0.6 g (37%) of a product with mp 177-179° (from 80% ethanol). IR spectrum: 3400 and 3280 (NH_2), 1680 (CO) cm^{-1}. Found: C 71.1; H 6.1; N 12.0%. $C_{20}H_{19}N_3O \cdot H_2O$. Calculated: C 71.6; H 6.0; N 12.5%.

B) A total of 200 ml of 2 N NaOH and 5 g (0.3 mole) of sodium hydrosulfite were added to a solution of 2.3 g (5 mmole) of XII in 200 ml of 80% ethanol, and the mixture was gradually heated to 80° and allowed to stand at this temperature until it became completely colorless (1 h). It was then filtered, and the filtrate was cooled and extracted with ether. The ether extract was evaporated to give 0.3 g (19%) of a product with mp 177-179°. The product was identical to the product obtained by method A.

LITERATURE CITED

1. A. A. Druzhinina and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 12, 1658 (1976).
2. F. S. Babichev, G. P. Kutrov, and M. Yu. Kornilov, Ukr. Khim. Zh., 36, No. 9, 909 (1970).
3. P. M. Kochergin, Yu. N. Sheinker, A. A. Druzhinina, R. M. Palei, and L. M. Alekseeva, Khim. Geterotsikl. Soedin., No. 6, 826 (1971).
4. A. A. Druzhinina, P. M. Kochergin, and L. M. Alekseeva, Khim. Geterotsikl. Soedin., No. 3, 405 (1972).
5. A. A. Druzhinina and P. M. Kochergin, USSR Author's Certificate No. 196,867; Byul. Izobr., No. 12, 40 (1967).
6. A. A. Druzhinina and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 3, 532 (1967).
7. R. M. Palei and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 3, 536 (1967).
8. A. A. Druzhinina and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 3, 527 (1967).
9. A. A. Druzhinina, P. M. Kochergin, and N. P. Bychkova, Khim. Geterotsikl. Soedin., No. 5, 856 (1969).

REACTIONS WITH ELECTRON TRANSFER TO N-ACYLHETEROAROMATIC CATIONS

A. K. Sheinkman, A. P. Kucherenko,
I. V. Kurkurina, N. A. Klyuev,
and E. N. Kurkutova

UDC 547.785.5'82'833'836

The behavior of some benzoquinolines and imidazoles in reactions with acylating agents in the presence of zinc dust was investigated. The possibility of free-radical hetarylation under these conditions of organic compounds by the intermediately formed N-acylheteroaromatic radicals was established. The structure of 2,2'-diacetyl-1,1',2,2'-tetrahydro-1,1'-diisoquinolyl was determined by means of x-ray diffraction analysis.

The electrophilicity of N-heteroaromatic cations increases as the electron-acceptor properties of the substituents attached to the heteroatom increases [1] and becomes particularly high in the case of N-acylheteroaromatic cations. The high electrophilicity of the latter is manifested not only by the fact that they can readily add to reaction centers with increased electron density (the so-called hetarylation reaction [2]): reactions involving one-electron transfer to the heteroring, which leads to the formation of N-acylheteroaromatic radicals, are also facilitated in this series. The anions themselves of the corresponding salts [2] and various metals can act as electron donors for cations of this sort, and, in contrast to N-alkylpyridinium salts, which are reduced only by sodium amalgam under severe conditions, the reduction of N-acyl salts proceeds at room temperature under the influence of zinc and even less active metals [3]. The resulting N-acylpyridine radicals are extremely stable in some cases and may exist in the crystalline state for a rather long time, but they most often immediately recombine to give 1,1'-diacyl-1,1',4,4'-tetrahydro-4,4'-dipyridyls. This reaction has been extended to N-acylpyridinium and benzopyridinium salts [4, 5]. However, N-acyl salts of acridine were re-

