162. Specifically ($\pi \rightarrow \pi^*$)-Induced Cyclohexenone Reactions 4a-(*Z*-1-Propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-one and 4a-(*Z*-1-Propenyl-bicyclo[4.4.0]deca-1(8a), 7-dien-2-one[1])[2])

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Dedicated to Professor *Oskar Jeger* on his 60th anniversary

(20.IV.77)

Summary

4a-(*Z*-1-Propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-one (**6**) and 4a-(*Z*-1-propenyl)-bicyclo[4.4.0]deca-1(8a), 7-dien-2-one (**17**) undergo an intramolecular hydrogen transfer from the methyl group of the propenyl substituent to the α-carbon atom of the enone group, and cyclization to the [4.4.3]propellane derivatives **9** and **30**, respectively, when excited in the $\pi \rightarrow \pi^*$ wavelength region. The quantum yield for *(Z)*-**6**$\rightarrow$**9** under optimum conditions is 0.29 at 254 nm. These reactions occur specifically from the $S_2(\pi,\pi^*)$ state, competing with the $S_2 \rightarrow T$ decay. The triplet reactions of **6** are *E-Z* double-bond isomerization, double-bond shift to *(E, Z)*-**8**, and rearrangement to *(E)*-**10**. Further investigations concern some structural limitations in the scope of the reaction type **6**$\rightarrow$**9** and enone S_2 reactivity in general.

We have shown recently [2] [3] that $\pi \rightarrow \pi^*$ excitation of 4-dimethoxymethyl-2-cyclohexenones results in two reactions from an upper excited state which compete with internal conversion $S_2 \rightarrow S_1$ and intersystem crossing to the n,π^* and π,π^* triplets (both are of lower energy than S_1). The reactive state is almost certainly the second excited singlet (S_2) which represents the lowest-lying $^1(\pi,\pi^*)$ configuration in enones; a less likely alternative would be a T_3 state. The specifically $\pi \rightarrow \pi^*$ induced photochemical processes are an intramolecular transfer of a methoxyl hydrogen atom to the enone α-carbon atom (C(1)) followed by cyclization of the resulting diradical (*e.g.*, **1**$\rightarrow$**2** in *Scheme 1*), and bond cleavage to a cyclohexenonyl dimethoxymethyl radical pair and recombination (**1**$\rightarrow$**3**). The triplet reactions include the well-known rearrangement to bicyclo[3.1.0]hexanone (**1**$\rightarrow$**4**) and isomerization to β,γ-unsaturated ketone (**1**$\rightarrow$**5**).

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[1]) Taken in part from the Doctoral Thesis by *F. Nobs* (ETH Zürich, 1976).

[2]) Preliminary reports on some of the results have already appeared elsewhere [1].

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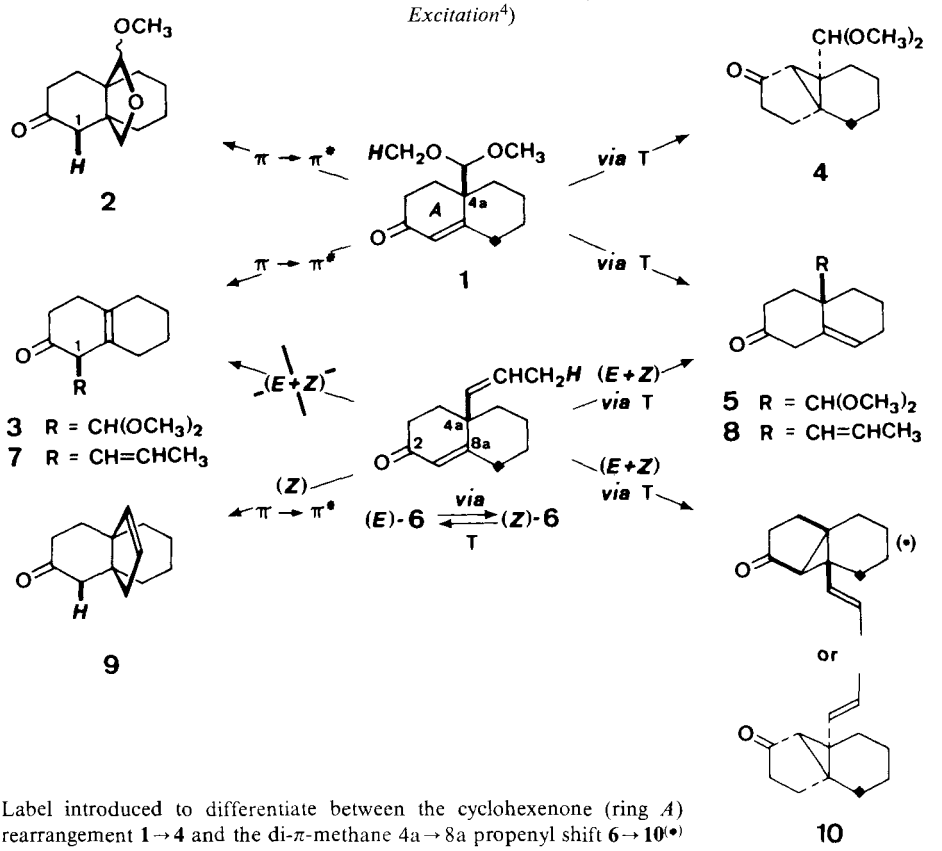
Scheme 1. *Photochemical Transformations of 4a-Dimethoxymethyl-bicyclo[4.4.0]dec-1(8a)-en-2-one* (**1**) *[2] and the 4a-(1-Propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-ones* (E)-**6** *and* (Z)-**6** *on* $n \rightarrow \pi^*$ *and* $\pi \rightarrow \pi^*$ *Excitation*[4])



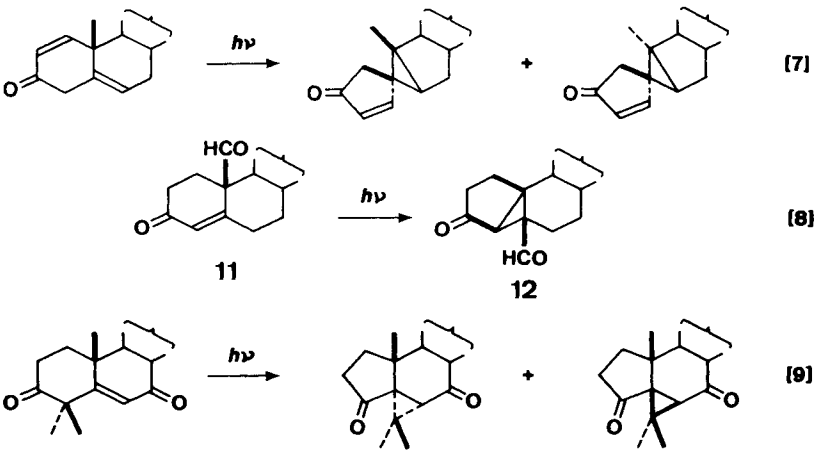
◆ Label introduced to differentiate between the cyclohexenone (ring *A*) rearrangement **1** → **4** and the di-π-methane 4a → 8a propenyl shift **6** → **10**(•)

In the present report the photochemical results with the propenylbicyclodecenones *(E)*-**6** and *(Z)*-**6**, as summarized in *Scheme 1*, are described. These two diastereoisomeric dienones were chosen for the following reasons: In view of the potential synthetic utility of the photocyclization (preparative yields of 40% for **1** → **2** and up to 80% in related cases [2]) a search for transformations similar to this intramolecular β-hydroxymethylation of a cyclohexenone was initiated. The allylic methyl-hydrogen atoms of the *(Z)*-propenyl group in **6** could be expected to meet the requirements with respect to geometric disposition and reactivity just as well as do the methoxyl hydrogen atoms in **1**. Furthermore, the compounds **6** will offer, in a subsequent study, the possibility also to probe into the relative efficiencies of two possibly competing triplet reactions, the cyclohexenone rearrangement and a di-π-methane-type transformation, both of which would lead to products of identical structure in the absence of an appropriate label. Di-π-methane type rearrangements of α,β-conjugated cyclohexenones with olefinic and carbonyl double bonds in

[4]) All formula shown stand for racemic compounds.

δ-position have been observed on several occasions[5]), *inter alia* with the steroidal compounds shown in *Scheme 2*. Among these examples the enone-aldehyde **11** is the closest structural analog of **6**. The triplet rearrangement to **12** clearly occurs with a 1,2-($\gamma \rightarrow \beta$)-formyl shift whereas in similar enones possessing a saturated angular substituent the formation of a bicyclo[3.1.0]hexanone isomer involves a skeletal rearrangement of the cyclohexenone partial structure (*cf.* testosterone [5] and **1**→**4**). The first example of a triplet cyclohexenone→bicyclohexanone isomerization including $\gamma \rightarrow \beta$-migration of a π-substituent has been established for 4,4-diphenylcyclohexenone by *Zimmerman* [6].

