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PROPELLANES—LII

THE REACTION OF CONJUGATED DIENIC PROPELLANES WITH SINGLET OXYGEN[a]

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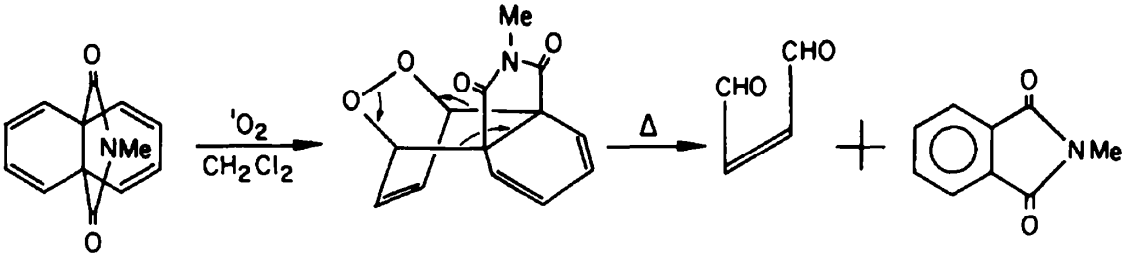
Abstract—The reactions of propellanes containing one or two cyclohexadiene rings with singlet oxygen take the course of exclusive *syn*-attack with respect to a hetero-ring containing two CO groups. When only one or no CO group is found in the hetero-ring, both *syn*- and *anti*-attack occur. The former course is interpreted in terms of secondary orbital interactions which stabilize the transition state for *syn*-attack.

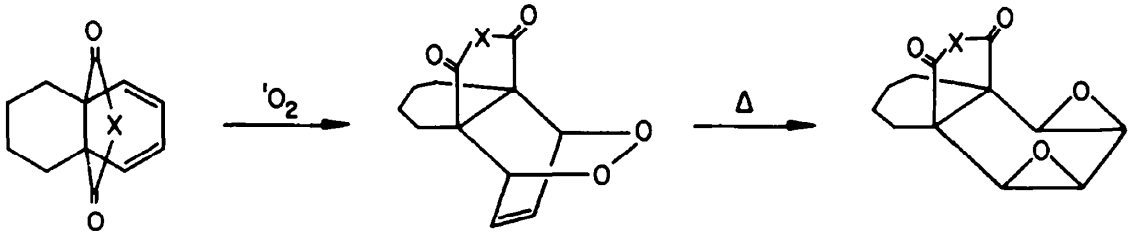
During the investigation of electronic and steric effects in Diels–Alder cycloadditions to propellanes[1] it has been suggested[2] that singlet oxygen is capable of undergoing secondary orbital interaction with the π^* orbitals of the CO groups in propellanes of type **1**. We have reported preliminary results regarding the thermal route taken by the endo-peroxide formed from a tetraenic propellane (Scheme 1).[3] It is true that we had not reported unequivocal proof that singlet oxygen indeed attacks the dienic component at the *syn*-face with respect to the hetero-ring as shown in Scheme 1, for the intermediate endo-peroxide could not be studied due to its desire to aromatize. We wrote its configuration in analogy to that obtained for the dienic propellanes described in Scheme 2 (see, however, Scheme 4 below).

The dienic methylimide[4] gave the corresponding endo-peroxide on treatment with $^1O_2$ in acetonitrile, $t_{1/2} \sim 35$ min at 140°; as a result of this thermal rearrangement the *bis*-epoxide **3**, X=NMe was obtained. The dienic anhydride[4] similarly afforded **2**, X=O, $t_{1/2} \sim 30$ min at 140°, leading thermally to a more complex mixture of products. Besides the *bis*-epoxide **3**, X=O, two further products were identified, **4** and **5**. The structure of **4** was assigned on the basis of its NMR spectrum and IR spectrum in its particular fraction in the reaction mixture. The structure of **5** was formulated after its isolation and comparison with an authentic specimen. The formation of these by-products may be rationalized as shown in Scheme 3.

Alternatively **2**, X=O gave **3**, X=O upon irradiation, uncontaminated by other products. X-ray



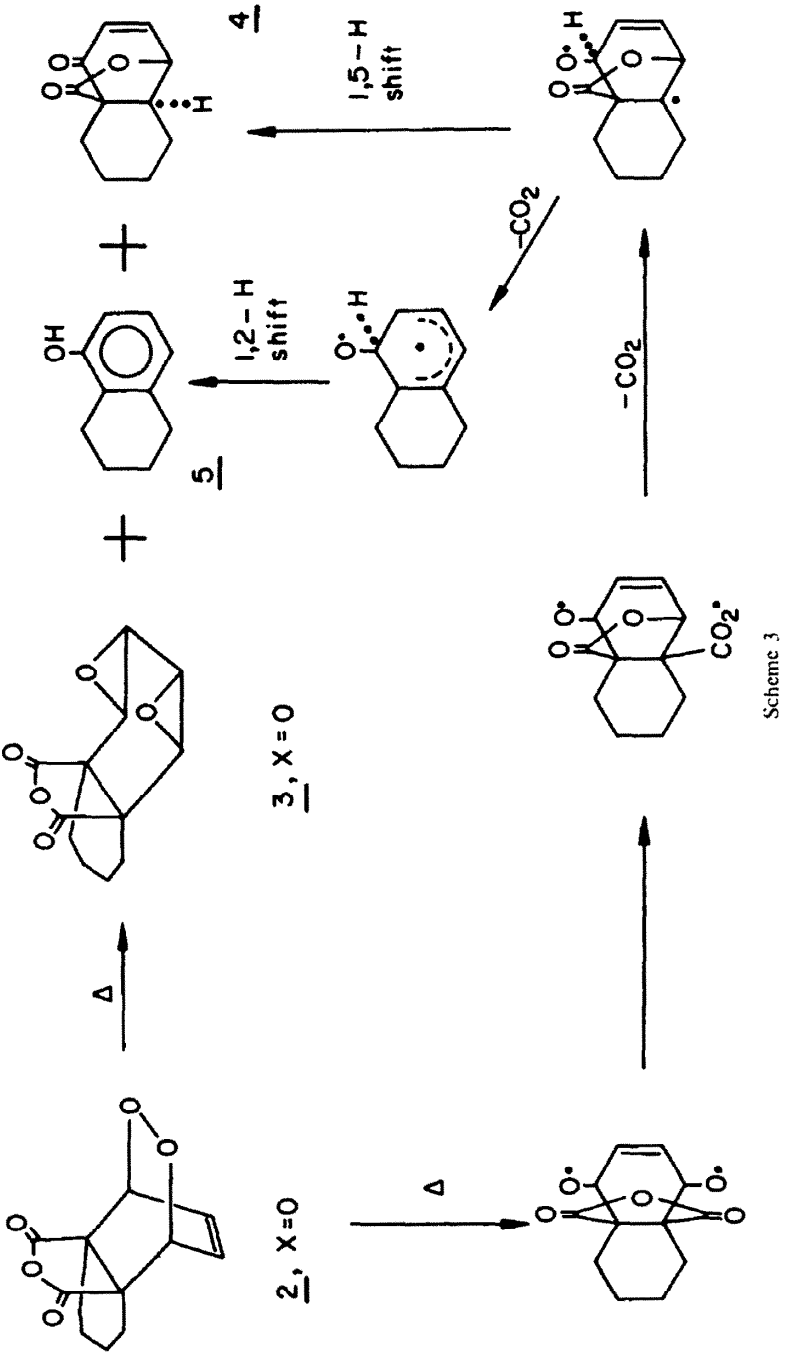
Scheme 1



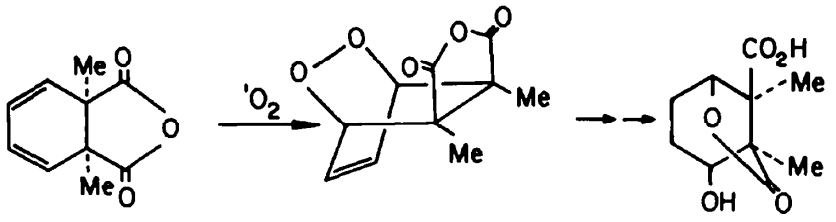
1, X=O, NMe **2** **3**

Scheme 2

[a]Part LI. P. Ashkenazi, R. Gleiter, W. von Philipsborn, P. Bigler and D. Ginsburg, *Tetrahedron* in press.



