224. Photoreaction of (*RS,SR*)-3-Phenyl-6-hepten-2-ol. Benzene-Olefin Cycloadditions as a Synthetic Route to [5.5.5.5]Fenestranes

Part III[1])

by **Jürg Mani, Jung-Hyuck Cho**[2]), **Rameshchandra R. Astik**[3]), **Erich Stamm**[4]), **Peter Bigler, Veronika Meyer,** and **Reinhart Keese***

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

(13.VIII.84)

Summary

Irradiation of (*RS,SR*)-3-Phenyl-6-hepten-2-ol (**3n**) gave the photoproducts **6n–10n**. Some reactions of **6n** and **8n** are reported. The regio- and diastereoselectivity observed in the photoreaction of substituted 5-phenylpentenes is discussed with respect to conformational preferences of the compounds to be irradiated.

Introduction. – Polycyclic hydrocarbons in which four rings are annulated in such a way that they share a common C-atom are of interest for a study of the planarization of the tetracoordinate C-atom [1]. The [5.5.5.5]fenestranes (= 'tetraquinacanes' or 'stauranes'; systematic name: tetracyclo[5.5.1.$0^{4,13}$.$0^{10,13}$]tridecanes) are particularly attractive since they eventually might be transformed into a [12]annulene with a central C-atom [2]. Although a few syntheses of fenestranes have been reported [1c] [3], short and efficient routes for their preparation are still in need. We report our results of the intramolecular photocycloaddition of 3-phenyl-6-hept-en-2-ol (**3n**).

Results. – *Synthesis and Configuration of* **3**. The preparation of the diastereoisomeric 5-(α-hydroxyethyl)-5-phenylpentenes **3n**[5]) and **3p**[5]) is outlined in *Scheme 1*. Alkylation of phenylacetone (**1**) with 4-bromobutene gives **2**, which is reduced by treatment with $NaBH_4$ to a 5:1 mixture of the diastereoisomers **3n**[5]) and **3p**[5]). The pure alcohols are obtained by preparative GLC separation.

The configuration of the diastereoisomers **3n** and **3p** has been determined by comparison of ^{1}H-NMR and IR data with those of *threo*- and *erythro*-3-phenylbutan-2-ol (**5**, see below) [6], respectively *(Table)*. To exclude the possibility that interaction of the

[1]) For part II of the series 'Planarization of Tetracoordinate Carbon Atom', see [1b].

[2]) Postdoctoral fellow 1982–1984.

[3]) Postdoctoral fellow 1980–1982.

[4]) Postdoctoral research assistant 1978–1980.

[5]) The configurational relationship of the two chiral centers is specified as **n** (= *RS,SR*) of **p** (= *RR,SS*) [4]. Alternatively, the diastereoisomers of **3** can be distinguished by *u* and *l* according to [5]; the two configurations are depicted by the *Fischer* projections in *Scheme 1*.

Scheme 1. *Synthesis and Configuration of (RS,SR)- and (RR,SS)-3-Phenyl-6-hepten-2-ol*

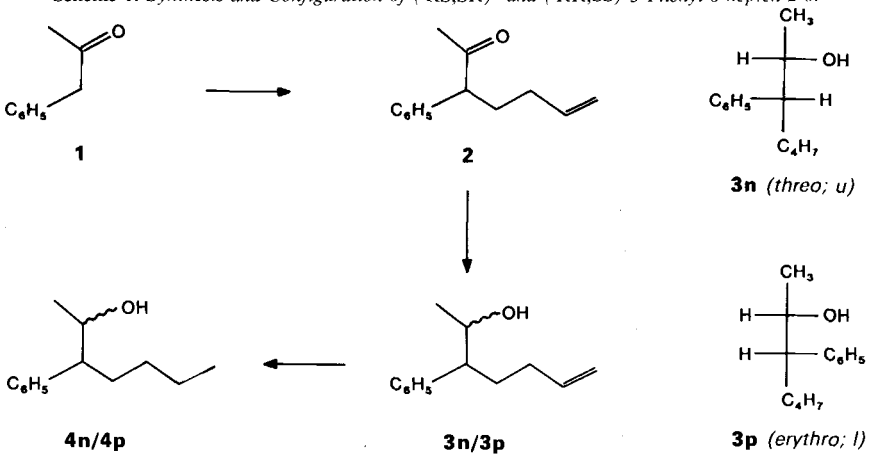
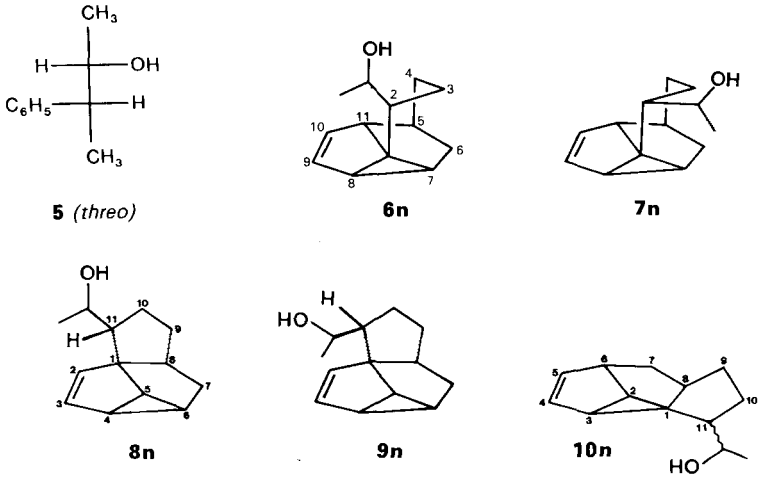


Table. *Comparison of ^{1}H-NMR and IR Data of the Pure Diastereoisomers* **3n** *and* **3p** *with* threo- *and* erythro-*3-Phenylbutan-2-ol* (**5**)

		3	4	5
^{1}H-NMR: $\delta(CH_3)$ [ppm]	*threo* (**n** or *u*)	1.025	1.12	1.08
	erythro (**p** or *l*)	0.962	0.95	0.93
IR: $\tilde{\nu}$(OH) [cm^{-1}]	*threo* (**n** or *u*)	3675, 3585	3610, 3585	3622, 3592
	erythro (**p** or *l*)	3679, 3618	3680, 3610	3629, 3601

OH-group with the double bond might lead to the alternative assignment, the 5:1 mixture of **3n**/**3p** was hydrogenated to give, after separation, **4n** and **4p**. Since the relationship of signals remained unchanged, the major isomer has **n**(*threo* or *u*)[5]) configuration. Further proof of the configuration of **3n** is provided by the X-ray structure analysis of one of the photoproducts **7n** (see below). Concerning the preferential formation of **3n** by reduction of **2**, it should be noted that this result is compatible with the *Cram-Felkin-Anh* rule [7].

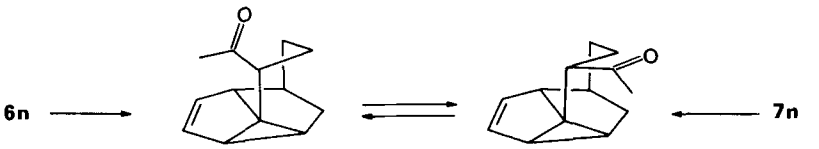


Photolysis of **3n**. When **3n** was photolyzed in degassed hexane, 6 products were formed, from which the major 5, *i.e.* **6n–10n**, could be obtained in pure form by preparative HPLC separation. Structure elucidation revealed 3 different types of tetracycloundecenes[6]), 2 of which are formed as pairs of configurational isomers (**6n**/**7n** and **8n**/**9n**, resp.). The ratio **6n**/**7n**/**8n**/**9n**/**10n** was 1:0.5:0.6:0.08:0.4.

