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SYNTHESIS OF ENDOPEROXIDES DERIVED FROM CYCLOOCTATETRAENES VIA SINGLET OXYGENATION

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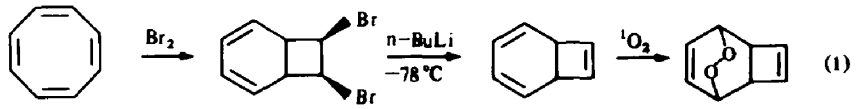
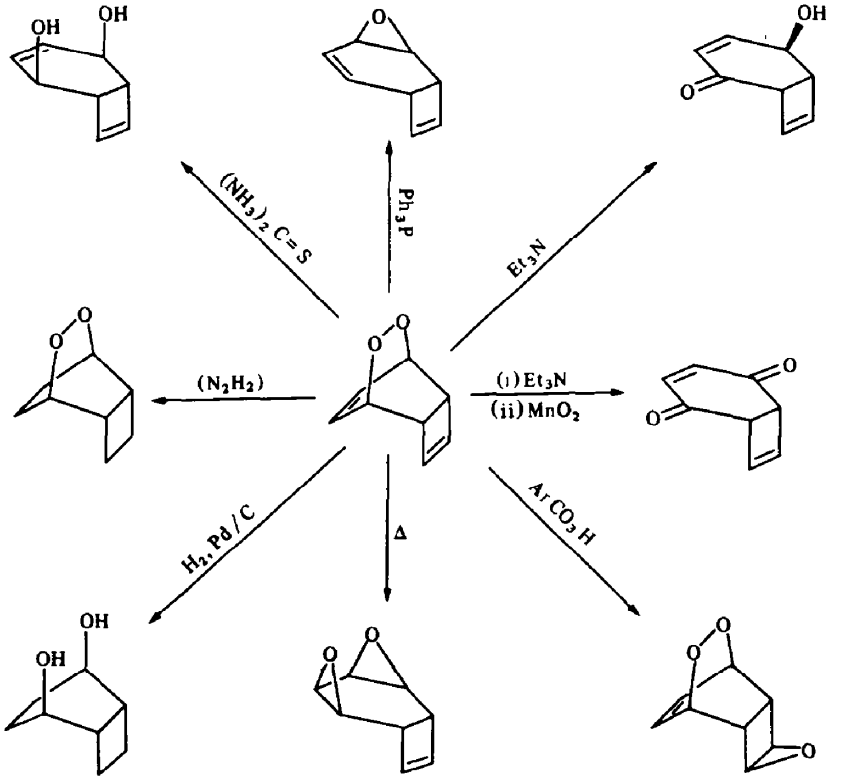
Abstract—Cyclooctatetraene (**1**) reacted with photo-generated singlet oxygen to give the endoperoxide 7,8-dioxabicyclo[4.2.2]deca-2,4,9-triene (**1a**), which was further transformed to the *cis*-diepoxide **1b** by catalytic rearrangement with Co-TTP to the unsaturated *cis*-diol **1c** and the saturated *cis*-diol **1d** by catalytic hydrogenation, to the saturated endoperoxide **1e** by reaction with diimide, and to the epoxycyclooctatetraene **1f** by deoxygenation with dimethylphosphine. Similarly, the methoxy-, phenyl- and methyl-substituted cyclooctatetraenes **3–5**, respectively, gave the corresponding endoperoxides with the substituents located at the 1-position (**3a**, **5a**), the 2-position (**5b**) and the 9-position (**3b**, **4a**). Their structures were determined on the basis of their ^{1}H- and ^{13}C-NMR data and by means of chemical transformation to the corresponding *syn*-diepoxides, i.e. 5,10-dioxatricyclo[7.1.0.0^{4,6}]deca-2,7-dienes. The formation of the endoperoxides is postulated to involve an electron transfer mechanism to give the radical cation of cyclooctatetraene and the superoxide ion. The latter couples into the homotropylium-type zwitterionic intermediate and subsequent cyclization leads to the endoperoxides.

The endoperoxide derived from the singlet oxygenation of the bicyclic valence isomer of cyclooctatetraene (Eq. 1) has proved itself as convenient and valuable synthetic intermediate in the preparation of a variety of complex oxygen-functionalized products (Scheme 1).[1] Anyone of these substances would constitute difficult synthetic targets by using classical chemical methods.



(1)

In principle the opportunity offers itself to prepare a variety of such oxygen-functionalized derivatives of cyclooctatetraene, if convenient access to its endoperoxide could be provided. Unfortunately, in view of its relatively low triplet state energy, cyclooctatetraene is an efficient quencher of triplet states derived from dyestuff sensitizers,[2] so that for a long time

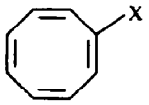


Scheme 1.

direct singlet oxygenation of cyclooctatetraene was left untried. The fact that the more electron-rich methoxycyclooctatetraene did afford the corresponding endoperoxides under direct singlet oxygenation conditions[3a] encouraged us to reinvestigate cyclooctatetraene as substrate. Using a more efficient photooxygenation apparatus, we indeed succeeded in obtaining the desired endoperoxide.[3b] Presently we report the full details on the singlet oxygenation of cyclooctatetraene and its methoxy, methyl and phenyl derivatives and the chemical transformations of the corresponding endoperoxides.

RESULTS

Starting materials. The monosubstituted cyclooctatetraene derivatives **2–7** were all prepared from



1 X = H **5** X = Me
2 X = Br **6** X = CO_2H
3 X = OMe **7** X = CO_2Me
4 X = Ph

cyclooctatetraene (**1**), following literature procedures. The bromocyclooctatetraene (**2**), which was the key intermediate for the others, was obtained by bromination (Br_2, −60°) and subsequent dehydrobromination (KOtBu, −45°).[4] For the methoxycyclooctatetraene (**3**) it turned out to be more advantageous to treat the *cis*-7,8-dibromo-1,3,5-cyclooctatriene directly with sodium methoxide in dimethylsulfoxide rather than using the bromocyclooctatetraene (**2**).

The methyl and phenyl derivatives **4** and **5** were obtained from **2** by reaction with phenyl and methyl cuprates, respectively.[4] Attempts to prepare the carboxylic acid **6** and its methyl ester **7** according to the Cope procedure[5] turned out to be problematic. For that purpose the procedure was modified by preparing the cyclooctatetraenylmagnesium bromide from bromocyclooctatetraene and Mg metal under the action of ultrasound, followed by treatment with carbon dioxide and acidification to give the carboxylic acid **6**. Reaction with diazomethane afforded the methyl ester **7**.

Photooxygenation apparatus. In view of the lack of reactivity of cyclooctatetraene towards singlet oxygen,[2,6] it was essential to develop an efficient photooxygenation apparatus (Fig. 1) for preparative scale applications. The key feature of this apparatus is that the Na-lamp (Osram Vialox NaV/TS 250 W) is used as internal irradiation source, contained in an immersion well.[7] Efficient cooling was necessary to remove the substantial heat produced by this high pressure Na-lamp. For this reason an efficient cooling jacket was provided, through which coolant from a cryostat was circulated. In addition, it was essential to submerge the entire apparatus in an efficient cooling bath. A contact thermometer was introduced as a safety measure, to disconnect the lamp in case of excessive temperatures, especially during overnight operation.

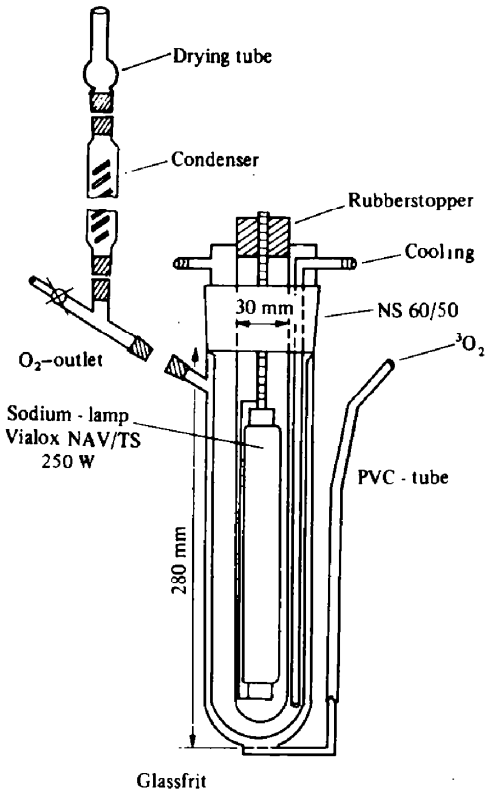


Fig. 1. Photooxygenation apparatus.

Stirring was achieved by percolating a stream of predried oxygen gas through a sintered glass inlet at the bottom of the reaction chamber. In view of the low ultraviolet output of the lamp, in our applications no filter was needed.

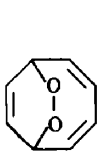
Comparative experiments revealed that this apparatus was *ca* 100-fold more efficient than an equivalent set-up using external irradiation sources. The scale of operation consisted typically of 100 mg to 20 g, the temperature from −80 to +30° and the time a few hours to several weeks. This permitted the successful singlet oxygenation of rather reluctant substrates yielding unstable peroxides in preparative quantities.

