210. The Intramolecular Ene Reaction: the Thermal Rearrangement of Linalool and 1,2-Dehydrolinalool

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Summary

A kinetic analysis of the thermal rearrangement of linalyl trimethylsilylether (1b) shows that four diastereoisomeric 1,2-dimethyl-3-isopropenyl-1-cyclopentyl trimethylsilyl ethers (2b–5b) are formed directly in parallel first order reactions. Kinetic analysis of the thermal rearrangement of dehydrolinalool (6) shows that two diastereoisomeric 1-methyl-2-methylidene-3-isopropenyl-1-cyclopentanols (7 and 8) are formed in parallel first order reactions. The configurations of 7 and 8 are determined by correlations with the known iridenols.

On heating (−)-(R)-linalool is converted into a mixture of four diastereoisomeric iridenols [1] [2] *(Scheme 1)*. This was interpreted in terms of four distinct intramolecular ene reactions, but the possibility that some of the iridenols were formed by secondary reactions could not be excluded. In the present paper we describe a kinetic analysis of the thermolysis of linalyl trimethylsilyl ether (1b) and of dehydrolinalool (6).

Scheme 1
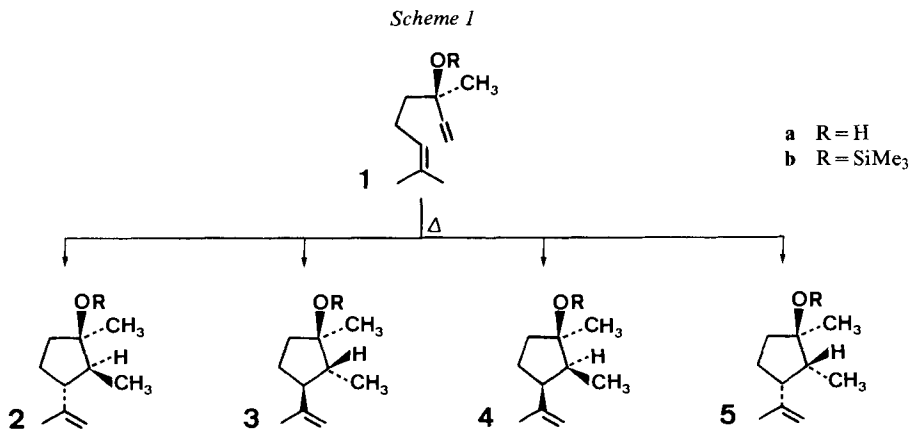
Thermolysis of **1a** in the gas phase at temperatures between 200 and 300° gave besides the iridenols **2a–5a** compounds whose rates of formation were dependent on the surface of the reactor and which were believed to be the products of dehydration. We were unable to avoid the formation of these compounds, even by carefully conditioning the reactor. Therefore, instead of the kinetics of the free alcohol **1a** we studied those of the rearrangement of the corresponding trimethylsilyl ether **1b**, whose products are much more stable under the reaction conditions.

The reactor was a 20 l pyrex flask in a conventional gas phase thermostat with a temperature deviation of ±0.1° [3]. Product analysis was performed by gas chromatography (GC.). The four products found in the thermolysis of **1b** were shown to be identical (GC.) with the compounds **2b–5b**, prepared independently from **2a–5a** [2]. Thermolysis of **6** at temperatures between 170 and 230° gave **7** and **8** [4] whose configurations were determined by hydrogenation and comparison with the hydrogenation products **9** and **10**, obtained from **5a** and **4a**, respectively *(Scheme 2)*.