Structure of **6n** *and* **7n**. The structure of **7n** was determined by X-ray structure analysis [8]. It revealed a bridged tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene skeleton with an equatorial α-hydroxyethyl substituent. Since the chirality in this substituent is opposite to the adjacent tertiary C-center, **7n** has *threo*-configuration.[7])

To establish the diastereoisomeric relationship between **6n** and **7n**, alcohol **6n** was oxidized to ketone **11**; similarly, alcohol **7n** gave the ketone **12**. Base-catalyzed equilibration of **11** and **12** each produced nearly the same mixture of **11** and **12**.

Scheme 2. *Equilibration of* **11** *and* **12**, *Obtained after Oxidation of* **6n** *and* **7n**, *Respectively*



Structure of **8n** *and* **9n**. The structure and configuration of the two isomers **8n** and **9n** has essentially been established by NMR spectroscopy. The ^{1}H-NMR spectrum of **8n**, the major isomer, is different from that of **6n** or **7n**. From the pattern of the olefinic protons, which revealed an *ABX* system and not an *ABXY* system, it is evident that only one of the olefinic protons has an adjacent CH group.

As revealed by a 200-MHz ^{1}H-NMR of **8n**, the coupling pattern of H–C(4) is *td* (J_t = 6.5 Hz, $J_{d(AX)}$ = 2 Hz). In addition to the coupling with H–C(3), H–C(4) shows coupling to 2 further H's, which give rise to the observed *t*. These 2H must be at different centers (C(5) and C(6)), because of the absence of an *AB* system with a large *J* in the methylene region. The presence of 3 tertiary C-atoms, which form a three-membered ring is supported by the ^{13}C-NMR spectrum of **8n**: experiments with delayed ^{1}H-decoupling by which signals with larger $J_{C,H}$ are amplified clearly indicate the presence of 3H's, which are each bound to cyclopropyl C-atoms. The assignment of the chemical shift of H–C(5) (2.3 ppm) and H–C(6) (1.3 ppm) is based on INDOR experiments and the observation that H–C(6) exhibits a complex coupling pattern, whereas H–C(5) appears as a *t*.

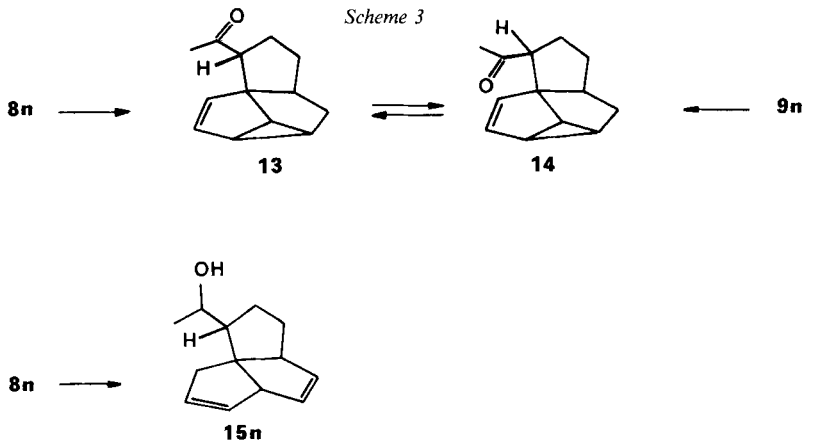
Based upon these observations and the ^{13}C-NMR spectrum which gave the expected number and type of C-atoms, it is concluded that **8n** has the C–C connectivity pattern shown. The *'exo'*-configuration assigned to the α-hydroxyethyl substituent is based on lanthanide-induced shifts, which is strongest for H–C(2). The alternative structure in which C(9) would be connected to C(7) instead of to C(8) can be ruled out because on heating, **8n** gave the diene **15n** *(Scheme 3) via* a [1,5]-H shift and not a diene with a bridgehead double bond.

---

[6]) Tetracyclo[5.4.0.0.^{1,8}.0^{5,11}]undecene, tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undecene, and tetracyclo[6.3.0.0^{1,3}.0^{2,6}]undecene.

[7]) To maintain the configurational relationship between **3n** (*threo*) and its photoproducts, only the relative configuration of the side chain is specified. The tetracyclic structures each have 5 centers of chirality, which are dependent on each other.

Scheme 3



Similarly, the connectivity pattern of **9n** has been established by combined ^{1}H and ^{13}C-NMR spectroscopy and lanthanide-shift experiments.

In the ^{13}C-NMR spectrum of **9n**, the signal of C(2) appears at much lower field than in **8n**, whereas that of C(4) is shifted upfield in comparison with C(4) in **8n**. The *'endo'*-configuration is deduced from lanthanide-shift experiments, which showed that H–C(4) is strongly shifted in comparison with H–C(4) in **8n**.

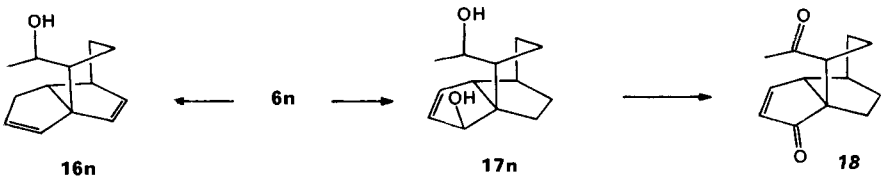
To establish beyond doubt that **8n** and **9n** are diastereoisomers, **8n** and **9n** were each oxidized to the corresponding ketones **13** and **14**. Upon equilibration under basic conditions, both ketones gave similar mixtures of **13** and **14**. Surprisingly, the *'endo'*-isomer **14** is more stable than the *'exo'*-isomer **13**.

Structure of **10n**. The structure of the photoproduct **10n** was established by its NMR spectra.

The *ABXY* coupling pattern of the olefinic protons in the ^{1}H-NMR of **10n** is similar to that of **8n** and **9n** (J_{AB} = 5 Hz, $J_{AC} \approx J_{BY} \approx$ 2 Hz). In a 300-MHz spectrum, H–C(6) appeared at 3.15 ppm with a *td* (degenerate *ddd*) coupling pattern (J = 5.8 Hz, $J_{5,6}$ = 2 Hz), whereas H–C(3) gave a *dd* (J = 7.8 Hz, $J_{4,3}$ = 2 Hz) at 2.38 ppm. The ^{13}C-NMR spectrum and delay-time experiments indicated the presence of a three-membered ring with only 2 C-atoms (C(3) and C(2)) each attached to 1H. A 2D ^{13}C-^{1}H correlation revealed that H–C(2) (2.2 ppm) has a *dd* coupling pattern ($J_{2,3}$ = 7.8 Hz, $J_{2,6}$ = 5.8 Hz). Ignoring the substituent, the missing C-atoms of the ring system consist of 2 CH- and 3 CH_3-groups.

Together with the observation that this photoproduct also undergoes a [1,5]-H shift, it is concluded that **10n** has the ring structure shown (see above). The position of the side-chain follows from the general mechanism of the photoinduced *meta*-cycloaddition (see below). Although lanthanide-shift experiments gave no definite information, we presently prefer the *'exo'*-configuration for the α-hydroxyethyl side chain.

