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PROPELLANES—XLIII

INHIBITION OF SECONDARY ORBITAL CONTROL IN DIELS–ALDER REACTIONS OF CERTAIN PROPELLANES WITH 4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES†

P. ASHKENAZI, J. KALO, A. RÜTTIMANN and D. GINSBURG*
Department of Chemistry, Israel Institute of Technology, Haifa, Israel

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Abstract—A number of propellane substrates were prepared with special structural features, such that attack by dienophiles would be (a) from below—due to repulsive interactions, both electronic and steric, or (b) if the electronic influence from above was less efficient, than the attack would be from both directions. The predicted course of all the reactions has been realised experimentally.

We have devoted much effort to test the hypothesis that in propellanes of type **1** steric control by the H atoms adjacent to the hetero-atom (or CH_2) causes attack by the title-dienophiles to occur from below, affording mono-adduct of the configuration explicated by **2**. On the other hand, when CO groups flank the hetro-atom, as in propellanes of type **3**, attack occurs from the reverse direction, from above, i.e. *syn* with respect to the CO groups due to secondary orbital control of the reaction course, leading to mono-adducts of the configuration exhibited by **4**[1].

In the tetraenic lactone **5**, secondary orbital overlap with the dienophile cannot be as effective as in the corresponding anhydride **4** (X=O). Indeed, a mixture of products is obtained by attack of **5** from both possible directions.[2]

It was of interest to prepare additional propellane substrates in which such secondary orbital overlap be rendered inefficient *a priori* as in the cases **6a–c** in which a steric factor is superimposed upon a repulsive electronic one and in **7** which, being a β-diketone would be expected to exist at least in part in the enolic form in which overlap cannot be as efficient as in substrates of type **3**.

As shown in Scheme 1, the starting material for the preparation of compounds of type **6** is isotetralin **8**.[3] Although the *trans*-glycol **9** has been prepared,[4] we are not aware of its *cis*-isomer **11** having been reported hertofore. The synthesis of the *cis*-glycol employed the known *trans*-dibromide.[4] Needless to say, the OH groups in **11** are amply hindered but it was nevertheless possible to prepare **6a–c** as described in the Experimental.

Conversion of **12a–c** into the corresponding tetraenes **6a–c** via a bromination-dehydrobromination sequence presented experimental difficulties owing to the lability of reactants and products towards acid (**6a,b**, **12a,b**) and towards base (**6c**, **12c**), respectively. Sufficient quantities of the products could nevertheless be husbanded so as to enable testing their behavior in the Diels–Alder reaction with the title-dienophiles.

That **6a** is attacked first from below, then from above, due to steric hindrance by the hydrogens of the $-OCH_2O$ bridge is supported by their doublet in the NMR spectrum of the bis-adduct and by the fact that **6b** gives only a mono-adduct. Presumably, the second Me group in the $-OCMe_2O-$ bridge does not allow a second mole of dienophile to react from the top side. By analogy, we

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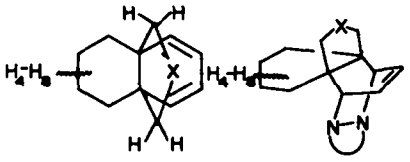
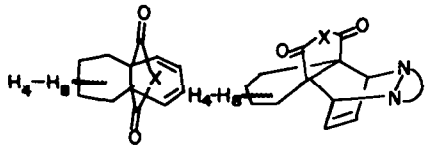
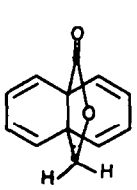


1: X = O, S, NH_2^+, CH_2 **2**:



3: X = O, NH, NMe, NPh **4**:



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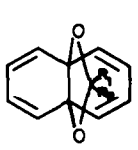
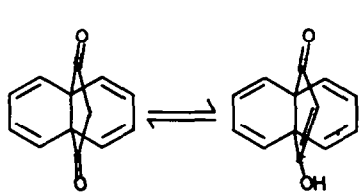