Scheme 2
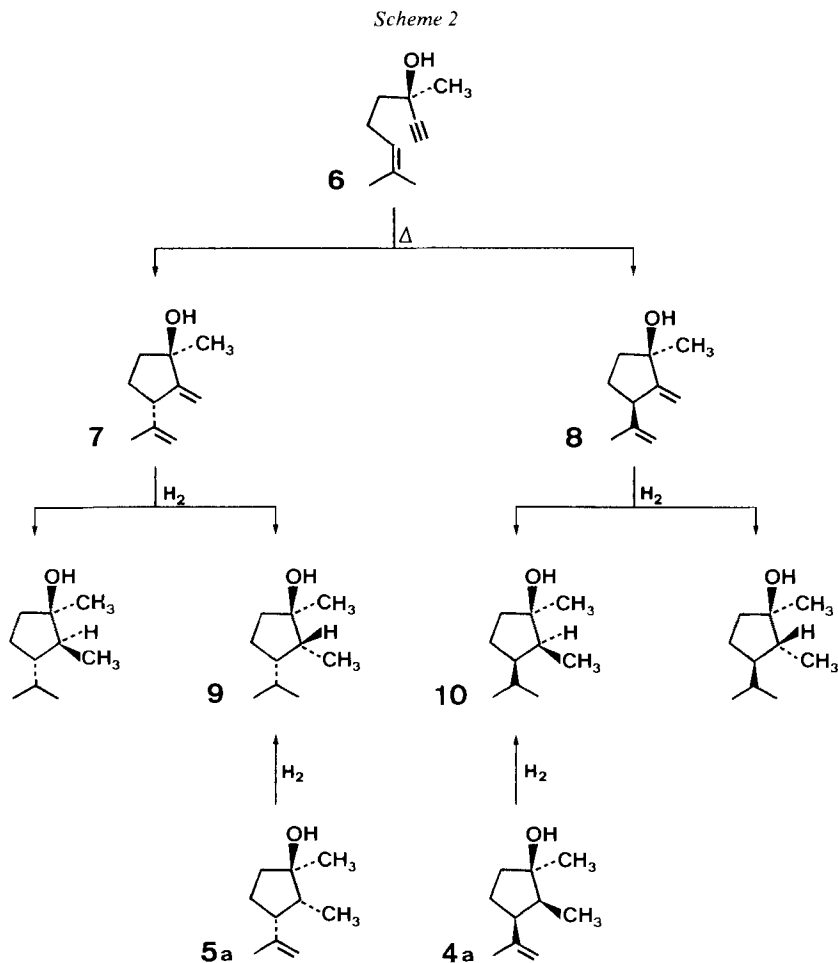
Thermolysis of **1b** or **6** for long reaction periods led to the formation of small amounts of non-identified products which are considered to be the result of dehydration of the alcohols, formed by partial cleavage of the silyl ethers on the glass surface. However, under the conditions of the kinetic analysis this reaction represented less than 1% of the total transformation of **1b**, and a maximum of 5% for the transformation of **6**. For the calculation of the k-values, these secondary products were estimated together with the main products in proportional amounts, assuming that in the case of **1b** the four iridenyl trimethylsilyl ethers **2b–5b** decompose at the same rate. The two diastereoisomeric 1-methyl-2-methylidene-3-isopropenyl-1-cyclopentanols (**7** and **8**) should dehydrate at comparable results. The proportions of the reaction products were constant for more than two half lives, which indicates parallel first order reactions in each case. The rate constants for the reactions of **1b** and **6** are listed in *Tables 1* and *2*.

Table 1. *Rate constants for the intramolecular ene reactions of* **1b**

Temp. °C	**1b → 2b** $k \cdot 10^5$	**1b → 3b** $k \cdot 10^5$	**1b → 4b** $k \cdot 10^5$	**1b → 5b** $k \cdot 10^5$
289.15	0.75398	0.29621	6.77255	5.46635
279.17	0.41896	0.16919	4.07688	3.28728
269.17	0.24264	0.08865	2.37512	1.85716
259.33	0.12610	0.04200	1.34210	1.03740
238.82	0.03446	0.01378	0.39807	0.30588

Table 2. *Rate constants for the intramolecular ene reactions of* **6**

Temp. °C	**6 → 7** $k \cdot 10^5$	**6 → 8** $k \cdot 10^5$	Temp. °C	**6 → 7** $k \cdot 10^5$	**6 → 8** $k \cdot 10^5$
227.1	21.290	15.427	198.4	3.762	2.366
221.8	15.590	10.826	186.3	1.506	0.851
209.8	7.235	4.990	175.1	0.738	0.472

The temperature dependence of the rate constants can be described by the *Arrhenius* equation $k = A \exp(-\mathrm{Ea}/RT)$. The corresponding activation parameters are listed in *Table 3*.