Scheme 4

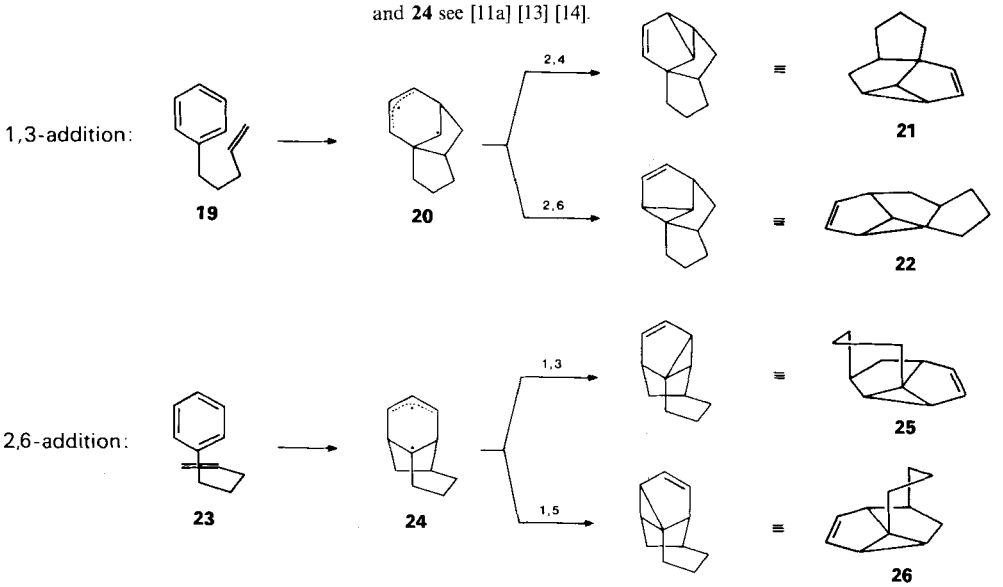


Some Transformations of **6n**. As already mentioned, **8n** as well as **10n** undergo a [1,5]-H shift on heating; treatment of **8n** with $HClO_4$ led to the same diene **15n**. Similarly, **6n** was transformed into **16n** on heating *(Scheme 4)*. In support of the structure, the ^{1}H-NMR spectrum of the olefinic region shows 4 olefinic protons. When **6n** was treated with $HClO_4$, the expected diene **16n** was not formed; instead, the cyclopropane ring was hydrated to give **17n**. This unexpected reactivity may be due to the more strained cyclopropane ring in **6n**. In support of this suggestion it should be pointed out that the X-ray structure of **7n** reveals a bond angle C(2)–C(1)–C(8) of 142° [8]. Oxidation of **17n** leads to the tricyclic enone **18**.

After identification of the 5 major photoproducts, it remains to be shown that **8n** and **9n** can be transformed into [5.5.5.5]fenestranes.

Discussion. – Common feature of the photoinduced cycloaddition reaction between benzene or some of its substituted derivatives and olefins is the formation of compounds with a tricyclo[3.3.0.$0^{4,6}$] oct-2-ene structure (photoinduced oxa-di-π-methane rearrangement of bicyclo[2.2.2]oct-2-en-5-ones provide another efficient entry into this class of compounds; see for example [9]). Since the preparation of such structural units usually is a multistep task, it is not surprising that the synthetic potential of this reaction has found attention. Particularly noteworthy are the results of *Wender et al.*, who used the intramolecular photocycloaddition of substituted 5-phenylpentenes for efficient, short syntheses of several natural products [10]. Mechanistic studies of this reaction, particularly by *Bryce-Smith, Gilbert* [11], and *Morrison* [12], have provided evidence that a) *meta*-cycloaddition occurs preferentially if the olefin and the substituted benzene have similar or identical ionization potentials, b) an exciplex is formed from the excited phenyl ring and the olefin leading after bond formation to an electronic state described as a diradical or a zwitterionic species [13] [14] which eventually leads to the three-membered ring.

Scheme 5. *Conformational Aspects of the Photocycloaddition of 5-Phenylpentene*. For the electronic nature of **20** and **24** see [11a] [13] [14].



In addition to the electronic nature of intermediates, it is of interest, how conformational restrictions may control intramolecular photocycloadditions, particularly those of substituted 5-phenylpentenes. For polysubstituted 5-(*ortho*-methoxyphenyl)pentenes, *Wender* has discussed some of these features [10b].

Excitation of 5-phenylpentene could lead to two different exciplexes, which are formed from the structures **19** and **23**. After cycloaddition, the intermediates **20** and **24** could give the products **21**/**22** and **25**/**26**, respectively (for a discussion of the electronic nature of intermediates such as **20** and **24**, see [11a] [13] [14]). For the relative rate with which the two exciplexes – and eventually the different products – are formed, we have to consider two limiting cases [15]: if, after excitation of the phenyl ring, the conformational changes in the side chain are faster than any of the individual rates, the product ratio **20**/**24** should be controlled by the difference in energies of the respective transition states (*Curtin-Hammett* principle) [16]. If the conformational changes are much slower, the ratio **20**/**24** should essentially be controlled by the energy difference of the different conformers. We wish to propose that high selectivity in formation of the primary cycloadduct (1,3- *vs.* 2,6-addition) is due to high conformational mobility of the vinyl group, whereas diastereoselectivity caused by substituents is controlled by conformational restrictions imposed by them.

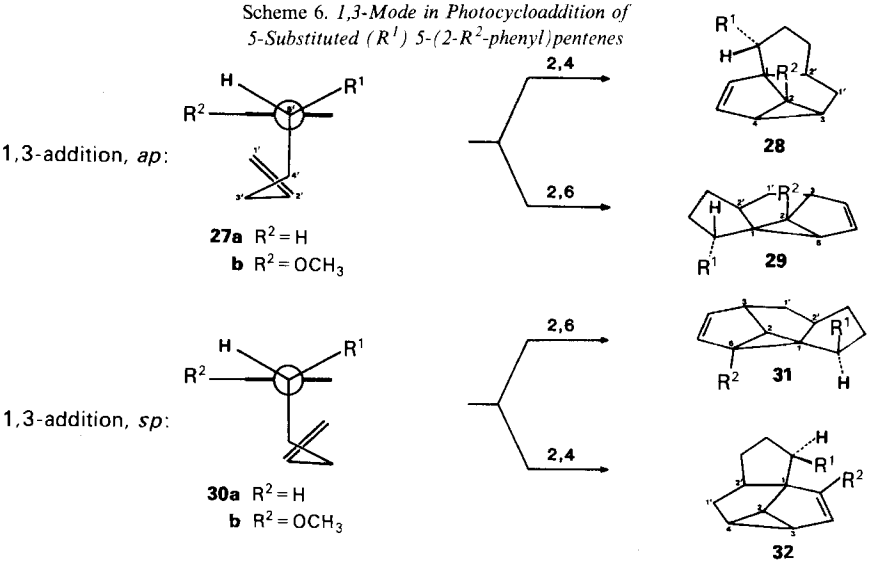
Based upon the fluorescence lifetime of *cis*-6-phenyl-2-hexene, estimated to $2.5 \cdot 10^{-9}$ sec, and the observation that its emission is quenched in comparison with hexylbenzene, it has been concluded that the rate of exciplex formation k_E must be faster than $0.5 \cdot 10^9$ sec^{-1} [12]. Since rotational barriers in alkanes, which do not involve alkyl-alkyl eclipsing, are 3–3.5 kcal/mol, and hence bond rotations $k_{rot} \geq 10^{10}$ sec^{-1}, it may be concluded that $k_E \approx 10^9$–10^{10} sec^{-1}. This conclusion is based upon the assumption that rotation of the alkenyl side chain is similar or equal in ground and excited state. This appears reasonable, because excitation is essentially limited to the phenyl ring. Also, it is assumed that no complexation betweeen the two chromophores occurs in the ground state [17]. Under these conditions, the vinyl group is sufficiently mobile to reach the optimal orientation **19** and **23**, respectively, for exciplex formation.