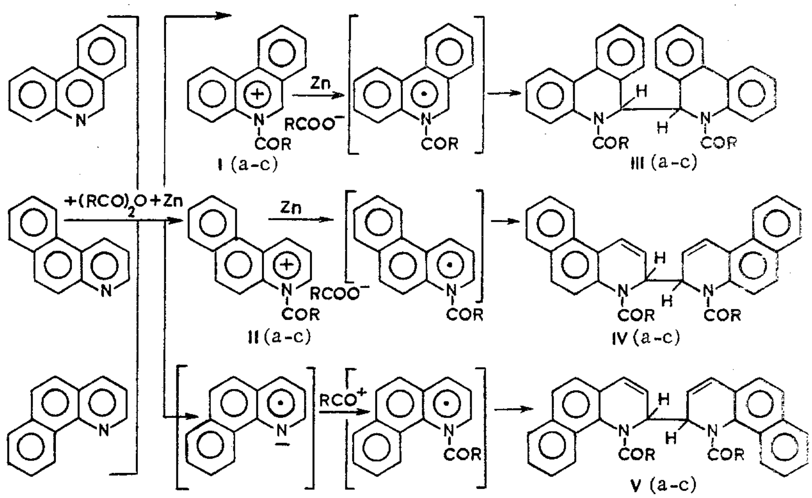
---

Donetsk State University, Donetsk 340055. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 229-237, February, 1977. Original article submitted December 29, 1975; revision submitted May 13, 1976.

duced under similar conditions to N-acylacridans without forming dimers [6]. This can evidently be explained by the higher stability of the N-acylacridinyl radical, which, under the reaction conditions does not have time to recombine but rather is reduced to the anion, which in acidic media adds a proton to give N-acrylacridans.

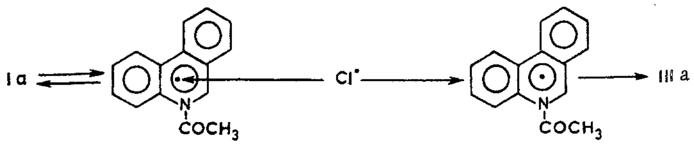
It seemed of interest to investigate the behavior, under similar conditions, of N-acyl salts of various dibenzopyridines — acridine isomers — and of some imidazoles and benzimidazoles, for which this reaction is generally unknown. In addition, it seemed of interest to us to attempt to use N-acylheteroaromatic radicals not only for the preparation of "doubled" heterocycles by their recombination but also for the hetarylation of various organic compounds.

It was found that, in contrast to acridine, phenanthridine and benzo[f]- and benzo[h]quinolines react with carboxylic acid anhydrides or chlorides in the presence of zinc dust to give the corresponding N,N'-diacyltetrahydro derivatives. The participation in the reaction of benzo[h]quinoline, which does not form N-acyl salts because of steric hindrance [7], can be explained by a change in the sequence of the individual reaction steps. In contrast to phenanthridine and benzo[f]quinoline, where N-acylheteroaromatic cations (I, II), which are subsequently reduced under the influence of Zn to N-acylheteroaromatic radicals (II), are formed as a result of initial attack of the acylating agents on the heteroatom, in the case of benzo[h]quinoline one observes the initial formation of an anion radical as a result of one-electron reduction with zinc dust, as in the reaction of zinc dust and other metals with pyridine and quinoline [8]. The resulting anion radicals subsequently undergo dimerization and acylation:



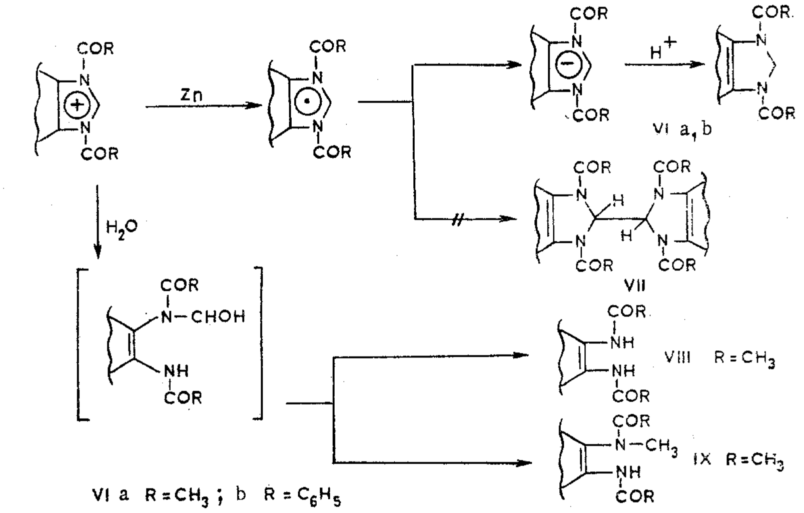
I—V a $R = CH_3$; b $R = C_2H_5$; $R = C_3H_7$

Compounds of the III and IV type (but not of the V type) are also formed by simple heating of benzoquinolines with acyl halides as a result of one-electron reduction of cation I (II) by the chloride ion:

