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LETTERS TO THE EDITOR

TRANSFORMATIONS OF 1-FURYLISOQUINOLINIUM SALTS BY THE ACTION OF METHYLAMINE

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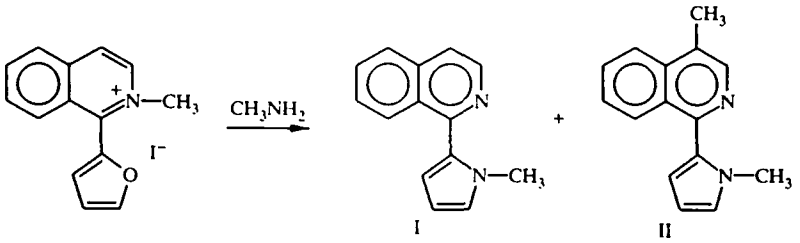
1-Methylisoquinolinium salts rearrange upon the action of nucleophiles to give 1-aminonaphthalenes [1]. We have studied the transformations of isoquinolinium salts containing an electron-rich heterocyclic substituent at $C_{(1)}$ upon the action of methylamine.

Samples of starting 1-(2-furyl)- and 1-(5-methyl-2-furyl)isoquinolinium salts were obtained by the reaction of the corresponding isoquinolines [2] with methyl iodide. Mixtures of these salts with excess 36% ethanolic methylamine were heated in sealed ampules at 160°C. However, recyclization under ordinary conditions led to unexpected results. In the case of 1-(2-furyl)-N-methylisoquinolinium iodide, column chromatography of the crude product gave a mixture of I and II, which have very similar retention indices. The total yield of I and II was 10%. The ^{1}H NMR spectrum of I coincided completely with the spectrum of 1-(N-methyl-2-pyrrolyl)isoquinoline [2], while II differed in the presence of an additional methyl group at $C_{(4)}$. The reaction mixture also contained tarry products, which were not identified. While the formation of I may be attributed to the Yur'ev reaction and dealkylation of the azinium salts by the action of base, the formation of 4-methyl analog II was entirely unexpected.

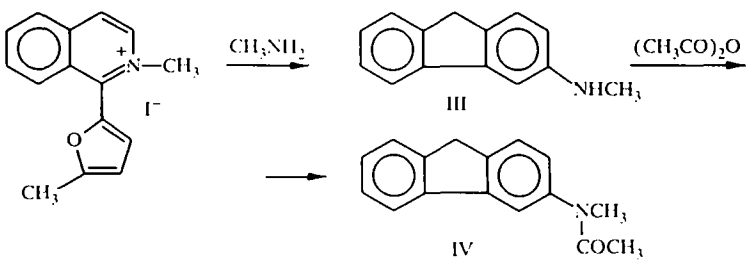


I II

The ratio of I and II depends on the reaction time. The yield of isoquinoline II is greatest when the reaction time was 5 h (I:II = 2:7).

We unexpectedly found that the reaction direction is markedly altered upon introducing a methyl group at $C_{(5)}$ of the furyl substituent.

The mass and ^{1}H NMR spectra show that the reaction product preparatively isolated is N-(9H-fluoren-2-yl)- or N-(9H-fluoren-3-yl)-N-methylamine. The existence of a methylamino group was indicated by the facile acylation of this compound. Fletcher et al. [3] reported mp 128°C for N-(9H-fluoren-2-yl)-N-methylacetamide, while isolated product IV has mp 102°C. Hence, we identified IV as N-(9H-fluoren-3-yl)-N-methylacetamide.



III IV

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EXPERIMENTAL

Mixture of 1-(N-methyl-2-pyrrolyl)isoquinoline (I) and 4-Methyl-1-(N-methyl-2-pyrrolyl)isoquinoline (II) (10% total yield). ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz (J, Hz(compound)): 8.56 (1H, d, J = 6.0, 3-H(I)), 8.46 (1H, d.d, J = 0.9, 8.5, 8-H(I)), 8.38 (1H, s, H-3(II)), 8.39 (d.d, 8-H(II)), 7.96 (1H, d, J = 8.1, 6-H(II)), 7.83 (1H, d, J = 8.1, 6-H(II)), 7.83 (1H, d, J = 8.1 (6-H(I)), 7.72 (1H, d.d.d, J = 1.2, 8.0, 8.5, 7-H(II)), 7.66 (1H, d.d.d, J = 1.2, 8.0, 8.5, 7-H(I)), 7.54 (3H, m, 4-H(I), 6-H(I)), 6.85 (1H, d.d, J = 2.5, 1.6, 5′-H(I)), 6.82 (1H, d.d, J = 2.5, 1.6, 5′-H(II)), 6.54 (1H, d.d, J = 3.6, 1.6, 3′-H(I)), 6.48 (1H, d.d, J = 3.6, 1.6, 3′-H(II)), 6.29 (1H, d.d, J = 2.5, 3.6, 4′-H(I)), 6.27 (1H, d.d, J = 2.5, 3.6, 4′-H(II)), 3.79 (3H, s, CH_3(I)), 3.74 (3H, s, N$-CH_3$(II)), 2.64 ppm (3H, s, CH_3(II)). Mass spectrum (II), m/z (I, %): M^+ 222(45), 221(100), 110(10, M^{++}). The composition of the molecular ion was confirmed by high-resolution mass spectrometry.

N-Methyl-N-(9H-fluoren-3-yl)amine (III) (10% yield). ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz (J, Hz): 7.74 (1H, d.d.d, J = 7.44, 1.23, 0.75, 5-H), 7.28 (1H, d.d.d, J = 7.44, 7.44, 1.27, 6-H), 7.36 (1H, d.d.d, J = 7.44, 7.44, 1.23, 7-H), 7.51 (1H, d.d.d, J = 7.44, 0.92, 1.21, 8-H), 7.35 (1H, d.d, J = 8.05, 0.70, 4-H), 7.05 (1H, d.d, J = 2.29, 0.77, 1-H), 6.62 (1H, d.d, J = 8.05, 2.29, 2-H), 3.78 (2H, s, CH_2), 2.90 ppm (3H, s, CH_3). ^{13}C NMR spectrum in $CDCl_3$ at 400 MHz: 31.38 (CH_3), 36.46 (CH_2), 103.4, 112.70, 119.90, 125.74, 125.34, 126.79, 126.85, 132.53, 142.38, 142.92, 144.90, 149.39 ppm. Mass spectrum, m/z (I, %): 195 ($M^{+\cdot}$, 100), 194(90), 180(10), 165(20), 152(15), 69(15). The composition of the molecular ion was confirmed by high-resolution mass spectrometry.

N-(9H-Fluoren-3-yl)-N-methylacetamide (IV) was obtained by heating amine III in acetic anhydride at reflux for 1 min. ^{1}H NMR spectrum in $CDCl_3$ at 400 MHz: 7.78 (1H, d, J = 7.40, 5-H), 7.58 (2H, m, 4-H, 8-H), 7.56 (1H, s, 1-H), 7.41 (1H, m, 6-H), 7.35 (1H, m, 6-H), 3.92 (2H, s, CH_2), 3.35 (3H, s, CH_3), 1.95 ppm (3H, s, CH_3). Mass spectrum, m/z (I, %): 237 ($M^{+\cdot}$, 70), 195(100), 194(86), 165(48), 152(20), 56(23).

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