neutralized with ammonia. The precipitated VIa, e were removed by filtration, while VIb and VIc, which separated in the form of oils, were extracted with ether. The extract was then dried over anhydrous sodium sulfate, the solvent was removed by evaporation, and the residue was chromatographed on aluminum oxide. In the preparation of VId, 4 ml of formalin and 12 ml of a saturated solution of sodium carbonate were added to a solution of 0.01 mole of phosphonium salt IVd in 200 ml of water, and the mixture was stirred for 1 h. It was then worked up as described for VIb, c.

2-Vinylbenzimidazole Methiodides (VIIb-d). Methiodides VIIb-d were obtained by refluxing VIb-d with methyl iodide in alcohol for 8-10 h and were crystallized from alcohol—ether. The yields and melting points were as follows: 80% VIIb, mp 219°C; 92% VIIc, mp 172°C; 94% VIId, mp 190°C. The results of elementary analysis of VIIb-d were in agreement with the calculated values; the halogen content was determined by potentiometric titration.

LITERATURE CITED

1. I. I. Popov, P. V. Tkachenko, A. A. Zubenko, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 5, 663 (1978).
2. J. A. Preis, US Patent No. 2606175 (1952); Chem. Abstr., 47, 350 (1958).
3. C. Schuster, West German Patent No. 865304 (1953); Chem. Abst., 52, 18472 (1958).
4. C. C. Overberger, Kosters, T. St. Pierre, J. Pol. Sci., A-1, 5, 1987 (1967).
5. C. G. Overberger and K. Gerberding, J. Pol. Sci., Pol. Lett. Ed., 11, 465 (1973).
6. N. G. Kumar, J. Pol. Sci., Pol. Lett. Ed., 11, 461 (1973).
7. I. I. Popov, A. M. Simonov, and A. A. Zubenko, Khim. Geterotsikl. Soedin., No. 8, 1145 (1976).
8. C. B. Bachman and L. V. Heisei, J. Am. Chem. Soc., 7, 1985 (1949).
9. J. R. Merchant and D. S. Chothia, Indian J. Technol., 13, 814 (1975).
10. H. Scolnik, J. G. Miller, and A. R. Day, J. Am. Chem. Soc., 65, 1854 (1943).
11. W. Ozegowski, D. Krebs, and M. Wunderwald, J. Prakt. Chem., 20, 166 (1963).
12. N. P. Bednyagina and I. Ya. Postovskii, Zh. Obshch. Khim., 30, 3193 (1960).
13. H. Walba, W. I. Murrai, G. Knitson, and A. Diaz, J. Am. Chem. Soc., 88, 1692 (1966).
14. G. Drefal, G. Plotner, and F. Rudolph, Chem. Ber., 93, 998 (1960).
15. M. T. Le Bris, Bull. Soc. Chim. France, 3411 (1967).

PYRROLO[1,2-a]BENZIMIDAZOLES IN THE HETARYLATION REACTION

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The direct incorporation of isoquinoline, benzimidazole, and acridine residues in pyrrolo[1,2-a]benzimidazole and its derivatives was accomplished by the reaction of N-heteroaromatic compounds with pyrrolo[1,2-a]benzimidazole and its analogs in the presence of acylating agents.

The increased electron density in the pyrrole ring [1, 2] is responsible for the ease of electrophilic substitution reactions in pyrrolo[1,2-a]benzimidazoles (I). In the case of protonation [1, 2], acylation [3], nitration, diazo coupling, and nitrosation [4] it has been shown that the 1 position is the most reactive position in the benzimidazole (I) molecule; if the 1 position is occupied, the 3 position is then the most reactive. It seemed possible to us to accomplish the direct introduction of N-heterocyclic residues in such compounds under the influence of N-acyl heteroaromatic cations in situ under the conditions of the hetarylation reaction [5]. In fact, in the case of the reaction of I with isoquinoline and benzoyl chloride we obtained both the previously described benzoyl derivative and