Scheme 2. *Examples of Di-π-methane-type Rearrangements of Cyclohexenones Possessing Olefinic and Carbonyl δ-Double Bonds*



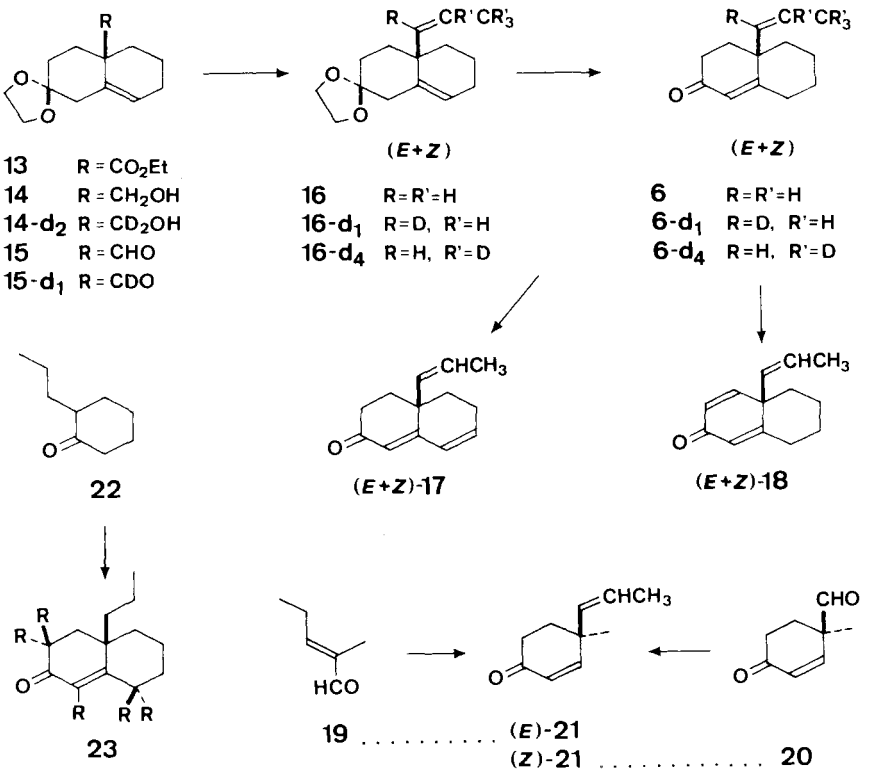
Synthesis of Compounds 6, 17, 18, 21, and 23. – A mixture of the propenyl-bicyclodecenones *(E)*- and *(Z)*-**6** was prepared in 47% overall yield from the alcohol **14** [10] by oxidation to aldehyde **15** with pyridinium chromate in methylene chloride, *Wittig* reaction to **16** with triphenylethylphosphonium bromide, and hydrolysis of the acetal with hydrogen chloride in aqueous acetone. The resulting mixture consisted of 7% *(E)*-**6** and 93% *(Z)*-**6**. The two diastereoisomers could only be separated by preparative gas chromatography, and isolation of one component without prohibitive loss required that this compound constituted at least *ca.* 50% of the two-component mixture. A method to increase accordingly the percentage of *(E)*-isomer was found when the irradiation of the 7:93 mixture of *(E+Z)*-**16** with wavelengths >300 nm in benzene and in the presence of naphthalene proved to effect the desired $Z \rightarrow E$ double bond isomerization[6]). The

[5]) For reviews see [4].

[6]) A mechanistic study of this sensitized isomerization is currently in progress. An alternative method to effect the $Z \rightarrow E$ isomerization of the propenyl side chain in boiling cyclohexene/ethanol over palladium on charcoal has been reported previously by *Fürst & al.* [11][7]) who prepared the 19-ethylidene-androst-4-ene-3,17-diones in a reaction sequence analogous to **14**→**15**→**16**→**6**.

[7]) We thank Dr. *A. Fürst*, F. Hoffmann-La Roche & Co. AG., Basel, for the communication of these results.

Scheme 3. *Synthesis of Compounds* **6**, **17**, **18**, **21**, *and* 23[4])



reaction was accompanied by the formation of insoluble material in appreciable amounts. Under optimum conditions, a 1:1 mixture of *(E+Z)*-**6** was obtained in 40% yield after hydrolysis of the acetals **16**.

The initial steps in the preparations of the deuterated ketones **6-d**$_1$ and **6-d**$_4$ were reduction with lithium aluminium deuteride of the ester **13** [10] to alcohol **14-d**$_2$ and reaction of the aldehyde **15** with pentadeuterioethyl phosphonium iodide, respectively. The remaining steps were, in each sequence, identical with those used for the synthesis of **6**.

The configurational assignments to the angular 1-propenyl chain rest on the characteristic infrared out-of-plane C–H deformation frequencies of the disubstituted double bond and the vicinal NMR. coupling constants of the olefinic protons, 980 cm^{-1} and 17 Hz in *(E)*-**6** and 710 cm^{-1} and 12 Hz in *(Z)*-**6**[8]).

Dehydrogenation of *(E+Z)*-**6** with chloranil and with dichlorodicyano-*p*-benzoquinone in the presence of a catalytic amount of benzoic acid gave the linearly and the crossed conjugated dienones **17** and **18**, respectively.

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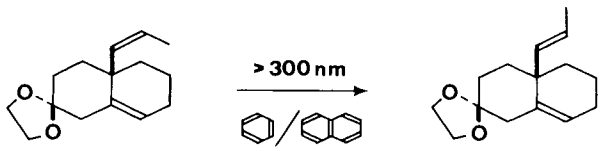
[8]) Although the preferential formation of *Z*-configurated double bonds is characteristic for *Wittig* reactions, the highly stereoselective reaction course in **15** → **16** is notable in view of the considerable steric crowding in *(Z)*-**16** between the *(Z)*-propenyl side chain and the bicyclodecene system. A *ca.* 19:1 preference for the *Z*-configuration was also reported in the steroid series[6]).



(Z)-6 (E)-6

The 4-propenylcyclohexenone *(E)*-**21** was obtained by base-catalysed addition of methylvinylketone to the methylpentenal **19** [12], cyclization and dehydration. *Wittig* reaction of the aldehydo-enone **20** [2] with ethyltriphenylphosphonium bromide afforded the *Z*-isomer **21**.

The synthesis of 4a-propyl-bicyclo[4.4.0]dec-1(8a)-en-2-one (**23**) was carried out by ring annelation with methyl vinyl ketone and 3M ethanolic sodium ethoxide [13] to 2-propylcyclohexanone (**22**) which in turn was prepared by catalytic hydrogenation of the readily accessible 2-allylcyclohexanone [14].

***n*→π* Irradiation and Triplet Sensitization of the 4a-(1-Propenyl)-bicyclo[4.4.0]-dec-1(8a)-en-2-ones (6).** – The irradiation of *(E)*- and *(Z)*-**6** at >300 nm led to geometrical isomerization of the propenyl double bond and to the formation of *(E+Z)*-**8** and *(E)*-**10**. The product distribution was strongly dependent on the solvents used *(Table 1)*, and the quantum yield of the formation of *(E)*-**10** strongly decreased with increasing conversion of *(E)*-**6** and isomerization to *(Z)*-**6**. Accordingly, Φ_{10} from *(Z)*-**6** was at least ten times smaller than the corresponding value measured with the *(E)*-isomer *(Table 2)*.

The double-bond shift **6**→**8** was negligible in ether and isooctane. In a preparative run, 1-(*E*-1-propenyl)-tricyclo[4.4.0.$0^{2,6}$]decan-3-one (**10**) was obtained in 55% yield after irradiation at >300 nm of a mixture of *(E+Z)*-**6** in 0.05M ether solution to *ca.* 90% conversion.

Table 1. *Solvent-dependent Distribution of the Photoproducts of the 4a-(1-Propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-ones* **6**

Starting Ketone	Solvent	Excitation Wavelength [nm]	Product Distribution, %[a])			
			(E)-**6**+**8**	*(Z)*-**6**+**8**	**9**	*(E)*-**10**
(E)-**6**	Hexane	254	74	9	2	15
(E)-**6**	Benzene	>300	77	18	–	5
(E)-**6**	Ether	>300	20	75	–	5
(Z)-**6**	Isooctane	254[b])	11	57	30	2
(Z)-**6**	Ether	254[b])	18	71	9	2
(Z)-**6**	*t*-Butyl alcohol	254[b])	12	84	3	1
(Z)-**6**	Methanol	254[b])	5	93	1	<1
(Z)-**6**	Benzene	>300[c])	4	40	–	56
(Z)-**6**	Isooctane	>300[c])	5	42	–	53
(Z)-**6**	Ether	>300[c])	4	50	–	46
(Z)-**6**	*t*-Butyl alcohol	>300[c])	5	66	–	29
(Z)-**6**	Methanol	>300[c])	5	81	–	14

[a]) Product analysis by VPC. under conditions which isomerize the β,γ-unsaturated ketones **8** to the conjugated enones **6**.

[b]) Identical irradiation times at 254 nm for these runs.

[c]) Identical irradiation times at >300 nm for these runs.