Endoperoxides and their transformations. As expected,[2] the cyclooctatetraenes **1–7** were all rather sluggish in reacting with singlet oxygen. That singlet oxygen was responsible for the formation of the endoperoxides was shown by means of control experiments. For example, in the absence of the dyestuff sensitizer or in the presence of DABCO no endoperoxides were produced. Even prolonged (several days) photooxygenation of the bromo, carboxy and carbomethoxy derivatives **2**, **6** and **7**, respectively, gave only high-molecular-weight peroxides (CAUTION!) or very little reaction with $^1O_2$. The others did afford endoperoxides as well as other products, especially high-molecular-weight peroxides (CAUTION!), and the results are summarized below for the individual cases.

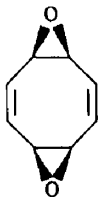
Cyclooctatetraene (**1**). After *ca* 350 hr irradiation of an acetone solution of cyclooctatetraene (**1**) at −15°, using tetraphenylporphine as sensitizer and hydroquinone as radical inhibitor, the endoperoxide **1a** was

obtained in 26% yield. In addition, a very explosive (CAUTION!) high-molecular-weight peroxide was produced (*ca* 53%), which was immediately destroyed and discarded. Careful chromatographic work-up revealed the presence of *ca* 2% diepoxide **1b** and *ca* 4% terephthaldehyde. The former is presumably a photolysis product of endoperoxide **1a**, the latter a thermal decomposition product. The mechanistic details of the thermolysis of the endoperoxide **1a** is the subject of a separate report.

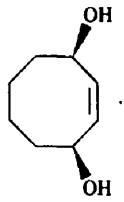
The chemical characterization of endoperoxide **1a** is summarized below. Thus, photolysis using the 333, 351



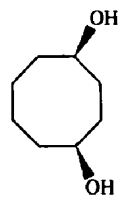
1a



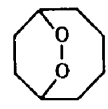
1b



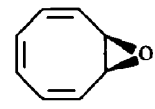
1c



1d



1e



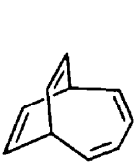
1f

and 364 lines of an 18 W Argon Ion Laser, but more effectively isomerization with catalytic amounts of the cobalt complex of tetraphenylporphine, Co(TPP),[8] afforded the known[9] *syn*-diepoxide **1b**. Catalytic reduction (Pd–C) led to a mixture of the known[10,11b] *cis*-dihydroxycyclooctane (**1d**) and the known *cis*-3,8-dihydroxycyclooctene (**1c**). On more persistent hydrogenation the endoperoxide **1a** gave only the expected diol **1d**. Diimide reduction led to the known[12] saturated endoperoxide **1e**. Finally, although endoperoxide **1a** was unreactive towards triphenyl-, tri-n-butyl- and even trimethylphosphine, when treated with dimethylphosphine, small amounts of the known[13] epoxide **1f** were isolated.

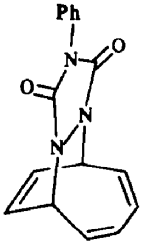
These chemical transformations unequivocally establish the structure of endoperoxide **1a**. Also the spectral data are in accord with this assignment (Table 1). As expected for this symmetrical structure, four distinct carbon resonances are exhibited in the 100 MHz ^{13}C-NMR spectrum, one aliphatic and three olefinic doublets at the appropriate chemical shift values.

The similarity of the 400 MHz ^{1}H-NMR spectrum of endoperoxide **1a** with those of the known[14] bicyclodecatetraene **8** and the known[15] urazole **9** speaks in favor of the proposed structure. The bridgehead protons appear as an XX′ multiplet at δ 4.90 and the olefinic protons as complex AA′ and AA′BB′ multiplets at δ 6.01 and 6.03–6.19, respectively. Decoupling experiments helped in this assignment. Thus, irradiation of the bridgehead protons at δ 4.90 led to a singlet for the AA′ pattern and simplification of the AA′BB′ pattern.

Methoxycyclooctatetraene (**3**). This derivative was considerably more reactive towards singlet oxygen so that photooxygenation at −20° for 23 hr under the



8



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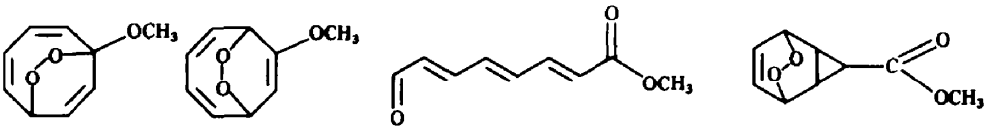
same conditions as cyclooctatetraene led to the two endoperoxides **3a,b** in *ca* 8 and 10% yield, respectively after low temperature (*ca* −25°) silica gel chromatography. Besides the explosive (CAUTION!) high-molecular-weight endoperoxide (*ca* 60%), *ca* 4% of the known[16] triene **3c** were isolated. Control experiments showed that the photooxygenation mixture obtained at −60° gave no appreciable chemiluminescence[17] on warm-up to *ca* 20–30° in the presence of dibromoanthracene as fluorophor. Neither could by means of low temperature (*ca* −60°) ^{1}H-NMR directly on the mixture any evidence for an intermediary dioxetane,

Table 1. Selected ^{1}H-* and ^{13}C-† chemical shifts of the endoperoxides

Endoperoxide	Chemical shifts (δ)					
	1-H	6-H	Olefinic-H	C-1	C-6	Olefinic-C
1a	4.90	4.90	6.03–6.19	72.89	72.89	119–132
3a	‡	4.75	5.87–6.32	100.5§	72.0§	121–136§
3b	4.92	4.98	5.08–6.15	75.0§	72.8§	90–152§
4a	5.34	5.12	5.97–6.32	75.06	72.88	116–136
5a	‖	4.88	5.83–6.20	76.65	71.76	116–137
5b	4.84	4.80	5.83–6.20			

* At 400 MHz except where indicated and in $CDCl_3$.
† At 100 MHz except where indicated and in $CDCl_3$.
‡ Substituted by methoxy group.
§ At 22.6 MHz in $CDCl_3$.
‖ Substituted by methyl group.



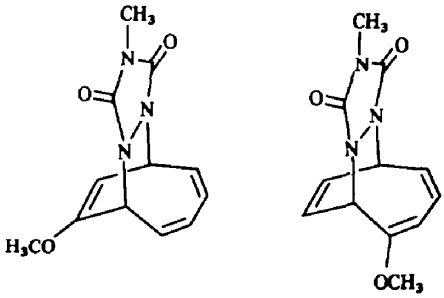
3a 3b 3c 3d

potential precursor to the triene **3c**,[16] be provided. However, the complex ^{1}H-NMR spectrum of the mixture could easily mask the presence of small amounts of the sought-for dioxetane.

When the photooxygenation was carried out in the presence of DMSO, in addition to the endoperoxides **3a,b** also the known[18] endoperoxide **3d**, derived from 7-carbomethoxycycloheptatriene, and dimethylsulfone were obtained. Increasing the DMSO content from 20 to 300 mol %, resulted in an increase of the ratio of endoperoxides **3d** and **3b** from 1.3 to 2.5. Since the endoperoxides **3a,b** were inert towards DMSO, the latter intercepted an oxidizing intermediate affording endoperoxide **3d** and dimethylsulfone.

In the structure elucidation of endoperoxide **3a** by spectral means, the urazoles **3e,f**, which were obtained in the 4-methyl-1,2,4-triazole-1,3-dione addition with methoxycyclooctatetraene, proved quite helpful, because X-ray structures of the urazoles **3e** (Fig. 2) and **3f** (Fig. 3) were on hand. Therewith a direct comparison of the NMR spectra was definitive. Indeed, the great similarity between the ^{1}H-NMR spectra of endoperoxide **3b** and urazole **3e**, but not with **3f**, provided compelling support in favor of the proposed structure.

The ^{13}C-NMR spectrum (Table 1) of endoperoxide **3b** exhibits a total of nine resonances, one quartet for the OMe carbon at δ 54.8, two doublets for the bridgehead carbons at δ 72.8 and 75.0, five doublets for the olefinic carbons in the range δ 90–135 and one



3e 3f

singlet for the OMe-substituted olefinic carbon at δ 152.2. Endoperoxides of cycloheptatriene show their bridgehead carbons at δ 70–78.[19]

The 400 MHz ^{1}H-NMR spectrum (Table 1) of endoperoxide **3b** displays the OMe group as singlet at δ 3.59, a complex multiplet of three protons at δ 4.92–5.08 corresponding to the bridgehead protons and the olefinic proton adjacent to the OMe group. A complex multiplet at δ 5.95–6.15 corresponds to the four olefinic protons of the 1,3-butadiene moiety. Decoupling experiments confirmed that the OMe substituent is located in the etheno-bridge.

The endoperoxide **3a** shows nine carbon resonances, a quartet for the OMe group at δ 51.2, a doublet for the

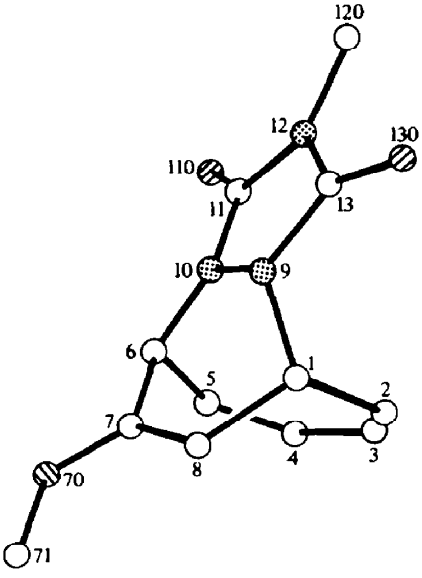


Fig. 2. Perspective drawing of urazole **3e** with the labelling of the atoms corresponding to that given in Tables 4 and 5. Nitrogen atoms are presented with dots and oxygen atoms with lines, respectively.

