

## 81. Conformational Analysis of Endoperoxides Grafted onto Bicyclo[2.2.n]alkanes as a Test of the Rigidity of the Bicyclic Skeleton. Photo-oxidation of [2.2.2]Hericene and 2,3,5,6-Tetramethylidene-bicyclo[2.2.n]alkanes<sup>1)</sup>

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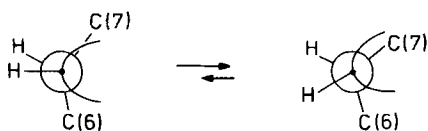
The photo-oxidation of [2.2.2]hericene (**6**) gave successively the endoperoxides **11** (9,10,11,12-tetramethylidene-4,5-dioxatricyclo[6.2.2.0<sup>2,7</sup>]dodec-2(7)-ene), the bis-endoperoxide **16** (15,16-dimethylidene-4,5,11,12-tetraoxatetracyclo[6.6.2.0<sup>2,7</sup>.0<sup>9,14</sup>]hexadeca-2(7),9(14)-diene), and the tris-endoperoxide **19** (4,5,11,12,17,18-hexaoxapentacyclo[6.6.6.0<sup>2,7</sup>.0<sup>9,14</sup>.0<sup>15,20</sup>]icosa-2(7),9(14),15(20)-triene). The endoperoxides **11**, **16**, and **19** were formed in the presence or in the absence of a dye sensitizer. The sensitized photo-oxidations of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**4**), 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**5**), 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**7**), and 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**8**) gave successively the corresponding mono-endoperoxides **9**, **10**, **12**, and **13** and the bis-endoperoxides **14**, **15**, **17**, and **18**, respectively. Low-temperature NMR spectra of the bis-endoperoxides **14** and **16** indicated that their *C*<sub>2</sub> and *C*<sub>s</sub> conformers have the same stability. Similarly, there was no difference in the enthalpy of the *D*<sub>3</sub> and *C*<sub>2</sub> conformers of the tris-endoperoxide **19**. The following reactivity sequence was observed for the sensitized photo-oxidations of **6–8** and 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**23**): **6** + <sup>1</sup>O<sub>2</sub> → **11** > **7** + <sup>1</sup>O<sub>2</sub> → **12** > **8** + <sup>1</sup>O<sub>2</sub> → **13** > **23** + <sup>1</sup>O<sub>2</sub> → **24**, a trend parallel with that reported for the ethylenetetra-carbonitrile (TCNE) cycloadditions to the same polyenes. The rate-constant ratios *k*<sub>1</sub>/*k*<sub>2</sub> and *k*<sub>2</sub>/*k*<sub>3</sub> for the three successive photo-oxidations of [2.2.2]hericene (**6**) did not differ significantly from unity, in contrast with the *Diels-Alder* additions of **6**. Similarly, the rate-constant ratios *k*<sub>1</sub>/*k*<sub>2</sub> for the two successive photo-oxidations of tetraenes **7** and **8** were significantly smaller than those reported for the successive TCNE cycloadditions to **7** to **8**. The endoperoxide formations are not sensitive to the change in the exothermicity of the reactions but they are sensitive to the electronic properties (IP's) of the polyenes.

**Introduction.** – According to *Houk* and coworkers [1b], the pyramidalization of the double bond in bicyclo[2.2.1]hept-2-ene (**1**) and *syn*-sesquiorbornene **2** [2] is due to torsional interactions between the alkene and the allylic substituents. This can be visualized by using the model of 'banana' bonding orbitals for the  $\sigma$  and  $\pi$  electrons of the C=C



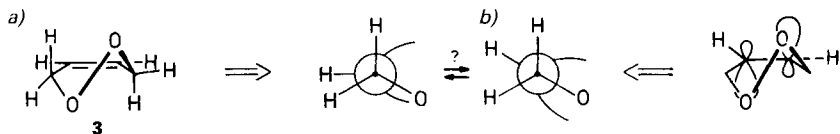
<sup>1)</sup> Interaction between non-conjugated chromophores, Part 24. Part 23, see [1a]. For a preliminary report, see communication No. ONII-10, Autumn Meeting of the Swiss Chemical Society, Bern, Oct. 18, 1985.

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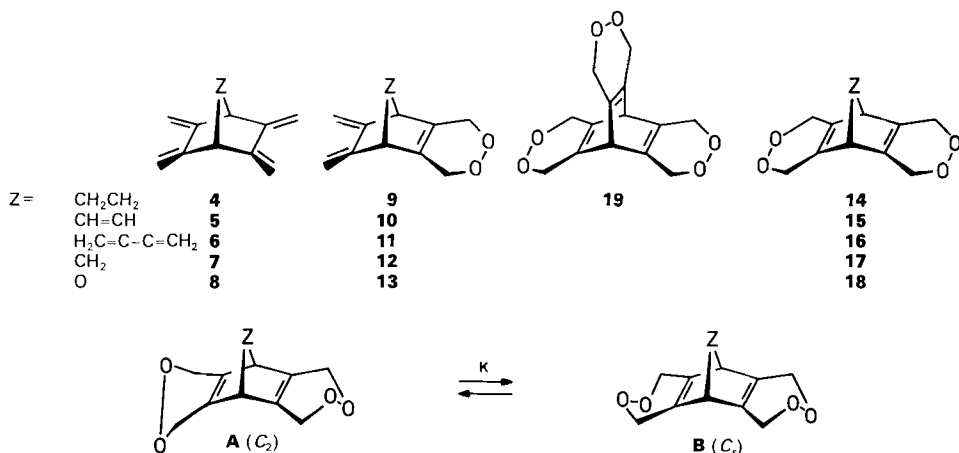
Fig. 1. Newman projections along bond  $C(1)-C(2)$  in **1**

bonds (Fig. 1). The same model allows one to interpret also the eclipsed structure of propene [3].

