(24) D. F. R. Gilson and C. A. McDowell, *Nature (London)*, **183**, 4669, 1183 (1959).
(25) H. R. Allcock, R. W. Allen, E. C. Bissell, L. A. Smeltz, and M. Teeter, *J. Am. Chem. Soc.*, **98**, 5120 (1976).
(26) (a) C. J. Finder, M. G. Newton, and N. L. Allinger, *Acta Crystallogr., Sect. B*, **30**, 411 (1974); (b) J. Bernstein, *ibid.*, **31**, 1268 (1975); (c) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966); (d) *ibid.*, **21**, 153 (1966).
(27) G. W. Frank, R. M. Myasnikova, and A. I. Kitaigorodskii, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **16**, 270 (1971).
(28) G. N. Ramachandran and V. Sasisekharan, *Adv. Protein Chem.*, **23**, 284 (1968).
(29) M. Lahav, F. Laub, E. Gati, L. Leiserowitz, and Z. Ludmer, *J. Am. Chem. Soc.*, **98**, 1620 (1976).
(30) D. D. MacNicol and F. B. Wilson, *J. Chem. Soc., Chem. Commun.*, 786 (1971).
(31) I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, **6**, 217 (1973).
(32) E. Hadjoudis, *Isr. J. Chem.*, 11, 63 (1973).
(33) D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 594 (1974); F. H. Quina and D. G. Whitten, *ibid.*, **99**, 877 (1977).
(34) The molecular volume of related carboxylic acids can be estimated from their unit cell dimensions or densities. The cis isomers are invariably found to have larger molecular volumes (lower densities) than the corresponding trans olefins in ring-substituted cinnamic acids such as *o*-methoxycinnamic acids,[20] chain-substituted cinnamic acids,[35] and related compounds.[36]
(35) S. E. Filippakis, L. Leiserowitz, D. Rabinovich, and J. M. G. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1750 (1972).
(36) A. L. Bednowitz and B. Post, *Acta Crystallogr.*, **21**, 566 (1966).
(37) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).
(38) A. R. Olson and F. L. Hudson, *J. Am. Chem. Soc.*, **55**, 1410 (1933).
(39) J. Saltiel, J. D'Agostino, and E. Dennis, "Organic Photochemistry", O. L. Chapman, Ed., Marcel Dekker, New York, 1973, pp 1-111.
(40) A. P. Downing, W. D. Ollis, I. O. Sutherland, J. Mason, and S. F. Mason, *Chem. Commun.*, 329 (1968).
(41) Although the chemical consequences of light absorption by TOT have not been studied here, transfer of energy from host to guest, if it occurs, would almost certainly not change our conclusions.
(42) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Am. Chem. Soc.*, **85**, 829, (1963); K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 662 (1967), and references cited therein.
(43) We thank Dr. K. A. Muszkat and Dr. Z. Ludmer for advice and assistance, and for putting their instruments at our disposal for these measurements.
(44) Enclathration generally affords stabilization and protection against oxidation, etc.; see, for example, M. Hagan "Clathrate Inclusion Compounds", Reinhold, New York, 1962, p 153.
(45) Three additional novel crystal forms of TOT inclusion complex have recently been uncovered in our laboratories: *Pbcn* containing *dl*-2,3-dibromobutane; $P2_1/c$ containing *meso*-2,3-dibromobutane; $C2/c$ containing 3-bromooctane. The details of these structures have not yet been studied. The variety and generality of complex formation by TOT are thus especially noteworthy.
(46) C. K. Johnson, Program ORTEP, Oak Ridge National Laboratory, Oak Ridge, Tenn., Report ORNL-3794, 1965.

Photooxygenation of 1,3,5-Cycloheptatriene: Isolation and Characterization of Endoperoxides[1]

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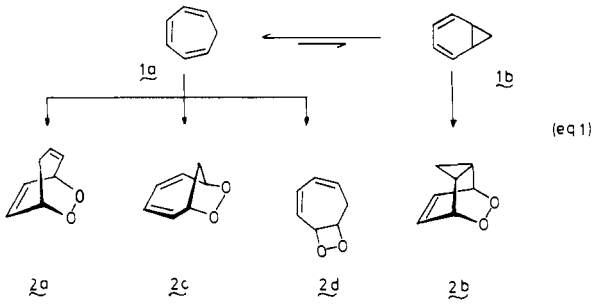
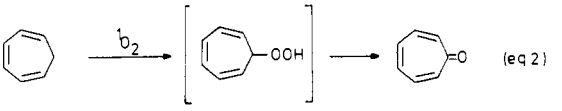
Abstract: The tetraphenylporphyrin-sensitized photooxygenation of 1,3,5-cycloheptatriene at subambient conditions affords the norcaradiene (2+4)-cycloadduct **2b** (3.5%), the tropilidene (2+4)-**2a** (40%) and (2+6)-cycloadducts **2c** (37%), benzaldehyde (5%), and benzene (5%). The characterization of these novel endoperoxides was made on the basis of ^1H and ^{13}C NMR spectral data, elemental analyses, diimide reduction to the corresponding saturated cyclic peroxides, and catalytic reduction.