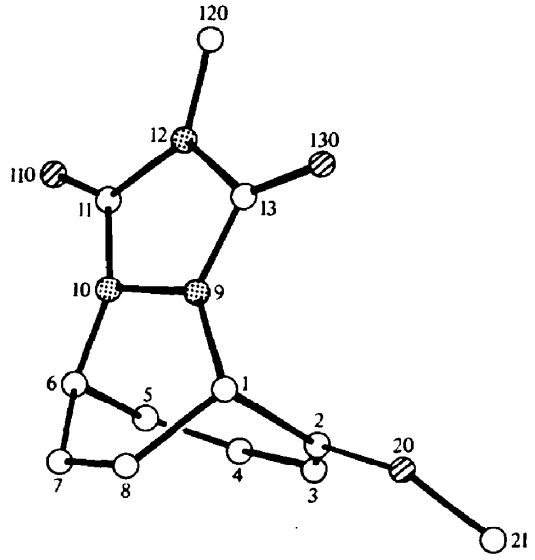
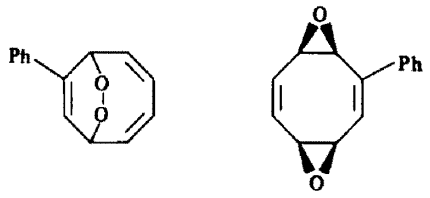


Fig. 3. Perspective drawing of urazole **3f**, with the labelling of the atoms corresponding to that given in Tables 4 and 5. Nitrogen atoms are presented with dots and oxygen atoms with lines, respectively.

bridgehead carbon at δ 72.0, a singlet for the OMe-substituted bridgehead carbon at δ 100.5 and six doublets for the olefinic carbons in the δ 121.0–135.9 range. Also the ^{1}H-NMR spectrum shows three groups of protons in the ratio *ca* 3 : 1 : 6, corresponding to the OMe singlet at δ 3.40, the bridgehead multiplet at δ 4.75 and the olefinic multiplets at δ 5.87–6.32. Decoupling experiments support this structure assignment.

Phenylcyclooctatetraene (**4**). Photooxygenation of phenylcyclooctatetraene (**4**) gave besides *ca* 55% high-molecular-weight peroxides (CAUTION!) only the endoperoxide **4a**, which was isolated in 34% by means



4a **4b**

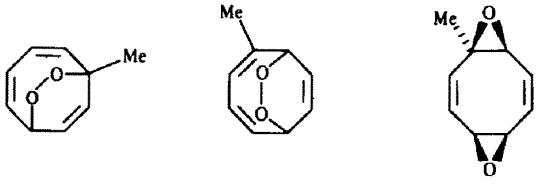
of low temperature (*ca* −20°) silica gel chromatography. The ^{13}C-NMR spectrum (Table 1) shows besides the typical set of four resonances of the phenyl substituent eight distinct carbons, two bridgehead doublets at δ 72.88 and 75.06, five olefinic doublets at δ 116–133 and an olefinic singlet at δ 135.94 bearing the phenyl group.

Its 400 MHz ^{1}H-NMR spectrum (Table 1) is complex. The bridgehead protons appear as ddd and mc at δ 5.12 and 5.34, respectively of which the latter is adjacent to the phenyl substituent. The four protons of the butadieno-bridge form a complex multiplet in the δ 5.97–6.26 range, while the olefinic proton next to the phenyl group resonates at δ 6.32 as a doublet, being coupled to the 6-H bridgehead proton. Extensive decoupling experiments confirm this assignment.

As chemical structure proof, the endoperoxide **4a** was converted into the *cis*-diepoxide **4b** on treatment with Co-TPP. The ^{13}C-NMR spectrum reveals eight distinct resonances in addition to the characteristic four resonances of the phenyl substituent. Four of these are doublets corresponding to the epoxide carbons located in the expected δ 54–56 range. The olefinic carbons appear as three doublets in the δ 122–128 range and as one singlet at δ 137.54, the latter corresponding to the phenyl-substituted carbon.

Its 400 MHz ^{1}H-NMR spectrum reveals four epoxide protons as complex multiplets in the δ 3.75–4.10 range and three olefinic protons also as complex multiplets in the δ 5.77–6.06 range. Decoupling experiments manifest that the four epoxide protons are coupled to at least one olefinic proton, with coupling constants $J \sim 1$–2 Hz. In view of the tub-shaped conformation of such *cis*-diepoxides,[9] the dihedral angle between adjacent epoxide and olefin protons is nearly 90° (Dreiding models), so that the magnitude of such adjacent coupling is about as large as allylic coupling. Decoupling experiments also confirm that the phenyl group is located in the etheno-bridge. Furthermore, the similar ^{1}H-NMR spectrum of *cis*-diepoxide **4b** compared to the parent *cis*-diepoxide **1b**, except that the former consists of complex multiplets due to its unsymmetrical nature, must be stressed. On the basis of these findings and the fact that the parent endoperoxide **1a** gave the *cis*-diepoxide **1b**, we propose the *cis*-diepoxide **4b** structure. The two epoxide units are separated by olefinic linkages rather than being adjacent.

Methylcyclooctatetraene (**5**). This substrate afforded a complex mixture of labile peroxide products including *ca* 63% of the explosive (CAUTION!) high-molecular-weight peroxide. By means of low temperature (*ca* −10°) silica gel chromatography a mixture of peroxides, containing the endoperoxides **5a,b** as main products, was isolated in *ca* 29%. All attempts of separating these labile endoperoxides by means of chromatography or crystallization failed. Either no separation or decomposition occurred.



5a **5b** **5c**

The ^{13}C-NMR spectrum (Table 1) of the mixture of endoperoxides **5a,b** exhibits one doublet at δ 71.76 and six doublets in the δ 115–137 range, all of nearly equal intensity. These resonances are tentatively assigned to the bridgehead carbon and the six olefinic carbons of isomer **5a**. Indeed, a singlet resonance for the Me-bearing bridgehead carbon can be located at δ 76.65. Furthermore, in the 400 MHz ^{1}H-NMR spectrum (Table 1) the etheno-bridge could be clearly identified, consisting of a doublet at δ 5.83 with J = 10 Hz and a doublet of doublets at δ 5.95. The smaller coupling of J = 5 Hz corresponds to the bridgehead proton at δ 4.88. This pattern is only possible if the Me group is at one of the bridgehead positions as in isomer **5a**. Furthermore, the well defined broad doublet at δ 4.80 and pseudo-triplet at δ 4.84 with $J \sim 6$ Hz could correspond to the bridgehead protons of isomer **5b**. Unfortunately no other resonances in the spectra could be assigned in the mixture of endoperoxides **5a,b**.

The most convincing evidence that the endoperoxides **5a,b** were formed in the singlet oxygenation of methylcyclooctatetraene came from the chemical transformation of **5a,b**, catalyzed by the Co(TPP)-complex. Only the *cis*-diepoxide **5c** was formed in *ca* 70% yield from the isomeric mixture **5a,b**. The mixture showed no other diepoxides in the ^{1}H-NMR spectrum. It is difficult to explain this, other than to suppose that the isomeric endoperoxides **5a,b** serve as precursors to the single *cis*-diepoxide **5c**.

Spectral data support this supposition. The ^{13}C-NMR spectrum of **5c** shows the Me quartet at δ 23.00, the three epoxide doublets in the δ 55–62 range, the epoxide singlet at δ 61.39 corresponding to the Me-substituted carbon, and the four olefinic doublets in the δ 125–131 range.

Also the 400 MHz ^{1}H-NMR spectrum speaks in favor of the diepoxide **5c** structure. Besides the Me singlet at δ 1.51, the multiplets of the three epoxide protons appear in the δ 3.0–3.1 range. The four olefin protons appear in the δ 5.4–5.5 range. These narrow ranges are similar to the parent diepoxide **1b**,[9] for which

these singlets can be better reconciled in terms of the **5c** structure. Extensive decoupling experiments reveal that the three epoxide protons are all coupled to at least one olefinic proton. The tub-shaped conformation obliges *ca* 90° dihedral angles between adjacent epoxide and olefin protons and is responsible for the small (J ~ 1 Hz) couplings.

DISCUSSION

The following experimental facts on the singlet oxygenation of the cyclooctatetraenes **1–7** need to be rationalized in terms of a reasonable mechanism concerning the formation of the corresponding endoperoxides:

(a) The reactivity order entails MeO > Ph > Me > H ≫ Br > CO_2H ~ CO_2Me, with the last two being essentially inert.

(b) No endoperoxides derived from the corresponding bicyclic valence isomers are formed.

(c) No preferred regiochemistry among the four possible (4 + 2)-cycloaddition modes, except that in all cases localization of the substituent at the 3-position is avoided.

(d) In the singlet oxygenation of methoxycyclooctatetraene appreciable amounts of cleavage product, the triene **3c**, are formed.

(e) In the presence of DMSO, oxygen transfer to give dimethylsulfone is observed with methoxycyclooctatetraene leading to the cycloheptatriene-derived endoperoxide **3d** in addition to the endoperoxides **3a,b**.

