

Stereochemistry and Product Distribution in the Singlet Oxygen Cycloaddition with 7,7-Disubstituted 1,3,5-Cycloheptatrienes

Waldemar Adam^{*a,b}, Friedhelm Adamsky^d, Frank-Gerrit Klärner^d,
Eva-Maria Peters^c, Karl Peters^c, Hector Rebollo^{a,b}, Wolfgang Rüngeler^d,
and Hans Georg von Schnering^c

Institut für Organische Chemie, Universität Würzburg^a,
Am Hubland, D-8700 Würzburg,

Departamento de Química, Universidad de Puerto Rico^b,
Rio Piedras, Puerto Rico 00931, USA,

Max-Planck-Institut für Festkörperforschung^c,
Postfach 800665, D-7000 Stuttgart 80, and

Abteilung für Chemie, Universität Bochum^d,
Postfach 102148, D-4630 Bochum

Received September 20, 1982

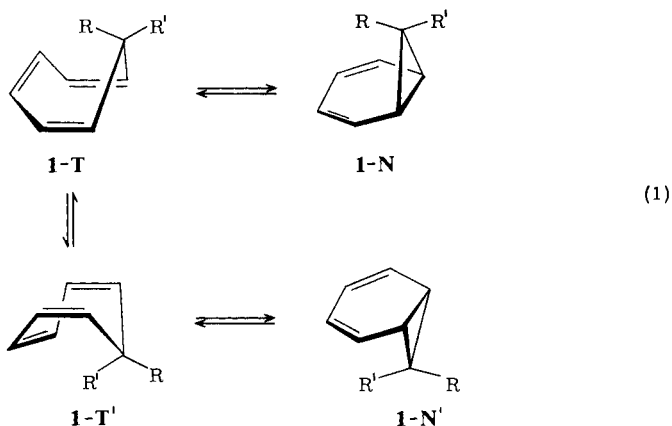
The photosensitized singlet oxygenation of 7,7-dimethyl- (**1a**), 7-(methoxycarbonyl)-7-methyl- (**1b**), 7-methyl-7-phenyl- (**1c**) and 7-[4-(methoxycarbonyl)phenyl]-7-methyl- (**1d**) 1,3,5-cycloheptatrienes has been investigated. While **1b**–**1d** give only the respective norcaradiene endoperoxides **2b-N**–**2d-N**, the dimethyl derivative **1a** affords a 60:40 mixture of tropilidene (**2a-T**) and norcaradiene (**2a-N**) endoperoxides. In addition to full spectral characterization, the norcaradiene endoperoxides **2b-N**–**2d-N** were thermally isomerized to their diepoxides **3b**–**3d**. X-ray analysis confirmed that for **3b** the stereochemistry of the substituents is 7-*endo*-methyl and 7-*exo*-methoxycarbonyl and for **3c** it is 7-*endo*-phenyl and 7-*exo*-methyl, showing that the steric size of the substituents in the cycloheptatrienes is Ph < Me < CO₂Me. While the tropilidene endoperoxide **2a-T** was a stable compound and could be fully characterized, the norcaradiene derivative **2a-N** was too labile and had to be reduced with diimide to the saturated endoperoxide **4a** to enable complete characterization.

It is shown that the cycloaddition of singlet oxygen is a useful method to assess qualitatively the substituent effects on the tropilidene-norcaradiene valence isomerization, especially for those cycloheptatrienes in which the N/T ratio is too low for measurement by dynamic NMR methods. Stabilization of the norcaradiene isomer by 7-methyl substitution is rationalized in terms of steric effects.

Stereochemie und Produktverteilung bei der Cycloaddition von Singulett-Sauerstoff an 7,7-disubstituierte 1,3,5-Cycloheptatriene

Die photosensibilisierte Oxygenierung von 7,7-Dimethyl- (**1a**), 7-(Methoxycarbonyl)-7-methyl- (**1b**), 7-Methyl-7-phenyl- (**1c**) und 7-[4-(Methoxycarbonyl)phenyl]-7-methyl-1,3-cycloheptatrien (**1d**) wurde durchgeführt. Während **1b**–**1d** nur die jeweiligen Norcaradien-endoperoxide **2b-N**–**2d-N** lieferten, führte das Dimethylderivat **1a** zu einem 60:40-Gemisch von Endoperoxiden **2a-T** und **2a-N**. Zusätzlich zu der spektroskopischen Charakterisierung wurden die Norcaradien-endoperoxide **2b-N**–**2d-N** thermisch in ihre Diepoxide **3b**–**3d** isomerisiert. Röntgenstrukturanalyse bestätigte, daß die Substituenten in **3b** 7-*endo*-Methyl und 7-*exo*-Methoxycarbonyl und in **3c** 7-*endo*-Phenyl und 7-*exo*-Methyl angeordnet sind. Die sterische Größe dieser 7-Substituenten

in Cycloheptatrienen ist daher $\text{Ph} < \text{Me} < \text{CO}_2\text{Me}$. Das Tropiliden-endoperoxid **2a-T** ist eine stabile Verbindung und konnte vollständig charakterisiert werden, während das Norcaradien-endoperoxid **2a-N** thermisch zu labil war und mit Diimid in das gesättigte Endoperoxid **4a** umgewandelt werden mußte, um eine vollständige Charakterisierung zu ermöglichen. – Es wird gezeigt, daß die Cycloaddition von Singulett-Sauerstoff eine brauchbare Methode darstellt, Substituenteneffekte in der Tropiliden-Norcaradien-Valenzisomerie qualitativ zu erfassen. Besonders geeignet ist diese Methode für Cycloheptatriene, für die das N/T-Verhältnis zu klein ist, um es mit dynamischen NMR-Methoden zu bestimmen. Die Stabilisierung des Norcaradiens durch 7-Methylsubstitution wird durch sterische Einflüsse erklärt.

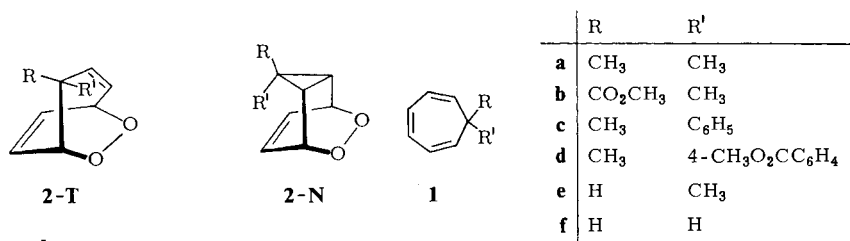


Electronic and steric effects of substituents on the tropilidene-norcaradiene equilibrium [Eq. (1)] have been investigated actively in recent years¹⁾ with the purpose of understanding the mechanistic subtleties of such valence isomerizations. For monosubstitution at the 7-position, the general conclusion obtains that π -electron acceptors, e.g. CN , CO_2R , Ph , etc., displace the equilibrium towards the norcaradiene form **1-N**, while electron donors, e.g. CH_3 , MeO , R_2N , etc., displace the equilibrium towards the tropilidene form **1-T**, relative to the unsubstituted cycloheptatriene²⁾. In fact, spectroscopic evidence for the existence of the norcaradiene isomer **1-N** ($\text{R} = \text{R}' = \text{H}$) in such equilibria is still lacking even at very low temperatures. However, by means of matrix isolation at -196°C , the authentic norcaradiene **1-N** ($\text{R} = \text{R}' = \text{H}$) was prepared via photodecarbonylation of tricyclo[3.2.2.0^{2,4}]non-6-ene-8,9-dione and spectroscopically characterized³⁾. Indeed, on warm-up of the matrix to -163°C , **1-N** isomerized as expected swiftly into the tropilidene **1-T** ($\text{R} = \text{R}' = \text{H}$).

