Conformational dependence in the photochemistry of (E,E)-germacra-1(10),4,7(11)-triene

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Crystal structure determination of $\text{Ni}(\text{Et}_2\text{dte})_2(\text{AsI}_3)_2$

Crystal data: $a = 8.428(1)$, $b = 19.692(2)$, $c = 9.194(1)$ Å,
 $\beta = 102.24(2)^\circ$, $V = 1487.21$, $D_x = 2.84$ gcm $^{-3}$.

Space group: $P2_1/c$; $Z = 2$.

2070 independent reflections with $\sin \theta/\lambda = 0.55$ Å $^{-1}$ were measured on a Nonius CAD4 single crystal diffractometer (9 – 29 scan), using monochromated Zr-filtered MoK α radiation. No absorption corrections were applied. The structure was solved by the Multan method⁵. In the best E-map the iodine and arsenic atoms could be assigned. The other atoms except hydrogen, were located by Fourier syntheses.

1523 reflections with $I > 3\sigma_c(I)$ (σ_c based on counting statistics) were used in the refinement by full-matrix least-squares methods, with anisotropic vibration for As, I, Ni and S.

The weight (w) for each reflection was calculated in accordance with the formula $w = [\sigma_c^2 + (0.0011F_o)^2]^{-1}$. The final conventional R value was 0.042 for the 1523 reflections.

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Conformational dependence in the photochemistry of (E,E) -germacra-1(10),4,7(11)-triene

Peter J. M. Reijnders*, Rob G. van Putten, Jan W. de Haan, Henk N. Koning and Henk M. Buck

Laboratories of Organic Chemistry and Instrumental Analysis, Eindhoven University of Technology, The Netherlands

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Abstract. Irradiation of (E,E) -germacra-1(10),4,7(11)-triene **1** gives intramolecular reactions of the endocyclic double bonds. Products can be correlated with the crossed and parallel conformation of the title compound and the parallel conformation of its (Z,Z) -isomer **2**.

Introduction

Ground state conformations may play an important role in the photochemistry of alkenes. Examples can be found in the work of Havinga¹ demonstrating the relation between the ground state conformers of hexatriene and their photo-products. In the title compound **1** we can discern, with respect to the endocyclic double bonds, two conformers: one in which they form a parallel (**1a**) and one in which they have a crossed orientation (**1b**) (Fig. 1).

Fig. 1. Parallel (**1a**) and crossed (**1b**) conformation of (E,E) -germacra-1(10),4,7(11)-triene **1**.

In contrast with **1**, the (Z,Z) -isomer **2** can only adopt the parallel orientation (Fig. 2). Photochemical studies of related 1,5-cyclodiene structures, like (E) -caryophyllene **3**², reveal a conformational dependence. The influence of small structural changes was demonstrated by Yoshioka et al.³ in their study of the photochemical behaviour of isabelin **4** and dihydroisabelin **5**. Although isabelin exists in solution in the form of two conformers, viz. the crossed and parallel conformation of the endocyclic double bonds, reaction takes place only from the latter conformer. It may be of interest to note that **5**, in which the exocyclic double bond of **4** is hydrogenated, exists only in the crossed conformation.

Fig. 2. Parallel conformation of (Z,Z) -germacrene **2**.

Apparently³, this is caused by a change in hybridization of the carbons in the exocyclic methylene double bond which results in a ring contraction of the 1,5-cyclodecadiene skeleton which allows of the crossed conformer and not of the parallel conformer.

Results and discussion

(E,E) -Germacra-1(10),4,7(11)triene ((E,E) -germacrene) **1** has been synthesized by deoxygenation of (E,E) -germacra-

¹ E. Havinga, *Chimia* **30**, 27 (1976).

² K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta* **54**, 370 (1971).

³ H. Yoshioka, T. J. Mabry and A. Higo, *J. Am. Chem. Soc.* **92**, 923 (1970).