In view of the facile valence isomerization (eq 1)[3] in 1,3,5-cycloheptatriene (**1**) between the tropilidene (**1a**) and

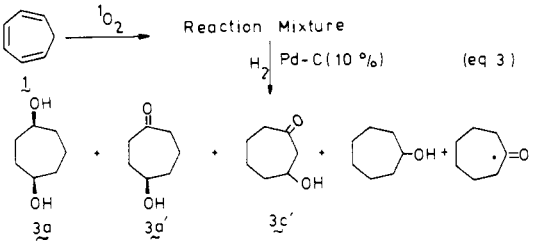


norcaradiene (**1b**) forms, its dienic reactivity is abundant and varied. For example, taking singlet oxygen as dienophilic agent for illustration, one may expect formation of the (2+4)-cycloadducts **2a** (tropilidene type) and **2b** (norcaradiene type). However, (2+6)-cycloadducts similar to **2c** are known,[4] and consequently one should expect as well the (2+6)-cycloadduct **2c.** Furthermore, the ability of singlet oxygen to (2+2)-cycloadd is well established,[5] and thus it is possible that the 1,2-dioxetane **2d** might be formed as well. Clearly, 1,3,5-cycloheptatriene is a fascinating substrate for singlet oxygenation.

Indeed, several studies have been reported after Schenck's observation[6] that singlet oxygenation of **1** affords tropone (eq 2) postulated to be derived from the intermediary tropilidene



hydroperoxide by dehydration. Thus, Kende and Chu[7] observed a complex product mixture after catalytic hydrogenation of the singlet oxygenated reaction mixture of cycloheptatriene (eq 3). Clearly, reduction products **3a** and **3a′** are



derived from the endoperoxide **2a,** the 1,4-diol **3a** by hydrogenolysis of the peroxide linkage and subsequent saturation of the double bonds, and the ketol **3a′** by isomerization of **2a** and subsequent saturation. The ketol **3c′** bespeaks the presence of the unusual (2+6)-endoperoxide **2c,** i.e., isomerization followed by saturation, since otherwise it would be difficult to rationalize the observed substitution pattern. The cycloheptanol and cycloheptanone have a more complex history, probably dehydration followed by saturation of the precursors to **3a, 3a′,** and **3c.** NMR investigation of the singlet oxygenated

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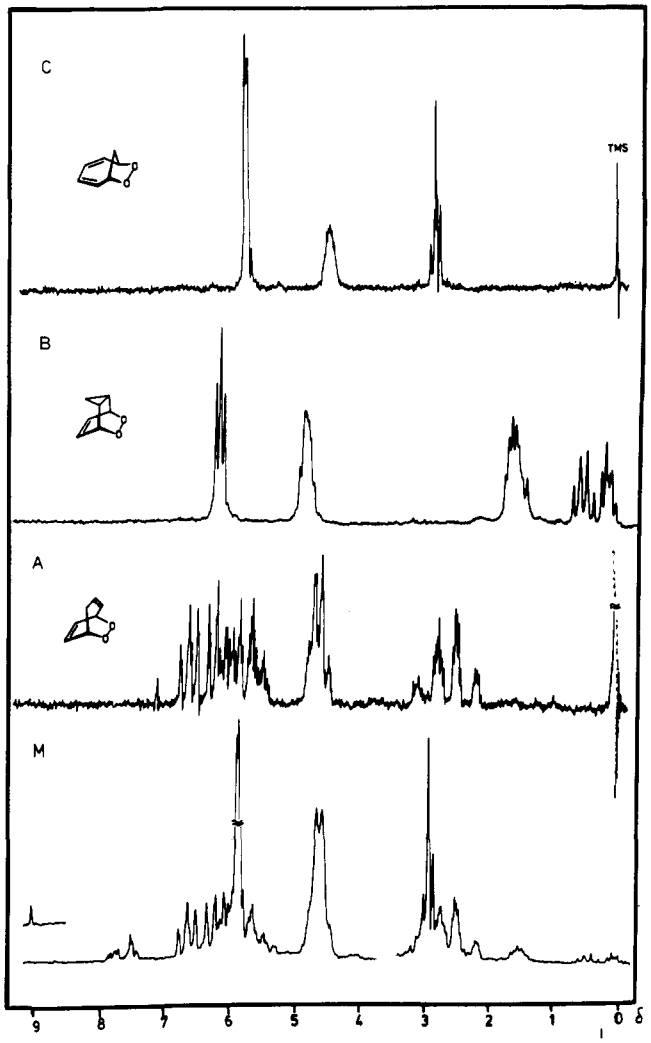
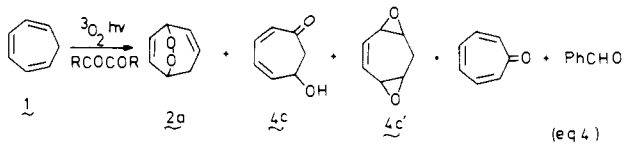


Figure 1. ^{1}H NMR spectra of the cycloheptatriene photooxygenation mixture (spectrum M) and individual endoperoxides (TMS = Me_4Si).

reaction mixture did not reveal any aldehydic nor cyclopropyl protons. Attempts to isolate the postulated intermediary endoperoxides **2a** and **2c** by distillation or chromatography failed.[7]