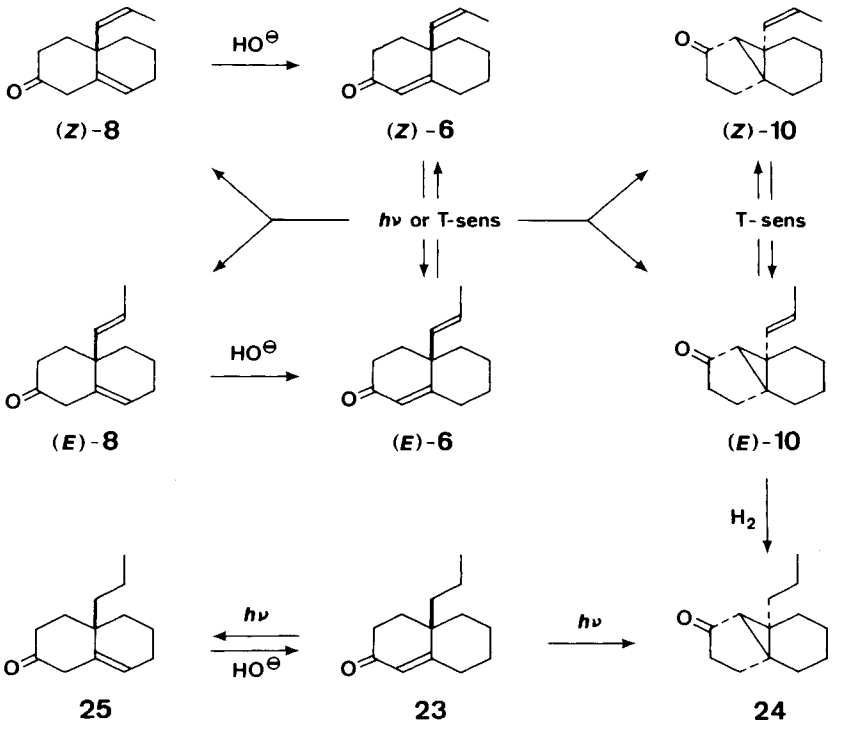
Table 2. n→π* *Excitation of* **6**: (E–Z)-*Isomerization and Quantum Yields of Product* (E)-**10** *Formation*[a])

Starting Ketone	Conversion of *(E+Z)*-**6**, %	Isomeric Composition of **6**, %	$\Phi_{(E)\text{-}10}$
(E)-**6**	12	85 *E*, 15 *Z*	0.037
(E)-**6**	20	75 *E*, 25 *Z*	0.015
(E)-**6**	48	13 *E*, 87 *Z*	0.0085
(Z)-**6**	9	5 *E*, 95 *Z*	0.0015

[a]) Irradiation at 366 nm of 0.015M benzene solution. Product analysis, see note a) in *Table 1*.

Triplet sensitizations of *(E)*- and *(Z)*-**6** with acetophenone in benzene and *t*-butyl alcohol furnished in each case mixtures composed of *(E+Z)*-**6**, *(E+Z)*-**8**, and *(E)*-**10**. The product distributions were similar to those of the direct irradiations summarized in *Table 1*. After *ca.* 50% conversion the formation of *(Z)*-**10** commenced as well. The two stereoisomers interconverted, *(E)*-**10** ⇄ *(Z)*-**10**, on acetophenone-sensitized photolyses in separate runs.

Scheme 4. n→π* *Irradiation (>300 nm) and Triplet Sensitization of* (E)- *and* (Z)-**6**, *and Structural Elucidation of Products*[4])

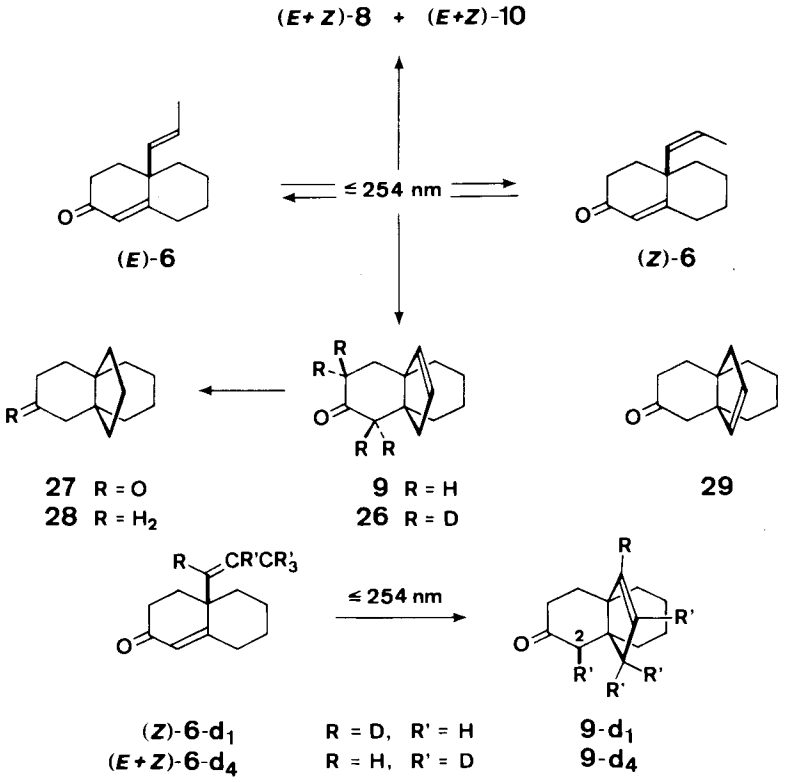


The mixture *(E+Z)*-**8** exhibited the appropriate IR. bands at 705/960 and 1720 cm^{-1} for the isomeric propenyl double bonds and the nonconjugated ketone, respectively. It was not separated but directly converted to the conjugated enones *(E+Z)*-**6** by treatment with ethanolic potassium carbonate solution.

The double-bond configuration of the *(E)*-propenyltricyclodecanone **10** is assigned on the basis of an NMR. coupling constant of 14 Hz and an IR. out-of-plane vibration of 975 cm^{-1} [*(Z)*-**10**: 710 cm^{-1}] of the olefinic protons. The constitution of **10** was correlated with that of product **24** which was obtained together with **25** on irradiation of 4a-propyl-bicyclo[4.4.0]dec-1(8a)-en-2-one (**23**) in *t*-butyl alcohol. Catalytic hydrogenation of *(E)*-**10** with tris(triphenylphosphin)-rhodium(I)chloride in benzene gave **24** (IR.: 1720 cm^{-1}) and a tetrahydrocyclopentanone derivative (1750 cm^{-1}) which probably resulted from an additional hydrogenolysis of the 1,2-cyclopropane bond.

$\pi \rightarrow \pi^*$ Irradiation of the 4a-(1-Propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-ones (6). – The irradiation in the wavelength region of the second absorption band afforded the tricyclic isomer **9** in addition to the product pattern observed also with longer-wavelength radiation. When a 0.05M solution of *(E+Z)*-**6** in hexane was photolysed at 254 nm to *ca.* 70% conversion, the new compound **9** was isolated in 47% yield besides 13% *(E+Z)*-**8** and 4% *(E)*-**10** (based on converted **6**). The product distribution was again dependent on the nature of the solvent *(Table 1)*. Furthermore, the quantum yield of the formation of product **9**, Φ_9, was practically invariant within the $\pi \rightarrow \pi^*$ region (at 235 and 245 nm), but it decreased strongly

Scheme 5. *$\pi \rightarrow \pi^*$ Irradiation of* (E)- *and* (Z)-**6**, *and Structural Elucidation of Product* **9**[4])



with increasing concentration of the starting ketone *(Z)*-**6** whereas Φ_{-6} remained constant *(Table 3)*. The measured value for Φ_9 with *(E)*-**6** as the starting material was about an order of magnitude smaller than with the *(Z)*-isomer under comparable conditions.

The $\pi \rightarrow \pi^*$-induced cyclization of *(Z)*-**6-d**$_1$ and *(E+Z)*-**6-d**$_4$ in hexane gave **9-d**$_1$ and **9-d**$_4$, respectively, without loss of deuterium.

Attempts to sensitize the reaction **6** → **9** failed even when sensitizers with triplet energies as high as *ca.* 78 (acetone) and 85 kcal/mol (benzene) were used. In photolyses of 0.05M *(Z)*-**6** at 254 nm in these solvents, the product ratio **9/10** was considerably smaller than the ratio formed in ether under comparable conditions (0.49 and 0.75 *vs.* 13.3.; *Table 4*). The residual cyclization to **9** in the former two experiments is attributable to the partial direct light absorption by **6** rather than to inefficient sensitization.

The tricyclo[4.4.3.0]decane (propellane) skeleton of **9** was established by catalytic hydrogenation of the double bond (→ **27**) and *Huang-Minlon* reduction of the ketone which gave the known hydrocarbon **28** [15]. The ketone position in a six-membered ring follows from an IR. carbonyl band at 1710 cm^{-1}, and a base-catalysed H/D exchange experiment afforded a tetradeuterated derivative (**26**) and thus demonstrates the presence of two methylene groups adjacent to the ketone group. In the NMR. spectrum of **9** an *ABXY* system at δ 2.1, 2.4, 5.6 and 5.72 with a vicinal coupling constant of 5 Hz of the olefinic protons indicates the existence of a

Table 3. $\pi \rightarrow \pi^*$ *Excitation of* **6**: (E–Z)-*Isomerization and Quantum Yields of Conversion and Product* **9** *Formation*[a])

Starting Ketone	Excitation Wavelength [nm]	Conversion of *(E+Z)*-**6**, %	Quantum Yields Φ_{-6}	Quantum Yields Φ_9	Isomeric Composition of **6**, %
0.011M *(E)*-**6**	245	8		0.005	95 *E*, 5 *Z*
0.011M *(E)*-**6**	245	20		0.016	88 *E*, 12 *Z*
0.071M *(Z)*-**6**	235	10	0.35	0.04	6 *E*, 94 *Z*
0.002M *(Z)*-**6**	245	12	0.35	0.29	8 *E*, 92 *Z*
0.027M *(Z)*-**6**	245	15	0.28	0.12	10 *E*, 90 *Z*
0.071M *(Z)*-**6**	245	8	0.34	0.07	4 *E*, 96 *Z*
0.071M *(Z)*-**6**	265	5	~ 0.001	< 0.0001	≳ 99 *Z*

[a]) Irradiation in isooctane. Product analysis by VPC. under conditions which reverse the negligible double-bond shift **6** → **8**.