6a: $R_1 = R_2 = H$
b: $R_1 = R_2 = Me$
c: $R_1, R_2 = O$



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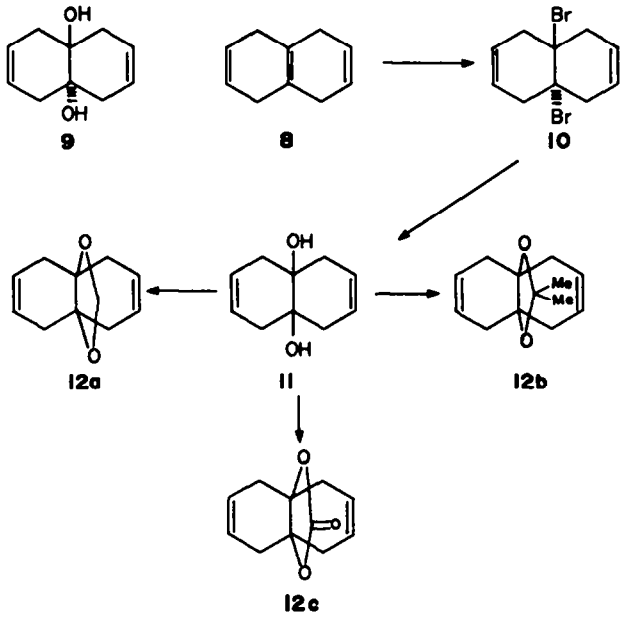


Scheme 1.

believe that **6c** also reacts by the same chronological sequence (below, then above). (Its *bis*-adduct with MTD exhibits two different NCH_3 signals). This thesis will be checked by X-ray crystallography.

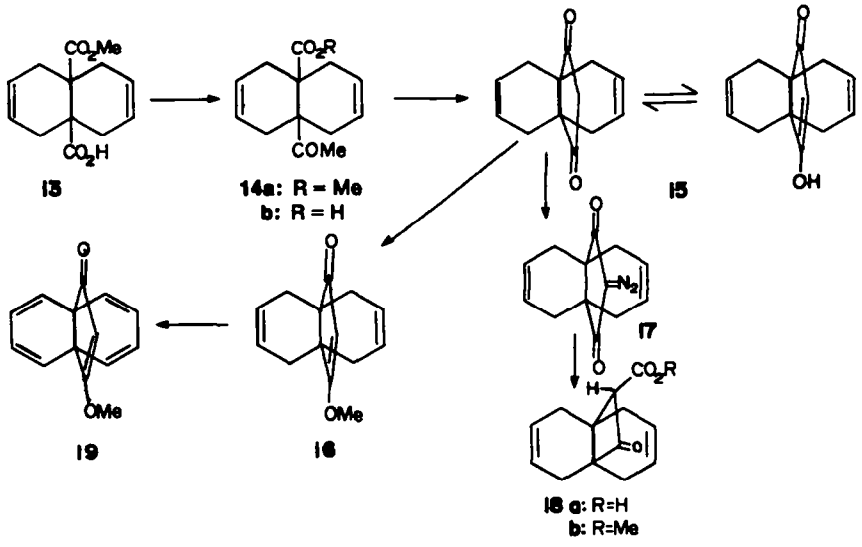
Scheme 2 summarizes the reactions carried out in the attempt to prepare the β-diketone **7**. The ester–ketone **14** was prepared from the half-ester **13**. Treatment of **14** with potassium hydride afforded the β-diketone **15** whose NMR spectrum in deuteriochloroform shows it to be 45% enolized in this solvent. Methylation of **15** with diazomethane afforded a quantitative yield of the methyl ether **16**. On the other hand, the diazodiketone **17** may be prepared from **15** using tosyl azide in the presence of triethylamine. Irradiation of the latter afforded either the acid **18a** or its methyl ester **18b** depending upon the solvent used for the irradiation. Finally, bromination of **16** followed by dehydrobromination afforded the pentaene **19** which, albeit suitable for study in the Diels–Alder reaction, was expected to give a complex mixture of products. It indeed gave an intractable mixture including mono-adducts having formed by attack from both directions and the corresponding *bis*-adducts. This is not surprising since this substrate ought to behave like the lactone **5**.

EXPERIMENTAL

IR spectra were measured on a Perkin–Elmer model 257 grating spectrometer. NMR spectra were measured on a Varian T-60 spectrometer. Mass spectra were measured on a Varian 711 spectrometer using the direct inlet system. The electron energy was maintained at 100 eV. Only the major fragments are listed. All m.ps are uncorrected. All Diels–Alder reactions were conducted at room temp.

Preparation of cis-*glycol* **11**

(a) *Direct way.* Isotetralin (13.2 g; 0.1 mole), glacial AcOH (450 ml) and water (2 ml; 0.11 mole) were placed in a 1 l.



Scheme 2.

