Chemistry of Heterocyclic Compounds, Vol. 33, No. 9, 1997

LETTERS TO THE EDITOR

SYNTHESIS OF 2,3-DIHYDRO-3H-PYRANO[2,3-*f*]-1,3-BENZOXAZINES

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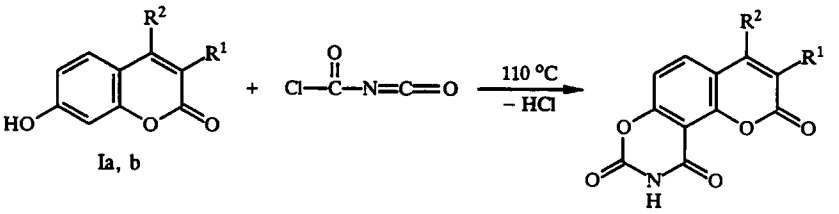
A simple synthetic approach to previously unknown angular pyranobenzoxazines consists of cyclocondensation of 7-hydroxycoumarins (Ia, b) with chlorocarbonyl isocyanate [1, 2]. Heating these reagents in boiling chlorobenzene for 2 h results in 2,3-dihydro-3H-pyrano[2,3-*f*]-1,3-benzoxazine derivatives (IIa, b) with a good yield. In all probability, this conversion takes place according to the scheme of the reaction of chlorocarbonyl isocyanate with phenols [2], while the formation of systems of the angular type is probably the result of the highest susceptibility of position 8 in the coumarin ring to electrophilic attack [3].



I, II a R^1 = H, R^2 = Me; b R^1R^2 = $(CH_2)_3$

A mixture of 0.01 mole of 7-hydroxycoumarin Ia, b and 1.05 g (0.01 mole) of chlorocarbonyl isocyanate in 25 ml of chlorobenzene was boiled for 2 h, cooled, and the sediment formed was filtered off and crystallized from dioxane–DMF mixture (5:1).

8-Methyl-2,4,6-trioxo-3H-pyrano[2,3-*f*]-1,3-benzoxazine (IIa). mp = 171-173°C. IR spectrum (KBr): 1730, 1810 (C=O), 3230 cm^{-1} (N–H). PMR spectrum (in DMSO-D_6): 2.35 (3H, s, CH_3); 6.12 (1H, s, CH=); 7.44 (1H, d, J = 7 Hz, 6-H); 7.88 (1H, d, J = 7 Hz, 5-H); 11.94 (1H, s, NH). Yield of 64%. Found, %: C 59.04; H 2.72; N 5.75. $C_{12}H_7NO_5$. Calculated, %: C 58.78; H 2.88; N 5.71.

7,8-Trimethylene-2,4,6-trioxo-3H-pyrano[2,3-*f*]-1,3-benzoxazine (IIb). mp = 220-221°C. IR spectrum (KBr): 1735, 1810 (C=O), 3235 cm^{-1} (N–H). PMR spectrum (in DMSO-D): 2.12-3.04 (6H, m, $3CH_2$); 7.35 (1H, d, J = 7 Hz, 6-H); 7.62 (1H, d, J = 7 Hz, 5-H); 11.73 (1H, s, NH). Yield of 69%. Found, %: C 62.33; H 3.40; N 4.94. $C_{14}H_9NO_5$. Calculated, %: C 62.00; H 3.32; N 5.16.

REFERENCES

1. A. Kamal, Heterocycles, **31**, 1377 (1990).
2. V. I. Gorbatenko, Tetrahedron, **49**, 3227 (1993).
3. D. Barton and W. D. Ollis, Comprehensive Organic Chemistry, Pergamon Press, Oxford, England (1979).

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 0009-3122/97/3309-1112$18.00