Table 3. *Activation parameters of the intramolecular ene reactions of* **1b** *and* **6**

Reaction	Ea [kcal mol^{-1}]	A [s^{-1}]	$\Delta H^{\neq}_{264°}$ [kcal mol^{-1}]	$\Delta S^{\neq}_{264°}$ e.u.
1b → 2b	35.1 ± 0.4	3.2 · 10^8	34.0	− 18.8
1b → 3b	35.4 ± 1.5	1.7 · 10^8	34.3	− 20.4
1b → 4b	32.3 ± 0.1	2.4 · 10^8	31.2	− 19.4
1b → 5b	32.9 ± 0.2	3.5 · 10^8	31.9	− 18.7
6 → 7	30.0 ± 0.4	9.8 · 10^8	28.0 (200°)	− 20.3 (200°)
6 → 8	30.5 ± 0.9	3.3 · 10^9	29.6 (200°)	− 17.9 (200°)

Discussion. The kinetic analysis of the thermolysis of **1b** shows that the formation of the 2,3-*cis* products **4b** and **5b** is energetically preferred over that of the 2,3-*trans* compounds **2b** and **3b**. The configuration of the reaction products is

obviously not determined by their thermodynamic properties. These observations correspond to the results of *Huntsman et al.* [5] and *Oppolzer et al.* [6] who have shown that the thermolysis of 1,6-diene systems leads preferentially to *cis*-di-substituted cyclopentanes.

Scheme 3

endo   *exo*

A $1 \rightarrow 4$ B

C $1 \rightarrow 5$ D

E $1 \rightarrow 3$ F

G $1 \rightarrow 2$ H
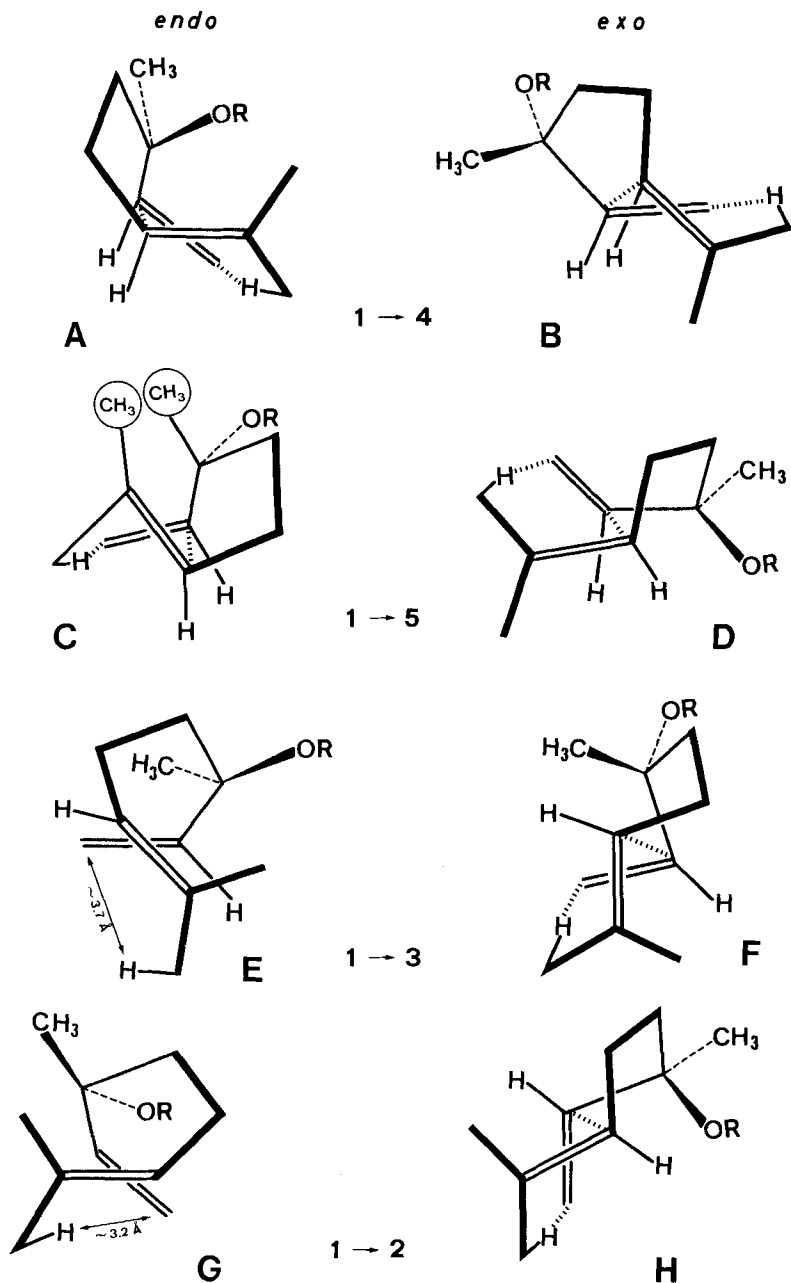
The thermal ene reaction is considered to be a concerted process [7] and it has been shown that for intermolecular ene reactions an *endo* transition state is preferred [8], but this preference is very susceptible to steric effects [9]. Intramolecular ene reactions also prefer an *endo* transition state if sterically possible [6].

