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LETTERS TO THE EDITOR

FIRST EXAMPLE OF A SYNTHESIS OF THE TETRACYCLIC 2,4-DI(*tert*-BUTYL)-6,7-DIHYDROFURO[2',3':3,4]CYCLOHEPTA-[1,2-*b*]INDOLE SYSTEM

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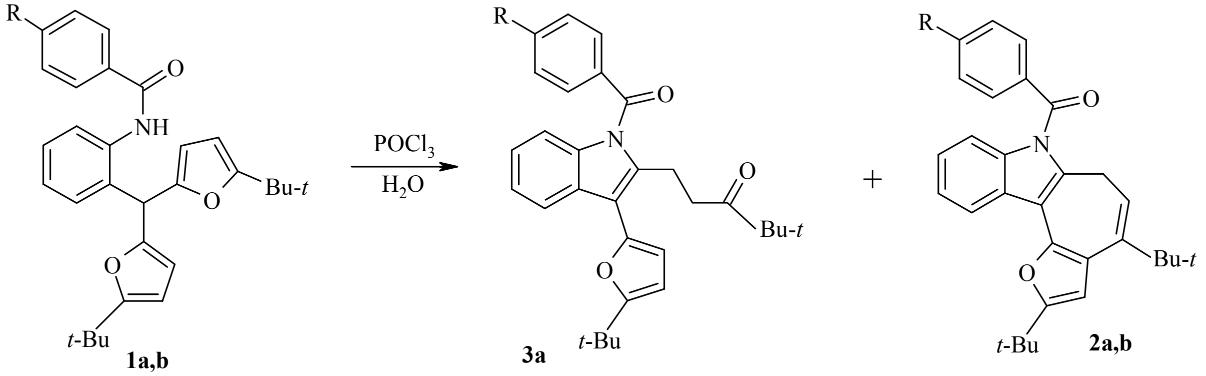
We have recently studied the acid-catalyzed recyclization of *ortho*-substituted benzylfurans. In these reactions, the furan ring acts as a formal equivalent of a 1,4-diketone: one carbonyl group participates in the formation of a new heterocycle, while the other is liberated. In the case of arylbis(5-methyl-2-furyl)methanes, the recyclization may be accompanied by a secondary cyclization involving the liberated carbonyl group [1-5], which leads to fused tetracyclic heterocycles. In contrast, the secondary cyclization does not occur when a bulky *tert*-butyl group is present at C-5. [6].



1–3 a R = NO$_2$, **1**, **2** **b** R = Br

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In a continuation of a study of the behavior of (2-benzoylaminoaryl)bis(5-*tert*-butyl-2-furyl)methanes in the presence of acids [7, 8], we found that the action of $POCl_3$ and a drop of water on benzene solutions of **1a** and **1b** at room temperature leads to tetracyclic derivatives **2a** and **2b**. The reaction proceeds through the intermediate formation of ketones **3**. Ketone **3a** was isolated from the reaction mixture and characterized, while ketone **3b** could not be isolated due to its low concentration.

The IR spectra were taken on a Shimadzu IR Prestige-21 spectrometer for KBr pellets. The ^1H and ^{13}C NMR spectra were taken on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively, in $CDCl_3$. The shifts were measured related to the solvent signal (^1H: $\delta = 7.25$, ^{13}C: $\delta = 77.13$ ppm).

Synthesis of Compounds 2 and 3 (General Method). A sample of 10 ml $POCl_3$ and one drop of water was added to a solution of compound **1** (2 mmol) in benzene (40 ml). The reaction mixture was maintained for 24 h at room temperature. Then, the mixture was poured into 200 ml water, neutralized by adding a solution of 20 g NaOH in 150 ml water, and extracted with three 50-ml portions of methylene chloride. The combined organic fractions were dried over anhydrous sodium sulfate. The solvent was evaporated in vacuum. The residue was separated on a column packed with Sorbpolimer KSK silica gel (fraction 5-40 μm) using 1:8 benzene–petroleum ether as the eluent.

