Photooxygenation of 5- and 6-chloro-1,3-cycloheptadienes and reactions of their endoperoxides with base: effects of the chloro substituent on the reactions

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Photooxygenation reactions of 5- and 6-chlorocycloheptadienes **6** and **7** gave bicyclic endoperoxides **10–13**. The endoperoxides **10** and **13** are major products due to the steric effects of the chloro substituent. The reactions of endoperoxide **10** with NEt_3 under different conditions gave 1,4-epoxide **14**, hydroxyenone **15**, diketone **16**, acetates **17–19** and diacetate **20**. The reaction of endoperoxide **10** with pyridine and Ac_2O gave diacetate **20** and dienone **21**. The reaction of endoperoxide **13** with NEt_3 gave tropone. The effects of the chloro substituent are discussed.

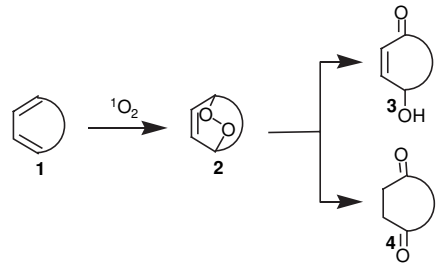
Keywords: base-catalysed rearrangement, chlorocycloheptadiene, endoperoxide, photooxygenation, steric effect, triethylamine

The reactions of 1,3-dienes with singlet oxygen are commonly used for the synthesis of unsaturated bicyclic endoperoxides, which have become increasingly significant in a variety of chemical transformations.[1]

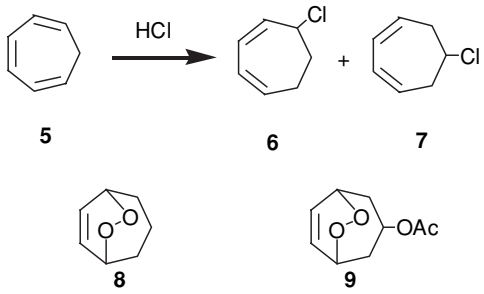
One of the common reactions of unsaturated [n.2.2] bicyclic endoperoxides is base-catalysed rearrangement (Scheme 1).[1] Triethylamine (NEt_3) is usually used as the reagent. Unsaturated bicyclic endoperoxides[1,2] derived from cyclo-heptatriene (CHT) and cycloheptatriene derivatives, usually give hydroxyenones with the structure **3**, but some give diketones with the structure **4**.[3]

The reaction of cycloheptatriene with HCl in acetic acid gives 5- and 6-chlorocycloheptadienes (**6** and **7**).[4] Unsaturated endoperoxide **8** was synthesised[5] from the reaction of 1,3-cycloheptadiene with singlet oxygen, and its reactions were investigated.[5,6,7]

The endoperoxides derived from **6** + **7** may be important because they have a double bond, an oxygen-oxygen bond and a chlorine substituent as functional groups. The endoperoxides derived from **7** should have properties similar to those of the endoperoxide acetate **9**.[7] Therefore, the photooxygenation of chlorocycloheptadienes **6** and **7** was performed, and the reactions of the endoperoxides with NEt_3 and pyridine were investigated.



Scheme 1

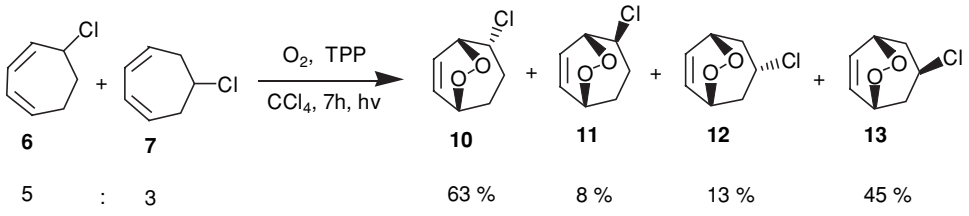


Scheme 2

Results and discussion

A mixture of chlorocycloheptadienes **6** and **7** was synthesised, as described in the literature (Scheme 2),[4] and they were obtained in a ratio of 5:3 (Scheme 3). The photooxygenation reaction of this mixture in CCl_4 at 15 ± 3 °C was accomplished with tetraphenylporphin (TPP) as sensitiser (Scheme 3). The ^1H NMR spectrum of the crude material showed that endoperoxides were formed, and careful chromatography of the mixture on silica gel provided four bicyclic endoperoxides, **10**–**13**.