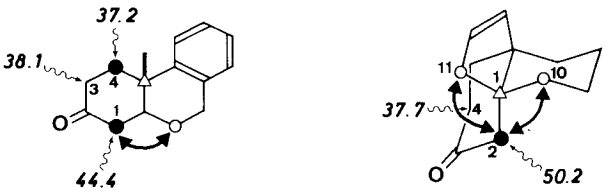
Table 4. *Product Distribution on Direct* $\pi \rightarrow \pi^*$ *Irradiation and Partially Triplet-sensitized Photolysis of* (Z)-**6**[a])

Solvent	Conversion of *(E+Z)*-**6**, %	Product Distribution, %		
		9	*(E)*-**10**	*(Z)*-**10**
Ether	70	93	7	–
Acetone	65	33	50	17
Benzene	30	43	57	trace

[a]) 0.05M *(Z)*-**6**; 254 nm. Product analysis, see note a) in *Table 1*.

propenylene bridge. The spectra of these latter protons were reduced to one-proton signals in **9-d**$_1$ and **9-d**$_4$, with a triplet at δ 5.7, $J = 5$ Hz, and a broadened singlet at δ 5.6, respectively. Treatment of **9-d**$_4$ with base removed selectively the deuterium at C(2).

The localization of the double-bond position and differentiation between the structures **9** and **29** was finally achieved by ^{13}C-NMR. spectroscopy of **9**, **9-d**$_1$ and **26** making use of the off-resonance technique and deuterium isotope shift effects on ^{13}C-resonance frequency. The combinatory analysis of the chemical shifts and signal multiplicities in **9** and of the disappearance of the signals for deuterium-labeled carbon atoms in **9-d**$_1$ and **26** permits unequivocal individual assignments to the carbon atoms C(1), C(3), C(6), C(7), C(11), C(12), and C(13) *(Table 5)*. Furthermore, assignments to C(2) and C(4) are possible by comparison with the data of the hexahydrophenanthrenone **a** which have recently been analysed [16]. The α-ketomethylenes C(3) of **a** and C(4) of **9** (=**b**) have an approximately similar sur-



a **b (=9)**

rounding and their carbon shifts are almost the same. The arguments which have been advanced by *Wenkert et al.* [16] to rationalize the shifts of C(1) and C(4) of **a** to lower field can also be applied to **9** and explain the still greater downfield shift of the α-ketomethylene carbon atom C(2) in this compound: C(2) of **9** suffers deshielding through both an adjacent quaternary bridgehead (C(1)) and the β-effects from two neighbouring ring methylenes (C(10) and C(11)).

In accordance with previous reports [17] the introduction of deuterium causes upfield resonance shifts of neighbouring carbon atoms. In the spectrum of **26** the signals of one bridgehead and three methylene carbon atoms are shifted by 2.5–3.8 Hz, whereas in **9-d**$_1$ the only shifts observed are for the olefinic carbon C(12) by 2.4 Hz and for the second bridgehead carbon atom by a mere 1.2 Hz which is already close to the error limit of ± 0.8 Hz. These results cannot be reconciled with formula **29** and structure **9** alone can account for all the observed isotope shifts.

Irradiation of Compounds *(E+Z)*-17, *(E+Z)*-18, *(E)*-21, and *(Z)*-21. – The irradiation of *(E+Z)*-**17** at 254 nm furnished in 33% yield the isomer **30**. The remainder of the photolysed mixture was composed of compounds of higher molecular weights which constituted the sole products when the irradiation was carried out at > 300 nm. Catalytic hydrogenation of **30** gave the saturated propellane ketone **27**.

The cross-conjugated compound *(E+Z)*-**18** gave at 50% conversion a mixture containing ketone *(Z)*-**31** and phenol **32** at either 254 and > 300 nm. No specifically $\pi \rightarrow \pi^*$ induced cyclization analogous to **6**$\rightarrow$**9** and **17**$\rightarrow$**30** was found. The γ,γ-di-

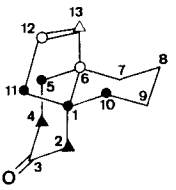
Table 5. *^{13}C-FT-NMR. Spectra of the Tricyclo[4.4.3.0]tridec-12-en-3-ones* **9**, **9-d$_1$**, *and* **26**[a])

Carbon Atom No.	Off-resonance Multiplicity	Chemical Shift [δ]	Deuterium Isotope Shift Effect [Hz] in **9-d$_1$**	in **26**
1	*s*	48.8		−2.5
2	*t*	50.2[b])		
3	*s*	212.8	[c])	[c])
4	*t*	37.7[b])		
5 and 10	two *t*	33.2		−3.3
		33.6		−3.6
6	*s*	46.9	−1.2	
7	*t*	32.9		
8 and 9	two *t*	20.3, 20.6		
11	*t*	44.9		−3.8
12	*d*	128.8	−2.4	
13	*d*	140.6[b])		

[a]) Measured in $CDCl_3$ at 25.2 MHz. Chemical shifts are expressed in δ (ppm) relative to internal TMS; error ±0.8 Hz.

[b]) Signals missing in the spectra of **9-d$_1$** (C(13)) and **26** (C(2) and C(4)).

[c]) C(3) signals of **9-d$_1$** and **26** not measured.



△ and ▲: deuteriated positions and disappearance of ^{13}C signal in **9-d$_1$** and **26**, respectively

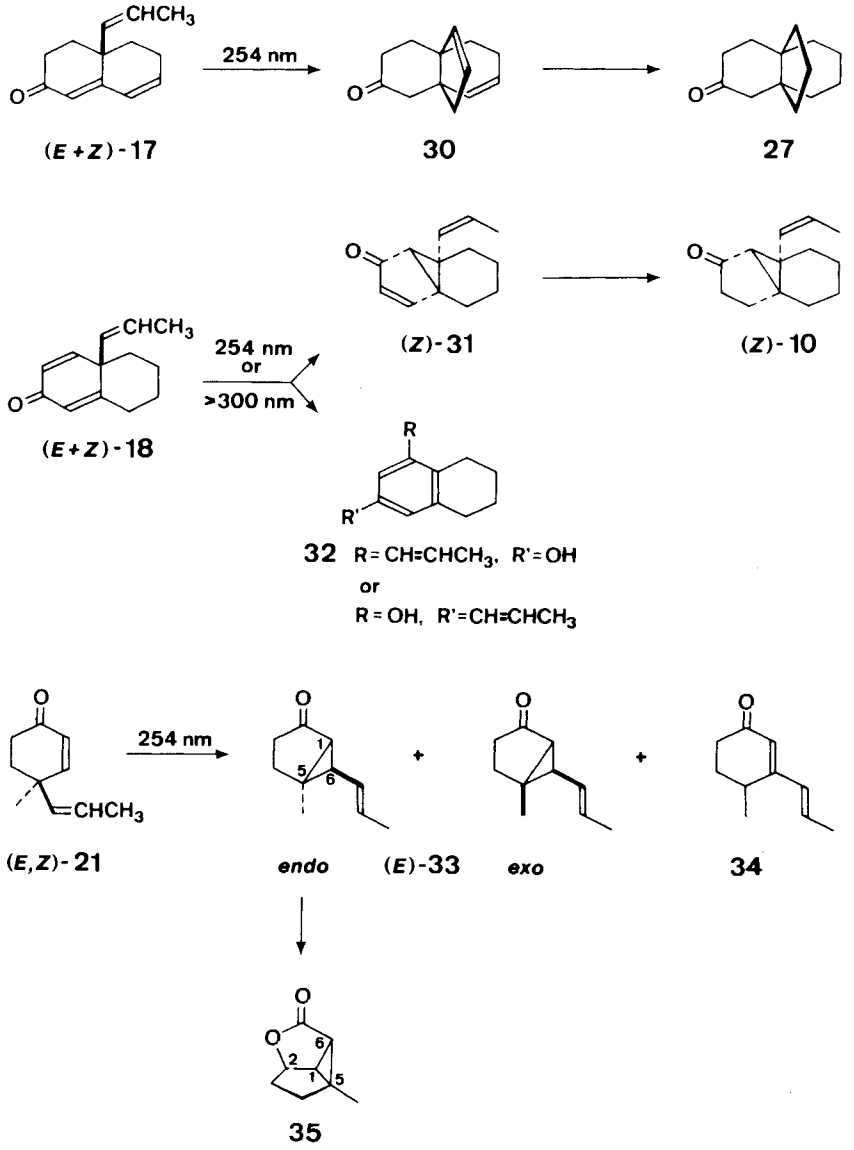
○ and ●: deuterium isotope effect on ^{13}C chemical shifts in **9-d$_1$** and **26**, respectively

substituted cyclopentenone partial structure of **31** is characterized in the IR. spectrum by a carbonyl frequency of 1705 cm^{-1} and in the NMR. by an *AB* system at δ 5.6 and 7.1, $J=6$ Hz, for the olefinic α- and β-protons. A 710 cm^{-1} band indicates the *Z*-configuration of the propenyl substituent. Sodium borohydride reduction of **31** and subsequent oxidation with *Collins* reagent yielded *(Z)*-**10**. The *meta*-substitution of the phenolic tetrahydronaphthylene **32** is derived from the *AB* pattern at δ 6.6 and 6.9 with $J=3$ Hz of the aromatic protons, and a band at 970 cm^{-1} points to the *E*-configuration of propenyl. A more detailed structural analysis of **32** was not attempted.