1(10),4,7(11)-trien-8-one⁴. Direct irradiation of **1** in methanol led to the formation of five products. Spectral analysis (see experimental part) indicated that structures **6** to **10** were formed. Irradiation of **1**, using *p*-xylene as sensitizer, led mainly to the formation of the completely isomerized (*Z,Z*)-derivative **2**, accompanied in minor amounts by compounds **6**, **7** and **9** (Scheme 1). Direct irradiation of isolated (*Z,Z*)-germacrene **2** in methanol only led to the formation of **7** and **9** together with unreacted **2**. These results can be compiled into a scheme in which the photo-products are related to the ground state conformers of **1** and **2** (Scheme 1). Formation

Scheme 1. Photochemistry of (E,E)-germacrene **1**.

of **6** and **7** can be explained by a photochemical cycloaddition reaction of the double bonds. Reaction of two olefinic bonds may occur in two ways⁵: a crossed one, comparable to that of (*Z,Z*)-1,5-cyclooctadiene⁶, would lead with **1** to compound **11**, whereas a [$\pi_s^2 + \pi_s^2$] cycloaddition reaction, comparable with that of isabelin³, results in the formation of product **6**. Structure **6** in contrast to **11** has an isomer, namely the *cis-syn-cis* derivative **7**, arising from [$\pi_s^2 + \pi_s^2$] cycloaddition of the *endocyclic* double bonds of (*Z,Z*)-isomer **2**. The presence of **7** obtained by direct irradiation of **1** is evidently due to partial isomerization of **1** into **2** via its excited singlet state⁷. In compound **8** ¹³C NMR (*vide infra*) indicated the presence of a trisubstituted cyclopropane ring at the expense of the two *endocyclic* double bonds. Photochemical reactions of two olefinic bonds generating a cyclopropane ring may arise from two kinds of reactions. The first one is the di- π -methane rearrangement⁸ occurring in 1,4-dienes. This possibility can be eliminated, since such a reaction would lead to **12**, in which one *endocyclic* double bond is saved. The second possibility is the Ohloff rearrangement. Reaction takes place via a six-centre mechanism which can arise from the singlet excited state² of the crossed conformer **1b** (Fig. 3).

Fig. 3. Ohloff rearrangement of **1b** leading to **8**.

The condition that the reaction originates from the singlet excited state explains why **8** is not found in the sensitized irradiation of **1**. It seems reasonable to assume that the formation of **9** takes place via a biradical intermediate which is quenched by intramolecular hydrogen transfer^{3,9}. The *cis*-geometry of **9** can only be rationalized via the crossed conformer **1b** and the parallel conformer **2** (Fig. 4).

Fig. 4. Formation of **9** from **1b** and **2**.

Compound **10** is formed via a Cope rearrangement. Its structure is identical with γ -elemene which is obtained under thermal conditions^{4a}. Since a photochemical Cope rearrangement is a forbidden process¹⁰, we assume that **10** is generated from the high vibrational manifold of the ground state of conformer **1b**. So the parallel conformer **1a** leads to **6**, while the crossed conformer **1b** initiates the Ohloff-type rearrangement leading to product **8**, the thermal Cope product **10**, and the bicyclo[5.3.0]-decane derivative **9**. The latter product is also formed from the (*Z,Z*)-isomer **2**. For the Ohloff-type rearrangement we suggest a mechanism which is based on the phenomenon "sudden polarization" as was proposed by Dauben and fully explained by Salem¹¹. This means that the charge separation is effectuated by the allylic anion ($C_2C_1C_{10}$) and the corresponding cation ($C_3C_4C_5$). (See Fig. 3, for the numbers see Figure 1, in particular compound **1a**.) Apparently, the $\sigma(C_2C_3) \rightarrow \pi$ mixing provokes rearrangement into **8**.

Structure elucidation

a. Compounds 6 and 7. The ¹³C-NMR spectrum indicated that the two compounds were present in a ratio of about 3/1 (based on a comparison of ¹³C-peak intensities of similar type of carbons). Each compound contained a tetrasubstituted olefinic bond. ¹H-NMR revealed that the isopropylidene group is still present. Apparently, we are dealing with an intramolecular reaction of the two *endocyclic* double bonds. The presence of two singlet and two doublet signals for each compound in the aliphatic region of the ¹³C NMR spectrum confirmed this assignment. A further confirmation of structures **6** and **7** could be found in their ¹H NMR spectrum. Dreiding models suggest that **7** has two angular methyl groups which are rather similar as far as the neighbouring surroundings are concerned, while in **6** they are more different. This is reflected in the ¹H NMR spectrum; for **7** the two methyl singlets appear at δ 1.03 and δ 1.08, while the methyl groups of **6** resonance at δ 0.68 and δ 0.82 ppm.

