

Par recristallisation fractionnée de la phase hydrophobe dans l'éthanol on a isolé les sulfones **8** et **9** (resp. F. 203° et F. 150°), identifiées par l'analyse élémentaire, leur spectre RMN. et leurs propriétés polarographiques.

Nous remercions le Dr. *U. Burger* qui a enregistré et interprété les spectres RMN.

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### 193. Thermal and Photochemical Rearrangements of Divinylcyclopropanes to Cycloheptadienes. – A Model for the Biosynthesis of the Cycloheptadiene Derivatives found in a Seaweed (*Dictyopteris*)

Preliminary Communication

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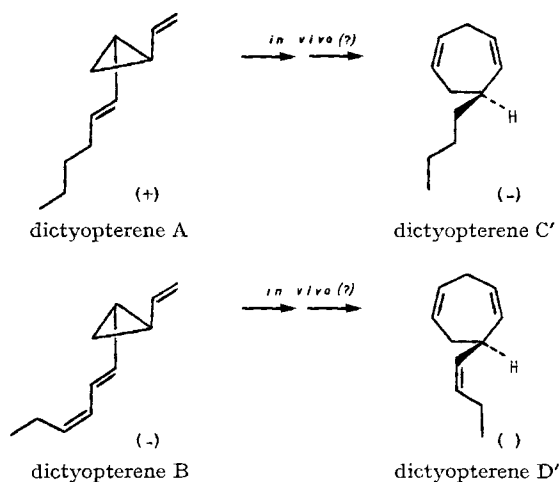
Dedicated to Professor *Edgar Lederer* on the occasion of his 65th birthday

(20. V. 73)

**Summary.** The activation parameters of the thermal rearrangements of the *trans*-divinylcyclopropanes **1** and **2**, and of *cis*-divinylcyclopropane **3** to give cycloheptadiene **5** have been determined. In addition it has been shown that *trans*-divinylcyclopropane-cycloheptadiene rearrangements also occur under irradiation by a mercury lamp in benzene at 40°. These low-temperature *in vitro* rearrangements suggest that the biosynthesis of the cycloheptadienes in *Dictyopteris* (dictyopterenes C' and D') may proceed by the same reaction(s).

**Introduction.** – In the course of a project [1] for the synthesis of unsaturated hydrocarbons isolated from the essential oil of *Dictyopteris* [2], an odoriferous seaweed, the interesting question arose as to whether the presence of 1,4-cyclohepta-

dienes, namely dictyopterene C' and D'<sup>1)</sup>, can be accounted for by *in vivo* sigmatropic rearrangements of the divinylcyclopropanes dictyopterenes A and B. A preliminary communication by Moore *et al.* [2c] showed that thermal rearrangement of *trans*-

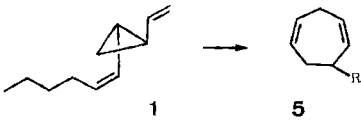
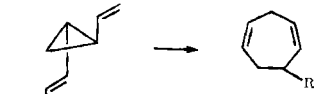

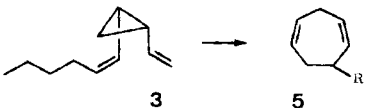


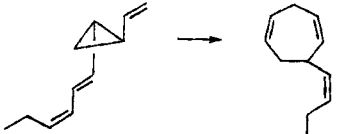


divinylcyclopropanes cannot account for the formation of heptadienes, firstly because of the high activation parameters of these rearrangements, and secondly because of the different optical properties of the heptadienes isolated from *Dictyopteris* compared with the heptadienes from a thermal *in vitro* rearrangement. The dictyopterenes A and B have therefore been ruled out as possible precursors of the natural heptadienes, and a hypothetical *cis*-divinylcyclopropane, which has not been detected in nature, was postulated as a precursor. However, Moore *et al.* only considered thermal rearrangements in order to explain the presence of cycloheptadienes in *Dictyopteris*. As *Dictyopteris* is a seaweed fully exposed to irradiation by sunlight, photochemical *in vivo* reactions must also be considered. Photochemical reactions complement the thermal ones; they readily progress at room temperature and often show a stereochemical course opposite to the thermal process [4]. In the present study we therefore investigated the rearrangements of racemic **1** and **2** to **5** not only thermally but also photochemically. The thermal rearrangements were kinetically monitored to obtain accurate activation parameters while the photochemical studies gave only qualitative results which nevertheless demonstrate a low-temperature pathway for the isomerization of *trans*-divinylcyclopropanes **1** or **2** to *cis*-divinylcyclopropanes **3** or **4** and for the formation of cycloheptadiene **5**.

