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PROPELLANES—XXIII[1]

THE SYNTHESIS OF [4.4.3]PROPELLANES CONTAINING ONE CYCLOHEXADIENE RING

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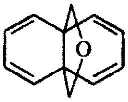
Abstract—Several propellanes containing in common a cyclohexane and a cyclohexadiene ring but varying in the structure of the third, 5-membered ring—an ether, a thioether, an anhydride or a methylimide ring—have been prepared.

We have studied the steric course of Diels–Alder addition of 4-phenyl-1,2,4-triazoline-3,5-dione to the *tetra*enic ether, **1** and methylimide, **2**.[2] The interpretation given for their difference in behavior towards the first equivalent of dienophile required us to adduce further evidence to support (or disprove) our contention[2] and an obvious set of substrates for Diels–Alder reaction was the set of tetrahydroderivatives **3** and **4**. In such compounds we would expect the cyclohexane ring to attain the chair conformation in analogy to that which obtains in [4.4.4]propellane.[3]

Another motive was to prepare the irontricar-



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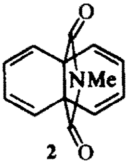

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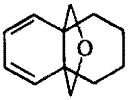

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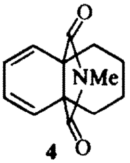

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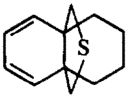

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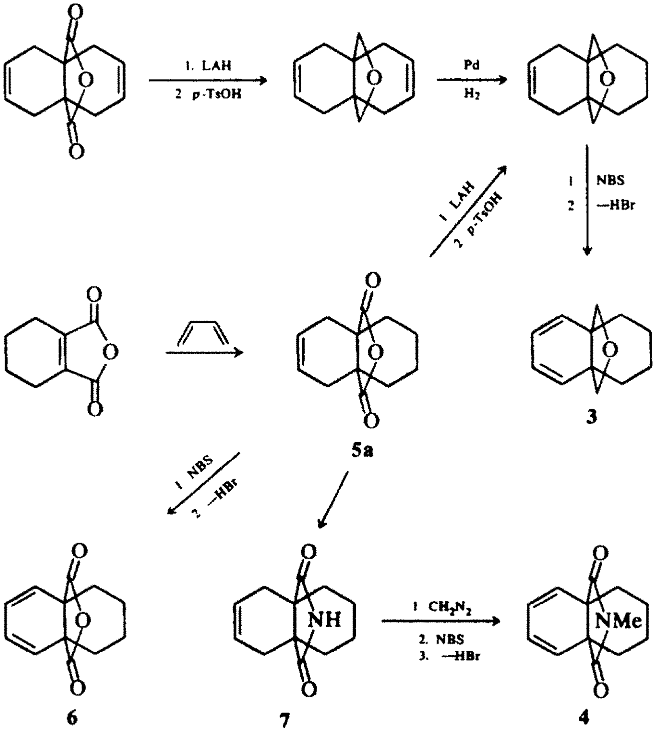

SCHEME 1

bonyl complexes of **3** and **4**, study their configuration and their reactions with excess 4-phenyl-1,2,4-triazoline-3,5-dione. In the case of **1** and **2** this reagent displaced the metal ligand with *retention* of configuration.[2] We wanted to compare to this, the behavior of the corresponding complexes of **3** and **4**.[4]

Thirdly, we wished to study the photochemistry of **3** and **4** as well as that of the analogous thioether **5**.[5]

The propellanes **3** and **4** were prepared as shown in Scheme 1.

Attempted reduction of **6** to the corresponding diol with LAH, even in ether solution, led to concurrent 1,4-reduction of the diene. Thus the sulfide **5** as well as its corresponding sulfone were prepared not *via* **6** but rather by the published method.[6]

The 1,4-reduction of a diene within a propellane system has been observed long ago in imides of this series. It was impossible to effect reduction to the amine without concomitant attack of the conjugated diene.[7] However, this is not so in the case of the dienic sulfide.[6]

EXPERIMENTAL

1-Cyclohexene-1,2-dicarboxylic anhydride. Following the published procedure[8] 4-cyclohexene-1,2-dicarboxylic anhydride (400 g) was stirred at 200° with P_2O_5 (10 g) for 60 hr. An additional portion (10 g) of P_2O_5 was added after 20 hr. Distillation afforded the rearranged product (324 g), b.p. 140° (0·5 mm), m.p. 67–70° (Lit.[8] m.p. 71–72°).