Their ^1H and ^{13}C NMR spectra, including double resonance and NOE experiments, were carefully investigated. Figure 1 contains their ^1H NMR spectra and ratios of the endoperoxides are given in Scheme 3. The yields of **10** and **11** are based on reactant **6**, and those of **12** and **13** on reactant **7**. In their ^{13}C NMR spectra, two have a four-line while the others have a seven-line spectrum. The former should be symmetric, and the later should be non-symmetric. This showed that endoperoxides **12** and **13** have symmetrical structures and were obtained from compound **7**. The configurations of Cl at the C-3 carbon atoms in endoperoxides **12** and **13** were determined by comparing their chemical shifts. Protons at the C-3 carbon atoms in **12** and **13** resonate at 4.87 and 3.86 ppm as *tt* (a triplet of triplets), respectively (Figure 1). The proton in **13**



Scheme 3

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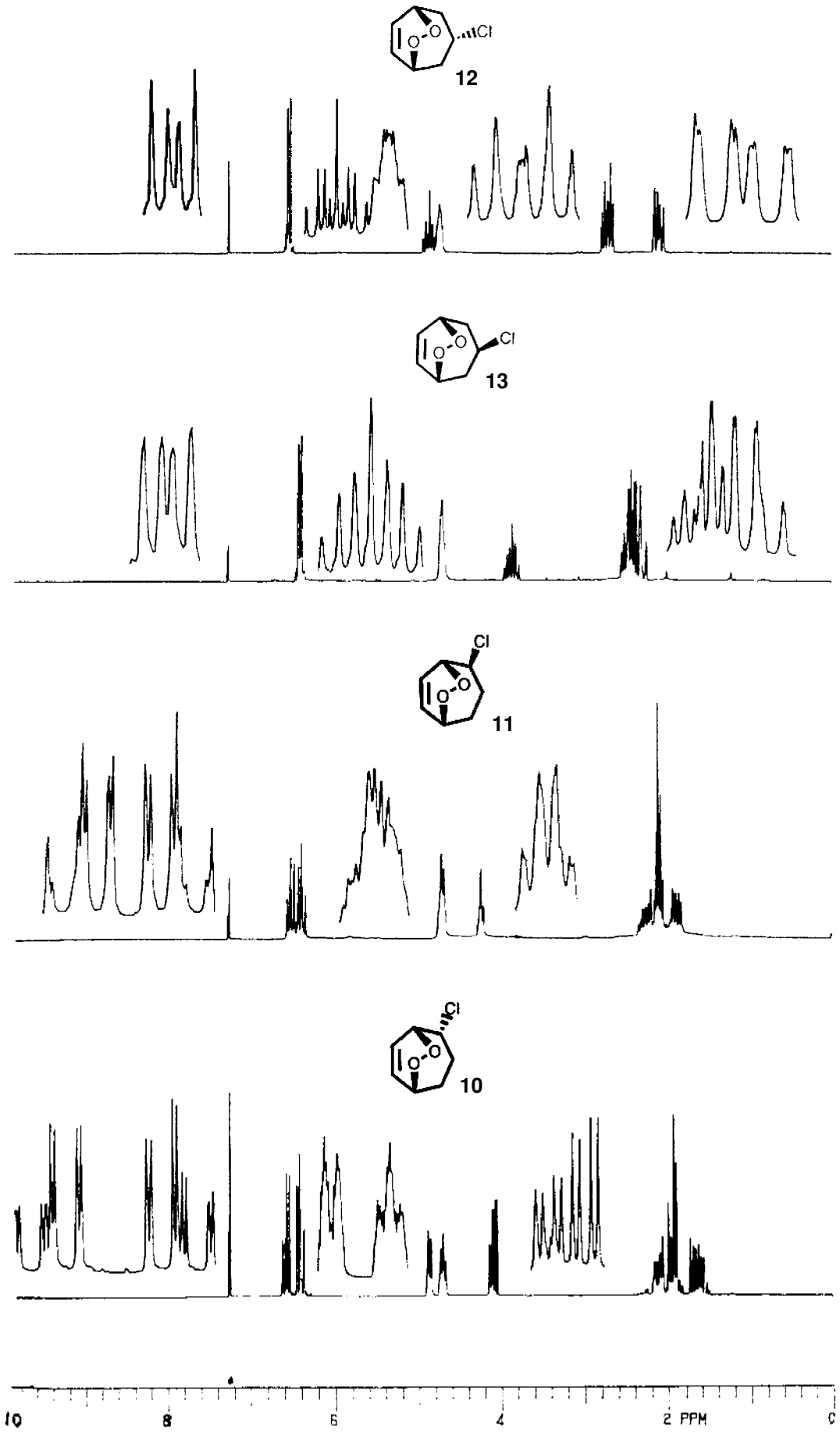
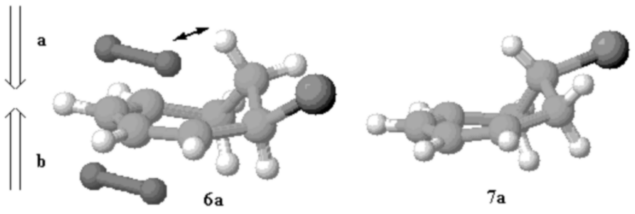
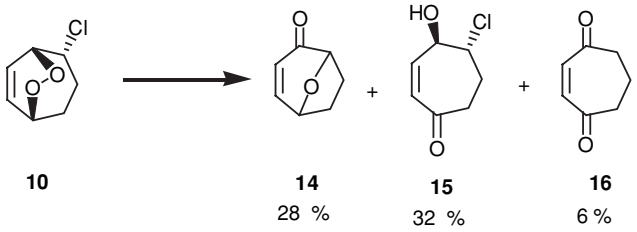