**Results.** - *Thermal rearrangements.* The energy parameters of the *trans*-divinylcyclopropanes **1** and **2**, both identical within the limits of error, and of the *cis*-divinylcyclopropane **3**, support the existence of two distinct pathways leading to cycloheptadiene **5**, which is in full agreement with recent work on the divinylcyclopropane rearrangement [5-6]. Our measured energy parameters accord well with the

<sup>1)</sup> This compound has also been isolated from the brown alga *Ectocarpus siliculosus*, and it has been shown to be a male attracting substance produced by the female gametes of the alga [3].

Table 1. Energy parameters of the thermal first-order divinylcyclopropane-1,4-cycloheptadiene rearrangement

Rearrangement	$E_a$ [kcal/mol]	log A	$\Delta H^\ddagger$ at 25° [kcal/mol]	$\Delta S^\ddagger$ at 25° [e. u.]	
1 	32.8 $\pm 0.8$	14.54	32.2 $\pm 0.8$	- 0.1 $\pm 1.8$	<i>l</i> <sup>a)</sup>
2 	32.2 $\pm 0.6$	13.23	31.7 $\pm 0.6$	- 1.6 $\pm 1.4$	<i>l</i>
3 	37.4	-	-	-	[2c]
4 	20.5 $\pm 1.4$	10.70	19.9 $\pm 1.4$	-17.8 $\pm 4$	<i>l</i>
5 	32.6 <sup>b)</sup> $\pm 0.8$	12.4 <sup>b)</sup>	-	- 1.94 <sup>b)</sup> $\pm 2$	<i>g</i> <sup>a)</sup> [5]
6 	34.3 $\pm 0.9$	13.1	-	0.61 <sup>b)</sup> $\pm 1$	<i>g</i> [6a]
7 	28.5	-	-	-	[2c]

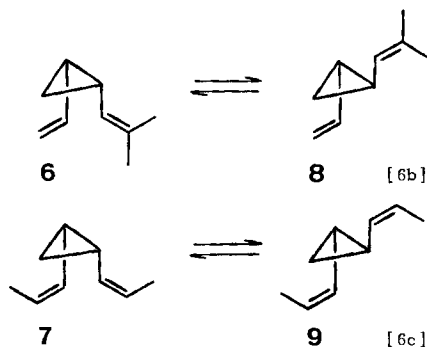
a) Abbreviations: *l* = liquid phase thermolysis; *g* = gas phase thermolysis.

b) These values have been calculated from the experimental data of [5] and [6a] using our computer programme.

available kinetic data of related compounds (see Table 1) with the exception of a preliminary measurement of Moore *et al.* [2c] (Table 1, Entry 3). *cis*-Divinylcyclopropane **3** with its low activation energy ( $E_a = 20.5$  kcal/mol) and its rather high negative entropy of activation ( $\Delta S^\ddagger = -17.8$  e.u. at 25°) rearranges, probably through highly ordered boat-like transition state, in a concerted fashion (*cf.* [6b, c] and [7]).



Unsubstituted *cis*-divinylcyclopropane has never been isolated because of its high reactivity even at  $-45^\circ$  [8]<sup>2)</sup>, and the methyl disubstituted homologues **6** or **7** no longer yield the cycloheptadienes, due to steric repulsion at the transition state, but only isomerize to the corresponding *trans*-isomers **8** [6b] and **9** [6c]; our monoalkylated example **3** is so far the only monocyclic case for which kinetic data have been obtained.