Interestingly, irrespective of the electronic nature of the substituent, disubstitution at the 7-position promotes the norcaradiene isomer. Thus, 7,7-dicyanonorcaradiene is a stable compound at room temperature⁴⁾.

Recently we have shown⁵⁾ that singlet oxygen is sufficiently reactive to intervene in the tropilidene-norcaradiene equilibrium via cycloaddition. Thus, ratios of tropilidene-type (**2-T**) and norcaradiene-type (**2-N**) endoperoxides are obtained which *qualitatively* reflect the distribution of the valence isomer in the substituted cycloheptatrienes that are found by dynamic ^{13}C and ^1H NMR. It was, therefore, of interest to determine the N/T-ratios of the endoperoxides **2** in the singlet oxygenation of the 7,7-disubstituted 1,3,5-cycloheptatrienes **1**. We hoped to acquire useful mechanistic information on sub-

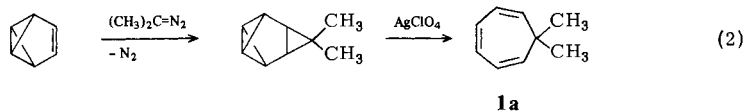
stituent effects in such valence isomerization using this simple chemical probe. Herein we report the results of the singlet oxygenation of the cycloheptatrienes **1a–d**.



Results

Preparation of Cycloheptatrienes

The 7,7-dimethyl-1,3,5-cycloheptatriene (**1a**), previously made by *Hoffmann* and *Frickel*⁶, was prepared in 11% overall yield, starting from the known⁷ 7-(methoxycarbonyl)-7-methyl-1,3,5-cycloheptatriene (**1b**). Since the cycloheptatriene **1b** was needed anyway in this work, we expected this synthetic route to be more efficient and time saving. Unfortunately the overall yields were low and chromatographic separation was necessary to isolate **1a** from α -methylstyrene, a by-product formed in appreciable amounts. Larger quantities of **1a** were then made via the sequence in Eq. (2), developed by *Christl* and *Brunn*⁸.



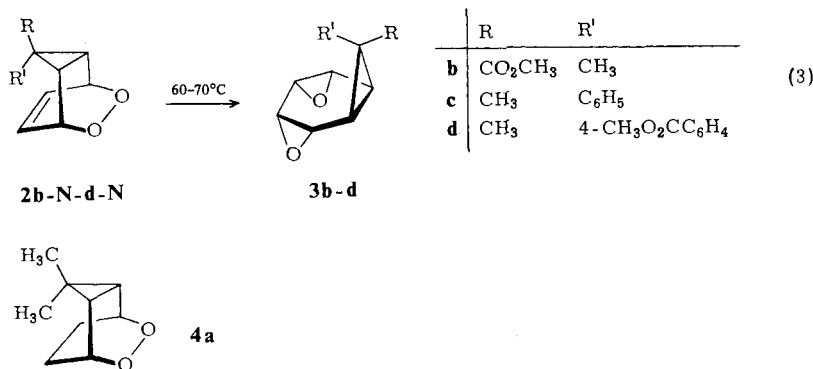
The 7-methyl-7-phenyl-1,3,5-cycloheptatriene (**1c**) was prepared in 78% overall yield starting from the known⁹ 7-phenyl-1,3,5-cycloheptatriene via formation of its carbanion with potassium amide and methylation with methyl iodide.

Quite analogously the cycloheptatriene **1d** was prepared from the 7-(4-carboxyphenyl)-1,3,5-cycloheptatriene by methylation and subsequent esterification with diazomethane in 84% overall yield. Treatment of the known⁹ 7-(4-bromophenyl)-1,3,5-cycloheptatriene with *n*-butyllithium and subsequent carboxylation with carbon dioxide provided the precursor to **1d**.

Singlet Oxygenation of Cycloheptatrienes

The required singlet oxygen was generated in situ via photosensitization by tetraphenylporphine (TPP) in dichloromethane at -20°C ¹⁰. All cycloheptatrienes, except the 7,7-dimethyl derivative **1a**, gave exclusively the norcaradiene-type endoperoxides **2-N**. These relatively stable endoperoxides were isolated and purified in good yields and characterized on the basis of correct elemental composition by combustion analysis and spectral data. Particularly definitive were the olefinic protons at $\delta = 5.6 - 6.6$ in the ¹H NMR and the cyclopropyl carbons at $\delta = 18 - 23$ and $24 - 29$ in the ¹³C NMR.

The stereochemistry of the substituents at the 7-position in the **2-N** endoperoxides was rigorously established by their thermal isomerization (ca. $60 - 70^\circ\text{C}$) into the corresponding diepoxides **3b–d** in high yield [Eq. (3)].



X-ray structure determinations of these diepoxides confirmed that in the case of **3b** the 7-methyl group is located *endo* (Figure 1) and in the case of **3c** it is located *exo* (Figure 2). By spectral comparison with **3c**, the stereochemistry of the 7-methyl group in diepoxide **3d** and thus in the endoperoxide **2d-N** is also *exo*. A full characterization of these diepoxides rests on satisfactory elemental composition by combustion analysis and spectral data.

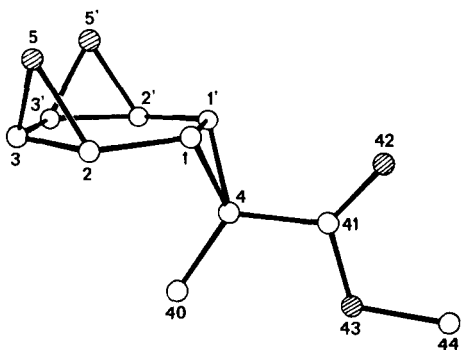


Fig. 1

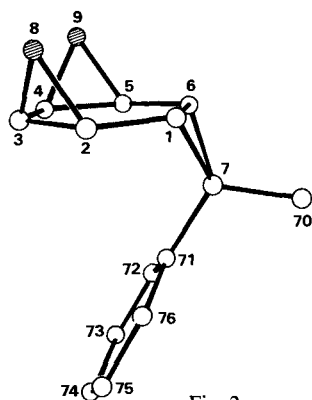


Fig. 2

Figure 1. Perspective drawing of diepoxide **3b**. The labeling corresponds to that of Tables 2 and 3. White and hatched circles represent carbon and oxygen atoms, respectively

Figure 2. Perspective drawing of diepoxide **3c**. The labeling corresponds to that of Tables 4 and 5. White and hatched circles represent carbon and oxygen atoms, respectively

More problematic and, therefore, also more interesting was the singlet oxygenation of cycloheptatriene **1a**. First of all, both the **2a-T** and the **2a-N** endoperoxides were formed in a ratio of 60:40 (determined by ¹H NMR of the crude product mixture). The **2a-T** endoperoxide could be isolated by column chromatography on silica gel at -25°C (dichloromethane as eluant) and fully characterized by means of elemental composition by exact mass count (high resolution mass spectrometry) and spectral data. However, unexpectedly considerable difficulty was encountered in isolating the **2a-N** endoperoxide. Silica gel chromatography even at low temperature (ca. -30°C)

led to deterioration of this endoperoxide. Similarly, thermal isomerization into the diepoxide **3a** and attempted purification by subambient silica gel chromatography proved unsuccessful. Finally, diimide reduction of **2a-N** to the stable saturated bicyclic peroxide **4a** and its isolation by silica gel chromatography and sublimation, permitted full characterization on the basis of elemental composition analysis and spectral data.