The stable conformation of 3,6-dihydro-1,2-dioxines (endoperoxides) is a half-chair [4]. In the case of **3**, partial eclipsing is expected between the alkene and the allylic bonds as shown in Fig. 2. Following Houk's arguments, some distortion from planarity is thus

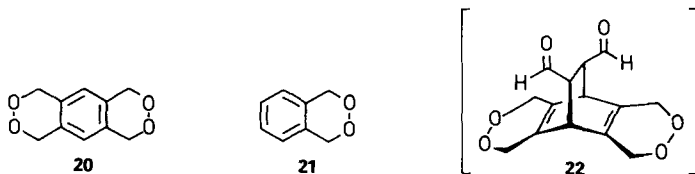
Fig. 2. Newman projections along bond  $C(3)-C(4)$  in **3**. a) For planar, b) for pyramidalized alkene.

expected for the olefinic C-atoms. In order to test this hypothesis, we have prepared the bis-endoperoxides **14-18** and the tris-endoperoxide **19** by photo-oxidation of the corresponding polyenes **4-8**. By low-temperature NMR spectroscopy [4], one expects to observe two conformers **A** and **B**, in the case of the bis-endoperoxides. If the bicyclic skeleton is a flexible one (see *e.g.* [5]), the hypothetical distortions shown in Fig. 2b for the alkenes should induce distortions of the bicyclic framework (*e.g.* a twist about the axis passing through the bridgehead centres) and make **A** and **B** of different stability ( $K \neq 1$ ). In contrast, if the bicyclic skeleton is rigid (see for example the structure of [2.2.2]hericene (**6**) [6] and related molecules [7]), **A** and **B** are expected to have similar stability and thus  $K \approx 1$ . We show that the latter hypothesis fits better the results obtained for the bis-endoperoxides **14** and **16**, and for the tris-endoperoxide **19**.



We have also evaluated the rates of photo-oxidation of polyenes **6-8** and compared them with those reported for their *Diels-Alder* additions to strong dienophiles.

**Results and Discussion.** – Sensitized (5,10,15,20-tetraphenylporphine (TPP)) photo-oxidation ( $\text{CH}_2\text{Cl}_2$ ,  $\text{O}_2$  bubbling,  $-25$  to  $0^\circ$ ,  $\text{I}_2$  lamp) of polyenes **4–8** gave the corresponding endoperoxides **9–13** which were oxidized under the same conditions into the corresponding bis-endoperoxides **14–18**. In the case of [2.2.2]hericene (**6**), prolonged irradiation led to the formation of the tris-endoperoxide **19**. The endoperoxides **9–19** were unstable compounds, and their isolation as pure materials was problematic. Their tendency to polymerise increased rapidly on concentrating the solutions of the photo-oxidations. These compounds were very sensitive to traces of acid or base, thus making their purification by the usual chromatography techniques low-yield processes. In the case of **19**, decomposition was accompanied by the formation of the unstable bis-endoperoxide **20**. The latter polymerized rapidly at  $20^\circ$  in dilute solutions. This was no surprise as the known mono-endoperoxide **21** was also reported to be an unstable compound [8].



The formation of **20** can be interpreted in terms of the intermediacy of the bis-aldehyde **22** which undergoes a facile cycloreversion giving **20**. Weak bases or acids are capable of promoting the rearrangement **19**→**22** [9]. The aromaticity of **20** provides the driving force for the cycloreversion.

The photo-oxidation of **4–8** could also be performed in the presence of a heterogenous sensitizer such as 'Sensitox' (Rose Bengal fixed on a polymer). Under these conditions, the endoperoxides **9** and **11** could be isolated.

The mono-endoperoxide **13** has already been reported [9]. It was then found that the photo-oxidation of **13** into the bis-endoperoxide **18** was a very slow process. By monitoring the reaction using 360-MHz  $^1\text{H-NMR}$  (without concentrating the irradiated solutions), we were able to observe **18**, a compound which decomposed rapidly at  $-20^\circ$  on concentration of the solution. The photo-oxidation of triene **23**, an analog of **8**, was also found to be an extremely slow process [9]. Again, using high-field  $^1\text{H-NMR}$  to monitor the reaction, the corresponding endoperoxide **24** could be observed at  $-20^\circ$ . The latter was rapidly decomposed on concentrating the irradiated solution.



The structures of the mono-endoperoxides **9**, **11**, and **13** (see [7]), of the bis-endoperoxides **14–18**, and of the tris-endoperoxides **19** were given by their mode of formation and their spectral data (see *Exper. Part*). With the exception of **11** which could be purified by recrystallization, no elemental analysis could be obtained as the endoperoxides decomposed rapidly in the condensed state.

*Conformation of the Bis- and Tris-endoperoxides.* At  $-100^\circ$ , the ring inversion of the 3,6-dihydro-1,2-dioxines is blocked on the NMR time scale [4] [10]. The low-temperature 360-MHz  $^1\text{H}$ -NMR spectrum of the bis-endoperoxide **16** (Fig. 3a) displayed an apparent  $t$  for the bridgehead protons. At  $25^\circ$  this signal was a  $s$  at 3.76 ppm. Thus, the low-temperature spectrum was consistent with a 1:1 equilibrium of the two conformers **A** and **B**. The central peak of the  $t$  belongs to **A** which possesses two identical bridgehead protons because of the  $C_2$  axis of symmetry. The two lateral peaks correspond to the two magnetically different bridgehead protons of **B**. The low-temperature 90-MHz  $^{13}\text{C}$ -NMR spectrum of **16** (Fig. 3b) gave also a 1:1 ratio for the two slowly interconverting conformers **A** and **B**. The comparison of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **16** (Fig. 3a, b) established a correlation factor for the integration of the  $^{13}\text{C}$  peaks in the  $^{13}\text{C}$ -NMR spectra of these endoperoxides (see below).