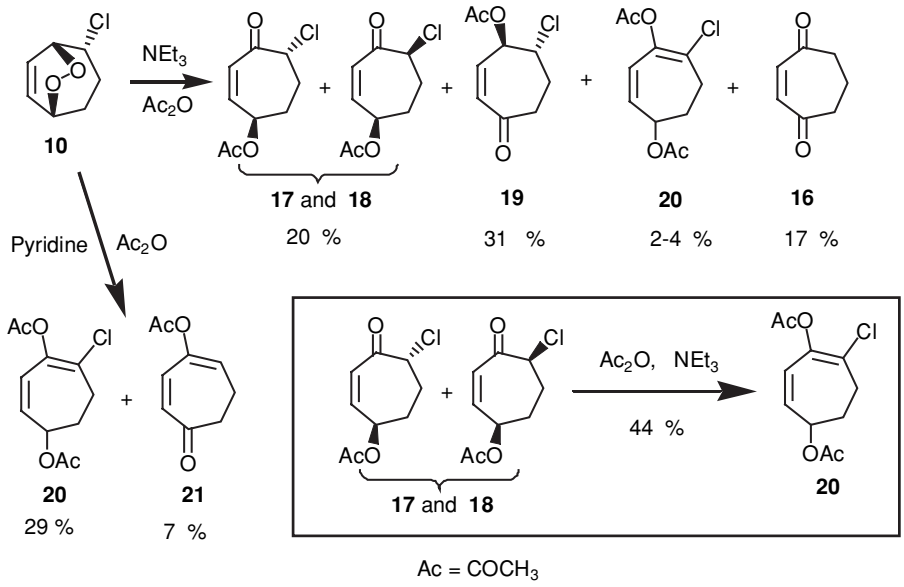
Fig. 1. 200 MHz ^{1}H NMR sectra of the endoperoxides **10–13**.



Scheme 4



Scheme 5



Scheme 6

is at a higher field than the proton in **12** because the double bond in **13** shields this proton. The structure of **13** has further been confirmed by NOE studies. Irradiation of H-3 proton in **13** at 3.86 ppm induces an enhancement of the olefinic resonances which indicates clearly the orientation of the H-3 proton.

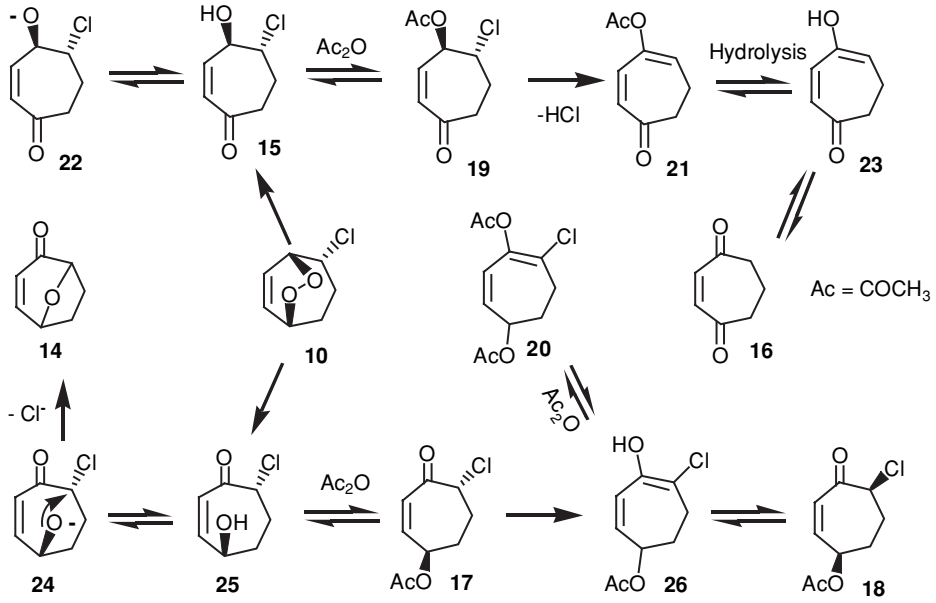
As also seen in Fig. 1, all the protons are non-equivalent in the other endoperoxides **10** and **11**, which have nonsymmetric structures. Endoperoxide **10** is the major product, and the ratio of **10** to **11** is approximately 8:1. The oxygen and chloro groups in **11** are in the same direction with respect to the ring, and it is expected that endoperoxide **11** should be more polar than endoperoxide **10**. In the column chromatography, endoperoxide **10** was eluted first, while endoperoxide **11** was eluted last due to this difference in their polarities. We have calculated the dipole moments of endoperoxides **10** +**11**, by the semi-empirical AM1 method and these are 2.58 Debye (D) and 4.01 D respectively.