If the relative stability of the primary cycloadduct formed *via* exciplex either from **19** or **23** would reflect the relative rate with which the excited phenyl ring reacts with the olefin, we may use the stability of tertiary over secondary radicals or cations [11a] [13] [14] to conclude that 2,6-addition should be favoured over 1,3-addition. In the case the phenyl ring has an *o*-CH_3O-substituent, 1,3-addition is favoured over 2,6-addition [18]. The cycloadducts **20** and **24** would then lead to formation of the three-membered ring and give the products **21** and **22**, and **25** and **26**, respectively. Whereas **21**, **22**, and **26** have regularly been found in intramolecular *meta*-cycloadditions, **25** has not been observed[8]). The reasons for the preferential formation of one cyclopropane ring over the other remain to be elucidated.

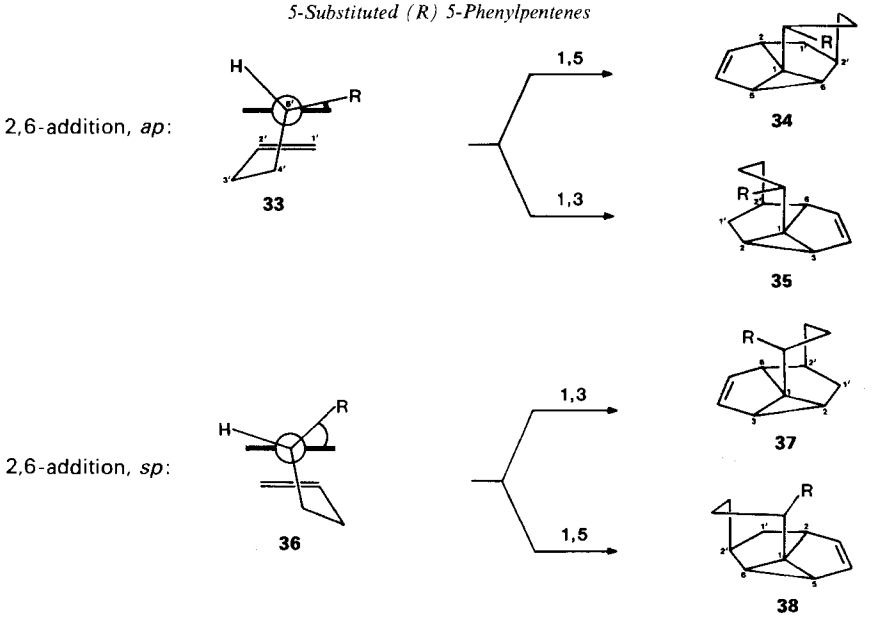
5-Substituted 5-Phenylpentenes. The 1,3- and 2,6-modes each have essentially two conformations (**27** and **30**, and **33** and **36**, resp.) leading to the corresponding exciplexes (see *Scheme 7* and *8*, resp.). The allylic group could either be antiperiplanar (*ap*) or synperiplanar (*sp*) with respect to the substituent R^1 or R in 5 (benzylic) position.

[8]) **Note added in proof:** A structure of type **25** has recently been found in an intramolecular photocycloaddition [29].

Scheme 6. *1,3-Mode in Photocycloaddition of 5-Substituted (R^1) 5-(2-R^2-phenyl)pentenes*



Scheme 7. *2,6-Mode in Photocycloadditions of 5-Substituted (R) 5-Phenylpentenes*



Depending on the regioselectivity of the final ring closure which leads to the cyclopropyl substructure, two pairs of bridged and two linear isomers could be formed. The four sets of isomers are distinguished by the configuration of the substituent R or R^1 (R^2 = H). The structural outcome for the 1,3-mode is shown in *Scheme 6*[9]). The

[9]) For more clarity, only one of the enantiomers of 5-substituted 5-phenylpentenes is used in *Scheme 7* and *8*.

structural and configurational consequences of the different conformational possibilities for the 2,6-mode are shown in *Scheme 7*. As mentioned above, there is presently no evidence that structures **34** and **38** are formed[8]).

As shown above, 1,3- as well as 2,6-cycloaddition occurs with **3n** (R^1, R = α-hydroxyethyl and R^2 = H in *Scheme 6* and *Scheme 7*). An analysis of observed product ratios shows that in the 1,3-mode, it is the *ap*-conformation **27a** which leads to the major configurational isomers (**28a**(↔**8n**) over **32a**(↔**9n**); only **29a**(↔**10n**) but not **31a** has been found). However, in the 2,6-mode, it is the *sp*-conformation **36** which leads to the major isomer **37**(↔**6n**), whereas the *ap*-conformation **33** gives the minor isomer **35**(↔**7n**). A model study suggests that the angle between the substituent R and the phenyl ring becomes smaller, if the 2,6-exciplex is formed from the *ap*- but not from the *sp*-conformation. If this repulsive interaction becomes stronger then the *sp*-interaction between the allylic chain and the substituent R, the predominant formation of **37** can be explained. Preliminary results with other 5-substituted phenylpentenes ($R=COOC_2H_5$) indicate a similar ratio of the diastereoisomeric products [19][10]).

5-(o-Methoxy-phenyl)pentenes. The strong effect of a CH_3O-substituent in the phenyl ring in directing regioselectivity is apparent in the intermolecular [18] as well as in the intramolecular [10a] benzene-olefin photocycloaddition. If the $(CH_2)_n$-chain by which the benzene ring and the olefin are connected is short ($n = 3$), the strong directing effect of a CH_3O-substituent is limited to the *ortho*-position. Under these conditions, the 1,3-mode should dominate over the 2,6-mode. The wealth of results published by *Wender et al.* [10] provide unambiguous evidence for this preference. In presence of a benzylic substituent in the $(CH_2)_n$-chain in addition to an *o*-CH_3O-group ($R^2 = OCH_3$, *Scheme 6*), model studies indicate that **27b** and **30b** have less repulsive interactions than those conformers where R^1 and the *o*-CH_3O-group approach each other. Major products should be formed *via* the 1,3-*ap*-mode **27**. If, however, the benzylic substituent R (R^1 = OH) and the *o*-CH_3-group could form a hydrogen bond, the 1,3-*sp*-mode might be preferred.

Preliminary experimental evidence indicates that the major photoproducts of 3-(*ortho*-methoxyphenyl)-6-hepten-2-ol are formed *via* the 1,3-*ap* mode [20][11]). The high regioselectivity of *o*-CH_3O-substituted 5-phenylpentenes in photo-induced 1,3-cycloaddition, combined with the higher yield are clear indicators for starting materials to be preferred in these reactions.

Conclusions. – The regioselectivity with which the primary cycloadducts are formed can be discussed in terms of a highly mobile vinyl group in substituted 5-phenylpentenes and dominating electronic stabilities in the intermediates **20** and **24**, respectively [11a] [13] [14]. The configuration of substituents in the photoproducts, determined in the same step, can be analyzed with respect to their restricted conformational mobility in the substituted 5-phenylpentenes. The parameters which control the formation of specific cyclopropane substructures in intra- and inter-molecular *meta*-photocycloadditions remain to be elucidated. Arene-olefin cycloadditions are at

---

[10]) The relative stability of conformers provides also a rationale for the observation [12] that (*Z*)-6-phenyl-2-hexene reacts preferentially *via* 1,3-mode, whereas the major products of the (*E*)-isomer are formed by the 2,6-mode [10b].