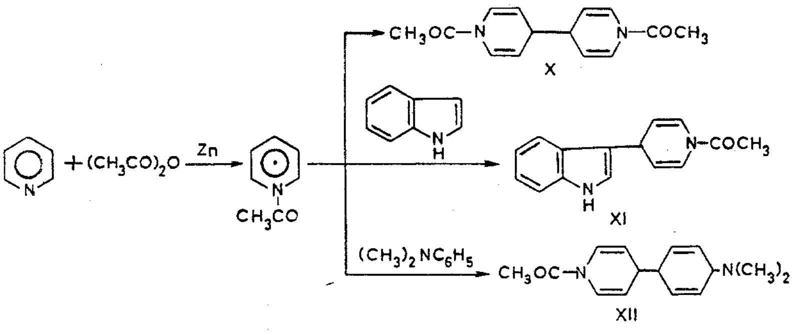


In the reaction of imidazole and benzimidazole with acylating agents and zinc dust under similar conditions, like acridine, they are reduced to 1,2-dihydroimidazoles also evidently due to the reduction of the intermediately formed N-acyl radicals to the corresponding anions and subsequent addition of a proton. Among the reaction products we also detected compounds with an open imidazole ring, which are formed in a side reaction probably as a result of decomposition of the unchanged 1,3-diacylimidazolium cations by water during isolation of the reaction products. Dimers of the VII type are not formed under these conditions.

In the case of pyridine we were able to show that the N-acylheteroaromatic radicals formed by the action of acetic anhydride on pyridine in the presence of zinc dust can be successfully used in situ for the hetarylation of nucleophilic organic compounds. In this case, in addition to dimers X, hetarylation products in which the



4 position of the pyridine ring and the position of the substrate with the maximum electron density were always found to be fused, are formed. For example:



Quinoline, isoquinoline, and benzoquinolines, which also form hetarylation products of the XI and XII type in addition to dimers of the III-V type when a nucleophilic organic compound is added to the reaction medium, behave similarly. Imidazole and benzimidazole form a difficult-to-separate mixture of reaction products under the investigated conditions.

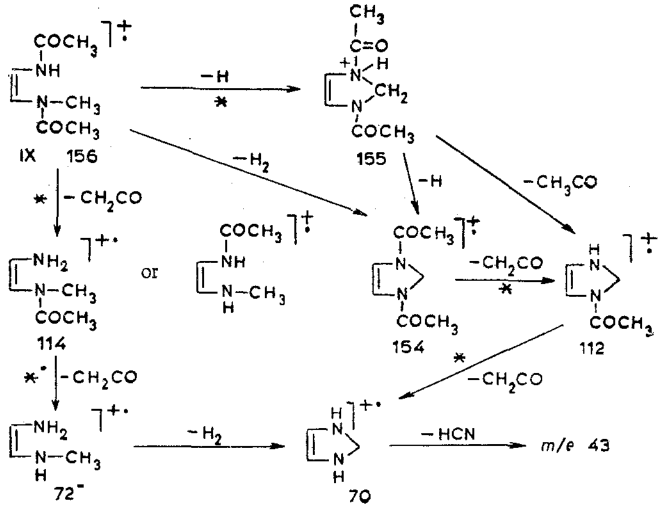
In order to establish the structure of the synthesized compounds we studied their IR and mass spectra and also used x-ray diffraction analysis and chemical transformations. It was expected that the corresponding dimers of the X type — 1,3,1',3'-tetraacyl-1,2,1',2'-tetrahydro-2,2'-diimidazolyls and benzimidazolyls — would be obtained during the reaction of imidazole and benzimidazole. We have previously shown [7] that these classes of compounds have molecular ions (M^+) with low stabilities with respect to electron impact ($W_M \approx$ 1-7% of the total ion current). We therefore used the following methods to record the $M^{+\cdot}$ peaks in the spectra of VI, VIII, and IX: We lowered the ionizing-electron energy to values close to the ionization potential of the sample (12-15 eV), and we adjusted the mass spectrometer and also lowered the accelerating voltage in order to detect the apparent mass of the metastable transition, which would correspond to fragmentation of $M^{+\cdot}$. It is known [7, 9] that elimination of a benzoyl grouping from M^+ is always realized in heterocycles containing this grouping. Then, according to the relationship