Discussion

The fact that the cycloheptatrienes **1b-d** gave exclusively the norcaradiene endoperoxides **2-N** clearly manifests the limitations of singlet oxygen as chemical diagnostic tool in elucidating the mechanistic details of the **1-T** \rightleftharpoons **1-N** valence isomerization. However, except for cycloheptatriene **1b**⁷⁾, also dynamic NMR techniques are equally limited for these cycloheptatrienes since within the experimental error only the tropilidene isomer **1-T** can be observed in the ¹H NMR spectra. Therefore, although the amounts of norcaradiene isomers **1-N** are too small for ¹H NMR detection, it is high enough to give exclusively the **2-N** endoperoxides with singlet oxygen. It is expected that the reactivity of the planar diene moiety in the norcaradiene isomer **1-N** is considerably greater than for the twisted tropilidene isomer **1-T**. Considering Eq. (4),

$$[2-N]/[2-T] = k_N[1-N]/k_T[1-T] \quad (4)$$

the relative amounts of endoperoxides **2-N** and **2-T** that are produced are given by the relative rates of singlet oxygen cycloaddition with the norcaradiene and tropilidene isomers, respectively $k_N[1-N]$ and $k_T[1-T]$, where k_N and k_T are the respective rate constants. Conservatively speaking, even if **1-N** were only 100-fold more reactive than its **1-T** isomer, on the basis of Eq. (4) we see that at equal concentrations of **1-T** and **1-N** a **2-N/2-T** ratio of ca. 100 would result. By conventional quantitative NMR techniques detection of the **2-T** product in that endoperoxide mixture would be difficult. On the other hand, if the upper limit of the **1-N/1-T** ratio were ca. 0.01, the **1-N** valence isomer would also go undetected in the error limits of dynamic NMR methods. Thus, the singlet oxygen cycloaddition and the dynamic NMR method complement each other in studying the T \rightleftharpoons N valence isomerization. Consequently, dynamic NMR techniques are applicable at high N/T ratios of cycloheptatrienes **1**, while singlet oxygen cycloaddition is for low N/T ratios.

Such an optimal case for singlet oxygen cycloaddition is presumably the 7,7-dimethyl-1,3,5-cycloheptatriene (**1a**). The N/T ratio of endoperoxides is 40:60, as determined by quantitative ¹H NMR. However, via dynamic NMR methods not even traces of the norcaradiene isomer **1a-N** can be detected down to -120°C . Thus, the complementary nature of these two methods is brought out very nicely in this case. According to Eq. (4), on one hand an upper limit of ca. ≤ 0.01 is placed on the **1-N/1-T** ratio for the dimethyl derivative **1a**, or on the other hand a lower limit in the relative rates of **1a-N** versus **1a-T** of ca. ≥ 100 .

Unfortunately, the singlet oxygen method in its present form is only a qualitative tool for studying such valence isomerizations because it is difficult to measure the absolute rates of singlet oxygen with the individual valence isomers **1-N** and **1-T**. Possibly competition experiments are feasible to determine such relative rates. Once such rate data

becomes available, singlet oxygen cycloaddition would constitute a powerful and convenient tool in studying tropilidene-norcaradiene valence isomerizations with low 1-N/1-T ratios.

As to the effect of 7,7-dimethyl substitution on the 1-T \rightleftharpoons 1-N isomerization, it is instructive to compare the N/T ratios of endoperoxides **2** of the dimethyl derivative **1a** with that for 7-methyl-1,3,5-cycloheptatriene (**1e**) and unsubstituted cycloheptatriene (**1f**). The N/T ratios of endoperoxides **2** are 40:60, 27:73 and ca. 5:95, respectively, for **1a**, **1e**¹²⁾, and **1f**⁵⁾. Clearly, with increasing methyl substitution the N/T ratio increases. While the stabilizing influence of the methyl substituent on the T \rightleftharpoons N isomerization is not well understood in terms of electronic factors²⁾, we believe that it is dominated by steric as well as hybridizational effects¹¹⁾. Thus, for the monomethyl derivative **1e** we have argued¹²⁾ that in the preferred *exo*-stereochemistry, nonbonded interaction between the methyl group and the adjacent 1,6-hydrogens is more serious for the tropilidene than for the norcaradiene isomer, respectively **1a-T** and **1a-N**. However, for the dimethyl derivative **1a**, besides this destabilization also unfavorable nonbonded interactions between the *endo*-methyl group and the C-3 – C-4 double bond must come into play¹⁴⁾. Consequently, steric energy is minimized by channeling the valence isomerization towards the norcaradiene form **1a-N**. Furthermore, the strain effect of *gem*-dimethyl substitution would be less in the norcaradiene form **1a-N** relative to the tropilidene form **1a-T** in view of a geminal bond angle of ca. 120° in cyclopropanes.

The steric effect of an *endo*-substituent with the C-3 – C-4 double bond of the tropilidene form is nicely brought out for the cycloheptatrienes **1b** and **1c**. As the crystal structures (Figures 1 and 2) for the respective diepoxides **3b** and **3c** show, the steric size must be Ph < Me < CO₂Me. Thus, in the cycloheptatrienes **1b** and **1c**, the preferred stereochemistry of the 7-substituents must be *endo*-methyl in **1b**, but *exo*-methyl in **1c**, confirming that the relative order of steric effects is Ph < Me < CO₂Me.

In conclusion, although the results of the singlet oxygen cycloaddition are necessarily qualitative in nature, this method reflects very nicely the trends caused by substituents on the T \rightleftharpoons N valence isomerization. Particularly valuable is this tool for those cycloheptatrienes for which the N/T ratio is too low for elucidation by dynamic NMR techniques.

Acknowledgements are made to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous financial assistance. H. Rebollo thanks the *Thyssen-Stiftung* for a travel grant. We thank Professor G. Maier and his staff (University of Gießen) for their swift and reliable service on elemental analyses. Gift samples of 7,7-dimethyl-1,3,5-cycloheptatriene (**1a**) from Professor M. Christl and Dipl.-Chem. E. Brunn are gratefully appreciated. We thank Dr. D. Scheutzwow for his assistance in the NMR work.