^{4a} E. D. Brown, T. W. Sam, J. K. Sutherland and A. Torre, J. Chem. Soc., Perkin Trans. 1, 2326 (1975).

^b P. J. M. Reijnders and H. M. Buck, Recl. Trav. Chim. Pays-Bas 97, 263 (1978).

⁵ J. R. Scheffer and M. L. Lungle, Tetrahedron Lett. 845 (1969).

⁶ I. Haller and R. Srinivasan, J. Am. Chem. Soc. 88, 5084 (1966).

⁷ Isomerization from the triplet state of **1** is unlikely due to the small i.c. rate of alkenes.

⁸ S. S. Hixson, P. S. Mariano and H. E. Zimmerman, Chem. Rev. 73, 531 (1973).

⁹ R. E. K. Winter and R. F. Lindauer, Tetrahedron 32, 955 (1976).

¹⁰ N. Trong-Anh, Die Woodward-Hoffmann Regeln und ihre Anwendung, Verlag Chemie, 1972, Weinheim/Bergstr., Chapters 2 and 3.

¹¹ L. Salem, Acc. Chem. Res. 12, 87 (1979).

b. Compounds 8 and 9. The second eluted product on column chromatography appeared, according to subsequent GLC analysis, to be composed of a 3/2 mixture of two compounds each with the same molecular mass as germacrene (*m/e* 204). Comparison of the multiplicity of the aliphatic signals in ^{13}C NMR indicated that the isomers had different skeletal structures. The relative positions of the olefinic signals in ^{13}C NMR supported this indication. The olefinic parts for each compound contained three singlet and one triplet olefinic carbon atom. This inferred the presence of one tetrasubstituted and one *exocyclic* double bond in these compounds. ^1H NMR showed that the isopropylidene moiety was still present in both compounds. Thus, as far as the olefinic part is concerned, we may conclude that an *intra*-molecular reaction of the two *endocyclic* double bonds took place which led to the formation of one *exocyclic* double bond. In the aliphatic region of the ^{13}C NMR spectrum one high field carbon singlet (δ 20.42 ppm) indicated that one product contained a cyclopropane ring. This was further confirmed by the existence of two carbon atoms with doublet and triplet multiplicity of $J_{\text{CH}} \sim 160$ Hz. Thus, besides the already mentioned olefinic elements, one product contains a tri-substituted cyclopropane ring. Further mechanistical deductions (*vide supra*) led to structure 8 formed *via* an Ohloff rearrangement. Subtraction of the signals of product 8 from the combined ^{13}C NMR spectrum of the mixture of 8 and 9 revealed that besides the aforementioned olefinic region, eleven signals with the following multiplicity had to be assigned: doublet (3), triplet (5) and quadruplet (3). This implies that two annelated ring systems are present and that accordingly one methyl group of 1 participated in the reaction. A comparable reaction was observed in the photochemistry of dihydroisabelin³ and dihydrocostunolide⁹. Applied to 1b this mechanism (Fig. 4) gives a product in agreement with the observed spectra of 9.

c. Compound 10. The third product obtained by column chromatography was one compound according to ^{13}C NMR. ^1H NMR and ^{13}C NMR revealed the existence of two vinylic parts. As in compounds 6 to 9 the *exocyclic* isopropylidene moiety was still present. ^1H NMR also revealed the presence of one singlet methyl group (δ 1.07 ppm). These elements combined suggest that a "Cope" structure was formed. To clarify the attachment of the vinyl groups to the cyclohexane ring a comparison was made with γ -elemene, the thermal rearrangement product of 1, which has the *trans*-divinyl geometry^{4a}. Comparison of the ^1H NMR and ^{13}C NMR spectra revealed that product 10 and γ -elemene were identical.

Experimental part

General remarks

Irradiations were carried out in a nitrogen atmosphere, using a Hanau TQ718 high pressure mercury vapour lamp of 700 W. During irradiation the temperature was kept between 15 and 20°C. ^1H NMR data were obtained on a Varian EM 360A spectrophotometer using TMS (δ 0.00 ppm) as internal standard. ^{13}C NMR data were recorded on a Varian HA100 equipped with a

digilab FTS-NMR-3. Mass spectra were recorded with a Finnigan 4000 GC-MS system by electron excitation (70 eV). HPLC separations were carried out with a Jobin Yvon Chromatospac Prep 100.