$$m^* = \frac{(m/e(M-\mathrm{PhCO})^+)^2}{m/eM^+},$$

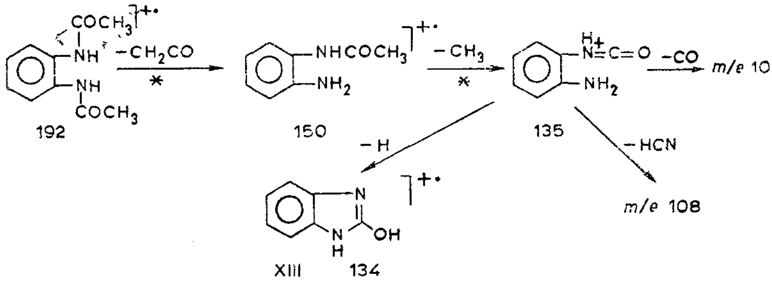
where m* is the apparent mass of the metastable transition, the mass number of M^+ of the starting compound can be determined [10]. However, these methods did not enable us to record the M^+ peak of the corresponding dimer. In all cases the molecular weights and the character of the fragmentation of the M^+ peaks of the compounds corresponded to structures VI, VIII, and IX. The formation of the open forms of the diacylated derivatives of the imidazoles (VIII, IX) was particularly unexpected.

The M^+ ion in the spectrum of IX undergoes fragmentation via two pathways: 1) successive dehydrogenation of M^+ (synchronous ejection of an H_2 molecule is also possible) leading ultimately to cyclization of the molecule through nitrogen [11] (to an imidazole structure); 2) stepwise splitting out of two ketene molecules rather than of an acetyl fragment (rearrangement with migration of the labile α-hydrogen atom of the methyl group to nitrogen [10-12]).

The second pathway in the fragmentation of M^+ is retained in the case of N,N'-diacetyl-o-phenylenediamine (VIII), but the absence of a methyl group attached to the amine nitrogen atom excludes the possibility of cyclization of the molecule in the first step of the fragmentation of M^+.



The elimination of a methyl group in the step involving the formation of the $(M - H_2C=C=O)^+$ ion (the apparent mass of the metastable transition m/e $150 \rightarrow$ m/e $135 + CH_3$ is 121.5) leads to the characteristic amide ion with m/e 135 [13], which by losing neutral HCN and CO fragments gives, in turn, fragment ions with m/e 108, 107, and 80:



The elimination of hydrogen from the amide ion entails a rearrangement process, as a result of which a fragment ion with a 2-hydroxybenzimidazole structure (XIII) is formed. The fragmentation of a molecule of this structure was studied in [14], and there is no doubt regarding the interpretation of the fragment ions formed as a result of its fragmentation.

In addition to bands of a carbonyl group 1660-1680 cm^{-1}, the IR spectra of VIII and IX contain absorption bands of an NH group at 3200-3500 cm^{-1}, and this, together with the mass spectra, confirms the proposed

TABLE 1. N,N'-Diacyl Derivatives of Tetrahydrodibenzoquinolines (III-V)

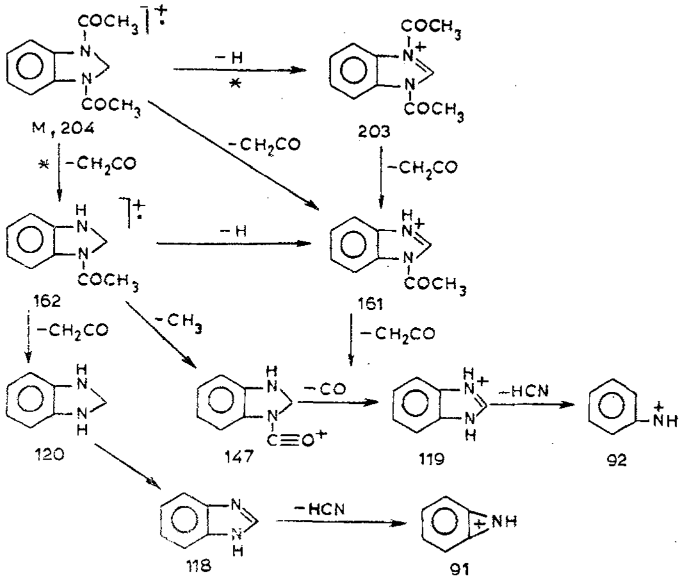
Compound	mp, °C*	M found†	M calc.	Found, % C	Found, % H	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N	Yield, %
IIIa	269—271	438,9	444,5	79,9	5,6	6,4	$C_{30}H_{24}N_2O_2$	81,1	5,4	6,3	25
IIIb	237—238	468 ‡	472,5	81,0	5,8	6,3	$C_{32}H_{28}N_2O_2$	81,2	6,0	6,0	16
IIIc	227—228	491	500.5	81,4	6.0	5,4	$C_{34}H_{32}N_2O_2$	81,6	6,4	5,6	10
IVa	239—241	459 ‡	444,5	81,1	5,8	6,6	$C_{30}H_{24}N_2O_2$	81,1	5,4	6,3	20
IVb	254—256	476,0	472,5	80.8	6,1	6,1	$C_{32}H_{28}N_2O_2$	81,2	6,0	6,0	13
IVc	232—234	521	500,5	81,2	6.1	5,4	$C_{34}H_{32}N_2O_2$	81,6	6,4	5,6	12
Va	245—247	462,6	444,5	81,1	5,8	6,5	$C_{30}H_{24}N_2O_2$	81,1	5,4	6,3	20
Vb	224—226	181	472,5	80,9	6.0	6,3	$C_{32}H_{28}N_2O_2$	81,2	6,0	6,0	16
Vc	218—220	489	500,5	81,2	6,3	5,3	$C_{34}H_{32}N_2O_2$	81,6	6,4	5,6	10