Experimental Part

Boiling and melting points are uncorrected. – Infrared spectra: Beckman Acculab 4 or Perkin-Elmer 157G spectrophotometer. – ¹H NMR spectra: 90 MHz Varian EM 390. – ¹³C NMR spectra: Bruker 100.61 MHz spectrometer. – Elemental analyses: All new compounds were kindly run for us by Prof. Dr. G. Maier's staff at the University of Gießen. – Commercial

reagents and solvents were purified according to literature procedures until reported constants or spectral data matched. Known compounds used in this study were either prepared according to known literature procedures or purchased from standard suppliers and purified to match the reported physical and spectral data.

7,7-Dimethyl-1,3,5-cycloheptatriene (1a): 7-(Hydroxymethyl)-7-methyl-1,3,5-cycloheptatriene was obtained in 94% yield (11.7 g, 86 mmol), b.p. 50°C/0.05 torr, by addition of a solution of 15.0 g (91.5 mmol) of 7-(methoxycarbonyl)-7-methyl-1,3,5-cycloheptatriene⁷⁾ in 100 ml of ether to a stirred suspension of 2.0 g (52.6 mmol) of lithium aluminium hydride in 80 ml of ether within 2 h at 0°C. The excess lithium aluminium hydride was hydrolyzed with ice water, the formed aluminium hydroxide precipitate dissolved with dilute hydrochloric acid, and the carbinol isolated on usual work-up of the ethereal solution. – IR (CCl₄): 3370 cm⁻¹. – ¹H NMR (CCl₄) at 60 MHz: δ = 1.0 (s, 3H, CH₃), 3.0 (s, 1H, OH), 3.3 (s, 2H, CH₂), 5.15 (d, *J*_{1,2} = *J*_{5,6} = 9.5 Hz, 2H, 1-, 6-H), 5.97–6.62 (m, 4H, 2-, 3-, 4-, 5-H).

The above carbinol (34.7 g, 0.26 mol) was converted into **1a** in 20% yield (6.2 g, 0.52 mol), b.p. 70–75°C/15 torr (molecular distillation), by addition of 38.0 g (0.38 mol) of triethylamine and 32.4 g (0.28 mol) of methanesulfonyl chloride in 300 ml of absolute tetrahydrofuran at –25°C within 10 min. After 15 min stirring, the precipitated triethylammonium chloride was removed by filtration in the cold and the filtrate without further purification added while stirring to a suspension of 5.4 g (0.15 mol) of lithium aluminium hydride in 140 ml of tetrahydrofuran. The reaction mixture was warmed for 30 min to 65°C and after cooling worked up as above, resulting in a 65:35 mixture of **1a** and α-methylstyrene. The pure **1a**, matching the reported spectral data⁶⁾, was obtained by preparative gas chromatography on a 4-m column packed with 3% SE-30 on Varaport® at a column temperature of 55°C and helium as carrier gas. – IR (CCl₄): 3010, 2960 cm⁻¹. – UV (cyclohexane): λ_{max} = 267 (ε = 2500), 203 nm (10 800). – ¹H NMR (CCl₄) at 60 MHz: δ = 1.0 (s, 6H, CH₃), 5.1 (d, *J*_{1,2} = *J*_{5,6} = 9.5 Hz, 2H, 1-, 6-H), 5.9–6.6 (m, 4H, 2-, 3-, 4-, 5-H).

7-Methyl-7-phenyl-1,3,5-cycloheptatriene (1c) was obtained in 78% yield (5.1 g, 30.0 mmol), b.p. 58°C/0.003 torr, by addition of 6.0 g (36.0 mmol) of 7-phenyl-1,3,5-cycloheptatriene⁹⁾ in 50 ml of absolute ether to a solution of potassium amide in 500 ml of dry liquid ammonia obtained from 14 g (0.37 mol) of potassium and a few crystals of iron(III) chloride as catalyst, while stirring at –78°C under an argon atmosphere. After reflux at –33°C while stirring for 15 min, 52 g (0.37 mol) of methyl iodide was added, stirred for additional 30 min, 150 ml of ether was added and the ammonia allowed to evaporate. Neutralization with 100 ml of concentrated ammonium chloride solution, separation of the ethereal layer, washing twice with water and drying over anhydrous magnesium sulfate, the pure **1c** was isolated on distillation and subsequent preparative gas chromatography on a 1-m x 1/4 in. (ID) column packed with 10% Silicon DC710 on Chromosorp PA/W DMCS (60/80 mesh), operated at a column temperature of 150°C and helium as carrier gas. – IR (CCl₄): 3050, 3010, 2950, 2920, 2860, 1597 cm⁻¹. – UV (*n*-hexane): λ_{max} = 264 (ε = 3000), 258 (3140), 254 nm (3080). – ¹H NMR (CCl₄) at 60 MHz: δ = 1.48 (s, 3H, CH₃), 5.29 (br. d, *J*_{1,2} = *J*_{5,6} = 9.5 Hz, 2H, 1-, 6-H), 6.0–6.3 (m, 4H, 2-, 3-, 4-, 5-H), 6.85–7.35 (m, 5H, C₆H₅). – MS (70 eV): *m/e* = 182 (M[⊕]), 167 (100%, M[⊕] – CH₃), 77 (C₆H₅[⊕]).

7-[4-(Methoxycarbonyl)phenyl]-7-methyl-1,3,5-cycloheptatriene (1d): 7-(4-Carboxyphenyl)-1,3,5-cycloheptatriene was obtained in 43% yield (2.8 g, 13 mmol), m.p. 142°C, by adding to a solution of 7.5 g (30.5 mmol) 7-(4-bromophenyl)-1,3,5-cycloheptatriene⁹⁾ in 100 ml absolute ether a 15% solution of 16 ml (31 mmol) of *n*-butyllithium in hexane diluted with 35 ml of absolute ether while stirring at –20°C under an argon atmosphere. After warm-up to 0°C and stirring for an additional 15 min, 10 g of solid dry ice (should be as dry as possible) are added to the yellow

reaction mixture. To the white suspension of the carboxylate salt are added 150 ml of water for dissolution, extracted twice with ether, and acidified with concentrated sodium bisulfate in the cold (ice bath). The crude acid is taken up in ether, dried over anhydrous magnesium sulfate and the ether removed by roto-evaporation, resulting in the crystalline acid ready for use without further purification.

The above acid (6.4 g, 30 mmol) is converted into 7-(4-carboxyphenyl)-7-methyl-1,3,5-cycloheptatriene in 83% yield (5.6 g, 24.8 mmol), m. p. 185 – 188 °C with decomposition (from ether), by treatment first with potassium amide (prepared from 14 g (37 mmol) of potassium) and subsequently with 52 g (37 mmol) of methyl iodide in 500 ml of liquid ammonia, following the procedure described above for **1c**. – IR (KBr): 3300 – 2400, 1690, 1675, 1660, 1605, 1572 cm⁻¹. – ¹H NMR ([D₆]acetone) at 60 MHz: δ = 1.55 (s, 3H, CH₃), 5.54 (d, $J_{1,2} = J_{5,6} = 9.5$ Hz, 2H, 1-, 6-H), 6.20 – 6.45 (m, 4H, 2-, 3-, 4-, 5-H), 7.45 (m, 4H, C₆H₄). – MS (70 eV): $m/e = 226$ (M[⊕]), 225 (M[⊕] – 1), 211 (M[⊕] – CH₃), 181 (100%, M[⊕] – CO₂H).