The intramolecular ene reaction of linalool leads to four diastereoisomeric products [1] which could be formed *via* either an *endo* or an *exo* transition state *(Scheme 3)*. For the formation of the 2,3-*cis*-substituted cyclopentanes **4** and **5** a hydrogen atom from the *E*-methyl group would be transferred through an *endo* transition state (**A** and **C**, respectively), whereas a hydrogen atom from the *Z*-methyl group would be transferred through an *exo* transition state (**B** and **D**, respectively). The situation would be inverse for the formation of the 2,3-*trans*-substituted rings **2** and **3**. An analysis of the transition states could give an explanation for the proportions of the reaction products. Molecular models *(Scheme 3)* show that only the transition states **A**, **B**, **C** and **D** leading to the 2,3-*cis* products **4** and **5** have a favorable geometry for a concerted ene reaction. The preferred formation of **4b** over **5b** could be explained by the steric hindrance of the two *quasi* diaxial methyl groups in the *endo* transition state **C** leading to **5b**. For the transformation **1** → **2** and **1** → **3** forming the 2,3-*trans*-substituted cyclopentanes, only the transition states **F** and **H** correspond to the conditions for a concerted ene reaction, but the approach of the reacting centers is more difficult because of the *quasi trans* junction of a five-membered ring with a six-membered transition state. This fact could explain the observed higher activation energy for the formation of **2b** and **3b**.

The transformation of **6** to **7** and **8** has activation energies comparable to those of the reactions of **1b** despite the less favored transition state, but this is offset by its higher reaction enthalpy, which can be estimated from group increments to be *ca.* 10 kcal · mol^{-1} [10].

Conclusion. On thermolysis of linalool four distinct intramolecular ene reactions with comparable activation energies lead to four diastereoisomeric iridenols (**2–5**). This shows that the thermodynamically preferred 2,3-*trans* isomers **2** and **3** are formed directly, and not by a secondary reaction from the kinetically preferred 2,3-*cis*-substituted cyclopentanes **4** and **5**. Whether the reactions proceed through *endo* or *exo* transition states cannot be determined without appropriate labeling experiments.

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