give 0.43 g (63%) of the 2-imidazoline with mp 122-124°C. Found; C 64.5; H 4.2; N 13.9%, $C_{11}H_9N_2Cl$. Calculated: C 64.7; H 4.4; N 13.7%. IR spectrum: 1630 (C=N), 2220 (C≡C), and 3260 cm^{-1} (NH). PMR spectrum: 7.56 (m, 4H, C_6H_4), 7.49 (br s, 1H, NH), and 3.27 ppm (m, 4H, CH_2CH_2).

LITERATURE CITED

1. A. V. Eremeev, D. A. Tikhomirov, and E. E. Liepin'sh, Khim. Geterotsikl. Soedin., No. 2, 207 (1977).
2. A. V. Eremeev, D. A. Tikhomirov, and Yu. V. Shubina, Khim. Geterotsikl. Soedin., No. 3, 334 (1979).
3. G. E. Ham, J. Org. Chem., 29, 3052 (1964).
4. H. B. Sullivan and A. R. Day, J. Org. Chem., 29, 326 (1964).
5. A. V. Shchelkunov, Synthesis of Monosubstituted Acetylenes [in Russian], Nauka, Alma-Ata (1970), p. 148.
6. K. V. Auwers and E. Riss, Ber., 64, 220 (1931).

INTRAMOLECULAR REARRANGEMENT OF N-ACETYLINDOXYL OXIME

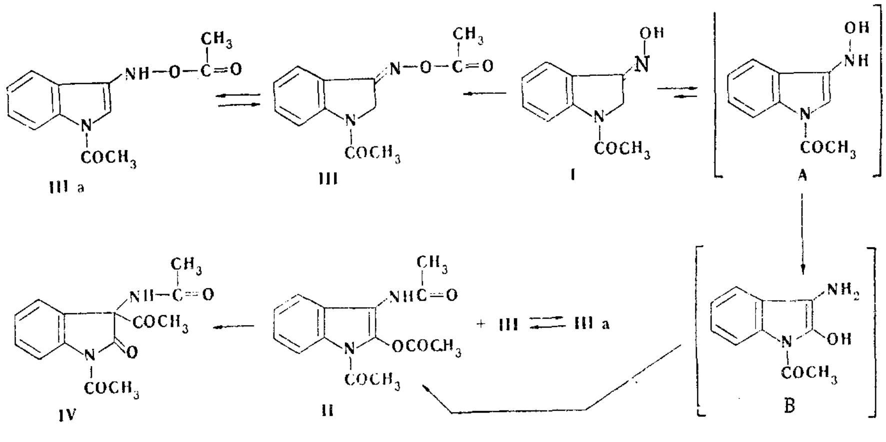
A. N. Grinev, S. Yu. Ryabova,
G. N. Kurilov, and K. F. Turchin

UDC 547.756:542.952

It was established that N-acetylindoxyl oxime is converted to N-acetylindoxyl acetyloxime when it is heated to 50°C in a mixture of acetic acid and acetic anhydride. If the reaction is carried out by refluxing, N-acetyl-2-acetoxy-3-acetamidoindole, which undergoes rearrangement to 1,3-diacetyl-3-acetamidooxindole when it is heated, is also formed.

We have previously demonstrated that N-acetylindoxyl arylhydrazones undergo a rearrangement of the o-benzidine type and form indolo[1,2-c]quinazolines [1].

In the present research we studied the behavior of N-acetylindoxyl oxime (I) under similar conditions, i.e., in the case of heating a solution of oxime I in acetic acid in the presence of acetic anhydride to the boiling point. As a result, we obtained N-acetyl-2-acetoxy-3-acetamidoindole (II) and N-acetylindoxyl acetyloxime (III).



In acidic media oxime I in tautomeric form A evidently undergoes a rearrangement of the type that phenylhydroxylamines undergo, in which the hydroxy group migrates to the α position of the indole ring to give N-acetyl-2-hydroxy-3-aminoindole (B). Under the reaction conditions rearrangement product B is acetylated to give II.

S. Ordzhonikidze All-Union Scientific-Research Institute of Pharmaceutical Chemistry, Moscow 119815. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1068-1070, August, 1980. Original article submitted January 9, 1980.

It might be assumed that acetyl derivative III rather than the N-acetylindoxyl oxime undergoes the rearrangement. We isolated III in 87% yield when the reaction mixture was heated to 50°C. However, refluxing N-acetylindoxyl acetyloxime in a mixture of acetic acid and acetic anhydride does not lead to the formation of II. This fact serves as a confirmation of the scheme proposed above for the formation of N-acetyl-2-acetoxy-3-acetamidoindole (II).