The formation of endoperoxides **10**–**13** may also be explained as follows: the most stable conformations of chlorocycloheptadienes **6** and **7** are shown in Scheme 4 as **6a** and **7a**, respectively. The approach of singlet oxygen to **6a** from **a** (above) and **b** (below) is possible, and the latter is much more likely due to the steric effect between *endo* H_7 and singlet oxygen; **10** is therefore obtained in a larger yield than **11**. In the same way, endoperoxide **13** is also obtained in a larger yield than **12** in the reaction of singlet oxygen with H_7 due to a similar steric effect. The structures of the endoperoxides **10**-**13** were assigned on this argument based on yields and polarities.

The reaction of endoperoxide **10** with NEt_3 at room temperature in $CHCl_3$ and subsequent careful chromatography of the reaction mixture on preparative thick layer chromatography (PLC) gave the known 1,4-epoxide **14**[8] and diketone **16**[9] in addition to hydroxyenone **15** (Scheme 5). Products **14** and **16** should be formed via intermediates as illustrated (Scheme 7). Hydroxyenone **15** is not symmetric and this is consistent with its NMR spectra.

To determine the intermediates formed in the reaction of endoperoxide **10** with NEt_3, this reaction was started at a low temperature and Ac_2O was also added to the reaction medium (Scheme 6). Careful chromatography of the reaction mixture gave **17–20** and **16**. Compounds **17** and **18** were obtained as a mixture and could not be isolated separately. Compound **17** is converted into **18** in the reaction. It was seen that **17** and **18** were converted into diene (or diacetate) **20** when they were reacted with NEt_3 and Ac_2O (Scheme 6). However, the reaction of endoperoxide **10** with pyridine and Ac_2O and subsequent careful chromatography of the reaction mixture on PLC gave diene **20** and dienone **21**. Dienone **21** could not be observed in the reaction of **10** with NEt_3 and Ac_2O.

The following reaction mechanism is proposed to rationalise the formation of products **14–21** (Scheme 7). The rearrangement of endoperoxides with a base has been investigated many times.[1,2,3,10] The rearrangements of endoperoxide **10** with NEt_3 or pyridine to **15** and **25** may be via the Kornblum-Delamare reaction mechanism. Base-catalysed rearrangements of **10** give **15** and **25** as is shown by the fact they leave two different α-protons and are therefore not symmetric. Intermediate **24** undergoes intramolecular chloride displacement to give epoxide **14**.[8] Compound **17**, formed from the reaction of **25** with Ac_2O, is converted into **18** via intermediate **26**. Diacetate **20** is formed from **17** and **18** via **26** because the reactions of **17** and **18** with NEt_3 give **20**. Compound **19**, formed from the reaction of **15** with Ac_2O, is converted into **21** by elimination



Scheme 7

of HCl in the presence of pyridine. Hydrolysis of compound **21** gives ketone **16** via intermediate **23**.

It was observed that the reaction of endoperoxide **13** with NEt_3 in $CHCl_3$ gave tropone **29** (Scheme 8). Intermediates **27** and **28** should be involved in this reaction. Firstly, intermediate **27** is formed from endoperoxide **13** by base catalysed-rearrangement. The other intermediate **28**, formed from **27** by the elimination of HCl in the presence of base, is converted into tropone **29** by dehydration. The photooxygenation of cycloheptatriene and subsequent treatment of cycloheptatriene endoperoxides with NEt_3 similarly gives tropone **29**.[11] In these reactions, the (2+4) adduct is the major product and it rearranges with NEt_3 to give compound **28**.

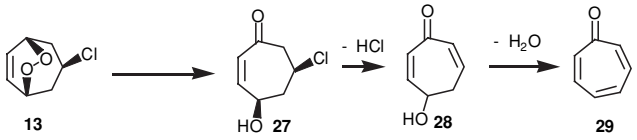
Conclusions

Photooxygenation reactions of chlorocycloheptadienes **6** and **7** as a mixture gave endoperoxides **10-13** (Scheme 3). Endoperoxides **10** and **13** are major products in these reactions due to the steric effects of the chloro substituent in compounds **6** and **7**. The reaction of endoperoxide **10** with NEt_3 gave 1,4-epoxide **14**[8], hydroxyenone **15** and diketone **16**[9] (Scheme 5). The 1,4-epoxide **14** and diketone **16** are secondary rather than primary reaction products. To determine the intermediates, this reaction was carried out in the presence of Ac_2O, and acetates **17–19**, diacetate **20** and ketone **16** were isolated by chromatographic separation. Compound **20** was prepared separately from the reaction of **26** with Ac_2O. The reaction of endoperoxide **10** with pyridine and Ac_2O gave diacetate **20** and dienone **21**. Dienone **21** is probably converted into other compound(s) because it could not be observed in the presence of NEt_3. The reaction of endoperoxide **13** with NEt_3 gave tropone.

From the reactions of endoperoxides **10** and **13**, products such as epoxide **14**, diketone **16**, diacetate **20**, dienone **21** and tropone were obtained. The presence of the chlorine atoms in endoperoxides **10** and **13** is responsible the formation of these products.