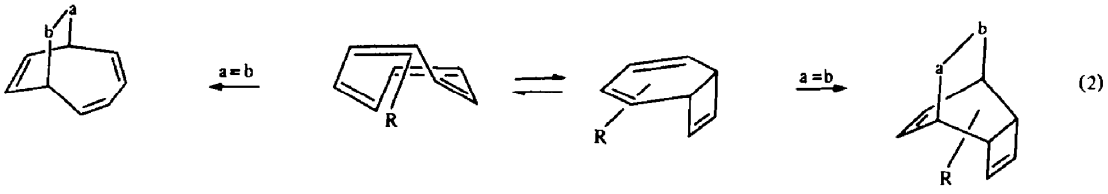
Clearly, the electrophilic nature of $^1O_2$ as dienophile is evident (point a). Thus, electron-donating substituents such as MeO, Me and Ph activate the cyclooctatetraene, while electron-withdrawing substituents such as Br, CO_2Me and CO_2H deactivate it. In this respect, $^1O_2$ resembles triazoledione (TAD) as electrophilic dienophile, except that for $^1O_2$ the differentiation in the electronic character of the substituent is so pronounced that cyclooctatetraenes with the electron-withdrawing groups Br, CO_2Me and CO_2H do not react. A still more significant difference between these two dienophiles is the fact (point b) that with $^1O_2$ only the bicyclic and no tricyclic endoperoxides (Eq. 2) are formed in the singlet oxygenation of cyclooctatetraene, while with TAD the tricyclic urazoles are produced preferentially if not exclusively.[20] An exception is methoxycyclooctatetraene, which affords only the urazoles **3e,f**. This dichotomy in cycloaddition behavior for $^1O_2$ and TAD has been amply documented[19a] for the 7-substituted cycloheptatrienes. Consequently, distinct mechanisms obtain for the cycloaddition of $^1O_2$ and TAD with cyclooctatetraenes. Since for TAD the formation of the bicyclic urazoles has been rationalized in terms of homotropylium ions as intermediates, the fact that with $^1O_2$ bridgehead-substituted endoperoxides are obtained (point c) but no corresponding urazoles with TAD, implies that the first step in the singlet oxygenation cannot entail homotropylium ions.

On the basis of these arguments and the fact (point d) that the cleavage product **3c**, presumably derived from an intermediary dioxetane, we propose the mechanism shown in Scheme 2 for the cycloaddition of singlet oxygen with cyclooctatetraenes. In view of the relatively low oxidation potential of cyclooctatetraene,[21] the first step involves electron transfer with $^1O_2$ to afford the radical cation of cyclooctatetraene and the superoxide ion.[22] While such electron transfer is facile for the activated cyclooctatetraenes **3–5**, it is energetically prohibitive for the deactivated derivatives **2**, **6** and **7**. Consequently, the latter are unreactive towards $^1O_2$ (point a).

Radical coupling[23] of the radical pair **10** leads preferentially to the two dipolar ions **11a** and **11b**, in which the electron-donating R-substituent (MeO, Me, Ph) stabilizes the positive center. Cyclization via charge annihilation leads to the various endoperoxides (point c). In the case of methoxycyclooctatetraene the dipolar ion **11b** also collapses into the dioxetane **3g**, which cleaves[24] and isomerizes[25] to the triene **3c** (point d).

To explain the formation of the rearranged endoperoxide **3d** in the singlet oxygenation of methoxycyclooctatetraene when DMSO is present (point e), an additional branching step is essential. We propose that the dipolar ion **11b** cyclizes into the perepoxide **12**,[26] which rearranges to the carbonyl oxide **13**.[27] Oxygen transfer to DMSO[28] affords dimethylsulfone and 7-carbomethoxycycloheptatriene, which adds singlet oxygen to lead to the known endoperoxide **3d**.[29] In the absence of DMSO, the carbonyl oxide **13** goes astray, giving undefined products.[30]

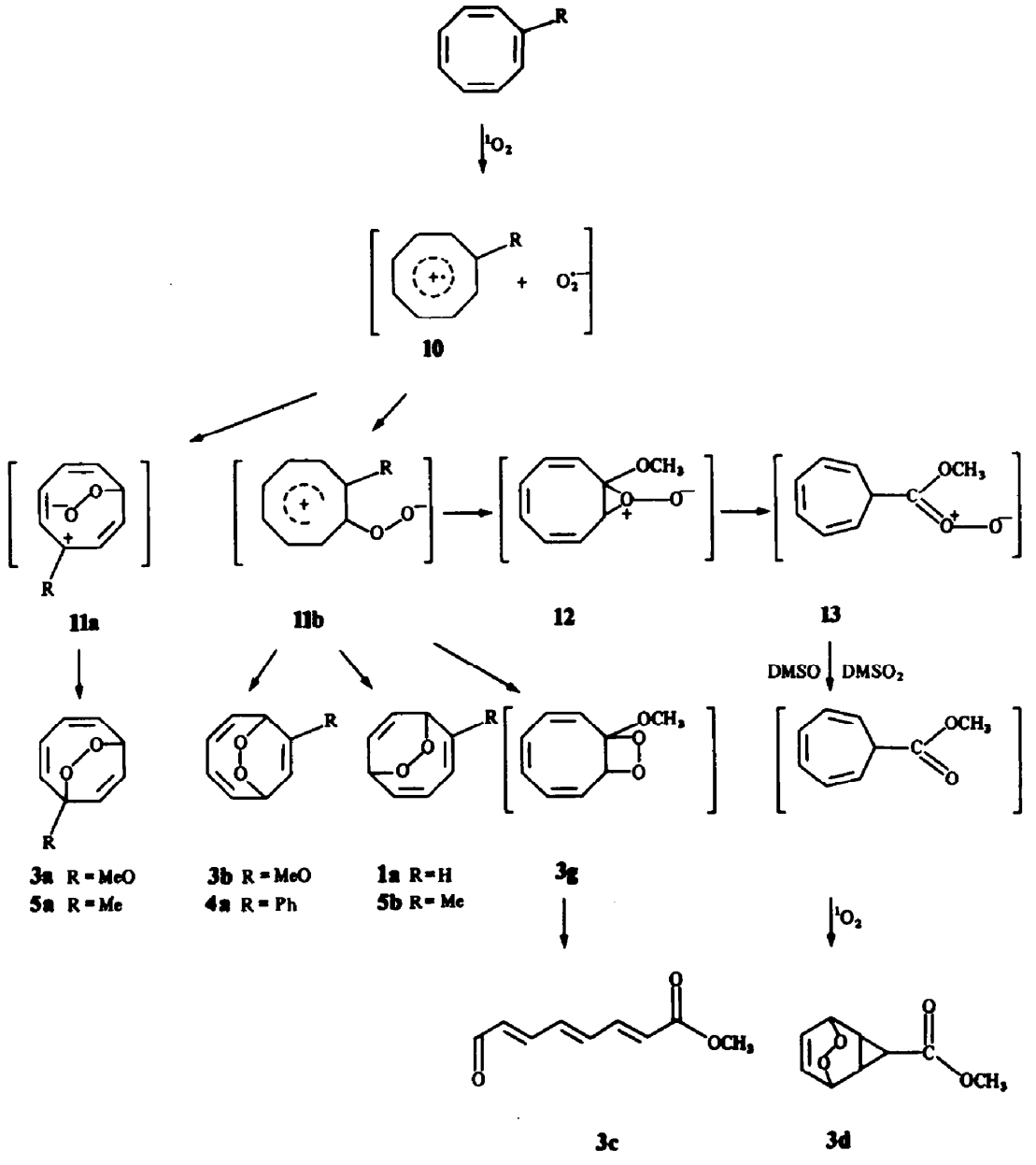
The mechanistic suggestions in Scheme 2 provide a reasonable account of the experimental facts (points a–e) observed in the singlet oxygenation of cyclooctatetraenes. The relatively low yields of isomeric endoperoxides produced, imply limiting synthetic value for this process.



(2)

EXPERIMENTAL

General aspects. All m.ps were taken on a Kofler hot stage and are uncorrected. IR spectra were recorded on a Beckmann Acculab 4 spectrometer. NMR spectra were obtained, unless otherwise stated, in $CDCl_3$ with TMS as reference, on a Varian EM 390 (90 MHz), Bruker WH 90 (22.6 MHz), Bruker WM 400 (400 MHz) or a Hitachi Perkin–Elmer R-24B spectrometer. Mass spectral (MS) data (70 eV) were obtained on a Varian CH-7 and elemental analyses were performed in-house. For the TLC runs Machery and Nagel Polygram SIL G/UV 40 × 80 mm plates were used, eluting with the appropriate solvent system, which is specified for each case. For column chromatography silica gel 70–230 mesh activity grade I (Merck Co.) was employed. Commercial reagents and solvents were purified according to the literature procedures



Scheme 2.

to match reported physical and spectral data. Known compounds used in this research were either purchased or prepared according to literature procedures and purified. Metal-free dichloromethane was obtained by first distilling from alumina (Woelm B activity grade I) and then from ethylenediaminetetraacetate (EDTA).

General procedure for photooxygenation. Through a soln of the particular cyclooctatetraenes (*ca* 15–150 mmol), *ca* 0.01–1.0 mmol hydroquinone and *ca* 5–500 mg tetraphenylporphine (TPP) in 100 ml acetone, contained in the photooxygenation apparatus described in Fig. 1, was bubbled a gentle stream of dry O_2 gas at subambient temps, while the mixture was irradiated with an Osram Vialox (NaV-TS) 250-W lamp. The reaction progress was monitored either by TLC or ^{1}H-NMR until *ca* 95% consumption of the starting material. Work-up and isolation consisted of roto-evaporation of the solvent at *ca* 0° and 15 Torr, followed by low temp chromatography. The details are given in the specific cases. CAUTION! The crude products contain dangerous peroxidic high-molecular-weight material, which may explode spontaneously when warmed above 10°. Also the endoperoxides are potentially dangerous and should be handled with care.