*Compound IVa was recrystallized from ethanol acetone, and the remaining compounds were recrystallized from acetone.

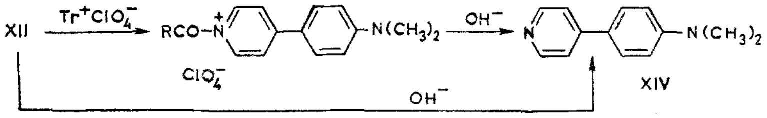
† By the Rast method.

‡ By a cryoscopic method.

structures. These absorption bands are absent in the spectra of VI at 3200-3500 cm^{-1}, whereas the characteristic absorption for the stretching vibrations of a carbonyl group is retained at 1660-1680 cm^{-1}. Two processes – elimination of only one hydrogen atom with aromatization of the imidazole ring and trivial detachment of a ketene molecule or a benzoyl residue – are always distinctly recorded in the fragmentation of the M^+ ions of compounds of this sort. Both processes ultimately, although via different pathways, lead to the formation of pseudomolecular ions of imidazole or benzimidazole, the fragmentation of which is well known [15]. The overall scheme of the fragmentation of compounds of the VI type is presented in the case of VIa:



Thus the IR spectra and the observed fragment ions completely confirm the structures of VI, VIII, and IX, formed in the reaction of imidazoles with acylating agents in the presence of zinc dust. All of the compounds of the XI and XII type obtained by reaction of pyridine and benzopyridines with indole and dimethylaniline in the presence of acetic anhydride and zinc dust were found to be identical to the previously described substances formed by hetarylation of the appropriate N-acyls salts in situ without zinc dust; this once again confirms the previously noted radical character of the hetarylation reaction [2]. Compound XII, which is formed only by radical pyridylation of dimethylaniline, constitutes an exception to this. However, dimethylaminophenylpyridines XIV are obtained immediately in the reaction of the corresponding N-acylpyridinium cations in the presence of Lewis acid catalyst [2] due to splitting out of a hydride ion from the intermediately formed XII and aromatization of the latter. In our case XII were also easily converted to XIV, and this proves their structure:



The hetarylation of N-acylpyridine radicals stops at the step involving the formation of XII because of the low electrophilicity of such radicals, which are incapable of splitting out a hydride ion, as occurs in the reactions of the corresponding N-acyl cations. The structures of compounds of the XII and XIV type were proved by determination of their molecular weights and comparison of their IR spectra with the spectrum described in [4] and the spectrum that we obtained for comparison under similar conditions of 2,2'-diacetyl-1,1',2,2'-tetrahydro-1,1'-diisoquinolyl (XV) (ν_{CO} 1660-1680 cm^{-1}). Compounds of this sort exist in three isomeric (d,*l*, and meso) forms [4], but we did not attempt to obtain the individual stereoisomers of the synthesized compounds.

It seemed of interest to determine the structure of one of the established stereoisomeric forms of such compounds in the case of the well-studied XV (Figs. 1 and 2). The structure of XV was deciphered by the Sayre–Zachariasen–Cochran method by means of Rentgen-70 automated programs [16]. The chief features of the structure of 2,2'-diacetyl-1,2,1',2'-tetrahydro-1,1'-diisoquinolyl (XV) are apparent from Fig. 1. The structure is composed of discrete molecules linked by van der Waals forces. The geometry of this compound is shown in Fig. 2. The intramolecular bond lengths and the valence angles are in satisfactory agreement with the literature data [17]. The C_1-C_9 (1.48 Å), $C_{1'}-C_{9'}$ (1.49 Å), C_4-C_{10} (1.46 Å), $C_{4'}-C_{10'}$ (1.42 Å), and $C_1-C_{1'}$ (1.55 Å) distances range from ~1.48 to 1.50 Å, which is the normal length for the $C_{sp^2}-C_{sp^2}$ bond, whereas the decrease in the C_3-C_4 and $C_{3'}-C_{4'}$ distances to 1.31 and 1.37 Å, respectively, indicates an increase in the order of this bond. The $N-C_{11}$ (1.37 Å) and $N'-C_{11'}$ (1.34 Å) distances between the heteroatom and the carbonyl carbon