Experimental

General remarks: All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. M.p.: *Thomas-Hoover* cap. Melting apparatus and are uncorrected. IR spectra were obtained from solutions in 0.1 mm cells



Scheme 8

with a Perkin-Elmer spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a 200 (50)-MHz Varian spectrometer; δ in ppm, Me_4Si as the internal standard. Elemental analyses were performed on LECO CHNS-932 apparatus. All column chromatography was performed on silica gel (60-mesh, Merck). PLC is preparative thick-layer chromatography: 1 mm of silica gel 60 PF (Merck) on glass plates.

Photooxygenation of 5- and 6-chloro-1,3-cycloheptadienes (**6** and **7**): To a stirred solution of chlorides[5] **6** and **7** (8.1 g, 63.04 mmol, **6**:**7** =5:3) in 250 ml of CCl_4 was added 100 mg of tetraphenyl-porphyrin (TPP). The resulting mixture was irradiated with a projection tungsten lamp (500 W) while oxygen was being passed through solution and the mixture was stirred for 7 h at 15 ± 3 °C. Evaporation of the solvent (30 °C, 20 mm-Hg) and chromatography of residue (9.87 g) on a silica gel (110 g) eluting with ethyl acetate/hexane (1:9) gave as the first fraction endoperoxide **10** (4.0 g, 25.3 mmol, 63 %), second fraction endoperoxide **12** (500 mg, 3.12 mmol, 13 %), third fraction endoperoxide **13** (1.697 g, 10.6 mmol, 45 %), and fourth fraction **11** (521 mg, 3.25 mmol 8 %). The yields of endoperoxides are given separately for **6** and **7.**

1S(R),2S(R),5S(R)-2-Chloro-6,7-dioxa-bicyclo[3.2.2]non-8-ene (**10**): M.p. 27–29 °C; white crystals were obtained an cooling in refrigerator; Anal. Calc. For $C_7H_9ClO_2$: C 52.35, H 5.65; found: C 52.3, H 5.6; ν_{max} ($CHCl_3$/ cm^{-1}) 3064, 2948, 1451, 1381, 1247, 1208, 1054, 985, 931, 741; δ_H (200 MHz, $CDCl_3$) 6.59 (ddd, A part of AB system, olefinic, *J*=9.3, 7.0 and 1.1 Hz, H_9, 1H), 6.42 (ddd, B part of AB system, olefinic, *J*=9.3, 7.0 and 1.2 Hz, H_8, 1H), 4.88 (brd, *J* =6.9 Hz, bridgehead, H_1, 1H), 4.85–4.69 (m, bridgehead, H_5, 1H), 4.10 (ddd, A part of AB system, *J*=11.0, 5.5 and 2.2 Hz, H_2, 1H), 2.18–1.98 (m, methylenic, 1H), 1.97–1.88 (m, methylenic, 2H), 1.75–1.57 (m, methylenic, 1H); δ_C (50 MHz; $CDCl_3$) 132.9 (CH), 126.0 (CH), 82.5 (OCH), 78.7 (OCH), 60.7 (ClCH), 31.0 (CH_2) 30.1 (CH_2).

1S(R),2R(S),5S(R)-2-Chloro-6,7-dioxa-bicylo[3.2.2]non-8-ene (**11**): M.p. 39–41 °C; white crystals were obtained an cooling in a refrigerator; Anal. Calc. For $C_7H_9ClO_2$: C 52.35, H 5.65; found: C 52.3, H 5.7; ν_{max} ($CHCl_3$/ cm^{-1}) 3080, 2953, 1395, 1370, 1293, 1191, 1165, 1038, 987, 936; δ_H (200 MHz, $CDCl_3$) 6.57–6.35 (m, olefinic, H_9, H_8, 2H), 4.77–4.68 (m, bridgehead, H_1, H_5, 2H), 4.28–4.21 (m, H_2, 1H), 2.35–2.20 (m, methylenic, 1H), 2.18–2.03 (m, methylenic, 2H), 2.01–1.83 (m, methylenic, 1H); δ_C (50 MHz;

APT, $CDCl_3$) 134.1 (CH), 128.9 (CH), 81.3 (OCH), 78.4 (OCH), 62.4 (ClCH), 32.5 (CH_2) 30.7 (CH_2).

Endo-3-Chloro-6,7-dioxa-bicylo[3.2.2]non-8-ene (**12**): M.p. 47–49 °C; white crystals from ether/hexane; Anal. Calc. For $C_7H_9ClO_2$: C 52.35, H 5.65; found: C 52.3, H 5.7; ν_{max} ($CHCl_3$/ cm^{-1}) 3064, 2941, 2871, 1447, 1381, 1354, 1277, 1081, 1023, 939, 715; δ_H (200 MHz, $CDCl_3$) 6.57–6.53 (m, olefinic, H_8, H_9, 2H), 4.87 (tt, J =9.1 and 5.9 Hz, H_3, 1H), 4.78–4.71 (m, bridgehead, H_1, H_5, 2H), 2.72 (brdt, A part of AB system, J =13.9 and 5.9 Hz, H_2, H_4, 2H), 2.12 (ddd, B part of AB system, J =13.9, 9.1 and 1.2 Hz, H_2, H_4, 2H); δ_C (50 MHz; $CDCl_3$) 133.1 (CH), 76.2 (OCH), 56.8 (ClCH), 43.9 (CH_2).