7,8-*Dioxabicyclo*[4.2.2]*deca*-2,4,9-*triene* (**1a**)

A soln of 15.0 g (0.144 mmol) freshly distilled **1**, *ca* 100 mg hydroquinone and *ca* 500 mg of TPP in 100 ml of acetone was photooxygenated at −15° for 14 d. The solvent was roto-evaporated at 0° and 15 Torr and the yellow, oily residue (CAUTION!) was taken up in 125 ml of CH_2Cl_2. On standing a yellowish green solid precipitated. Precipitation was completed by storing the mixture at −25° for 8 hr. The high-molecular-weight peroxidic ppt was removed by filtration (CAUTION!) and immediately destroyed by dissolving it in 100 ml of acetone and reducing with 25 ml of a 40% $Na_2S_2O_5$ aq. The green colored mother liquor was evaporated at 0° and 15 Torr to give 10.0 g of a green colored viscous oil, which was purified by silica gel chromatography (50:1 adsorbant–substrate ratio) at −10° eluting with 600 ml CH_2Cl_2. After roto-evaporation of the solvent at 0° and 15 Torr, 7.00 g of a

pale yellow oil were isolated, which by ^{1}H-NMR contained 90% **1a**, 4% terephthalaldehyde, 4% **1** and 2% of **1b**. This oil was taken up in 10 ml pentane and on standing at −25° it slowly crystallized. Recrystallization of the colorless solid from 2-propanol gave 5.20 g (26%) of colorless needles of **1a**, m.p. 35.5–37.5°. IR (CCl_4): 3060, 3040, 2910, 1400, 1290, 985, 880, 700, 665 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.90 (mc, 2H, 1,6-H), 6.01 (mc, 2H, 9,10-H), 6.03–6.19 (m, 4H, 2,3,4,5-H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 72.89 (d, C-1,6), 119.72 (d), 127.97 (d), 131.57 (d). MS (70 eV) *m/e*: 136 (15%, M^+), 107 (71%), 91 (100%, $C_7H_7^+$), 28 (60%), $C_8H_8O_2$ (136.2). (Found: C, 70.59; H, 6.19. Calc: C, 70.57; H, 5.92%.)

1α,4α,6α,9α,5,10-*Dioxatricyclo*[7.1.0.0^{4,6}]*deca*-2,7-*diene* (**1b**)

(A) *From* **1a** *by irradiation with UV-light.* A soln of 100 mg (0.734 mmol) **1a** in 10 ml CH_2Cl_2 was irradiated at −15° with the full UV-output (2.5 W) of an argon ion laser (Coherent Argon Ion Laser, Supergraphite Series CR 18 with UV Optics) for 2.5 hr (333, 351 and 364 nm lines). After roto-evaporation of the solvent at 30° and 15 Torr, the pale yellow solid (97.0 mg) was dissolved in 2 ml EtOAc and 0.5 ml pentane and on standing at −25° colorless needles crystallized. Recrystallization from 1 : 1 $CHCl_3$–EtOH gave 25.1 mg (25%) colorless needles, m.p. 162.5–163.5 (lit.[9] 165°).

(B) *From* **1a** *by reaction with the* Co(II) *complex of tetraphenylporphine* (Co-TTP). A soln of 50.0 mg (0.367 mmol) **1a** and 3.00 mg Co-TPP in 1 ml $CDCl_3$ was stirred 2 hr at 20°. High-molecular-weight material was removed by passing the mixture through a short silica gel column (*ca* 2 g). ^{1}H-NMR (90 MHz) and TLC showed **1b** as main product.

cis-*Cyclooct*-2-*en*-1,4-*diol* (**1c**)

A soln of 500 mg (3.67 mmol) **1a** in 70 ml MeOH was stirred with *ca* 10 mg Pd–C catalyst under a H_2-atmosphere for 3 hr at *ca* 20°. The mixture was concentrated by roto-evaporation at 20° and 15 Torr to 3 ml and particular matter removed by filtration over *ca* 0.5 g Celite. On standing, from the clear soln separated 300 mg colorless crystals, which were recrystallized from water to give 270 mg (51%) of **1c** as colorless plates, m.p. 159.5–160° (lit. 154°,[11a] 143–151°[11b]).

cis-1,4-*Cyclooctandiol* (**1d**)

(A) *From the unsaturated diol* **1c**. A suspension of 74.1 mg (0.520 mmol) of **16** and *ca* 10 mg Pd–C catalyst was stirred magnetically 12 hr at *ca* 20° under H_2. The catalyst was removed by filtration over 0.5 g Celite and the clear soln roto-evaporated at 20° and 15 Torr, to give 75 mg (95%) of a colorless oil. Molecular distillation at 100° and 0.01 Torr gave a viscous oil, which was recrystallized from CH_2Cl_2, affording 65 mg (81%) of **1d**, colorless needles, m.p. 84–86° (lit. 84–87°,[11b] 81–83°[10]).

(B) *From the endoperoxide* **1a**. A soln of 103 mg (0.758 mmol) **1a** and 10 mg Pd–C catalyst in 4 ml MeOH and 26 ml EtOAc was stirred for 24 hr at 0°. Removal of the catalyst by filtration over *ca* 0.5 g Celite and roto-evaporation of the solvent at 40° and 15 Torr yielded 98.1 mg (89%) of a colorless oil. Molecular distillation at 100° and 0.01 Torr afforded a highly viscous oil, which was crystallized from CH_2Cl_2 to give 85.0 mg (77%) of **1d**, colorless needles, m.p. 85–87° (lit. 84–87°,[11b] 81–83°[10]).

7,8-*Dioxabicyclo*[4.2.2]*decane* (**1e**)

To a suspension of 12.8 g (66.1 mmol) potassium azodicarboxylate in 250 ml CH_2Cl_2 were added, while stirring magnetically, 300 mg (2.21 mmol) **1a** in 40 ml CH_2Cl_2 at 0°. Into this mixture was administered dropwise a soln of 7.34 (122 mmol) AcOH in 60 ml CH_2Cl_2 over a period of 60 min while stirring. After complete addition, the mixture was stirred for 24 hr at *ca* 20°. Water (200 ml) was added and the aqueous layer extracted with 3 × 20 ml ether, the combined ether layers were washed with 20 ml 5% $KHCO_3$ aq and with 20 ml water and dried over $MgSO_4$. Roto-evaporation of the solvent at 20° and 15 Torr yielded 290 mg of a yellow viscous oil, which crystallized on standing at −25°. Chromatography on silica gel (50 : 1 adsorbant–substrate ratio) at −20° gave 100 mg unreacted **1a** and 54.3 mg (18%) of a colorless oil, which crystallized on standing at −25°. Sublimation at 40° and 0.01 Torr afforded 45.2 mg (14%) of colorless plates, m.p. 95–97° (lit.[12] 96–98°).

Epoxycyclooctatetraene (**1f**)

A soln of 285 mg (2.09 mmol) **1a** and *ca* 170 mg (*ca* 2.7 mmol) dimethylphosphine in 6 ml abs ether were stirred magnetically at −78° for 1 hr, then at 8° for 14 hr. Roto-evaporation of the solvent at 30° and 15 Torr afforded a black tar, which was distilled at 80° (bath temp) and 15 Torr to give 60 mg (24%) of **1f**. IR- and ^{1}H-NMR spectra (60 MHz) were in accordance with those, which were obtained by an independent synthesis of epoxide **1f** by oxidizing cyclooctatetraene with *m*-chloroperbenzoic acid.[13]

1 - *Methoxy- and* 9 - *methoxy* - 7,8 - *dioxabicyclo*[4.2.2*deca* - 2,4,9-*triene* (**3a**) *and* (**3b**)

A soln of 20.0 g (0.149 mmol) of **3**, *ca* 20 mg hydroquinone and *ca* 50 mg TPP was photooxygenated at −20° for 23 hr. After roto-evaporation of the solvent at 0° and 15 Torr, there were obtained 24.1 g of a yellow viscous oil, which was quickly (*ca* 2 min each time) triturated with 4 × 30 ml of a 12 : 1 mixture of cyclohexane and EtOH at 70°. On cooling the combined triturates to 0°, a yellow semi-solid separated, which was removed from the clear supernatant liquid by decantation and recrystallized from EtOAc affording 800 mg (4%) of **3c** as pale yellow needles, m.p. 132–133° (lit.[16] 128–130°).

Roto-evaporation of the solvent from the mother liquor of the aldehyde-ester **3c** at 0° and 15 Torr gave 27.6 g of a brown oil. Silica gel chromatography at −25° (100 : 1 adsorbant–substrate ratio) eluting with CH_2Cl_2 afforded two fractions, which were identified as **3a** and **3b**. Endoperoxide **3b** was eluted as first fraction (R_f = 0.39). After roto-evaporation of the solvent at 0° and 15 Torr there was obtained 2.25 g (11%) of a colorless liquid, which crystallized on standing at −25°. Recrystallization from cyclohexane gave 1.94 g (10%) of colorless plates, m.p. 52–53°. IR ($CDCl_3$): 3040, 2975, 2940, 2920, 2850, 1675, 1365, 1225, 1050, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.59 (s, 3H, OCH_3), 4.92 (ddd, 1H, 1-H), 4.98 (ddd, 1H, 6-H), 5.08 (dd, 1H, 10-H), 5.95 (dd, 1H, 4-H), 6.07 (mc, 1H, 2-H), 6.13 (ddd, 1H, 5-H), 6.15 (mc, 1H, 3-H); $J_{1,2}$ = 6.9 Hz, $J_{1,6}$ = 1.0 Hz, $J_{1,10}$ = 1.0 Hz, $J_{2,3}$ = 12.0 Hz, $J_{3,4}$ = 7.0 Hz, $J_{3,5}$ = 1.0 Hz, $J_{4,5}$ = 12.0 Hz, $J_{5,6}$ = 6.2 Hz, $J_{6,10}$ = 6.7 Hz. ^{13}C-NMR ($CDCl_3$, 22.6 MHz): δ 54.8 (q, OCH_3), 72.8 (d, C-1), 75.0 (d, C-6), 90.3 (d, C-10), 125.5 (d), 129.4 (d), 131.1 (d), 134.7 (d), 152.2 (s, C-9). MS (70 eV): *m/e* = 166 (11%, M^+), 151 (10%, $M-CH_3^+$), 135 (10%, $M-OCH_3^+$), 77 (100%, $C_6H_5^+$). (Found: C, 65.04; H, 5.99. Calc $C_9H_{10}O_3$ (166.2): C, 65.05; H, 6.07%.)