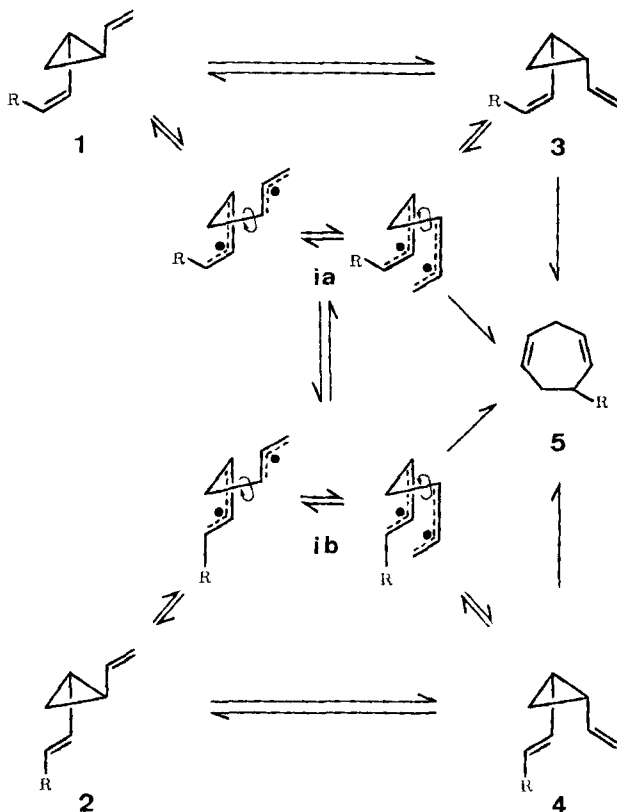


For the rearrangement of the *trans*-isomers **1** and **2** three mechanisms can be considered. The first two mechanisms are associated with the *cis*-divinylcyclopropanes **3** or **4** as intermediates, the rate limiting formation of which can be explained either by a diradical intermediate or a thermally allowed *Smith* inversion [9]. A subsequent fast concerted rearrangement of **3** or **4** yields **5** as already discussed. The third mechanism, namely direct cyclization of the diradicals **1a** or **1b** to give **5**, must also be considered. The isomerization of the *trans* compounds **1** and **2** is characterized by their rather low entropy of activation ( $\Delta S^\ddagger = -0.14$  and  $-1.5$  e.u., respectively), in sharp contrast to the value of  $\Delta S^\ddagger = -17$  e.u. for the *cis*-divinylcyclopropane **3**. This entropy value might indicate that the rearrangement of **1** and **2** proceeds through a 'loose' transition state, while the *Smith* inversion would require a highly ordered transition state with an entropy of activation comparable to that of concerted *Cope* rearrangements.

*Photochemical reactions of trans-divinylcyclopropanes.* Irradiation of a mixture of **1** and **2** in benzene at  $40^\circ$ , using a mercury lamp, gave (*Z*)-*cis*-divinylcyclopropane **3** and cycloheptadiene **5** in an extremely clean reaction. In addition, the ratio of the starting materials had changed from  $1/2 = 94/6$  to  $1/2 = 72/10$  after 12h of irradiation. When the reaction mixture was heated to  $110^\circ$  for 3h, **3** disappeared from the mixture to give **5** by thermal rearrangement. The photochemical isomerization of **1** to give **3** is the first example of a photochemical divinylcyclopropane *trans-cis*-isomerization and provides strong evidence for possible *in vivo* photochemical steps during the *trans*-divinylcyclopropane-cycloheptadiene rearrangement.

The reactions observed may be rationalized as follows. Photochemical isomerization of **1** *via* the diradical **1a** (which differs from the thermally generated diradical **1a**)

<sup>2)</sup> Note added after completion of the present manuscript: A preliminary determination of the activation parameters of the *cis*-divinylcyclopropane-cycloheptadiene rearrangement gives:  $\Delta H^\ddagger = 19.38 \pm 1.8$  kcal mol<sup>-1</sup>,  $\Delta G^\ddagger = 20.6$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = 5.3 \pm 6.75$  e.u. [11].



Only one enantiomer of the racemic compounds **1**-**5** has been drawn.

gives **3** (cf. *cis-trans*-isomerization of diphenylcyclopropane [10]). This intermediate (**3**) can undergo either thermal or photochemical *Cope* rearrangement to yield **5**. An analogous mechanism can be proposed for **1** → **5**, although the intermediate **4** has not been detected due to its low thermal stability. A further pathway is direct cyclization of the photochemically generated diradicals **ia/ib** to give **5**. However, the experiments undertaken so far do not allow any definite statements concerning the mechanisms involved. Further work bearing on this question is in progress.

The present low-temperature *in vitro* pathways from *trans*-divinylcyclopropanes **1** and **2** to cycloheptadiene **5** suggest that the biosynthesis of the cycloheptadienes in *Dictyopteris* (dictyopterenes C' and D') may proceed by the same reactions.

### Experimental Part

(with the collaboration of Mr. P. Deladoey)

1. *Pyrolysis of 1, 2 and 3.* a) *Apparatus and methods.* All thermolyses were carried out in 50% solutions of gas chromatographically pure *trans*-decaline in the case of **1** and **2**, and of the pentyl ester of isovaleric acid in the case of **3**. These solutions (3  $\mu$ l) were placed in glass tubes (20  $\times$  2 mm) which were sealed and placed in an oil bath closed by an asbestos cover. The bath was kept in a temperature controlled room, so that the reaction temperature varied by  $\pm 0.1^\circ$ . The temperature was measured with a Mettler TM 15 digital thermometer and continuously recorded.