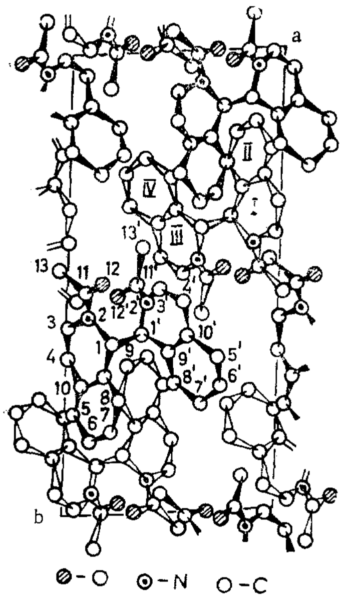


Fig. 1

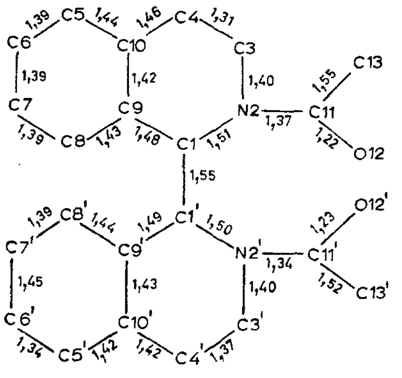


Fig. 2

Fig. 1. Crystal structure of 2,2'-diacetyl-1,2,1',2'-tetrahydro-1,1'-diisoquinolyl.

Fig. 2. Bond lengths in the 2,2'-diacetyl-1,2,1',2'-tetrahydro-1,1'-diisoquinolyl molecule.

TABLE 2. Deviations (σ) of Some Atoms from the Planar Fragments of the Molecule

Pyridine ring (I)		Benzene ring (II)		N-Acetyl group		Pyridine ring (III)		Benzene ring (IV)		N-Acetyl group	
$-6,16x+2,66y+$ $+7,26z+2,41=0$		$6,96x+0,44y-$ $-6,36z-4,37=0$		$5,47x-3,64y+$ $+7,59z-5,14=0$		$6,04x-3,12y-$ $-7,35z-0,10=0$		$-5,08x+7,92y+$ $+7,38z-2,18=0$		$0,80x-6,17y+$ $+9,46z-0,63=0$	
atoms	σ, Å	atoms	σ, Å	atoms	σ, Å	atoms	σ, Å	atoms	σ, Å	atoms	σ, Å
C (1)	0,24	C (5)	−0,01	N (2)	−0,15	C (1')	−0,26	C (5')	0,00	N (2')	−0,04
N (2)	−0,15	C (6)	0,03	C (11)	0,15	N (2')	0,21	C (6')	−0,02	C (11')	−0,12
C (3)	−0,02	C (7)	−0,01	O (12)	0,04	C (3')	−0,01	C (7')	0,02	C (12')	0,12
C (4)	−0,09	C (8)	−0,02	C (13)	0,00	C (4')	−0,13	C (8')	0,00	C (13')	0,03
C (9)	−0,14	C (9)	0,03			C (9')	0,13	C (9')	0,01		
C (10)	−0,08	C (10)	−0,01			C (10')	0,05	C (10')	0,01		

atom of the acetyl group constitute evidence for an increase in the order of the exocyclic C−N bond. To determine the real conformation of the molecule we obtained the equations of the planes drawn through the individual fragments of the model. The deviations of the atoms from these planes are given in Table 2. The dihedral angles between the planes passing through the benzene and pyridinium rings of the molecule are ~10°. The angles between the planes through the N-acetyl groups and the isoquinoline rings are ~50°.

EXPERIMENTAL

The mass spectra of the compounds were obtained with a Varian Mat-311 spectrometer at an accelerating voltage of 3 kV, an ionizing voltage of 70 eV, and a cathode emission current of 300 μA (by direct introduction of the samples into the ion source at 70°). The IR spectra of $CHCl_3$ solutions of the compounds were also obtained. Thin-layer chromatography (TLC) was carried out on activity II Al_2O_3 in a benzene−hexane−chloroform−acetone system (1 : 6 : 30 : 1) with development by iodine vapors.