3-necked flask equipped with stirrer, dropping funnel, N_2 inlet and thermometer. Silver acetate (37.0 g; 0.22 mole, Fluka purum) was added under N_2. Br_2 (17.0 g; 0.107 mole) in glacial AcOH (20 ml) was added to this slurry at room temp. whilst stirring during 1 hr. Stirring was continued at 75° for 2 hr and the mixture was cooled to room temp. The AgBr formed was removed by filtration and the solvent removed at the water pump at 50–60°. MeOH (300 ml) was added to the residue and the whole was neutralized with solid KOH to pH 10. More KOH (6 g) was added with stirring and cooling in an ice bath at 0°. The brown suspension was removed by filtration and the filtrate set aside at room temp. overnight. The MeOH was removed in a vacuum at room temp. and the residue poured into satd NaCl aq (100 ml) and then extracted with $CHCl_3$ (3 × 100 ml). The combined organic extracts were washed with satd NaCl aq (50 ml) and the latter phase again extracted with $CHCl_3$ (2 × 50 ml). The combined organic phases were dried ($MgSO_4$), the solvent removed in a vacuum to afford a brown oil which crystallized on standing. Recrystallization was affected by dissolution in boiling ether and slow cooling to −10°. The *cis*-diol **11** (4.83 g; 29%) had m.p. 82–85°.

(b) *Indirect way.* (1) *Bromination.* Into a 2 l. 3-necked flask equipped with stirrer, dropping funnel and thermometer were placed isotetralin (80 g; 0.605 mole) and $CHCl_3$ (1 l.). The soln was cooled to −10° in an ice-salt bath and Br_2 (103 g; 0.64 mole) in $CHCl_3$ (50 ml) was added with stirring during 1 hr maintaining the temp. at −10 to −5°. After warming to room temp. the solvent was removed in a vacuum and the colorless crystalline residue was recrystallized and washed with pentane, affording the *trans*-angular dibromide (104.0g; 59%), m.p. 145–150° (dec, chloroform). Lit.[4] m.p. 156–157°. IR (KBr) and NMR ($CDCl_3$) were identical with the reported data,[4] but NMR showed slight impurity at τ5.4 and 7.5. The product is pure enough to be used in the next step.

(2) *cis-Hydroxylation.* Glacial AcOH (750 ml) and water (3.9 ml; 0.22 mole) were placed in a 1 l. 3-necked flask equipped with stirrer, N_2 inlet, thermometer and reflux condenser. Silver acetate (55.0 g; 0.33 mole, Fluka purum or prepared from KOAc and $AgNO_3$ in water) was added under N_2. The slurry was heated to 60° and powdered dibromide (from part b, 40.0 g; 0.137 mole) was added in portions with vigorous stirring during 90 min at 60–63°. Stirring was continued for 90 min more at 70–75°. After cooling to room temp. the workup was as described in part a. Finally, evaporation of the MeOH in a vacuum gave a residue of **11**, worked up as above (10.4 g; 46%), m.p. 86–88°. The analytical sample had m.p. 86–88° (ether). (Found: C, 72.20; H, 8.43; M.W. 166.1000. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%; M.W. 166.1006). IR ($CHCl_3$): 3560, 3440, 2910, 2840, 1655, 1425, 1370, 1330, 1295, 1100, 1075, 1040, 995, 920, 890, 880 cm^{-1}. NMR ($CDCl_3$): τ4.43 (t, J = 1.5 Hz, 4 vinylic H); 7.71 (s + m, 8 allylic H); 7.87 (s, 2 OH). With TFA the latter band moved to τ2.23. MS: M^+, 166 (2); 148 (11); 112 (100); 111 (6); 101 (14); 95 (41); 94 (6).

Preparation of **12a–c** *from* **11**

(a) Into a 500 ml flask equipped with reflux condenser and N_2 inlet were placed para-formaldehyde (40 g; 1.33 mole, Fluka purum), conc. HCl (110 ml; 32%, C.P.) and distilled water (110 ml). The suspension was stirred magnetically at room temp. for 5 hr when it turned into a nearly clear soln. To this slightly turbid soln was added a soln of **11** (5.0 g; 0.03 mole) in $CHCl_3$ (110 ml, EtOH-free, filtered through basic alumina). Vigorous stirring was maintained under reflux and nitrogen at 80° bath temp.