Subsequently, Mori and Takeshita[8] reported the α-diketone-sensitized photooxygenation of cycloheptatriene, leading to the products shown in eq 4. The stable endoperoxide **2a** could



be isolated and characterized, but the unsaturated ketol **4c** and bisepoxide **4c'** products imply that the labile endoperoxide **2c** intervened in this photooxygenation. Finally, Kitahara et al.[9] showed in a more detailed investigation that singlet oxygenation affords a product mixture similar to that observed in the α-diketone-sensitized photooxygenation (eq 4).[8]

Thus, while our work on the singlet oxygenation of cycloheptatriene was in progress, the only peroxide of the four possible ones that was reported as fully characterized was the stable tropilidene-type (2+4)-cycloadduct **2a**;[8,9] the labile (2+6)-adduct **2c** was implied from the final product composition. As described in our preliminary report,[10] by low temperature column chromatography we were able to isolate, besides **2a**, the endoperoxides **2b** and **2c** and fully characterize them. Furthermore, we suspect that the novel tropilidene-type (2+6)-cycloadduct **2c** is derived via rearrangement of an intermediary 1,2-dioxetane **2d**. Herein we present the full details of our investigation.

Results and Discussion

Isolation of Endoperoxides. The ^{1}H NMR spectrum of the singlet oxygenated cycloheptatriene product mixture is shown in Figure 1 (spectrum M). Its great complexity is immediately apparent. Even then, several spectral features suggest the presence of certain products. Before rotoevaporation of the solvent, the NMR showed a sharp spike at δ 7.10 ppm which was identified as benzene (ca. 5% by NMR). It is significant to mention that this spike continuously increased during monitoring of the progress of singlet oxygenation by NMR. The aldehydic resonance at δ 9.2 ppm implies the presence of benzaldehyde (isolated in 5% yield in the silica gel chromatography), and cyclopropyl protons at δ 0.0–0.8 ppm are conspicuous for the presence of norcaradiene-type products. The lack of the olefinic resonance at δ 6.7–6.9 of tropone clearly established that this previously observed product must be of secondary origin.

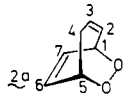
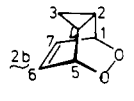
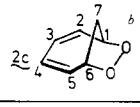
After silica gel chromatography at −50 °C, the three endoperoxides **2a** (spectrum A), **2b** (spectrum B), and **2c** (spectrum C) were isolated in 40, 3.5, and 38% yields, eluting in the order **2c** > **2a** > **2b** with 1:1 CH_2Cl_2/n-C_5H_{12}. Superposition of the individual spectra A, B, and C leads to spectrum M for the crude product mixture, provided that due account is made for the presence of benzaldehyde. Thus, better than 90% of the product mixture is accounted for. This indicates that the singlet oxygenation of cycloheptatriene is a rather clean and well-defined reaction, provided that the essential care is taken in the photooxygenation and silica gel chromatography. The latter is particularly critical, especially the choice of the adsorbant. We found that the activity grade I (0.05–0.2 mm) silica gel from Woelm gave consistently best results; but even then the success of the separation of the endoperoxides **2** depended from batch to batch of the silica gel used. In our experience, unless the endoperoxides moved rather swiftly on the low temperature column, extensive decomposition and thus poor separation would result.

Characterization of Endoperoxides: Spectral Data. The ^{1}H and ^{13}C NMR spectra have been definitive in assigning the proposed structures of the endoperoxide. Because of the complexity of ^{1}H NMR spectra, double resonance experiments were essential and decisive.

The most complex ^{1}H NMR (Table I) was that of the tropilidene (2+4)-adduct **2a** with singlet oxygen. Since this product was already characterized,[8,9] we will not discuss its complex ^{1}H NMR spectrum in further detail. Although there is little question on the structural assignment of endoperoxide **2a** as the tropilidene (2+4)-cycloadduct with $^1O_2$ (correct elemental analysis, molecular ion at *m/e* 124, matched reported physical constants), we also obtained the ^{13}C NMR for this product (Table I). Each carbon resonance is distinctly resolved and located at the expected chemical shift. In addition, the IR shows characteristic bands for the olefinic and aliphatic C—H and C=C stretchings.

The ^{1}H NMR of endoperoxide **2b** is straightforward (Table I) and highly characteristic. The cyclopropyl H_3 and $H_{3'}$ protons constitute a resonance at 0.0–0.8 ppm consisting of two multiplets of which the high-field multiplet was assigned to the *endo*-H_3 in view of the anisotropy effect of the double bond and the coupling constants. These are coupled to the neighboring cyclopropyl H_2 and H_4 protons, a multiplet at 1.3–1.8 ppm with $J_{3,2} = J_{3,4} = 4.0$ Hz and $J_{3',2} = J_{3',4} = 6.5$ Hz, as confirmed through double resonance. Irradiation at 1.5 ppm resolves the H_3 and $H_{3'}$ multiplet into an AB pattern. The H_2 and H_4 multiplet at 1.3–1.8 ppm is further coupled to the bridgehead protons H_1 and H_5, located as a multiplet at 4.6–4.9 ppm,