Scheme 3



analysis of **3**, X=O showed that the two epoxy-oxygens are *syn*-with respect to the anhydride ring. Here, as in the analogous case of **3**, X=NMe already reported[3,5] the cyclohexane rings are both twisted away from possible symmetrical conformations due to the position of one of the epoxy-oxygens which is held more or less equidistant to both carbonyls with one of its lone pairs pointing towards the opposite CO function.

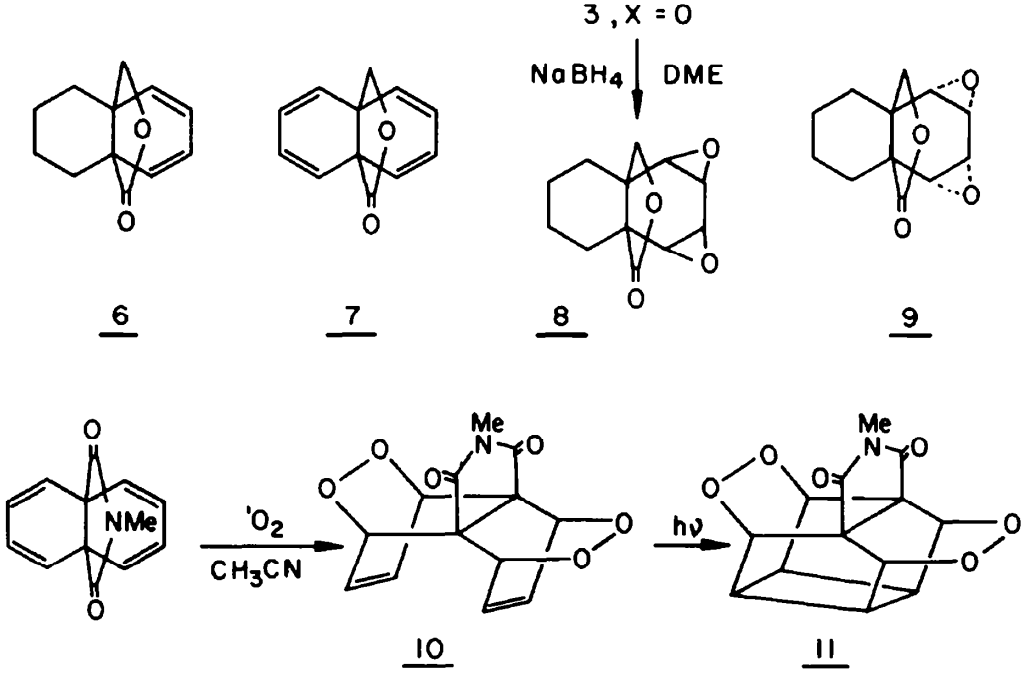
It is of interest in connection with Scheme 3 that there is precedent for a similar intermediate in the case of a bicyclic compound, in the reaction of a dimethylcyclohexadienecarboxylic anhydride with singlet oxygen.[6]

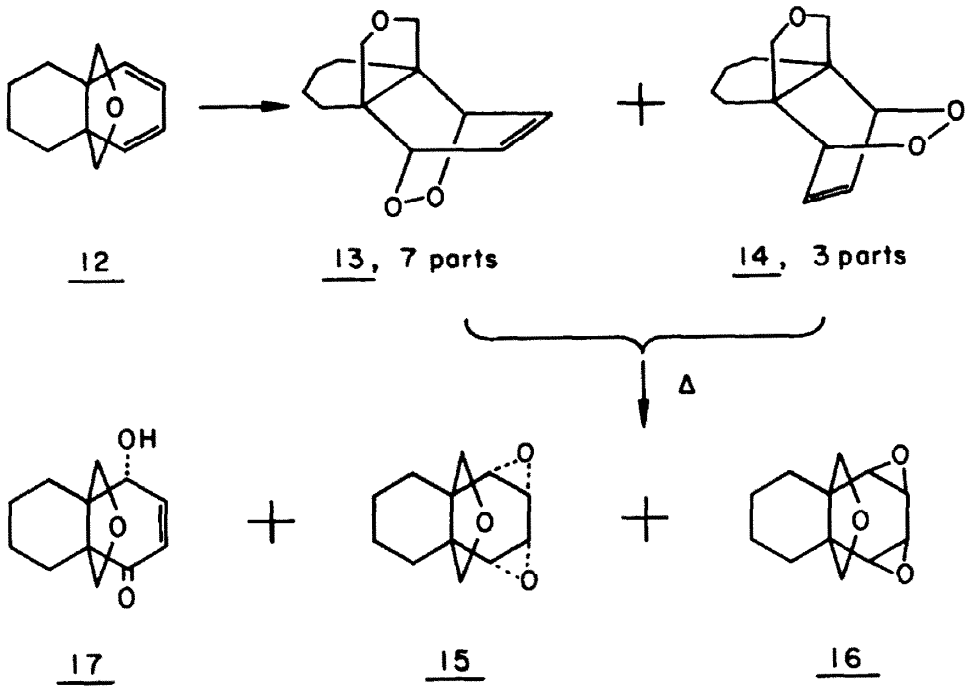
The *bis*-epoxide **3**, X=O was reduced in high yield to the corresponding lactone **8**.[7] This was of importance in order to have a configurational frame of reference for the mode of attack of $^1O_2$ upon the dienic lactone **6** for on the basis of Diels–Alder reactions of the tetraenic lactone **7** with triazolinediones we know that we get both possible mono-adducts.[8]

We would therefore expect to obtain both 8 and 9 from a mixture of two endoperoxides (*syn* and *anti*) by treating **6** with $^1O_2$.