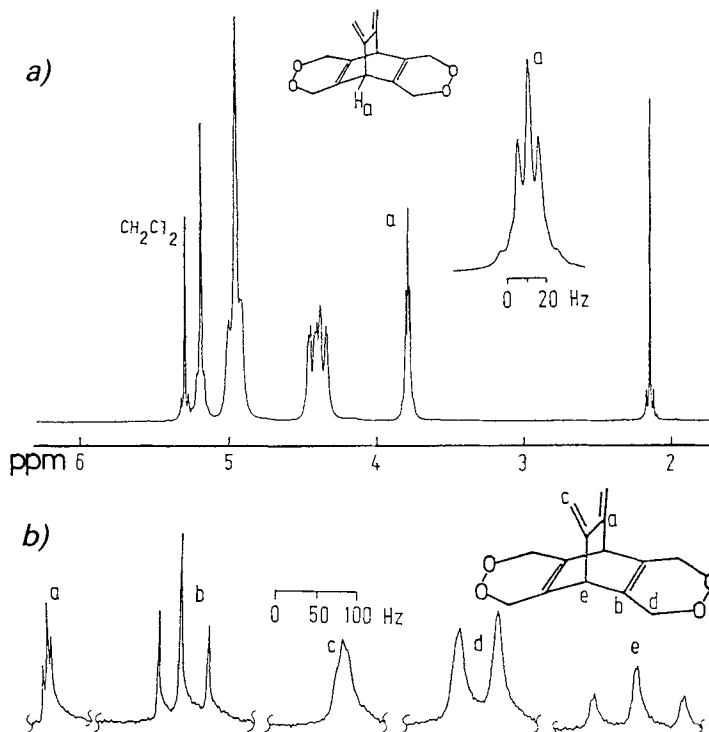


Fig. 3. a)  $^1\text{H}$ -NMR (360 MHz) and b)  $^1\text{H}$ -decoupled  $^{13}\text{C}$ -NMR (90 MHz) spectrum of **16** in  $\text{CD}_2\text{Cl}_2/(\text{CBrF}_2)_2$  1:1 at  $-100^\circ$

The low-temperature  $^1\text{H}$ -NMR spectra of **14**, **15**, and **17–19** did not allow one to distinguish the signals of the corresponding conformers. The low-temperature 90-MHz  $^{13}\text{C}$ -NMR spectra were no better in resolving the C-signals, except in the cases of the bis-endoperoxides **14** (Fig. 4), **16** (Fig. 3b), and of the tris-endoperoxide **19** (Fig. 5). The spectrum of **14** was consistent with the existence of two conformers of type **A** and **B** of similar stability. This indicates that the hypothetical pyramidalization of the olefinic C-atoms of one of the endoperoxide moiety of **15** is not perturbed by the distortions

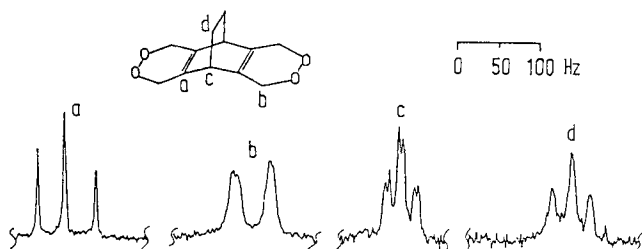
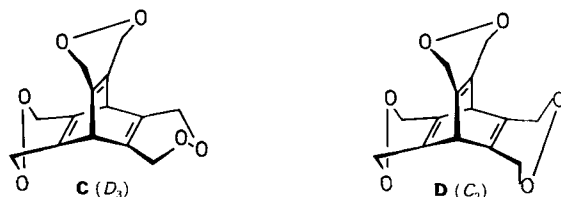


Fig. 4.  $^1\text{H}$ -Decoupled  $^{13}\text{C}$ -NMR (90 MHz) spectrum of **14** in  $\text{CDCl}_2/(\text{CBrF}_2)_2$  1:1 at  $-100^\circ$

imposed by the second endoperoxide moiety. The hypothetical transmission effect due to the flexibility of the bicyclic skeleton is, therefore, not detected by the low-temperature spectra of **14** and **16**. With these results, the chances of detecting such an effect with the other endoperoxides were very slim as **14** was expected to possess the most flexible skeleton out of **14**–**19** [7].



The low-temperature  $^1\text{H}$ -decoupled 90-MHz  $^{13}\text{C}$ -NMR spectrum of the tris-endoperoxide **19** (Fig. 5) showed to broad *s*'s for the  $\text{CH}_2$  (72.0 ppm) and the bridgehead C-atoms (47.0 ppm). However, 4 peaks of similar intensity were observed for the olefinic C-atoms. This was consistent with a 1:3 equilibrium of conformers **C** and **D**. This implies that **C** and **D** have the same enthalpy. The 1:3 ratio arises from their difference in symmetry which makes **D** with the  $\text{C}_2$  axis of symmetry (three pairs of enantiomers) three times more abundant than **C** with its  $\text{C}_3 \times \text{C}_2$  axes of symmetry (2 enantiomers). In fact, there are three equivalent possibilities to convert **C** into **D** by ring inversion of one endoperoxide moiety, whereas there is only one possibility to convert **D** into **C** by ring

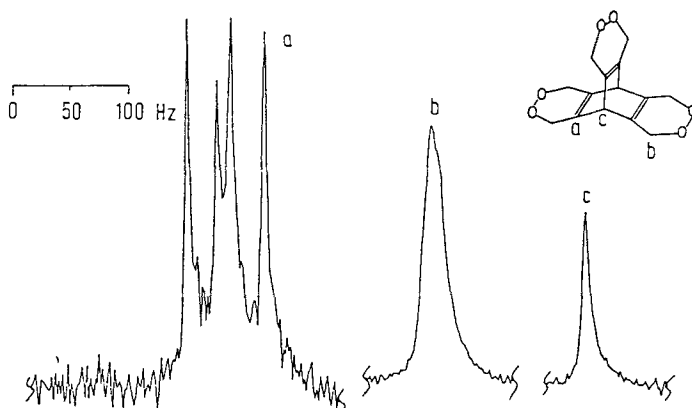
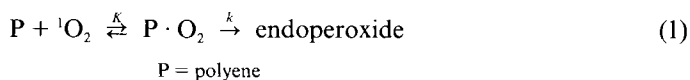


Fig. 5.  $^1\text{H}$ -Decoupled  $^{13}\text{C}$ -NMR (90 MHz) spectrum of **19** in  $\text{CD}_2\text{Cl}_2$  at  $-90^\circ$

inversion of the endoperoxide moieties. One expects one *s* for the 6 olefinic C-atoms of **C** and 3 signals of equal intensity for those of **D**, consistently with the <sup>13</sup>C-NMR spectrum reproduced in Fig. 5.

