# 59. Direct Formation of a Substituted [5.5.5.5]Fenestrane by Intramolecular Arene-Olefin Photocycloaddition

by **Jürg Mani, Stefan Schüttel, Cong Zhang, Peter Bigler, Christian Müller,** and **Reinhart Keese***

Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH–3012 Bern

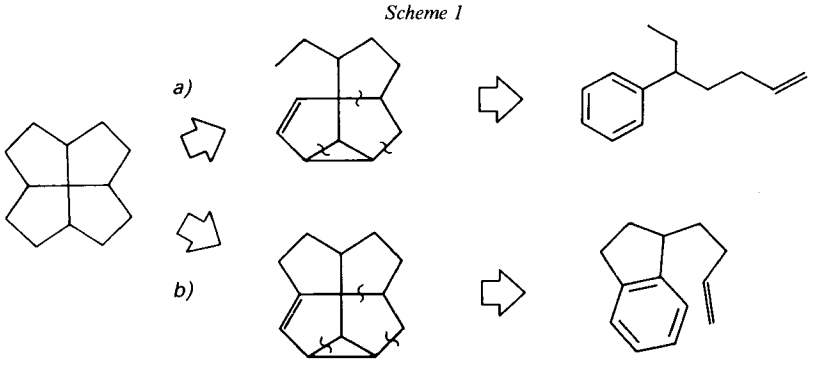
In admiration and memory of Prof. *Egbert Havinga*

(16. XII. 88)

In a search for further synthetic routes to substituted [5.5.5.5]fenestranes, compound **1a**, a derivative of 7-methoxyindane, was photolyzed. Two of the three photoproducts, *viz.* the [3.5.5.5]fenestrane **3a** and the isomer **4a**, are formed according to the expected intramolecular *meta*-cycloaddition. A different mechanism is suggested for the formation of the major component **2a**.

**Introduction.** – The photoinduced intramolecular *meta*-cycloaddition of an olefinic double bond to an aromatic $\pi$-system provides an efficient route for the synthesis of natural products and a variety of other tri- and tetracyclic structures [1]. We have used this method for the synthesis of tetracyclic intermediates, suitable for the formation of substituted [5.5.5.5]fenestranes [2]. The first approach required the formation of one additional cyclopentane moiety after the photoreaction *(Scheme 1, Route a)*. In order to

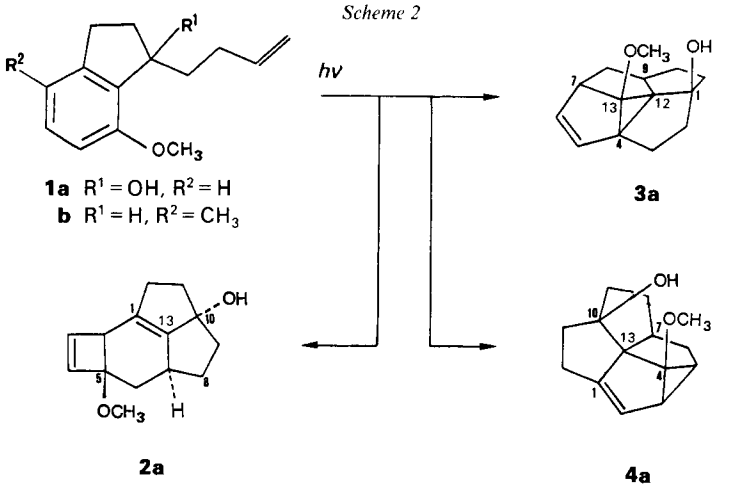
*Scheme 1*




further shorten the synthesis of fenestranes, we explored the possibility of direct formation of such compounds in the photochemical step. A retrosynthetic analysis clearly showed that for direct formation of [5.5.5.5]fenestranes, substituted indanes instead of 5-substituted 5-phenylpentenes had to be irradiated *(Scheme 1, Route b)*. In order to enhance the formation of the appropriate *meta*-cycloadduct, a donor substituent in 7-position of the indane moiety was desirable [1b]. Thus, 7-methoxyindanone was used for the preparation of **1a**, suitable for direct formation of a substituted [5.5.5.5]fenestrane.

**Results.** – When **1a** was irradiated in hexane or *tert*-butyl methyl ether, the three photoproducts **2a, 3a,** and **4a** were formed in an approximate ratio of 4–5:3–4:1 *(Scheme 2)*. The structure of all components was unambiguously established by NMR spectroscopy.

