3$ | H | H | 107—108 | 1758 | 49,2 | 3,8 | 11,2 | 9,5 | $C_{15}H_{14}N_3O_6Cl$ | 48,9 | 3,8 | 11,4 | 9,6 | 40,6 |
| IIId |  [b] | H | H | 175—176 | 1750 | 50,1 | 2,9 | 8,4 | 7,0 | $C_{21}H_{14}N_3O_6ClS_2$ | 50,0 | 2,8 | 8,3 | 7,0 | 99,0 |
| IIIe |  | H | H | 140—141 | 1752 | 64,3 | 3,9 | 6,8 | 5,2 | $C_{35}H_{26}N_3O_8Cl$ | 64,5 | 3,9 | 6,4 | 5,4 | 76,9 |
| IIIf | $CH_3$ | H | H | 186—187 | 1760 | 54,9 | 4,1 | 10,1 | 8,3 | $C_{19}H_{16}N_3O_6Cl$ | 54,6 | 3,8 | 10,0 | 8,5 | 60,0 |
| IIIg | $CH_3$ | H | $CH_3$ | 189—190 | 1760 | 55,2 | 4,0 | 10,0 | 8,4 | $C_{20}H_{18}N_3O_6Cl$ | 55,5 | 4,2 | 10,0 | 8,2 | 44,0 |
| IIIh | $CH_3$ | $CH_3$ | H | 191—192 | 1755 | 55,3 | 4,0 | 10,2 | 8,5 | $C_{20}H_{18}N_3O_6Cl$ | 55,5 | 4,2 | 10,0 | 8,2 | 65,0 |

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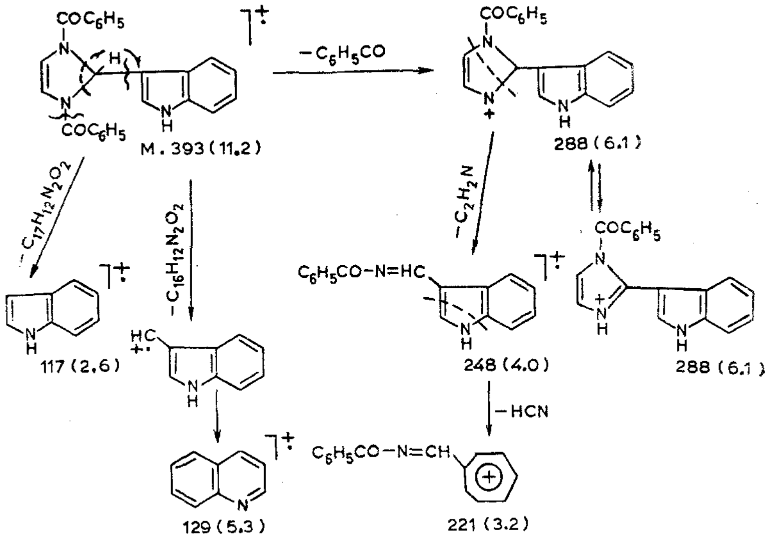
[a] From acetonitrile—ether.

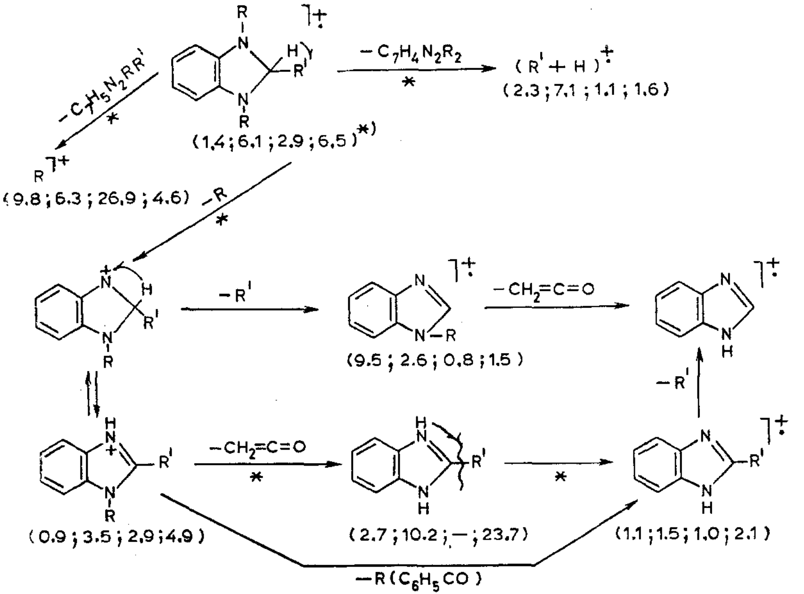
[b] Found: S 12.5%. Calculated: S 12.7%.