Table I. Spectral Data of Endoperoxides **2**

endoperoxides	^{1}H NMR (CCl_4, Me_4Si) type	no.	δ, ppm	multiplicity	J, Hz	^{13}C NMR ($CDCl_3$)[a] type	δ, ppm	IR (CCl_4) ν, cm^{-1}
	1, 5	2	4.2-4.7	m	$J_{2,3}$ = 10.6	1	75.59	3070
	2	1	5.9	m	$J_{3,4}$ = 3.0	2	130.58	3040
	3	1	5.5	m	$J_{3,4'}$ = 3.0	3	134.04	2940
	4[c]	1	2.28	m	$J_{4,4'}$ = 18.6	4	35.67	1650
	4′	1	2.78	m	$J_{4,5}$ = 2.3	5	73.42	
	6	1	6.15	m	$J_{4',5}$ = 3.99	6	125.00	
	7	1	6.5	m	$J_{6,7}$ = 9.3	7	128.84	
	1, 5	2	4.6-4.9	m	$J_{2,3}$ = 4.0	1, 5	73.70	3070
	2, 4	2	1.3-1.8	m	$J_{2,3'}$ = 6.5	2, 4	5.98	3040
	3, 3′	2	0.0-0.8	m	$J_{3,3'}$ = 5.9	3	4.30	3000
	6, 7	2	6.0-6.3	m	$J_{3,4}$ = 4.0	6, 7	126.57	2900
					$J_{3',4}$ = 6.5			1530
	1, 6	2	4.3-4.6	m		1, 6	73.59	3030
	2, 3, 4, 5	4	5.7-5.8	m		2, 5	128.52	2950
	7, 7′	2	2.7-2.9	m		3, 4	132.15	1630
						7	38.92	

[a] We thank Professor D. Traficante (Yale University) for recording these spectra for us. [b] UV (*n*-hexane) λ_{max} 294 nm (ϵ 818) for endoperoxide **2c**. [c] H_4 refers to exo and $H_{4'}$ to endo protons.

which in turn are coupled to the multiplet of the olefinic protons H_6 and H_7 at 6.0-6.3 ppm. In fact, the 1.5-ppm irradiation uncovers the $H_{1,5}$ and $H_{6,7}$ multiplets as an AA′XX′ pattern. Line broadening of the X portion indicates long-range coupling between the bridgehead H_1 and H_5 protons with the geminal cyclopropyl H_3 and $H_{3'}$ protons.

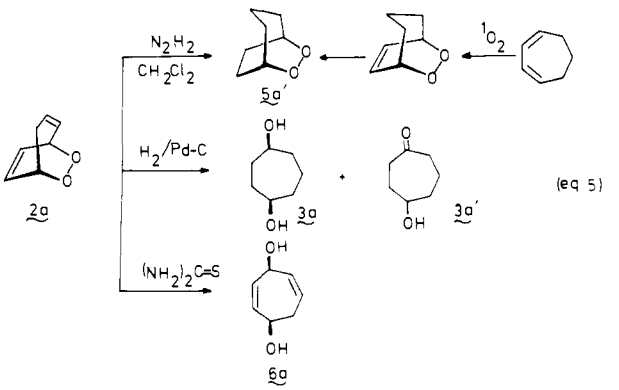
Again, the ^{1}H NMR spectrum secures the proposed structure for the endoperoxide **2b.** Further confirmation is provided by the ^{13}C NMR spectrum (Table I). As expected for such a symmetrical structure, the cyclopropyl carbons C_2 and C_4, the bridgehead carbons C_1 and C_5, and the olefinic carbons C_6 and C_7 are degenerate and are located at the appropriate chemical shifts. The IR spectrum exhibits olefinic, cyclopropyl, and aliphatic C—H and C=C stretching bands. A correct elemental analysis and a molecular ion at *m/e* 124 substantiate the structure of **2b** as the norcaradiene endoperoxide.

The endoperoxide **2c** is of course the most novel of the three since it represents one of the few known (2+6)-cycloadducts of tropilidene and the first for singlet oxygen. Its ^{1}H NMR is quite straightforward (Table I) with the methylenic H_7 and $H_{7'}$ protons forming a quasi-quartet at 2.7-2.9 ppm, the bridgehead H_1 and H_6 protons a multiplet at 4.3-4.6, and the olefinic H_3, H_4, H_5, and H_6 protons a multiplet at 5.7-5.8 ppm. Irradiation of the bridgehead protons at 4.45 ppm collapses the methylenic and the olefinic protons into singlets, clearly showing coupling of the bridgehead H_1 and H_6 protons to $H_{7,7'}$ and H_{3-6}.

In addition, the ^{13}C NMR spectrum (Table I) confirms our structure assignment beyond any reasonable doubt. Thus, in view of its symmetry, the ^{13}C resonances of the bridgehead carbons $C_{1,6}$, the olefinic carbons $C_{2,5}$ and $C_{3,4}$ are degenerate and located at the expected chemical shifts. The IR shows olefinic and aliphatic C—H and conjugated C=C stretchings. Inspection of Dreiding models reveals that the dienic structure is essentially planar, resulting in a rather strained molecule. The λ_{max} at 294 nm (ϵ 818) in the UV spectrum clearly corroborates the planarity of the dienic moiety.