After cooling to room temp., the $CHCl_3$ was separated and the aq phase extracted with $CHCl_3$ (2 × 30 ml). The combined organic phase was washed with satd $NaHCO_3$ aq (50 ml), then with satd NaCl aq (50 ml) and the combined organic phases dried $MgSO_4$), the solvent removed in a vacuum affording a nearly colorless oil which was distilled in a bulb to bulb apparatus (100° at 0.1 mm) to give **12a** (3.74 g; 70%) as an oil at room temp. It solidifies upon refrigeration. (Found: C, 73.87; H, 7.78. $C_{11}H_{14}O_2$ requires: C, 74.13; H, 7.92%). IR ($CHCl_3$): 2910, 2880, 2850, 1660, 1420, 1355, 1330, 1300, 1160, 1135, 1080, 1000, 970, 850 cm^{-1}. NMR (CCl_4): τ4.40 (t, J = 2.5 Hz, 4 vinylic H); 5.02 (s, $2OCH_2O$); 7.30–8.20 (m, 8 allylic H). MS: 132 (29); 130 (6); 128 (11); 124 (100); 123 (10); 117 (10); 117 (10); 104 (25); 94 (25); 93 (7); 91 (18).

(b) Into a 100 ml flask equipped with reflux condenser and $CaCl_2$ tube were placed **11** (3.0 g; 0.018 mole), dimethylsulfoxide (40 ml, distilled from CaH_2) and 2,2-dimethoxypropane (5 ml; 0.041 mole, Fluka purum), *p*-Toluenesulfonic acid monohydrate (100 mg, Fluka puriss freshly recrystallized from boiling benzene before use) was added and the whole was stirred magnetically and slowly heated within 30 min to 110° bath temp. and so maintained for 4 hr more. The dark soln was cooled to room temp. and $NaCO_3$ aq (5%; 20 ml) was added in one portion with ice cooling and then the whole was diluted with water (300 ml). The soln was extracted with hexane (2 × 200 ml). The combined organic phase was washed with water (2 × 100 ml), with satd NaCl aq (100 ml) and dried ($MgSO_4$). The solvent was removed in a vacuum to afford **12b** as a yellow oil, b.p. 100 (0.1 mm) in a bulb to bulb distillation (1.53 g; 41%). It partly solidified and had m.p. 52–53° (MeOH) by cooling to −70° during recrystallization. (Found: C, 75.48; H, 8.93; M.W. 206.1316. $C_{13}H_{18}O_2$ requires: C, 75.69; H, 8.80%; M.W. 206.1326). IR ($CHCl_3$): 2980, 2940, 2890, 2855, 2830, 1640, 1430, 1380, 1370, 1295, 1170, 1115, 1050, 1000, 955, 885 cm^{-1}. NMR (CCl_4): τ4.18 (t, J = 3 Hz, 4 vinylic H); 7.35–8.20 (m, 8 allylic H); 8.70 (s, $6CH_3$). MS: M^+, 206 (3); 191 (38); 153 (12); 152 (100); 149 (18); 148 (43); 147 (7); 137 (12); 133 (29); 132 (7); 131 (52); 130 (10); 129 (12); 128 (8); 119(6); 112 (15); 107 (13); 105 (12); 100 (13); 94 (81).

(c) Into a 250 ml 3-necked flask equipped with reflux condenser, argon inlet (dried over P_2O_5) and serum cap was placed **11** (3.0 g; 0.018 mole). To this was added dry THF (150 ml, distilled from CaH_2 and filtered through basic Alox), under dry argon. While stirring magnetically at room temp. a soln of n-BuLi (1.88 M, 19.0 ml; 0.036 mole) in hexane was added through the serum cap. At the end of the addition the soln turned pink. Stirring was continued at room temp. for 1 hr more. The whole was cooled to 0° in an ice bath and a toluene soln of phosgene (11%, 23 ml; *ca.* 0.023 mole) was added during 10 min. Stirring was continued 20 min more at 0°, 30 min at room temp. and then 20 min at reflux.

After cooling to 0°, HCl aq (1.5 N, 40 ml) was added with cooling and stirring. The THF was removed in a vacuum and the residue was taken up in CH_2Cl_2 (200 ml) and water (100 ml). The organic phase was separated, washed with satd $NaHCO_3$ aq (50 ml), with satd NaCl aq (50 ml), dried ($MgSO_4$) and the solvent removed. The already crystalline **12c** was recrystallized (2.83 g), m.p. 214–215° (EtOAc-hexane). The mother liquor afforded more material (0.19 g), m.p. 205–207° pure enough for further use, total **12c** 87.5%. (Found: C, 68.90; H, 6.20; M.W. 192.0751. $C_{11}H_{12}O_3$ requires: C, 68.73; H, 6.29%; M.W. 192.0715). IR ($CHCl_3$): 2950, 2900, 1787, 1430, 1330, 1310, 1115, 1040 cm^{-1}. NMR ($CDCl_3$): τ4.00 (t, J = 3 Hz, 4 vinylic H); 7.00–8.30(m, 8 allylic H). MS: M^+, 192 (5); 133 (12); 120 (7); 106 (10); 105 (15); 94 (35); 92 (25).