*Relative Rates of Endoperoxide Formation.* Singlet O<sub>2</sub> [4 + 2]-cycloadditions to conjugated dienes have activation parameters that make them different in character from the topologically similar *Diels-Alder* additions. Endoperoxide formations, like many reactions of singlet O<sub>2</sub> [11], have enthalpies of activation near zero [12]. *Diels-Alder* additions, on the other hand, have relatively large activation enthalpies [7] [13]. It was suggested that the near zero activation enthalpy for the endoperoxide formation is indicative of the reversible formation of an exciplex on the reaction coordinate [11] [12] [14] [15]. Recently, *Clennan et al.* [15] have shown that the rate of reaction of <sup>1</sup>O<sub>2</sub> with a large number of furan and cyclopentadiene derivatives varies with the electron-density distribution in the dienes. For exocyclic *s-cis*-butadienes grafted onto rigid bicyclo[2.2.1]heptane skeletons, we have found that the rates of formation of the corresponding endoperoxides depend on the ionization potentials of the conjugated dienes, as do the rates of their *Diels-Alder* reactions toward a strong dienophile such as ethylenetetracarbonitrile (TCNE) [7]. These data imply that the equilibrium constant *K* for the exciplex (PO<sub>2</sub>) formation or/and the rate constant *k* of the collapse of PO<sub>2</sub> into the corresponding endoperoxide (Eqn. 1) depend on the electronic structure of the diene [15].



We have shown that the *Diels-Alder* reactivity of the polyenes **4–8** and of the corresponding mono-adducts depends not only on their ionization potentials but also on the exothermicity of the cycloaddition [7] [16], in agreement with the *Dimroth* [17] or the *Bell-Evans-Polanyi* principle [18]. For instance, while the two first successive cycloadditions of TCNE to the [2.2.2]hericene (**6**) have similar rate constants (*k*<sub>1</sub>/*k*<sub>2</sub> = 8 at 298 K) and the same activation enthalpy ( $\Delta H_2^\ddagger = 11.3 \pm 0.2$  kcal/mol;  $\Delta H_2^\ddagger = 10.9 \pm 0.5$  kcal/mol), the addition of the third equivalent of TCNE was a much slower reaction (*k*<sub>2</sub>/*k*<sub>3</sub> = 312 at 298 K) with a higher activation enthalpy ( $\Delta H_3^\ddagger = 15 \pm 3$  kcal/mol) [7]. The reactions yielding the tris-adducts generate barrelene derivatives that are more strained than the corresponding bis-adducts and mono-adducts. Thus, the cycloadditions giving barrelene derivatives were less exothermic than those giving adducts that are not barrelene derivatives; the former were found to be slower reactions than the latter. We were interested to find out whether the successive photo-oxidations of **6**, and of the tetraenes **7** and **8** would yield rate ratios that did or did not parallel those measured for the *Diels-Alder* additions of **6–8** to TCNE.

Our kinetic data for the sensitized (TPP) photo-oxidation of **6–8** and of triene **23** are reported in the *Table*. They were obtained by measuring the rate of disappearance of the polyenes **6–8** and **23** and the rate of appearance of the corresponding endoperoxides **11–13**, **16–19**, and **24** by 360-MHz <sup>1</sup>H-NMR spectroscopy (see *e.g.* Fig. 6). Polyenes **6–8** and **23** were found to be poor physical quenchers of the photo-oxidation of cyclopentadiene (see *e.g.* [9] [11] [19]). No evidence was obtained for the corresponding endoperoxides to act as physical quenchers of <sup>1</sup>O<sub>2</sub>. In the presence of DABCO (1,4-diazabicyclo[2.2.2]octane), the photo-oxidations were retarded [9]. Moreover, when <sup>1</sup>O<sub>2</sub> was generated by thermal decomposition of the endoperoxide derived from 9,10-diphenylanthracene

Table. Global First-Order Rate Constants  $k_i$  (see Eqn. 9) for the 5,10,15,20-Tetraphenylporphine-Sensitized Photo-oxidation of **6-8, 11-13, 16, and 23** in  $CDCl_3^a$ 

Poly-ene	Initial concentration [mol/dm <sup>3</sup> ]	$k_i \cdot 10^5$ [s <sup>-1</sup> ]	Temperature [K]	$k_i/k_{i+1}$ ( <sup>1</sup> O <sub>2</sub> ) <sup>b</sup>	$k_{TCNE}^H \cdot 10^4$ at 298 K [dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ]	$k_i/k_{i+1}$ (TCNE) <sup>b</sup>	IP [eV]
<b>6</b>	$9.0 \cdot 10^{-3}$	$k_1 = 3960 \pm 10$	$253 \pm 2$		1360 [7]		8.38 [25]
<b>11</b>	$(4 \cdot 10^{-4})^c$	$k_2 = 1420 \pm 40$		$k_1/k_2 = 1.8$	156 <sup>d</sup>	6	
<b>16</b>		$k_3 = 175 \pm 10$		$k_2/k_3 = 4.1$	0.5 <sup>d</sup>	146	
<b>6</b>	$8.2 \cdot 10^{-3}$	$k_1 = 2.94 \pm 0.06$	$268 \pm 2$				
<b>11</b>	$(0.0)^c$	$k_2 = 3.54 \pm 0.5$		$k_1/k_2 = 0.6$			
<b>16</b>		$k_3 = 7.5 \pm 3.3$		$k_2/k_3 = 0.2$			
<b>7</b>	$1.27 \cdot 10^{-2}$	$k_1 = 500 \pm 35$	$258 \pm 2$		255 [16c]		8.34 [27]
<b>12</b>	$(4 \cdot 10^{-4})^c$	$k_2 = 37 \pm 3$		$k_1/k_2 = 6.8$	0.7	182	
<b>8</b>	$1.33 \cdot 10^{-2}$	$k_1 = 25 \pm 3$	$268 \pm 2$		1.5 [16c]		8.74 [27]
<b>13</b>	$(6 \cdot 10^{-4})^c$	$k_2 = 0.8 \pm 0.4$		$k_1/k_2 = 15.6$	0.004	188	
<b>23</b>	$2.5 \cdot 10^{-2}$ $(2 \cdot 10^{-3})^c$	$k_1 = 0.17 \pm 0.02$	$268 \pm 2$	-	$\leq 0.5$ [16c]		8.87 [26]

<sup>a</sup>) The reactions were monitored by 360-MHz-<sup>1</sup>H-NMR.