Chemical Reductions. As further proof for the endoperoxide structures, we have examined a number of chemical transformations including diimide, catalytic, and thiourea reductions. Of these the diimide reduction is the most significant for structural assignment since this mild and double bond specific reduction[11] preserves the bicyclic peroxide skeleton. The use of the nonprotic CH_2Cl_2 as solvent was essential, because in methanol some of the endoperoxides, especially the (2+6)-adduct **2c,** suffered rearrangements.

The diimide reduction **2a** → **5a** went relatively smoothly in 89% yield by saturation of the more strained 6-ene bond. Repetitive reduction with diimide was necessary to effect the subsequent reduction **5a** → **5a′** by saturation of the less strained 2-ene bond; however, it could be achieved in 65% yield. The saturated bicyclic peroxide **5a′** was synthesized independently via the sequence shown in eq 5.[12] Furthermore, the ^{1}H



NMR, IR, and MS data and correct elemental analyses confirm the structures **5a** and **5a′.**

Catalytic hydrogenation of 2a over Pd/C in ethyl acetate gave the reported[12] *cis*-1,4-diol **3a** and the 4-ketol **3a′** in 64% and 13% yields, respectively, isolated by silica gel chromatography while eluting with $CHCl_3$. Also this transformation, although sacrificing the bicyclic peroxide skeleton, confirms the tropilidene-type (2+4)-adduct structure for the endoperoxide **2a.**

Also the thiourea reduction of **2a** in methanol proceeded smoothly, affording the extremely labile *cis*-diol **6a** in 72% yield, purified by silica gel chromatography while eluting with $CHCl_3$/MeOH (95:5). This viscous oil resisted crystallization and was too labile for even Kugelrohr distillation at maximum vacuum. Already on standing at room temperature (ca. 30 °C), it quickly deteriorated. For this reason it was impossible to obtain satisfactory elemental analysis; however, by ^{1}H NMR it is clear that this product was better than 97% pure. Furthermore, the ^{1}H NMR, IR, and MS data clearly establish the diene *cis*-diol structure for **6a**. Again, the geometrical arrangement of the double bonds confirms (2+4)-cycloaddition of $^1O_2$ to the tropilidene tautomer.

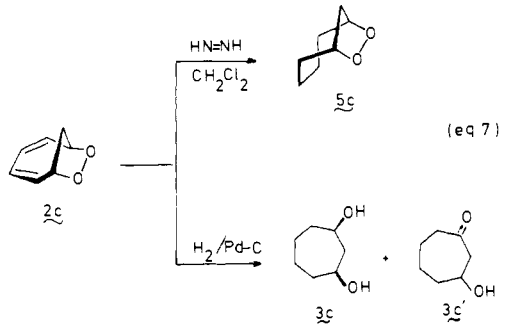
With respect to the chemical transformations of the norcaradiene endoperoxide **2b**, we have carried out the diimide

reduction **2b** → **5b** in CH_2Cl_2 in order to provide additional evidence for its structural assignment. The reduction proceeded smoothly, affording the norcarane-derived tricyclic peroxide **5b** in 85% yield (eq 6). In addition to the satisfactory elemental

(eq 6)

analysis, the ^1H NMR, IR and MS data unequivocally support the assigned structure **5b**.

Also the diimide reduction **2c** → **5c** went well, affording the saturated bicyclic **5c** in 73% yield. However, in this case particularly, CH_2Cl_2 as solvent was critical because in methanol complex rearrangements took place. Apparently this unsaturated endoperoxide **2c** is sufficiently more strained than **2a**, so that the diimide reduction occurs more readily. Again the satisfactory elemental analysis and spectral data substantiate the bicyclic peroxide structure **5c**. Catalytic hydrogenation of endoperoxide **2c** over Pd/C in ethyl acetate afforded the known *cis*-1,3-diol **3c**[12] and 3-ketol[7] **3c'** in 55 and 38% yields, respectively (eq 7). Both reduction methods convincingly es-

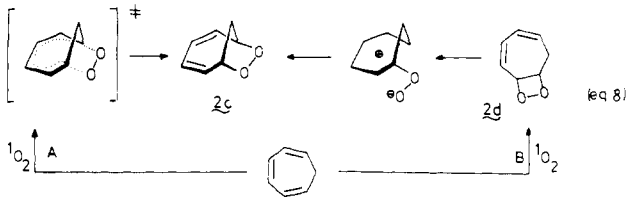


(eq 7)

tablish the structure of the tropilidene (2+6)-cycloadduct **2c**.