Exo-3-Chloro-6,7-dioxa-bicylo[3.2.2]non-8-ene (**13**): M.p. 52–54 °C; white crystals from ether/hexane; Anal. Calc. For $C_7H_9ClO_2$: C 52.35, H 5.65; found: C 52.3, H 5.7; ν_{max} ($CHCl_3$/ cm^{-1}) 3106, 3080, 3040, 2953, 2927, 1446, 1395, 1370, 1344, 1293, 1063, 1038, 987, 936; δ_H (200 MHz, $CDCl_3$) 6.43–6.39 (m, olefinic, H_8, H_9, 2H), 4.75 (m, bridgehead, H_1, H_5, 2H), 3.86 (tt, J =11.5 and 5.9 Hz, H_3, 1H), 2.48 (ddd, A part of AB system, J =14.6, 5.9 and 5.1 Hz, H_2, H_4, 2H), 2.33 (dd, B part of AB system, ^2J =14.6 and 11.5 Hz, H_2, H_4, 2H); δ_C (50 MHz; $CDCl_3$) 130.4 (CH), 70.3 (OCH), 54.3 (ClCH), 44.0 (CH_2).

Reaction of endoperoxide **10** *with Ac_2O and NEt_3*
A solution of endoperoxide **10** (1090 mg, 6.79 mmol) and acetic anhydride (2.0 g, 19.59 mmol) in ether (20 ml) was cooled to –8 ± 5 °C (ice-salt), and then to this solution was added dropwise a solution of triethylamine (2.5 g, 24.73 mmol) in ether (10 ml) for 10 minutes. A white solid appeared while NEt_3 was being added. After the mixture was stirred for 30 minutes, the cold bath was removed and the mixture was stirred at room temperature (rt) for 45 h. The solvent was evaporated, and then $CHCl_3$ (50 ml) was added to the residue. The resulting solution was poured into dilute HCl solution (150 g) with ice and checked to be acid with pH paper. After the organic layer was separated, the aqueous phase was extracted with $CHCl_3$ (2 × 30 ml). The combined organic layers were washed with $NaHCO_3$ (5 %, 100 ml) and water (100 ml), dried over $CaCl_2$ and the solvent was evaporated. The residue was submitted to silica gel (60 g) column chromatography with EtOAc/hexane (1/9). Diacetate **20** which is together with another unidentified product (91 mg, **20** =2–4 %), acetate **17** which is together with **18** (280 mg, 20 %, their ratio is approximately ½ or 1:2, 1.39 mmol), acetate **19** (420 mg, 2.08 mmol, 31 %) and diketone[10] **16** (140 mg, 1.13 mmol, 17 %) were obtained.

1S(R),5R(S)-Acetic acid 5-chloro-4-oxo-cyclohept-2-enyl ester (**17** or **18**) and *1S(R),5S(R)-acetic acid 5-chloro-4-oxo-cyclohept-2-enyl ester* (**17** or **18**): Colourless liquid; Anal. Calc. For $C_7H_9ClO_2$: C 53.35, H 5.47; found: C 53.4, H 5.5; for mixture of **17** and **18**. For major product: δ_H (200 MHz, $CDCl_3$) 6.28 (dm, J =12.8 Hz, A part of AB system, olefinic, 1H), 6.06 (dd, J =12.8 and 2.6 Hz, B part of AB system, olefinic, 1H), 5.61–5.47(m, HC-OAc, 1H), 4.62–4.56 (m, HC-Cl 1H), 2.53–1.93 (m, methylenic, 4H), 2.09 (s, OAc, 3H); δ_C (50 MHz; $CDCl_3$) 196.4 (CO), 171.9 (CO), 143.9 (CH), 130.4 (CH), 73.7 (OCH), 65.3 (ClCH), 30.6 (CH_2), 30.3 (CH_2), 23.0 (CH_3). *For minor product*: The peaks of this compound are in the same places as those of the major product except for, OAc (2.06 ppm, s) in the δ_H (200 MHz, $CDCl_3$) spectrum; δ_C (50 MHz; $CDCl_3$) 197.1 (CO), 171.8 (CO), 146.6 (CH), 131.3 (CH), 72.5 (OCH), 65.4 (ClCH), 31.0 (CH_2), 30.5 (CH_2), 23.0 (CH_3).