When the lithium salt of t-butyl-cyclohexylamine was used instead of n-BuLi, the yield of **12c** was 68%.

Preparation of **6a**

A mixture of **12a** (345 mg) and Br_2 (0.2 ml) in CCl_4 (50 ml) was stirred at 0° for 4 hr. The solvent was removed, the residue taken up in benzene (30 ml), diazabicyclononane (0.99 g) was added and the whole was stirred at room temp. for 48 hr. After removal of solvent and extracting with EtOAc, crude **6a** was obtained (76 mg; 15%). Purification was effected on a preparative silica plate with benzene as eluant, affording **6a** as an oil. (Found: M.W. 174.0673. $C_{11}H_{10}O_2$ requires: 174.0681). NMR ($CDCl_3$): τ 3.90–4.50 (m, 8 vinylic H); 5.10 (s, $2CH_2O$). MS: M^+, 174 (31); 144 (100).

Reaction of **6a** *with* 4 - *methyl* - 1,2,4 - *triazoline* - 3,5 - *dione*

(a) Crude **6a** obtained as above in benzene soln was treated with MTD (77 mg to give unstable mono-adduct (180 mg; 30% based on **12a**), m.p. 151–152° (hexane). IR ($CHCl_3$): 1780, 1720 cm^{-1}. NMR ($CDCl_3$): τ 3.50 (t, 2 vinylic H); 3.50–4.10 (m, 4 dienic H); 5.00 (t, $2CH_2N$); 5.10, 5.50 (d, $2OCH_2O$); 7.00 (s, $3NCH_3$). MS: 165 (100); 121 (20). This product was accompanied by the mono-adduct of MTD with the trienic propellane accompanying **6a** in the mixture. It was an oil. IR ($CHCl_3$): 1780, 1720 cm^{-1}. NMR ($CDCl_3$): τ 3.50 (t, 2 vinylic H); 4.00 (t, 2 vinylic

H); 5.10 (m, CHN + OCH_2O); 6.95 (s, $3NCH_3$); 7.45 (d, $4CH_2CH$=). MS: M^+–CH_2O. 258 (2.5); 165 (100).

(b) Reaction of **6a** with excess MTD gave the *bis*-adduct, m.p. 290° (ethyl acetate). (Found: N, 20.96. $C_{17}H_{16}N_6O_6$ requires: N, 20.99%). IR ($CHCl_3$): 1780, 1720 cm^{-1}. NMR ($CDCl_3$): τ 3.50 (t, 2 vinylic H); 3.70 (t, 2 vinylic H); 4.70 (t, 4CHN); 4.80 (m, $2OCH_2O$); 6.95, 7.00 (d, $6NCH_3$). NMR (DMSO-d_6): τ 3.40 (t, 2 vinylic H); 3.70 (t, 2 vinylic H); 4.65 (m, 4CHN); 4.90, 5.00 (d, $2OCH_2O$); 7.10, 7.15 (d, $6NCH_3$). MS: 165 (100).

The same *bis*-adduct (15 mg) identical by mixed m.p. and spectroscopically was obtained from mono-adduct (10 mg) and MTD (5 mg) in CH_2Cl_2 (3 ml) after 24 hr, m.p. 290° (EtOAc-hexane).

Preparation of **6b** *and its Diels–Alder reaction*

The diene **12b** (327 mg) was brominated and dehydrobrominated as described for **12a** and without isolation the crude product, a mixture of tetraene **6b** and its corresponding triene was treated with excess MTD.

The mono-adduct of **6b** (35 mg; 7%) had m.p. 148–150° (benzene–hexane). (Found: C, 61.30; H, 5.58; N, 13.05. $C_{16}H_{17}N_3O_4$ requires: C, 60.94; H, 5.43; N, 13.33%). IR ($CHCl_3$): 1780, 1720, 1070 cm^{-1}. NMR ($CDCl_3$): τ 3.50 (t, 2 vinylic H); 3.85 (m, 4 dienic H); 5.15 (t, 2CHN); 7.00 (s, $3NCH_3$); 8.70, 8.80 (d, $6C(CH_3)_2$). MS: M^+–CH_3, 300 (9); 165 (100).