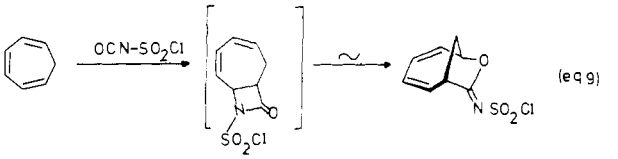
Mechanistic Aspects. The tropilidene–norcaradiene equilibrium **1a** ⇌ **1b** (eq 1) is unquestionably on the side of the tropilidene tautomer **1a** down to −150 °C.[13] Not even traces of the norcaradiene tautomer **1b** could be detected by ^1H NMR. Thus, that the tropilidene-derived endoperoxide **2a** is the prefered product over the norcaradiene endoperoxide **2b** is not surprising. In fact, it is well established that electron-withdrawing groups by resonance such as cyano, or carbmethoxy, help stabilize the norcaradiene isomer[14] sufficiently to permit NMR detection. For example, at −150 °C ca. 3% of the norcaradiene tautomer of the carbmethoxy derivative was observed by ^1H NMR in the valence tautomerism **1a** ⇌ **1b**.[15] Consequently, for the unsubstituted cycloheptatriene the equilibrium **1a** ⇌ **1b** must be still more shifted in favor of the tropilidene isomer **1a**. Indeed, while for cycloheptatriene we obtain 40% tropilidene and 3.5% norcaradiene (2+4)-adducts with $^1O_2$, for 7-cyano-1,3,5-cycloheptatriene the norcaradiene (2+4)-adduct was formed quantitatively.[16] Whether a bona fide norcaradiene tautomer **1b** is essential for (2+4)-cycloaddition with $^1O_2$ or whether merely a norcaradiene-type conformation of the cycloheptatriene ring system on the way toward the endoperoxide product **2b** is involved is difficult to answer under the circumstances. In either case, the planar diene geometry of the norcaradiene structure or transition state is highly favored over the nonplanar diene geometry of the tropilidene structure. Otherwise, an appreciable amount of tropilidene (2+4)-adduct should have been formed in the singlet oxygenation of 7-cyano-1,3,5-cycloheptatriene.[16]

Mechanistically the more challenging product is the tropilidene (2+6)-adduct **2c** (38%). Two possibilities come to mind (eq 8). Path A contemplates a formally forbidden concerted



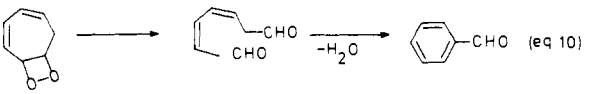
(eq 8)

transition state for (2+6)-cycloaddition of the singlet oxygen. Alternatively, in path B first (2+2)-cycloaddition to afford the 1,2-dioxetane is proposed. Subsequently the 1,2-dioxetane rearranges via a dipolar intermediate into the (2+6)-adduct **2c**. In fact, a precedent for such a stepwise cycloaddition process exists, namely, the formation of the (2+6)-adduct **7** between chlorosulfonyl isocyanate and cycloheptatriene (eq 9).[17]



(eq 9)

It is obviously a difficult task to sort out these two mechanistic possibilities A and B. However, accepting the intervention of 1,2-dioxetanes **2d** in the formation of the (2+6)-cycloadduct **2c**, the 5% benzaldehyde product is conveniently rationalized in terms of the mechanism suggested in eq 10. We



(eq 10)

are presently designing specific experiments to probe this challenging mechanistic problem of whether or not the 1,2-dioxetane **2d** intervenes in the formation of the endoperoxide **2c**.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 283 spectrophotometer and ^1H NMR spectra on an Hitachi Perkin-Elmer Model R-24B spectrometer. Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this research were purchased from standard suppliers (if available) or prepared according to published procedures and purified to match reported physical and spectral data. The elemental analyses were performed by the Atlanta Analytical Laboratories, P.O. Box 80569, Atlanta, Ga. 30366. Mass spectra were recorded on an Hitachi Perkin-Elmer Model RMS-4 spectrometer.

Singlet Oxygenation of 1,3,5-Cycloheptatriene (1). A 250-mL, one-necked, pear-shaped flask was charged with 200 mL of a 0.1 M solution of the cycloheptatriene in CCl_4, containing 5 mg of tetraphenylporphyrin (TPP) and sealed with a rubber septum. Dry oxygen gas was introduced by means of an 18-gauge stainless steel needle, which reached the bottom of the flask, using a 24-gauge needle as air vent. While passing a steady oxygen stream and cooling at 0 °C by means of an ice bath, the flask was irradiated by means of a 150-W General Electric sodium street lamp. The progress of singlet oxygenation was monitored by ^1H NMR. Usually within 7 h, singlet oxygenation was complete.

The solvent was rotoevaporated (ca. 25 °C at 20 Torr) and the residue chromatographed on 100 g of silica gel (0.05–0.2 mm; activated) at ca. −50 °C, eluting with CH_2Cl_2/*n*-C_5H_{12} (1:1). The progress of the separation was monitored by TLC. Fractions with same retention times were combined, rotoevaporated (ca. 25 °C at 20 Torr), and further purified by repeated silica gel chromatography, recrystallization, and/or fractional distillation.

Endoperoxide 2a. This material was isolated in 40% yield as second eluate and bulb-to-bulb distilled at a bath temperature of 50 °C and 0.1 Torr, resulting in a colorless oil (n_D^{20} 1.5249) which gave a satisfactory elemental analysis based on the empirical formula $C_7H_8O_2$. The spectral data are summarized in Table I.

Endoperoxide 2b. This material was isolated in 3.5% yield as third eluate, mp 64 °C, colorless needles from pentane, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_8O_2$. The spectral data are summarized in Table I.

Endoperoxide 2c. This material was isolated in 38% yield as first eluate, a colorless oil (n_D^{20} 1.5316) which gave a satisfactory elemental analysis based on the empirical formula $C_7H_8O_2$. The spectral data are summarized in Table I.