After the reaction time the tubes were withdrawn from the bath and cooled in liquid nitrogen. GC.-analyses were carried out on a *Carlo-Erba* Fractovap 2400 T on  $1.6 \times 0.02$  m packed columns, Chromosorb W 60/80 with 10% Carbowax as stationary phase. The peak areas were calculated with a *Hewlett-Packard* integrator 337 B.

In the case of **3**, the reaction mixtures were hydrogenated over 10% Pd/C for 16 h at atmospheric pressure before GC.-analyses.

The calculations of the *Arrhenius* parameters were carried out on a computer; error  $\equiv$  two standard deviations.

Table 2. *Isomerization of 1  $\rightarrow$  5<sup>3)</sup>*

Temp. °C $\pm$ 0.1	Time (min)	% of <b>5</b>	k (min <sup>-1</sup> )
129.9	1320	53.73	$5.672 \cdot 10^{-4}$
137.5	1320	83.10	$1.350 \cdot 10^{-3}$
147.0	360	66.43	$3.025 \cdot 10^{-3}$
156.4	180	76.47	$8.144 \cdot 10^{-3}$
165.0	140	87.84	$1.522 \cdot 10^{-2}$

Table 3. *Isomerization of 2  $\rightarrow$  5*

Temp. °C $\pm$ 0.1	Time (min)	% of <b>5</b>	k (min <sup>-1</sup> )
128.8	1590	56.30	$5.088 \cdot 10^{-4}$
138.0	1290	81.11	$1.283 \cdot 10^{-3}$
147.4	425	68.30	$2.776 \cdot 10^{-3}$
157.5	220	82.29	$7.752 \cdot 10^{-3}$
165.0	120	81.91	$1.420 \cdot 10^{-2}$

Table 4. *Isomerization of 3  $\rightarrow$  5*

Temp. °C $\pm$ 0.1	Time (min)	% of <b>5</b>	k (min <sup>-1</sup> )
65.6	270	65.85	$2.614 \cdot 10^{-3}$
71.8	140	62.79	$5.067 \cdot 10^{-3}$
77.2	120	74.08	$8.692 \cdot 10^{-3}$
81.6	110	75.79	$9.859 \cdot 10^{-3}$
87.3	74	79.76	$1.746 \cdot 10^{-2}$

Table 5. *Photolysis of 1 and 2  $\rightarrow$  3 and 5*  
Peak 1 = **1**; peak 2 = **2+3**; peak 3 = **5**

time (h)	photolysis			photolysis and pyrolysis (3 h 110°)		
	peak 1 %	peak 2 %	peak 3 %	peak 1 %	peak 2 %	peak 3 %
0	93.3	6.0	0.8	92.2	5.8	2.0
6	80.0	14.4	5.6	80.1	7.6	12.3
10	77.1	16.6	6.3	75.8	8.7	15.5
12	75.3	17.2	7.6	72.7	10.4	16.9

<sup>3)</sup> In order to shorten the paper, only the last measurement of each series is mentioned. Up to this point 9 more control data were obtained at different times for each temperature and the proportion of rearranged product was shown to fall on a line of a first order reaction. The complete data can be obtained from the authors.

2. *Photolysis of 1 and 2.* A mixture of **1** and **2** (94:6)<sup>4)</sup> (150 mg), was dissolved in 10 ml of benzene and irradiated in a quartz tube with a Philips HPK 125 W mercury medium pressure lamp. The reaction tube was cooled in an air stream to keep the temperature below 40°. The reaction was monitored by GC-analysis of the solution. A sample withdrawn at the same time was pyrolyzed at 110° and analyzed as above.

The peak with the same retention time as **5** was isolated by preparative GC. and identified as 6-butyl-1,4-cycloheptadiene by comparison of the NMR. spectra.

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- 4) UV. spectra of the mixture:  $\lambda_{\max}$  210  $\mu\text{m}$ ,  $\epsilon = 4360$  (ethanol).

## 194. Circular dichroismus

62. Mitteilung<sup>1)</sup>

### Chiroptische Eigenschaften einiger Trimethylcyclohexen-Derivate: Die Jonone, Irone und Abszisinsäuren

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(14. VI. 73)

*Summary.* The absolute configuration of (+)- $\alpha$ -ionone **3** (*R*), the absolute configurations at C(6) of (+)-*cis*- $\alpha$ -irone **5** (6*S*) and (-)-*trans*- $\alpha$ -irone **6** (6*R*), and the absolute configurations of (+)-*cis*-abscisic acid **10** (*S*) and (+)-*trans*-abscisic acid **11** (*S*) are deduced from the CD-spectra.

<sup>1)</sup> Teil 61 dieser Reihe der Bonner Autoren siehe [1].

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