

SHORT COMMUNICATIONS

Synthesis of 6,12-Di(adamantane-2'-spiro)-6*H*,12*H*-dibenzo[*b,f*][1,5]dioxocine

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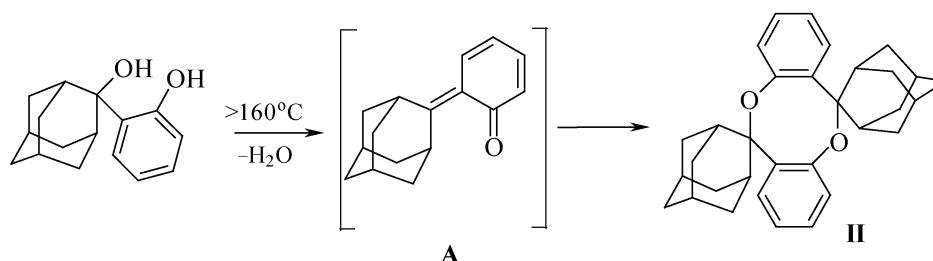
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In the absence of nucleophilic agents *O*-hydroxybenzyl alcohols through the formation of *O*-methylenequinones suffer di- and trimerization by [4+2]-cycloaddition [1, 2]. At the same time the cases of formal [4+4]-cycloaddition of *O*-methylenequinones are extremely seldom [3, 4]. We showed that the sterically hindered 2-(2-hydroxyphenyl)-2-adamantanol (**I**) [5] at a temperature higher than the melting point (>160°C) underwent a dimerization into 6*H*,12*H*-dibenzo[*b,f*][1,5]dioxocine (**II**).

The heating for long hours in the boiling *O*-xylene or

DMF did not result in the formation of the spiro dimer **II**.

In the ¹H NMR spectrum of compound **II** the group of signals from aromatic protons was observed in the region 6.74–7.05 ppm, and the signals from the adamantane fragment, in the region 1.36–3.43 ppm. In the ¹³C NMR spectrum the most deshielded in the adamantane fragment is atom C² (89.28 ppm), and in the aromatic fragment, carbon atoms attached to oxygen (156.86 ppm). In the mass spectra the most abundant peak belongs to the product of the dimer decomposition, *O*-methylenequinone **A**.



The reverse transformation of dioxocine **II** into alcohol **I** easily occurs at its dissolution in CF₃COOH and pouring the reaction mixture in water.

6,12-Di(adamantane-2'-spiro)-6*H*,12*H*-dibenzo[*b,f*][1,5]dioxocine (II**).** Yield 87%, mp 240–242°C (DMF). IR spectrum, ν, cm⁻¹: 3059 (CH_{arom}), 2939, 2901, 2851 (CH_{Ad}), 1597, 1481, 1447, 1234 (C–O–C), 1099, 1038 (C–O–C), 968, 918, 768, 741. ¹H NMR spectrum (400 MHz, CDCl₃), δ, ppm: 1.36 δ (2H_{Ad}, *J* 12.47 Hz), 1.67–1.80 m (12H_{Ad}), 1.99 s (4H_{Ad}), 2.30 d (4H_{Ad}, *J* 12.48 Hz), 2.59 s (2H_{Ad}), 2.69 d (2H_{Ad}, *J* 12.47 Hz), 2.90–2.97 m (2H_{Ad}), 3.43 s (2H_{Ad}), 6.74–6.77 m (4H_{arom}–

2,4,8,10), 6.96 t (2H_{arom}^{–3,9}, *J* 7.34 Hz), 7.05 d (2H_{arom}^{–1,7}, *J* 8.08 Hz). ¹³C NMR spectrum (50 MHz, CDCl₃), δ, ppm: 27.13, 27.46, 33.12, 34.22, 35.00, 35.68, 36.05, 36.85, 38.45 (18C_{Ad}^{–1,3-10}), 89.28 (2C_{Ad}^{–2}), 122.78 and 124.85 (4C_{arom}^{–2,4,8,10}), 128.25 and 129.28 (4C_{arom}^{–1,3,7,9}), 135.72 (2C, C_{arom}, C_{Ad}^{–2}), 156.86 (2C_{arom}–O). Mass spectrum, *m/z* (*I*_{rel}, %): 452 (1) [*M*]⁺, 226 (82) [C₁₆H₁₈O], 225 (100), 219 (10), 183 (27), 169 (18), 145 (19), 131 (20), 107 (21), 71 (48), 69 (43), 57 (66), 55 (49), 43 (48). Found, %: C 84.78; H 7.98. C₃₂H₃₆O₂. Calculated, %: C 84.84; H 7.95.

The IR spectrum was recorded on a spectrophotometer Shimadzu FTIR-8400S from KBr pellet. ¹H and ¹³C NMR

spectra were taken on a spectrometer Bruker AM400 (400 MHz), internal reference TMS. Mass spectrum was obtained on an instrument Finnigan Trace DSQ, ionizing electrons energy 70 eV. The elemental analysis was carried out on an automatic CHNS-analyzer Euro-Vector EA-3000.

REFERENCES

1. Van De Water, R. W., and Pettus, T.R.R., *Tetrahedron*, 2002, vol. 58, p. 5367.
2. Cavitt, S.B., Sarrafizadeh, H., and Gardner, P.D., *J. Org. Chem.*, 1962, vol. 27, p. 1211.
3. Pisova, M. and Soucek, M., *Coll. Czech. Chem. Commun.*, 1982, vol. 47, p. 838.
4. Patel, A., Mazzini, F., Netscher, T., and Rosenau, T., *Res. Lett. Org. Chem.*, 2008, p. 1.
5. Talley, J.J. and Evans, I.A., *J. Org. Chem.*, 1984, vol. 49, p. 5267.