The mono-adduct of the corresponding triene had m.p. 232–234° (benzene–hexane). IR ($CHCl_3$): 1780, 1720, 1080 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (t, 2 vinylic H); 3.70 (m, 2 vinylic H); 5.30 (t, 2CHN); 7.00 (s, $3NCH_3$); 7.30 (m, 4 allylic H); 8.60, 8.70 (d, $6C(CH_3)_2$). MS: 300 (1.2); 165 (100); 152 (2); 150 (3); 135 (7).

12 - *Oxo* - 11,13 - *dioxa*[4.4.3]*propella* - 2,4,7,9 - *tetraene*, **6c**

A mixture of **12c** (227 mg) and Br_2 (0.1 ml) in CCl_4 (25 ml) was stirred at 0° for 4 hr. The solvent was removed and replaced by CH_2Cl_2 (25 ml) and DBN (0.73 g) was added. The whole was stirred at room temp. for 48 hr. The solvent was removed and the residue extracted with EtOAc. The product was purified on a preparative silica plate (kieselgel 60 PF_{254}, Merck, 20 × 20) and the pure product (217 mg; 95%) had m.p. 134–135° (EtOAc-hexane). (Found: M.W. 188.0453. $C_{11}H_8O_3$ requires: 188.0474).

Diels–Alder reactions of **6c**

(a) A mixture of **6c** (44 mg) and MTD (20 mg) in CH_2Cl_2 (20 ml) gave recovered tetraene and mono-adduct (25 mg), m.p. 218–219° (benzene–hexane). (Found: N, 14.45. $C_{14}H_{11}N_3O_5$ requires: N, 13.95%) IR ($CHCl_3$); 1810, 1780, 1720, 1060 cm^{-1}. NMR ($CDCl_3$): τ 3.30 (t, J = 3.5 Hz, 2 vinylic H); 3.30–4.00 (A_2B_2, 4 dienic H); 4.90 (t, J = 3.5 Hz 2CHN); 7.00 (s, $3NCH_3$). MS: 165 (100); 136 (2.4).

(b) In several preparations of **6c**, less of the equivalent amount of bromine was used as described above. Conducting the Diels–Alder with crude triene-containing product gave the mono-MTD-adduct of **6c** accompanied by the corresponding derivative of the triene (11 mg; 4%), m.p. 258–260°, after separation on a preparative silica plate with hexane as eluant. (Found: N, 13.19; M.W. 303.0852. $C_{14}H_{13}N_3O_5$ requires: N, 13.86%; M.W. 303.0854). IR ($CHCl_3$): 1810, 1780, 1720 cm^{-1}. NMR ($CDCl_3$): τ 3.40 (t, 2 vinylic H); 3.90 (m, 2 vinylic H); 5.00 (t, 2CHN); 6.95 (s, $3NH_3$); 7.35 (d, 4 allylic H). MS: M^+, 303 (9.9); 165 (100).

(c) Reaction of **6c** (27 mg; 1 eq) with MTD (32 mg; 2 eq) in CH_2Cl_2 (20 ml) gave the *bis*-adduct (44 mg; 73%), m.p. 275° (EtOAc–hexane). (Found: N, 19.58; M.W. 414.0935. $C_{17}H_{14}N_6O_7$ requires: N, 20.29%; M.W. 414.0924). IR ($CHCl_3$): 1830, 1780, 1720, 1080 cm^{-1}. NMR ($CDCl_3$): τ 3.45 (t, 2 vinylic H); 3.70 (t, 2 vinylic H); 4.80 (m, 4CHN); 6.95 (s, $3NCH_3$); 7.00 (s, $3NCH_3$). NMR (DMSO-d_6): τ 3.30 (t, 2 vinylic H); 3.65 (t, 2 vinylic H); 4.30 (m, 4CHN); 7.10 (s, $3NCH_3$); 7.15 (s, $3NCH_3$). MS: M^+, 414 (15); 166 (9); 165 (100); 136 (65).

(d) The mono-adduct of **6c** with MTD (10 mg) with MTD (8 mg) in CH_2Cl_2 (5 ml) afforded after 24 hr *bis*-adduct as a ppt (15 mg), m.p. 275°, identical spectroscopically and by m. m.p. with *bis*-adduct described above.

