Chemistry of Heterocyclic Compounds, Vol. 41, No. 7, 2005

LETTERS TO THE EDITOR

NOVEL APPROACH TO SYNTHESIS OF DIMETHYL-1-OXA-AZULENIO[7,8-*b*]INDOLE SALTS

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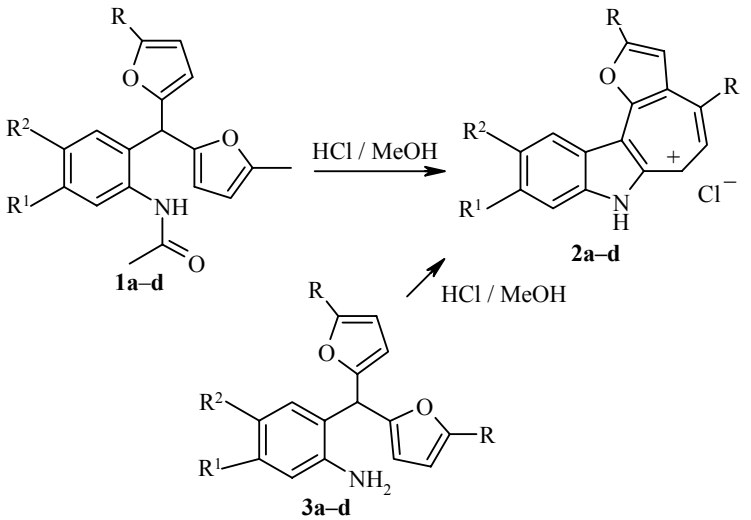
Keywords: indole, oxaazulenium, tropylium, furan, recyclization reaction.

Planar tetracyclic systems including an indole moiety, a seven-membered carbocycle, and a heterocycle are structural analogs of natural furocarbazole alkaloids [1-3] and are of interest in searching for new substances with useful biological action [4, 5].

Earlier we obtained planar tetracyclic tropylium salts including an indole moiety by reaction of 2-acetylaminoaryl(difuryl)methanes **1a,c** with trityl perchlorate [6].



1-3 a-c R = Me; **a** $R^1 = R^2 = H$; **b** R^1 = Br, R^2 = H; **c** $R^1 = R^2$ = OMe; **d** R = Et, $R^1 = R^2$ = OMe

In this paper, we report on a novel approach to such compounds. We know [7] that in acid medium, 2-R-phenyl(difuryl)methanes undergo recyclization, which leads to formation of ketones of benzannelated heterocycles and may be accompanied by a secondary reaction of intramolecular cyclization. We observed such

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0009-3122/05/4107-0929

a reaction, leading to tetracyclic derivatives of cycloheptatriene, during synthesis of derivatives of isocoumarin [8] and isoquinolone [9] when 2-carboxyaryl(difuryl)methanes and their amides were treated with an alcoholic solution of hydrogen chloride.

Such a reaction under harsher conditions (boiling in dioxane in the presence of equimolar amounts of perchloric acid) may lead to disproportionation of cycloheptatriene derivatives and may be accompanied by formation of the corresponding tetracyclic salts, as observed in the case of benzofuran derivatives [10].

We have studied recyclization of 2-acetylaminoaryl(difuryl)methanes **1** when treated with alcoholic solutions of hydrogen chloride, and we have established that the tetracyclic salts **2** are formed as a result of this conversion.

We should note that the indicated conversions are accompanied by cleavage of the acetyl group, and salts **2** can be obtained directly from the corresponding amines **3**.

The ^{1}H NMR spectra were recorded on a Bruker AM 300 (250 MHz) in CF_3COOD, internal standard TMS.

2,4-Dimethyl-1-oxaazulenio[7,8-*b*]indole Chloride (2a). Compound **1a** (3.13 g, 0.01 mol) was dissolved with heating to 50-55°C in methanol (50 ml); at that same temperature, gaseous hydrogen chloride was passed through the solution until precipitation of crystals stopped (~1-1.5 h). The reaction mixture was held for 10 h at room temperature; the precipitate was separated by filtration, washed with a small amount of ethanol, and dried. We obtained 0.87 g (39.6%) of compound **2a** as a yellow powder; decomposes at 200-202°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.98 (3H, s, CH_3); 3.22 (3H, s, CH_3); 7.30 (1H, s, H_{Fur}); 7.78-7.85 (1H, m, H_{Ar}); 7.96-8.08 (2H, m, H_{Ar}); 8.48 (1H, d, J = 11.0, H_{Trop}); 8.90 (1H, d, J = 11.0, H_{Trop}); 9.03-9.07 (1H, m, H_{Ar}). Found, %: C 72.09; H 4.79; N 4.85. $C_{17}H_{14}ClNO$. Calculated, %: C 71.96; H 4.97; N 4.94.

Compounds 2b-d were obtained as for **2a**.

9-Bromo-2,4-dimethyl-1-oxaazulenio[7,8-*b*]indole Chloride (2b). Yield 56%; decomposes at 211-213°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.97 (3H, s, CH_3); 3.23 (3H, s, CH_3); 7.33 (1H, s, HFur); 7.93 (1H, d, J = 8.7, H_{Ar}); 8.16 (1H, s, H_{Ar}); 8.53 (1H, d, J = 11.0, H_{Trop}); 8.88 (1H, d, J = 8.7, H_{Ar}); 8.90 (1H, d, J = 11.0, H_{Trop}). Found, %: C 56.21; H 3.78; N 4.01. $C_{17}H_{13}BrClNO$. Calculated, %: C 56.30; H 3.61; N 3.86.

9,10-Dimethoxy-2,4-dimethyl-1-oxaazulenio[7,8-*b*]indole Chloride (2c). Yield 58%; decomposes at 203-205°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95 (3H, s, CH_3); 3.18 (3H, s, CH_3); 4.21 (3H, s, OCH_3); 4.26 (3H, s, OCH_3); 7.28 (1H, s, H_{Fur}); 7.49 (1H, s, H_{Ar}); 8.34 (1H, d, J = 11.0, H_{Trop}); 8.49 (1H, s, H_{Ar}); 8.78 (1H, d, J = 11.0, H_{Trop}). Found, %: C 66.52; H 5.15; N 4.00. $C_{19}H_{18}ClNO_3$. Calculated, %: C 66.38; H 5.28; N 4.07.

9,10-Dimethoxy-2,4-diethyl-1-oxaazulenio[7,8-*b*]indole Chloride (2d). Yield 47.2%; decomposes at 198-199°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.62 (3H, t, J = 7.6, CH_3); 1.72 (3H, t, J = 7.6, CH_3); 3.33 (2H, q, J =7.6, CH_2); 3.51 (2H, q, J = 7.6, CH_2); 4.23 (3H, s, OCH_3); 4.27 (3H, s, OCH_3); 7.33 (1H, s, H_{Fur}); 7.50 (1H, s, H_{Ar}); 8.38 (1H, d, J = 11.0, H_{Trop}); 8.50 (1H, s, H_{Ar}); 8.82 (1H, d, J = 11.0, H_{Trop}). Found, %: C 67.72; H 6.09; N 3.83. $C_{21}H_{22}ClNO_3$. Calculated, %: C 67.83; H 5.96; N 3.77.

This work was done with the financial support of the Russian Foundation for Basic Research (grant No. 03-03-32759) and Bayer Health Care AG.

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