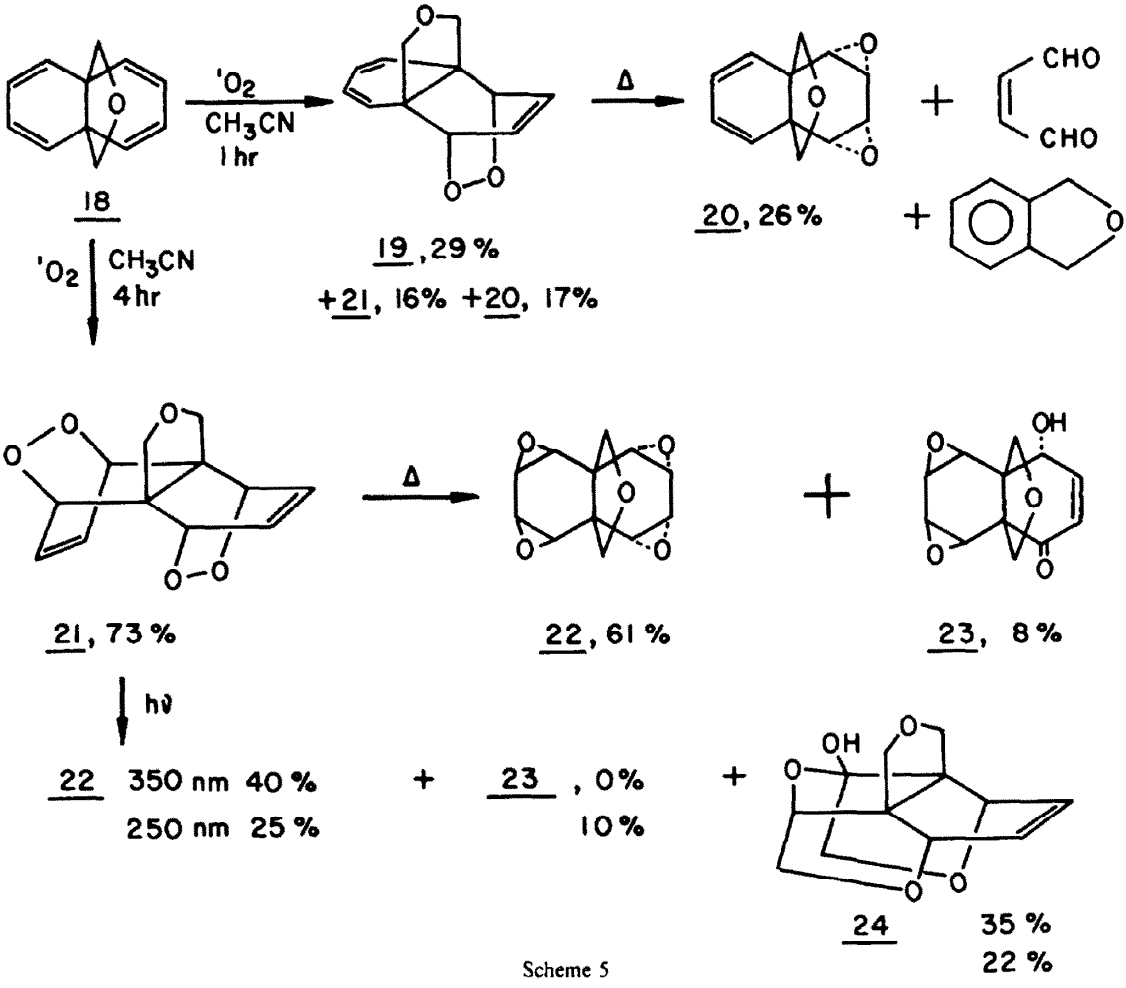
Before turning to this subject we should add several results to those already published[3] with respect to the tetraenic methylimide. We had obtained its mono-endoperoxide by reaction with $^1O_2$ in CH_2Cl_2 and as stated above this was not fully characterized and was converted into N-methylphthalimide (identical with an authentic specimen) and malealdehyde[9,10] (identity established by comparison of NMR spectra of product and an authentic specimen as well as the corresponding *bis*-2,4-dinitrophenylhydrozones, m.p. 304° (dec)). But when reaction between the tetraene and $^1O_2$ was conducted in CH_3CN the *bis*-endoperoxide **10** was obtained in 64% yield. This was rearranged thermally to the endoperoxide-*bis*-epoxide but the latter could not be converted by further rearrangement into the tetra-epoxide. All attempts failed to give isolable material. However, irradiation of **10** in acetone solution at 250 nm proved that $^1O_2$ attacks only from the *syn*-face of each diene for **11** was obtained in 40% yield (Scheme 4). No tetra-epoxide accompanied the reaction product. Although the tetraenic anhydride also reacted smoothly with 2 moles of $^1O_2$ during 30 min, no definite products could be obtained from the crude reaction mixture which turned black on standing.

It was, of course, of great interest to study the behavior of the dienic ether **12** with singlet oxygen. In the case of Diels–Alder reactions with carbocyclic or heterocyclic dienophiles the ether undergoes exclusive *anti*-attack.[11] However, in the case of $^1O_2$ both configurational isomers of the endoperoxides were obtained **14** and **13**, in a ratio of *syn*:*anti* = 3:7 as

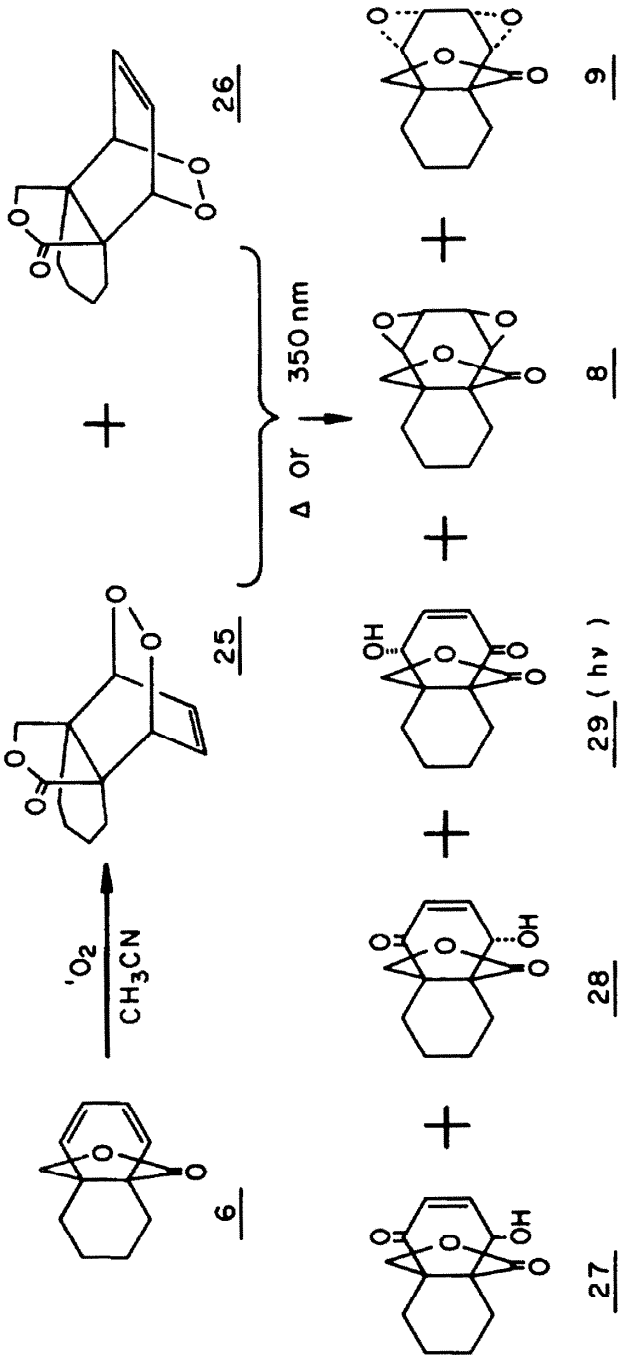




Scheme 4



Scheme 5



Scheme 6

determined after thermal rearrangements into the *bis*-epoxides, **16** and **15**, respectively (Scheme 4).

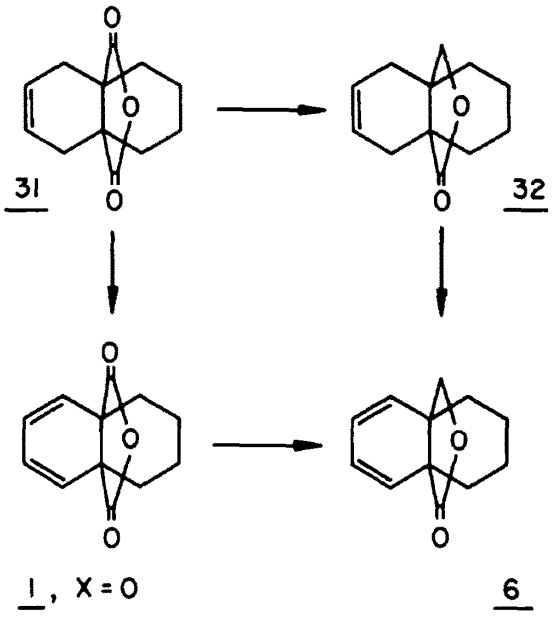
The endo-peroxides were not separated. Their mixture had $t_{1/2} \sim 5$ min in thermal rearrangement at 140° and the *bis*-epoxide mixture thus obtained was separated into its components by glc. The two-*bis*-epoxides were accompanied by the hydroxy-ketone **17** which was evidently formed from the major endo-peroxide **13**.[12] The *anti*-configuration of the epoxide rings in **15** vis-a-vis the 5-membered ether ring was assigned on the basis of comparison of the NMR spectra of other members of the series, e.g. **16** and its lactone analog **8** as well as derivatives of the anhydride and imide series; the signals for the AB systems of the CH_2O protons and the protons of the epoxide rings were correlated. Finally, unequivocal confirmation of this assignment was obtained by X-ray crystallography.[5]

The tetraenic ether **18** was also treated with singlet oxygen. In 1 hr in CH_3CN the mono-endo-peroxide **19** was obtained with some *bis*-product **21**. In 4 hr a good yield of *bis*-product **21** is formed.