<sup>b</sup>) Taking into account the number of equivalent *s-cis*-butadiene moieties.

<sup>c</sup>) Concentration of the sensitizer (TPP).

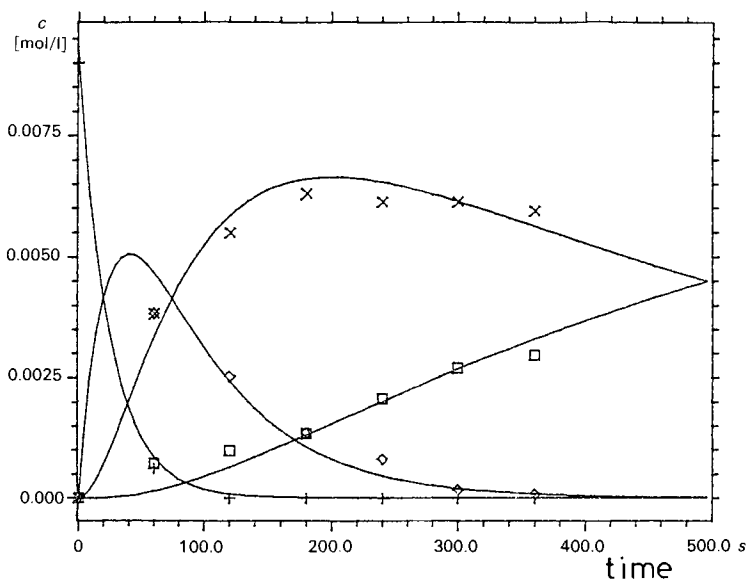


Fig. 6. Example of kinetic measurements of the successive sensitized photo-oxidations **6** (+)→**11**(◇)→**16**(x)→**19**(□)

[20], the same endoperoxides were generated with relative rate constants similar to those reported in the Table. Under the conditions of Midden and Wang (the solution of the polyene is not in touch with the sensitizer (TPP) which is deposited on a plate placed with the sensitizer-side down on top of a shallow disk of the solution, leaving 1–2 mm of air space between the sensitizer and the solution) [21], **6** was also oxidized into the endoperoxides **11**, **16**, and **19** with relative rates similar to those obtained under the usual photo-oxidation conditions with the TPP dissolved in  $CDCl_3$  or in  $CCl_4$ . All these results

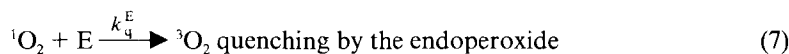
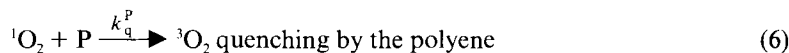
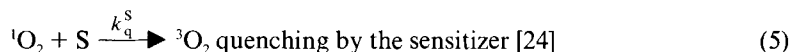
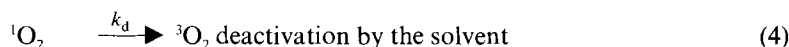
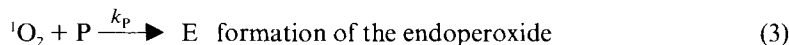
confirmed that  $^1\text{O}_2$ , and not another oxidant [22], was responsible for the formation of the endoperoxides.

We have observed that **6** was stable in the dark in the presence of  $\text{O}_2$  for several days at room temperature. This indicates that triplet  $\text{O}_2$  is not capable of oxidizing **6**. We also found that **6** was slowly photo-oxidized into **11**  $\rightarrow$  **16**  $\rightarrow$  **19** in the absence of any sensitizer ( $\text{I}_2$  lamp). This can be explained by the fact that there is a relatively large bathochromic shift for the maximum of absorption of **6** on increasing the concentration. For instance, the maximum at 295 nm for  $10^{-4}\text{M}$  solution on  $\text{CCl}_4$  was shifted to 311 nm for a  $10^{-2}\text{M}$  solution. These spectra were the same for degassed solution with Ar or saturated with  $\text{O}_2$ . Therefore, we were not capable of detecting any oxygen-**6** complex by UV/VIS absorption spectroscopy [23]. Under the conditions employed for the preparation of the endoperoxides, **6** absorbs some incident light and acts as an auto-sensitizer, although with a low efficiency.

The rate of disappearance of a polyene P giving the endoperoxide E is given by Eqn. 2.

$$-\frac{d[\text{P}]}{dt} = I\phi \frac{k_p[\text{P}]}{(k_p + k_q^p)[\text{P}] + k_d + k_q^s[\text{S}] + k_q^e[\text{E}]}, \quad (2)$$

where the parameters  $k_p, k_q^p, k_d, k_q^s$  and  $k_q^e$  are given by Eqns. 3-7,



where  $I$  is the number of photons absorbed per time and volume unit, and  $\phi$  is the quantum yield for the formation of  $^1\text{O}_2$ . If one admits that the endoperoxides E are not better physical quenchers than the corresponding substrates P, hence  $k_q^p = k_q^e = k_q$  and  $k_q^p[\text{P}] + k_q^e[\text{E}] = k_q[\text{P}]_0 = \text{constant}$ , one thus can write after integration:

$$\frac{k'}{k_p} \ln \frac{[\text{P}]}{[\text{P}]_0} + [\text{P}] - [\text{P}]_0 = -I\phi(t - t_0), \quad (8)$$

with  $k' = k_d + k_q^s[\text{S}] + k_q[\text{P}]_0$ . Since  $[\text{P}]_0 = 10^{-2}$  to  $10^{-3}\text{M}$ ,  $|[\text{P}] - [\text{P}]_0| \ll \left| \ln \frac{[\text{P}]}{[\text{P}]_0} \right|$ . This yields:

$$[\text{P}] = [\text{P}]_0 \exp(-I\phi(k_p/k')t) = [\text{P}]_0 \exp(-k_1 t) \quad (9)$$

The first-order rate constant  $k_1 = I\phi k_p/k'$  is thus proportional to the second-order rate constant  $k_p$  for the endoperoxide formation. Assuming the validity of the hypotheses made above, the rate-constant ratios  $k_1/k_2$  and  $k_2/k_3$  measured for the three successive photo-oxidations of [2.2.2]hericene (**6**) (and  $k_1/k_2$  for the two successive photo-oxidations of **7** and **8**) are directly proportional to the corresponding second order rate constant ratios.