1,1'-Diacyl-1,2,1',2'-tetrahydro-2,2'-dibenzo[f]quinolines (III) (Typical Method). A 1.5-g sample of zinc dust was added uniformly in the course of 2 h at 80-90° in a stream of dry nitrogen to a solution of 1.79 g (0.01 mole) of benzo[f]quinoline in 0.1 mole of the appropriate anhydride, after which the mixture was allowed to stand at the same temperature for 7-8 h. The contents of the flask were then subjected to steam distillation, and the residue in the distillation flask was extracted repeatedly with ether. The ether was removed by distillation, and the residue was chromatographed and recrystallized from acetone (IVa was recrystallized from acetone−ethanol). The III-V obtained by this method are presented in Table 1. The same compounds were formed by refluxing benzene solutions of the benzoquinoline bases with the appropriate acid chlorides.

2,2'-Diacetyl-1,1',2,2'-tetrahydro-1,1'-diisoquinolyl (XV). This compound, with mp 196-198° (from butanol) (according to the data in [4] the d*l* isomer has mp 190-191°), was obtained as described above. Two compounds with mp 255-257° (from hexanol) and mp 196-198° (from butanol), corresponding to the meso and d*l* isomers [4], were obtained by refluxing 0.1 mole of isoquinoline and 0.05 mole of acetyl chloride in benzene for 5 h without zinc dust.

Hetarylation with N-Acylheteroaromatic Radicals (Typical Method). Activated zinc dust (7 g) was added gradually at 25-30° in a dry nitrogen atmosphere to a solution of 0.1 mole of N-heteroaromatic compounds in 28 ml of acetic anhydride, after which 0.1 mole of nucleophilic organic compound was added, and the mixture was maintained at 70-75° for another 8 h. It was then subjected to steam distillation, and the residue in the distillation flask was dried and recrystallized from a suitable solvent. This method was used to obtain the previously described 1-acetyl-4-(3'-indolyl)-1,4-dihydropyridine (in 40% yield), 2-acetyl-4-(p-dimethylaminophenyl)-1,2-dihydroquinoline (in 34% yield) and others in 35-45% yields, as well as the previously undescribed 1-acetyl-4-(p-dimethylaminophenyl)-1,4-dihydropyridine (XII), with mp 82-83° (from cyclohexane) and R_f 0.35 in 35% yield. IR spectrum: ν_{CO} 1660 cm^{-1}. Found: C 74.2; H 7.5; N 11.9%. $C_{15}H_{18}N_2O$. Calculated: C 74.3; H 7.5; N 11.6%. 4-(p-Dimethylaminophenyl)pyridine, with mp 233-234° [from dimethylformamide (DMF)] [18], was obtained by refluxing the latter in ethanolic KOH.

Reaction of Benzimidazoles with Acetic Anhydride in the Presence of Zinc Dust. Activated zinc dust (7 g) was added at room temperature in a stream of dry nitrogen to a solution of 11.8 g (0.1 mole) of benzimidazole in 40 ml of acetic anhydride, and the mixture was then stirred for 24 h. The white precipitate was removed by filtration and recrystallized from acetone. The yield of 1,3-diacetyl-1,2-dihydrobenzimidazole (VIa), with mp 146-147°, was 3.4 g (16%). IR spectrum: 1660 cm^{-1}. Mass spectrum:* 43 (67.5), 63 (27.5), 64 (32.5), 65 (90.8), 66 (13.3), 77 (15.0), 78 (8.3), 90 (20.0), 21 (40.0), 92 (45.0), 93 (14.2), 118 (48.3), 119 (98.7), 120 (96.2), 121 (13.3), 147 (17.2), 161 (30.8), 162 (90.0), 163 (14.2), 203 (9.3), 204 (100.0), 205 (12.4). Found: C 64.6; H 5.6; N 14.0%, $C_{11}H_{12}N_2O_2$. Calculated: C 64.7; H 5.9; N 13.7%.

After separation of the crystals of VIa, the acetone mother liquor was evaporated in vacuo, and the residue was recrystallized from isopropyl alcohol. The yield of N,N'-diacetyl-o-phenylenediamine VIII, with mp 183-185°, was 4.2 g (21%). IR spectrum: ν_{CO} 1660 cm^{-1} and 3210 cm^{-1}. Mass spectrum: 43 (58.6), 53 (23.7), 54 (5.5), 80 (100.0), 81 (12.0), 89 (10.0), 106 (10.0), 107 (79.6), 108 (91.1), 134 (18.9), 135 (32.3), 150 (39.5), 192 (8.9), 193 (1.3).