7,9-Dioxo-8-oxa[4.4.3]*propell-3-ene.* Following the published procedure[9] the above anhydride (120 g), butadiene (200 ml), dioxan (250 ml, rather than benzene) and hydroquinone (20 g) were heated in an autoclave for 17 hr at 170–180°. After cooling to room temp and removing solvent in a vacuum the residue was heated under reflux with 10% KOH aq (800 ml) for 2 hr. After cooling, filtration and acidification with conc HCl the corresponding dicarboxylic acid precipitated. It was collected, washed with water and dried overnight in a vacuum oven at 70°, affording the diacid (54 g; 31%), m.p. 76–77° (dec). Heating this (48 g) under reflux with acetic anhydride (300 ml) for 16 hr and removal of solvent gave the anhydride, m.p. 66–68° (40–60 pet ether). Lit.[9] m.p. 67–68°.

9, 10-Dihydroxymethyl-1, 4, 5, 6, 7, 8, 9, 10-octahydronaphthalene. A soln of the anhydride **5** (20 g) in dry THF (100 ml) was added dropwise to a stirred suspension of LAH (6 g) in THF (300 ml) and the mixture was heated under reflux overnight. After the usual workup the *diol* (16 g) was obtained, m.p. 144–148° (acetone). Lit.[9] m.p. 155–156°, prepared by a different route.

8-Oxa[4.4.3]*propell-3-ene* was prepared as reported,[10] b.p. 50° (0·2 mm). Lit.[10] b.p. 136° (22 mm). The compounds were compared and had identical spectral properties.

8-Oxa[4.4.3]*propella-2,4-diene*, **3**. A mixture of the ether monoene (8·6 g), N-bromosuccinimide (8·9 g), dibenzoyl peroxide (50 mg) and CCl_4 (600 ml) was heated under reflux over a sunlamp for 35 min. After the usual workup the allylic bromide was stirred in DMF (600 ml) at 100° for 15 hr. After the usual workup a red-brown oil (7·8 g) was obtained. Distillation afforded the pure diene (5·3 g; 62%). b.p. 78° (0·6 mm). (Found: C, 81·75; H, 8·99; M.W. 176. $C_{12}H_{16}O$ requires: C, 81·77; H, 9·15%, M.W. 176·25); NMR ($CDCl_3$): τ 3·80–4·65 (m, 4 dienic H); 6·16 (s, 4 $C\underline{H}_2O$); 8·52 (br s, 8 $C\underline{H}_2$); UV (MeOH): λ_{max} 261 nm, (ε 3300).

Irontricarbonyl complex of **3**. A soln of **3** (0·6 g) and iron pentacarbonyl (1·2 ml) in di-n-butyl ether (100 ml) was heated under reflux for 16 hr under N_2. After cooling, the black ppt was collected (under N_2), washed with CH_2Cl_2 and the solvents removed from the filtrate and washings. The residue was triturated with hexane and afforded the light yellow product (0·79 g; 73%). The analytical sample had m.p. 91–92° (CH_2Cl_2-hexane). (Found: C, 57·04; H, 5·02; Fe, 17·50; M.W. 316. $C_{15}H_{16}O_4Fe$ requires: C, 56·98; H, 5·10; Fe, 17·67%, M.W. 316·13); IR($CHCl_3$): 2920, 2850 (CH), 2050, 1975 (CO), 1140, 1110 cm^{-1} (ether); NMR ($CDCl_3$): τ 4·90 (m, 2 cent. dienic H), 6·45 (ABq, $J_{AB} = 9$ Hz; 4 $C\underline{H}_2O$); 7·27 (m, 2 term. dienic H); 8·75 (br s, 8 $C\underline{H}_2$).

11,13-Dioxo-12-aza[4.4.3]*propell-3-ene*, **7**. A mixture of **5** (9 g) and conc NH_4OH (300 ml) was heated under reflux for 16 hr. The ppt was collected by filtration, washed with water and dried, affording the *imide* (6·9 g). Extraction with EtOAc gave a second crop (1·7 g; total, 95%). It had m.p. 175–176° (95% EtOH). (Found: C, 70·60; H, 7·43; N, 6·66; M.W. 205. $C_{12}H_{15}NO_2$ requires: C, 70·22; H, 7·37; N, 6·82%; M.W. 205·25). IR($CHCl_3$): 3400 (NH); 2940, 2890, 2850 (CH), 1785, 1735 (imide CO), 1600 cm^{-1} (C=C); NMR ($CDCl_3$): τ 1·30 (br, $N\underline{H}$); 4·18 (m, 2 vinylic H); 7·20–8·66 (m, 12 allylic and $C\underline{H}_2$).