The global rate constants  $k_i$  are reported in the *Table*. They were obtained by non-linear least-squares regressions (see e.g. *Fig. 6*) for three consecutive, irreversible reactions, in the case of **6**, and for two consecutive irreversible reactions in the cases of **7** and **8**. Because of the relatively large uncertainties of our measurements and because of the instability of the endoperoxides formed during these sensitized photo-oxidations, the kinetic data reported here must be taken as indicative only. Nevertheless, we feel that they can be used to define the general trends of the reactivity of polyenes **6–8** and **23** toward  $^1\text{O}_2$ .

First of all, one observes the following reactivity sequence:  $\mathbf{6} + ^1\text{O}_2 \rightarrow \mathbf{11} > \mathbf{7} + ^1\text{O}_2 \rightarrow \mathbf{12} > \mathbf{8} + ^1\text{O}_2 \rightarrow \mathbf{13} > \mathbf{23} + ^1\text{O}_2 \rightarrow \mathbf{24}$ . This trend is parallel with that observed for the TCNE cycloadditions [9] [16]. As expected for a strong dienophile [13], the tetraene **7** and [2.2.2]hericene (**6**) with the lowest *IP*'s react about  $10^4$  as fast toward  $^1\text{O}_2$  than 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**23**) with a significantly higher *IP* value (see *Table*). As in the case of the TCNE additions, the rate-constant ratio  $k_1/k_2$  is small for the photo-oxidation of **6**. The rate constant ratio  $k_2/k_3(^1\text{O}_2)$  is also small whereas it has a much higher value for the *Diels-Alder* reactivity toward TCNE. The differences between the  $k_i + k_{i+1}$  values obtained for the photo-oxidations of **6** in the presence of TPP, on one hand, and in the absence of a dye sensitizer, on the other hand, are somewhat surprising. At the moment, we consider these differences not to be significant because of the hypotheses made in order to extract the  $k_i$  values from our kinetic data and our ignorance concerning the ability of the endoperoxides **11** and **16** to generate  $^1\text{O}_2$  under our irradiation conditions. One cannot yet exclude the possibility of a change in the mechanism of the formation of the endoperoxides when going from the conditions with the dye to those in absence of sensitizer.

Our results on the reactivity of **6** and its endoperoxides **11** and **16** toward  $^1\text{O}_2$  are consistent with the hypothesis that the photo-oxidations have near zero activation enthalpies and consequently, are not sensitive to the variation of the exothermicity of the reaction. For this reason, both the rate-constant ratios  $k_1/k_2$  and  $k_2/k_3$  for the three successive photo-oxidations of **6** have similar values, close to unity, in contrast with the corresponding rate-constant ratios measured for the three successive cycloadditions of TCNE to **6**. The relatively small values evaluated for  $k_1/k_2$  in the case of the two successive photo-oxidations of tetraenes **7** and **8** (*Table*) confirm our findings with the photo-oxidations of **6**. The large  $k_1/k_2$  values observed for the TCNE additions to **7** and **8** have been attributed to a change in the exothermicity of the two successive *Diels-Alder* reactions [16]. The  $k_i/k_{i+1}(^1\text{O}_2)$  reported in the *Table* must be considered as upper limits as the sensitizer was found to be slowly decomposing over a prolonged irradiation time, thus leading to a smaller flux of  $^1\text{O}_2$  as the photo-oxidations progressed. This could explain also the smaller  $k_i/k_{i+1}$  values obtained for the photo-oxidation of **6** in the absence of dye.

**Conclusion.** – There is no difference in stability between the  $C_2$  and  $C_s$  conformers of the bis-endoperoxides **14** and **16** resulting from the photo-oxidations of 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**4**) and [2.2.2]hericene (**6**), respectively. Similarly, there is no difference in the enthalpy of the  $D_3$  and  $C_2$  conformers of the tris-endoperoxide **19** resulting from the photo-oxidation of **16**. These results indicate that the half-chair conformation of the 3,6-dihydro-1,2-dioxines does not induce distortions of the bicyclo[2.2.2]octane skeleton which would make the endoperoxide moiety of one side of these

molecules 'feel' the conformation of the endoperoxide moiety on the other side of the bicyclic system.

The approximate, relative rate constants for the sensitized photo-oxidations of [2.2.2]-hericene (**6**), 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**7**), 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**8**), and 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**23**) parallel those reported for the TCNE cycloadditions of these polyenes. The rate-constant ratios  $k_i/k_{i+1}$  for the successive photo-oxidations of **6–8** do not deviate significantly from unity, in contrast with the corresponding  $k_i/k_{i+1}$  values found for the TCNE cycloadditions. The results are in accord with mechanisms for the endoperoxide formations having near zero activation enthalpies.

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### Experimental Part

*General.* See [28].