Similarly, the reaction of 3.4 g (0.05 mole) of imidazole in acetic anhydride with zinc dust at 30-35° for 4 h gave 1.1 g (14%) of N,N'-diacetyl-N-methylethylenediamine (IX) with mp 213-220° (from acetone). IR spectrum: ν_{CO} 1680 cm^{-1}, ν_{NH} 3150 cm^{-1}. Mass spectrum: 42 (12.5), 43 (24.5), 53 (6.3), 55 (5.0), 70 (100.0), 71 (7.3), 72 (5.8), 112 (16.5), 114 (6.8), 154 (20.7), 155 (13.2), 156 (41.4), 157 (3.3). Found: C 53.8; H 7.6; N 18.3%. $C_7H_{12}N_2O_2$. Calculated: C 53.8; H 7.8; N 17.9%.

The reaction of imidazole with benzoyl chloride and zinc dust gave N,N'-dibenzoyl-1,2-dihydroimidazole (VIb), with mp 300-301° (from isopropyl alcohol), in 32% yield. IR spectrum: ν_{CO} 1670 cm^{-1}. Mass spectrum: 67 (5.3), 68 (6.3), 69 (5.6), 77 (7.8), 105 (100.0), 106 (7.6), 121 (6.3), 122 (14.3), 145 (6.8), 146 (5.4), 172 (16.5), 173 (8.2), 201 (5.3), 277 (25.7), 278 (10.6), 279 (2.3). Found: C 74.0; H 5.3; N 10.0%. $C_{17}H_{14}N_2O_2$. Calculated: C 73.4; H 5.1; N 10.0%.

LITERATURE CITED

1. A. K. Sheinkman, L. M. Kapkan, L. G. Gakh, E. V. Titov, S. N. Baranov, and A. N. Kost, Dokl. Akad. Nauk SSSR, 193, 366 (1970).
2. A. K. Sheinkman, Khim. Geterotsikl. Soedin., No. 1, 3 (1974).
3. N. F. Kazarinova, E. P. Babin, K. A. Solomko, M. I. Kotelenets, A. A. Artamonov, and A. K. Sheinkman, Zh. Prakt. Khim., 36, 649 (1963).
4. A. Nielsen, J. Org. Chem., 35, 2498 (1970).
5. P. Altani and J. Bielmann, Compt. Rend., 271, 688 (1970).
6. A. Blont and J. Corley, J. Am. Chem. Soc., 69, 763 (1947).
7. A. K. Sheinkman, M. N. Mestechkin, A. P. Kucherenko, N. A. Klyuev, V. N. Poltavets, G. A. Mal'tseva,
8. L. A. Palagushkina, and Yu. B. Vysotskii, Khim. Geterotsikl. Soedin., No. 8, 1096 (1974).
9. A. K. Sheinkman, V. A. Ivanov, N. A. Klyuev, and G. A. Mal'tseva, Zh. Org. Khim., 9, 2550 (1973).

J. F. Bielmann and C. C. Hirth, Organic Mass Spectrometry, Vol. 2 (1969), p. 723.

---

*Here and subsequently, the intensity of the ion peaks in percent of the maximum peak in the spectrum is presented in parentheses.

10. A. A. Polyakova and R. A. Khmel'nitskii, Introduction to the Mass Spectrometry of Organic Compounds [in Russian], Khimiya, Moscow–Leningrad (1966).
11. R. T. Contts and K. W. Hindmarsh, Organic Mass Spectrometry, Vol. 2, (1969), p. 681.
12. O. Buchardt, A. M. Duffield, and C. Djerassi, Acta Chem. Scand., 22, 2329 (1968).
13. S. W. Tam, Organic Mass Spectrometry, 2, 729 (1969).
14. B. J. Millard and A. F. Temple, Organic Mass Spectrometry, 1, 285 (1968).
15. R. A. Khmel'nitskii, A. N. Kost, Reddi K. Kendal, and V. I. Vysotskii, Zh. Org. Khim., 5. 1153 (1969).
16. V. I. Andrianov. Z. Sh. Safina, and B. L. Tarnopol'skii, Zh. Strukt. Khim., 12, 1052 (1971).
17. G. B. Bokii, Crystal Chemistry [in Russian], Izd. Mosk. Gos. Univ., Moscow (1972).
18. E. Koenigs and E. Ruppelt, Ann., 509, 142 (1934).

IMIDAZOLES IN THE HETARYLATION REACTION

A. K. Sheinkman, T. V. Stupnikova,
N. A. Klyuev, L. Yu. Petrovskaya,
and V. G. Zhil'nikov

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:

---

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

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.