[11]) Surprisingly, 1-(*ortho*-(trimethylsilyl)phenyl)-4-penten-1-ol is photo-inert [21].

present the most attractive transformations with which de-aromatization [22] [23] of a phenyl ring leading to complex structures can be achieved. It is obvious that photoproducts like **8n** can be transformed into functionalized [5.5.5.5]fenestranes [24].

We thank Dr. *Richarz, Varian AG,* Zug, for 2D-correlation spectra. We gratefully acknowledge the support of this work by the *Stiftung zur Förderung der Forschung an der Universität Bern* and by the *Swiss National Science Foundation* (project 2.690-0.80 and 2.421-0.82).

Experimental Part

General. See [25]. For capillary and prep. GLC, *Carbowax 20M* was used as stationary phase. 2D-NMR spectra were obtained in $CDCl_3$ using *Varian XL-300,* operated in FT-mode; specific ^{1}H-NMR coupling pattern reported are based on simplified spin-system analyses. Prep. HPLC was done on a 21 mm × 25 cm column with 7 μm silica; mobile phase hexane/*tert*-butyl methyl ether 9:1. *k* values were calculated according to [26].

3-Phenyl-6-hepten-2-one (**2**). A solution prepared from KOH (20 g, 0.36 mol) and phenylacetone (**1**; 20 g 0.15 mol) in DMSO (400 ml) at 10° was stirred rigorously for 2 min. After slow addition of 4-bromo-1-butene (25 g, 0.19 mol) in DMSO (10 ml) at 10°, stirring was continued for 18 h at r.t. The mixture was poured on ice, extracted with Et_2O and worked up to yield 26.8 g (87%) of **2** of 92% purity. Distillation (72–75°/0.09 Torr) gave an anal. pure sample. IR: 2940, 1710, 1638, 1600, 1492, 1453, 1355, 1210, 1162, 920. ^{1}H-NMR: 0.75–2.5 (stack, *s* at 2.03, 7H); 3.65 (*t*, *J* = 7, 1H); 4.8–5.15 (2*m*, 2H); 5.5–6.05 (*m*, 1H); 7.3 (*m*, 5H). MS: 188 (M^+), 145, 134, 91, 67, 43. Anal. calc. for $C_{13}H_{16}$ (188.1): C 82.94, H 8.57; found: C 82.77, H 8.40.

threo- *and* erythro-*3-Phenyl-6-hept-en-2-ol* (**3n** and **3p**, *resp.*). To a cooled solution of **2** (28 g, 0.15 mol) in MeOH (600 ml) was added $NaBH_4$ (25 g, 0.66 mol) in small portions. After evaporation of the solvent, 20% aq. KOH (200 ml) was added. Subsequent workup gave 26.1 g (91.6%) of a 5:1 mixture **3n**/**3p**. **3n** (*threo*): GLC (150°), 17.8 min. IR: 3675, 3590, 3000, 2980, 2940, 1640, 1600, 1491, 1451, 918, 700. ^{1}H-NMR: 1.05–1.4 (stack, with *d* at 1.25, *J* = 7, 14H); 1.8 (stack, 4H); 2.5 (*m*, 1H); 3.9 (*ca. quint.*, *J* = 6, 1H); 4.8 (*m*, 1H); 4.95 (*m*, 1H); 5.5–5.95 (*m*, 1H); 7.25 (*m*, 5H). MS: 146, 117, 105, 104, 92, 91, 79, 77. Anal. calc. for $C_{13}H_{18}O$ (190): C 82.06, H 9.54; found: C 81.85, H 9.31.

3p (*erythro*): GLC (150°), 19.2 min. IR: 3675, 3618, 3000, 2980, 2935, 1640, 1600, 1491, 1451, 915, 700. ^{1}H-NMR: 1.0 (*d*, *J* = 7, 3H); 1.45 (br., 1H); 1.65–2.1 (stack, 4H); 2.6 (*m*, 1H); 3.9 (*ca. quint.*, 1H); 4.8 (*m*, 1H); 5.0 (*m*, 1H); 5.5–6.0 (*m*, 1H); 7.25 (*m*, 5H). MS: 146, 117, 105, 104, 91, 77, 45. Anal. calc. for $C_{13}H_{18}O$ (190): C 82.06, H 9.54; found: C 81.98, H 9.48.

threo- *and* erythro-*3-Phenylheptan-2-ol* (**4n** *and* **4p**, *resp.*). A sample of a 5:1 mixture **3n**/**3p** was hydrogenated in MeOH over Pd/C and separated by GLC. **4n**: IR: 3610, 3585, 2960, 2940, 1600, 1490, 1451. ^{1}H-NMR: 0.4–1.9 (stack with *d* at 1.08, *J* = 7, 11H); 2.2–2.6 (*m*, 1H); 3.75 (*ca. quint.*, *J* = 6, 1H); 7.2 (*m*, 5H). MS: 148, 105, 92, 91, 78. Anal. calc. for $C_{13}H_{20}O$ (192): C 81.20, H 10.48; found: C 81.13, H 10.48.

4p: IR: 3680, 3610, 3000, 2960, 2930, 2875, 2860, 1600, 1490, 1450, 1380. ^{1}H-NMR: 0.5–3.0 (stack with *d* at 0.94, *J* = 7, 14H); 3.7 (*quint.*, *J* = 6, 1H); 7.15 (*m*, 5H). MS: 148, 105, 92, 91, 78. Anal. calc. for $C_{13}H_{20}O$ (192): C 81.20, H 10.48; found: C 81.18, H 10.45.

Photolysis of threo-*Alcohol* **3n**. A degassed solution of **3n** (2.0 g, 0.011 mol) in hexane (375 ml) was irradiated with a 500-W lamp under continuous stirring. After 36–40 h when more than 90% of **3n** had reacted (control by capillary GLC), the solvent was removed and the residue submitted immediately to flash chromatography [27] with hexane/*tert*-butyl methyl ether 3:4. Subsequent prep. HPLC gave 6 products from which the 5 major photoalcohols were identified.

(1RS, 2SR)-2-((RS)-1'-Hydroxyethyl)-tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**6n**)[7]. *k'* (HPLC) 3.2. IR: 3620, 3592, 3060, 3000, 2970, 2935, 2860, 1590, 1450, 1440, 1050, 920, 880. ^{1}H-NMR: 0.88 (*m*, 1H); 1.1–2.1 (stack, with *d* at 1.2, *J* = 7, 11H); 2.2–2.8 (stack, 3H); 3.83 (*dq*, *J* = 8.5, 6.5, 1H); 5.50 (*ca. dd*, *J* = 5, 2, 1H); 5.70 (*ca. dd*, *J* = 5, 2, 1H). ^{13}C-NMR: 21.1 (*q*, C(2')); 26.0 (*t*); 27.2 (*d*, C(7)); 27.4 (*t*); 30.6 (*t*); 42.3 (*d*, C(8)); 47.7 (*s*, C(1)); 51.6 (*d*); 51.8 (*d*); 68.8 (*d*, 2C); 128.8 (*d*, C(9)); 130.0 (*d*, C(10)). MS: 146, 117, 115, 105, 104, 91.