*9,10-Dimethylidene-4,5-dioxatricyclo[6.2.2.0<sup>2,7</sup>]dodec-2(7)ene (9).* A mixture of **4** [29] (107 mg, 0.68 mmol),  $\text{CH}_2\text{Cl}_2$  (80 ml), and *Sensitox* (1 g) was stirred by bubbling with  $\text{O}_2$  in a *Pyrex* vessel and cooled to  $-20^\circ$ . After irradiation (halogen lamp 150 W/24 V, *Philips No. 7178*, 'Tauschlampe' system) for 20 min, the mixture was filtered and the soln. evaporated. The residue was purified by column chromatography on silica gel (*Lobar*,  $\text{CHCl}_3/\text{hexane}$  2:1). The first fraction contained traces of unreacted **4**, the second 29 mg (0.15 mmol, 22%) of **9**, and the third 68 mg (0.31 mmol, 45%) of **14**. **9**: Colourless crystals, m.p. 126–128°. UV ( $\text{CH}_3\text{CN}$ ): 245 (7100). IR (KBr): 2950, 2880, 2840, 1620, 1430, 1350, 1130, 995, 960.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 5.15 (s, 2H); 4.78 (s, 2H); 4.60 (s, 4H); 3.05 (br. s, H–C(1), H–C(8)); 1.9–1.2 (m,  $\text{CH}_2$ (11),  $\text{CH}_2$ (12)). MS (70 eV): 191 (9), 190 (63,  $M^+$ ), 172 (28), 162 (100), 144 (36), 130 (14), 115 (40), 103 (15), 91 (14), 77 (15).

*4,5,11,12-Tetroxatetracyclo[6.6.2.0<sup>2,7</sup>.0<sup>9,14</sup>]hexadeca-2(7),9(14)-diene (14).* Colourless solid, m.p. 130° (dec.). UV ( $\text{CH}_3\text{CN}$ ): final absorption. IR (KBr): 2960, 2940, 2890, 1675, 1430, 1355, 1300, 1135, 1040, 1020, 1000, 960.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 4.62 (s, 8H); 3.26 (br. s, H–C(1), H–C(8)); 1.49 (br. s,  $\text{CH}_2$ (15),  $\text{CH}_2$ (16)).  $^{13}\text{C-NMR}$  ( $\text{CD}_2\text{Cl}_2/\text{CBrF}_3$  1:1), see Fig. 4. MS (70 eV): 222 (61,  $M^+$ ), 194 (73), 162 (100), 158 (23), 115 (20), 91 (39), 77 (43).

*4,5,11,12-Tetroxatetracyclo[6.6.2.0<sup>2,7</sup>.0<sup>9,14</sup>]hexadeca-2(7),9(14),15-triene (15).* A mixture of **5** [29] (180 mg, 1.15 mmol), 5,10,15,20-tetraphenylporphine (TPP, 20 mg), and  $\text{CH}_2\text{Cl}_2$  (70 ml) was cooled to  $-20^\circ$  and stirred by bubbling with  $\text{O}_2$ . After 15–20 min of irradiation (as above), the mono-endoperoxide **10** and **5** had disappeared (TLC). The mixture was evaporated to ca. 10 ml and filtered through *Florisil*. The soln. was purified by column chromatography on silica gel (*Lobar*,  $\text{CH}_2\text{Cl}_2$ ) yielding 8 mg (0.04 mmol, 3%) of **15**, colourless powder, m.p. 148–150° (dec.). IR (KBr): 2900, 2840, 1670, 1590, 1350, 1300, 1100, 1000.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 6.88 (m, H–C(15), H–C(16)); 4.68 (s, 8H); 4.28 (m, H–C(1), H–C(8)). MS (70 eV): 221 (12), 220 (84,  $M^+$ ), 202 (3), 160 (16), 131 (27), 128 (29), 115 (66), 103 (59), 91 (51), 77 (100).

*9,10,11,12-Tetramethylidene-4,5-dioxatricyclo[6.2.2.0<sup>2,7</sup>]dodec-2(7)ene (11).* [2.2.2]Hericene (**6**; 100 mg, 0.55 mmol) [**7**], *Sensitox* (1 g), and  $\text{CH}_2\text{Cl}_2$  (200 ml) were stirred by bubbling of  $\text{O}_2$  and cooled to  $-25^\circ$ . After irradiation (as above) for 90 min (control by TLC), the mixture was filtered and the soln. evaporated. The residue was purified by column chromatography on *Florisil* (20 g, petroleum ether/ $\text{CHCl}_3$  1:1) yielding 45 mg (34%) of **11**, colourless crystals, m.p. 250° (dec.). UV (96% EtOH): 220 (10 500), 228 (10 200), 237 (8900), 257 (9000) (compare with the UV of **5** [29a]). IR (KBr): 2890, 1810, 1610, 1420, 1380, 1350, 1030, 995, 960, 900.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 5.25 (s, 4H); 4.95 (s, 4H); 4.63 (s, 4H); 3.66 (s, H–C(1), H–C(8)).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ): 143.8 (s, C(9), C(10)); 132.5 (s, C(2), C(7)); 104.4 (t,  $^1J(\text{C,H}) = 159$ , 4  $\text{CH}_2=\text{C}$ ); 69.7 (t,  $J = 145$ ,  $\text{CH}_2\text{O}$ ); 53.3 (dm,  $J = 140$ , C(1), C(8)). MS (70 eV): 215 (16), 214 (100,  $M^+$ ), 196 (39), 182 (40), 167 (35), 152 (43), 141 (43), 128 (45), 115 (69). Anal. calc. for  $\text{C}_{14}\text{H}_{14}\text{O}_2$  (214.27): C 78.48, H 6.59; found: C 78.47, H 6.52.

*15,16-Dimethylidene-4,5,11,12-tetroxatetracyclo[6.6.2.0<sup>2,7</sup>.0<sup>9,14</sup>]hexadeca-2(7),9(14)-diene (16).* A mixture of **6** (270 mg, 1.48 mmol), TPP (20 mg, 0.03 mmol), and  $\text{CH}_2\text{Cl}_2$  (70 ml) was cooled to  $-20^\circ$ . Irradiation (halogen lamp, *Pyrex*) and  $\text{O}_2$  bubbling was maintained until disappearance (TLC) of **6** after ca. 10 min. The soln. was