12 - Methyl - 11, 13 - dioxo - 12 - aza[4.4.3]*propell - 3 - ene.* A soln of **7** (10 g) in dry MeOH was treated with excess ethereal diazomethane. After removal of solvent the methylimide was obtained in quant yield, m.p. 80–81° (95% EtOH). (Found: C, 71·27; H, 7·93; N, 6·52. $C_{13}H_{17}NO_2$ requires: C, 71·20; H, 7·82; N, 6·39%); IR($CHCl_3$): 2940, 2870, 2840 (CH); 1770, 1700 (imide CO); 1620 cm^{-1} (C=C); NMR ($CDCl_3$): τ 4·16 (m, 2 vinylic H), 7·01 (s, 3 $NC\underline{H}_3$); 7·10–8·00 (m, 4 allylic $C\underline{H}_2$), 8·10–8·70 (m, 8 $C\underline{H}_2$).

12 - Methyl - 11, 13 - dioxo - 12 - aza[4.4.3]*propella - 2, 4 - diene*, **4**. Bromination of the monoene (10 g) was carried out as above with NBS (9·1 g), dibenzoyl peroxide (50 mg) and CCl_4 (700 ml) during 30 min over a sunlamp. After workup as above the oily allylic bromide was stirred under N_2 in DMF (700 ml) for 15 hr at 100°. After the usual workup the *diene* was obtained (7·0 g; 70%) after sublimation at 55° (0·2 mm), m.p. 66–72°. (Found: C, 71·65; H, 6·85; N, 6·34; M.W. 217. $C_{13}H_{15}NO_2$ requires: C, 71·86; H, 6·96; N, 6·45%; M.W. 217·26); IR($CHCl_3$): 2950–2850 (CH); 1780, 1700 (imide CO); 1600 cm^{-1} (C=C) NMR($CDCl_3$): τ 3·75–4·54 (AA′BB′m, 4 dienic H); 7·00 (s, $NC\underline{H}_3$); 7·80–8·80 (m, 8 $C\underline{H}_2$); UV (MeOH): λ_{max} 260 (ε 4400), 2·68 nm (sh, ε 4200).

Irontricarbonyl complex of **4**. A soln of **4** (0·5 g) and $Fe(CO)_5$ (1 ml) in di-n-butyl ether (100 ml) was heated under reflux for 16 hr under N_2. After workup as above for the complex of **3** and trituration with hexane the complex (0·37 g; 45%) was obtained. It formed light yellow crystals, m.p. 118–118·5° (CH_2Cl_2-hexane). (Found: C, 53·62; H, 4·18; N, 3·84; M.W. 357. $C_{16}H_{15}NO_5Fe$ requires: C, 53·78; H, 4·23; N, 3·92%; M.W. 357·14); IR ($CHCl_3$): 2950, 2880 (CH); 2060, 1990 (CO); 1770, 1700 cm^{-1} (imide CO); NMR ($CDCl_3$): τ 4·62 (m, 2 central dienic H); 6·68 (m, 2 term dienic H); 7·00 (s, 3 $NC\underline{H}_3$); 7·60–9·20 (br m, 8 $C\underline{H}_2$).

7, 9 - Dioxo - 8 - oxa[4.4.3]*propella - 2, 4 - diene*, **6**. The anhydride **5** (1·05 g) in CCl_4 (50 ml) was treated with NBS (0·95 g) and a trace of dibenzoyl peroxide and the mixture was heated under reflux for 45 min whilst irradiating with a sunlamp. After filtration and removal of solvent in a vacuum, DMF (50 ml) was added and the whole was heated at 100° overnight. After cooling and dilution with water (50 ml), the whole was extracted with ether affording after evaporation crude material (720 mg). The anhydride **5** had m.p. 78–79° (light petroleum 40–60° followed by sublimation). (Found: C, 70·63; H, 6·04. $C_{12}H_{12}O_3$ requires: C, 70·57; H, 5·92%); IR(KBr): 1870, 1780 cm^{-1} (CO); NMR(CCl_4): τ AA'BB' 3.80 (dd, $J_1 = 8$ Hz, $J_2 = 3$ Hz, 2 vinylic H); 4·36 (dd, $J_1 = 8$ Hz, $J_2 = 3$ Hz, 2 vinylic H); 7·8–8·5 (m, 4H); 8·5 (br s, 4H). UV (hexane): $\lambda\lambda_{max}$ 257 (3470); 264 (3390), 247 (sh), 275 nm (sh).

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