(1RS, 9RS)-2-((SR)-1'-Hydroxyethyl)tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**7n**)[7]: *k'* (HPLC) 5; crystallized on standing, m.p. 110°. IR: 3600, 3060, 3000, 2920, 2855, 1590, 1450, 1090, 935, 890, 870, 640. ^{1}H-NMR: 0.75–1.4 (stack, with *d* at 1.15, *J* = 7, 5H); 1.4–2.0 (stack, 5H); 2.0–2.55 (stack, 4H); 2.65 (*dd*, *J* = 6.5, 2, 1H); 3.25 (*dq*, *J* = 8.5, 6.5, 1H); 5.50 (*ca. dd*, *J* = 5, 2, 1H); 5.68 (*ca. dd*, *J* = 5, 2, 1H). ^{13}C-NMR: 20.2 (*q*, C(2')); 22.5 (*d*, C(7)); 27.2 (*t*); 29 (*t*); 33.3 (*t*); 43.3 (*d*, C(8)); 48.7 (*s*, C(1)); 50.3 (*d*); 52.0 (*d*); 60.2 (*d*); 68.3 (*d*, C(1')); 128 (*d*, C(9)); 130.3 (*d*, C(10)). MS: 146, 131, 117, 105, 104, 92, 91, 45.

(1RS,11RS)-11-((RS)-1'-Hydroxyethyl)tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**8n**)[7]: *k'* (HPLC) 2.7. IR: 3600, 3555, 3000, 2915, 2890, 2860, 1442, 1390, 1055, 920. ^{1}H-NMR: 0.75–2.5 (stack, with *d* at 1.12, J = 7, 15H); 3.90 (*dq*, J = 8.5, 6.5, 1H); 5.43 (*d*, J = 5, 1H); 5.60 (*dd*, J = 5.2, 2, 1H). ^{13}C-NMR: 20.7 (*q*, C(2')); 27.1 (*t*); 29.6 (*d*); 31.3 (*t*); 31.6 (*t*); 32.0 (*d*); 43.7 (*d*,C(4)); 54.3 (*d*, C(11)); 61.0 (*d*); 68.8 (*s*, C(1)); 70.6 (*d*, C(1')); 128.0 (*d*, C(3)); 132.1 (*d*, C(2)); 27.1 (*t*); 29.6 (*d*); 31.6 (*t*); 32.0 (*d*); 61.0 (*d*). MS: 190 (M^+), 146, 129, 117, 115, 105, 104, 91, 79, 77, 51.

(1RS,11RS)-11-((SR)-1'-Hydroxyethyl)-tetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**9n**)[7]: *k'* (HPLC) 2.2. IR: 3560, 3018, 2940, 2865, 1448, 1395, 1375, 1090, 1035, 907. ^{1}H-NMR: 0.75–2.5 (stack, with *d* at 1.17, J = 7, *ca.* 15H); 3.90 (*m*, J = 9, 7, 1H); 5.43 (*B* of *ABX*, J_{AB} = 5, J_{BX} < 1, 1H); 5.60 (*A* of *ABX*, J_{AX} = 2, 1H). ^{13}C-NMR: 21.8 (*q*, C(2')); 28.0 (*t*); 29.0 (*t*); 29.4 (*d*); 29.7 (*t*); 32.5 (*d*); 35.6 (*d*, C(4)); 51.6 (*d*, C(11)); 60.7 (*d*, C(8)); 70.4 (*s*, C(1)); 71.7 (*d*, C(1')); 127.2 (*d*, C(3)); 136.3 (*d*, C(2)). MS: 190 (M^+), 146, 145, 129, 118, 117, 115, 105, 104, 92, 91.

(1RS,11RS)-11-((SR)-1'-Hydroxyethyl)tetracyclo[6.3.0.0^{1,3}.0^{2,6}]undec-4-ene (**10n**)[7]: *k'* (HPLC) 6.8. IR: 3555, 2930, 1450, 1100, 908. ^{1}H-NMR: 1.0–1.4 (stack, with *d* , J = 7, *ca.* 5H); 1.4–2.45 (stack, *ca.* 9H); 3.15 (*m*, J = 6, 2, 1H); 3.7 (*m*, J = 7, 7, 1H); 5.38 (*A* of *ABXY*, J_{AB} = 5, J_{AX} = 2, J_{AY} < 1, 1H); 5.58 (*B* of *ABXY*, J_{BY} = 2, J_{BX} < 1, 1H). ^{13}C-NMR: 21.3 (9, C(2')); 29.5 (*t*); 31.0 (*t*); 34.7 (*d*, C(3)); 40.3 (*d*, C(8)); 41.2 (*d*, C(2)); 49.0 (*t*, C(7)); 50.3 (*s*, C(1)); 50.8 (*d*, C(11)); 51.5 (*d*, C(6)); 69.8 (*d*, C(1')); 128.0 (*d*, C(4)); 133.8 (*d*, C(5)). MS: 190 (M^+), 172, 157, 146, 145, 129, 117, 105, 91, 80.

(1RS,2SR)-2-Acetyltetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**11**)[7]. A small sample of **6n** was oxidized in CH_2Cl_2 with *Sarett*'s reagent [28]; pure **11** was obtained by chromatography, R_f (CH_2Cl_2) 0.60. IR: 3010, 2925, 2860, 1705, 1190, 1170, 1360, 1350. ^{1}H-NMR: 1.0 (*m*, 1H); 1.45–2.5 (stack with *s* at 2.13, 11H); 2.8 (*m*, 2H); 5.5 (*B* of *ABXY*, J_{AB} = 5, J_{BY} = 2, J_{BX} < 1, 1H); 5.7 (*A* of *ABXY*, J_{AX} = 2, 1H). ^{13}C-NMR: 24.4 (*t*); 27.1 (*t*); 28.0 (*d*); 28.1 (*q*); 30.7 (*t*); 43.2 (*d*); 48.9 (*s*); 52.9 (*d*); 54.4 (*d*); 55.9 (*d*); 128.4 (*d*); 130.5 (*d*); 209.7 (*s*). MS: 188 (M^+), 145, 134, 117, 115, 91.

(1RS,2RS)-2-Acetyltetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**12**)[7] was obtained from **7n** like **11** from **6n** (see above), R_f (CH_2Cl_2) 0.60. IR: 3010, 2925, 2875, 1705, 1355, 1190. ^{1}H-NMR: 0.95 (*m*, 1H); 1.5–2.0 (stack, 6H); 2.1 (*s*, 3H); 2.28 (*Y* of *ABXY*, J_{BY} = 2, J_{AY}, J_{XY} < 1, 1H); 2.4 (*m*, 1H); 2.63 (*X* of *ABXY*, J_{AX} = 2, J_{BX} < 1, 1H); 3.3 (*m*, 1H); 5.08 (*B* of *ABXY*, J_{AB} = 5, 1H); 5.68 (*A* of *ABXY*, 1H). MS: 188 (M^+), 145, 134, 117, 115, 91, 87, 77, 75.

(1RS,11RS)-11-Acetyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**13**)[7]. A solution of **8n** (0.12 g, 0.63 mmol) in CH_2Cl_2 was oxidized according to [28]. After decantation, the precipitated material was washed with Et_2O; the combined org. phases were washed with 5% NaOH, 5% HCl, and conc. $NaHCO_3$. After drying and evaporation of the solvent, 0.1 g (83%) of crude **13** was isolated, R_f (CH_2Cl_2) 0.45. IR: 3030, 2930, 1705, 1360, 1175. ^{1}H-NMR: *ca.* 1.4–2.5 (stack with *s* at 2.15, 13H); 3.15 (*t*, 1H); 5.15 (*B* of *ABX*, J_{AB} = 5, $J_{BX} \approx$ 0,1H); 5.55 (*A* of *ABX*, J_{AX} = 2, 1H). ^{13}C-NMR: 27.2 (*t*); 28.4 (*t*); 29.3 (*d*); 30.6 (*t*); 31.5 (*q*, C(2')); 32.2 (*d*); 43.0 (*d*, C(4)); 57.2 (*d*); 59.8 (*d*); 69.8 (*s*, C(1)); 126.6 (*d*, C(3)); 132.5 (*d*, C(2)); 209.0 (*s*, C(1'). MS: 188 (M^+), 145, 134, 117, 115, 91, 79, 77.