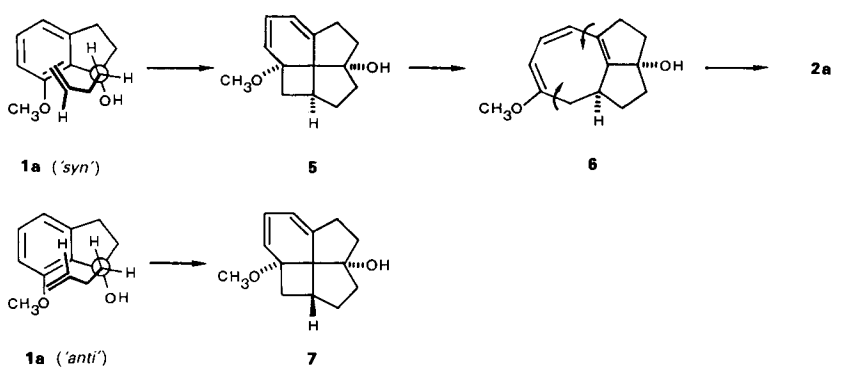
*Scheme 2*




Based on heteronuclear NOE measurements with a modified pulse sequence, the linkage between the proton-bearing substructures *via* the quaternary C-atom was established. Homonuclear NOE measurements were used to verify the configuration of **2a**: the OH group and the proton at the adjacent bridgehead position are *trans* to the MeO substituent [3].

A possible mechanism for the formation of the major photoproduct **2a** is based on an initial [2 + 2] instead of a [2 + 3] cycloaddition *(Scheme 3)*. The *cis*-relationship between the OH group and the bridgehead proton in the primary photoproduct **5** can only be generated, if it is formed *via* the *'syn'* conformation of **1a** rather than the *'anti'* arrangement of **1a**. The [4.5.5.6]fenestradiene **5** contains a highly strained, *trans*-

*Scheme 3*



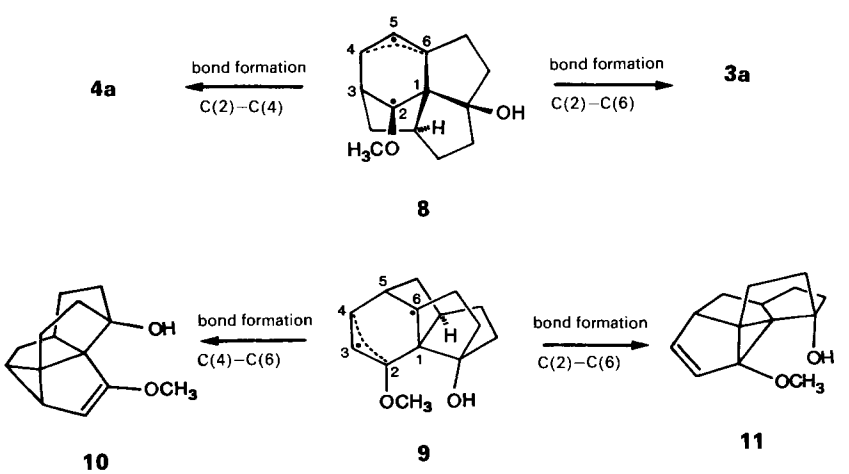
fused bicyclo[3.2.0]heptane subunit. Opening of the cyclohexadiene ring of **5** in a thermally allowed disrotatory 6-electron ring cleavage removes the *trans*-fused bicyclo[3.2.0]heptane subunit and gives the tricyclic compound **6**. A further photoinduced reaction leads *via* a disrotatory 4-electron ring closure to the observed photoproduct **2a**. If the initial [2 + 2] cycloaddition would occur *via* the *'anti'* conformation of **1a, 7,** a derivative of all-*cis*-[4.5.5.6]fenestrane[1]), would be formed. It could have been expected that this more stable isomer is less reactive than **5** and could be detected or isolated[2])[3]).

On the reasonable assumption that **3a** and **4a** are direct photoproducts, their formation can be explained by a photoinduced [2 + 3] cycloaddition which is followed by the closure of the cyclopropane ring [2a]. The structure of both these photoproducts has been established by NMR spectroscopy.

Major structural features of **3a** were extracted from INADEQUATE and $^1H,^{13}C$ hetero-COSY measurements (*Table 1*[4])). The $^{13}C,^{13}C$ connectivity was indicative of two ethylidene moieties, bonded to the same tertiary C(OH) group. Further connectivities led from C(3) to C(5) *via* the quaternary bridgehead C(4), and from C(10) *via* C(9)–C(8)–C(7) to C(6) and C(13); also the direct bonding C(9)–C(12) could be observed. Additional details of the C-skeleton and an independent assignment of all the quaternary $^{13}C$-NMR signals could be obtained by COLOC and heteronuclear NOE measurements. The presence of a cyclopropane substructure was apparent from the independently determined $^1J(C(4), C(13)) = 13.6$, $^1J(C(4), C(12)) \approx 7.9$, and $^1J(C(12), C(13)) = 18.1$ Hz. Structural features, apparent from $^1H,^1H$-COSY measurements, supported the adjacency of the protons at C(11), C(10), C(9), and C(8), and indicated the coupling of both H–C(8) to the bridghead H–C(7). Further structural information was obtained from homonuclear NOE measurements: upon irradiation of H–C(6), H–C(5) and H–C(7) showed a positive NOE effect, whereas irradiation of H–C(7) led to a signal enhancement of H–C(6), $H_{'exo'}$–C(8), and $H_{'endo'}$–C(8).