1R(S),7R(S)-4 Acetic acid 7-chloro-4-oxo-cyclohept-2-enyl ester (**19**): Colourless liquid; Anal. Calc. For $C_9H_{11}ClO_3$: C 53.35, H 5.5; found: C 53.2, H 5.5; ν_{max} ($CHCl_3$/ cm^{-1}) 2937, 1753, 1688, 1375, 1236, 1051; δ_H (200 MHz, $CDCl_3$) 6.26 (dd, J =12.4 and 4.0 Hz, A part of AB system, olefinic, 1H), 5.99 (ddd, J =12.4, 3.1 and 1.1 Hz, B part of AB system, olefinic, 1H), 5.71 (ddd, J =8.2, 4.0 and 2.0 Hz, HC-OAc, 1H), 4.30 (dt, J =8.2 and 4.7 Hz, HC-Cl 1H), 2.76 (ddd, A part of AB system, J =16.7, 9.2 and 3.6 Hz, methylenic, HC-CO, 1H), 2.69–2.64 (m, methylenic, HC-CO, 1H), 2.44–2.13 (m, methylenic, 2H), 2.11 (s, OAc, 3H); δ_C (50 MHz; $CDCl_3$) 203.2 (CO), 171.6 (CO), 142.1 (CH), 133.7 (CH), 77.4 (OCH), 61.2 (ClCH), 40.2 (CH_2), 31.1 (CH_2), 22.7 (CH_3).

5(S)R-Acetic acid 5-acetoxy-2-chloro-cyclohepta-1,6-dienyl ester (**20**): Pale yellow liquid; Anal. Calc. For $C_{11}H_{13}ClO_4$: C 54.0, H 5.36; found: C 54.1, H 5.4; ν_{max} ($CHCl_3$/ cm^{-1}) 2933, 1739, 1434, 1374, 1227, 1181, 1120, 1042 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.90 (dd, A part of AB system olefinic, J =12.4 and 4.4 Hz, 1H), 5.77 (d, B part of AB system olefinic, J =12.4 Hz, 1H), 5.46–5.39 (m, CH-O, 1H), 2.80-2.72 (m, methylenic, 2H), 2.13 (s, CH_3, 3H), 2.11-2.03 (m, methylenic, 2H), 2.07 (s, CH_3, 3H); δ_C (50 MHz; APT, $CDCl_3$) 171.7 (CO), 169.8 (CO), 142.2 (C), 133.3 (CH), 130.5 (C), 126.4 (CH), 72.3 (OCH), 33.4 (CH_2), 32.3 (CH_2) 23.1 (CH_3), 22.4 (CH_3).

Reaction of chlorides **17** *and* **18** *with Ac_2O and NEt_3*
A solution of chloride **17** and **18** (265 mg, 1.31 mmol) and acetic anhydride (300 mg, 2.94 mmol) and triethylamine (400 mg, 3.96 mmol) in ether (15 ml) was stirred at room temperature (rt) for 25 days. The other parts of the reaction were studied in the same manner as that of endoperoxide **10** with NEt_3 and Ac_2O, and diacetate **20** (142 mg, 0.58 mmol, 44 %) was obtained as the sole product.

*Reaction of endoperoxide **10** with NEt_3*
To solution of endoperoxide **10** (750 mg, 4.67 mmol) in $CHCl_3$ (20 ml) was added dropwise a solution of triethylamine (1180 mg, 11.67 mmol) in $CHCl_3$ (10 ml) for 5 minutes and the reaction mixture was stirred at room temperature for 5 days. The other parts of the reaction were studied in the same manner as that of endoperoxide **10** with NEt_3 and Ac_2O. The residue was submitted to PLC with EtOAc/hexane (3/7). The mixture of 1,4-epoxide **14**[9] and ketone **16**[10] as a mixture (200 mg, 1.6 mmol, 34.6 % as total) and alcohol **15** (240 mg, 1.5 mmol, 32 %) was obtained. According to the ^1H NMR spectrum of this mixture, the ratio of **14** and **16** in the mixture is 9 and 2, respectively (**14**: **16** =9:2).

4R(S),5R(S)-5-Chloro-4-hydroxy-cyclohept-2-enone (**15**): Colourless liquid; Anal. Calc. For $C_7H_9ClO_2$: C 52.35, H 5.65; found: C 52.2, H 5.7; ν_{max} ($CHCl_3$/ cm^{-1}) 3442, 2948, 2864, 1670, 1447, 1343, 1254, 1073, 951, 902; δ_H (200 MHz, $CDCl_3$) 6.20 (dd, J =12.5 and 3.4 Hz, A part of AB system, olefinic, H_3, 1H), 5.97 (dm, J =12.5 Hz, B part of AB system, olefinic, H_2, 1H), 5.71 (dm, J =8.7 Hz, A part of AB system, H_4, 1H), 4.22 (dt, J =8.7 and 4.8 Hz, B part of AB system, H_5,1H), 3.19 (m, OH, 1H), 2.81–2.58 (m, methylenic, 2H), 2.55–2.21 (m, methylenic, 2H); δ_C (50 MHz; APT, $CDCl_3$) 203.9 (CO), 146.2 (CH), 132.3 (CH), 77.0 (OCH), 66.7 (ClCH), 40.5 (CH_2), 31.6 (CH_2).

