

## Photochemistry of Germacrenes. A [1,3]-OH and -OMe Shift

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The primary process in the irradiation of (*E,E*)-germacra-1(10), 4,7(11)-trien-8-ol and (*E,E*)-8-methoxygermacra-1(10), 4,7(11)-triene is a photochemically induced [1,3]-OR shift (R = H, Me).

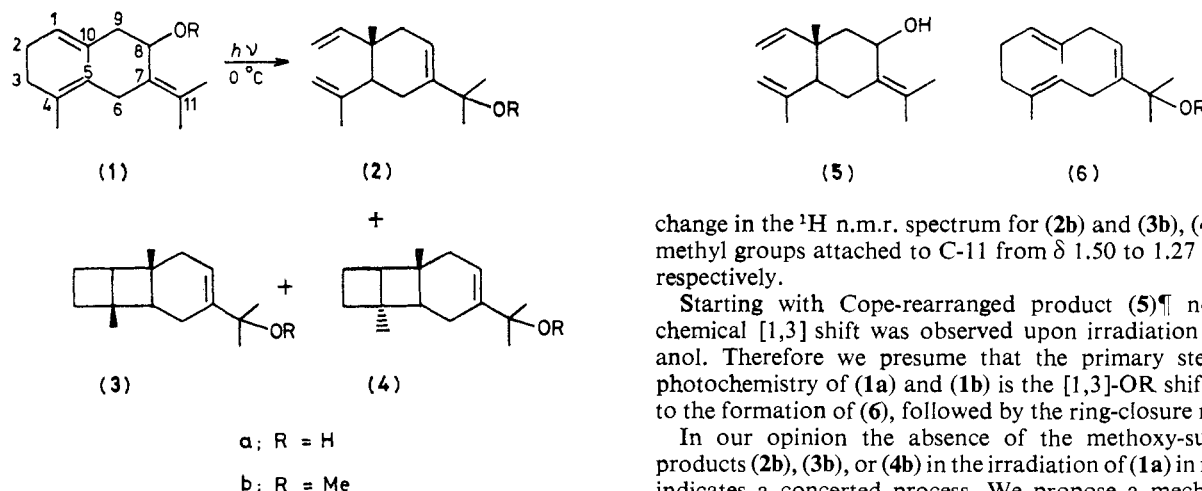
Previous investigations by our group have shown the unique properties of the 1,5-diene chromophore enclosed in a medium-sized ring system.<sup>1</sup> Extension of this study to the oxygen derivatives (**1a**, **1b**)† of germacrene B revealed that in addition to the intramolecular reactions of the endocyclic double bonds a photochemical [1,3]-OR shift (R = H, Me) of the allylic oxygen substituent takes place. To our knowledge a similar

shift has been proposed only in the irradiation of 2,5-dihydrofuran yielding 3,4-epoxybut-1-ene.<sup>2</sup>

When 8-hydroxygermacrene B (**1a**) was irradiated‡ at 0 °C in methanol or n-pentane for 3 h, t.l.c. (silica gel, hexane-5% ethyl acetate) indicated that three major products were formed. Separation by column chromatography (Woelm silica, hexane-5% ethyl acetate) yielded the compounds (**2a**),

† The synthesis of (**1a**) is described in ref. 1. The preparation of (**1b**) was carried out according to ref. 3.

‡ Irradiations were performed using a 500 W medium-pressure mercury lamp (Hanau), through quartz. The solution ( $6 \times 10^{-3}$  M) was purged with dry nitrogen prior to, and during, irradiation.



(3a), and (4a) in relative yields of 5:2:1 whose structures were elucidated by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy. $^{\S}$  The allylic rearrangement was demonstrated by a shift in the  $^1\text{H}$  n.m.r. spectrum of the methyl signals of the isopropylidene group from  $\delta$  1.47 to 1.33 and 1.30 for (2a) and (3a), (4a), respectively. In the  $^1\text{H}$  spectrum of (3a) and (4a) a triplet was found for the olefinic proton at  $\delta$  5.80 and 5.33, respectively. Further evidence was found in the multiplet structure of the relevant signals in the  $^{13}\text{C}$ -n.m.r. spectra; (2a):  $\delta$  117.49 (d, C-8), 143.51 (s, C-7), and 73.13 p.p.m. (s, C-11); (3a):  $\delta$  120.12 (d, C-8), 146.61 (s, C-7), and 74.08 p.p.m. (s, C-11); (4a):  $\delta$  120.99 (d, C-8), 142.90 (s, C-7), and 74.41 p.p.m. (s, C-11). The remaining part of the structure could be established by comparison with the spectral data of the germacrene irradiation products. $^1$  Irradiation of (1b) under similar conditions yielded completely analogous results. The [1,3]-methoxy shift was proved by a

$^{\S} ^1\text{H}$ -N.m.r. data were obtained on a Varian EM-360A spectrometer with  $\text{Me}_4\text{Si}$  ( $\delta$  0.0) as an internal standard.  $^{13}\text{C}$  N.m.r. data were recorded on a Bruker HX90 spectrometer. In all cases  $\text{CDCl}_3$  was used as solvent.

change in the  $^1\text{H}$  n.m.r. spectrum for (2b) and (3b), (4b) of the methyl groups attached to C-11 from  $\delta$  1.50 to 1.27 and 1.28, respectively.

Starting with Cope-rearranged product (5) $^{\parallel}$  no photochemical [1,3] shift was observed upon irradiation in methanol. Therefore we presume that the primary step in the photochemistry of (1a) and (1b) is the [1,3]-OR shift, leading to the formation of (6), followed by the ring-closure reactions.

In our opinion the absence of the methoxy-substituted products (2b), (3b), or (4b) in the irradiation of (1a) in methanol indicates a concerted process. We propose a mechanism in which the 1,5-diene fragment is used as a chromophore, initiating the [1,3]OR shift. If the chemistry is controlled by the conservation of orbital symmetry then it is to be expected that the [1,3] shift occurs in a suprafacial fashion.

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## References

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$^{\parallel}$  Prepared by a thermally induced Cope-rearrangement of 8-oxo-germacrene B followed by  $\text{LiAlH}_4$ -reduction.