A convenient synthesis of some new 2-oxazolidone derivatives

Syed Sulaiman Hussaini, V. Sriraman and C. A. M. A. Huq*

P.G. and Research Department of Chemistry, The New College, Chennai-600 014, India

E-mail : sshussainichem@rediffmail.com

Manuscript received 29 October 2002, revised 26 May 2003, accepted 4 September 2003

One of the general approaches to the synthesis of 2-oxazolidones involves the reaction of glycols with urea. The synthesis of some novel 2-oxazolidone derivatives **3**, **5a** and **5b** by the reaction of **1**, **2** diols **2**, **4a** and **4b** with urea have been reported.

Lunsford *et al.*¹ have reported the synthesis of 5-aryloxymethyl-2-oxazolidone in fairly good yield. We report here the synthesis of some interesting 2-oxazolidone derivatives 1,10,10-trimethyl-6-phenyl-3-oxa-5-aza-tricyclo[5.2.1.0^{2,6}]decan-4-one (**3**), 3a,11b-di-1'-naphthyl-3a,11b-dihydro-3H-phenanthro[9,10-d]oxazol-2-one (**5a**) and 3a,11b-diphenyl-3a,11b-dihydro-3H-phenanthro[9,10-d]oxazol-2-one (**5b**) using the above reaction.

Results and discussion

Camphor was treated with selenium dioxide in the presence of acetic anhydride to give 2,3-bornanedione². It was converted to the corresponding β -keto alcohol (**1**) by the addition of two equivalents of phenylmagnesium bromide in dry THF. Reduction of **1** with sodium borohydride gave the diol (**2**) which on heating with two equivalents of urea gave the 2-oxazolidone (**3**) (Scheme 1).

Scheme 1

The addition of four equivalents of arylmagnesium bromide to phenanthrene-9,10-dione in dry THF gave the corresponding diols **4a** reported³ by us and **4b**, which on heating with two equivalents of urea gave the 2-oxazolidones

(**5a**) and (**5b**) (Scheme 2).

Scheme 2

Experimental

All m.ps. are uncorrected. The purity of the compounds was checked by TLC on silica gel. IR spectra were recorded on a Perkin-Elmer 598 spectrophotometer, ¹H NMR spectra (CDCl₃) on a Varian EM 390 spectrometer and mass spectra on a Varian MatCH-7 spectrometer.

3-Hydroxy-1,7,7-trimethyl-3-phenyl-bicyclo[2.2.1]heptan-2-one (1): To a solution of phenylmagnesium bromide (0.08 mol, 18.0 g), (prepared from 2.0 g magnesium and 12.6 g bromobenzene) in dry THF (200 ml) was added 2,3-bornanedione (0.04 mol, 6.64 g). The mixture was refluxed for 3 h in dry nitrogen atmosphere and quenched with a saturated solution of ammonium chloride (50 ml). The organic layer was separated. The aqueous layer was extracted with diethyl ether (3 × 20 ml). On removal of the solvent from the combined organic layer a viscous liquid 8.0 g was obtained. It was chromatographed over a column of silica gel. Elution with ethyl acetate : petroleum ether (1 : 20) gave a solid (5.2 g, 85%), m.p. 105° (Found : C, 78.61; H, 8.55. C₁₆H₂₀O₂ requires : C, 78.69; H, 8.60%); $\nu_{\max}$ (CDCl₃) 1600 (C=C, arom), 1740 (C=O), 2800–3100 (C–H), 3550 cm⁻¹ (OH); δ (CDCl₃) 7.24 (5H, s, ArH), 2.70 (1H, s, OH, D₂O exchangeable), 2.29 (1H, t, CH), 1.64

(4H, m, CH₂), 0.9, 1.0, 1.1 (9H, 3 × s, 3 × CH₃); *m/z* 244.

2,3-Dihydroxy-1,7,7-trimethyl-3-phenyl-bicyclo[2.2.1]heptane (2) : The β-keto alcohol (1) was reduced with sodium borohydride to the diol (2) by the reported⁴ procedure, (yield 90%), m.p. 157–159° (Found : C, 77.91; H, 8.90. C₁₆H₂₂O₂ requires : C, 78.00; H, 8.94%); *v*_{max} (CDCl₃) 2850–3100 (C–H), 3450 and 3600 cm^{–1} (OH); δ (CCl₄) 7.2 (5H, m, ArH), 3.90 (1H, d, OH, D₂O exchangeable), 3.1 (1H, d, CH), 2.7 (1H, s, OH, D₂O exchangeable), 2.1 (4H, m, CH₂), 1.7 (1H, t, CH), 0.9, 1.0, 1.1 (9H, 3 × s, 3 × CH₃); *m/z* 246.