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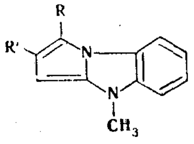
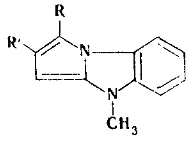
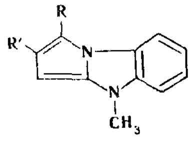
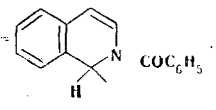
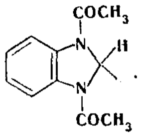
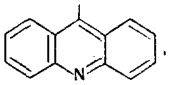
the isoquinoline derivative of pyrrolo[1,2-a]benzimidazole (II) in a ratio of ∿1:1, whereas acylation of I [3] rather than hetarylation was mainly observed in the presence of pyridine or quinoline. Both reaction pathways are also realized in the reaction of I with benzimidazole and acetic anhydride, where, in addition to the acetyl derivative of benzimidazole I, we obtained III. As in the case of the hetarylation of indolizine [6], the introduction of an acridine residue in I is easily accomplished by the action on it of acridine hydrochloride in dimethylformamide (DMF). As established previously in the case of acridinylation of dimethylaniline [7], the mechanism of this reaction involves hydride transfer from the intermediately formed dihydro derivative of acridine to acridine hydrochloride to give acridan and hetarylation product IV:


II


III


IV

II R =  , a R' = C_6H_5, b R' = CH_3, III R =  , R' = C_6H_5;

IV R =  , R' = C_6H_5

The direct incorporation of an acridine residue in the pyrrolo[4,5-b]thiazole and imidazo[1,2-a]pyridine molecules was similarly accomplished.

Characteristic $\nu_{C=O}$ bands (1660-1685 cm^{-1}) are observed in the IR spectra of II and III. Signals at δ 5.8-6.5 ppm (2-H, II and III), as well as at 1.85 ppm (CH_3) and 2.35 ppm ($COCH_3$) for III, and a complex multiplet at 6.80-8.42 ppm (aromatic protons) are recorded in the PMR spectra. Molecular-ion (M^+) peaks (479) and peaks of $[COC_6H_5]^+$ (105) and $[M - COC_6H_5]^+$ (374) fragment ions, which are formed by cleavage of the exocyclic C—N bond, are observed in the mass spectrum of IIa. Another process involving the fragmentation of the molecular ion is cleavage of the C—C bond between the two hetaryl rings to give $[M—R]^+$ (245) and $[R]^+$ (234) ions. Correspondingly, M^+ (417), $[M—R]^+$ (183) and $[R]^+$ (234) ion peaks are observed in the spectrum of IIb, and $[M]^+$ (448), $[R]^+$ (203), $[M—R]^+$ (245), $[M - CH_2{=}C{=}O]^+$ (375), and other ion peaks are observed in the spectrum of III. The mass spectrometric data completely confirm the structures of the synthesized compounds.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The mass spectra were obtained with a Varian MAT-311 spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 μA, an ionizing voltage of 70 eV, and an ion-source temperature of 115-130°C. The PMR spectra of solutions of the compounds in hexadeuterated dimethylsulfoxide (DMSO) were recorded with an XL-100 spectrometer at room temperature with tetramethylsilane as the internal standard. Chromatography in a loose thin layer of activity II aluminum oxide (Brockmann scale) was accomplished by elution with chloroform—benzene—hexane (30:6:1) and development with iodine vapors and in UV light.

1-(2-Benzoyl-1,2-dihydro-1-isoquinolyl)-2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole (IIa). A mixture of 2.5 g (50 mmole) of 2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole, 0.6 g (50 mmole) of isoquinoline, and 0.7 g (50 mmole) of benzoyl chloride in 10 ml of dry benzene was refluxed for 5 h, after which it was subjected to steam distillation, and the residue in the distillation flask was separated and recrystallized from methanol to give 0.8 g (32%) of a product with mp 275-276°C and R_f 0.5. Found: C 82.5; H 5.1; N 8.9%. $C_{33}H_{25}N_3O$. Calculated: C 82.7; H 5.2; N 8.8%. Workup of the reaction mixture also yielded 0.5 g (28%) of 1-benzoyl-2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole with mp 210-211°C (from methanol) and R_f 0.8. Found: C 82.5; H 5.0; N 8.3%. $C_{24}H_{18}N_2O$. Calculated: C 82.3; H 5.1; N 8.0%. According to the data in [3], this compound has mp 210-211°C.

1-(2-Benzoyl-1,2-dihydro-1-isoquinolyl)-2,4-dimethylpyrrolo[1,2-a]benzimidazole (IIb). This compound, with mp 155-156°C (from methanol) and R_f 0.3, was similarly obtained in 48% yield. Found: C 80.9; H 5.2; N 10.1%. $C_{28}H_{23}N_3O$. Calculated: C 80.6; H 5.5; N 10.3%. Workup of the reaction mixture yielded 1-benzoyl-2,4-dimethylpyrrolo[1,2-a]benzimidazole, with mp 144-145°C (from ethanol) and R_f 0.8 (mp 145°C [3]), in 35% yield.

