RECYCLIZATION OF 4-OXO-1,3-BENZOXAZINIUM PERCHLORATES TO 4-SUBSTITUTED 5-(o-HYDROXYPHENYL)-1,2,4-OXADIAZOLIUM SALTS

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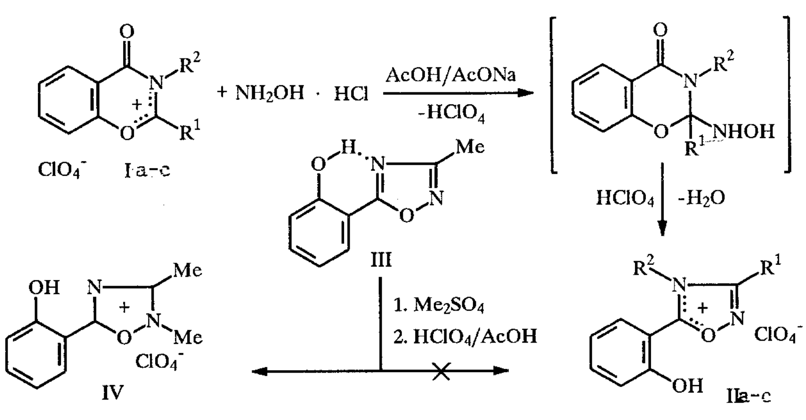
It was observed that N-substituted salts I are converted to the previously unknown oxadiazolium perchlorates II in 36-50% yields by the action of hydroxylamine.

Perchlorates II cannot be obtained by alkylation of the corresponding oxadiazoles of the III type, which were described in [1]. Thus the isomeric (with respect to salt IIa) perchlorate IV is formed when III is heated in dimethyl sulfate with subsequent dilution of the mixture with ether and treatment of the oily methylsulfonate with $HClO_4$ in AcOH. This reaction pathway is explained by the fact that the electron density on the $N_{(2)}$ atom of oxadiazole III is significantly higher than on $N_{(4)}$ [2] and by the fact that the $N_{(4)}$ atom is chelated by an intramolecular hydrogen bond.



I, IIa R¹=R²=Me; b R¹=Et, R²=Me; c R¹=Me, R²=Ph

High-intensity absorption bands of an OH group and a perchlorate anion at 3200-3300 and 1096-1127 cm^{-1}, respectively, and a group of bands of heteroaromatic absorption at 1487-1617 cm^{-1} are present in the IR spectra of salts II.

A 1.41-g (20 mmole) sample of hydroxylamine hydrochloride was added to a suspension of 1.64 g (20 mmole) of anhydrous AcONa in 5 ml of glacial AcOH, and the precipitated NaCl was removed by filtration after 10 min. A 20-mmole sample of perchlorate I was added to the filtrate, after which the suspension was heated until the solid had dissolved. The solution was cooled and diluted with ether, and perchlorate II was removed by filtration.

5-(o-Hydroxyphenyl)-3,4-dimethyl-1,2,4-oxadiazolium Perchlorate (IIa, $C_{10}H_{11}ClN_2O_6$). This compound had mp 184-186°C (from AcOH). PMR spectrum (CD_3CN): 2.55 (3H, s, CH_3), 3.72 (3H, s, N—CH_3), 6.88-7.92 (4H, m, C_6H_4), 9.30 ppm (1H, s, OH). The yield was 50%.

5-(o-Hydroxyphenyl)-4-methyl-3-ethyl-1,2,4-oxadiazolium Perchlorate (IIb, $C_{11}H_{13}ClN_2O_6$). This compound had mp 136-138°C (from AcOH). PMR spectrum (CD_3CN): 1.35 (3H, t, CH_2CH_3), 2.95 (2H, q, CH_2CH_3), 3.72 (3H, s, N—CH_3), 6.95-7.90 (4H, m, C_6H_4), 9.08 ppm (1H, s, OH). The yield was 36%.

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5-(o-Hydroxyphenyl)-3-methyl-4-phenyl-1,2,4-oxadiazolium Perchlorate (IIc, $C_{15}H_{13}ClN_2O_6$). This compound had mp 188-190°C (from AcOH). PMR spectrum (CD_3CN): 2.40 (3H, s, CH_3), 6.76-7.86 (9H, m, C_6H_4 and C_6H_5), 8.90 ppm (1H, s, OH). The yield was 41%.

5-(o-Hydroxyphenyl)-2,3-dimethyl-1,2,4-oxadiazolium Perchlorate (IV, $C_{10}H_{11}ClN_2O_6$). This compound had mp 257-258°C (from AcOH). PMR spectrum (CF_3COOH): 2.57 (3H, s, CH_3), 4.1 (3H, s, N—CH_3), 6.58-7.83 ppm (4H, m, C_6H_4). The yield was 47%.

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SYNTHESIS OF 5-AMINO-3*a*,4-DICYANO-2,3,3*a*,6*a*-TETRAHYDROFURO[2,3-b]PYRROLES

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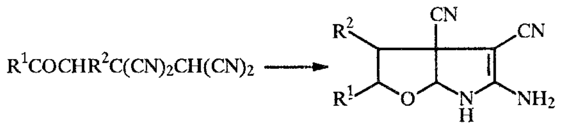
We have observed that substituted 2,3,3*a*,6*a*-tetrahydrofuro[2,3-b]pyrroles IIa-d are formed in the reduction of β,β,γ,γ-tetracyano ketones with sodium borohydride in water at room temperature.



I a-d

II a-d

I, II a R^1=CH_3, R^2=H; b R^1=CH_3, R^2=C_3H_7; c R^1=C_6H_5, R^2=H; d R^1=C_4H_9, R^2=H

A solution of 0.1 mole of $NaBH_4$ in 20 ml of water was added in portions with water cooling to a suspension of 0.05 mole of 4,4,5,5-tetracyano-2-pentanone in 30 ml of water, after which the mixture was stirred for 30-40 min. It was then neutralized with dilute hydrochloric acid, and the precipitate was removed by filtration, washed with water, dried, and recrystallized from isopropyl alcohol to give IIa ($C_9H_{10}N_4O$), with mp 176-178°C, in 67% yield. IR spectrum (here and subsequently, suspension in mineral oil): 3200-3450; 1650 (NH_2); 2250, 2180 (CN); 1590 cm^{-1} (C=C). The structure of IIa was established by x-ray diffraction analysis.

The following compounds were similarly obtained [the compound, empirical formula, melting point (°C), yield (%), and principal bands in the IR spectrum are presented]: IIb, $C_{12}H_{16}N_4O$, 204-205, 68, 3185-3450, 1645 (NH_2), 2185, 2250 (CN), 1590 (C=C); IIc, $C_{14}H_{12}N_4O$, 208-210, 50, 3200-3430, 1650 (NH_2), 2190, 2250 (CN), 1590 (C=C); IId, $C_{12}H_{16}N_4O$, 198-200, 57, 3200-3450, 1645 (NH_2), 2180, 2250 (CN), 1590 (C=C).

^{13}C NMR spectrum of 5-amino-2-phenyl-3*a*,4-dicyano-2,3,3*a*,6*a*-tetrahydrofuro[2,3-b]pyrrole (data for a second diastereomer are presented in parentheses): C(1) 161.65 (161.33), C(2) 49.89, C(3) 119.09, C(4) 49.29, C(5) 120.68 (119.93), C(6) 92.85 (93.65), C(7) 45.85 (45.11), C(8) 78.83 (78.29), C(9) 138.43 (140.05), C(10) 128.26 (127.48), C(11) 126.21 (125.46).

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