1,10,10-Trimethyl-6-phenyl-3-oxa-5-aza-tricyclo[5.2.1.0^{2,6}]decan-4-one (3) : A mixture of diol 2 (0.001 mol, 0.246 g) and urea (0.002 mol, 0.120 g) was heated at 180–200° for 5 h. The reaction mixture was poured into water (20 ml) and extracted with chloroform (50 ml). It was dried over anhyd. Na₂SO₄. On removal of the solvent, a solid was obtained (0.240 g, 90%), C₁₇H₂₁NO₂, m.p. 123–124°; *v*_{max} (CDCl₃) 1740–1800 (C=O), 3540 cm^{–1} (NH); δ (CDCl₃) 7.0 (5H, s, ArH), 2.90 (1H, s, CH), 2.2 (4H, m, CH₂), 1.7 (1H, t, CH), 1.4 (1H, s, NH₂, D₂O exchangeable), 0.9, 1.0, 1.1 (9H, 3 × s, 3 × CH₃); *m/z* 271.

9,10-Di-1¹-naphthylphenanthrene-9,10-diol (4a) : was synthesised by the reported procedure³.

3a,11b-Di-1¹-naphthyl-3a,11b-dihydro-3H-phenanthro[9,10-d]oxazol-2-one (5a) : A mixture of diol 4a (0.001 mol, 0.464 g) and urea (0.002 mol, 0.120 g) was rapidly heated at 180–200° for 5 h, then poured into water and extracted with chloroform (50 ml). The chloroform layer was dried over anhyd. Na₂SO₄. On removal of the solvent, a solid was obtained (0.200 g, 40%), m.p. 154–155° (Found : C, 85.82; H, 4.68; N, 2.83. C₃₅H₂₃NO₂ requires : C, 85.88; H, 4.70; N, 2.86%); *v*_{max} (CDCl₃) 1640–1700 (C=O), 3520 cm^{–1} (NH); δ (CDCl₃) 8.1 (2H, m, peri-protons), 7.3 (20H, m, ArH), 2.0 (1H, br s, NH, D₂O exchangeable); *m/z* 489.

9,10-Diphenylphenanthrene-9,10-diol (4b) : It was synthesised from phenanthrene-9,10-diol (0.025 mol, 7 g) using phenylmagnesium bromide (prepared from 2.4 g magnesium and 15.6 g bromobenzene) in dry THF adapting the same procedure as for 4a, (yield 6.0 g, 49%), m.p. 171–173 (Found : C, 85.66; H, 5.47. C₂₆H₂₀O₂ requires : C, 85.71; H, 5.49%); *v*_{max} (KBr) 1600 (C=C, arom), 3520 cm^{–1} (OH); δ (CDCl₃) 7.2 (18H, m, ArH), 4.1 (2H, s, OH, D₂O exchangeable); *m/z* 364.

3a,11b-Diphenyl-3a,11b-dihydro-3H-phenanthro[9,10-d]oxazol-2-one (5b) : A mixture of diol 4b (0.0005 mol, 0.182 g) and urea (0.001 mol, 0.060 g) was heated at 180–200° for ~7 h, then extracted with chloroform (50 ml) and dried over anhyd. Na₂SO₄. On removal of the solvent, a white solid was obtained (yield 0.076 g, 40%), m.p. 163–165° (Found : C, 83.28; H, 4.86; N, 3.55. C₂₇H₁₉NO₂ requires : C, 83.29; H, 4.88; N, 3.59%); *v*_{max} (CDCl₃) 3520 cm^{–1} (NH); δ (CDCl₃) 7.1 (18H, m, ArH), 1.6 (1H, s, NH, D₂O exchangeable); *m/z* 389.

Acknowledgement

The authors are thankful to SPIC Science Foundation, Chennai, R.S.I.C., I.I.T., Chennai, for providing the spectral data and the management of New College, Chennai, for facilities.

References

1. C. D. Lunsford, R. P. Mays and R. S. Murphey, *J. Am. Chem. Soc.*, 1960, **82**, 1166.
2. F. G. Mann and B. C. Saunders, "Practical Organic Chemistry", 4th. ed., ELBS and Longman, London, 1974, p. 147.
3. A. K. Rahiman, S. S. Hussaini and C. A. M. A. Huq, *Curr. Sci.*, 2002, **82**, 1138.
4. P. Dimroth, H. Pasedoch and K. Scheffezik, *Chem. Abstr.*, 1964, **60**, 2934.