(e) Reduction of *bis*-adduct (50 mg) in EtOAc (100 ml) in presence of PtO_2 gave the tetrahydro-derivative (36 mg; 72%), m.p. > 280°. (Found: M.W. 418.1225. $C_{17}H_{18}N_6O_7$ requires: 418.1236). IR ($CHCl_3$): 1840, 1780, 1725, 1080 cm^{-1}. NMR (DMSO-d_6): τ 4.90 (m, 4CHN); 7.00 (s, $6NCH_3$); 7.70–8.20, 8.50–8.80 ($8CH_2$). MS: M^+, 418 (14); 167 (10); 166 (100).

(f) Reaction of **6c** with excess PTD (1:2) gave the EtOAc-insoluble *bis*-adduct (90%), m.p. > 280°. (Found: M.W. 538.1230. $C_{27}H_{18}N_6O_7$ requires: 538.1236). IR ($CHCl_3$): 1810, 1780, 1720 cm^{-1}. NMR ($CDCl_3$) τ 2.50 (m, 10 arom H); 3.30 (m, 4 vinylic H); 4.80 (m, 4CHN). MS: M^+, 538 (58); 227 (100); 119 (43); 136 (4). This was accompanied by the mono-adduct with PTD of the corresponding triene (10%), m.p. 150° (EtOAc-hexane). (Found: M.W. 365.1016. $C_{16}H_{15}N_3O_5$ requires: 365.1011). IR ($CHCl_2$): 1830, 1780, 170 cm^{-1} NMR ($CDCl_3$): τ 2.50 (m, 5 arom H); 3.20 (t, 2 vinylic H); 3.80 (m, 2 vinylic H); 4.80 (t, 2CHN); 7.25 (d, 4 allylic H). MS: M^+, 365 (7.6), 227 (100); 136 (8); 119 (38).

Methyl 8a - acetyl - 1,4,4a5,8,8a - hexahydronaphthalene - 4a - carboxylate, **14a**

The half-ester **13** (4 g) in dry benzene (50 ml) was treated with oxalyl chloride (5 ml) and the whole was maintained at 70° for 90 min. Revoval of solvent afforded the crude acid chloride. A soln of the latter in dry ether (5 ml) was added at 0° to $LiCu(CH_3)_2$ prepared from CuI (3.45 g) in dry ether (10 ml) and MeLi (2M in ether) at 0°. After 10 min the reaction was terminated by addition of satd NH_4Cl aq. The ether phase was separated and dried. Evaporation gave crude **14a**. Distillation at 130° (0.5 mm) afforded the pure product (2.61 g), m.p. 57–59° (hexane). IR ($CHCl_3$): 2920, 2840, 1720, 1700, 1430 cm^{-1}. NMR ($CDCl_3$): τ 4.37 (br s, 4 vinylic H); 6.34 (s, $3OCH_3$); 7.10–7.70 (m, 8 allylic H); 7.80 (s, $3COCH_3$).

11,13-*Dioxo*[4.4.3]*propella*-3,8-*diene*, **15**

To a suspension of potassium hydride (4 ml, 50% in oil, after washing with hexane) in dry THF (300 ml) was added a soln of **14a** (2.55 g) in dry THF (10 ml). After stirring at room temp. for 1 hr the mixture was treated with water and HCl (10%) to acidic pH. The aq phase was extracted with $CHCl_3$ and the combined organic phase evaporated to dryness. The crude residue afforded upon crystallization pure **15** (1.25 g; 55%), m.p. 196–197° ($CHCl_3$). From the aq mother liquor an additional oil (0.8 g) was isolated from which the free acid **14b** was obtained (0.3 g) by crystallization from benzene–hexane, m.p. 148–150°. The rest of the oil was **14a** which could be recycled with KH affording more of **15** (total yield 65–70%).

Compound **15**. (Found: C, 77.26; H, 6.86. $C_{13}H_{14}O_2$ requires: C, 77.20; H, 6.98%). IR ($CHCl_3$): 2960, 2880, 2820, 1730, 1700, 1620 cm^{-1}. NMR ($CDCl_3$): τ 4.00–4.30 (m, 4 vinylic H); 4.80 (s, $COCH$=); 5.10 (s, =COH); 6.83 (s, $COCH_2CO$); 7.34–8.17 (m, 8 allylic H).

Compound **14b**. IR ($CHCl_3$): 3500, 3150, 2920, 2850, 1770, 1730 cm^{-1}. NMR ($CDCl_3$): τ 1.50 (br s, $1CO_2H$); 4.36 (br s, 4 vinylic H); 7.00–7.80 (m, 8 allylic H); 7.90 (s, $3COCH_3$).

Treatment of **14b** with ethereal diazomethane gave **14a** quantitatively, identical in all respects to **14a** described above.

