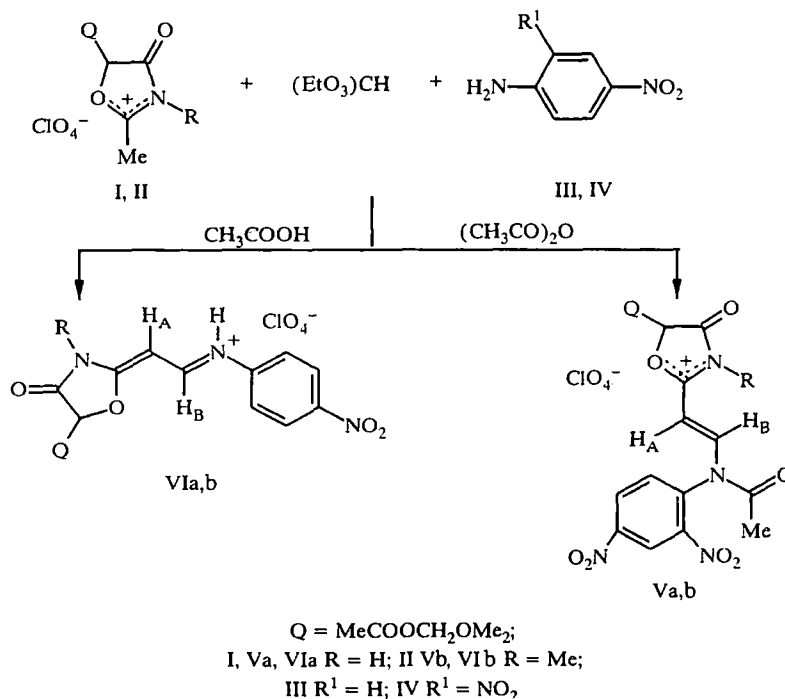


2-METHYL-4(5H)-OXAZOLONIUM SALTS IN REACTION WITH ETHYL ORTHOFORMATE AND AROMATIC AMINES

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Earlier we have described three-component condensation of 2-methyl- and 2,3-dimethyl-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium perchlorates I, II as active CH-acids with orthoformic ester and amides of furancarboxylic acids in acetic anhydride medium, with formation of salts containing the enamine moiety C=C-N [1]. However, the three-component condensation of 4(5H)-oxazolonium salts with ethyl orthoformate and aromatic amines has not yet been studied (see review [2]).

We have shown that under conditions suggested earlier [1] it is possible to obtain β -vinylamino derivatives starting from arylamines III and IV with acceptor substituents. For example, 2,4-dinitroaniline IV first is acylated by acetic anhydride, and then its anilide enters the condensation, being converted to N-acyl-substituted perchlorates Va,b. The products VIa,b based on *p*-nitroaniline III were synthesized in a single step in acetic acid at 50-60°C for 3.5-4 h. Amines with donor substituents, due to the higher basicity of the NH₂ group (higher than in arylamines with acceptor substituents) do not react, since they are previously protonated by perchloric acid and are crystallized as the corresponding perchlorates. According to the PMR spectra taken in trifluoroacetic acid, the



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enamines Va,b have *trans* configuration and VIa,b exist in the mesomerically stabilized *s-E*-form, which is consistent with the data in [3].

2-{2-[(2,4-dinitrophenyl)acetylamino]ethenyl}-5-(1,1-dimethyl-2-acetoxyethyl-4(5H)-oxazolonium perchlorate (Va). Yield 64%; mp 184°C. IR spectrum: 3080, 1790, 1740, 1575, 1530, 1510, 1230, 1100 cm⁻¹. PMR spectrum (CF₃COOH): 0.85 and 0.93 [6H, two s, (Me)₂]; 1.81 (3H, s, COMe); 2.00 (3H, s, NCOMe); 3.71 and 3.95 (2H, two d, ²J = 11.9 Hz, CH₂); 4.87 (1H, s, CH); 6.32 and 7.75 (2H, two d, ³J_{AB} = 15 Hz, HB, HA); 6.68-7.41 ppm (3H, m, H_{Ar}). Found, %: C 41.90; H 3.98; N 10.47; Cl 6.63. C₁₉H₂₁ClN₄O₁₃. Calculated, %: C 41.55; H 3.86; N 10.21; Cl 6.46.

Compound Vb. Yield 70-80%. PMR spectrum (CF₃COOH): 0.80 and 0.87 [6H, two s, (Me)₂]; 1.80 (3H, s, COMe); 2.02 (3H, s, NCOMe); 3.14 (3H, s, N-Me); 3.68 and 3.90 (2H, two d, ²J = 11.9 Hz, CH₂); 4.83 (1H, s, CH); 6.39 and 7.80 (2H, two d, ³J_{AB} = 15 Hz, HB, HA); 6.75-7.50 ppm (3H, m, H_{Ar}). Found, %: C 42.81; H 4.30; N 10.1; Cl 6.45. C₂₀H₂₃ClN₄O₁₃. Calculated, %: C 42.63; H 4.12; N 9.95; Cl 6.30.

2-{2-[(4-nitrophenyl)amino]ethenyl}-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium Perchlorate (VIa). Yield 78%; mp 228-230°C. IR spectrum: 3240, 3090, 1775, 1730, 1665, 1600, 1560, 1540, 1230, 1210, 1120 cm⁻¹. PMR spectrum (CF₃COOH): 0.80 and 0.87 [6H, two s, (Me)₂]; 1.78 (3H, s, COMe); 3.81 and 3.92 (2H, two d, ²J = 11.9 Hz, CH₂); 4.81 (1H, s, CH); 5.73 (1H, d, ³J_{AB} = 12 Hz, HA); 8.51 (1H, dd, ³J_{AB} = 12, ³J_{NHCH} = 16 Hz, HB); 7.11 and 7.92 ppm (4H, two d, ³J = 9 Hz, H_{Ar}). Found, %: C 44.43; H 4.54; N 9.52; Cl 7.90. C₁₇H₂₀ClN₃O₁₀. Calculated, %: C 44.21; H 4.37; N 9.10; Cl 7.68.

Compound VIb: Yield 84%; mp 158-160°C. IR spectrum: 3250, 3080, 1775, 1730, 1730, 1600, 1560, 1230, 1210, 1110 cm⁻¹. PMR spectrum (CF₃COOH): 0.80 and 0.90 [6H, two s, (Me)₂]; 1.90 (3H, s, COMe); 3.13 (3H, s, N-Me); 3.93 and 4.13 (2H, two d, ²J = 11.9 Hz, CH₂); 5.08 (1H, s, CH); 6.03 (1H, d, ³J_{AB} = 12 Hz, HA); 9.13 (1H, dd, ³J_{AB} = 12, ³J_{NHCH} = 16 Hz, HB); 7.67 and 8.47 ppm (4H, two d, ³J = 9 Hz, H_{Ar}). Found, %: C 45.60; H 4.63; N 8.99; Cl 7.95. C₁₈H₂₂ClN₃O₁₀. Calculated, %: C 45.44; H 4.66; N 8.83; Cl 7.45.

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