Endoperoxide **3a** eluted as second fraction (R_f = 0.34). After roto-evaporation of the solvent at 0° and 15 Torr, there was obtained 1.78 g (9%) of a colorless oil, which crystallized on standing at −25°. Recrystallization from pentane gave 1.54 (8%) colorless plates, m.p. 50–51.5°. IR ($CDCl_3$): 3025, 2970, 2940, 2840, 1485, 1480, 1445, 1425, 1230, 1150, 1060 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 270 MHz): δ 3.40 (s, 3H, OCH_3), 4.75 (dd, 1H, 6-H), 5.87 (mc, 2H, 2,3-H), 5.96 (d, 1H, 9-H), 6.00 (dd, 1H, 10-H), 6.12 (dd, 1H, 5-H), 6.32 (ddd, 1H, 4-H); $J_{3,4}$ = 5.0 Hz, $J_{4,5}$ = 13.0 Hz, $J_{5,6}$ = 7.0 Hz, $J_{6,10}$ = 5.5 Hz, $J_{9,10}$ = 10.0 Hz. ^{13}C-NMR ($CDCl_3$, 22.6 MHz): δ 51.2 (q, OCH_3), 72.0 (d, C-6), 100.5 (s, C-1), 121.0 (d), 121.5 (d), 125.4 (d), 129.3 (d), 130.5 (d), 135.9 (d). MS (70 eV) *m/e*: 166 (8%, M^+), 135 (15%, $M-OCH_3^+$), 134 (97%, $M-O_2^+$), 77 (100%, C_6H_5). (Found: C, 64.86; H, 6.40. Calc $C_9H_{10}O_3$ (166.2): C, 65.05; H, 6.07%.)

3-*Carbomethoxy*-6,7-*dioxatricyclo*[3.2.2.0^{2,4}]*non*-8-*ene* (**3d**)

A soln of 2.00 g (14.8 mmol) **3**, 230 mg (2.95 mmol) DMSO and *ca* 5 mg TPP was photooxygenated for 20 hr at −20°. After roto-evaporation of the solvent at 0° and 15 Torr, a red oily residue was obtained, which was dissolved in 3 ml EtOH at 40°. On standing at −30°, the product crystallized affording 500 mg light green needles, which were sublimed at 30° and 0.01 Torr to give 250 mg (91%) dimethylsulfone, m.p. 110°

(lit.[31] 110°). Roto-evaporation of the solvent from the mother liquor of the sulfone and silica gel chromatography at −20° eluting with $CHCl_3$ afforded 150 mg (7.5%) of **3d** as colorless plates, m.p. 94–95° (lit.[18] 95°).

9-and 2-Methoxy-7,8-diazabicyclo[4.2.2]deca-2,4,9-triene-N-methyl-7,8-dicarboximide (**3e**) *and* (**3f**)

A soln of 1.00 g (7.45 mmol) **3** and 930 mg (8.23 mmol) 4-methyl-1,2,4-triazole-3,5-dione (MTAD) in 25 ml CH_2Cl_2 was stirred at 20° for 4 hr. The solvent was roto-evaporated at 0° and 15 Torr to give 2.14 g of a yellow, viscous oil. Chromatography on silica gel (50:1 adsorbant–substrate ratio) eluting with 4:1 CH_2Cl_2–EtOAc afforded 759 mg of a yellow solid, consisting of a mixture of 9-methoxy- and 2-methoxyurazoles **3e** and **3f**, which were separated by fractional recrystallization from EtOH.

Urazole **3e**. 400 mg (22%), colorless needles, m.p. 138°. IR ($CDCl_3$): 3020, 2940, 2840, 1760, 1700, 1660, 1475, 1400, 1180, 1000 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 3.06 (s, 3H, NCH_3), 3.59 (s, 3H, OCH_3), 5.03 (dd, 1H, 6-H), 5.04 (d, 1H, 10-H), 5.13 (d, 1H, 1-H), 5.89 (dd, 1H, 4-H), 6.01 (dd, 1H, 2-H), 6.13 (dd, 1H, 3-H), 6.26 (dd, 1H, 5-H); $J_{1,2}$ = 6.2 Hz, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 6.4 Hz, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 5.2 Hz. ^{13}C-NMR ($CDCl_3$, 22.6 MHz): δ 25.3 (q, N−CH_3), 47.0 (d), 51.2 (d), 55.4 (q, OCH_3), 88.9 (d, C-10), 125.3 (d), 127.7 (d), 131.4 (d), 134.3 (d), 150.1 (s, C=O), 150.3 (s, C=O), 150.9 (s, C-9). MS (70 eV) *m/e*: 247 (45%, M^+), 232 (5%, M−CH_3^+), 216 (4%, M−OCH_3^+), 134 (38%, M−MTAD$^+$), 91 (100%, $C_7H_7^+$). (Found: C, 58.56; H, 5.11; N, 16.99. Calc $C_{12}H_{13}N_3O_3$ (247.3): C, 58.29; H, 5.30; N, 17.00%.)

Urazole **3f**. 80 mg (4%), colorless needles, m.p. 158°. IR ($CDCl_3$), 3060, 3010, 2950, 2840, 1760, 1700, 1630, 1590, 1475, 1400, 1210, 1175 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 3.05 (s, 3H, N−CH_3), 3.65 (s, 3H, OCH_3), 5.00 (dd, 1H, 6-H), 5.10 (d, 1H, 1-H), 5.13 (d, 1H, 3-H), 5.85 (dd, 1H, 5-H), 5.94 (mc, 2H, 9-,10-H), 6.01 (dd, 1H, 4-H). MS (70 eV) *m/e*: 247 (60%, M^+), 232 (6%, M−CH_3^+), 216 (5%, M−OCH_3^+), 134 (31%, M−MTAD$^+$), 91 (100%, C_7H_7). (Found: C, 57.92; H, 5.15; N, 17.04. Calc $C_{12}H_{13}N_3O_3$ (247.3): C, 58.29; H, 5.30; N, 17.00%.)

X-Ray crystallography of urazoles (**3e**) *and* (**3f**)

Clear, colorless crystals were optically centered on a Syntex four circle diffractometer. The intensities of all reflections were measured according to the ω-technique (MoKα, graphite-monochromator) using a scan-range of 1° and a scan-speed between 0.5 and 24.0 degrees min^{-1} as a function of the intensities of the reflections. In the range between $3.0° \leqslant 2\theta \leqslant 55.0°$ all reflections hkl with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL-System on an Eclipse S250 at the Max-Planck-Institut für Festkörperforschung was employed. All structures were solved by the direct phase determination. The parameters of the complete structure could be refined by anisotropic least squares cycles to the given *R*-values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Details of the measurements of the crystallographic results, positional and thermal parameters of the atoms of **3e** and **3f** and bond lengths and angles are given in Tables 2–5, respectively. Perspective drawings are given in Figs 2 and 3, respectively.

Table 2. X-Ray operations and results of urazoles **3e** and **3f**

Sample	**3f**	**3e**
Crystal size (mm)	0.5 × 0.3 × 0.25	0.35 × 0.2 × 0.2
Number of measured intensities	2005	3458
Number of observed reflections	1862	3186
Number of structure factors of the direct phase determination	75	374
R_{aniso}	0.044	0.050
Space group	C2/c	P $\bar{1}$
a (pm)	2286.6(13)	1011.8(4)
b (pm)	842.7(3)	1389.1(6)
c (pm)	1407.3(8)	976.5(4)
α (°)		99.10(3)
β (°)	120.55(3)	116.72(3)
γ (°)		78.18(3)
Number of formula units/cell	8	4
Calculated density ($g \cdot cm^{-3}$)	1.406	1.372

9-Phenyl-7,8-dioxabicyclo[4.2.2]deca-2,4,9-triene (**4a**)

A soln of 2.00 g (11.1 mmol) **4**, *ca* 10 mg hydroquinone and *ca* 15 mg TPP in 100 ml of acetone was photooxygenated at −10° for 34 hr. The solvent was removed by roto-evaporation at 0° (CAUTION!) and the residue taken up in 75 ml of CH_2Cl_2. On standing at −25°, a brown solid precipitated, which was removed by filtration. The clear orange filtrate was concentrated at 0° and 15 Torr to *ca* 5 ml volume and submitted to silica gel chromatography at −20°, eluting with 5:1 CH_2Cl_2–pentane (100:1 adsorbant–substrate ratio). After roto-evaporation of the solvent at 0° and 15 Torr, there was obtained 1.08 g (48%) of a colorless solid. Recrystallization from 2-propanol afforded 741 mg (33%) of **4a**, colorless plates, m.p. 73–74°. IR (KBr): 3020, 2920, 1600, 1500, 1080, 1000, 770, 670 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.12 (ddd, 1H, 6H), 5.34 (mc, 1H, 1-H), 5.97 (mc, 1H, 4-H), 6.08 (dd, 1H, 5-H), 6.26 (mc, 2H, 2,3-H), 6.32 (d, 1H, 10-H), 7.27–7.34 (m, 5H, phenyl-H); $J_{1,2}$ = 4.1 Hz, $J_{1,6}$ = 1.5 Hz; $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 11.1 Hz, $J_{5,6}$ = 5.5 Hz, $J_{6,10}$ = 5.0 Hz. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 72.88 (d), 75.06 (d), 116.00 (d), 125.78 (d), 126.14 (d), 127.74 (d), 128.73 (d), 130.11 (d), 130.99 (d), 132.10 (s), 132.85 (d), 135.94 (s). MS (70 eV) *m/e*: 212 (19%, M^+), 196 (12%, M−O^+), 167 (100%, M−$OOCH^+$), 77 (48%, C_6H_5). (Found: C, 79.37; H, 5.63. Calc $C_{14}H_{12}O_2$ (212.3): C, 79.23; H, 5.70%.)