Thermal rearrangement afforded the *anti-bis*-epoxide **20** and the *syn, anti*-tetraepoxide **22**, respectively. Scheme 5 shows also that some retro-reaction occurs and **20** is not surprisingly accompanied by maleic dialdehyde[3,9] and phthalan.[11] The tetra-epoxide **22** is accompanied by a small amount of **23**. Irradiation of **21** also affords **22**, **23** and the very interesting cage compound **24**, as shown in the Scheme.

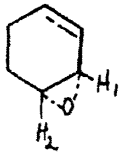
X-ray analysis of **20** established its configuration.[5] The structure of **24**, although understandable under the circumstances of its formation, was also established unequivocally by X-ray analysis.[5] It supports the possibility of formation of hemi-ketals as intermediates in this work, for instance during formation of **17**. It is our intention to study further the formation of **24** during irradiation at 250 nm as well as at 350 nm. This may imply that two different diradicals may be implicated. At 250 nm perhaps a triplet is formed by excitation of the double bond which then reacts with the proximate ends of the peroxide oxygens (route a). At 350 nm perhaps a direct formation of a dioxy diradical may be conceived and this reacts with the double bond (route b).

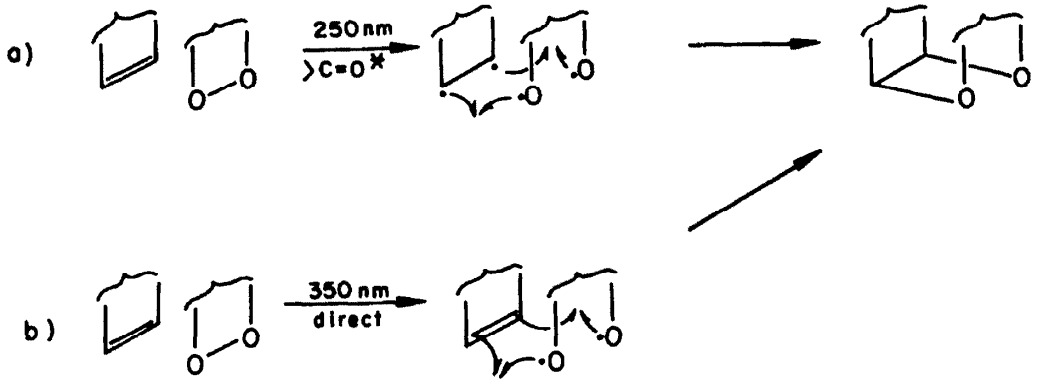
Finally the reaction of the dienic lactone **6**, already mentioned above, with singlet oxygen, amply fulfilled our expectations for a complex reaction mixture. Not only were two endo-peroxides obtained as evidenced



by the two isomeric *bis*-epoxides **8** and **9** derived by thermal rearrangement in a ratio of isolated product, *syn* (**8**): *anti* (**9**) = 8:1 but this rearrangement afforded a wealth of by-products as shown in scheme 6. However, measuring the ratio of the AB signals for the $C\underline{H}_2OCO$ protons in the crude NMR spectrum of endo-peroxides **25** and **26** gave 4:3 for the *syn-anti*-ratio.

Assignment of the structures of the keto-alcohols in scheme 6 (and one isolated in the methylimide series; Experimental) was based on comparison of positions of signals for olefinic protons as well as noting H-bonding in IR spectrum and lowering of C=O frequencies therein. Thus, for example, **27** exhibited such H-bonding and we decided it is *syn* whilst **28** is *anti*. The structure of **29** was assigned on the basis of the position of the AB of the $C\underline{H}_2OCO$ protons: in this case it had collapsed into a broad singlet. The epoxide protons of **30** give a broad multiplet at τ 6.61. H_2 must





be in the neighborhood of the carbonyl, otherwise its signal would be much lower. Hence, the epoxide ring must be *anti*. The H_1-signals are usually higher for propellanes in which the epoxide ring is *syn*. We do not understand, however, how **30** is formed.

It appears from the above results that in the cases where the hetero ring contains two CO groups, secondary orbital interaction occurs between the appropriate orbitals of the dicarbonyl system and of singlet oxygen.

The dienic lactone **6** could be prepared in two ways: by reduction of **31** with sodium borohydride[13] followed by NBS bromination and dehydrobromination by DMF (66% overall) or similarly by sodium borohydride reduction of the dienic anhydride[4] **1**, X=O (89%; 63% overall from mono-enic anhydride).

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 237 spectrometer. NMR spectra were measured on a Varian T-60 or a Bruker WP-60 spectrometer. Mass spectra were measured on a Varian MAT-711 spectrometer. M.ps and b.ps are uncorrected.

Singlet oxygen was generated photochemically using methylene blue (MB) as sensitizer by means of a water-cooled tungsten-halogen lamp, Osram-64663, 400 W, 36 V or an ordinary halogen projection lamp, 150 W, 24 V. The light was filtered by a sodium bichromate solution (20 g/l). The mixture was vigorously stirred by a magnetic stirrer in a reaction vessel cooled by an ice bath. Oxygen uptake was measured by a gas burette. After completion, checking by tlc on silica, methylene blue was removed by stirring the reaction with carbon black followed by filtration. Evaporation of the solvent afforded the crude product.

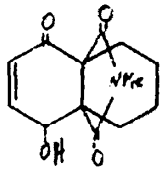
Alox-n = grade I, neutral alumina

Alox = grade I, basic alumina.

Reaction of **1**, X=NMe *with* $^1O_2$

A soln of the diene (587 mg; 2.7 mmol) and methylene blue (6 mg) in dry acetonitrile (35 ml) was irradiated for 1 hr. Workup as described above gave a solid (623 mg) which after trituration with diethyl ether afforded *syn*-2 **2**, X=NMe (521 mg; 77%). The m.p. of the product is actually that of the thermal rearrangement product **3**, X=NMe, 175–180°. (Found: C, 62.43; H, 6.01; N, 5.59; M.W. 249.0995. $C_{13}H_{15}NO_4$ requires: C, 62.64; H, 6.07; N, 5.62%; M.W. 249.1001). IR (KBr): 2915, 2840, 1772, 1702, 1461, 1445, 1430, 1380, 1342, 1302, 1273, 1063, 1035, 985, 956, 942, 919, 825, 713 cm^{-1}. NMR ($CDCl_3$): δ 6.68 (pseudo t, 2H); 4.72 (pseudo t; 2H); 3.09 (s, 3H); 2.07–1.05 (m, 8H). MS: M$^+$, 249 (16); 218 (16); 217 (86); 166 (96); 165 (35); 135 (37); 132 (67); 108 (81); 104 (29); 79 (100).