Diimide Reduction of Endoperoxides 2. A 100-mL, three-necked, round-bottomed flask, provided with a magnetic spinbar, 20-mL pressure-equalizing addition funnel, and nitrogen inlet and outlet tubes, was charged with 25 mmol (5-30 molar excess based on **2**) of potassium azodicarboxylate in 40 mL of dry CH_2Cl_2. The slurry was cooled to 0 °C and a solution of 1.0 mmol of the endoperoxide **2** in 10 mL of CH_2Cl_2 was added. While cooling and stirring magnetically, a solution of 50 mmol (10-50 molar excess based on **3**) of HOAc in 20 mL of CH_2Cl_2 was added dropwise (ca. 45 min) and stirred until disappearance of the yellow azodicarboxylate color. Subsequently, 20 mL of water was added slowly and the organic layer was washed with 2 × 20 mL of saturated $NaHCO_3$ solution and water. After drying over $MgSO_4$, the solvent was evaporated at 0 °C and 15 Torr. The saturated cyclic peroxides **5** were purified by column chromatography on silica gel at 0 °C eluting with CH_2Cl_2/*n*-C_5H_{12} (1:1), by recrystallization from the appropriate solvent, and/or sublimation at 30 °C and 2 Torr.

8,9-Dioxabicyclo[3.2.2]non-2-ene (5a). Reduction of **2a** with a fivefold molar excess of diimide afforded **5a** in 89% yield, mp 32-33 °C, colorless needles from pentane, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_{10}O_2$. The spectral data are: ^{1}H NMR (CCl_4, Me_4Si, ppm)[18] $\delta_{6,7}$ 1.2-2.4 (4 H, multiplet), $\delta_{4,4'}$ 2.2-3.1 (2 H, AB system, J = 16.6 Hz with $J_{3,4}$ = 4 Hz and $J_{4,5}$ = 3.5 Hz, $J_{34'} \approx J_{4'5}$ = 0), $\delta_{1,5}$ 4.1-4.5 (2 H, multiplet), and $\delta_{2,3}$ 5.5-5.9 (2 H, multiplet); IR (CCl_4, cm^{-1}) 3045 (olefinic C—H), 2970 (aliphatic C—H), 1650 (C=C), 1460 (CH_2 bending), 1420 and 1345; MS (70 eV) *m/e* 126.

8,9-Dioxabicyclo[3.2.2]nonane (5a'). Repetitive reduction of **2a** with a tenfold molar excess of diimide four times gave **5a'** in 65% yield, mp 122-123 °C (sublimed at 30 °C and 1 mm Torr), colorless wax, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_{12}O_2$. The spectral data are: ^{1}H NMR (CCl_4, Me_4Si, ppm)[18] $\delta_{2,3,4,6,7}$ 1.4-2.4 (10 H, multiplet) and $\delta_{1,5}$ 4.0-4.4 (2 H, multiplet); IR (CCl_4, cm^{-1}) 2965, 2930, and 2835 (aliphatic C—H), 1470, 1450, and 1435 (CH_2 bending), 1365, 1335, and 1035; MS (70 eV) *m/e* 128.

The authentic **5a'** could be prepared alternatively by reduction of 8,9-dioxabicyclo[3.2.2]non-6-ene, prepared by singlet oxygenation of cycloheptadiene,[12] with a tenfold molar excess of diimide in 72% yield, mp 122-123 °C (sublimed at 30 °C and 1 mm Torr), colorless wax, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_{12}O_2$.

8,9-Dioxatricyclo[3.2.2.0^{2,4}]nonane (5b). Reduction of **2b** with a fivefold molar excess of diimide afforded **5b** in 85% yield, mp 98 °C, colorless plates from pentane, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_{10}O_2$. The spectral data are: ^{1}H NMR (CCl_4, Me_4Si, ppm)[18] $\delta_{2,3,4}$ 0.45-1.0 (4 H, multiplet), $\delta_{6,7}$ 1.05-2.2 (4 H, multiplet), $\delta_{1,5}$ 4.0-4.4 (2 H, broad singlet); IR (CCl_4, cm^{-1}) 3030 (cyclopropyl C-H), 2945 and 2860 (aliphatic C-H), 1465 (CH_2 bending), 1350 and 1300; MS (70 eV) *m/e* 126.

7,8-Dioxabicyclo[4.2.1]nonane (5c). Repetitive reduction of **2c** with a tenfold molar excess of diimide two times produced **5c** in 73% yield, mp 69-70 °C (after silica gel chromatography at −20 °C, eluting with CH_2Cl_2/*n*-pentane and subliming at 30 °C and 2 Torr), colorless plates, which gave a satisfactory elemental analysis based on the empirical formula $C_7H_{12}O_2$. The spectral data are: ^{1}H NMR (CCl_4, Me_4Si, ppm)[18] δ_{2-5} 1.0-2.0 (8 H, multiplet), $\delta_{7,7'}$ 2.1-2.8 (2 H, multiplet), and $\delta_{1,6}$ 4.2-4.6 (2 H, broad doublet, $J_{7,7'}$ = 11.6, $J_{6,7'} = J_{1,7'}$ = 7.01, $J_{6,7} = J_{1,7} < 1.3$ Hz); IR (CCl_4, cm^{-1}) 2985, 2920, and 2855 (aliphatic C—H), 1465 and 1445 (CH_2 bending), 1365, 1325, 1290, and 1205; MS (70 eV) *m/e* 128.