Irradiations of *(E)*- and *(Z)*-**21** at 254 nm gave rise to *(E−Z)*-isomerization of the starting material and to the formation of the bicyclohexanone *endo-(E)*-**33** as the major product and the *exo*-isomer and other compounds including **34** as minor components. In a preparative run with *(E)*-**21** in dioxan the yields were 40% *endo-(E)*-**33**, 4% *exo-(Z)*-**33**, and 6% **34**, based on 50% converted **21**. Again, a product due to a specifically $\pi \rightarrow \pi^*$ induced cyclization could not be isolated.

The bicyclo[3.1.0]hexanones **33** exhibit a ketone IR. band at 1735–1740 cm^{-1}. The ^{1}H-NMR. spectroscopic analysis including decoupling and Eu(fod)$_3$ shift experiments established the presence of a tertiary methyl group (at C(5)) and the proton sequence at C(1), C(6) and the propenyl chain in the two isomers. Further-

Scheme 6. *Irradiations of* (E+Z)-**17**, (E+Z)-**18**, *and* (E)- *and* (Z)-**21**, *and Structural Elucidation of Products*[4])



more, the *(E)*-configuration of both is shown by IR. out-of-plane frequencies around 970 cm^{-1} and NMR. olefinic coupling constants of $J \sim 15$ Hz. The configuration of the propenyl attachment was determined by reduction of the carbonyl group of *endo*-**33** with sodium borohydride, followed by ozonolysis of the double bond and oxidative cleavage of the ozonide in formic acid, accompanied by ring closure and formation of lactone **35**. The ring size of the lactone is determined by an IR. band at 1780 cm^{-1}. In the NMR. spectrum, the methyl singlet appears at δ 1.30, and the

protons at C(1) (δ 2.04), C(2) (δ 4.98) and C(6) (δ 2.78) couple with $J_{1,2}<0.5$, $J_{1,6}=7$, and $J_{2,6}=5$ Hz. A *W* coupling similar to that of HC(2)–HC(6) has also been observed for a C(5) phenyl analog of **35** [6c]. The *endo-exo* assignment of **33** is in accord with the magnitudes of the *cis*- and *trans*-cyclopropane CH–CH couplings in the two stereoisomers (*endo*-**33**: $J_{1,6}=10$ Hz; *exo:* 3 Hz)[9]).

The ketone group in product **34** exhibits an IR. band at 1675 cm^{-1} which is shifted to 1720 cm^{-1} in the saturated tetrahydro derivative obtained by catalytic hydrogenation. In the NMR. spectrum of **34**, the secondary methyl group (doublet at δ 1.25, $J=7$ Hz) was located at C(4) by a decoupling experiment involving an allylic one-proton multiplet at δ 2.9. A singlet at δ 5.80 and an ABX_3 system at δ 6.12/6.31 and 1.91 are attributable to the proton at C(2) and to those of the propenyl chain, respectively. The *E*-configuration derives from a vicinal coupling constant of $J=15.5$ Hz of the olefinic protons. The NMR. chemical shift data and in particular a pair of IR. bands at 1590 and 1645 cm^{-1} of **34** are in good agreement with the published values for 3-(*E*-1-propenyl)-cyclohex-2-enone [18], whereas the UV. absorption maximum at 266 nm ($\varepsilon=25\,000$) is closer to the value for the *Z*-isomer, possibly owing to a steric influence of the additional methyl group in **34**.

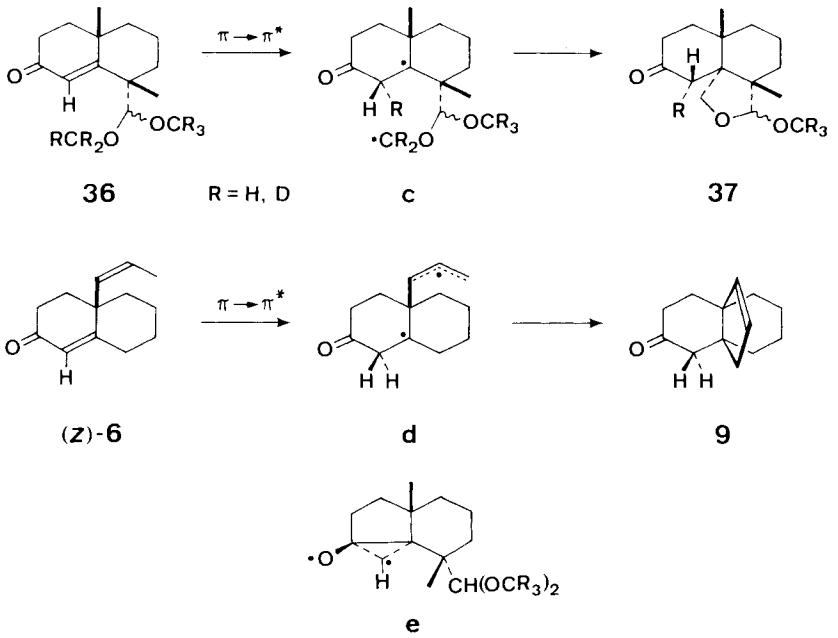
Discussion. – The specifically $\pi\rightarrow\pi^*$ induced cyclizations *(Z)*-**6**$\rightarrow$**9** and *(Z)*-**17**$\rightarrow$**30** provide a comparatively short and facile synthetic access to functionalized [4.4.3]propellane systems.

The characteristics of the reaction reveal a close mechanistic relationship with the corresponding process of the dimethoxymethyl analog, **1**$\rightarrow$**2**. Both specifically require excitation to the S_2 state. The quantum yields are essentially invariant with wavelength within the region of $\pi\rightarrow\pi^*$ absorption (see *Table 3* and [2]). While the quantum yields for the disappearance of starting material are also independent of the initial concentration, the values for the formation of cyclization product strongly decrease with increasing concentration in the previous and the present series. The molecular mechanism of the reaction as proposed for the case of the dimethoxymethyl enones [2] appears equally applicable to *(Z)*-**6**$\rightarrow$**9** and is shown in *Scheme 7*.

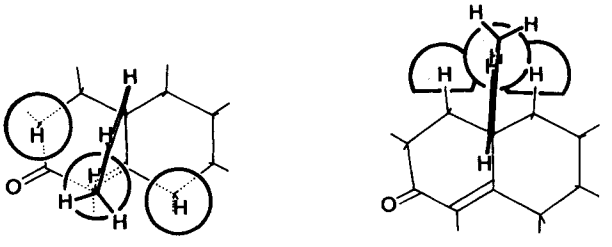
The spatial arrangement of the enone and the dimethoxymethyl groups in **36** had been chosen to restrict the choice for intramolecular hydrogen abstraction routes to the direct transfer from the methoxyl to the α-ketone position (C(1);$\rightarrow$**c**). The formation of the 1α-deuterated compound **37** (R=D) eliminated a structure such as **e** (which would have given the 1β-deuterio analog of **37**) as a possible directing factor in the transfer process. A similar stereochemical determination (by NMR.) of the C(1) deuterium in **9-d**$_4$ was not possible. Nevertheless, the sequence *(Z)*-**6**$\rightarrow$**d**$\rightarrow$**9** appears the most plausible mechanistic path. Particularly so as a temperature NMR. study combined with a stereochemical analysis of the ground-state geometry of *(Z)*-**6** suggest that the propenyl chain is conformationally locked into a position which brings a methyl hydrogen very close to the reaction site. In the temperature range $-85°$ to $+175°$ the methyl multiplet ($d\times d$ at δ 1.63) remained unchanged in signal shape and chemical shift apart from an unsignificant

[9]) See references [6b,c] for vicinal cyclopropane (CH–CH)-coupling in similar 5,6-disubstituted bicyclo[3.1.0]hexan-2-ones.

Scheme 7. *Proposed Molecular Mechanism for the Specifically $\pi \rightarrow \pi^*$ Induced Cyclization*[4])



loss of resolution at low temperature, whereas the methylene proton signals underwent extensive changes at elevated temperatures owing to increasing conformational mobility of the ring system *(Fig. 1)*. We interpret this result in terms of the practically exclusive presence of the conformationally rigid rotamer **f** rather than as the consequence of facile rotation of the *(Z)*-propenyl substituent around its angular bond throughout the entire temperature range. A molecular model of *(Z)*-**6** reveals an extremely dense steric packing of the propenyl chain onto the ring system which is likely to prevent rotational equilibration. Conformation **f** presents the sterically somewhat preferred of the two least crowded arrangements (*cf.* rotamers **f** and **g**; half chair-chair conformations). Conformational changes of the ring system do not seem to relieve the barriers to rotation to any important extent. In rotamer **f**, a methyl hydrogen can approach the α-carbon C(1) to within *ca.* 1.2 Å almost exactly along the *p*-orbital axis (in a *Dreiding* model). This hydrogen should therefore be ideally placed for the transfer process.