In a run using unfiltered light, after Alox-I (MeOAc) the NMR spectrum of the crude reaction mixture showed signals attributed to but this was not further investigated. NMR (CD_3CN): δ 7.17 (dd, 1H); 6.00 (dd, 1H); 4.63 (dd, 1H); 3.8 (br s, 1H); 3.02 (s, 3H; 1.50 (br s, 8H).



syn-syn,2,3-4,5-*Diepoxy*-11,13-*dioxo*-12-*methyl*-12-*aza*-[4.4.3]*propellane*, **3** (X=NMe)

The endoperoxide **2** (208 mg) was heated under reflux in *m*-xylene (10 ml, filtered through Alox-n) for 2 hr. Solvent was removed and the residual solid crystallized, giving the *bis*-epoxide **3** (177 mg; 85%), m.p. 184–185° (CCl_4). It could be sublimed at 140–150°/10^{-1} mm, m.p. 184–185°. (Found: C, 62.66; H, 5.87; N, 5.67; M.W. 249.1001. $C_{13}H_{15}NO_4$ requires: C, 62.64; H, 6.07; N, 5.62%; M.W. 249.1001). IR (KBr): 3010, 2962, 2920, 2902, 2840, 1773, 1706, 1449, 1436, 1421, 1378, 1362, 1310, 1272, 1259, 1227, 1079, 1068, 1039, 1018, 1007, 978, 930, 886, 851, 836, 817, 774, 740, 725, 666 cm^{-1}. NMR ($CDCl_3$): δ 3.54 (pseudo d, 2H); 3.05 (pseudo d, 2H); 2.99 (s, 3H); 2.00–1.31 (m, 8H). MS: M$^+$, 249 (25); 166 (74); 164 (17); 152 (15); 136 (21); 135 (71); 108 (22); 107 (22); 84 (100). X-ray structure has been published.[5]

An NMR tube containing **2** (50 mg) and $CDCl_3$ (0.4 ml) was sealed under vacuum. It was immersed in an oil bath at 140° and the NMR spectrum recorded at 15 min intervals. $t_{1/2}$ of **2** at 140° was *ca* 35 min

syn,syn-2,5-7,10-bis-*Epidioxy*-11,13-*dioxo*-12-*methyl*-12-*aza*[4.4.3]*propella*-3,8-*diene*, **10**

A soln of the tetraenic imide (Scheme 1); 400 mg) and MB (20 mg) in dry CH_3CN (35 ml) was irradiated with a halogen projection lamp (150 W, 24 V). After the usual workup (carbon black, MeOAc) crude solid (600 mg) was obtained. Trituration with MeOAc and recrystallization gave the *bis*-endoperoxide **10**, (332 mg; 64%), m.p. 170–175° (dec, acetone). (Found: C, 56.38; H, 3.94; N, 4.83; M.W. 277.0563. $C_{13}H_{11}NO_6$ requires: C, 56.32; H, 4.00; N, 5.05%; M.W. 277.0586). IR (KBr): 2950, 1785, 1705, 1440, 1380, 1363, 1294, 1277, 1190, 1177, 1113, 1058, 1040, 989, 975, 937, 880, 828, 767, 710, 689, 653 cm^{-1}. NMR (DMSO-d_6): δ 6.54 (pseudo t, 4H); 5.20 (pseudo t, 4H); 3.13 (s, 3H). (Acetone-d_6): δ 6.52–6.39 (ps t, 4H); 5.09–4.95 (ps t, 4H); 3.05 (s, 3H). MS: M$^+$, 277 (24); 194 (91); 193 (100); 177 (20); 166 (48); 165 (27); 164 (85); 161 (19); 150 (95); 147 (49); 145 (14); 144 (58); 138 (26); 137 (34); 136 (25); 131 (62); 128 (12); 121 (14).

Heating in *m*-xylene gave a mixture which appeared from the NMR spectrum to contain bis-epoxy-epidioxy product, m.p. 178–181° (acetone). (Found: M.W. 277.0628. $C_{13}H_{11}NO_6$ requires: 277.0586). IR (KBr): 2955, 1776, 1701, 1441, 1387, 1371, 1308, 1276, 1259, 1201, 1053, 1030, 1021, 987, 957, 930, 901, 838, 740 cm^{-1}. NMR (CD_3CN): δ 6.86 (ps t, 2H); 5.26 (ps t, 2H); 3.55 (ps d, 2H); 3.29 (ps d, 2H); 2.99 (s, 3H). MS: M$^+$, 277 (7); 245 (29); 194 (100); 193 (40); 177 (24); 166 (25); 164 (50); 144 (19); 137 (21); 136 (23). A minute amount of tetraepoxide was obtained by sublimation of the former at 150–160°/10^{-2} mm. This thermal product was insufficiently characterized.

Irradiation of **10**

The *bis*-endoperoxide **10** (50 mg) and acetone (40 ml) were sealed under vacuum in an ampoule and irradiated (250 nm) in a Rayonette instrument for 24 hr. Solvent was removed at the water pump and the residual cage product **11** was crystallized affording analytical sample (20 mg; 40%), m.p. 218–220° (dec, acetone). (Found: C, 56.16; H, 4.01; N, 4.79; M.W. 277.0566. $C_{13}H_{11}NO_6$ requires: C, 56.32; H, 4.00; N, 5.05%; M.W. 277.0568). IR (KBr): 2930, 1783, 1707, 1439, 1367, 1295, 1213, 1040, 982, 939, 846, 753, 720, 678 cm^{-1}. NMR (DMSO-d_6): δ 3.75 (ps d, 4H); 3.50 (ps d, 4H); 2.88 (s, 3H). MS: M$^+$, 277 (14); 235 (14); 203 (7); 178 (7); 177 (22); 176 (9); 175 (18); 162 (8); 161 (17); 160 (7); 149 (11); 148 (8); 147 (65); 135 (8); 134 (7); 133 (7); 131 (12); 121 (18); 120 (12); 119 (25); 118 (12); 111 (8); 106 (9); 105 (26); 91 (100).

syn-2,5-*Epidioxy*-11,13-*dioxo*-12-*oxa*[4.4.3]*propell*-3-*ene*, **2** (X=O)

A soln of di **1** X=O; 460 mg) and MB (5 mg) in dry acetonitrile (35 ml) was irradiated with the Osram lamp for 90 min. The usual workup afforded crude solid (483 mg) which upon trituration with diethyl ether gave the *endo*-peroxide (403 mg; 76%), m.p. 165–168° (with rearrangement). It could be recrystallized from benzene. (Found: C, 60.74; H, 5.15; M.W. 236.0703. $C_{12}H_{12}O_5$ requires: C, 61.01; H, 5.12%; M.W. 236.0685). IR (KBr): 2930, 2910, 2850, 1871,

1850, 1786, 1452, 1357, 1248, 1235, 1230, 1203, 1182, 1174, 1038, 1018, 1001, 976, 963, 937, 922, 909, 711, 701 cm^{-1}. NMR ($CDCl_3$): δ 6.74 (ps t, 2 H); 481 (ps t, 2 H); 2.18–1.09 (m, 8 H). MS: M^+, 236 (6); 204 (22); 184 (6); 163 (9); 153 (16); 152 (9); 148 (29); 147 (14); 135 (15); 133 (11); 132 (72); 131 (18); 129 (8); 128 (10); 127 (7); 121 (4); 120 (36); 119 (6); 117 (19); 116 (9); 115 (15); 109 (7); 108 (53); 107 (19); 105 (19); 104 (100); 103 (12).

syn,syn-2,3-4,5-*Diepoxy*-11,13-*dioxo*-12-*oxa* [4.4.3]-*propellane*, **3**, X=O

(a) The *endo* peroxide (115 mg) in *m*-xylene (10 ml; filtered through Alox-n) was heated under reflux for 2 hr. After removal of solvent the NMR spectrum exhibited signals in addition to those of the *bis*-epoxide. Prep tlc silica plates using benzene, then $CHCl_3$ as eluant gave in ascending order of polarity material (12 mg; 17%) assigned the structure 5,6,7,8-tetrahydro-1-naphthol; the desired *bis*-epoxide (45 mg; 39%), m.p. 145–147°; an impure fraction (33 mg; 30%) believed on the basis of NMR to be 12-*oxa*-*tricyclo* [4.4.0.$2^{1,5}$]*dodec*-3-*ene*, **4** (Scheme 2). $t_{1/2}$ of the *endo*-peroxide was *ca* 30 min as observed by disappearance of its signals at δ 6.74 and 4.81 and the appearance of the corresponding signals of the *bis*-epoxide at 3.53 and 3.11.