concentrated to ca. 10 ml and filtered through *Florisil*. Column chromatography on silica gel (*Lobar*, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:2) yielded a first fraction containing 85 mg (23%) of **16** and a second fraction containing 30 mg (6%) of **19**. **16**: Colourless solid, m.p. > 200° (dec.). UV (96% EtOH): 244 (9100), 237 (8800), 212 (8000). IR (KBr): 2920, 2860, 1720, 1455, 1420, 1375, 1345, 1105, 1000, 960. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 5.13 (s, 2 H); 4.90 (s, 2 H); 4.66 (s, 8 H, CH<sub>2</sub>O); 3.76 (s, H-C(1), H-C(8)); see also *Fig. 3a*. <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 142.1 (s, C(15), C(16)); 134.4 (s, C(2), C(7), C(9), C(14)); 103.1 (t, <sup>1</sup>J(C,H) = 162, 2 CH<sub>2</sub>=C); 70.5 (t, J = 149, CH<sub>2</sub>O); 48.5 (dm, J = 144, C(1), C(8)); see also *Fig. 3b*. MS (70 eV): 247 (15), 246 (88, M<sup>+</sup>), 228 (12), 210 (11), 199 (25), 186 (35), 171 (18), 169 (19), 162 (32), 154 (42), 141 (48), 128 (94), 115 (100), 91 (68), 77 (73).

*4,5,11,12,17,18-Hexaoxapentacyclo[6.6.6.0<sup>2,7</sup>.0<sup>9,14</sup>.0<sup>15,20</sup>]jicosa-2(7),9(14),15(20)-triene (19)*. Colourless solid, m.p. > 250° (dec.). IR (KBr): 2960, 2900, 2840, 1425, 1350, 1200, 1120, 1010, 960. <sup>1</sup>H-NMR (CD<sub>3</sub>CN): 4.74 (s, 12 H, CH<sub>2</sub>O); 4.28 (s, H-C(1), H-C(8)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 142.1 (s, C(sp<sup>2</sup>)), 72.0 (t, <sup>1</sup>J(C,H) = 146, CH<sub>2</sub>O); 47.0 (d, <sup>1</sup>J(C,H) = 139, C(1), C(8)); see also *Fig. 5*. CI-MS (CH<sub>4</sub>, 200 eV): 279 (1, (M + 1)<sup>+</sup>), 193 (1), 178 (3), 123 (5), 89 (15), 73 (42), 61 (58), 41 (100).

*5,6,12,13-Tetroxatricyclo[8.2.0.0<sup>3,8</sup>]tetradeca-1,3(8),9-triene (20)*. When the irradiation of **6** (see above) was continued for 40 min, the purification by column chromatography yielded only one fraction containing 5% of a white solid, m.p. > 250° (dec.). IR (KBr): 3050, 2920, 2840, 1730, 1440, 1420, 1370, 1290, 1220, 1040, 980, 970. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.01 (s, H-C(2), H-C(9)); 5.19 (s, CH<sub>2</sub>O). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 131.0 (s, C(1), C(3), C(8), C(10)); 120.5 (d, J = 155, C(2), C(9)); 71.7 (td, <sup>1</sup>J(C,H) = 145, <sup>4</sup>J(C,H) = 5, CH<sub>2</sub>O). MS (70 eV): 194 (13, M<sup>+</sup>), 176 (25), 167 (28), 162 (12), 149 (100), 105 (10), 91 (20), 77 (15), 57 (29).

*4,5,11,12-Tetroxatetracyclo[6.6.1.0<sup>2,7</sup>.0<sup>9,14</sup>]pentadeca-2(7),9(14)-diene (17)*. As for the preparation of **15**, using **7** [16c] (130 mg, 0.9 mmol). Purification by filtration through *Florisil* and column chromatography on silica gel (*Lobar*, CHCl<sub>3</sub>/hexane 1:1). The first fraction contained TPP. The second contained 20 mg (13%) of the unstable mono-endoperoxide **12**. The third fraction contained 15 mg (0.07 mmol, 8%) of **17**, colourless solid, m.p. 114–117° (dec.). IR (KBr): 2950, 2910, 1660, 1270, 1120, 980. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 5.06–4.40 (m, CH<sub>2</sub>O); 3.46 (br. s, H-C(1), H-C(8)); 2.25 (br. s, CH<sub>2</sub>(15)). MS (70 eV): 209 (12), 208 (100, M<sup>+</sup>), 176 (26), 144 (32), 129 (16), 117 (12), 115 (15), 105 (17), 91 (69), 77 (59).

*Kinetic Measurements*. The polyenes (100–200 mg) were dissolved in CDCl<sub>3</sub> (67 ml). Then TPP (10–20 mg, 2.5–5 × 10<sup>-4</sup>M) was added, and the mixture was cooled to ca. -25° under bubbling of O<sub>2</sub> in a *Pyrex* Tauschlampe (I<sub>2</sub> lamp, 24 V/10A, *Philips*) apparatus. Aliquots of 0.5 ml were used for 360-MHz-<sup>1</sup>H-NMR analyses, without concentration and purification. Corrections for the loss of solvent were made. The temp. of the irradiated soln. was thermostated within ± 2°. Concentrations of the polyenes and of the corresponding endoperoxides were determined by integration of the <sup>1</sup>H-NMR signals accumulated on a 8 K memory. The signal of CHCl<sub>3</sub> was used as internal reference. The data were treated on a NORISK computer using the program ITERAT [30] for the non-linear regressions. The kinetic equations assumed irreversible first-order rate laws, with no parallel side-reactions [31]. Although the bis-endoperoxide **18** resulting from the photo-oxidation of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**8**) was unstable at -20°, the following <sup>1</sup>H-NMR (CDCl<sub>3</sub>) characteristics were observed: 5.25 (s, H-C(1), H-C(8)); 5.02 (d, J = 14.3); 4.63 (d, J = 14.3, CH<sub>2</sub>O). For the mono-endoperoxide **12**, see [9]. Similarly, the following <sup>1</sup>H-NMR (CDCl<sub>3</sub>) characteristics were observed for the unstable endoperoxide **24** derived from the photo-oxidation of 5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane (**23**): 7.17 (s, H-C(sp<sup>2</sup>)); 5.42 (s, bridgehead protons); 5.01 (d, J = 14.3) and 4.49 (d, J = 14.3, CH<sub>2</sub>O). This spectrum was in agreement with that reported for 7-oxabicyclo[2.2.1]hepta-2,5-diene [32].

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