(1RS,11RS)-11-Acetyltetracyclo[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene (**14**)[7]. A small sample of **9n** was oxidized with CrO_3 as described above and the crude mixture purified by repeated chromatography, R_f (CH_2Cl_2) 0.54. Capillary GLC: 9.48 min. IR: 3020*s*, 2930*s*, 2870*s*, 1705*s*, 1590*w*, 1465*m*, 1450*s*, 1420*m*, 1360*s*, 1335*m*, 1180*s*, 1085*m*, 1055*m*, 915*m*. ^{1}H-NMR: 1.5–2.5 (stack, with *s* at 2.1, *ca.* 13H); 3.13 (*t*, J = 7, 1H); 5.5 (*B* of *ABX*, J_{AB} = 5, J_{BX} < 1, *ca.* 1H); 5.65 (*A* of *ABX*, J_{AX} = 2, *ca.* 1H). MS: 188 (M^+), 145, 130, 117, 115, 91, 79.

Equilibration of **11**. A small sample was refluxed for 10 h in KOH/EtOH. Capillary GLC: 2.3:1 mixture **11**/**12**. Equilibration of **12** under the same conditions gave **11**/**12** in ratio of 2:1.

Equilibration of **13**. A small sample of **13** was refluxed for 1 h in KOH/EtOH. Capillary GLC: 1:2.8 mixture **13**/**14**. Equilibration of **14** for 10 h under the same conditions gave **13**/**14** in a ratio of 1:2.7.

(1RS,11RS)-11-((RS)-1'-Hydroxyethyl)tricyclo[6.3.0.0^{1,5}]undeca-3,6-diene (**15n**)[7]. A sample of **8n** (40 mg, 0,21 mmol) under vacuum in a small ampoule and heated to 275° for 0.5 h. After chromatography (CH_2Cl_2), 0.015 g (38%) of **15n** was obtained, R_f (CH_2Cl_2) 0.36. IR: 3605, 3560, 3050, 3005, 1448, 1395, 1375, 1349, 1250, 1135, 1040, 1020, 950. ^{1}H-NMR: 1.1–2.2 (stack with *d* at 1.2, J = 7, 10H); 2.65–3.05 (*m*, 2H); 3.68 (*m*, 1H); 3.9 (*m*, 1H); 5.43–5.8 (stack with *s* at 5.58, 4H). ^{13}C-NMR: 23.3 (*q*); 31.3 (*t*); 40.5 (*t*); 57.1 (*d*); 60.6 (*s*); 62.3 (*d*); 66.3 (*d*); 70.0 (*d*); 128.3 (*d*); 130.0 (*d*); 133.2 (*d*); 134.3 (*d*). MS: 190 (M^+), 172, 157, 143, 130, 129, 117, 115, 104, 91.

(1RS,9SR)-9-((RS)-1'-Hydroxyethyl)tricyclo[4.3.2.0^{1,5}]undeca-2,10-diene (**16n**)[7]. After photolysis of **3n**, the product mixture was separated by prep. GLC at 200° and gave **16n** (3.8%) as solid material. Pure **16n** was obtained by crystallization from hexane and sublimation, m.p. 66°. Capillary GLC: 18.67 min. IR (KBr):

3600–3100 (br.), 3070, 3050, 2580–2800, 1445, 1368, 1348, 1155, 1119, 1090, 1076, 990, 950, 915, 755, 732, 708. ^{1}H-NMR: 1.1–1.5 (stack, with *s* at 1.23, $J = 7$, 5H); 1.53–2.58 (stack, 7H); 2.7 (*m*, 1H); 4.06 (*m*, 1H); 5.3 (*d*, $J = 6$, 1H); 5.7 (*m*, 2H), 6.05 (*m*, 1H). ^{13}C-NMR: 21.6 (*t*); 22.6 (*q*); 25.7 (*t*); 34.7 (*t*); 43.6 (*d*); 43.9 (*d*); 52.6 (*d*); 63.1 (*s*); 69.2 (*d*); 127.7 (*d*); 129.7 (*d*); 133.1 (*d*); 135.5 (*d*). MS: 190 (M^+), 175, 172, 157, 145, 143, 129, 117, 115, 105, 91. Anal. calc. for $C_{13}H_{18}O$ (190): C 82.06, H 9.54; found: C 81.89, H 9.6.

*(1*RS*,9*SR*)-9-Acetyltricyclo[4.3.2.0^{1,5}]undec-3-en-2-one* (**18**)[7]). A small sample of **17n** was oxidized according to [28]. After workup, crude **18** was isolated in 50% yield, R_f (hexane/Et_2O 1:1) 0.32. IR: 3005, 2938, 2878, 1705, 908. ^{1}H-NMR: 1.45–2.2 (stack, with *s* at 2.13, 11H); 2.48 (*m*, 1H); 3.05 (*X* of *AMX* and 1 additional H); 5.90 (*M* of *AMX*, $J_{MA} = 5$, $J_{MX} = 2$); 7.30 (*A* of *AMX*, $J_{AX} = 2$). ^{13}C-NMR: 21.6 (*t*); 28.1 (*t*); 29.5 (*q*); 29.7 (*s*); 31.8 (*t*); 34.1 (*t*); 39.2 (*d*); 52.2 (*d*); 56.8 (*d*); 132.3 (*d*); 160 (*d*); the signals of the carbonyl C-atoms were not visible. MS: 204 (M^+), 161, 155, 133, 112, 97, 84.

*(1*RS*,9*SR*)-2-*'exo'*-Hydroxy-9-((*RS*)-1'-hydroxyethyl)tricyclo[4.3.2.0^{1,5}]undec-3-ene* (**17n**)[7]). A sample of **6n** (50 mg, 0.26 mmol) was stirred with 57 mg of 70% $HClO_4$ in monoglyme (8 ml) at r.t. for ½ h. Et_2O extraction yielded **17n** (50 mg, 92%), R_f (hexane/Et_2O 1:1) 0.77. IR: 3500–3300 (br.), 1340, 1135, 1085, 1040, 1010, 985, 975, 945, 935, 908, 855. ^{1}H-NMR: 1.2 (*d*, $J = 7$, 3H); 1.2–1.95 (stack, 11H); 2.41 (*m*, 1H); 2.90 (*X* of *ABMX*, $J_{XA} = 2$, $J_{XB} = 3$); 4.0 (*m*, $J = 7$, 9, 1H); 4.48 (*M* of *ABMX*, $J_{MB} = 2$, $J_{MA} < 1$); 5.80 (*B* of *ABMX*, $J_{BA} = 5$); 6.07 (*A* of *ABMX*). ^{13}C-NMR: 19.03 (*t*); 21.5 (*q*); 28.3 (*t*); 29.3 (*t*); 32.3 (*t*); 36.6 (*d*); 53.0 (*d*); 56.8 (*d*); 63.5 (*s*); 85.2 (*d*); 86.3 (*d*); 131.4 (*d*); 140.4 (*d*); from (^{13}C) of C(2), it could be concluded that the OH-group has *'exo'*-configuration; this is supported by the broad CH-band of the IR. MS: 190 ($M^+ - 18$), 175, 146, 131, 119, 118, 117, 105, 104, 91, 86, 84, 79.