(b) Alternatively, the crude *endo*-peroxide obtained from 840 mg of dienic anhydride was dissolved in acetone, the soln degassed, sealed in an ampoule and irrad at 350 nm in a Rayonette apparatus for 4 hr. Removal of solvent and passing a soln of the residue in C_6H_6 through Alox-n gave the *bis*-epoxide (330 mg; 34%), m.p. 145–147° (ether–EtOAc). No by-products were detected. It may be sublimed at 140–150°/0.1 mm. When a KBr plate containing the endoperoxide was heated at about 170° for 15 min a new signal appeared at 2430 cm^{-1}, probably due to CO_2 and at 1688 cm^{-1} (C=C–C=O).

The pure *bis*-epoxide had the same m.p. when crystallized from CCl_4–$CHCl_3$. (Found: C, 61.03, H, 5.02; M.W. 190.0587. $C_{12}H_{12}O_5$ requires: C, 61.01; H, 5.12%; M.W. 190.0630). IR (KBr): 2975, 2920, 2835, 1850, 1793, 1444, 1233, 1200, 1175, 1042, 1010, 980, 936, 888, 855, 838 cm^{-1}. NMR ($CDCl_3$): δ 3.53 (ps d, 2 H); 3.11 (ps d, 2 H); 2.11–1.41 (m, 8 H). MS: 190 (4); 164 (5); 135 (49); 120 (23); 79 (100). The two crystalline forms (from the different solvents of crystallization) were subjected to X-ray analysis affording slightly different structures.[5]

The tetraenic anhydride reacted smoothly with $^1O_2$, taking up 2 moles of oxygen but it could not be purified; it decomposed on standing and on silica.

Preparation of **6**

A mixture of **32** (2.26 g),[13] NBS (2.38) and dibenzoylperoxide (5 mg) in CCl_4 (110 ml) was heated under reflux using a sun lamp for 30 min. Evaporation of solvent gave crude allylic bromide (4.11 g). This was stirred in dry DMF (120 ml) at 95–100° for 13 hr. The whole was poured into ice water (700 ml) saturated with salt and extracted with ether (4 × 100 ml). After drying (Na_2SO_4) and removal of solvent crude **6** (2.63 g) was obtained. Its benzene solution was passed through Alox-n, affording pure **6** (1.83 g; 82%), b.p. 85°/10^{-1} mm, as an oil. (Found: C, 75.14; H, 7.40; M.W. 190.0991. $C_{12}H_{14}O_2$ requires: C, 75.76; H, 7.42%; M.W. 190.0993). IR ($CHCl_3$): 2915, 2845, 1774, 1447, 1356, 1300, 1099, 1001, 962, 902, 876 cm^{-1}. NMR ($CDCl_3$): δ 6.25–5.24 (m, 4 H); 3.84 (s, 2 H); 2.24–0.97 (m, 8 H). MS: M^+, 190 (19); 146 (20); 132 (14); 131 (43).

Reaction of **6** *with* $^1O_2$

A soln of the dienic lactone (600 mg) and MB (30 ml) was irradiated with the halogen lamp for 30 hr. The NMR spectrum of the crude mixture after the usual workup showed a 30% conversion. The solid residue was dissolved in xylene (25 ml) which had been filtered through alox-n I and heated under reflux for 2 hr. Column chromatography with benzene on alox-n I gave starting material (360 mg). Elution with $CHCl_3$ gave a mixture (350 mg) which was subjected twice to tlc on silica, first EtOAc (2): hexane (3) affording main fractions which on a second plate using hexane (1): ether (4) gave pure compounds. Isolated in ascending order of polarity: 71 mg starting material; 36 mg (8%) of **27**, distilled bulb to bulb, b.p. 190°/10^{-2} mm; 17 mg (4%) of **9**, b.p. as above, 170°/10^{-2} mm; 118 mg (27%) of **8**, m.p. 143–145° (EtOAc), b.p. 180°/10^{-2} mm; 26 mg (6%) of **28**, b.p. 200°/10^{-1} mm. Structures **27** and **28** were assigned on the basis of spectral (NMR) comparisons of these with **29**, **30**, **16**, and **17**.

Compound **8**. (Found: C, 64.40; H, 6.31; M.W. 222.0860. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35; M.W. 222.0892). IR ($CHCl_3$): 2965, 2915, 2845, 1779, 1450, 1300, 1133, 1102, 1001, 863 cm^{-1}. NMR ($CDCl_3$): δ 4.41–3.72 (AB, 2 H, J=8 Hz); 3.50 (ps d, 2 H); 3.08 (ps d, 1 H); 2.92 (ps d, 1 H); 2.11–1.22 (m, 8 H). MS: M^+, 222 (0.5); 206 (3); 190 (34); 146 (28); 145 (17); 132 (22); 131 (77); 105 (100).

An X-ray analysis has been carried out.[5]

Compound **9**. (Found: C, 64.30; H, 6.28; M.W. 222.0865). IR ($CHCl_3$): 2955, 2915, 2845, 1776, 1448, 1351, 1100, 1008, 948, 885 cm^{-1}. NMR ($CDCl_3$): δ 4.27–3.93 (AB, 2 H, J = 9 Hz); 3.44 (ps d, 2 H, J = 3 Hz); 3.08 (ps d, 1 H, J = 3 Hz); 2.92 (ps d, 1 H, J = 3 Hz); 2.11–1.25 (m, 8 H). MS: M^+, 222 (2); 175 (10); 165 (12); 160 (10); 150 (13); 149 (100); 148 (22); 147 (29); 145 (13); 139 (67); 138 (27); 137 (15); 136 (14); 135 (56); 134 (16); 133 (27); 132 (11); 131 (45); 129 (10); 128 (11); 122 (23); 121 (42); 120 (3); 119 (40).

Compound **27**. (Found: M.W. 222.0922. $C_{12}H_{14}O_4$ requires M.W. 222.0892). IR ($CHCl_3$): 3630, 3540, 3450, 2915, 2840, 1762, 1720, 1676, 1479, 1444, 1362, 1303, 1278, 1102, 1066, 1014, 989, 978, 948 cm^{-1}. NMR ($CDCl_3$): δ 7.07 (dd, 1 H); 6.03 (dd, 1 H); 4.61 (t, 1 H); 4.68–4.20 (AB, 2 H, J = 9 Hz); 4.00 (br s, 1 H); 1.58 (br s, 8 H). MS: M^+, 222 (1.6); 221 (1); 206 (1.5); 178 (3); 150 (2); 149 (9); 148 (7); 147 (6); 140 (26); 139 (100); 138 (4); 135 (5); 131 (5).

Compound **28**. (Found: M.W. 222.0895). IR ($CHCl_3$): 3630, 3570, 3455, 2915, 2840, 1780, 1724, 1678, 1610, 1447, 1364, 1302, 1097, 1050, 1001, 951, 935 cm^{-1}. NMR ($CDCl_3$): δ 6.98 (dd, 1 H); 6.11 (dd, 1 H); 4.82 (t, 1 H); 4.31–3.83 (AB, 2 H, J = 9 Hz); 4.00 (br s, 1 H); 1.49 (br s, 8 H). MS: M^+, 222 (6); 206 (8); 192 (12); 178 (9); 176 (7); 150 (14); 149 (15); 148 (11); 147 (8); 140 (9); 139 (100); 138 (14); 137 (5); 136 (7); 135 (9); 134 (5); 133 (11); 131 (14); 122 (8); 121 (16); 120 (10); 119 (5); 118 (6); 117 (11).

When the chloroform solution obtained from 772 mg **6** as above irrad for 36 hr (conversion 37%) was chromotag as above returning 360 mg starting material and the residue dissolved in EtOAc (40 ml) in an ampoule, sealed in vacuum and irrad (Rayonette) at 350 nm for 4 hr, the solvent removed at water pump and crude residue purified as above by tlc on silica, 7 fractions were isolated: 32 mg of **6**; 26 mg (6%) of **30**; 31 mg (7%) of **27**; 25 mg (6%) of **9**; 127 mg (29%) of **8**; 18 mg (4%) of **29** and 35 mg (8%) of **28**.

