ISSN 0018-019X

Erscheint 9mal jährlich – Paraît 9 fois par an

241. Propellanes, XXXII. Preparation of Propellane Lactones by Means of the Chloronitrone Reaction[1])

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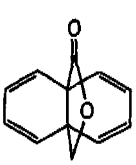
(13.IX.75)

Summary. Two [4.4.3]propellane lactones **3** and **8** were prepared by employing the chloronitrone reaction. The intermediate propellanes **9** and **12** were also isolated in pure form.

For the first time a propellane has been synthesized by using the chloronitrone reaction [1]. We have studied the behaviour of the lactone **1** [2] prepared from the dienic lactone **2** [3]. The chloronitrone reaction makes possible the synthesis of **3**, a positional isomer of **2**.

For the purpose of preparing the analogous tetraenic positional isomer and comparing its course of *Diels-Alder* reaction, we considered isotetralin **4** as a reasonable starting material. It is known that carbenoid attack of **4** [4] affords more of the corresponding propellane **5** rather than the tricyclic isomer **6** because the tetrasubstituted double bond is mechanistically more prone to attack [5]. We thus expected by the same token that more of **3** would be obtained as compared to **7**. Of course, a [4.4.3]-propellane lactone rather than an analog of **7** could be guaranteed by reducing **3** catalytically.

The tetrasubstituted double bond cannot be reduced under these conditions and the chloronitrone reaction as applied to **11** would then lead exclusively to **8** (tetrahydro-**3**) [6].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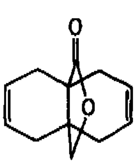
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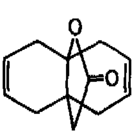
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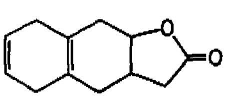
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The reaction sequences are shown in the scheme and the details are given in the experimental section.

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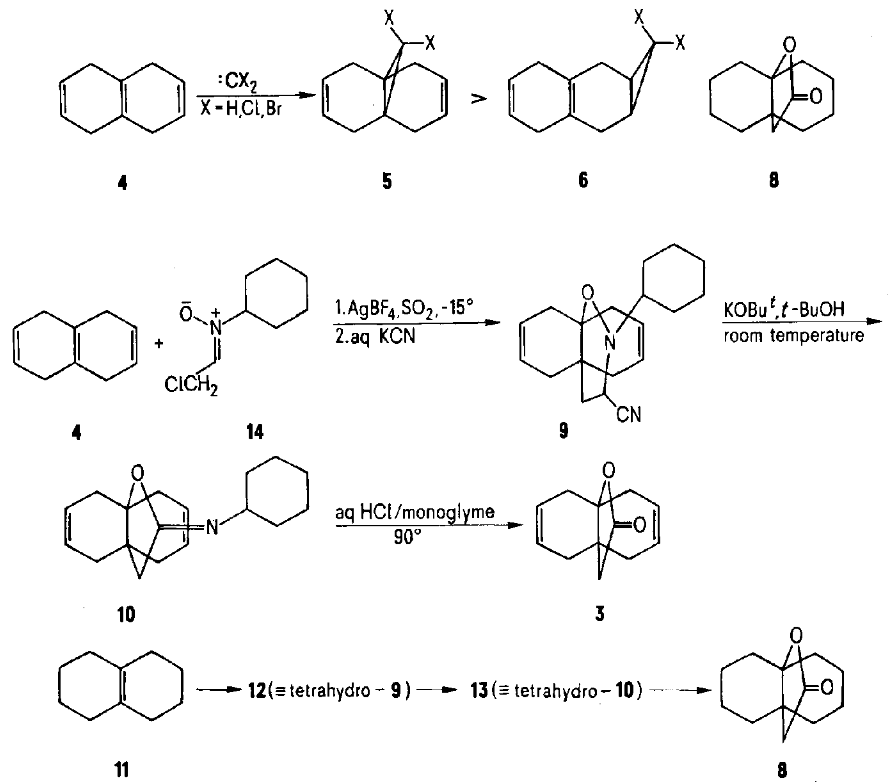
[1] Propellanes, XXXI. *J. Kalo, J.M. Photis, L.A. Paquette, E. Vogel & D.Ginsburg*, Tetrahedron, in press.



Experimental Part

12-Oxo-11-oxa[4.4.3]propella-3,8-diene (**3**). a) A mixture of isotetralin (**4**) (m.p. 55°; 0.8 g) and silver fluoroborate (*Fluka*, purum, anhydrous; 1.17 g) was placed in a 100 ml 3-necked flask equipped with nitrogen inlet (dry nitrogen) and an SO_2 condenser (maintained at $-70°$ with dry ice – MeOH). The flask was cooled with an ice/salt bath (*ca.* $-15°$) and SO_2 was condensed in it (*ca.* 50 ml, dried over P_2O_5). At $-15°$ (bath temp) a solution of α-chloroacetaldehyde-N-cyclohexylnitrone **14** [1] (1.08 g) in 1,2-dichloroethane (*Fluka*, puriss, filtered through Alox; 10 ml) was added during 75 min with vigorous stirring. Then $AgBF_4$ (577 mg) and **14** (540 mg) in dichloroethane (5 ml) were added in turn and again the same reagents (350 mg and 320 mg in 5 ml, respectively) during 45 min. The whole was allowed to warm to room temp. and the liquid SO_2 removed with a stream of dry nitrogen at room temp. The residue was freed at the water pump of any remaining SO_2 and the partly insoluble material (AgCl) was suspended in CH_2Cl_2 (50 ml) and shaken in a separatory funnel with aqueous (50 ml) potassium cyanide (5 g) for 1 min at room temp. The organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 30 ml). The combined organic phase was dried ($MgSO_4$) and after removal of solvent in a vacuum the crude yellow product was chromatographed on a column of neutral Alox (deactivated with 6% water; 35 g) using 200 ml hexane/benzene 9:1 starting with pure hexane. A slightly yellow oil was eluted (960 mg; 53%). Crystallization at 0° gave **9** (570 mg; 31%), m.p. 104° (pentane). – NMR. (CCl_4)[2]: 5.48 (*m*, 4 vinylic H); 4.03 (*t*, $J = 6$, CHCN); 3.1–3.2 (br. *m*, *ca.* 21H). – IR. ($CHCl_3$): 2930, 2860, 2230, 1660, 1455, 1375, 1360, 1135, 1020, 1000, 900, 880 cm^{-1}. – MS. (*m/e*): 298 (M^+, 2), 130(20), 115(38), 91(37), 83(32), 72(41), 55(62), 54(44), 41(100).