The cycloheptatriene **1d** is obtained in 84% yield (0.53 g, 2.2 mmol), m. p. 58 °C (from *n*-pentane), by esterification of 0.6 g (2.6 mmol) of the above 7-(4-carboxyphenyl)-7-methyl-1,3,5-cycloheptatriene in 20 ml of ether with excess diazomethane at room temperature. – IR (CCl₄): 3015, 2980, 2975, 2920, 1735, 1720, 1607, 1275, 1100, 1010 cm⁻¹. – UV (*n*-hexane): λ_{max} = 283 (ε = 3020), 274 (4030), 236 (18300), 195 nm (62200). – ¹H NMR (CCl₄) at 60 MHz: δ = 1.52 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 5.45 (d, $J_{1,2} = J_{5,6} = 9.5$ Hz, 2H, 1-, 6-H), 6.10 – 6.40 (m, 4H, 2-, 3-, 4-, 5-H), 7.43 (m, 4H, C₆H₄). – MS (70 eV): $m/e = 240$ (M[⊕]), 225 (100%, M[⊕] – CH₃), 181 (M[⊕] – CO₂CH₃).

General procedure for the singlet oxygenation: A 15-ml sample of a ca. 0.1 M solution of cycloheptatriene **1** in dichloromethane, containing ca. 5 mg of tetraphenylporphine (TPP) as sensitizer, was irradiated by means of a General Electric 150 W sodium street lamp at –20 °C while continuously passing a vivid stream of dry oxygen gas. The progress of the reaction was monitored by ¹H NMR and/or TLC (KI/AcOH test) on silica gel, CH₂Cl₂/hexane (2:1) as eluant. After completion of the photooxygenation (ca. 3 h), the solvent was roto-evaporated (ca. 20 °C/15 torr) and the crude endoperoxides **2** chromatographed on silica gel (20:1 ratio of SiO₂ versus substrate), eluting with CH₂Cl₂/hexane (2:1). By means of TLC, endoperoxide fractions were detected using the potassium iodide in acetic acid test. Final purification to obtain analytical samples was achieved by repeated recrystallizations.

4,4-Dimethyl-6,7-dioxabicyclo[3.2.2]nona-2,8-diene (**2a-T**) was obtained from 250 mg (2.08 mmol) of **1a** in 50% yield (110 mg; 0.73 mmol), b. p. 130 °C/0.1 torr. – IR (CCl₄): 3040, 3015, 2980, 2955, 2940, 1475, 1400, 1385, 1370, 1015, 1005, 980, 875 cm⁻¹. – ¹H NMR (CDCl₃) at 90 MHz: δ = 0.85 (s, 3H), 1.20 (s, 3H), 4.15 (d, 1H), 4.40 (t, 1H), 5.25 (d, 1H), 5.80 (dd, 1H), 6.20 (t, 1H), 6.65 (t, 1H); $J_{1,8} = 7.5$, $J_{8,9} = 9.0$, $J_{5,9} = 7.5$, $J_{1,2} = 7.5$, $J_{2,3} = 10.5$ Hz. – ¹³C NMR (CDCl₃) at 100.61 MHz: δ = 23.03 (q), 27.42 (q), 43.01 (s), 72.67 (d), 84.11 (d), 125.27 (d), 126.34 (d), 141.74 (d).

C₉H₁₂O₂ Calc. 152.0837 Found 152.0839 (MS)

3,3-Dimethyl-6,7-dioxatricyclo[3.2.2.0^{2,4}]non-8-ene (**2a-N**) could not be isolated because it decomposed on attempted silica gel column chromatography even at low (ca. –30 °C) temperature. By quantitative ¹H NMR (CDCl₃) it could be estimated that ca. 40% of this norcaradiene endoperoxide **2a-N** was present in the photooxygenation product mixture. – ¹H NMR (CDCl₃) at 90 MHz: δ = 1.0 (s, 3H), 1.17 (s, 3H), 1.37 (m, 2H), 4.95 (m, 2H), 6.40 (m, 2H).

exo-3-(Methoxycarbonyl)-endo-3-methyl-6,7-dioxatricyclo[3.2.2.0^{2,4}]non-8-ene (**2b-N**) was obtained from 500 mg (3.0 mmol) of **1b** in 64% yield (390 mg; 1.48 mmol), m. p. 97 – 98 °C (from dichloromethane/hexane). – IR (CCl₄): 3075, 2995, 2980, 1725, 1440, 1380, 1300, 1260, 1230,

1140, 1120, 950, 885, 875 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.35$ (s, 3H), 2.25 (t', 2H), 3.65 (s, 3H), 5.0 (m, 2H), 6.4 (t', 2H); $J_{1,8} = 3.90$, $J_{1,2} = 2.25$ Hz. – $^{13}\text{C NMR}$ (CDCl_3) at 100.61 MHz: $\delta = 12.10$ (q), 22.72 (d), 24.63 (s), 52.56 (q), 72.66 (d), 130.97 (d), 174.62 (s).

$\text{C}_{10}\text{H}_{12}\text{O}_4$ (196.3) Calc. C 61.22 H 6.56 Found C 60.98 H 6.53

exo-3-Methyl-endo-3-phenyl-6,7-dioxatricyclo[3.2.2.0^{2,4}]non-8-ene (**2c-N**) was obtained from 200 mg (1.09 mmol) of **1c** in 90% yield (211.5 mg; 0.99 mmol), m.p. 147–149 °C (from dichloromethane/hexane). – IR (CHCl_3): 3050, 3020, 3005, 2980, 2960, 1600, 1500, 1450, 1380, 1295, 1260, 1090, 1020, 940, 860 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.25$ (s, 3H), 1.90 (t', 2H), 5.00 (m, 2H), 5.60 (t', 2H), 6.90–7.35 (m, 5H); $J_{1,2} = 2.7$, $J_{1,8} = 4.0$ Hz. – $^{13}\text{C NMR}$ (CDCl_3) at 100.61 MHz: $\delta = 21.66$ (d), 29.76 (s), 30.57 (q), 73.15 (d), 125.79 (d), 128.21 (d), 128.58 (d), 129.65 (s), 142.41 (d).

$\text{C}_{14}\text{H}_{14}\text{O}_2$ (214.3) Calc. C 78.48 H 6.59 Found C 78.17 H 6.47

endo-3-[4-(Methoxycarbonyl)phenyl]-exo-3-methyl-6,7-dioxatricyclo[3.2.2.0^{2,4}]non-8-ene (**2d-N**) was obtained from 200 mg (0.83 mmol) of **1d** in 54% yield (123 mg, 0.45 mmol), m.p. 135–136 °C (from dichloromethane/hexane). – IR (CCl_4): 3050, 2990, 1720, 1610, 1430, 1380, 1260, 1110, 1020, 900 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.40$ (s, 3H), 2.00 (t', 2H), 4.90 (s, 3H), 5.15 (m, 2H), 6.55 (t', 2H), 7.34 and 8.05 (AB, 4H); $J_{1,2} = 2.70$, $J_{1,8} = 4.35$, $J_{\text{AB}} = 9.0$. – $^{13}\text{C NMR}$ (CDCl_3) at 100.61 MHz: $\delta = 18.50$ (d), 20.77 (q), 28.42 (s), 51.97 (d), 73.40 (q), 128.12 (d), 128.20, 130.22 (d), 130.90 (d), 154.27 (s), 166.79.