Apart from C(1)–C(2), C(1)–C(13), C(3)–C(5), C(4)–C(13), and C(10)–C(13), all $^{13}C,^{13}C$ connectivities of the ring skeleton of **4a** could be established by INADEQUATE measurements (*Table 2*[4])). COLOC results

*Scheme 4*




[1]) For specification of stereoisomerism in fenestranes, *cf.* [4].

[2]) MNDO calculations suggest that **5** is more than 200 kJ/mol less stable than **7**, whereas **6** and the stereoisomeric tricyclic compound to be formed from **7** by disrotatory cleavage of the cyclohexadiene subunit have similar stability [5].

[3]) Appropriate experiments to establish the stability of **7** and **5** are planned [6].

[4]) The terms *'endo'*/*'exo'* refer to the position of substituents below/above the mean plane of the C-skeleton.

Table 1. *NMR Data of* **3a**[4])

| | $^{13}$C-NMR[a]) $\delta$[ppm] | Adjacent[b]) C-atoms | $^{1}$H-NMR[c])[d]) $\delta$[ppm] | $^{1}$H,$^{1}$H Connectivity[e]) | Long-range $^{13}$C,$^{1}$H connectivities[f]) | NOE results[g]) | |
|---|---|---|---|---|---|---|---|
| | | | | | | H-atom irradiated | signal enhancement at |
| C(1) | 88.335 (*s*) | C(2), C(11), C(12) | – | – | $CH_2$(3) | | |
| $CH_2$(2) | 47.979 (*t*) | C(1), C(3) | 2.16 (*dd*, $H_{'exo'}$) | $CH_2$(3) | – | | |
| | | | 1.97 (*m*, $H_{'endo'}$) | | | | |
| $CH_2$(3) | 28.191 (*t*) | C(2), C(4) | 2.32 (*dd*, $H_{'exo'}$) | $CH_2$(2) | – | $CH_2$(3) | C(4) |
| | | | 2.31 (*dd*, $H_{'endo'}$) | | | | |
| C(4) | 54.817 (*s*) | C(3), C(5) | – | – | H–C(6) | | |
| H–C(5) | 131.905 (*d*) | C(4) | 5.70 (*d*) | H–C(6), H–C(7) | $CH_2$(3), H–C(7) | H–C(5) | C(4) |
| H–C(6) | 128.564 (*d*) | C(7) | 5.39 (*dd*) | H–C(5), H–C(7) | $CH_2$(8) | | |
| H–C(7) | 56.608 (*d*) | C(6), C(8), C(13) | 3.41 (*dd*) | H–C(6), $H_{'exo'}$–C(8) | – | H–C(7) | C(13) |
| $CH_2$(8) | 41.917 (*t*) | C(7), C(9) | 1.80 (*dd*, $H_{'exo'}$) | H–C(7), H–C(9) | – | H–C(8) | C(12) |
| | | | 1.66 (*ddd*, $H_{'endo'}$) | | | | |
| H–C(9) | 41.490 (*d*) | C(8), C(10), C(12) | 2.04 (*ddd*) | $CH_2$(8), $CH_2$(10) | – | | |
| $CH_2$(10) | 36.158 (*t*) | C(9), C(11) | 2.02–1.97 (*m*, 2H) | H–C(9), $CH_2$(11) | – | | |
| $CH_2$(11) | 45.131 (*t*) | C(1), C(10) | 2.12 (*m*, $H_{'exo'}$) | $CH_2$(10) | – | $H_{'exo'}$–C(11) | C(1) |
| | | | 1.79 (*m*, $H_{'endo'}$) | | | | |
| C(12) | 71.196 (*s*) | C(1), C(9) | – | – | $CH_2$(2), H–C(7), $CH_2$(8) | | |
| C(13) | 97.021 (*s*) | C(7) | – | – | $CH_2$(3), $CH_2$(8) | | |
| $CH_3O$ | 57.582 (*q*) | | 3.45 (*s*) | – | | $CH_3O$ | C(1), C(13) |
| OH | – | | 3.79 (*s*) | – | | OH | C(1), C(12), C(13) |

[a]) Multiplicity determined by DEPT.
[b]) INADEQUATE results.
[c]) Assigned according to hetero-COSY measurements.
[d]) Approximate multiplicity.
[e]) COSY results.
[f]) COLOC results.
[g]) Heteronuclear NOE.