2,4-Di(*tert*-butyl)-7-(4-nitrobenzoyl)-6,7-dihydrofuro[2',4':3,4]cyclohepta[1,2-*b*]indole (2a) was obtained in 21% yield (0.20 g) as an orange powder, mp 191-192°C (CH_2Cl_2-hexane). IR spectrum, ν, cm^{-1}: 2964, 1680, 1524, 1452, 1346, 1324, 1206. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.20 (9H, s, t-C_4H_9); 1.43 (9H, s, t-C_4H_9); 2.83 (2H, d, $J = 7.2$, CH_2); 5.17 (1H, t, $J = 7.2$, =CH); 6.46 (1H, s, H Fur); 7.19-7.24 (1H, m, H Ar); 7.31-7.37 (1H, m, H Ar); 7.47-7.51 (1H, m, H Ar); 7.97-8.01 (1H, m, H Ar); 7.98 (2H, d, $J = 9.0$, H Ar); 8.39 (2H, d, $J = 9.0$, H Ar). ^{13}C NMR spectrum, δ, ppm: 25.8, 29.1 (3C), 30.8 (3C), 32.7, 35.9, 104.1, 112.2, 113.7, 114.9, 120.3, 122.9, 124.0 (2C), 124.1, 124.3, 126.6, 130.7 (2C), 131.0, 136.8, 141.0, 144.6, 146.8, 150.2, 162.3, 166.8. Found, %: C 74.61; H 6.57; N 5.92. $C_{30}H_{30}N_2O_4$. Calculated,%: C 74.67; H 6.27; N 5.80.

7-(4-Bromobenzoyl)-2,4-di(*tert*-butyl)-6,7-dihydrofuro[2',3':3,4]cyclohepta[1,2-*b*]indole (2b) was obtained in 41% yield (0.42 g) as yellow needles, mp 206-207°C (CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2952, 1680, 1592, 1448, 1324, 756. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.79 (9H, s, t-C_4H_9); 1.34 (9H, s, t-C_4H_9); 3.82 (3H, s, CH_3); 6.13 (1H, d, $J = 3.3$, H Fur); 6.38 (1H, d, $J = 12.0$, =CH); 6.48 (1H, d, $J = 3.3$, H Fur); 6.89 (2H, d, $J = 8.7$, H Ar); 7.19 (1H, d, $J = 12.0$, =CH); 7.44-7.50 (1H, m, H Ar); 7.52 (2H, d, $J = 8.7$, H Ar); 7.63-7.68 (1H, m, H Ar); 8.04-8.07 (1H, m, H Ar); 8.11-8.13 (H Ar). ^{13}C NMR spectrum, δ, ppm: 25.7, 29.1 (3C), 30.8 (3C), 32.7, 35.9, 104.1, 112.5, 112.9, 114.8, 120.1, 122.4, 123.6, 123.9, 126.3, 128.1, 131.4 (2C), 131.8, 132.1 (2C), 134.2, 137.0, 144.3, 147.1, 162.0, 168.0. Found, %: C 69.53; H 5.96; N 2.44. $C_{30}H_{30}BrNO_2$. Calculated, %: C 69.77; H 5.85; N 2.71.

1-{3-[5-*tert*-Butyl-2-furyl]-1-(4-nitrobenzoyl)-1H-indol-2-yl}-4,4-dimethyl-3-pentanone (3a) was obtained in 35% yield (0.35 g) as a red powder, mp 126-127°C (CH_2Cl_2–hexane). IR spectrum, ν, cm^{-1}: 2968, 1696, 1604, 1520, 1408, 1344, 1304, 1208, 1180. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (9H, s, *t*-Bu); 1.35 (9H, s, *t*-Bu); 3.06-3.11 (1H, m, CH_2); 3.28-3.37 (2H, m, CH_2); 6.14 (1H, d, $J = 3.3$, H Fur); 6.55 (1H, d, $J = 9.0$, H Fur); 6.57-6.59 (1H, m, H Ar); 6.99-7.05 (1H, m, H Ar); 7.20-7.26 (1H, m, H Ar); 7.87-7.89 (1H, m, H Ar); 7.94 (2H, d, $J = 9.0$, H Ar); 8.35 (2H, d, $J = 9.0$, H Ar). ^{13}C NMR spectrum, δ, ppm: 22.2, 26.4 (3C), 29.1 (3C), 32.7, 36.9, 44.0, 103.8, 108.4, 112.8, 113.8, 120.5, 123.3, 123.6, 124.0 (2C), 127.5, 131.0 (2C), 135.9, 137.5, 140.7, 146.0, 150.3, 163.7, 167.4, 214.7. Found, %: C 71.85; H 6.68; N 5.36. $C_{30}H_{32}N_2O_5$. Calculated, %: C 71.98; H 6.44; N 5.60.

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