11 - *Oxo* - 13 - *methoxy*[4.4.3]*propella* - 3,8,12 - *triene*, **16**

Methylation of **15** (20 mg) in ether (5 ml) with ethereal diazomethane gave a quant yield of **16**, m.p. 92–94° (EtOH). (Found: M.W. 216.1151. $C_{14}H_{16}O_2$ requires: 216.1150). IR ($CHCl_3$): 2980, 2940, 2840, 1680, 1600, 1450, 1160 cm^{-1}. NMR ($CDCl_3$): τ 4.07–4.27 (m, 4 vinylic H); 4.77 (s, $COCH$=); 6.12 (s, $3OCH_3$); 7.34–8.34 (m, 8 allylic H).

Hydrolysis of **16** (40 mg) in a mixture of AcOH (2 ml) and H_2SO_4 (6N, 2 ml) by boiling for 2hr, removal of AcOH, extraction with $CHCl_3$, drying and evaporating solvent gave **15** (24 mg) identical in all respects with **15** described above.

11-*Oxo*-13-*methoxy*[4.4.3]*propella*-2,4,7,9,12-*pentaene*, **19**

The crude bromide was prepared from **16** (520 mg), NBS (890 mg) in CCl_4 (50 ml). After the usual workup solvent was removed, dry benzene (50 ml) and DBN (2.5 g) added and the whole stirred over night at room temp. The soln was decanted and washed several times with HCl (10%), dried, solvent

removed and the residue purified on 5 prep. silica plates, benzene as eluant, affording pure **19** (180 mg), m.p. 128–129° (ether). (Found: M.W. 212.1146. $C_{14}H_{12}O_2$ requires: 212.1150). IR ($CHCl_3$): 2980, 2940, 1690, 1610, 1590, 1090 cm^{-1}. NMR ($CDCl_3$): τ 3.90–4.34 (m, 8 vinylic H); 4.40 (s, $COCH$=); 6.04 (s, $3OCH_3$).

11,13 - *Dioxo* - 12 - *diazo*[4.4.3]*propella* - 3,8 - *diene*, **17**

A soln of **16** (300 mg) in EtOH (5 ml) was treated with triethylamine (450 mg) and tosyl azide (450 mg) in EtOH (5 ml) and the whole was stirred overnight at room temp. The solvent was removed, the residue dissolved in ether (40 ml) and the organic phase washed with KOH aq (10%; 2 × 10 ml) and with water (2 × 10 ml), dried ($MgSO_4$) and the solvent removed. The crude residue was purified on 5 silica plates (Merck, 20 × 20) using acetone (1) : hexane (3). The product **17** was in the upper band (400 mg) but still impure. Chromatography on 5 more plates using hexane gave the pure product in the bottom band (200 mg) as an oil. This was purified by dry column chromatography on basic alumina (grade 1, 9 g). Elution by chloroform (1) : hexane (9) gave pure **17** (170 mg; 50%), m.p. 92–93°. (Found: C, 68.22; H, 5.34; N, 12.42; M.W. 228.0904. $C_{13}H_{12}N_2O_2$ requires: C, 68.41; H, 5.30; N, 12.27%; M.W. 228.0898). IR ($CHCl_3$): 2850, 2150, 1680 cm^{-1}. NMR ($CDCl_3$): τ 4.00–4.20 (m, 4 vinylic H); 7.10–8.10 (m, 8 allylic H). MS: M^+, 228 (21); 131 (100); 128 (16); 118 (25); 101 (23).

Irradiation of **17**

A soln of **17** (70 mg) in aq (10 ml) THF (15 ml) was irradiated in pyrex using as Osram HBO 200w lamp during 11 min. Removal of solvent gave crude **18a** which was purified by dissolving in Na_2CO_3 aq (10%), washing with ether, acidification of aq phase with HCl (20%) and extraction with $CHCl_3$. Removal of solvent gave **18a** (61 mg), m.p. 145–147° (benzene–hexane). (Found: C, 71.45; H, 6.49. $C_{13}H_{14}O_3$ requires: C, 71.54; H, 6.47%). IR ($CHCl_3$): 2950, 1780, 1715 cm^{-1}. NMR ($CDCl_3$): τ 2.80 (br s, $1CO_2H$); 3.90–4.16 (m, 4 vinylic H); 6.16 (s, 1 cyclobutane H); 7.16–8.34 (m, 8 allylic H). MS: 133 (16); 132 (100); 128 (10).

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