Compound **29**. (Found: M.W.–0: 206.0938. $C_{12}H_{14}O_3$ requires: 206,0942). IR ($CHCl_3$): 3630, 3555, 3465, 2915, 2840, 1776, 1724, 1680, 1602, 1443, 1364, 1296, 1093, 1016, 990, 953 cm^{-1}. NMR ($CDCl_3$): δ 6.80 (dd, 1 H); 6.07 (dd, 1 H); 4.62 (t, 1 H); 4.28 (s, 2 H); 4.00 (br s, 1 H); 1.63 (br s, 8 H). MS: 206.0938 (−0); 205.0877 (−OH); 204.1130 ($-H_2O$); 192.0798 ($-CH_2O$); 178.0984 ($-CO_2$); 147 (base peak).

Compound **30**. (Found: M.W.−O: 206.0902). IR ($CHCl_3$): 2945, 2910, 2840, 1770, 1639, 1445, 1390, 1363, 1350, 1294, 1094, 1045, 1032, 1000, 952, 881, 850, 836 cm^{-1}. NMR ($CDCl_3$): δ 6.27 (m, 1 H); 5.74 (dd, 1 H); 4.13–3.75 (AB, 2 H, J = 8 Hz); 3.39 (m, 2 H); 2.24–1.12 (m, 8 H). MS: 206 (19); 190 (3); 188 (2); 151 (3); 148 (40); 132 (23); 131 (72); 130 (11); 129 (22); 128 (12); 127 (4); 122 (6); 121 (18); 120 (43); 119 (33); 118 (39); 117 (68); 116 (21); 115 (32); 109 (40); 108 (15) 107 (90); 105 (97); 104 (100).

Preparation of **8** *by reduction*

To an ice-cooled soln of $NaBH_4$ (200 mg) in dimethoxyethane (distilled from CaH_2), under argon, wa:

added with stirring a soln of **3** (X=O; 20 mg) in dry DME (2 ml). When addition was complete the ice bath was removed and the mixture was stirred for 1 hr. It was carefully hydrolyzed with ice-cooling using HCl (6 N; 2 ml) and the solvent removed at the water pump. The residue was partitioned between water (20 ml) and ether (10 ml) and twice extracted with ether (10 ml portions). The aq layer was satd with NaCl and again extracted with ether (2 × 10 ml). The combined ether extracts were washed with satd NaClaq and dried (Na_2SO_4). Removal of solvent gave crude product (18 mg). tlc on silica ($CHCl_3$) gave **8** (11 mg; 59%), m.p. 143–145 (EtOAc) identical in all respects with the product described above.

Reaction of **12** *with* $^1O_2$

A soln of **12** (295 mg) and MB (5 mg) in dry acetonitrile (35 ml) was irradiated with the Osram lamp for 6 hr. The NMR spectrum of the crude mixture after the usual workup showed a conversion of 22% of the diene. Prep tlc on silica using EtOAc (1): hexane (9) gave **12** (185 mg) and a mixture of **13** and **14** (76 mg). This material was not further characterized. It was an oil. NMR ($CDCl_3$): δ 6.64 (ps t, 2 H); 4.17 (ps t, 2 H); 3.77–3.37 (AB, 4 H, J = 9 Hz); 1.77–1.13 (m, 8 H). It was sealed in an NMR tube with 0.4 ml $CDCl_3$ and the spectrum recorded at 5 min intervals; $t_{1/2}$ *ca* 5 min (140°). A mixture of **15** and **16** was obtained as well as a by-product, **17**. Rearrangement thermally of the product obtained as above but after irrad of 28 hr showed 63% conversion. The crude from 750 mg **12** afforded after heating under reflux in xylene for 90 min material which by tlc on silica (4 plates, hexane (2): ether (8)) gave 196 g of **12**, 300 mg of **15** + **16** and 70 mg of **17**. Chromatography on prep. silica plate using ether, two fractions were obtained, a mixture of **13** and **14** (1:1; 45 mg) and pure *anti*-isomer **13** (27 mg). The isomers may however be separated using glc, 2 m glass column, 1/4 inch, 5% SF-96 on chromosorb-W, column temp 150°. Semicrystalline isomers were obtained. Crystallization gave pure products which had been present in the reaction mixture as endoperoxides in the ratio *syn* (3): *anti* (7).

Compound **15**. (Found for mixture of **15** and **16**: C, 68.77; H, 7.71. $C_{12}H_{16}O_3$ requires: C, 69.21; H, 7.74%). M.p. 87–89° (ether). IR (CCl_4): 3010, 2970, 2935, 2890, 2865, 1490, 1478, 1462, 1450, 1422, 1275, 1244, 1178, 1112, 1087, 1068, 1032, 1000, 986, 962, 945, 925, 904, 866, 849, 643, 627, 582 cm^{-1}. NMR ($CDCl_3$): δ 3.90, 3.72 (AB, 4 H, J = 8.5 Hz); 3.42 (m, 2 H); 2.89 (m, 2 H); 2.00–1.47 (m, 8 H). MS: M^+, 208 (3); 191 (4); 190 (4); 179 (9); 178 (6); 177 (8); 163 (8); 162 (7); 161 (18); 160 (8); 150 (10); 149 (42); 147 (14); 145 (10); 137 (10); 136 (22); 135 (33); 134 (14); 133 (30); 132 (12); 131 (30); 129 (10); 124 (34); 123 (51); 122 (17); 121 (30); 120 (16); 119 (25); 118 (10); 123 (51); 121 (21); 120 (12); 119 (14); 117 (12); 109 (10); 108 (18); 107 (81); 105 (24); 104 (14); 91 (100).

Compound **16**. M.p. 101–104° (ether). IR (CCl_4): 3010, 2935, 2870, 1487, 1480, 1460, 1450, 1416, 1271, 1261, 1241, 1111, 1089, 1069, 1052, 1029, 1007, 962, 952, 922, 895, 870, 843, 636, 612, 582 cm^{-1}. NMR ($CDCl_3$): δ 4.02, 3.80 (AB, 4 H, J = 8.5 Hz); 3.45 (m, 2 H); 2.86 (m, 2 H); 1.57 (m, 8 H). MS: M^+ + 1, 209 (1.7); M^+, 208 (2.2); 207 (1); 206 (1); 192 (3); 191 (3); 190 (2); 178 (4); 177 (3); 176 (3); 163 (9); 162 (10); 161 (11); 149 (31); 147 (10); 146 (10); 145 (48); 142 (11); 137 (10); 136 (18); 135 (19); 134 (12); 133 (34); 132 (12); 131 (23); 124 (10); 123 (51); 121 (21); 120 (12); 119 (14); 117 (12); 109 (10); 108 (18); 107 (81); 105 (24); 104 (14); 91 (100).

The fraction comprising crude **17** was again subjected to tlc on silica using ether (2): $CHCl_3$ (8) giving 30 mg (5%) of material which after bulb to bulb distillation at 165°/10^{-2} mm was assigned structure **17** on the basis of the spectroscopic data.

Compound **17**: (Found: M.W. 208.1063. $C_{12}H_{16}O_3$ requires M.W. 208.1027). IR ($CHCl_3$): 3580, 3410, 2920, 2870, 2850, 1708, 1672, 1600, 1478, 1447, 1381, 1291, 1124, 1057, 994, 976, 949, 900 cm^{-1}. NMR ($CDCl_3$): δ 6.80 (dd, 1 H); 5.96 (dd, 1 H); 4.78 (t, 1 H); 4.48–3.90 (AB, 2 H, J = 9 Hz); 3.97–3.54 (AB; 2 H; J = 9 Hz); 2.70 (br s, 1 H); 1.55 (br s, 8 H). MS: M^+, 208 (13); 190 (22); 178 (17); 177 (27); 163 (12); 162 (66); 161 (44); 151 (26); 150 (25); 149 (71); 148 (38); 147 (81); 139 (35); 135 (15); 134 (69); 132 (28); 131 (23); 130 (20); 125 (23); 123 (52); 121 (45); 120 (100); 119 (42).

