

2-METHYL-4(5H)-OXAZOLONIUM

SALTS IN REACTION WITH

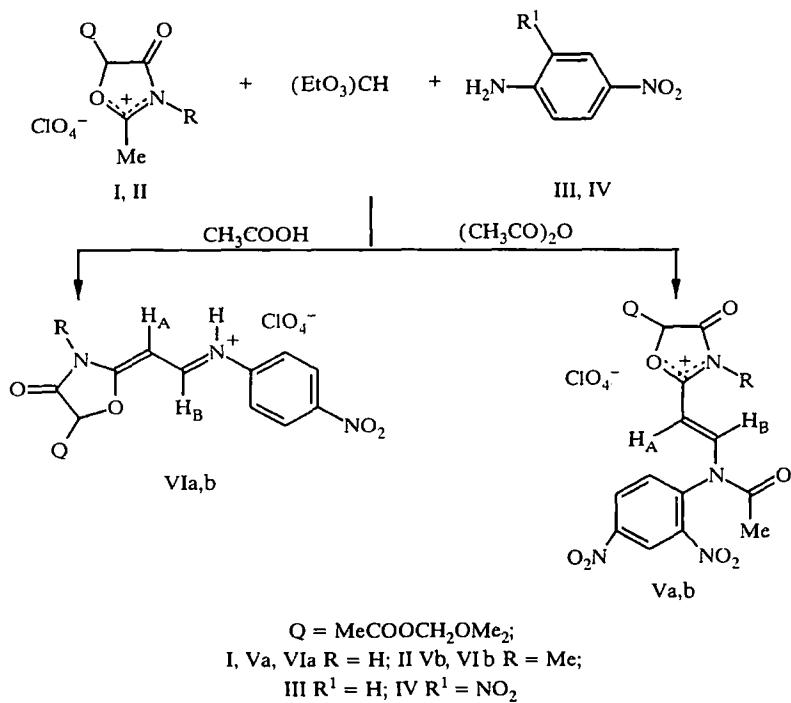
ETHYL ORTHOFORMATE

AND AROMATIC AMINES

T. P. Kosulina, K. S. Pushkareva, N. I. Bychenko, I. P. Morenets, and V. G. Kul'nevich

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



Kuban State Technological University, Krasnodar 350072, Russia; e-mail organics@kubstu.ru. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, pp. 705-706, May, 1999. Original article submitted February 17, 1999.

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 (CF_3COOH): 0.85 and 0.93 [6H, two s, (Me_2)₂]; 1.81 (3H, s, COMe); 2.00 (3H, s, NCOMe); 3.71 and 3.95 (2H, two d, $^2J = 11.9$ Hz, CH_2); 4.87 (1H, s, CH); 6.32 and 7.75 (2H, two d, $^3J_{\text{AB}} = 15$ 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. $\text{C}_{19}\text{H}_{21}\text{ClN}_4\text{O}_{13}$. Calculated, %: C 41.55; H 3.86; N 10.21; Cl 6.46.

Compound Vb. Yield 70-80%. PMR spectrum (CF_3COOH): 0.80 and 0.87 [6H, two s, (Me_2)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, CH_2); 4.83 (1H, s, CH); 6.39 and 7.80 (2H, two d, $^3J_{\text{AB}} = 15$ 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. $\text{C}_{20}\text{H}_{23}\text{ClN}_4\text{O}_{13}$. 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 (CF_3COOH): 0.80 and 0.87 [6H, two s, (Me_2)₂]; 1.78 (3H, s, COMe); 3.81 and 3.92 (2H, two d, $^2J = 11.9$ Hz, CH_2); 4.81 (1H, s, CH); 5.73 (1H, d, $^3J_{\text{AB}} = 12$ Hz, HA); 8.51 (1H, dd, $^3J_{\text{AB}} = 12$, $^3J_{\text{NHCH}} = 16$ 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. $\text{C}_{17}\text{H}_{20}\text{ClN}_3\text{O}_{10}$. 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 (CF_3COOH): 0.80 and 0.90 [6H, two s, (Me_2)₂]; 1.90 (3H, s, COMe); 3.13 (3H, s, N-Me); 3.93 and 4.13 (2H, two d, $^2J = 11.9$ Hz, CH_2); 5.08 (1H, s, CH); 6.03 (1H, d, $^3J_{\text{AB}} = 12$ Hz, HA); 9.13 (1H, dd, $^3J_{\text{AB}} = 12$, $^3J_{\text{NHCH}} = 16$ 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. $\text{C}_{18}\text{H}_{22}\text{ClN}_3\text{O}_{10}$. Calculated, %: C 45.44; H 4.66; N 8.83; Cl 7.45.

REFERENCES

1. T. P. Kosulina, I. N. Kozlovskaya, N. V. Bychenko, I. P. Morenets, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 2, 236 (1995).
2. Yu. I. Ryabukhin, L. N. Faleeva, T. P. Kosulina, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 6, 723 (1991).
3. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High-Resolution Nuclear Magnetic Resonance Spectroscopy* [Russian translation], Mir, Moscow (1969), Vol. 1.