(*E,E*)-Germacrene-1(10),4,7(11)-triene 1

Prepared according to ref. 4a.

Direct irradiations of 1

(*E,E*)-Germacrene 1 (5 g, 0.025 mol) dissolved in 650 ml of methanol was irradiated for 10 h. After TLC indicated that 1 was no longer present, the methanol was evaporated and the residue separated by means of column chromatography (silica gel; *n*-hexane). The following fractions were obtained: *a.* (1.39 g; 27.8%) containing compounds 6 and 7. Compound 6: ^1H NMR (CDCl_3); δ 0.68 (s, 3, CH_3); 0.82 (s, 3, CH_3); 1.61 (s, 6, CH_3); ^{13}C NMR (neat); δ 132.65 (s); 121.00 (s); 51.17 (s); 49.05 (s); 53.07 (d); 46.10 (d). Compound 7: ^1H NMR (CDCl_3); δ 1.03 (s, 3, CH_3); 1.08 (s, 3, CH_3); 1.61 (s, 6, CH_3); ^{13}C NMR (neat); δ 128.76 (s); 122.19 (s); 50.86 (s); 47.11 (d); 43.80 (d); 41.86 (s). *b.* (0.95 g; 19%) containing compounds 8 and 9 in a ratio of 3/2. Compound 8: ^1H NMR (CDCl_3); δ 1.20 (s, 3, CH_3); 1.57 (s, 6, CH_3); 1.70 (s, 3, CH_3); 4.47–4.77 (m, 2, olefinic H); ^{13}C NMR (neat); δ 147.11 (s); 133.35 (s); 126.07 (s); 110.10 (t); 40.45 (d); 24.30 (t); 21.04 (d); 20.42 (s). Compound 9: ^1H NMR (CDCl_3); δ 0.94 [d (J 4.2 Hz), 3, CH_3]; 1.57 (s, 6, CH_3); 4.47–4.77 (m, 2, olefinic H); ^{13}C NMR (neat); δ 152.45 (s); 133.61 (s); 123.03 (s); 110.63 (t); 50.33 (d); 49.63 (d); 41.95 (d). *c.* (1.66 g, 33.2%) consisting of compound 10. ^1H NMR (CDCl_3); δ 1.03 (s, 3, CH_3); 1.62 (s, 6, CH_3); 1.68 (s, 3, CH_3); 4.53–5.10 (m, 4, olefinic H); 5.80 (dd (J 10, 17 Hz), 1, olefinic H). ^{13}C NMR (neat); δ 150.20 (s); 147.78 (d); 131.50 (s); 121.09 (s); 112.71 (t); 11.59 (t); 40.45 (s); 53.73 (d).

Thermal Cope rearrangement of 1

(*E,E*)-Germacrene 1 (0.5 g, 0.0025 mol) was refluxed for 4 h at 200°C. Column chromatography (silica gel, *n*-hexane) yielded, according to ^1H and ^{13}C NMR spectra, 0.34 g (68%) of compound 10.

Sensitized irradiation of 1

(*E,E*)-Germacrene 1 (0.9 g, 0.0044 mol) was irradiated in 650 ml of methanol/*p*-xylene (9/1) for 7 h. After evaporation of the solvent, column chromatography (silica gel, *n*-hexane) afforded 0.11 g of 9 (12.2%), 0.13 g of 6 + 7 (14.4%) and 0.36 g of (*Z,Z*)-isomer 2 (40%). Compound 2: ^1H NMR (CDCl_3); δ 1.63 (s, 6, CH_3); 1.69 (s, 6, CH_3); 1.87–2.50 (m, 8, aliphatic H); 2.77 [d (J 7 Hz), 2, aliphatic H]; 4.96–5.48 (m, 2, olefinic H).

Direct irradiation of 2

Isolated 2 (0.25 g, 0.0013 mol) was irradiated in 650 ml of methanol for 7 h. After evaporation of the solvent, column chromatography (silica gel, *n*-hexane) gave, besides unreacted 2, 0.05 g of 6 + 7 (1/1) (20%) and 0.04 g of 9 (16%).

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