1α,4α,6α,9α,2-Phenyl-5,10-dioxatricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**4b**)

A soln of 212 mg (1.00 mmol) of **4a** and *ca* 25 mg Co-TPP in 10 ml CH_2Cl_2 was heated for 2 hr at 35°. Roto-evaporation of the solvent at 30° and 15 Torr and chromatography of the dark red, oily residue (250 mg) on silica gel (140:1 adsorbant–substrate ratio) eluting with CH_2Cl_2 afforded 85.3 mg of a red oil (R_f = 0.45). Sublimation at 95° and 15 Torr yielded 70.2 mg (33%) of **4b** as colorless needles, m.p. 133–135°. IR ($CDCl_3$): 3080, 3060, 3030, 2970, 2920, 1600, 1500, 1450, 1430, 1260, 1075, 1055, 820 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 3.75 (m, 1H, 4-H), 3.79 (m, 1H, 6-H), 3.85 (mc, 1H, 9-H), 4.10 (mc, 1H, 1-H), 5.77 (br d, 1H, 7-H), 5.81 (br d, 1H, 8-H), 6.06 (mc, 1H, 3-H), 7.25–7.54 (m, 5H, phenyl-H); $J_{1,3}$ = 1.1 Hz, $J_{1,9}$ = 3.6 Hz, $J_{3,4}$ = 1.5 Hz, $J_{3,6}$ = 1.8 Hz, $J_{4,6}$ = 3.9 Hz, $J_{6,7}$ = 1.2 Hz, $J_{7,9}$ = 1.7 Hz, $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 1.8 Hz. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 54.29 (d), 55.20 (d), 55.38 (d), 56.02 (d), 122.56 (d), 126.42 (d), 127.06 (d), 127.36 (d), 128.26 (d), 128.48 (d), 137.40 (s), 127.54 (s). MS (70 eV) *m/e*: 212 (33%, M^+), 196 (3%, M−O^+), 183 (98%, M−CHO), 115 (100%, $C_7H_6O_2$), 77 (82%, C_6H_5). (Found: C, 79.07; H, 5.83. Calc $C_{14}H_{12}O_2$ (212.3): C, 79.22; H, 5.70%.)

1-Methyl- and 2-methyl-7,8-dioxabicyclo[4.2.2]octa-2,4,7-triene (**5a**) *and* (**5b**)

A soln of 2.07 g (17.5 mmol) **5**, *ca* 50 mg hydroquinone and *ca* 10 mg TPP in 100 ml acetone was photooxygenated for 50 hr at −20°. After roto-evaporation of the solvent at 0° and 15 Torr (CAUTION!), the residual oil was triturated with 75 ml CH_2Cl_2 and the greenish resinous semi-solid (845 mg) was removed by filtration over Celite. The solvent of the filtrate was roto-evaporated at 0° and 15 Torr and the residue chromatographed on silica gel (100:1 adsorbant–substrate ratio) at −20° with CH_2Cl_2, affording 761 mg (29%) of a colorless oil (R_f = 0.52; 85% peroxidic titer), which failed to

Table 3. Positional ($\times 10^4$) and thermal ($\times 10^3$) parameters in $Å^2$ of the atoms of urazole **3e*** and urazole **3f**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Urazole 3e									
Molecule A									
C(1)	878(4)	8302(2)	−180(4)	67(2)	46(2)	74(2)	12(1)	46(2)	−9(1)
C(2)	−237(4)	8071(3)	−1827(4)	61(2)	99(3)	73(2)	43(2)	44(2)	22(2)
C(3)	−559(4)	7183(4)	−2431(4)	48(2)	134(3)	53(2)	−7(2)	21(2)	−15(2)
C(4)	−19(4)	6186(3)	−1855(4)	58(2)	100(3)	74(2)	−19(2)	36(2)	−35(2)
C(5)	956(4)	5791(2)	−523(4)	70(2)	61(2)	83(2)	−19(2)	50(2)	−30(2)
C(6)	1839(3)	6320(2)	915(3)	63(2)	42(2)	57(2)	5(1)	31(2)	−8(1)
C(7)	2901(3)	6759(2)	650(3)	46(2)	52(2)	46(2)	−3(1)	20(1)	−11(1)
C(8)	2468(3)	7674(2)	155(3)	60(2)	49(2)	60(2)	2(1)	32(2)	−16(1)
N(9)	434(3)	8114(2)	959(3)	72(2)	45(1)	62(2)	5(1)	45(1)	−7(1)
N(10)	860(3)	7126(2)	1436(3)	90(2)	42(1)	72(2)	−1(1)	57(2)	−15(1)
C(11)	−67(4)	7043(2)	2044(3)	79(2)	59(2)	48(2)	−9(1)	35(2)	−35(2)
N(12)	−1011(3)	8008(2)	1999(3)	61(2)	65(2)	53(1)	−13(1)	36(1)	−27(1)
C(13)	−780(3)	8661(2)	1241(3)	61(2)	56(2)	51(2)	−7(1)	32(2)	−18(1)
O(70)	4248(2)	6050(2)	925(3)	56(1)	60(1)	77(2)	13(1)	28(1)	−7(1)
C(71)	5259(4)	6332(3)	488(4)	55(2)	80(2)	80(2)	6(2)	37(2)	−10(2)
O(110)	−48(3)	6285(2)	2535(3)	124(2)	69(1)	79(2)	−8(1)	62(2)	−50(1)
C(120)	−2073(4)	8296(3)	2702(4)	80(2)	105(3)	73(2)	−18(2)	53(2)	−38(2)
O(130)	−1504(3)	9536(2)	911(3)	82(2)	64(1)	84(2)	6(1)	51(1)	0(1)
Molecule B									
C(1)	2362(3)	8287(2)	−3970(3)	58(2)	52(2)	59(2)	1(1)	39(2)	−9(1)
C(2)	3591(4)	8643(2)	−2524(4)	103(3)	53(2)	55(2)	−8(1)	48(2)	−29(2)
C(3)	5102(5)	8208(3)	−1843(4)	92(3)	83(2)	52(2)	−3(2)	23(2)	−47(2)
C(4)	6088(4)	7264(3)	−2077(4)	55(2)	99(3)	63(2)	11(2)	17(2)	−28(2)
C(5)	5886(3)	6591(3)	−3218(4)	50(2)	78(3)	70(2)	15(2)	30(2)	−12(2)
C(6)	4452(3)	6657(2)	−4696(3)	51(2)	48(2)	56(2)	4(1)	32(1)	−8(1)
C(7)	3255(3)	6471(2)	−4332(3)	50(2)	48(2)	51(2)	0(1)	27(1)	−15(1)
C(8)	2323(3)	7220(2)	−3930(3)	52(2)	54(2)	57(2)	−1(1)	32(1)	−17(1)
N(9)	2588(3)	8353(2)	−5339(3)	55(2)	48(1)	50(1)	4(1)	31(1)	−7(1)
N(10)	3900(3)	7639(2)	−5372(3)	55(2)	51(1)	59(2)	7(1)	36(1)	−9(1)
C(11)	4592(3)	8051(2)	−5947(3)	56(2)	63(2)	41(2)	−3(1)	23(1)	−24(1)
N(12)	3681(3)	9033(2)	−6296(3)	63(2)	60(2)	45(1)	3(1)	25(1)	−25(1)
C(13)	2535(3)	9252(2)	−5808(3)	63(2)	52(2)	41(2)	3(1)	21(1)	−14(1)
O(70)	3398(2)	5465(1)	−4390(3)	71(1)	49(1)	83(2)	0(1)	47(1)	−18(1)
C(71)	2405(4)	5174(2)	−3956(4)	85(2)	61(2)	83(2)	4(2)	47(2)	−31(2)
O(110)	5735(2)	7641(2)	−6146(3)	61(1)	83(2)	71(1)	3(1)	41(1)	−23(1)
C(120)	3959(4)	9750(3)	−7004(4)	95(3)	77(2)	64(2)	13(2)	35(2)	−39(2)
O(130)	1649(3)	69(2)	−5798(3)	90(2)	55(1)	73(2)	14(1)	43(1)	−2(1)
Urazole 3f									
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	3831(1)	8246(3)	2613(2)	43(1)	41(1)	41(1)	0(1)	24(1)	5(1)
C(2)	3060(1)	8363(3)	2052(2)	45(1)	40(1)	50(1)	−10(1)	27(1)	−7(1)
C(3)	2642(1)	9018(3)	1065(2)	39(1)	62(2)	55(2)	−7(1)	17(1)	−10(1)
C(4)	2769(1)	9803(4)	267(2)	49(1)	74(2)	47(2)	6(1)	9(1)	−5(1)
C(5)	3323(1)	260(3)	239(2)	59(2)	49(2)	47(1)	7(1)	21(1)	−3(1)
C(6)	4059(1)	58(3)	1115(2)	54(1)	25(1)	57(1)	3(1)	31(1)	1(1)
C(7)	4195(1)	762(3)	2189(2)	37(1)	33(1)	60(2)	−11(1)	21(1)	−2(1)
C(8)	4104(1)	9914(3)	2891(2)	33(1)	47(1)	45(1)	−13(1)	15(1)	2(1)
N(9)	4035(1)	7494(2)	1900(2)	65(1)	28(1)	61(1)	2(1)	46(1)	3(1)
N(10)	4269(1)	8387(2)	1323(2)	76(1)	27(1)	58(1)	2(1)	48(1)	2(1)
C(11)	4392(1)	7401(3)	687(2)	44(1)	34(1)	39(1)	0(1)	20(1)	3(1)
N(12)	4297(1)	5889(2)	974(2)	47(1)	27(1)	54(1)	−5(1)	29(1)	1(1)
C(13)	4076(1)	5937(3)	1726(2)	36(1)	30(1)	55(1)	1(1)	25(1)	1(1)
O(20)	2867(1)	7738(2)	2740(1)	54(1)	59(1)	66(1)	−3(1)	41(1)	−2(1)
C(21)	2169(1)	7925(4)	2448(3)	55(2)	88(2)	91(2)	−6(2)	48(2)	−12(2)
O(110)	4569(1)	7755(2)	31(1)	87(1)	50(1)	60(1)	5(1)	52(1)	8(1)
C(120)	4385(2)	4438(3)	498(3)	106(2)	33(1)	107(3)	−15(2)	74(2)	1(2)
O(130)	3952(1)	4824(2)	2144(2)	82(1)	31(1)	106(2)	11(1)	68(1)	2(1)