Table 2. *NMR Data of* **4a**[4])

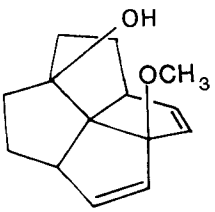
| | $^{13}$C-NMR[a]) $\delta$[ppm] | Adjacent[b]) C-atoms | $^{1}$H-NMR[c])[d]) $\delta$[ppm] | $^{1}$H,$^{1}$H Connectivity[e]) | Long range $^{13}$C,$^{1}$H connectivities[f]) | NOE results[g]) | |
|---|---|---|---|---|---|---|---|
| | | | | | | H-atom irradiated | signal enhancement at |
| C(1) | 155.185 (*s*) | C(12) | – | – | H–C(3) | | |
| H–C(2) | 110.384 (*d*) | C(3) | 5.01 (*dd*) | H–C(3), H–C(5), $CH_2$(12) | $CH_2$(12) | H–C(2) | C(1) |
| H–C(3) | 39.250 (*d*) | C(2), C(4) | 2.24 (*m*) | H–C(2), H–C(5) | H–C(2) | | |
| C(4) | 94.484 (*s*) | C(3), C(5) | – | – | – | | |
| H–C(5) | 35.937 (*d*) | C(4), C(6) | 2.25 (*m*) | H–C(3), $CH_2$(6) | – | | |
| $CH_2$(6) | 27.792 (*t*) | C(5), C(7) | 1.85 (*m*, 2H) | H–C(5), H–C(7) | – | | |
| H–C(7) | 57.103 (*d*) | C(6), C(8), C(13) | 2.10 (*m*) | $CH_2$(6), $CH_2$(8) | – | | |
| $CH_2$(8) | 30.620 (*t*) | C(7), C(9) | 1.95 (*m*, $H_{exo}$) 1.70 (*m*, $H_{endo}$) | H–C(7), $CH_2$(9) | – | | |
| $CH_2$(9) | 42.362 (*t*) | C(8), C(10) | 2.04 (*m*, 2H) | $CH_2$(8) | – | | |
| C(10) | 86.702 (*s*) | C(9), C(11) | – | – | $CH_2$(12) | | |
| $CH_2$(11) | 46.250 (*t*) | C(10), C(12) | 2.32 (*m*, $H_{exo}$) 2.14 (*m*, $H_{endo}$) | $CH_2$(12) | – | | |
| $CH_2$(12) | 23.007 (*t*) | C(1), C(11) | 2.45 (*m*, $H_{exo}$) 2.25 (*m*, $H_{endo}$) | $CH_2$(11) | – | $H_{exo}$–C(12) | C(1) |
| C(13) | 80.755 (*s*) | C(7) | – | – | H–C(2), $CH_2$(6) | | |
| $CH_3O$ | 55.321 (*q*) | – | 3.35 (*s*) | – | – | $CH_3O$ | C(4), C(10), C(13) |
| OH | – | – | 3.70 (*s*) | – | – | OH | C(4), C(10), C(13) |

[a]) Multiplicity determined by DEPT.
[b]) INADEQUATE results.
[c]) Assigned according to hetero-COSY results.
[d]) Approximate multiplicity.
[e]) COSY results.
[f]) COLOC results.
[g]) Heteronuclear NOE.

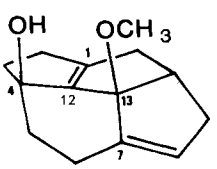
pointed to 1,3 relationships between C(13)/H–C(2), C(13)/$CH_2$(6), C(2)/$CH_2$(12), and C(5)/H–C(7). Dipolar interactions and, hence, spatial proximity between *H*–C(2)/C(1), $H_{exo}$–C(12)/C(1), $CH_3$O/C(4), C(10), and C(13), and O*H*/C(4), C(10), and C(13) could be detected by heteronuclear NOE measurements. Apart from COSY results, $^1$H,$^1$H relationships were extracted from homonuclear NOE measurements. Noteworthy are the enhancements of the signal of H–C(2) upon excitation of $H_{exo}$–C(12) and those of H–C(3) and H–C(5) by irradiation of H–C(2).

The formation of **3a** and **4a** is in accordance with mechanistic considerations of the photoinduced *meta*-cycloaddition [2a]. After excitation of **1a,** and directed by the MeO group in *ortho*-position, the olefinic double bond reacts to give an intermediate **8** which leads *via* formation of a bond between C(2) and C(6), and C(2) and C(4) to the photoproducts **3a** and **4a,** respectively *(Scheme 4)*. The alternate mode of [2 + 3] cycloaddition would have led *via* **9** to **10** and **11** *(Scheme 4)*. However, on the basis of the NMR results discussed above, these structures can be excluded.