Reaction of endoperoxide **10** *with Ac_2O and pyridine*
To solution of endoperoxide **10** (1000 mg, 6.23 mmol) in $CHCl_3$ (25 ml) was added acetic anhydride (4.0 g, 39.22 mmol) and pyridine (4.0 g, 50.6 mmol) for 5 minutes and the reaction mixture was stirred at room temperature for 1 month. The other parts of the reaction were studied in the same manner as that of endoperoxide **10** with NEt_3. The residue was submitted to PLC with EtOAc/hexane (1/4). Diacetate **20** (445 mg, 1.82 mmol, 29 %) and dienone **21** (70 mg, 0.42 mmol, 7 %) were obtained.

Acetic acid 5-oxo-cyclohepta-1,6-dienyl ester (**21**): Colourless liquid; Anal. Calc. For $C_9H_{10}O_3$: C 65.05, H 6.1; found: C 64.9, H 6.1; ν_{max} ($CHCl_3$/ cm^{-1}) 3080, 2978, 1778, 1676, 1446, 1395, 1342, 1140, 1063, 936; δ_H (200 MHz, $CDCl_3$) 6.34 (dd, A part of AB system olefinic, J =12.9 and 1.8 Hz, H , 1H), 6.15 (d, B part of AB system olefinic, ^3J =12.9 Hz, H_α, 1H), 6.08 (dd, oleifnic, J =12.9 and 1.8 Hz, 1H), 2.75–2.69 (m, methylenic, CH_2-CO, 2H), 2.48–2.39 (m, methylenic, CH_2-CH=, 2H), 2.19 (s, CH_3, 3H); δ_C (50 MHz; APT, $CDCl_3$) 201.9 (CO), 171.5 (CO), 148.2 (C), 137.9 (CH), 132.7 (CH), 128.2 (CH), 43.3 (CH_2) 22.8 (CH_3), 21.8 (CH_2).

Reaction of endoperoxide **13** *with NEt_3*
To solution of endoperoxide **13** (756 mg, 4.7 mmol) in $CHCl_3$ (2 5 ml) was added NEt_3 (570 mg, 5.6 mmol) for 5 minutes and the reaction mixture was stirred at room temperature for 1 day. The other parts of the reaction were studied in the same manner as that of endoperoxide **10** with NEt_3. Tropone **29** (400 mg, 3.8 mmol, 81 %) was obtained. The structure of **29** was checked by NMR.

The authors are indebted to the Department of Chemistry (Atatürk University) for financial support, and assistant Prof. Dr. Cavit Kazaz and Mr. BarışAnıl for recording all NMR spectra.

Received 22 October 2004; accepted 27 January 2005
Paper 04/2832

References

1 M. Balcı, *Chem. Rev.*, 1981, **81**, 91.
2 (a) W. Adam, M. Balcı, and J. Riveare, *Synthesis,* 1979, 807; (b) E. Mete, R. Altundaş, H. Seçen, and M. Balcı, *Turk. J. Chem.*, 2003, **27**(2), 145; (c) A. Menzek, N. Akbulut and M. Balcı, *Turk. J. Chem*., 1985, **9**(3), 282.
3 a) B. Atasoy and M. Balcı, *Tetrahedron,* 1985, **42**, 1461; (b) M.E. Şengül, Z. Ceylan and M. Balcı, *Tetrahedron,* 1997, **53**, 10401.
4 H. Mayr, W. Heilmann and R. Lammers, *Tetrahedron*, 1986, **42**, 6663.

5 A.C. Cope, T.A. Liss and G.W. Wood, *J. Am. Chem. Soc.*, 1957, **79**, 6287.
6 M. Balcı and N. Akbulut, *Tetrahedron*, 1985, **41**, 1315.
7 (a) D.M. Floyd and C.M. Cimarusti, *Tetrahedron Lett.*, 1979, **20**, 4129; (b) C.R. Johnson, A. Golebiowski, T.K. McGill and D.H. Steensma, *Tetrahedron Lett.*, 1991, **32**, 2597.
8 D. Fattori, S. Henry and P. Vogel, *Tetrahedron,* 1993, **49**, 1649.
9 (a) L.A. Paquette, G.D. Crouse and A.K. Sharma, *J. Am. Chem. Soc.*, 1979, **104**, 4441; (b) T. Bajorek and N.H. Werstuik, *J. Chem. Soc., Chem. Commun.*, 2002, 648; (c) O.L. Chapman and D.J. Pasto, *J. Am. Chem. Soc*., 1960, **82**, 3642.
10 (a) N. Kornblum and H.E. Delamare, *J. Am. Chem. Soc*., 1951, **73**, 880; (b) M.K. Schwaebe and R.D. Little, *Tetrahedron Lett.*, 1996, **37**, 6635; (c) D.R. Kelly, H. Bansel and J.J. G. Morgan, *Tetrahedron Lett*., 2002, **43**, 9331.
11 (a) T. Asao, M. Yagihara and Y. Kitahara, *Bull. Chem. Soc. Jpn,* 1978, **51**, 2131; (b) E. Garfunkel and D. Reingold. *J. Org. Chem.,* 1979, **44**, 3725; (c) K. M. Harmon, A.B. Harmon, T.C. Thomas and J.M. Fisk, *J. Org. Chem.,* 1968, **33**, 2567.