1-(1,3-Diacetyl-2-benzimidazolinyl)-2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole (III). This compound was obtained by reaction of 1.2 g (50 mmole) of 2-phenyl-4-methylpyrrolo-[1,2-a]benzimidazole and 0.6 g (50 mmole) of benzimidazole in acetic anhydride for 1 h at room temperature. Workup gave 0.7 g (31%) of a product with mp 136-137°C (from n-butanol) and R_f 0.4. Found: C 75.3; H 5.7; N 11.7%. $C_{28}H_{24}N_4O_2$. Calculated: C 75.0; H 5.4; N 12.0%. Workup of the reaction mixture also gave 0.06 g (5%) of 1-acetyl-2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole with mp 146-147°C (from ethanol) and R_f 0.7 (mp 147°C [3]).

1-(9-Acridinyl)-2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole (IV). A mixture of 1.2 g (50 mmole) of 2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole and 2.2 g (100 mmole) of acridine hydrochloride in 10 ml of dry DMF was maintained at room temperature for 15 min, after which the resulting precipitate was removed by filtration and recrystallized from DMF to give 0.8 g (38%) of a product with mp 190-191°C and R_f 0.8. Found: C 78.6; H 5.5; N 10.0%. $C_{30}H_{21}N_3$. Calculated: C 78.9; H 5.5; N 10.0%. Workup of the filtrate gave 0.6 g (60%) of acridine with mp 170-171°C (from methanol). No melting-point depression was observed for a mixture of this product with a genuine sample.

A similar procedure was used to obtain the compounds below.

3-(9-Acridinyl)-4-methylpyrrolo[4,5-b]thiazole. This compound, with mp 249-250°C (from DMF) and R_f 0.5, was obtained in 25% yield. Mass spectrum, m/e (%):* 31 (4.2); 39 (3.2); 44 (3.8); 71 (3.6); 151 (3.8); 178 (4.3); 179 (14.4); 180 (11.1); 181 (4.1); 194 (3.0); 194.5 (4.1); 195 (8.9); 195.5 (3.0); 213 (8.1); 389 (6.8); 390 (100.0). Found: C 80.3; H 4.9; N 7.5; S 8.0%. $C_{26}H_{18}N_2S$. Calculated: C 80.0; H 4.6; N 7.2; S 8.2%.

1-(9-Acridinyl)-2-phenylimidazo[1,2-a]pyridine. This compound, with mp 291-292°C (from DMF) and R_f 0.5, was obtained in 30% yield. Mass spectrum, m/e (%): 44 (5.7); 51 (5.2); 73 (6.7); 78 (9.3); 183 (5.5); 184 (6.7); 185 (6.4); 185.5 (16.6); 186 (5.3); 264 (5.0); 266 (12.5); 267 (15.9); 291 (8.3); 292 (11.8); 293 (9.9); 367 (5.0); 368 (10.9); 369 (7.3); 370 (59.8); 371 (100.0). Found: C 84.4; H 4.3; N 11.2%. $C_{26}H_{17}N_3$. Calculated: C 84.1; H 4.6; N 11.3%.

LITERATURE CITED

1. M. Yu. Kornilov, G. G. Dyadyusha, and F. S. Babichev, Khim. Geterotsikl. Soedin., No. 5, 905 (1968).
2. L. M. Alekseeva, T. G. Dvoryantseva, N. V. Cherepanova, Yu. N. Sheinker, R. M. Palei, and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 8, 1132 (1972).
3. F. S. Babichev, G. P. Kutrov, and M. Yu. Kornilov, Ukr. Khim. Zh., No. 10, 1020 (1968).
4. F. S. Babichev, G. P. Kutrov, and M. Yu. Kornilov, Ukr. Khim. Zh., No. 9, 909 (1970).
5. A. K. Sheinkman, Khim. Geterotsikl. Soedin., No. 1, 3 (1974).
6. A. K. Sheinkman, V. I. Zherebchenko, T. V. Stupnikova, É. Portsel', and N. A. Klyuev, Khim. Geterotsikl. Soedin., No. 11, 1510 (1977).
7. A. K. Sheinkman, S. G. Potashnikova, and S. N. Baranov, Zh. Org. Khim., 6, 614 (1970).

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*The intensities are given in percent relative to the maximum peak.