272. Propellanes

Part LXX

The Oximes of [4.3.3]Propellane-8,11-dione1)

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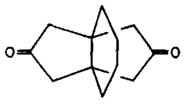
Summary

The mono-oxime and dioxime of the title compound have been prepared.

We wished to conduct the *Beckmann* rearrangement of [4.3.3]propellane-8,11-dione dioxime (**2**). In principle there may be two dioximes, *syn* or *anti* (with respect to the C=N hydroxy functions).



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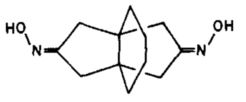
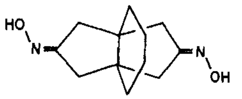


2a
(*syn*)



2b
(*anti*)

The diketone was prepared by the method of *Weiss* [2]. The mixture of dioximes was purified by repeated crystallization. This was shown by X-ray crystallography to be the *anti*-dioxime which is evidently the thermodynamically more stable isomer, m.p. 215–216°.

Beckmann rearrangement was attempted under a variety of conditions, without success. Hydrolysis competes with rearrangement (see *Experimental*) and the mono-oxime of **1** was obtained in this way together with recovered **2b** and **1**.

Experimental. – The diketone **1** (4.75 g), hydroxylamine hydrochloride (1.5 g), and anh. AcONa (12.5 g) were added to aq. (50 ml) EtOH (100 ml) and the whole was heated under reflux for 24 h. The solvent was removed at the H_2O pump and ice cold H_2O was added, affording a colorless solid. After filtration, washing and drying the dioxime was obtained (5.2 g, 94%), consisting of two isomers, m.p. 180–183° (MeOH). Repeated recrystallization gave one isomer, m.p. 215–216° (MeOH). IR (KBr): 3200–3100. ^{1}H-NMR (D_6DMSO): (br. *s*, 2=N–OH); 2.3 (*s*, 8CH_2C=NOH); 1.33 (*s*, 8CH_2). MS: 222 (100); 164 (64); 150 (26); 146 (33); 134 (24); 133 (74); 132 (35); 105 (43). M.W.: Calc. 222.1368, Found 222.1350.

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1) Part LXIX: [1].

Beckmann rearrangement failed with $SOCl_2$ in Et_2O, polyphosphoric acid, dry HCOOH, conc. H_2SO_4, H_3PO_4, AcOH, trifluoroacetic acid, Ac_2O. With benzenesulfonyl chloride, dioxime was recovered but some hydrolysis took place to give **1** and the mono-oxime, m.p. 164–165° (abs. MeOH). IR ($CHCl_3$): 3665,1735. ^{1}H-NMR ($CDCl_3$): 9.2–8.7 (*m*, 1N–OH); 2.5 (*m*, $4CH_2C=NOH$); 2.3 (*s*, $4CH_2CO$); 1.45 (*s*, $8CH_2$). MS: 207 (16); 191 (15); 164(10); 162(16); 150(34); 148(25); 136(26). M.W.: Calc. 207.1259, Found 207.1264.

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[3] *M. Kapon*, unpublished results.