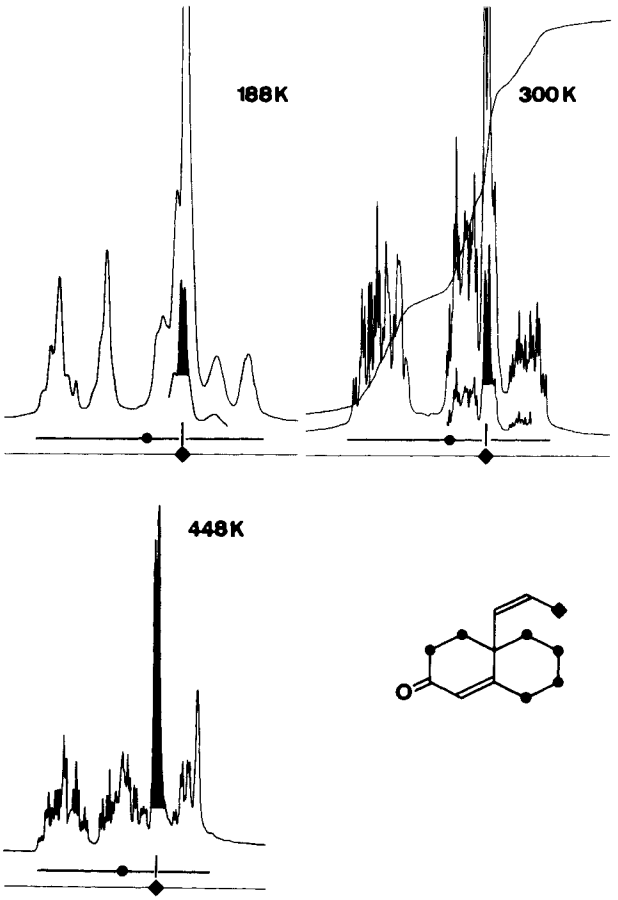


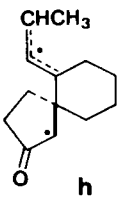
Fig. 1. *^{1}H-NMR. spectrum of the methyl and methylene protons of* (Z)-**6** *at various temperatures (270 MHz; solvents: toluene-d_8 at 188 and 300 K, dodecane-d_{24} at 448 K)*

The photochemical results with the dienones **17** and **18** parallel those with their dimethoxymethyl analogs [2]. Upper-excited state cyclization is observed only with the linear dienone, whereas the cross-conjugated isomer undergoes, irrespective of the excitation wavelength, the triplet rearrangements characteristics of such cyclohexadienones [19].

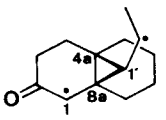
The photoreactions of **6** [*(E)*-**6** $\rightleftarrows$ *(Z)*-**6**; $\rightarrow$ *(E, Z)*-**8** + *(E)*-**10**] which occur also at long wavelengths and which compete with the specifically $\pi \rightarrow \pi^*$-induced process at short wavelengths, can be attributed to the lowest-lying triplet state(s) [20], as confirmed by the sensitization results. In the case of 4a-methyl-bicyclo[4.4.0]dec-1(8a)-en-2-one and related systems [5] [21] a double-bond shift similar to **6** $\rightarrow$ **8** has been shown to result from hydrogen abstraction processes between triplet-excited and ground-state enones[10]). For the rearrangements of both *(E)*- and *(Z)*-**6** to *(E)*-**10** there is

[10]) The present work gave no indication of any specific $\pi \rightarrow \pi^*$ induction of the double-bond shift as did the apparently still unique example of 10α-testosterone [22].

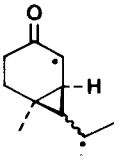
a choice of two mechanistic alternatives. Both involve a formal sequence of 1,2-shift and 1,3-ring closure, and both have been found to operate in certain α,β-conjugated cyclohexenones. In one alternative [5], the accompanying *(Z→E)*-isomerization of the aliphatic double bond would have to occur in the ring-contracted intermediate **h**[11]). A perhaps more likely reaction path for **6**→**10** is the di-π-methane process which involves bridging to the diradical **i** and would thus lead to the more favorable *(E)*-configuration of the propenyl chain in **10** on cleavage of the C(1′)–C(4a) bond followed by C(1)–C(4a) ring closure. Moreover, the substantial difference in the quantum yields with which *(E)*-**10** is formed from *(E)*- and *(Z)*-**6** *(Table 2)* is more easily rationalized with this mechanism. Bridging to **i** should be more difficult with the orientation of the π-orbital lobes of C(8a) and C(1′) in the preferred rotamers of *(Z)*-**6** (*cf.* **f** and **g**) – hence the lower quantum yield of reaction – than should be the case for the rotationally more mobile *(E)*-isomer.



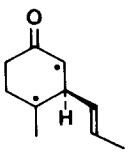
h



i



j



k

While a definitive differentiation between the two mechanisms for **6**→**10** has to await further experimentation, *e.g.*, with a dideuteriomethylene label as indicated in *Scheme 1*, the question is resolved in favor of the di-π-methane route in the case of the monocyclic enone **21** *(Scheme 6)*. The rearrangement *via* a 1,2-propenyl shift is evident from the structure of products **33** and **34**, and the reaction mechanism in the case of analogous diphenyl derivatives, involving intermediates of type **j** and **k** (and its zwitterionic counterpart), has been amply discussed by *Zimmerman* [28].

The species **i** and **h** are also plausible intermediates in the *(E–Z)*-isomerizations of **6** and **10**, respectively. Photochemical bridging of **6** to **i** and opening of either of the lateral cyclopropane bonds partitions between decay to the ground state potential surfaces of the cyclohexenones **6** *(E* and *Z)* and the bicyclohexanone product *(E)*-**10**. In the latter compound, photocleavage of the cyclopropane bond vicinal to both the ketone group and the double bond, leads to **h** which can again

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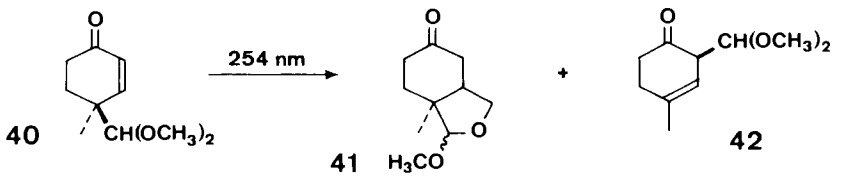
[11]) Despite the reasonably high configurational stability [23], *(E,Z)*-isomerization of allylic radicals has been observed occasionally (*cf.* [24]). However, the bond reorganization of the cyclohexenone skeleton leading to bicyclo[3.1.0]hexanones has been shown by *Schuster* [25] for the case of (+)-(*R*)-4-methyl-4-propyl-2-cyclohexen-1-one to be a concerted $_{\sigma}2_a+_{\pi}2_a$ triplet reaction. Such a process does not provide for concomitant double-bond isomerization as required for *(Z)*-**6**→*(E)*-**10**. Yet concertedness may be more difficultly attained in a bicyclic enone such as **6**[12]), and the possibility of the intervention of diradical **h** cannot be excluded with rigor.

[12]) Concertion of the skeletal rearrangement may profit [5] [25] from a relaxation of the monocyclic enone triplet by torsion around the C=C bond which in turn could facilitate $T_1 \rightarrow S_0$ crossing through the 'twisted π-bond biradicaloid funnel' [26]. A recent analysis by *Kearns* [27] shows that there is little change in the geometry of 4a-methyl-bicyclo[4.4.0]dec-1(8a)-en-2,5-dione upon excitation to its $^3(\pi,\pi^*)$ state at 4.2 K. A concerted reaction at room temperature would thus require a (possible) thermal activation of bicyclic enone triplets for ring distortion.

reclose to starting material (major path) and to the *(Z)*-isomer (minor path). Precedent for this mechanism can be seen in the rearrangement of the bicyclo-[3.1.0]hexanone photoproduct of testosterone back to enone on direct irradiation [5][13]). Intramolecular energy transfer as an alternative mechanism for the *(E–Z)*-isomerization is, at least for **6**, excluded in view of the exothermicity of such a process in the singlet and the triplet manifolds[14]).

The two cyclohexenones *(Z)*-**21** and **40** show an interesting difference in photoreactivity. While **40** *(Scheme 8)* [2] had been found to undergo the upper-excited state reactions to **41** and **42** characteristic of this class of compounds, *(Z)*-**21** does not exhibit any specifically $\pi \rightarrow \pi^*$ induced reactivity. This failure of **21** is

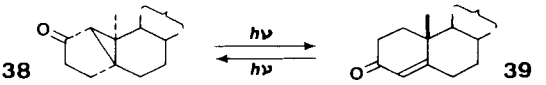
Scheme 8[4])



aggravated by the fact that the reaction *(Z)*-**6**→**9** under optimum conditions predominates over the reactions requiring prior internal conversion ($S_2 \rightarrow S_1$) and intersystem crossing ($S_1 \rightarrow T$; or direct $S_2 \rightarrow T$ crossing), by a factor of 4.8 (*Table 3*, Φ_9/Φ_{-6}-Φ_9)[15]). The absence of a $\pi \rightarrow \pi^*$ induced cyclization of *(Z)*-**21** is possibly attributable to a conformational reason. One may except that in the axial position – prerequisite for S_2 reaction – the propenyl chain points away from the ring rather than that it turns into the strongly crowded arrangement in which it is locked in *(Z)*-**6** (*cf.* **f**). This impediment toward reaction in the monocyclic compounds is certainly less stringent for the axial dimethoxymethyl substituent (**40**) which has both smaller steric interactions with the ring surface and, with two methyl groups *vs.* one in propenyl, a statistically greater choice of optimum reaction geometries.