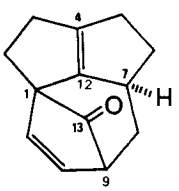
The structure of the photoproduct **4a** suggests that a homo-[1,5]-H shift might give the [5.5.5.5]fenestrane **12** with four functionalities well suited for introduction of further double bonds. When **4a** was heated in toluene in a sealed tube to 242° for 5 min, the tetracyclic compound **13** instead of **12** was obtained. In a similar reaction, **13** was also obtained from **3a**. The structure of this compound was determined by NMR methodology (*Table 3*[4])). On the basis of $^1$H,$^1$H and $^1$H,$^{13}$C-COSY data of **13**, five molecular fragments could be established. The connectivity among these fragments was proved by heteronuclear NOE experiments, whereas configurational information was obtained from homonuclear NOE data.




**12**




**13**




**14**

When **3a** or **4a** was refluxed in DMSO, the tetracyclic compound **14** was obtained. In the more polar solvent, fragmentation occurs in preference to the [1,5]-H shift. In the case of **4a**, fragmentation as well as [1,5]-H shift apparently follow, after rearrangement to **3a**. The selective homodienyl [1,5]-sigmatropic H shift, which is observed in **3a** (H–C(9)→C(6)) but not in **4a**, might be due to differences in steric constraints for the two compounds. According to model studies, the C-skeleton is much more rigid in **4a** than in **3a** and keeps the *'endo'*-proton[4]) at C(6) at a distance too large for the optimal *'endo'*-transition state [7]. According to MNDO calculations, it appears that **3a** is less stable than **4a** by 16 kJ/mol. The structure of **14** was established by NMR studies (*Table 4*[4])).

Analysis of the COSY results indicated the presence of an isolated $CH_2CH_2$ fragment and a separate $CH_2CH_2CHCH_2CH$ substructure. This led to the structure for **14**. Decoupling experiments showed that the bridgehead H–C(9) was coupled to the olefinic protons H–C(10) and H–C(11) ($J(9,10) \approx 2$, $J(10,11) \approx 6$ Hz) as well as to the neighbouring protons at C(8).

Table 3. *NMR Data of* **13**[4])

| | $^{13}$C-NMR[a]) $\delta$[ppm] | $^{1}$H-NMR[b])[c]) $\delta$[ppm] | NOE results | | |
|---|---|---|---|---|---|
| | | | H-atom irradiated | signal enhancements | |
| | | | | H-atom[d]) | C-atom[e]) |
| C(1) | 151.673 (*s*) | – | – | – | – |
| $CH_2$(2) | 28.595 (*t*) | 2.30 (*m*, $H_{'exo'}$) | $H_{'exo'}$–C(2) | $H_{'endo'}$–C(2), $CH_2$(3) | C(1) |
| | | 1.81 (*m*, $H_{'endo'}$) | $H_{'endo'}$–C(2) | $H_{'exo'}$–C(2), $CH_2$(3) | C(1) |
| $CH_2$(3) | 43.020 (*t*) | 2.25–2.19 (*m*, 2 H) | $CH_2$(3) | $CH_2$(2) | C(4) |
| C(4) | 79.158 (*s*) | – | – | – | – |
| $CH_2$(5) | 41.548 (*t*) | 1.94 (*m*, $H_{'exo'}$) | $H_{'exo'}$–C(5) | $H_{'endo'}$–C(5), $CH_2$(6) | C(4) |
| | | 1.18 (*ddd*, $H_{'endo'}$) | $H_{'endo'}$–C(5) | $H_{'exo'}$–C(5), $H_{'endo'}$–C(6) | C(4) |
| $CH_2$(6) | 22.751 (*t*) | 2.45 (*m*, $H_{'exo'}$) | $H_{'exo'}$–C(6) | $H_{'endo'}$–C(6), $H_{'exo'}$–C(5) | C(7) |
| | | 2.16 (*dddd*, $H_{'endo'}$) | $H_{'endo'}$–C(6) | $H_{'exo'}$–C(6), $CH_2$(5), H–C(8) | C(7) |
| C(7) | 144.801 (*s*) | – | – | – | – |
| H–C(8) | 122.936 (*d*) | 5.33 (*m*) | H–C(8) | $H_{'endo'}$–C(6), $CH_2$(9) | C(7) |
| $CH_2$(9) | 40.819 (*t*) | 2.80 (*m*, $H_{'exo'}$) | $H_{'exo'}$–C(9) | H–C(8), $H_{'endo'}$–C(9), H–C(10) | – |
| | | 1.93 (*dd*, $H_{'endo'}$) | $H_{'endo'}$–C(9) | H–C(8), $H_{'exo'}$–C(9), $H_{'endo'}$–C(11) | – |
| H–C(10) | 45.492 (*d*) | 3.01 (*ddd*) | H–C(10) | $H_{'exo'}$–C(9), $CH_2$(11) | C(13) |
| $CH_2$(11) | 39.156 (*t*) | 2.89 (*dd*, $H_{'exo'}$) | $H_{'exo'}$–C(11) | H–C(10), $H_{'endo'}$–C(11) | C(1) |
| | | 1.49 (*dd*, $H_{'endo'}$) | $H_{'endo'}$–C(11) | $H_{'endo'}$–C(9), H–C(10), $H_{'exo'}$–C(11) | C(1) |
| C(12) | 150.863 (*s*) | – | – | – | – |
| C(13) | 97.627 (*s*) | – | – | – | – |
| $CH_3O$ | 52.200 (*q*) | 3.20 (*s*) | $CH_3O$ | H–C(10) | – |
| OH | – | 2.34–2.13 (br.) | | – | – |