groups bonded to the carbonyl group and one $H_2$ methylidyne proton, respectively. This assignment is confirmed by the integral intensity ratio (6 : 1). In addition, it follows from the PMR spectra that the area of the broad signal in the region of the proton of the NH group corresponds to one proton rather than to two protons, as would be expected for the open form (VI) of these compounds. All nine of the aromatic protons of the aryl portion of the molecule give a complex multiplet at δ 6.75-8.05 ppm.

The structures of the imidazole and benzimidazole derivatives of indoles are also confirmed by their mass spectra. The fragmentation of the molecular ions of these compounds proceeds extremely specifically, and this makes it possible to easily interpret each fragment that makes up the starting molecule. In the general case the character of the fragmentation of 1,3-diacyl-2(3'-indolyl)-1,2-dihydroimidazoles IIa-k is illustrated by the following scheme (in the case of IId):



As seen from the above scheme, the fragmentation of the molecular ion can be realized via three pathways: 1) cleavage of the labile amide bond leads to the appearance in the mass spectra of ion peaks with masses 105 and 238 with the structures of the benzoyl and 1-benzoyl-2-(3'-indolyl)imidazolyl cation: 2) cleavage of the interannular bond is accompanied by migration of a hydrogen atom, and this leads to the formation of a pseudo-molecular ion with the indole structure (m/e 117); 3) destruction of the imidazoline ring leads to the formation of an ion peak with mass 129, evidently with a quinoline structure (because of expansion of the pyrrole ring in the indole fragment).



II l $R=COCH_3$; $R'=$3-indolyl; m $R=COCH_3$; $R'=$N-methyl-3-indolyl;
o $R=COC_6H_5$; $R'=$3-indolyl; p $R=COCH_3$; $R'=$ 2-pyrrolyl

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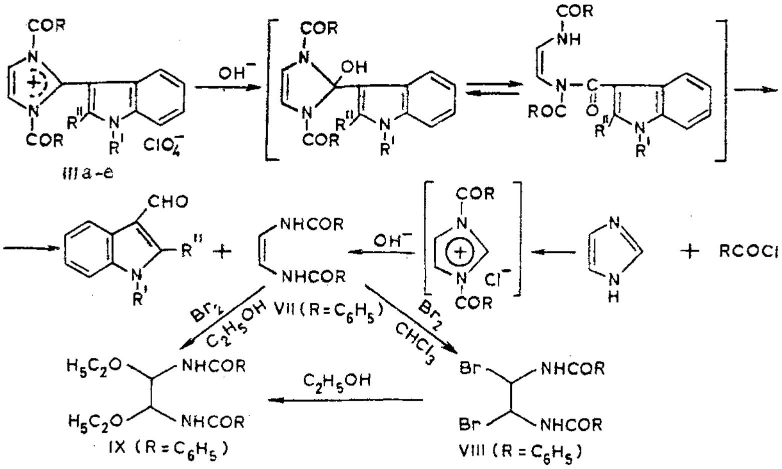
*The intensities of the ion peaks in percent of the total ion current for IIl, m, o, p, respectively, are presented.

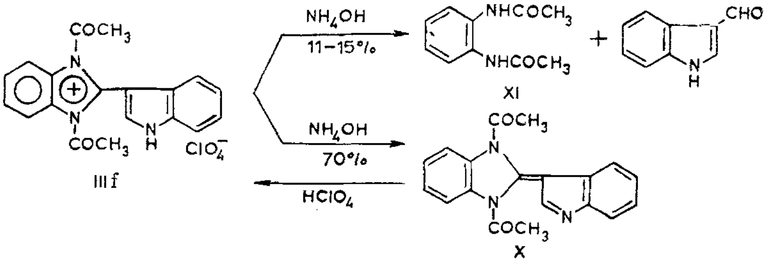
The overall picture of the dissociative ionization of benzimidazoline derivatives II*l*-p is illustrated by the scheme at the bottom of the previous page.