On the other hand, the high value of $\Phi_9 = 0.29$[16]) appears plausible when taken to reflect the particularly favorable conformation **f** of *(Z)*-**6**. It is interesting in this connection to recall that *Herz & al.* and *Nakanishi & al.* [30] have observed intramolecular transfers of hydrogen to the β-position of cycloalkenones in which the

[13]) Although the isomerizations of both bicyclo[3.1.0]hexanones (**10** and **38**) are triplet reactions, the reversal of the triplet rearrangement **39**→**38** could not be sensitized with acetophenone [5] in contrast to *(E)*-**10**→*(Z)*-**10**. Evidently the additional double-bond in **10** provides for lowering of the triplet energy of this compound below 74 kcal/mol.



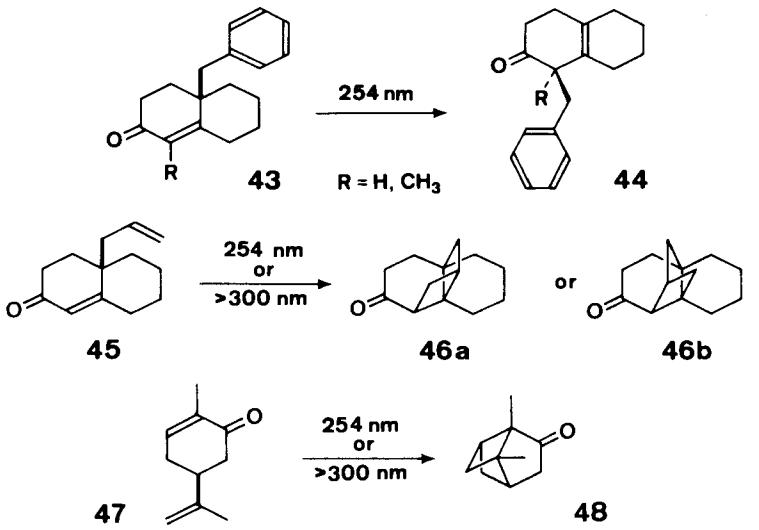
[14]) The phosphorescence spectra of *(E)*- and *(Z)*-**6** are quite similar to each other and to those of related octalones [20] [27], with $E_T(0-0) \sim 70.6$ kcal/mol (in ether/isopentane/ethanol 5:5:2 glass at 77 K).

[15]) The efficient competition of reaction with physical deactivation in the S_2 state is particularly striking in view of the relatively small energy gap between the $S_2(\pi,\pi^*)$ and the lower-lying excited states of these cyclohexenones; *e.g.*, $\Delta E(S_2 - S_1) \sim 20$ kcal/mol for cyclohexenones, $\gtrsim 40$ kcal/mol for thioketones (which also react from S_2 [29]).

[16]) By comparison also with $\Phi_{37} = 0.016$ *(cf. Scheme 7)* [2].

reaction sites are rigidly held in near-bonding distance closely along the π_β-axis (see also [31]). However, these reactions are triplet processes and are obviously of the same nature as the intermolecular hydrogen abstraction by the β-carbon atom of cycloalkenones [5] [32] which has been shown to be a property of the π,π^* triplet state [33]. Although the regioselectivity of the transformation *(Z)*-**6**→**9** could be supported by the conformational constraints, these are less important in **1**, *(Z)*-**17**, **36**, and **40**. There remains the interesting aspect then that the spin multiplicity alone appears qualitatively to change the reactivity of π,π^* enone states.

Preliminary experiments indicate further limitations in the scope of the reaction type **6**→**9** and enone S_2 reactivity in general. The octalones **43** rearranged with a 1,3-benzyl shift to **44** on 254 nm irradiation only ($\Phi_{44} \sim 0.1$ for both homologs) [34], whereas the vinyl analog **45** showed no specifically $\pi \rightarrow \pi^*$ induced reaction but rather formed a product of either structure **46a** or **46b** in a wavelength-



independent intramolecular 2+2 cycloaddition [35]. Similarly, $\pi \rightarrow \pi^*$ excitation of carvone (**47**) failed to introduce a reaction competing with the well-known formation of carvonecamphor (**48**) [36].

Financial support by the *Fonds National Suisse de la Recherche Scientifique* and *Firmenich SA*, Geneva, is gratefully acknowledged.

Experimental Part

General Remarks. – The usual *work-up* of crude reaction mixtures involved extraction with benzene/ether 1:1 or CH_2Cl_2, washing of the organic layer with H_2O or a saturated aqueous NH_4Cl solution to the neutral point, and drying over anhydrous $MgSO_4$. The solvent was then removed *in vacuo* in a rotary evaporator. – For *thin-layer chromatograms* (TLC.) *Merck* Fertigplatten F_{254} (silicagel) were used. The spots were located by fluorescence and by treatment with conc. sulfuric acid and heating. – *Preparative chromatography* was carried out on silicagel *Merck* (0.05–0.20 mm) in columns with decreasing diameter. – *In vapor phase chromatography* (VPC.) either capillary columns (150′ × 0.01″, with OV 101, K 1540, and Carbowax 1540) or packed columns (10′ × 1/4″; with 3% SE-30 and 15% Carbowax on Chromosorb

P-AW-DMCS, and 5% Apiezone L on Chromosorb G) were used. The composition of product mixtures was determined by calibrated electronic integration. – *Melting points* (m.p.) are not corrected. – *UV. spectra:* λ_{max} in nm, ε in parantheses. – *IR. spectra:* $\tilde{\nu}_{max}$ in cm^{-1}; in CCl_4 unless specified otherwise. – *^{1}H-NMR. spectra:* in CCl_4 unless specified otherwise; 100 MHz; chemical shifts in δ and coupling constants *(J)* in Hz; br. = broad; *s* = singlet, *d* = doublet, *m* = other than first-order multiplet. – *^{13}C-NMR. spectra:* 25.2 MHz, *Fourier* transformation mode. – *Mass spectra* (MS.): base peak in italics.

UV. Irradiations. – Light source for 254 nm: Ring-shaped Hg low-pressure lamps (Minerallight PCQX1, *Ultraviolet Products Inc.*), magnetically stirred solutions in quartz tubes in the center. – *For > 300 nm and > 340 nm:* 250 W Hg high-pressure lamp *(Philips)* in a water-cooled pyrex mantle which is surrounded with an additional mantle of 1-cm inner path containing one of the following filter solutions: for > 300 nm, aqueous 0.05% KH-phthalate solution [optical densities: 1.5 (295 nm), 0.6 (300), 0.05 (313)]; for > 340 nm, 750 g NaBr + 7 g $Pb(NO_3)_2$ per liter H_2O [optical densities: 1.5 (340 nm), 0.6 (345), 0.03 (360)]. – At > 300 nm, analytical irradiations were carried out in a turn-table reactor with magnetically stirred sample tubes, and for preparative experiments the lamp housing was placed into the solution which was stirred magnetically. – Prior to all irradiations the solution was flushed with argon.

Synthesis of Compounds 6, 17, 18, 21, and 23 (Scheme 3). – *2-Ethylenedioxy-4a-formyl-bicyclo[4.4.0]-8-decene* (**15**). 7 g CrO_3 were added in portions to a stirred mixture of 200 ml CH_2Cl_2 and 10 ml pyridine at 0°, followed after 30 min by a solution of 2 g 2-ethylenedioxy-4a-hydroxymethyl-bicyclo[4.4.0]-8-decene (**14**) [10] in 20 ml CH_2Cl_2. The mixture was stirred for another 30 min, then taken up in 150 ml ether and filtered through neutral Al_2O_3 (act. III). The filtrate was concentrated i.V. and pyridine was removed by azeotropic distillation with toluene. Chromatography of the residue in toluene/ethyl acetate 4:1 gave 1.5 g **15** (75% yield). – IR.: 1665, 1725, 2680, 2800, 2820. – NMR.: 3.89/*s*, $H_4C_2O_2C(2)$; 5.7/br., H–C(8); 9.52/*s*, CHO–C(4a). – MS.: 222 ($C_{13}H_{18}O_3^+$), *194*, 193, 149, 130, 121, 99.