Catalytic Hydrogenation of Endoperoxides 2. Into a 50-mL, two-necked, round-bottomed flask, provided with spinbar, were placed 5 mg of Pd/C (4%) catalyst and 1.0 mmol of peroxide **2** in 20 mL of AcOEt. One of the necks was attached to a hydrogen manifold with a three-way stopcock, the other neck was capped with a rubber septum and degassed and flushed with hydrogen gas, while stirring magnetically. After 45 min the solution was decanted from the catalyst, the solvent rotoevaporated (ca. 25 °C at 20 Torr) and the product purified by silica gel column chromatography, eluting with $CHCl_3$ and/or recrystallization from the appropriate solvent.

Reduction of Endoperoxide 2a. The 1,4-diol **3a**, mp 66-68 °C (lit.[12] mp 68.4-70 °C), colorless needles from AcOEt, and the ketol **3a'**, bp 115 °C at 0.1 Torr, Kugelrohr distillation, prepared independently by the catalytic reduction of 4-hydroxycyclohept-2-enone,[19] were isolated in 64 and 13% yields, after column chromatography on silica gel eluting with $CHCl_3$ and with $CHCl_3$/MeOH (95:5).

Reduction of Endoperoxide 2c. The 1,3-diol **3c**, mp 47-48 °C (lit.[12] mp 48.5-49.5 °C), colorless needles from AcOEt, and the ketol **3c'**, bp 90 °C at 1 Torr (lit.[7] bp 83-84 °C at 0.3 Torr), were isolated in 55 and 38% yield, respectively, after column chromatography on silica gel, eluting with $CHCl_3$/MeOH (95:5) and with MeOH.

Thiourea Reduction of Endoperoxide 2a. To a magnetically stirred slurry of 1.2 mmol of thiourea in 5 mL of MeOH was added a solution of 1.2 mmol of endoperoxide **2a** in 5 mL of MeOH at 25 °C. After complete addition (ca. 10 min) the mixture was stirred for 3 h, the solids were removed by filtration, the MeOH was rotoevaporated (ca. 30 °C at 15 Torr), and the residue purified by column chromatography on 15 g of silica gel, eluting with $CHCl_3$/MeOH (95:5), affording the pure *cis*-1,4-diol **6a** in 72% yield, n_D^{25} 1.5132. The material deteriorated even at room temperature, making it impossible to obtain a satisfactory elemental analysis. The spectral data are: ^{1}H NMR (CD_3COCD_3, Me_4Si, ppm)[18] δ_4 2.25 (2 H, multiplet), δ_1 4.4 (1 H, broad singlet), δ_5 4.9 (1 H, broad triplet), and $\delta_{2,3,6,7}$ 5.2-5.9 (4 H, multiplet); IR (NaCl, cm^{-1}) 3600-3100 (OH), 3030 (olefinic C—H), 2900 (aliphatic C—H), and 1605 (C=C).

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References and Notes

(1) Paper No. 89 in the Cyclic Peroxide Series.
(2) NIH Career Development Awardee (1975-1980).
(3) Maier, G. *Angew. Chem.* **1967**, *79*, 446.
(4) (a) Moriconi, E. J.; Hummel, C. F. *J. Org. Chem.* **1976**, *41*, 3583. (b) Moriconi, E. J.; Hummel, C. F.; Kelly, J. F. *Tetrahedron Lett.* **1969**, 5325. (c) Hutton, J.; Waters, W. A. *J. Chem. Soc., Chem. Commun.* **1966**, 634.
(5) Adam, W. *Chem.-Ztg.* **1975**, *99*, 142.
(6) Schenck, G. O. *Angew. Chem.* **1957**, *69*, 579.
(7) Kende, A. S.; Chu, J. Y.-C. *Tetrahedron Lett.* **1970**, 4837.
(8) Mori, A.; Takeshita, H. *Chem. Lett.* **1978**, 395.
(9) Asao, T.; Yagihara, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2131.
(10) Adam, W.; Balci, M. *Angew. Chem.* **1978**, *90*, 1014.
(11) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.
(12) Cope, A. C.; Liss, T. A.; Wood, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 6287.
(13) Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 458.
(14) (a) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907. (b) Günther, H. *Ibid.* **1970**, 5173.
(15) Günther, H.; Wehner, R. *J. Am. Chem. Soc.* **1975**, *97*, 924.
(16) Adam, W.; Balci, M. *J. Org. Chem.* **1979**, *44*, 1189.
(17) Moriconi, E. J.; Hummel, C. F. *J. Org. Chem.* **1976**, *41*, 3583.
(18) The numbering of the protons refers to that given for the endoperoxides structures **2**.
(19) (a) Adam, W.; Balci, M.; Rivera, J. I. Unpublished results. (b) Doering, W. von E.; Sayigh, A. A. *J. Org. Chem.* **1961**, *26*, 1365.