$\text{C}_{16}\text{H}_{16}\text{O}_4$ (272.3) Calc. C 70.58 H 5.92 Found C 70.43 H 5.83

General procedure for the thermal endoperoxide-diepoxide rearrangement: A 0.4 mmol sample of the endoperoxide **2** in 20 ml of CCl_4 was heated at 60 °C until complete consumption of the endoperoxide, monitoring the reaction progress by TLC on silica gel and spotting for active peroxide with potassium iodide in acetic acid. After roto-evaporation of the solvent (ca. 20 °C/15 torr), the quite clean (by $^1\text{H NMR}$) crude product was purified by recrystallization.

anti,anti-9-(Methoxycarbonyl)-9-methyl-3,6-dioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (**3b**) was obtained from 100 mg (0.51 mol) of endoperoxide **2b-N** in 98% yield (98 mg; 0.50 mol), m.p. 96–97 °C (from ether/pentane). – IR (CCl_4): 3000, 2950, 1730, 1460, 1445, 1300, 1250, 1140 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.40$ (s, 3H), 2.10 (s, 2H), 3.20 (br.s, 2H), 3.40 (br.s, 2H), 3.70 (s, 3H). – $^{13}\text{C NMR}$ (CDCl_3) at 100.61 MHz: $\delta = 10.39$ (q), 23.25 (d), 26.98 (s), 46.54 (d), 47.94 (d), 52.44 (q), 173.92 (s).

$\text{C}_{10}\text{H}_{12}\text{O}_4$ (196.3) Calc. C 61.22 H 6.56 Found C 61.40 H 6.29

anti,anti-9-Methyl-9-phenyl-3,6-dioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (**3c**) was obtained from 100 mg (0.47 mmol) of endoperoxide **2c-N** in 95% yield (95 mg; 0.44 mmol), m.p. 208–209 °C (from dichloromethane/hexane). – IR (CCl_4): 3040, 2980, 1460, 1430, 1270, 1220, 955, 940, 860, 710, 675 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.45$ (s, 3H), 1.60 (br.s, 2H), 2.80 (narrow m, 2H), 3.30 (narrow m, 2H), 7.30 (br.s, 5H). – $^{13}\text{C NMR}$ (CDCl_3) at 100.61 MHz: $\delta = 23.51$ (d), 30.21 (q), 48.22 (d), 49.27 (d), 126.88 (d), 128.58 (d), 129.94 (d), 140.53 (s).

$\text{C}_{14}\text{H}_{14}\text{O}_2$ (214.3) Calc. C 78.48 H 6.59 Found C 77.72 H 7.28

anti,anti-9-[4-(Methoxycarbonyl)phenyl]-9-methyl-3,6-dioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (**3d**) was obtained from 100 mg (0.37 mmol) of endoperoxide **2d-N** in 93% yield (93 mg; 0.34 mmol), m.p. 164–166 °C (from dichloromethane/hexane). – IR (CCl_4): 3040, 3000, 2980, 1725, 1615, 1450, 1410, 1305, 1275, 1195, 1180, 1125, 1025, 950, 935, 860 cm^{-1} . – $^1\text{H NMR}$ (CDCl_3) at 90 MHz: $\delta = 1.40$ (s, 3H), 1.60 (br.s, 2H), 2.70 (narrow m, 2H), 3.25 (narrow m, 2H), 3.85 (s,

3 H), 7.34–8.05 (AB pattern, $J = 9.0$ Hz, 4 H). – ^{13}C NMR (CDCl_3) at 100.61 MHz: $\delta = 23.60$ (d), 29.76 (q), 32.03 (s), 48.07 (d), 48.92 (d), 52.05 (q), 129.12 (d), 130.03 (d), 145.79 (s), 166.67 (s).

$\text{C}_{16}\text{H}_{16}\text{O}_4$ (272.3) Calc. C 70.58 H 5.92 Found C 70.38 H 6.14

3,3-Dimethyl-6,7-dioxatricyclo[3.2.2.0^{2,4}]nonane (4a): A 100-ml, three-necked, round-bottomed flask, provided with a magnetic stirrer, 20-ml pressure-equalizing addition funnel, was charged with 9.7 g (25 mmol) of potassium azodicarboxylate (5–30 molar excess based on the endoperoxide) in 40 ml of dry dichloromethane. The slurry was cooled to 0°C and a solution of 200 mg (1.3 mmol) of the **2a-T**, **2a-N** in 10 ml of dry dichloromethane was added. While cooling and stirring magnetically, a solution of 50 mmol of acetic acid in 10 ml of dichloromethane was added dropwise within ca. 45 min and stirred until disappearance of the yellow azodicarboxylate color. Subsequently 15 ml of distilled water were added slowly and the organic layer was washed with 2×10 ml of saturated aqueous sodium bicarbonate. After drying over anhydrous magnesium sulfate, the solvent was roto-evaporated (ca. 0°C/15 torr) and the residue purified by column chromatography on silica gel at 0°C, eluting with a 10:1 dichloromethane/ether mixture. Final purification was achieved by preparative layer chromatography on silica gel at 0°C, eluting with dichloromethane. The saturated endoperoxide **4a** eluted as second fraction after **2a-T** and several recrystallizations from dichloromethane/hexane afforded the colorless needles, m.p. 79–80°C, in 25% yield (38 mg, 0.25 mmol). – IR (CCl_4): 3000, 2965, 2945, 1455, 1350, 1300, 1015, 1000, 905 cm^{-1} . – ^1H NMR (CDCl_3) at 90 MHz: $\delta = 1.05$ (s, 3 H), 1.40 (s, 3 H), 1.70–2.25 (m, 6 H), 4.48 (m, 2 H). – ^{13}C NMR (CDCl_3) at 100.61 MHz: $\delta = 16.05$ (q), 18.90 (s), 23.45 (t), 26.57 (d), 31.67 (q), 73.71 (d).

$\text{C}_9\text{H}_{14}\text{O}_2$ (154.2) Calc. C 70.10 H 9.15 Found C 70.19 H 9.18

X-ray crystallography of diepoxides **3b** and **3c***)

Clear colorless crystals were optically centered on a Syntex-P3 four circle diffractometer. The intensities of all reflections were measured according to the ω technique (Mo- K_α graphite monochromator), using a scan range of 1° and a scan speed between 0.5 and 29.3 deg min^{-1} as a function of the intensities of the reflections. In the range between $3.0^\circ \leq 2\Theta \leq 55.0^\circ$ all

Table 1. X-ray operations and results of diepoxides **3b** and **3c**

	$\text{C}_{10}\text{H}_{12}\text{O}_4$ (3b)	$\text{C}_{14}\text{H}_{14}\text{O}_2$ (3c)
crystal size, mm	0.8 × 0.15 × 0.15	0.5 × 0.4 × 0.3
no. of measd intensities	1087	1238
no. of obsd reflections	907	1055
no. of struct factors of direct phase determination	190	143
R_{aniso}	0.072	0.053
space group	<i>Pnma</i>	<i>P2₁2₁2₁</i>
<i>a</i> , pm	1766.4 (9)	772.7 (8)
<i>b</i> , pm	779.3 (4)	1857 (1)
<i>c</i> , pm	703.4 (3)	769.0 (9)
no. of formula units/cell	4	4
calcd density, $\text{g} \cdot \text{cm}^{-3}$	1.346	1.291

*) Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 50272, author, and source.

reflections hkl with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL system on an Eclipse S250 was employed. All structures were solved by the direct phase determination. The parameters of the complete structures could be refined by anisotropic least-squares cycles to the given R -values. The positions of the hydrogen atoms were calculated

Table 2. Positional and thermal parameters of the atoms of diepoxide **3b** in \AA^2 . The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots 2U_{12}hka^*b^* \dots)]$ (the standard deviations are given in parentheses)

Atom	lage	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	8(d)	0.6420(2)	0.6540(5)	0.1031(5)	0.032(2)	0.050(2)	0.036(2)	0.006(2)	-0.003(1)	0.007(2)
C(2)	8(d)	0.6662(2)	0.5599(5)	-0.0720(5)	0.037(2)	0.055(2)	0.049(2)	-0.003(2)	0.006(2)	0.005(2)
C(3)	8(d)	0.6937(2)	0.6520(5)	-0.2372(5)	0.039(2)	0.082(3)	0.034(2)	-0.006(2)	-0.001(1)	0.009(2)
C(4)	4(c)	0.5669(3)	3/4	0.1024(6)	0.028(2)	0.046(3)	0.029(2)	0	-0.002(2)	0
O(5)	8(d)	0.7464(1)	0.5686(4)	-0.1127(4)	0.041(1)	0.087(2)	0.056(2)	-0.002(2)	0.004(1)	0.022(2)
C(40)	4(c)	0.5165(3)	3/4	-0.0716(7)	0.032(2)	0.064(3)	0.030(2)	0	-0.004(2)	0
C(41)	4(c)	0.5297(3)	3/4	0.2917(7)	0.035(3)	0.056(3)	0.033(3)	0	-0.001(2)	0
O(42)	4(c)	0.5624(2)	3/4	0.4416(5)	0.048(2)	0.145(5)	0.028(2)	0	-0.001(2)	0
O(43)	4(c)	0.4542(2)	3/4	0.2800(5)	0.032(2)	0.074(3)	0.035(2)	0	0.007(2)	0
C(44)	4(c)	0.4130(3)	3/4	0.4587(8)	0.051(3)	0.108(7)	0.042(3)	0	0.018(3)	0

Table 3. Bond lengths (pm) and angles (deg) for diepoxide **3b** (the standard deviations are given in parentheses)

Bond Lengths (pm)			
C(1) - C(1')	149.6(7)	C(2) - C(3)	145.0(5)
C(1) - C(2)	149.5(5)	C(2) - O(5)	144.6(4)
C(1) - C(4)	152.4(5)	C(3) - C(3')	152.7(8)
C(4) - C(40)	151.4(6)	C(4) - C(41)	148.5(6)
C(41) - O(42)	120.2(6)	C(41) - O(43)	133.5(6)
C(43) - C(44)	145.3(7)		
Angles (°)			
C(1') - C(1) - C(2)	119.4(2)	C(2) - C(3) - C(3')	119.7(2)
C(1') - C(1) - C(4)	60.6(2)	C(2) - C(3) - O(5)	60.2(2)
C(2) - C(1) - C(4)	119.2(3)	C(3') - C(3) - O(5)	117.0(2)
C(1) - C(2) - C(3)	120.9(3)	C(1) - C(4) - C(1')	58.8(3)
C(1) - C(2) - O(5)	114.8(3)	C(1) - C(4) - C(40)	121.0(3)
C(3) - C(2) - O(5)	59.4(2)	C(1) - C(4) - C(41)	112.5(3)
C(1') - C(4) - C(40)	125.0(3)		
C(1') - C(4) - C(41)	112.5(3)		
C(40) - C(4) - C(41)	117.7(3)		
C(4) - C(41) - O(42)	125.0(4)		
C(4) - C(41) - O(43)	112.7(4)		
O(42) - C(41) - O(43)	122.3(4)		
C(41) - O(43) - C(44)	116.6(4)		

Table 4. Positional and thermal parameters of the atoms of diepoxide **3c** in \AA^2 . The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots 2U_{12}hka^*b^* \dots)]$ (the standard deviations are given in parentheses)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.3899(5)	0.5947(2)	-0.0785(6)	0.037(2)	0.040(3)	0.051(2)	0.004(2)	-0.003(2)	0.002(2)
C(2)	0.2790(5)	0.6025(2)	0.0794(6)	0.047(2)	0.042(3)	0.061(3)	0.009(2)	0.002(2)	-0.004(2)
C(3)	0.3085(6)	0.5575(3)	0.2313(6)	0.054(3)	0.063(3)	0.047(2)	0.003(2)	0.004(2)	-0.007(2)
C(4)	0.4579(6)	0.5043(3)	0.2334(6)	0.062(3)	0.051(3)	0.052(3)	0.010(2)	-0.002(3)	-0.007(2)
C(5)	0.5702(5)	0.4980(2)	0.0853(6)	0.047(2)	0.035(3)	0.070(3)	0.004(2)	-0.001(3)	-0.002(2)
C(6)	0.5397(5)	0.5415(2)	-0.0750(6)	0.046(2)	0.031(3)	0.059(2)	-0.005(2)	0.003(2)	0.001(2)
C(7)	0.5755(5)	0.6222(2)	-0.0786(6)	0.040(2)	0.038(3)	0.046(2)	0.003(2)	0.006(2)	0.001(2)
O(8)	0.1688(4)	0.5416(2)	0.1183(4)	0.044(2)	0.065(2)	0.068(2)	0.008(2)	0.004(2)	-0.009(2)
O(9)	0.4426(4)	0.4435(2)	0.1229(5)	0.068(2)	0.034(2)	0.085(2)	0.012(2)	0.002(2)	-0.006(2)
C(70)	0.6429(6)	0.6518(3)	-0.2483(6)	0.060(3)	0.050(3)	0.049(2)	0.004(2)	0.011(2)	-0.003(2)
C(71)	0.6432(5)	0.6600(2)	0.0794(6)	0.043(2)	0.033(2)	0.049(2)	0.005(2)	0.005(2)	-0.003(2)
C(72)	0.7904(5)	0.6373(2)	0.1645(6)	0.047(2)	0.035(3)	0.062(3)	0.005(2)	-0.003(2)	0.002(2)
C(73)	0.8547(6)	0.6741(3)	0.3068(6)	0.058(3)	0.057(3)	0.061(3)	0.009(2)	-0.012(3)	-0.008(3)
C(74)	0.7749(7)	0.7367(3)	0.3600(6)	0.070(3)	0.058(3)	0.056(3)	-0.002(3)	0.002(3)	-0.017(3)
C(75)	0.6308(7)	0.7621(3)	0.2727(6)	0.068(3)	0.046(3)	0.065(3)	-0.009(2)	0.012(3)	-0.004(3)
C(76)	0.5660(6)	0.7243(2)	0.1330(6)	0.052(2)	0.037(3)	0.051(3)	0.002(2)	0.003(2)	0.002(2)