The successive elimination of two acyl residues leads to a stable bishetaryl system with nonequivalent heterocyclic rings. The subsequent trend of the fragmentation of this ion on electron impact follows the well-known scheme [9–11]. The fragmentation of the benzimidazole fragment is accompanied by the appearance in the spectra of ion peaks with the following mass numbers: 145, 117, 91, 90, 64, and 63 [13]. Thus the mass-spectrometric study of the synthesized compounds (IIa-p) completely confirms the structures assigned to them.

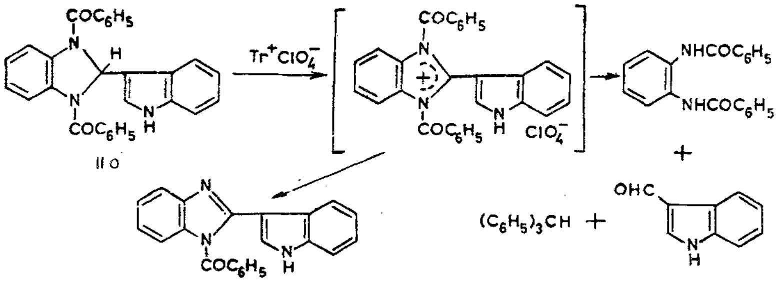
The structures of the 1,3-diacyl-2-(3'-indolyl)imidazolium (IIIa-e) and benzimidazolium salts (IIIf-h) are confirmed by their chemical behavior and their IR spectra. They are insoluble in ether, benzene, and other nonpolar solvents and decompose under the influence of alkali or weak ammonium hydroxide. In this case the imidazolium (IIIa-e) and benzimidazolium (IIIf-h) salts behave differently: Salts IIIa-e decompose rapidly to give 3-formylindole, which is subsequently converted under the reaction conditions to indole-3-carboxylic acid, and N,N'-diacylaminoethylene (VII), which is also obtained by alkaline decomposition of 1,3-diacylimidazolium salts in situ. The reaction of bromine with VII gave N,N'-dibenzoyldiamino-1,2-dibromoethane (VIII), which readily undergoes alcoholysis and on refluxing in ethanol solution is converted to N,N'-dibenzoyldiamino-1,2-diethoxyethane (IX), which can be obtained by direct bromination of VII in ethanol:



1,3-Diacetyl-2-(3'-indolyl)benzylimidazolium salts IIIf-H also undergo partial decomposition to give N,N'-diacetyl-o-phenylenediamine and indol-3-carboxylic acid under the influence of ammonium hydroxide but they are mainly (~70%) converted to indoline derivative X, which is converted to the starting salt by acidification:



The analogous 1,3-dibenzoyl salts of benzimidazolylindoles were found to be extremely unstable, and we were unable to obtain them, since transformation products are immediately formed in the reaction of the corresponding dibenzoyl derivative IIo with trityl perchlorate:



Triphenylmethylindole is not formed in this reaction. The band of the stretching vibrations of the C = O group in the IR spectra of salts IIIa-h (Table 2) is found at 1740-1760 $cm^{-1}$, i.e., it is shifted by 100-110 $cm^{-1}$ to the higher-frequency region as compared with the corresponding amides II. In addition the absorption band at 1610-1620 $cm^{-1}$ related to the stretching vibrations of the C = C bond of the imidazoline ring in IIa-k vanishes in the spectra of these salts. The data from the IR spectra of imidazolium salts IIIa-e, in particular the $\nu_{CO}$ position, are in good agreement with the position of the corresponding band of the carbonyl group in the spectra of N-acylpyridinium [14] and 1-acyl-2-amino-3-alkylbenzimidazolium [15] salts, and this completely confirms their structures.

All of our attempts to carry out the hetarylation of other nucleophilic organic compounds (dialkylanilines, acetoacetic ester, acetophenones, etc.) by a similar method were unsuccessful, and compounds of the VII and XI type, which do not contain a nucleophilic fragment and are formed during isolation as a result of opening of the imidazolium ring in salts I under the influence of water or by moisture entering the reaction medium, were obtained in all cases. We were also able to extend the reaction to pyrroles.