[a]) Multiplicity determined by DEPT.
[b]) Assigned according to hetero-COSY measurements.
[c]) Apparent multiplicity.
[d]) 2D NOESY.
[e]) Heteronuclear NOE.

Table 4. *NMR Data of* **14**[4])

| | $^{13}$C-NMR[a]) $\delta$[ppm] | $^{1}$H-NMR[b])[c]) $\delta$[ppm] | $^{1}$H,$^{1}$H Connectivity[d]) |
|---|---|---|---|
| C(1) | 62.495 (*s*) | – | – |
| $CH_2$(2) ($CH_2$(3)) | 27.112 (*t*) | 2.79 (*ddd*, $H_{'exo'}$) | $H_{'endo'}$–C(2), $CH_2$(3) |
| | | 2.18 (*m*, $H_{'endo'}$) | $H_{'exo'}$–C(2), $CH_2$(3) |
| $CH_2$(3) ($CH_2$(2)) | 29.164 (*t*) | 2.40 (*m*, 2 H) | $CH_2$(2) |
| C(4) (C(12)) | 142.151 (*s*) | – | – |
| $CH_2$(5) | 30.201 (*t*) | 2.35 (*m*, $H_{'exo'}$) | $H_{'endo'}$–C(5), $CH_2$(6) |
| | | 2.14 (*m*, $H_{'endo'}$) | $H_{'exo'}$–C(5), $CH_2$(6) |
| $CH_2$(6) | 37.579 (*t*) | 2.57 (*dtd*, $H_{'exo'}$) | $CH_2$(5), $H_{'endo'}$–C(6), H–C(7) |
| | | 1.83 (*ddt*, $H_{'endo'}$) | $CH_2$(5), $H_{'exo'}$–C(6), H–C(7) |
| H–C(7) | 32.520 (*d*) | 2.75–2.65 (*m*) | $CH_2$(6), $CH_2$(8) |
| $CH_2$(8) | 38.149 (*t*) | 2.27 (*ddd*, $H_{'exo'}$) | H–C(7), $H_{'endo'}$–C(8), H–C(9) |
| | | 1.54 (*ddd*, $H_{'endo'}$) | H–C(7), $H_{'exo'}$–C(8), H–C(9) |
| H–C(9) | 50.178 (*d*) | 2.88 (*ddd*) | $CH_2$(8) |
| H–C(10) (H–C(11)) | 128.435 (*d*) | 6.18 (*m*) | |
| H–C(11) (H–C(10)) | 134.569 (*d*) | | |
| C(12) (C(4)) | 152.497 (*s*) | – | – |
| C(13) | 213.498 (*s*) | – | – |

[a]) Multiplicity determined by DEPT. [b]) Assigned by $^{1}$H,$^{13}$C-hetero-COSY measurements. [c]) Apparent multiplicity. [d]) COSY results.

**Concluding Remarks.** – The intramolecular, photoinduced reaction of a 5-phenylpentene moiety, conformationally restricted by the indane skeleton, gives three products. These results are in contrast to the recent report where no monomeric products could be obtained from irradiation of **1b** in cyclohexane [8]. Despite the directing effect of a donor substituent in *ortho*-position of the phenyl ring, the photoreaction occurs preferentially *via* a [2 + 2] and not *via* a [2 + 3] cycloaddition. Mechanistic considerations for formation of the major product **2a** suggest that the highly strained *trans-cis-cis-cis*-[4.5.5.6]fenestrane[l]) **5** might be an intermediate. The products **3a** and **4a** are to be expected from the photoinduced *meta*-addition between an olefin and an arene. The formation of **3a** in preference to **4a** indicates that subtle structural changes control the closure of the cyclopropane ring. Thermolysis of **3a** in toluene leads, *via* a [1, 5]-H shift, to **13** which is also obtained from **4a**. Thermolysis of **3a** as well as **4a** in DMSO induces fragmentation and formation of **14**. The structures of **2a–4a, 13,** and **14** are established by the interplay of advanced NMR methods. This demonstrates the importance of advanced NMR spectroscopy for efficient elucidation of C,C and C,H connectivities in complex organic structures. The chemistry of the major photoproduct **2a** is under active investigation.

