Chemistry of Heterocyclic Compounds, Vol. 31, No. 2, 1995

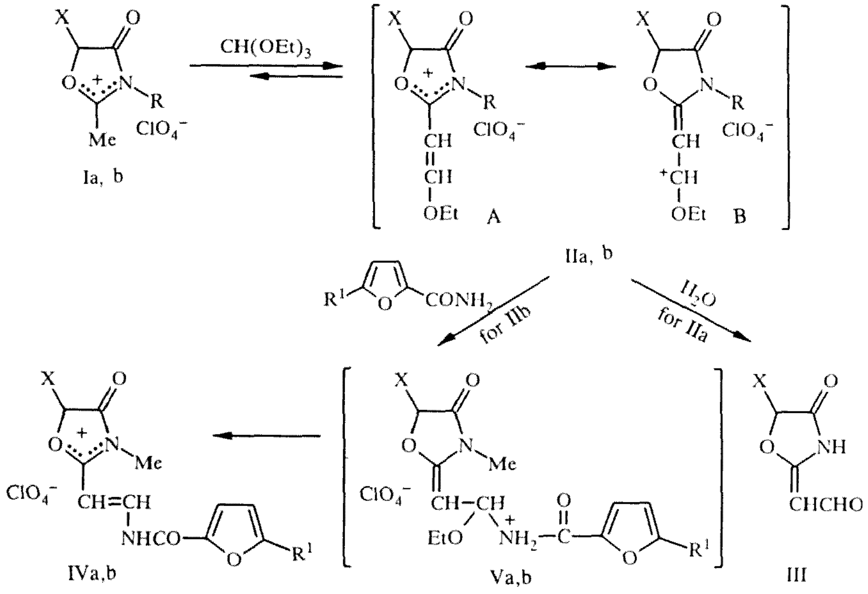
NEW 4(5H)-OXAZOLONIUM PERCHLORATE DERIVATIVES

T. P. Kosulina, I. N. Kozlovskaya, N. V. Bychenko,
I. P. Morenets, and V. G. Kul'nevich

The condensation of 2,3-dimethyl-4(5H)-oxazolonium salts with ethyl orthoformate and amides of 5-substituted 2-furancarboxylic acids gives the corresponding products derived by modification of the methyl group at $C_{(2)}$, *2-formylmethylene-4-oxazolidinone and 2-furoylaminoethenyl-4(5H)-oxazolonium perchlorates.*

We have already studied the activity of the α-methylene unit at the meso-carbon atom of the $O{=}C^{+}{=}N$ fragment of 2-methyl-4(5H)-oxazolonium with carbonyl compounds [1].

In a continuation of this work, we carried out the condensation of 4(5H)-oxazolonium salts (Ia) and (Ib) with ethyl orthoformate. Salt Ia yielded a bright yellow, oily product with the presumed structure (IIa), which proved difficult to crystallize. Hydrolysis of this product led to aldehyde (III).



I—V X = CMe₂CH₂OCOMe; I, II a R = H, b R = Me; IV, V a R¹ = Me, b R¹ = Br

The preference for the formation of aldehyde III and not for the ring opening products [2] is probably a consequence of the possibility of transfer of the electrophilic site from the $C_{(2)}$ in the ring to the β-carbon atom of the double bond in β-ethoxyvinyl-4(5H)-oxazolonium salt IIa (resonance structure B) in contrast to 2-methyl-substituted salt Ia.

Kuban State Technological University, 350072 Krasnodar. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 236-237, February, 1995. Original article submitted September 30, 1994.

0009-3122/95/3102-0206$12.50 ©1995 Plenum Publishing Corporation

The ternary condensation of 2,3-dimethyl salt Ib with ethyl orthoformate and amides of 5-methyl- and 5-bromo-2-furancarboxylic acids gives (IVa) and (IVb) containing an enamine C═C–NH fragment [3], which also indicates transfer of the electrophilic site and reaction through intermediate salts IIb (form B) and then Va and Vb.