## EXPERIMENTAL

The PMR spectra of dimethyl sulfoxide (DMSO) solutions of the compounds were recorded with a Varian XL-100 spectrometer (100 MHz) at 35°; the chemical shifts (δ, ppm) are presented relative to tetramethylsilane. The accuracy in the measurement of the chemical shifts was ±0.01. The mass spectra were obtained by using the technique of direct introduction of the samples into the ion source with a Varian MAT-311 spectrometer (the accelerating voltage was 3 kV, the cathode emission current was 1.0 mA, and the ionizing voltage was 70 eV). The apparent masses of the metastable transitions were recorded with a partially unadjusted MKh-1303 spectrometer. The IR spectra of solutions of the compounds in $CCl_4$, $CHCl_3$, n-butanol, tetrahydrofuran (THF), and acetonitrile were recorded with a UR-20 spectrometer. Chromatography in a loose thin layer of aluminum oxide (activity II on the Brockmann scale) was accomplished in a chloroform–benzene–hexane–methanol system (30 : 6 : 1 : 1) with development by iodine vapors and in UV light.

1,3-Diacetyl-2-(3'-indolyl)-4-imidazoline (IIc). A) A mixture of 0.68 g (0.01 mole) of imidazole, 0.58 g (0.005 mole) of indole, and 0.63 g (0.01 mole) of acetyl chloride in 20 ml of dry benzene was refluxed for 2 h, after which it was cooled and treated with 50 ml of water. The benzene layer was separated, washed with water, and dried, and the benzene was removed by distillation. The residue was recrystallized from butanol to give 0.3 g (22.4%) of a product with mp 214-215° (from n-butanol) and $R_f$ 0.23. Found: C 66.7; H 5.7; N 15.3%. $C_{15}H_{15}N_3O_2$. Calculated: C 66.9; H 5.6; N 15.6%.

B) A mixture of 1.1 g (0.01 mole) of N-acetylimidazole, 0.58 g (0.005 mole) of indole, and 0.3 g (0.005 mole) of acetyl chloride was refluxed for 2 h, after which it was worked up by the method described above to give 0.4 g (28%) of 1,3-diacetyl-2-(3'-indolyl)-4-imidazoline with mp 215° (from n-butanol) and $R_f$ 0.23. Found: C 66.9; H 4.7; N 15.4%. $C_{15}H_{15}N_3O_2$. Calculated: C 66.9; H 5.6; N 15.6%.

C) A mixture of 0.68 g (0.01 mole) of imidazole and 1.17 g (0.01 mole) of indole in 30 ml of acetic anhydride was heated at 125° for 2 h, after which it was worked up as described above to give 1.0 g (37%) of 1,3-diacetyl-2-(3'-indolyl)-4-imidazoline with mp 214-215° (from n-butanol) and $R_f$ 0.23. Found: C 66.7; H 5.7; N 15.4%. $C_{15}H_{15}N_3O_2$. Calculated: C 66.9; H 5.6; N 15.6%.

Compounds IIa-o were obtained by method A (the chief characteristics are presented in Table 1).

Reaction of 1,3-Dibenzoyl-2-(3'-indolyl)-4-imidazoline with Triphenylmethyl Perchlorate. A solution of 0.34 g (1 mmole) of triphenylmethyl perchlorate in 10 ml of dry acetonitrole was added to a solution of 0.4 g (1 mmole) of 1,3-dibenzoyl-2-(3'-indolyl)-4-imidazoline (IId) in 10 ml of dry acetonitrile, and the mixture was maintained at room temperature for 5 min. It was then poured into 150 ml of dry ether, and the resulting precipitate was removed by filtration and washed with ether. The salt was purified by reprecipitation from acetonitrile by the addition of ether. The yield of 1,3-dibenzoyl-2-(3'-indolyl)imidazolium perchlorate, with mp 160-161°, was 0.63 g (61.2%). Found: C 61.0; H 4.1; N 8.8; Cl 6.8%. $C_{25}H_{18}N_3O_6Cl$. Calculated: C 61.0; H 3.7; N 8.5; Cl 7.2%.

The other 1,3-diacyl-2-(3'-indolyl)imidazolium perchlorates IIIa-h (Table 2) were similarly obtained. After separation of the crystals of the salt in the filtrate, 50 ml of water was added, and the ether layer was separated, washed with water, and dried. The ether was removed by distillation, and the residue was recrystallized from butanol. The yield of triphenyl(3'-indolyl)methane, with mp 208-209° (from butanol) and $R_f$ 0.5, was 0.10 g (27.7%). Found: C 90.3; H 6.2; N 3.8%. $C_{27}H_{21}N$. Calculated: C 90.2; H 5.9; N 3.9%.