* The form of the thermal ellipsoid is $\exp -2^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)$.

Table 4. Bond lengths (pm) for urazoles **3f** and **3e***

	3f	3e(A)	3e(B)
C(1)—C(2)	152.5(3)	152.2(4)	149.5(4)
C(1)—C(8)	150.7(3)	158.0(4)	149.8(4)
C(1)—N(9)	145.0(4)	144.8(5)	147.3(5)
C(2)—C(3)	134.1(3)	131.8(6)	140.7(5)
C(4)—C(3)	145.5(5)	148.1(6)	153.0(5)
C(4)—C(5)	134.2(5)	134.7(5)	130.5(5)
C(6)—C(5)	150.8(3)	145.7(4)	151.6(4)
C(6)—C(7)	150.3(4)	147.0(5)	148.4(5)
C(6)—N(10)	146.9(3)	152.1(4)	150.0(4)
C(7)—C(8)	131.8(4)	134.8(4)	138.8(4)
N(9)—N(10)	139.8(4)	143.7(3)	149.5(3)
C(11)—N(10)	135.0(4)	134.6(6)	132.4(5)
C(11)—N(12)	138.6(3)	147.2(4)	147.5(4)
C(11)—O(110)	121.9(4)	121.7(4)	126.3(4)
N(12)—C(13)	138.5(4)	137.2(5)	140.4(5)
N(12)—C(120)	145.7(4)	147.9(6)	143.4(5)
C(13)—N(9)	134.8(3)	142.1(4)	138.0(4)
C(13)—O(130)	121.4(3)	129.0(3)	129.6(4)
O(20)—C(2)	135.8(4)	—	—
O(20)—C(21)	144.1(4)	—	—
O(70)—C(7)	—	145.1(3)	137.1(3)
O(70)—C(71)	—	141.1(5)	139.9(6)

* The standard deviations are given in parentheses.

Table 5. Bond angles for urazoles **3f** and **3e***

	3f	3e(A)	3e(B)
C(2)—C(1)—C(8)	106.9(2)	110.5(3)	110.3(2)
C(2)—C(1)—N(9)	111.3(2)	113.5(3)	112.0(3)
C(8)—C(1)—N(9)	110.5(2)	108.0(2)	106.0(2)
C(1)—C(2)—C(3)	126.2(3)	124.6(3)	127.6(3)
C(1)—C(2)—O(20)	108.3(2)	—	—
C(3)—C(2)—O(20)	125.4(2)	—	—
C(2)—C(3)—C(4)	132.1(3)	134.2(3)	138.2(3)
C(3)—C(4)—C(5)	135.6(2)	136.7(3)	132.7(6)
C(4)—C(5)—C(6)	128.5(3)	126.9(3)	121.6(3)
C(5)—C(6)—C(7)	110.5(2)	107.3(3)	107.0(3)
C(5)—C(6)—N(10)	112.8(2)	111.8(2)	116.1(2)
C(7)—C(6)—N(10)	107.4(2)	109.7(2)	105.4(2)
C(6)—C(7)—C(8)	120.6(2)	118.2(3)	123.2(3)
C(6)—C(7)—O(70)	—	109.5(2)	105.0(2)
C(8)—C(7)—O(70)	—	132.2(3)	131.7(3)
C(7)—C(8)—C(1)	120.9(2)	124.0(3)	122.0(3)
C(1)—N(9)—N(10)	121.4(2)	116.4(2)	112.0(2)
C(1)—N(9)—C(13)	129.0(2)	125.8(2)	121.4(2)
N(10)—N(9)—C(13)	109.6(2)	113.8(3)	110.9(3)
C(6)—N(10)—C(11)	127.9(2)	129.2(3)	124.9(3)
C(6)—N(10)—N(9)	116.7(2)	123.7(3)	125.4(3)
C(11)—N(10)—N(9)	108.9(2)	105.1(2)	109.3(2)
N(10)—C(11)—N(12)	104.9(2)	107.3(3)	103.0(3)
N(10)—C(11)—O(110)	127.8(2)	123.0(3)	125.4(3)
N(12)—C(11)—O(110)	127.3(2)	129.6(4)	131.6(3)
C(11)—N(12)—C(13)	111.6(2)	112.2(3)	114.9(3)
C(11)—N(12)—C(120)	124.0(3)	126.4(3)	124.1(3)
C(13)—N(12)—C(120)	124.3(2)	121.4(3)	120.9(3)
N(12)—C(13)—N(9)	104.7(2)	101.3(2)	101.2(2)
N(12)—C(13)—O(130)	127.8(2)	127.3(3)	130.2(3)
N(9)—C(13)—O(130)	127.5(3)	131.5(4)	128.6(4)
C(2)—O(20)—C(21)	117.9(2)	—	—
C(7)—O(70)—C(71)	—	114.6(2)	111.7(3)

* The standard deviations are given in parentheses.

crystallize at −30°. All efforts of purifying this complex product mixture by chromatography were unsuccessful, but the spectra data point out that the main products are **5a** and **5b**. This product mixture was used for further reactions.

1α,4α,6α,9α,1 - Methyl - 5,10 - dioxatricyclo[7.1.0.0^{4,6}]deca - 2,7-diene (**5c**)

A soln of 540 mg (3.60 mmol) of **5a** and **5b** and *ca* 30 mg Co-TTP in 10 ml CH_2Cl_2 was stirred 15 hr at *ca* 20°. Rotoevaporation of the solvent at 30° and 15 Torr and chromatography of the dark brown residue (580 mg) on silica gel (100:1 adsorbant–substrate ratio), eluting with CH_2Cl_2, yielded a red crystalline solid (385 mg). After sublimation at 40° and 15 Torr, 340 mg of a colorless crystalline product were obtained, which was recrystallized from pentane to give 320 mg (56%) of **5c** as colorless needles, m.p. 73–74°. IR (CCl_4): 3040, 2970, 2920, 1430, 1080, 1000, 920, 840 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ 1.11 (s, 3H, CH_3), 2.99–3.01 (m, 1H, 9-H), 3.12–3.4 (m, 2H, 4-H, 6-H), 5.43 (ddd, 1H, 3-H), 5.48 (dddd, 1H, 8-H), 5.50–5.53 (m, 2H, 2-H, 7-H); $J_{2,3}$ = 10.6 Hz, $J_{2,4}$ = 1.2 Hz, $J_{2,9}$ = 0.8 Hz, $J_{3,4}$ = 1.0 Hz, $J_{3,6}$ = 0.8 Hz, $J_{4,6}$ = 4 Hz, $J_{4,7}$ = 1.0 Hz, $J_{4,8}$ = 0.8 Hz, $J_{6,7}$ = 1.2 Hz, $J_{6,8}$ = 0.8 Hz, $J_{7,8}$ = 10.8 Hz, $J_{7,9}$ = 1.0 Hz, $J_{8,9}$ = 1.5 Hz. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 23.00 (q, CH_3), 54.75 (d), 54.80 (d), 61.39 (s, C-1), 61.63 (d), 124.93 (d), 126.49 (d), 128.17 (d), 130.75 (d). MS (70 eV) *m/e*: 150 (0.3%, M^+), 135 (4%, $M-CH_3$), 107 (61%, $M-COCH_3$), 77 (100%, C_6H_5). (Found: C, 72.23; H, 6.41. Calc $C_9H_{10}O_2$ (150.2): C, 71.98; H, 6.71%.)

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