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[2] Chemical shifts are given in δ (ppm), coupling constants in Hz.

b) To a solution of **9** (m.p. 104°, 550 mg) in *t*-butyl alcohol (distilled from CaH_2; 5 ml)was added under dry nitrogen at room temp. a solution of $KOBu^t$ in *t*-BuOH (0.78N; 2,6 ml). After 15 min the slightly yellow cloudy solution was poured onto brine (50 ml) and extracted with ether (3 × 50 ml). After drying ($MgSO_4$) the ether was removed in a vacuum affording crude **10** as an oil (580 mg) which crystallized on standing [IR. ($CHCl_3$): 2920, 1690, 1445, 1360, 1020, 965, 885 cm^{-1}]. This crude product was dissolved in 10 ml of hydrochloric acid (0.5N)-/monoglyme 1:1) and heated in a bath at 90° for 20 h. The solution was cooled to room temp, poured onto brine (5 ml) and extracted with ether (twice 30 ml). After drying ($MgSO_4$) and removal of ether in a vacuum the crude residue was chromatographed on a column of silica (deactivated with 15% water; 11 g) using benzene (150 ml). The oily lactone **3** (260 mg, 74%) showed presence of no other isomer by NMR. or GLC. (SE-30, 20%, ret. time 19.4 min at 195° at He flow rate of 40 ml/min). – NMR. ($CDCl_3$): 5.72 (*s*, 4 vinylic H); 2.53 (*s*, CH_2CO); 2.44 (*m*, 4 allylic H); 7.78 (*m*, 4 allylic H). – IR. ($CHCl_3$): 2900, 1775, 1760, 1655, 1448, 1410, 1330, 1255, 1120, 1065, 1015, 990, 905, 865 cm^{-1}. – MS. (*m/e*): 190 (M^+, 5), 145(21), 136(100), 131(15), 108(81), 94(22), 91(31), 80(52), 79(55), 77(33).

12-Oxo-11-oxa[4.3.3]propellane (**8**) a) In the same way as described above $\Delta^{9,10}$-octalin (0.8 g; 93% purity by GLC.) in 1,2-dichloroethane (5 ml) was treated with $AgBF_4$ (1.6 g) in SO_2 (*ca.* 60 ml) and **14** (1.46 g) in dichloroethane (5 ml) was added during 1 h with vigorous stirring. After work-up as above hexane (450 ml) eluted from the Alox column (30 g) pure **12** (1.16 g; 68%), m.p. 92–94°. The analytical sample had m.p. 95–96° (hexane).

$C_{19}H_{30}N_2O$ (302.45) Calc. C 75.45 H 10.00 N 9.26% Found C 75.66 H 9.83 N 9.26%

NMR. ($CDCl_3$): 4.15 (*m*, $CHCN$); 0.6–3.2 (br. *m* 29H). – IR. ($CHCl_3$): 2920, 2850, 2220, 1450, 1320, 1245, 1230, 985, 970, 930, 890, 870 cm^{-1}. – MS. (*m/e*): 302(M^+, 30), 285(30), 189(15), 174(20), 161(34), 141(100), 96(38), 91(25), 55(77), 41(60).

b) The nitrile **12** (m.p. 92–94°; 0.94 g) in *t*-butyl alcohole (10 ml) was treated as above with $KOBu^t$ in *t*-BuOH (0.78N; 4.5 ml). After work-up as above the crude iminolactone **13** (1.024 g) was obtained [IR. ($CHCl_3$): 2920, 1680, 1445, 1365, 1135, 980, 930, 905, 885 cm^{-1}]. This was treated for 20 h as above with 20 ml HCl (0.5 N)/diglyme 1:1. After work-up as above chromatography on silica (13 g) using benzene (250 ml) after starting with benzene/hexane 1:1, eluted **8** (267 mg; 45%), m.p. 70–71° (hexane).

$C_{12}H_{18}O_2$ (194.26) Calc. C. 74.19 H 9.34% Found C 74.20 H 9.26%

NMR. ($CDCl_3$): 2.45 (*s*, CH_2CO); 1.3–2.0 (*m*, 16H). – IR. ($CHCl_3$): 2940, 2870, 1755, 1455, 1300, 1150, 1075, 980, 970, 935, 915, 865 cm^{-1}. – MS. (*m/e*): 194(M^+, 98),166(20), 138(100), 137(40), 124(24), 109(61), 81(28), 77(43), 41(37).

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