Triphenyl(3'-indolyl)methane (IV). A mixture of 0.12 g (1 mmole) of indole and 0.34 g (1 mmole) of triphenylmethyl perchlorate in 10 ml of dry acetonitrile was refluxed for 5 min, after which it was cooled and treated with 50 ml of water. The aqueous mixture was extracted with ether, and the ether extracts were washed with water and dried. The ether was removed by distillation, and the residue was recrystallized from butanol. The yield of triphenyl(3'-indolyl)methane, with mp 207-208° (from n-butanol) and $R_f$ 0.5, was 0.3 g (83.3%). Found: C 90.3; H 6.0; N 3.6%. $C_{27}H_{21}N$. Calculated: C 90.2; H 5.9; N 3.9%.

N,N'-Dibenzoyl-1,2-diaminoethylene (VII). A) A mixture of 0.68 g (0.01 mole) of imidazole and 2.3 ml (0.02 mole) of benzoyl chloride in 25 ml of dry benzene was refluxed for 2 h, after which it was cooled and treated with 50 ml of 10% ammonium hydroxide. The benzene layer was separated, washed with water, and dried. The benzene was removed by distillation, and the residue was recrystallized from ethanol to give 1 g (37%) of a product with mp 195-196° (from ethanol) and $R_f$ 0.21. Found: C 72.3; H 5.2; N 10.3%. $C_{16}H_{14}N_2O_2$. Calculated: C 72.3; H 5.3; N 10.5%.

B) A 0.5-g (1 mmole) sample of 1,3-dibenzoyl-2-(3'-indolyl)imidazolium perchlorate was allowed to stand in 25 ml of 10% ammonium hydroxide at room temperature for 5 min. The solid residue was separated, washed with water, and recrystallized from ethanol to give 0.2 g (74%) of N,N'-dibenzoyl-1,2-diaminoethylene with mp 195-196° (from ethanol) and $R_f$ 0.21. Found: C 72.2; H 5.4; N 10.6%. $C_{16}H_{14}N_2O_2$. Calculated: C 72.2; H 5.3; N 10.5%.

N,N'-Dibenzoyl-1,2-(diaminodibromo)ethane (VIII). A mixture of 1.33 g (0.005 mole) of N,N'-dibenzoyl-1,2-diaminoethylene and 0.4 g (0.005 mole) of $Br_2$ in 25 ml of dry chloroform was refluxed for 5 min, after which it was cooled, and the resulting precipitate was removed by filtration and washed with dry chloroform to give 1.5 g (71.4%) of a product with mp 169-170° (from chloroform). Found: C 45.0; H 3.2; Br 37.5; N 6.8%. $C_{16}H_{14}Br_2N_2O_2$. Calculated: C 45.1; H 3.3; Br 37.6; N 6.6%.

N,N'-Dibenzoyl-1,2-(diaminodiethoxy)ethane (IX). A) A mixture of 1.33 g (0.005 mole) of N,N'-dibenzoyl-1,2-diaminoethylene and 0.4 g (0.005 mole) of $Br_2$ in 25 ml of dry ethanol was refluxed for 5 min, after which the precipitate was removed by filtration and recrystallized from n-butanol to give 1 g (56.1%) of a product with mp 240-241° (from butanol) and $R_f$ 0.58. Found: C 67.3; H 6.7; N 8.0%. $C_{20}H_{24}N_2O_4$. Calculated: C 67.4; H 6.7; N 7.8%.

B) A suspension of 0.43 g (1 mmole) of N,N'-dibenzoyl-1,2-(diaminodibromo)ethane in 25 ml of dry ethanol was refluxed for 5 min, after which it was cooled, and the resulting precipitate was removed by filtration and recrystallized from butanol to give 0.27 g (75%) of a product with mp 240-241° (from n-butanol) and $R_f$ 0.58. Found: C 67.3; H 6.5; N 8.2%. $C_{20}H_{24}N_2O_4$. Calculated: C 67.4; H 6.7; N 7.9%.

N,N'-Diacetyl-2-(2'-pyrrolyl)benzimidazoline (IIp). A mixture of 2.36 g (0.02 mole) of benzimidazole, 0.67 g (0.01 mole) of pyrrole, and 64 g (0.02 mole) of acetyl chloride in 25 ml of dry benzene was refluxed for 2 h, after which it was worked up as described for IIa-o. The yield of IIp, with mp 223-224° and $R_f$ 0.44, was 0.8 g (20%). PMR spectrum, δ: 2.20 ($CH_3$), 5.95 (CH), 10.55 (N–H), and 6.75-8.05 ppm (aromatic protons). The integral intensity ratio of the signals was 7 : 6 : 1 : 1. Found: C 66.7; H 6.0; N 15.2%. $C_{15}H_{15}N_3O_2$. Calculated: C 66.4; H 6.3; N 15.5%; M 269 (mass spectrometrically).