Table 5. Bond lengths (pm) and angles (deg) for diepoxide **3c** (the standard deviations are given in parentheses)

Bond lengths (pm)							
C(1) - C(2)	149.3(6)	C(3) - C(4)	151.9(7)	C(5) - C(6)	149.3(6)	C(7) - C(72)	137.9(6)
C(1) - C(6)	152.2(5)	C(3) - O(8)	141.7(5)	C(5) - O(9)	144.2(5)	C(71) - C(76)	139.7(6)
C(1) - C(7)	152.2(5)	C(4) - C(5)	143.7(5)	C(6) - C(7)	152.5(6)	C(72) - C(73)	138.2(7)
C(2) - C(3)	145.5(6)	C(4) - O(9)	141.8(6)	C(7) - C(70)	150.9(6)	C(73) - C(74)	137.7(7)
C(2) - O(6)	144.8(5)			C(7) - C(71)	149.7(6)	C(74) - C(75)	138.3(7)
						C(75) - C(76)	137.8(7)
Angles (deg)							
C(2) - C(1) - C(6)	119.0(4)	C(3) - C(4) - C(5)	120.2(4)	C(1) - C(7) - C(6)	59.9(3)	C(7) - C(71) - C(72)	122.1(4)
C(2) - C(1) - C(7)	120.5(4)	C(3) - C(4) - O(9)	116.6(4)	C(1) - C(7) - C(70)	116.6(4)	C(7) - C(71) - C(76)	119.4(4)
C(6) - C(1) - C(7)	60.1(3)	C(5) - C(4) - O(9)	60.7(3)	C(1) - C(7) - C(71)	119.1(3)	C(72) - C(71) - C(76)	118.2(4)
C(1) - C(2) - C(3)	120.5(4)	C(4) - C(5) - C(6)	120.9(4)	C(6) - C(7) - C(70)	115.9(4)	C(71) - C(72) - C(73)	121.5(4)
C(1) - C(2) - O(6)	115.5(4)	C(4) - C(5) - O(9)	59.0(3)	C(6) - C(7) - C(71)	120.6(4)	C(72) - C(73) - C(74)	119.4(4)
C(3) - C(2) - O(6)	58.5(3)	C(6) - C(5) - O(9)	115.9(4)	C(70) - C(7) - C(71)	114.2(3)	C(73) - C(74) - C(75)	120.3(4)
C(2) - C(3) - C(4)	120.1(4)	C(1) - C(6) - C(5)	119.2(4)	C(2) - O(8) - C(3)	61.0(3)	C(74) - C(75) - C(76)	119.8(4)
C(2) - C(3) - O(8)	60.5(3)	C(1) - C(6) - C(7)	60.0(3)	C(4) - O(9) - C(5)	60.3(3)	C(71) - C(76) - C(75)	120.7(4)
C(4) - C(3) - O(8)	116.7(4)	C(5) - C(6) - C(7)	121.3(4)				

geometrically and considered isotropically in all refinements. Special X-ray operations and results are listed in Table 1. The positional and thermal parameters of the atoms of the diepoxides **3b** and **3c** are given in Tables 2 and 4, respectively, and their bond lengths and angles in Tables 3 and 5.

- 1) ^{1a)} K. Takeuchi, M. Arima, and K. Okamoto, *Tetrahedron Lett.* **22**, 3081 (1981). — ^{1b)} K. Takeuchi, H. Fujimoto, and K. Okamoto, *Tetrahedron Lett.* **22**, 4981 (1981). — ^{1c)} K. Takahashi, K. Takase, and H. Toda, *Chem. Lett.* **1981**, 979. — ^{1d)} K. Takeuchi, T. Kitagawa, T. Toyama, and K. Okamoto, *J. Chem. Soc., Chem. Commun.* **1982**, 313. — ^{1e)} W. Bauer, J. Daub, G. Maas, M. Michna, and J. J. Stezowski, *Chem. Ber.* **115**, 99 (1982). — ^{1f)} F.-G. Klärner, E. K. G. Schmidt, and M. A. Abdel Rahman, *Angew. Chem. Suppl.* **1982**, 331. — ^{1g)} F.-G. Klärner, E. K. G. Schmidt, M. A. Abdel Rahman, and H. Kollmar, *Angew. Chem. Suppl.* **1982**, 338.
- 2) ^{2a)} R. Hoffmann, *Tetrahedron Lett.* **1970**, 2907. — ^{2b)} H. Günther, *Tetrahedron Lett.* **1970**, 5173. — ^{2c)} R. Hoffmann and W.-D. Stohrer, *J. Am. Chem. Soc.* **93**, 6941 (1971). — ^{2d)} W.-D. Stohrer and J. Daub, *Angew. Chem.* **86**, 54 (1974); *Angew. Chem., Int. Ed. Engl.* **13**, 86 (1974). — ^{2e)} R. Wehner and H. Günther, *J. Am. Chem. Soc.* **97**, 923 (1975). — ^{2f)} J. D. Dill, A. Greenberg, and J. F. Liebman, *J. Am. Chem. Soc.* **101**, 6814 (1979). — ^{2g)} S. Durmaz and H. Kollmar, *J. Am. Chem. Soc.* **102**, 6942 (1980). — ^{2h)} F. H. Allen, *Acta Crystallogr. B* **36**, 81 (1980). — ²ⁱ⁾ G. Maas and J. K. Ketting, *Chem. Ber.* **115**, 627 (1982).
- 3) M. B. Rubin, *J. Am. Chem. Soc.* **103**, 7791 (1981).
- 4) ^{4a)} E. Ciganek, *J. Am. Chem. Soc.* **93**, 2207 (1971). — ^{4b)} G. H. Hall and J. D. Roberts, *J. Am. Chem. Soc.* **93**, 2203 (1971).
- 5) W. Adam, M. Balci, and B. Pietrzak, *J. Am. Chem. Soc.* **101**, 6285 (1979).
- 6) R. W. Hoffmann and F. Frickel, *Synthesis* **1975**, 444.
- 7) ^{7a)} F.-G. Klärner, *Tetrahedron Lett.* **1974**, 19. — ^{7b)} F.-G. Klärner, S. Yaslak, and M. Wette, *Chem. Ber.* **110**, 107 (1977).
- 8) M. Christl and E. Brunn, unpublished results; gift samples and experimental details to prepare gram quantities of **1a** via Eq. (2) are gratefully acknowledged.
- 9) ^{9a)} W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.* **79**, 352 (1957). — ^{9b)} C. Jutz and F. Voithenleiter, *Chem. Ber.* **97**, 29 (1964).
- 10) W. Adam and H. G. Eggelte, *J. Org. Chem.* **42**, 2987 (1977).
- 11) Due to the higher s-character of cyclopropane-substituent bond and the fact that the C(sp²) - C(sp³) bond is energetically favored over the C(sp³) - C(sp³) bond, the N/T equilibrium is expected to shift towards the norcaradiene form by substitution of C-7 with methyl groups; cf. J. C. Barborak, S. Chari, and P. von R. Schleyer, *J. Am. Chem. Soc.* **93**, 5275 (1971).
- 12) W. Adam and H. Rebollo, *Tetrahedron Lett.* **23**, 4907 (1982).

[283/82]