Reaction of **18** *with* $^1O_2$

A soln of **18** (259 mg) and MB (20 mg) in dry acetonitrile (35 ml) was irradiated with the halogen lamp for 1 hr. TLC indicated complete disappearance of tetraene and the NMR spectrum showed besides the mono-adduct also ca 16% *bis*-adduct. After the usual workup the semi-solid residue was triturated with acetone and part of the less soluble *bis*-adduct **21** was removed by filtration. Evaporation of the mother liquor afforded 260 mg residue. Tlc of 60 mg of this on silica ($CHCl_3$) gave **19** (17 mg; 29%) and **21** (10 mg; 17%). **19**: IR ($CHCl_3$): 1596, 896 cm^{-1}. NMR ($CDCl_3$): δ 6.89 (ps t, 2 H); 6.24–5.53 (AA'BB', 4 H); 4.41 (ps t, 2 H); 3.90–3.38 (AB, 4 H, J = 9 Hz).

Rearrangement of 100 mg of the above crude residue containing **19** and **21** in 0.4 ml acetone-d_6 within a vacuum-sealed NMR tube was effected at 150°C. The NMR spectrum was recorded at 5 min intervals. Signals for the *bis*-epoxide **20** appeared as well as those for phthalan, δ 7.43 (s, 4 H); 5.11 (s, 4 H), and maleic dialdehyde, δ 10.13 (m, 2 H); 7.10 (m, 2 H); $t_{1/2}$ at 140°, *ca* 5 min.

Preparative tlc ($CHCl_3$) on silica gave in ascending order of polarity: phthalan (7 mg, 15%), low recovery due to high volatility; **20** (21 mg; 26%), **22** (14 mg; 74%).

Compound **20**. M.p. 145–148° (EtOAc). (Found: C, 69.01; H, 5.75; M.W. 204.0798. $C_{12}H_{12}O_3$ requires: C, 70.57; H, 5.92%; M.W. 204.0786). IR (KBr): 3015, 2990, 2965, 2915, 2850, 1574, 1484, 1427, 1412, 1370, 1359, 1282, 1254, 1163, 1125, 1114, 1056, 1031, 956, 939, 920, 860, 722, 705 cm^{-1}. NMR ($CDCl_3$): δ 6.08–5.55 (AA'BB', 4 H); 4.14–3.76 (AB, 4 H, J = 9 Hz); 3.46 (ps d, 2 H); 2.98 (ps d, 2 H). MS: M^+, 204 (19); 175 (23); 146 (15); 145 (100); 144 (15); 141 (12); 131 (24); 129 (15); 119 (23). X-ray analysis has been carried out.[5]

Irradiation of **18** (400 mg) and MB (30 mg) in CH_3CN (35 ml) as above for 4 hr gave after the usual workup **21** (400 mg; 73%), m.p. 163–167° (dec, acetone). (Found: C, 60.78; H, 4.83; M.W. 236.0669. $C_{12}H_{12}O_5$ requires: C, 61.01; H, 5.12%; M.W. 236.0684). IR (KBr): 3040, 2940, 2860, 1621, 1473, 1464, 1362, 1159, 1133, 1115, 1085, 1064, 938, 927, 910, 893, 848, 824, 813, 787 cm^{-1}. NMR (acetone-d_6): δ 6.21–5.92 (2 ps t, 4 H); 4.36–4.22 (2 ps t, 4 H); 3.87–3.26 (AB, 4 H, J = 9 Hz). ($CDCl_3$): δ 6.65 (m, 4 H); 4.55 (m, 4 H); 4.32–3.56 (AB, 4 H, J = 9 Hz). MS: M^+, 236 (3); 207 (2); 202 (2); 190 (11); 178 (6); 177 (11); 161 (23); 159 (8); 152 (17); 151 (11); 149 (14); 147 (27); 145 (10); 144 (19); 137 (9); 136 (29); 135 (37); 134 (13); 133 (34); 132 (13); 131 (56); 129 (9); 119 (100).

Thermal rearrangement of **21** (185 mg) in xylene (20 ml) at reflux for 2.5 hr gave after tlc using acetone (2): chloroform (8), in ascending order of polarity **22** (112 mg; 61%), m.p. 192–194° (acetone), accompanied by **23** (15 mg; 8%). The structure of **23** was assigned on the basis of comparison of NMR spectra of related products. Rearrangement of **21** (20 mg) in 0.4 ml acetone-d_6 in a sealed NMR tube gave $t_{1/2}$ at 140°, *ca* 7 min.

Compound **22**. (Found: C, 61.10; H, 5.06. $C_{12}H_{12}O_5$ requires: C, 61.10; H, 5.12%). It had b.p. 160°/10^{-2} mm. IR (KBr): 2990, 2965, 2945, 2915, 2875, 2850, 1486, 1469, 1438, 1418, 1400, 1372, 1353, 1279, 1172, 1157, 1124, 1110, 1081, 1046, 1032, 973, 959, 950, 931, 863, 854, 833, 822, 765, 753, 705, 669, 634 cm^{-1}. NMR ($CDCl_3$): δ 4.12–3.81 (AB, 4 H, J = 9 Hz); 3.53 (m, 4 H); 3.31 (ps d, 2 H); 3.08 (ps d, 2 H). X-ray structure has been determined.[5]

Compound **23**. IR ($CHCl_3$): 3615, 3565, 3475, 2960, 2940, 2905, 2845, 1712, 1679, 1354, 1075, 963, 922, 856 cm^{-1} NMR ($CDCl_3$): δ 6.86 (dd, 1 H); 5.98 (dd, 1 H); 5.08 (t, 1 H); 4.41–3.64 (AB, 2 H, J = 9 Hz); 4.08 (s, 2 H); 3.80 (br s, 1 H); 3.53 (m, 2 H); 3.27 (ps d, 1 H); 3.10 (ps d, 1 H).

Irradiation of **21**

The *bis-endoperoxide* **21** (100 mg) and acetone (50 ml) were sealed under vacuum and the ampoule irradiated (Rayonette) at 350 nm for 4 hr. After tlc on silica, using acetone (2): chloroform (8) the tetraepoxide **22** (40 mg; 40%) and the cagelike **24** (35 mg; 35%) were isolated; **22** was identical with the product described above.

Compound **24** was recrystallized from acetone and dec at 250–255° without melting. (Found: C, 60.68; H, 5.16; M.W. 236.0662. $C_{12}H_{12}O_3$ requires: C, 61.01; H, 5.12%; M.W. 236.0684). IR (KBr): 3200, 3030, 2990, 2960, 2910, 2870, 1482, 1467, 1390, 1327, 1293, 1283, 1232, 1203, 1154, 1133, 1076, 1052, 1039, 992, 976, 917, 895, 826, 800 cm^{-1}. NMR (acetone-d_6): δ 6.48 (ps t, 2 H); 4.75–4.52 (m, 4 H); 3.82, 3.38 (AB, 2 H, J = 10 Hz); 3.71, 3.12 (AB, 2 H, J = 10 Hz); 3.65 (br s, 1 H); 3.00 (br s, 1 H). MS: M^+ 236 (8); 207 (12); 191 (5); 179 (8); 178 (13); 177 (51); 161 (16); 160 (11); 159 (20); 149 (23); 148 (32); 147 (84); 146 (30); 136 (9); 135 (55); 134 (18); 133 (40); 132 (31); 131 (100); 121 (53); 120 (20); 119 (97); 103 (91).

In similar irradiation at 250 nm were obtained **22** (25 mg; 25%); **24** (22 mg; 22%) identical with the products described above as well as **23**, respectively identical with the product described above (10 mg; 10%).

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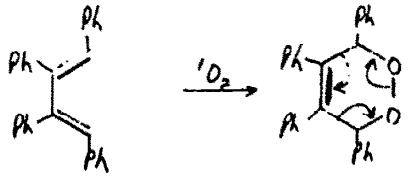

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