Reaction of N,N'-Diacetyl-2-(3'-indolyl)benzimidazolium Perchlorate with $NH_4OH$. A mixture of 1 g (0.0024 mole) of N,N'-diacetyl-2-(3'-indolyl)benzimidazolium perchlorate (IIIf) and 20 ml of concentrated $NH_4OH$ was allowed to stand at room temperature for 5 min, after which the resulting resin was separated, dried, and washed with methanol to give 0.05 g (14%) of indole-3-carboxylic acid with mp 210-218° (mp 210-218° [16]). The methanol filtrate was worked up to give 0.05 g (10.9%) of XI with mp 180-181° (mp 181-182° [16]). The ammoniacal filtrate remaining after separation of the resin was cooled to precipitate 0.5 g (65.8%) of yellow crystals of N,N'-diacetyl-2-(3'-indolenylidene)benzimidazoline (X) with mp 161-162° (from 70% ethanol). UV spectrum (in ethanol): $\lambda_{max}$ 360 nm (recorded with a Specord spectrophotometer). Found: C 71.6; H 5.0; N 13.3%. $C_{19}H_{15}N_3O_2$. Calculated: C 71.9; H 4.7; N 13.2%.

Reaction of N,N'-Dibenzoyl-2-(3'-indolyl)benzimidazoline with Triphenylmethyl Perchlorate. A mixture of 0.88 g (0.002 mole) of N,N'-dibenzoyl-2-(3'-indolyl)benzimidazoline and 0.6 g (0.002 mole) of triphenylmethyl perchlorate in 20 ml of dry acetonitrile was allowed to stand at room temperature for 5 min, after which the resulting white precipitate of N,N'-dibenzoyl-o-phenylenediamine was removed by filtration and recrystallized from glacial acetic acid to give 0.16 g (25.4%) of a product with mp 301-302°. Ether and water were added to the filtrate, and the ether layer was separated and dried. The ether was removed by distillation, and the residue was recrystallized from 70% ethanol. The yield of N-benzoyl-2-(3'-indolyl)benzimidazole, with mp 170-171° and $R_f$ 0.26, was 0.35 g (52.2%). IR spectrum, ν: 3480 (NH), 1665 (C=O), 1420 (C–N), 1550 (C=N) (characteristic for azoles), and 1590-1600 cm$^{-1}$ (CH) (aromatic). Found: C 78.0; H 4.7; N 12.1%. $C_{22}H_{15}N_3O$. Calculated: C 78.0; H 4.7; N 12.1%.

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# FORMATION OF 1-PYRAZOLINE 1,2-DIOXIDES BY OXIDATION OF 1,3-HYDROXYLAMINO OXIMES

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UDC 547.4'722.2'775:542.943

Cyclization with the formation of an N—N bond and simultaneous bromination, which lead to 3-bromo-1-pyrazoline 1,2-dioxides, apparently through a step involving the dinitroso derivative, occur in the reaction of sodium hypobromite with 1,3-hydroxylamino oximes. Dehydrobromination of the bromopyrazoline leads to the corresponding 3H-pyrazole. The same treatment of acetylacetone dioxime gives 4H-dibromo-3,5-dimethyl-4H-pyrazole 1,2-dioxide, which is readily hydrolyzed to the corresponding 4-oxo derivative. Data from the IR, UV, and PMR spectra are presented.

We have previously shown that the reaction of tertiary 1,2-hydroxylamino oximes with sodium hypobromite leads to 3-bromo-1,2-diazetine 1,2-dioxide [1]. In the present research we examine the possibility of the synthesis of 1-pyrazoline 1,2-dioxides from 1,3-hydroxylamino oximes.

A colorless crystalline compound (IIa) with the composition $C_6H_{11}BrN_2O_2$ is formed by treatment of N-(4-oximino-2-methyl-2-pentyl)hydroxylamine (Ia) with excess sodium hypobromite. Absorption with $\lambda_{max}$ 286 nm (log ε 3.88) is observed in the UV spectrum of IIa, and its IR spectrum contains two intense bands at 1380 and 1490 cm$^{-1}$, which is characteristic for cis-dimeric nitroso compounds [2], and an intense band at

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Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 248-251, February, 1944. Original article submitted January 28, 1976.