## SYNTHESIS OF BROMO-SUBSTITUTED 2-FORMYLPYRROLES

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Information regarding substitution reactions in the 2-formylpyrrole series is virtually confined to data on the introduction of an isochlorosulfonylisocyanato [sic] group in the 4 position of the pyrrole ring, which gives the product in low yield [1]. We have found that the bromination of 2-formylpyrrole (I) with dioxane dibromide at 5°C in the presence of the calculated amount of concentrated alkali leads, depending on the way in which the reaction mixture is worked up, to 4-bromo-2-formylpyrrole (II) or 4,5-dibromo-2-formylpyrrole (III).



The positions of the bromine atoms in the compounds obtained were established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by comparison of the spectra with one another and with the spectra of 2-formylpyrrole. Data on the chemical shifts (CS) in the <sup>1</sup>H and <sup>13</sup>C NMR spectra for unsubstituted pyrrole were taken into account [2]. A coupling of 1.4 Hz, which was assigned, taking into account the data for aldehyde I, to the <sup>4</sup>J<sub>35</sub> coupling, is observed between the two ring protons of II, and, on the basis of this, it was concluded that the bromine atom is located in the 4 position. Taking into account the effect of the electronegative nitrogen atom, one of the <sup>1</sup>J<sub>CH</sub> constants in the spectra of the ring carbon atoms of I and II (182 and 187 Hz, respectively), which is substantially greater than the other, was assigned to  $C_{(s)}$ -H coupling. The absence of this coupling in the case of III makes it possible to conclude that the second bromine atom is located in the <sup>13</sup>C CS are in good agreement with the conclusions drawn. The <sup>13</sup>C NMR spectrum of the reaction mixture showns the presence of at least four compounds and does not contradict the assumption of the presence of I-III in the mixture.

<u>4-Bromo-2-formylpyrrole (II).</u> A solution of 16 g (0.1 mole) of bromine in 160 ml of dioxane was added with vigorous stirring in the course of 2 h at 5°C to a mixture of 0.1 mole of 2-formylpyrrole, 30 ml of dioxane, and 5.6 g of KOH in 20 ml of H<sub>2</sub>O, after which the mixture was filtered. The filtrate was shaken with 15 ml of 40% KOH, and the solvents were removed by distillation. The residue was diluted with water, and the aqueous mixture was poured into water. The solvent was removed by filtration to give 3.3 g (20%) of aldehyde II with mp 122-123°C (from ethyl acetate-hexane, 1:9). PMR spectrum (CD<sub>3</sub>OD),  $\delta$ : 180.5 (C=O), 134.5 [C(2)], 127.7 [C(5)], 122.5 [C(3)], and 99.2 ppm [C(4)], <sup>1</sup>J<sub>C</sub>(5)<sub>H</sub> = 187, <sup>1</sup>J<sub>C</sub>(3)<sub>H</sub> = 173, <sup>3</sup>J<sub>C</sub>(3), 5-H = 6, <sup>2</sup>J<sub>C</sub>(4), 3<sup>-</sup> or 5-H = 5, and <sup>3</sup>J<sub>C</sub>(5), 5-H = 7 Hz.

<u>4,5-Dibromo-2-formylpyrrole (III)</u>. This compound was obtained in the same way as II. After completion of the reaction, the mixture was filtered, the filtrate was poured into water, and the resulting precipitate was removed by filtration to give 6 g (20%) of aldehyde III with mp 154-155°C [from ethyl acetate-hexane (1:9)]. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD),  $\delta$ : 179.5 (CO), 135.2 [C<sub>(2)</sub>], 123.2 [C<sub>(3)</sub>], 113.3 [C<sub>(5)</sub>], and 101.9 ppm [C<sub>(4)</sub>]; <sup>1</sup>J<sub>CHO</sub> = 175,

All-Union Scientific-Research Institute of the Technology of Blood Substitutes and Hormonal Preparations, Moscow 109044. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 998-999, July, 1986. Original article submitted October 22, 1985.  ${}^{1}J_{C(3)}H = 176$ ,  ${}^{3}J_{CO}$ ,  ${}_{3}-H = 2$ , and  ${}^{3}J_{C(5)}$ ,  ${}_{3}-H = 9$  Hz. The results of elementary analysis of II and III were in agreement with the calculated values.

 $\frac{2-\text{Formylpyrrole (I).}}{2-\text{Formylpyrrole (I).}} \text{ PMR spectrum (CD_3OD), } \delta: 9.33 (CHO), 7.05 (5-H), 6.88 (3-H), and 6.18 ppm (4-H); <math>{}^{3}J_{34} = 3.6$ ,  ${}^{3}J_{45} = 2.4$ ,  ${}^{4}J_{35} = 1.4$ ,  ${}^{5}J_{5-H}, CHO = 1$  Hz.  ${}^{13}C$  NMR spectrum (CD\_3OD),  $\delta: 180.8 (CO), 134.2 [C(_2)], 128.3 [C(_5)], 122.5 [C(_3)], and 111.9 ppm [C(_4)];$  ${}^{1}J_{CHO} = 170, {}^{1}J_{C}(_{5})H = 182, {}^{1}J_{C}(_{3})H = 168, {}^{1}J_{C}(_{4})H = 170, {}^{1}J_{C}(_{5}),_{3-H} = 4, {}^{3}J_{C}(_{3}),_{5-H} = 6,$  ${}^{2}J_{C}(_{4}),_{3-} \text{ or } {}_{5-H} = 7.5, {}^{2}J_{C}(_{4}),_{5-} \text{ or } {}_{3-H} = 3.5, {}^{2}J_{C}(_{5}),_{4-H} = 8, \text{ and } {}^{3}J_{C}(_{5}),_{3-H} = 8$  Hz.

## LITERATURE CITED

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## RECYCLIZATION OF 4-CYANOBENZO[c]PYRYLIUM SALTS UPON

REACTION WITH HYDRAZINE

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In a study of the reaction of benzo[c]pyrylium salt I with hydrazine we observed that the previously undescribed 5-methyl-7,8-dimethoxy-l-phenylpyrazolo[5,4-c]isoquinoline (II) is formed in 40% yield as a result of the reaction. The conversion of perchlorate I to pyrazoloisoquinoline II evidently includes the formation of intermediate 5-aminopyrazole derivative III.



Pyrylium Salt I. This salt, with mp 210-212°C (dec.), was obtained by treatment of  $\alpha$ -benzoylhomoveratronitrile with acetic anhydride in the presence of an equimolar amount of perchloric acid. IR spectrum (in Nujol): 1100 (C104"), 1605 (pyrylium cation), and 2250 cm<sup>-1</sup> (C=N). PMR spectrum (60 MHz, CF<sub>3</sub>COOH),  $\delta$ : 3.20 (3H, s, CH<sub>3</sub>), 3.97 (3H, s, OCH<sub>3</sub>), 4.13 (3H, s, OCH<sub>3</sub>), 7.30 (5H, s, C<sub>6</sub>H<sub>5</sub>), and 7.67 and 7.80 ppm (each 1H, s, 5- and 7-H).

Compound II. This compound had mp 272-273°C (from xylene). IR spectrum (in Nujol):  $1620 \text{ cm}^{-1}$  (ring C=N). PMR spectrum (60 MHz, CF<sub>3</sub>COOH),  $\delta$ : 3.23 (3H, s, CH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 4.07 (3H, s, OCH<sub>3</sub>), and 7.67 ppm (7H, s, H<sub>arom</sub>).

The results of elementary analysis of the compounds were in agreement with the calculated values.

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