The generous support by the *Swiss National Science Foundation* (project No. 2.421–0.82, 2.236–0.84, and 2.016–0.86), the *van't Hoff Fund* of the *Royal Netherlands Academy of Sciences*, the *Stipendienfonds der Basler Chemischen Industrie* and the *Stiftung zur Förderung der wissenschaftlichen Forschung an der Universität* is gratefully acknowledged.

## Experimental Part

*General.* See [2a]. NMR: *Varian-EM-360L, Varian-XL-100, Bruker-Spectrospin-AM-400* instruments. For the acronyms used, see [9].

*1-(But-3-enyl)-7-methoxyindan-1-ol* (**1a**). A soln. of 7-methoxyindanone [10] (6.15 g, 37.9 mmol) in THF (50 ml) was added to the *Grignard* reagent prepared from Mg (1.04 g, 42.8 mmol) and 4-bromobut-1-ene (5.77 g,

42.7 mmol) in THF (30 ml) at 0°. After 4 h at r. t. and workup, the crude material was purified by medium-pressure chromatography with hexane/$Et_2O$ 7:5 (0.05% $Et_3N$ added): 6.62 g (80%) of **1a** as a yellowish oil. $R_f$ (hexane/$Et_2O$ 1:1) 0.46. UV (hexane; log ε): 274 (2.87), 266 (2.86). IR: 3560, 3000, 2950, 2925, 1634, 1600, 1585, 1440, 1432, 1070, 905. $^1$H-NMR: 1.90–2.40 (stack, 6H); 2.70–3.00 (stack, 2H); 3.15 (*s*, 1H); 3.80 (*s*, 3H); 4.85–5.20 (stack, 2H); 5.60–6.20 (*m*, 1H); 6.80 (*t*, 2H); 7.25 (*t*, 1H). MS: 218 (1, $M^+$), 200 (37), *163*, 159 (44), 148 (9), 146 (14). Anal. calc. for $C_{14}H_{18}O_2$ (218.30): C 77.03, H 8.31; found: C 77.00, H 8.31.

*Irradiation of* **1a**. A soln. of **1a** (1.0 g, 4.58 mmol) in (*t*-Bu)MeO (350 ml) was irradiated with a 500-W high-pressure lamp *(Hanau TQ 718)* in quartz apparatus for 9 h. The yellow soln. was filtered through *Celite* and concentrated unter $N_2$. The yellow, viscous oil which contained 33% of **1a** and **2a/3a/4a** in the ratio of 2:2:1 was separated by HPLC (hexane/(*t*-Bu)MeO 9:1, 0.1% $Et_3N$ added). In other experiments, the ratio **2a/3a/4a** was 4–5:3–4:1 at 70% turnover.

rel-*(2 R,5 S,7 S,10 S)-5-Methoxytetracyclo[5.5.1.0$^{2,5}$0$^{10,13}$]trideca-1(13),3-dien-10-ol* (**2a**). HPLC: $k' = 2.29$. Yield: 0.141 g (18.6%; GC purity, 90%). IR: 3600, 3000, 2940, 2850, 1150, 1082, 1063, 1030, 918. NMR: see [3]. MS: 218 (32, $M^+$), 203 (61), 201 (47), 200 (77), 185 (82), 175 (61), *163*, 159 (45), 157 (43), 147 (49), 141 (43), 129 (66), 115 (81), 91 (69). HR-MS: 128.13087 (calc. 218.13068).

*13-Methoxypentacyclo[5.4.2.0$^{4,12}$.0$^{4,13}$.0$^{9,12}$]tridec-5-en-1-ol* (**3a**). HPLC: $k' = 1.50$. Yield: 0.153 g (20%, GC purity, 92%). IR: 3600–3400, 3000, 2950, 1645, 1620, 1450, 1345, 1125, 1110. NMR: see *Table 1*. MS: 218 (2, $M^+$), *163*, 148 (11), 129 (4), 115 (5), 91 (5). HR-MS: 218.12985 (calc. 218.13068).

*4-Methoxypentacyclo[5.5.1.0$^{3,5}$.0$^{4,13}$.0$^{10,13}$]tridec-1-en-10-ol* (**4a**). HPLC: $k' = 1.63$. Yield: 0.047 g (6.2%, GC purity, 90%). IR: 3600–3300, 3000, 2940, 2860, 1448, 1372. NMR: see *Table 2*. MS: 218 (1, $M^+$), *163*, 148 (12), 129 (8), 115 (8), 91 (9). HR-MS: 218.13005 (calc. 218.13068).