In addition to the signals of four protons of a phenyl ring at 7.15-8.40 ppm, singlet signals of the protons of three acetyl groups at 2.08, 2.37, and 2.58 ppm, as well as a broad singlet at 9.5 ppm corresponding to the NH proton of the $NHCOCH_3$ substituent in the 3 position, are observed in the PMR spectrum of II. One should especially note the absence in the spectrum of this compound of the signal of methylene protons of an indoxyl ring that is observed in the PMR spectra of I and III at 4.8-5.1 ppm.

In establishing the structure of III it was found that it exists in the different forms in the crystalline state and in solutions. A singlet signal at 5.02 ppm with an intensity of two proton units, which is characteristic for the methylene protons of indoxyl, appears in the PMR spectrum of acetyloxime III (~10% solution in d_7-dimethylformamide). The IR spectrum of a 0.02% solution of this compound in CCl_4 does not contain an absorption band characteristic for the NH group. In other words, the structure of N-acetylindoxyl acetyloxime in solutions corresponds to formula III. However, two absorption bands appear in the IR spectra of a mineral oil suspension and a KBr pellet of acetyloxime III at 3430 and 3520 cm^{-1}. This can be explained only by the fact that III exists in the IIIa tautomeric form in the crystalline state.

We also found that N-acetyl-2-acetoxy-3-acetamidoindole (II) undergoes rearrangement to 1,3-diacetyl-3-acetamidooxindole (IV) when it is heated. This sort of rearrangement was previously observed when 1-methyl-2-alkoxy-3-acetylindole was heated [2].

The structure of IV follows from the data from the IR spectrum, which contains four absorption bands of carbonyl groups at 1670, 1710, 1720, and 1750 cm^{-1}, and from the ^{13}C NMR spectrum, in which signals of carbonyl carbon atoms of a keto group at 194.8 ppm, three amide groups at 171.4, 170.4, and 168.7 ppm, six carbon atoms of a phenyl ring (four tertiary at 130.5, 125.7, 122.0, and 117.1 ppm and two quaternary at 141.2 and 124.7 ppm), three carbon atoms of methyl groups at 26.4, 23.7, and 22.2 ppm, and, finally, a quaternary sp^3-hybridized carbon atom bonded to a nitrogen atom (at 72.2 ppm) are observed.* In addition to the signals of the proton-containing groups enumerated above, a broad signal at 7.45 ppm corresponding to the proton of the NH group of the $NHCOCH_3$ substituent in the 3 position is observed in the PMR spectrum of IV.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of II-IV and of a KBr pellet and a 0.02% solution of III in CCl_4 (with a layer thickness of 50 mm) were recorded with a UR-10 spectrometer. The UV spectra of alcohol solutions of the compounds were recorded with an EPS-3 spectrophotometer. The PMR spectra were recorded with JEOL C60-HL (60 MHz) and Varian XL-100A (100 MHz) spectrometers with hexamethyldisiloxane as the internal standard. The ^{13}C spectrum was recorded with an XL-100A spectrometer (25.2 MHz) with tetramethylsilane as the internal standard. The course of the reaction and the individuality of the substances were monitored on Silufol UV-254 plates in ethyl acetate.

N-Acetyl-2-acetoxy-3-acetamidoindole (II). A mixture of 0.5 g (2.63 mmole) of N-acetylindoxyl oxime (I), 3 ml of glacial acetic acid, and 1 ml of acetic anhydride was heated to the boiling point, after which it was cooled and diluted with 8 ml of ether. The precipitate was removed by filtration, washed with ether, and dried to give 0.15 g (21%) of a product with mp 160-161°C (from methanol). IR spectrum: 1660, 1710, 1780 (3 C=O); 3270 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 234 (4.06), 272 (3.42) sh, and 300 nm (3.20) sh. PMR spectrum (in d_7-DMF): 2.08, 2.37, 2.58 (3 s, 3 $COCH_3$); 7.15-8.40 (m, aromatic protons); 9.5 ppm (br s, NH). Found: C 61.3; H 5.0; N 10.2%. $C_{14}H_{14}N_2O_4$. Calculated: C 61.3; H 5.2; N 10.2%.