REFERENCES

[1] a) *R. Keese, A. Pfenninger & A. Roesle*, Helv. Chim. Acta *62*, 326 (1979); b) *H. Schori, B. B. Patil & R. Keese*, Tetrahedron *37*, 4457 (1981); c) *M. Luyten & R. Keese*, Angew. Chem. *96*, 358 (1984); ibid. Int. Ed. *23*, 390 (1984); d) *M. Luyten & R. Keese*, Helv. Chim. Acta (1984) in press; e) *R. Keese*, Nachr. Chem. Techn. Lab. *30*, 844 (1982); for computational results of planar, tetracoordinate carbon see *K. Krogh-Jespersen, D. Cremer, D. Poppinger, J. A. Pople, P. v. R. Schleyer & J. Chandrasekhar*, J. Am. Chem. Soc. *101*, 4843 (1979); *E.-U. Würthwein, J. Chandrasekhar, E. D. Jemmis & P. v. R. Schleyer*, Tetrahedron Lett. *22*, 843 (1981); *P. v. R. Schleyer & E.-U. Würthwein*, J. Chem. Soc., Chem. Commun. *1982*, 542; *D. C. Crans & J. P. Snyder*, J. Am. Chem. Soc. *102*, 7152 (1980).

[2] *R. Hoffmann, R. W. Alder & C. F. Wilcox, Jr.*, J. Am. Chem. Soc. *92*, 4992 (1970); *M. C. Böhm, R. Gleiter & P. Schang*, Tetrahedron Lett. *1979*, 2575; *J. Chandrasekhar, E.-U. Würthwein & P. v. R. Schleyer*, Tetrahedron *37*, 921 (1981).

[3] *W. G. Dauben & D. M. Walker*, Tetrahedron Lett. *23*, 711 (1982); *R. Mitschka, J. M. Cook & U. Weiss*, J. Am. Chem. Soc. *100*, 3973 (1978).

[4] *E. Anders, E. Ruch & I. Ugi*, Angew. Chem. *85*, 16 (1973); ibid. Int. Ed. *12*, 16 (1973); *J. Blair, J. Gasteiger, G. Gillespie, P. D. Gillespie & I. Ugi*, Tetrahedron *30*, 1845 (1974).

[5] *D. Seebach & V. Prelog*, Angew. Chem. *94*, 696 (1982); ibid. Int. Ed. *21*, 654 (1982).

[6] *J. Sicher, M. Cherest, Y. Gault & H. Felkin*, Collect. Czech. Chem. Commun. *28*, 72 (1963); *C. A. Kingsbury & W. B. Thornton*, J. Org. Chem. *31*, 1000 (1966).

[7] *D. J. Cram & F. A. Abd Elhafez*, J. Am. Chem. Soc. *74*, 582 (1952); *D. J. Cram & K. R. Kopecky*, ibid. *81*, 2748 (1959); *M. Cherest, H. Felkin & N. Purdent*, Tetrahedron Lett. *1968*, 2199; *N. T. Anh & O. Eisenstein*, Nouv. J. Chim. *1*, 61 (1977).

[8] *K. Chandrasekhar & J. Hauser*, to be published.

[9] *M. Demuth & K. Schaffner*, Angew. Chem. *94*, 809 (1982); ibid. Int. Ed. *21*, 820 (1982).

[10] a) *P. A. Wender & J. J. Howbert*, J. Am. Chem. Soc. *103*, 688 (1981); b) *P. A. Wender & G. B. Dreyer*, Tetrahedron *37*, 4445 (1981); c) *P. A. Wender & G. B. Dreyer*, J. Am. Chem. Soc. *104*, 5805 (1982); d) *P. A. Wender & J. J. Howbert*, Tetrahedron Lett. *23*, 3983 (1982).

[11] a) *D. Bryce-Smith, B. Foulger, J. Forrester, A. Gilbert, B. H. Orger & H. M. Tyrell*, J. Chem. Soc., Perkin Trans. 1 *1980*, 55; b) *D. Bryce-Smith, G. A. Fenton & A. Gilbert*, Tetrahedron Lett. *23*, 2697 (1982) and earlier papers cit. there.

[12] *W. Feeree, Jr., J. B. Grutzner & H. Morrison*, J. Am. Chem. Soc. *93*, 5502 (1971); *H. Morrison*, Acc. Chem. Res. *12*, 383 (1979).

[13] *J. Mattay, J. Runsink, H. Leismann & H.-D. Scharf,* Tetrahedron Lett. *23,* 4919 (1982); *H. Leismann, J. Mattay & H. D. Scharf,* J. Am. Chem. Soc., in press; we thank Prof. *H.-D. Scharf* for this information prior to publication.

[14] *E. M. Osselton, E. L. M. Lempers & J. Cornelisse,* Proceedings of the Xth IUPAC Symposium on Photochemistry, July 22–27, 1984, Interlaken, p. 161.

[15] *F. D. Lewis & R. W. Johnson,* J. Am. Chem. Soc. *94,* 8914 (1972).

[16] *J. I. Seeman,* Chem. Rev. *83,* 83 (1983).

[17] *K. N. Houk,* Pure Appl. Chem. *54,* 1633 (1982).

[18] *J. A. Ors & R. Srinivasan,* J. Org. Chem. *42,* 1321 (1977).

[19] *J. Mani, R. R. Astik & R. Keese,* unpublished results.

[20] *J. Mani, D. Bourgin & R. Keese,* unpublished results.

[21] *J. Mani, D. Bourgin & R. Keese,* unpublished results.

[22] *S. H. Bertz,* J. Am. Chem. Soc. *103,* 3599 (1981).

[23] *J. B. Hendrickson,* J. Am. Chem. Soc. *99,* 5439 (1977).

[24] *M. Trachsel, J. Mani, J.-H. Cho, M. Frey, A. Kreuzer & R. Keese,* presented at the Xth IUPAC Symposium of Photochemistry, Interlaken, July 22–27, 1984; *J. Mani & R. Keese,* in press.

[25] *U. Aeberhard, R. Keese, E. Stamm, U.-C. Vögeli, W. Lau & J. K. Kochi,* Helv. Chim. Acta 66, 2753 (1983).

[26] *L. R. Snyder & J. J. Kirkland,* 'Introduction to Modern Liquid Chromatography', 2nd edn., Wiley-Interscience, New York, 1979, p. 24; *V. Meyer,* 'Praxis der Hochleistungs-Flüssigchromatographie', 2nd edn., Diesterweg-Salle-Sauerländer, Frankfurt, 1980, p. 16.

[27] *W. C. Still, M. Kahn & A. Mitra,* J. Org. Chem. *43,* 2923 (1978).

[28] a) *G. I. Poos, G. E. Arth, R. E. Beyler & L. H. Sarett,* J. Am. Chem. Soc. *70,* 3237 (1948); b) *J. C. Collins, W. W. Hess & F. J. Frank,* Tetrahedron Lett. *1968,* 3363.

[29] *G. C. R. Ellis-Davies, A. Gilbert, P. Heath, J. C. Lane, J. V. Warrington & D. L. Westover,* J. Chem. Soc., Perkin Trans 2, *1984.* We thank Prof. *A. Gilbert,* for communicating these results prior to publication.