The structures of newly synthesized products III, IVa, and IVb were confirmed by elemental analysis, PMR and IR spectroscopy (see Experimental section). PMR spectroscopy indicates that IVa and IVb have *trans* configuration ($^3J_{CH=CH}$ = 15.0 Hz).

EXPERIMENTAL

The IR spectra were taken on a Specord spectrometer for vaseline suspensions, while the PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz using HMDS as the internal standard. The UV spectrum was taken on a Specord UV-VIS spectrometer.

The elemental analysis data for C, H, Hal, and N for III, IVa, and IVb were in accord with the calculated values.

Perchlorates Ia and Ib were obtained according to our previous procedure [2].

2-Formylmethylidene-5-(1,1-dimethyl-2-acetoxyethyl)-4-oxazolidinone (III, $C_{11}H_{15}NO_5$). A mixture of 3.12 g (10 mmoles) perchlorate Ia, 6 ml (10 mmoles) ethyl orthoformate, 4 ml acetic anhydride, and 5 ml nitromethane was maintained for 2.5-3 h at room temperature. Then, 30 ml ether was added. The oil formed was separated and treated with water. The resultant yellow precipitate was extracted with ether. The solvent was removed and the residue was crystallized from heptane to give 1.5 g (62%) aldehyde III, mp 87-88°C. IR spectrum: 1780, 1740, 1680, 1610, 1580, 1480, 1420, 1260, 1200, 1160, 1100, 1020, 960 cm^{-1}.

2-[2-(5-Methyl-2-furoylamino)ethenyl-1]-3-methyl-5-(1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium perchlorate (IVa, $C_{18}H_{23}N_2O_{10}Cl$). A sample of 1.1 ml (12 mmoles) acetic anhydride was added to a mixture of 3.28 g (10 mmoles) perchlorate Ib, 1.25 g (10 mmoles) amide of 5-methylfuran-2-carboxylic acid, and 1.66 ml (10 mmoles) triethyl orthoformate. The reaction mixture was maintained at room temperature for 30-40 min and then diluted with ether. The resultant yellow precipitate was filtered to give 3.51 g (76%) IVa, mp 173-174°C. IR spectrum: 3260, 3120, 1790, 1700, 1570-1610, 1550, 1230, 1100, 800 cm^{-1}. UV spectrum in glacial acetic acid, λ_{max} (log ε): 357 nm (4.56). PMR spectrum in CF_3CO_2D: 0.85 (3H, s, CH_3), 0.92 (3H, s, CH_3), 1.82 (3H, s, CH_3), 2.06 (3H, s, 5-CH_3), 3.10 (3H, s, N–CH_3), 3.73 and 3.95 (2H, q, CH_2), 4.92 (1H, s, CH), 6.92 (1H, s, NH), 6.30 and 8.73 (2H, d.d, CH═CH), 6.07 (1H, d, 4-H), 7.35 ppm (1H, d, 3-H).

2-[2-(5-Bromo-2-furoylamino)ethenyl-1]-3-methyl-5-[1,1-dimethyl-2-acetoxyethyl)-4(5H)-oxazolonium perchlorate (IVb, $C_{17}H_{20}N_2O_{10}ClBr$) was obtained by analogy to IVa from perchlorate Ib and the amide of 5-bromofuran-2-carboxylic acid. The yield was 4.2 g (80%), mp 171-172°C. IR spectrum: 3280, 3130, 1770, 1720, 1590, 1560-1530, 1250, 1100, 800 cm^{-1}. PMR spectrum in CF_3CO_2D: 0.87 (3H, s, CH_3), 0.92 (3H, s, CH_3), 1.85 (3H, s, CH_3), 3.10 (3H, s, N–CH_3), 3.90 and 3.72 (2H, d.d, CH_2), 4.92 (1H, s, CH), 6.86 (1H, s, NH), 6.15 and 10.5 (2H, d.d, CH═CH), 6.25 (1H, d, 4-H), 7.22 ppm (1H, d, 3-H).

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