N-Acetylindoxyl Acetyloxime (III). A suspension of 1.2 g (6.3 mmole) of N-acetylindoxyl oxime (I) in 8 ml of glacial acetic acid and 2.4 ml of acetic anhydride was heated to 50°C

---

*The range of ^{13}C chemical shifts at 160-180 ppm may correspond to the carbonyl carbon atoms of both N—C=O and O—C=O groups [3]; however, the presence of an O—C=O group in this case can be excluded on the basis that all four oxygen atoms of IV are carbonyl oxygen atoms.

with stirring. The resulting solution was cooled immediately, and the precipitate was removed by filtration, washed with ether, and dried to give 1.27 g (87%) of a product with mp 137-138°C (from ethyl acetate). IR spectrum (in CCl_4): 1670, 1770 cm^{-1} (2 $C=O$). UV spectrum, λ_{max} (log ε): 241 (4.41), 248 (4.39), 268 (4.23), and 330 nm (4.85). PMR spectrum (in d_7-DMF): 2.22, 2.30 (2 s, 2 $COCH_3$); 5.02 (s, CH_2); 7.00-8.40 ppm (m, aromatic protons). Found: C 62.2; H 5.3; N 12.1%. $C_{12}H_{12}N_2O_3$. Calculated: C 62.1; H 5.2; N 12.1%.

1,3-Diacetyl-3-acetamidooxindole (IV). A 0.4-g (1.46 mmole) sample of N-acetyl-2-acetoxy-3-acetamidoindole was heated on a Wood's metal bath at 180-190°C for 1-2 min, 2-3 ml of methanol was added to the melt, and the mixture was cooled. The precipitate was removed by filtration, washed with methanol, and dried to give 0.26 g (64%) of a product with mp 176.5-178°C (from methanol). IR spectrum: 1670, 1710, 1720, 1750 (4 $C=O$); 3350 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 240 nm (3.90) sh. PMR spectrum (in $CDCl_3$): 1.95, 2.04, 2.72 (3 s, 3 $COCH_3$); 7.00-8.35 (m, aromatic protons); 7.45 ppm (broad s, NH). Found: C 61.4; H 5.2; N 10.3%. $C_{14}H_{14}N_2O_4$. Calculated: C 61.3; H 5.2; N 10.2%.

LITERATURE CITED

1. G. N. Kurilo, S. Yu. Ryabova, and A. N. Grinev, Khim. Geterotsikl. Soedin., No. 6, 832 (1979).
2. L. Julian and A. Magnani, J. Am. Chem. Soc., 71, 3207 (1949).
3. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, New York (1972).

TRANSFORMATIONS OF 1,2-DIMETHYLPYRIDINIUM IODIDE UNDER THE INFLUENCE OF SULFITES OF CYCLIC AMINES

A. N. Kost,* T. V. Stupnikova,
V. N. Kalafat, R. S. Sagitullin,
and V. P. Marshtupa

UDC 547.82.1.412:542.945.22

The transformations of 1,2-dimethylpyridinium iodide under the influence of sulfites of morpholine, piperidine, and piperazine were investigated. It was established that it undergoes demethylation and recyclization both with and without exchange of an amino group when it is heated with aqueous solutions of the cyclic amines.

Several reaction pathways that depend on the structures of the reagents are possible in the reaction of nucleophiles with 1-alkylpyridinium salts. The data from deuterium exchange and NMR spectroscopy indicate that the CH acidity of the N-methyl group in the 1-methylpyridinium salts is negligible, that deuterium exchange through the CH_2 group in the 1-benzylpyridinium salt proceeds slowly, and that the principal process under the influence of alkoxide ion is deprotonation in the α position of the pyridine ring [1, 2]. The process appears to be somewhat different under the influence of the NH_2^- ion, which adds to the C_2 atom to give a dihydropyridine structure [3]. A similar capacity for addition was noted for $NO_2CH_2^-$ and $C_2H_5S^-$ ions, but in this case addition occurred at both the C_2 atom and the C_4 atom in the case of 3-substituted 1-alkylpyridinium salts [4]. The cyanide ion adds virtually only to the C_4 atom, and the process is reversible [5]. It is known [6] that attack by the hydroxide ion takes place preferably at the C_2 atom and leads to hydrolytic ring opening. In the case of the 1-(2,4-dinitrophenyl)pyridinium salt this opening process is observed even under the influence of piperidine. Finally, one should take into account the possibility of attack by the nucleophile on the carbon atom of the alkyl group bonded to the ring nitrogen atom, which leads to dealkylation [7]. The same final result can be observed in the case of ring opening with subsequent replacement of the methylamine fragment by an amine fragment and

---

*Deceased.

Donetsk State University, Donetsk 340055. M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1071-1074, August, 1980. Original article submitted January 4, 1980.

0009-3122/80/1608-0830$07.50