*13-Methoxytetracyclo[5.4.2.0$^{4,12}$.0$^{10,13}$]trideca-1(12),7-dien-4-ol* (**13**). *From* **4a**: A soln. of **4a** (0.075 g, 0.34 mmol) in toluene (2 ml) was heated in an ampoule to 242° for 5 min. The brownish oily product was chromatographed with $CH_2Cl_2$/AcOEt 12:1 and then hexane/AcOEt 1:1: **13** as a yellowish oil (0.041 g 54.3%). $R_f$ ($CH_2Cl_2$/AcOEt 12.1) 0.07, $R_f$ (hexane/AcOEt 1:1) 0.22. IR: 3600, 3500–3300, 3000, 2920, 2845, 1450, 1438, 1250, 980, 960, 908. NMR: see *Table 3*. MS: 218 (12, $M^+$), *186*, 171 (47), 144 (19), 143 (42), 130 (20), 129 (71), 128 (26), 115 (16). HR-MS: 218.1307 (calc. 218.13068).

*From* **3a**: Similarly, **13** was obtained from **3a** (0.027 g, 0.12 mmol) in a yield of 0.015 g (54%). According to IR, $R_f$ (see above), and $t_R$ (cap. GC, *SE-54*, 20 m, isothermal, 150°), it was identical with **13** obtained from **4a**; a mixture of **13** from **3a** and **4a** gave a single peak in cap. GC.

*Tetracyclo[5.4.1.1.$^{1,9}$.0$^{4,12}$]trideca-4(12),10-dien-13-one* (**14**). *From* **3a**: A soln. of **3a** (0.190 g, 90% purity, 0.78 mmol) in ($D_6$)DMSO (0.5 ml) was heated in an ampoule to 200° for 1 min. After workup, the crude product was purified by medium-pressure chromatography with hexane/(*t*-Bu)MeO 20:1: **14** (0.100 g, 68.5%; GC: *ca.* 99%) as a colorless oil. $R_f$ (hexane/(*t*-Bu)MeO 20:1) 0.31. IR: 2935, 2850, 1755, 1105, 910. NMR: see *Table 4*. MS: 186 (1, $M^+$), 158 (78), 143 (24), *130*, 129 (49), 115 (30), 91 (19), 28 (25). Anal. calc. for $C_{13}H_{14}O$ (186.25): C 83.83, H 7.58; found: C 83.89, H 7.62.

*From* **4a**: Similarly, **14** was obtained from **4a** (0.046 g, 0.21 mmol) in a yield of 0.012 g (31%). According to IR, NMR, $R_f$, and $t_R$, it was identical with **14** obtained from **3a**.

## REFERENCES


[1] a) P. A. Wender, T. W. v. Geldern, B. H. Levine, *J. Am. Chem. Soc.* **1988**, *110*, 4858, and lit. cit. therein; b) A. Gilbert, *J. Chem. Soc., Perkin Trans. 2* **1984**, 1.

[2] a) R. Keese, J. Mani, J. H. Cho, E. Stamm, R. R. Astik, P. Bigler, V. Meyer, *Helv. Chim. Acta* **1984**, *67*, 1930; b) J. Mani, R. Keese, *Tetrahedron* **1985**, *41*, 5697; c) R. Keese, 'Organic Synthesis: Modern Trends', Ed. O. Chizhov, Blackwell Scientific Publications Ltd., Oxford, 1987; d) R. Keese, W. Luef, J. Mani, S. Schüttel, M. Schmid, C. Zhang, 'Strain and its Implications in Organic Chemistry', Ed. A. de Meijere, NATO ASI SERIES Kluver Academic Publishers, V. V. Dordrecht, The Netherlands, in press.

[3] P. Bigler, M. Kamber, *Magn. Reson. Chem.* **1986**, *24*, 972.

[4] W. Luef, R. Keese, *Helv. Chim. Acta* **1987**, *70*, 543.

[5] W. Luef, R. Keese, unpublished results.

[6] C. Zhang, part of the planned thesis.

[7] R. L. Loncharich, K. N. Houk, *J. Am. Chem. Soc.* **1988**, *110*, 2089.

[8] G. C. R. Ellis-Davis, J. Cornelisse, A. Gilbert, A. Kashoulis-Koupparis, *Tetrahedron Lett.* **1988**, *29*, 4319.

[9] A. E. Derome, 'Modern NMR Techniques for Chemistry Research', Pergamon Press, Oxford, 1987.

[10] H. J. E. Loewenthal, S. Shatzmiller, *J. Chem. Soc., Perkin Trans. 1* **1975**, 2149.