FORMATION OF PYRROLYLACETYLENE BY VILSMEIER FORMYLATION OF 3-METHYL-4-ACETYLPYRROLE

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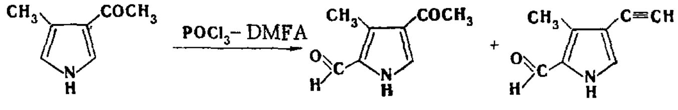
We have observed an unusual Vilsmeier reaction with 3-methyl-4-acetylpyrrole (I). In addition to the expected aldehyde (II), a pyrrole containing an ethynyl residue in place of the acetyl group in the 3 position was obtained. This is the first instance of this sort of conversion of acetylpyrroles to pyrrolylacetylenes. The reaction evidently includes attack on the acetyl group (possibly in the enol form [1]) by phosphorus oxychloride and subsequent splitting out of phosphoric acid with the formation of a triple bond. Pyrrolylacetylene III is a readily crystallizable stable substance. It is readily hydrogenated over palladium black to give 2-formyl-3-methyl-4-ethylpyrrole and is converted to pyrrole II in acidic media. The latter fact explains the predominant formation of acetylene derivative III during decomposition of the reaction mixture at pH 7-9 and of acetylpyrrole II during decomposition of the mixture at pH 2-4.



I II III

EXPERIMENTAL

2-Formyl-3-methyl-4-acetylpyrrole (II) and 2-Formyl-3-methyl-4-ethynylpyrrole (III). A solution of 0.5 g of pyrrole I in 20 ml of dichloroethane was added at 20° to a mixture of 4 ml of dimethylformamide and 0.55 ml of $POCl_3$ at 20°, after which the mixture was heated at 80° for 1 h. It was then cooled, and a saturated solution of sodium acetate was added to pH 7. The mixture was then refluxed for 15 min, the organic phase was separated, and the aqueous layer was extracted with ether. The extracts were washed with sodium carbonate solution and dried with magnesium sulfate. The solvent was evaporated, and the residue was chromatographed with a column (2 by 20) filled with L 40/100 μ silica gel. The column was eluted successively with petroleum ether-chloroform (1:1) and chloroform. The first fraction (50 ml) was discarded. The second fraction (120 ml) contained pyrrole III. The third fraction (150 ml) contained pyrrole II. The residues were triturated in CCl_4 at −70° to give 0.184 g (34%) of colorless prisms of III with mp 192° (from aqueous ethanol), and R_f 0.56. IR spectrum: 3380 and 3260 (N–H), 3300 (≡C–H) 3020 (=C–H), 2120 (C≡C), and 1650 cm^{-1}(C=O). UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 220 (15.3), 227 (15.8), 274 (10.2), and 306 nm (12.6). Mass spectrum, m/e (%): 133 (M^+, 100), 104 (48), 77 (47), 51 (30), 39 (10), and 28 (12). PMR spectrum ($CDCl_3$), δ, ppm: 11.3 (H, s, NH), 9.25 (H, s, CHO), 6.75 (H, d, α-H), 3.18 (H, s, ≡C-H), and 2.69 (3H, s, CH_3). Found: C 72.0; H 5.4; N 10.6%. C_8H_7NO. Calculated: C 72.2; H 5.3; N 10.5%. The yield of slightly yellowish prisms of pyrrole II, with mp 178-179° (from aqueous ethanol) and R_f 0.2, was 0.025 g (4%). IR spectrum: 3390 and 3280 (NH), 3020 (=C–H), 1670 (CHO), and 1640 cm^{-1} ($COCH_3$). UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 240 (23.0) and 293 nm (17.9). Mass spectrum, m/e (%): 151 (M^+, 80), 141 (7), 136 (100), 108 (12), 80 (13), 53 (18), 43 (14), and 28 (15). PMR spectrum (D_6-DMSO), δ, ppm: 9.75 (H, s, CHO), 7.9 (H, d, α-H), 2.5 (3H, s, $COCH_3$), and 2.4 (3H, s, CH_3). Found: C 63.2; H 6.3; N 9.5%. $C_8H_9NO_2$. Calculated: C 63.5; H 6.0; N 9.3%.

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LITERATURE CITED

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