Tetrahedron Vol. 40, No. 24, p. 5273, 1984
Printed in the U.S.A.

0040-4020/84 $3.00 + .00

PROPELLANES—LXXVII

SODIUM BOROHYDRIDE REDUCTION OF 10-OXA[3.3.3]PROPELLANE-3,7-DIONE†

Ella Cohen and David Ginsburg*
Department of Chemistry, Israel Institute of Technology, Haifa, Israel

(*Received in UK* 26 *January* 1984)

Abstract—The title diketone was reduced to give a mixture of the three possible diols which were isolated and characterized.

In connection with a related exercise in symmetry[1] we report unpublished work[2] with experimental detail.

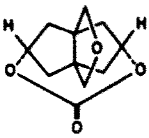
The diketone **1**[3] upon reduction to diols is expected for reasons of symmetry to give three configurational isomers **2–4**.

1

2

3

4



5

Sodium borohydride reduction of **1** gives the three diols in the ratio of 5:9:1, respectively. The relatively unsymmetric nature of the NMR spectrum of the *syn–anti*-diol **3** permits its characterization as such. In this case it would have been easier if we had more of the *anti–anti*-diol **4** in hand for its proof of structure depended upon preparation of a cyclic carbonate **5** but in accordance with the Robinson postulate this was therefore obtained in lowest yield.[4] The diol from which this carbonate was indeed prepared was therefore **4** and by ironclad logic, both chemical and symmetrical, the third diol **2** must have the *syn–syn* configuration.[5]

EXPERIMENTAL

Reductions of **1**. A mixture (1.2 g), $NaBH_4$ (1.28 g), MeOH (100 ml), and ether (20 ml) was allowed to stand overnight. The volume was concentrated to one third and submitted to continuous extraction with CH_2Cl_2 for 24 hr. Evaporation gave the diol mixture (1.08 g; 88%) as an oil which turned semi-solid. (Found: C, 65.03; H, 9.00; O, 26.05. $C_{10}H_{16}O_3$ requires C, 65.19; H, 8.75; O, 26.05%; the individual isomers do not give a molecular peak.) The diols were isolated by column chromatography on basic alumina, using $CHCl_3$ as eluent, in the following order:

Diol **2**. M.p. 192° (benzene–chloroform), 350 mg (5 parts). IR($CHCl_3$): 3600, 3500–3300, 2990, 2950, 2930, 2860 cm^{-1}. NMR($CDCl_3$: δ 3.81 (s, 4 $\mathrm{C\underline{H}_2O}$); 3.41 (br t, 2 $\mathrm{C\underline{H}OH}$); 3.67–3.48 (m, 2 $\mathrm{O\underline{H}}$, disappears with D_2O); 1.83 (d, 8 $\mathrm{C\underline{H}_2}$).

Diol **3**. M.p. 162° (benzene–chloroform), 627 mg (9 parts). IR($CHCl_3$): as for **2**. NMR($CDCl_3$): 4.42–4.20 (m, 2 $\mathrm{C\underline{H}OH}$); 3.90–3.39 (ABq, J = 10 Hz; 4 $\mathrm{C\underline{H}_2O}$); 2.30–1.32 (m, 8 $\mathrm{C\underline{H}_2}$ + 2$\mathrm{O\underline{H}}$).

Diol **4**. M.p. 188° (benzene–chloroform), 68 mg (1 part). IR($CHCl_3$): 3600, 3500–3300, 2950, 2930, 2850 cm^{-1}. NMR($CDCl_3$): 4.45 (br t, 2 $\mathrm{C\underline{H}OH}$); 3.55 (s, 4 $\mathrm{C\underline{H}_2O}$); 2.26–2.08 (m, 2 $\mathrm{O\underline{H}}$, disappears with D_2O); 1.98 (d, 8 $\mathrm{C\underline{H}_2}$).

Cyclic carbonate **5**. Diol **4** (14 mg) and diethyl carbonate (0.01 ml) were added to toluene heated under reflux containing Na (18 mg) and kept at this temp for 17 hr. After cooling to r.t., filtration and removal of solvent (water pump) a colorless solid was obtained (13 mg; 81.5%), m.p. 270° (dec, pet ether 60–70). (Found: C, 62.22; H, 6.87; O, 29.73. $C_{11}H_{14}O_4$ requires C, 62.84; H, 6.71; O, 30.44%.) IR($CHCl_3$): 2960, 2930, 2850, 1740 cm^{-1}. NMR($CDCl_3$): 5.18 (t, 2 $\mathrm{C\underline{H}O}$); 3.58 (s, 4 $\mathrm{C\underline{H}_2O}$); 2.05 (d, 8 $\mathrm{C\underline{H}_2}$).

REFERENCES

[1a] R. Askani, R. Kirsten, and B. Dugall, *Tetrahedron* **37**, 4437 (1981); [b] S. Bhanumati, P. Ashkenazi, S. Migdal, and D. Ginsburg, *Helv. Chim. Acta* in press.

[2] D. Ginsburg, *Propellanes—Structure and Reactions*, pp. 169–170. Verlag Chemie, Weinheim (1975).

[3] J. Altman, E. Cohen, T. Maymon, J. B. Petersen, N. Reshef, and D. Ginsburg, *Tetrahedron* **25**, 5115 (1969).

[4] This experimental fact of life may have been enuciated by others but we heard it many years ago from Sir Robert Robinson and the attribution to him in lectures has gone unchallenged.

[5] This is another case of obedience to the Prelog dictum: *The world is chiral and clinal. Enjoy symmetry wherever you find it.* Cf. D. Ginsburg, *Acc. Chem. Res.* **7**, 286 (1974).

---

†Part LXXVI: L. Senegör, P. Ashkenazi and D. Ginsburg, *Tetrahedron* **40**, 5271 (1984).