4a-(E- and Z-1-propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-ones (**6**). 20 ml of a *ca.* 2M solution of CH_3Li in ether were added dropwise to a vigorously stirred suspension of 18.5 g (50 mmol) of triphenylethylphosphonium bromide (cryst. from hexane/CH_2Cl_2) in 250 ml ether at RT. under an argon atmosphere. After 3 h reflux 5.5 g (25 mmol) **15** in 50 ml ether were dropped into the dark orange solution. The reaction mixture was kept at 50° for 2 h before the excess ylide was destroyed with acetone at RT. The work-up and chromatography in toluene/ethyl acetate 10:1 gave 3,9 g of an *(E+Z)*-mixture of **16** (VPC.: 7% *E* + 93% *Z*) which crystallized at −5° (69% yield). *2-Ethylenedioxy-4a-(Z-1-propenyl)-bicyclo[4.4.0]-8-decene* (**16**) was isolated by GC. – UV. (hexane): 216 (620), 243 (65, sh). – IR.: 705, 945, 1090, 1125, 1650, 1665. – NMR.: 1.85/ABX_3, $J_{1,3}$ = *ca.* 1.5, $J_{2,3}$ = 7, 3 H–C(3) of –CH=CH–CH_3; 4.0/*s*, $H_4C_2O_2C(2)$; 5.26 and 5.44/*AB*X_3, $J_{1,2}$ = 14, H–C(1) and H–C(2) of –CH=CH–CH_3, resp.; 5.40/br., H–C(8). – MS.: 234 ($C_{15}H_{22}O_3^+$), 216, 194, 181, *117*, 97.

3 g of the *(E+Z)*-mixture of **16** were hydrolysed for 5 h at RT. with 2 ml 5N HCl in 150 ml acetone. The acetone was distilled off after the addition of 200 ml toluene. The solution was then neutralized with K_2CO_3, filtered and concentrated i.V. Chromatography in toluene/ethyl acetate 20:1 gave 2.3 g of an *(E+Z)*-mixture of **6** (90% yield). *(Z)*-**6** was isolated by VPC. – UV. (hexane): 228 (14500), 270 (125, sh), 330 (47). – IR.: 710, 930, 1270, 1630, 1685, 2940, 3010. – NMR. ($CDCl_3$): 1.63/ABX_3, $J_{1,3}$ = 1.3, $J_{2,3}$ = 7.2, 3 H–C(3) of –CH=CH–CH_3; 5.15 and 5.62/*AB*X_3, $J_{1,2}$ = 12.0, double resonance at 1.63 decoupled to *AB*, H–C(1) and H–C(2) of –CH=CH–CH_3, resp.; 5.94/*s*, H–C(1). – MS.: *190* ($C_{13}H_{18}O_3^+$), 175, 148, 133, 119, 105, 91.

A solution of 2 g of the *(E+Z)*-mixture of **16** and 2 g naphthalene in 200 ml benzene was irradiated at > 300 nm at RT. In order to prevent excessive formation of insoluble material, the irradiation was carried only to a *(E/Z)*-ratio of *ca.* 1:1. The solution was taken to dryness and the residue was hydrolysed with 5N HCl as described above. Chromatography afforded 800 mg of the *(E+Z)*-mixture from which *(E)*-**6** was separated by VPC. (Apiezone L-200). – UV. (hexane): 225 (13600), 270 sh, 330 (40). – IR.: 930, 980, 1270, 1630, 1685, 2940, 3010. – NMR.: 1.74/*d*, $J_{2,3}$ = 5, 3 H–C(3) of –CH=CH–CH_3; 5.27 and 5.34/*AB*X_3, $J_{1,2}$ = 17, H–C(1) and H–C(2) of –CH=CH–CH_3, resp.; 5.92/*s*, H–C(1). – MS.: the same as for *(Z)*-**6**.

4a-(Z-1-Deuterio-1-propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-one (**6-d$_1$**). 500 mg Ethyl 2-ethylenedioxy-bicyclo[4.4.0]-8-decene-4a-carboxylate (**13**) [10] were reduced to **14-d$_2$** with $LiAlD_4$. An *(E+Z)*-mixture of **6-d$_1$** was obtained from the reaction sequence **14-d$_2$** → **15-d$_1$** → **16-d$_1$** → **6-d$_1$**, similar to that described above for the non-deuterated analogs. *(Z)*-**6-d$_1$** was isolated by VPC. – UV. and IR.: the same as for

(Z)-**6**. – NMR.: 1.65 and 5.27/AX_3, $J_{2,3}$ = 7, 3 H–C(3) and H–C(2) of –CH=CH–CH_3, resp.; 5.80/*s*, H–C(1). – MS.: *191* ($C_{13}H_{17}DO^+$), 176, 149, 120, 106, 92.

*4a-(*E- *and* Z*-2,3,3,3-tetradeuterio-1-propenyl)-bicyclo[4.4.0]dec-1(8a)-en-2-ones* (**6-d$_4$**). The aldehyde **15** was converted to *(E+Z)*-**16-d$_4$** with triphenylpentadeuterioethylphosphonium iodide and deacetalized to *(E+Z)*-**6-d$_4$** as described above for the non-deuterated analogs. – NMR.: 1.3–2.5/*m*, 12 H (ABX_3 at *ca.* 1.6 missing); 5.8/*m*, H–C(2) of –CH=CH–CH_3; 5.85/*s*, H–C(1). – MS.: *194* ($C_{13}H_{14}D_4O^+$), 176, 152, 137, 120, 109, 92.

4a-(Z-1-Propenyl)-bicyclo[4.4.0]deca-1(8a),7-dien-2-one (**17**). A solution of 950 mg (5 mmol) *(E+Z)*-**6** and 1.85 g (7.5 mmol) chloranil in 70 ml *t*-butyl alcohol was refluxed for 5 h, then concentrated i.v. and filtered in CH_2Cl_2 through neutral Al_2O_3 (act. III). Chromatography in benzene/ethyl acetate 4:1 gave 530 mg *(E+Z)*-**17** (55% yield), m.p. *ca.* 25°. *(Z)*-**17** was separated by VPC. – UV. (hexane): 268 (17000), 340 (500). – IR.: 705, 730, 920, 1620, 1675. – NMR.: 1.60/ABX_3, $J_{1,3}$ = 1.2, $J_{2,3}$ = 7, 3 H–C(3) of –CH=CH–CH_3; 4.85 and 5.90/*AB*X_3, $J_{1,2}$ = 12, H–C(1) and H–C(2) of –CH=CH–CH_3, resp.; 5.60/*s*, H–C(1); 6.2/br., H–C(7) and H–C(8). – MS.: *188* ($C_{13}H_{16}O^+$), 173, 160, 146, 131, 117.

*4a-(*E- *and* Z*-1-propenyl)-bicyclo[4.4.0]deca-1(8a),3-dien-2-one* (**18**). A solution of 190 mg (1 mmol) *(E+Z)*-**6**, 245 mg (2 mmol) benzoic acid and 227 mg (1 mmol) 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in 60 ml benzene was refluxed for 15 h and then filtered through neutral Al_2O_3 (act. III). Chromatography in toluene/ethyl acetate 4:1 afforded 110 mg *(E+Z)*-**18** (59% yield). – UV. (hexane): 235 (11000). – IR.: 880, 1600, 1630, 1660, 3020. – NMR. ($CDCl_3$): 1.2–2.5/*m*, 11 H, with *d* at 1.35, $J_{2,3}$ = 7, 3 H–C(3) of –CH=CH–CH_3; 5.3–5.8/*m*, double resonance at 1.35 decoupled to *AB*, $J_{1,2}$ = 11, H–C(1) and H–C(2) of –CH=CH–CH_3; 6.12/*d*, $J_{1,3}$ = 2, H–C(1); 6.25/*d*×*d*, $J_{3,4}$ = 10.5, H–C(3); 6.75/*d*, H–C(4). – MS.: *188* ($C_{13}H_{16}O^+$), 173, 160, 145, 131, 117.

*4-Methyl-4-(*E*-1-propenyl)-2-cyclohexenone* (**21**). 10 g 2-Methyl-2-pentenal (**19**) [12] and 8 g methylvinylketone in 20 ml C_2H_5OH were dropped into a 1N ethanolic solution of C_2H_5ONa within 15 min at RT. The mixture was then concentrated i.V. and worked up. Distillation at 60°/0.5 Torr gave 7.6 g *(E)*-**21**. – UV. (isooctane): 230 (18300), 282 (28), 243 (29). – IR.: 975, 1110, 1240, 1650, 1615, 1690, 3030. – NMR.: 1.20/*s*; 1.70/*d*, $J_{2,3}$ = 4, 3 H–C(3) of –CH=CH–CH_3; 5.3–5.6/*m*, H–C(1) and H–C(2) of –CH=CH–CH_3; 5.90+6.55/*AB*, $J_{2,3}$ = 10, H–C(2) and H–C(3), resp.). – MS.: *150* ($C_{10}H_{14}O^+$), 135, 122, 108, 93.

*4-Methyl-4-(*Z*-1-propenyl)-2-cyclohexenone* (**21**). 140 mg 4-Formyl-4-methyl-2-cyclohexenone (**20**) [2] and 400 mg triphenylethylphosphonium bromide were converted to 52 mg *(Z)*-**21** (after chromatography in hexane/ether 2:1, 34% yield) as described above for **15**→**16**. – UV.: same as for *(E)*-**21**. – IR.: 710, 1120, 1230, 1620, 1660, 1690, 3020. – NMR. ($CDCl_3$): 1.30/*s*, H_3C–C(4); 1.70/*d*, $J_{2,3}$ = 6, 3 H–C(3) of –CH=CH–CH_3; 5.3–5.6/*m*, double resonance at 1.7 decoupled to *AB* at 5.35 and 5.55, $J_{1,2}$ = 11, H–C(1) and H–C(2) of –CH=CH–CH_3, resp.; 5.88 and 6.95/*AB*, $J_{2,3}$ = 10, H–C(2) and H–C(3), resp. – MS.: *150* ($C_{10}H_{14}O^+$), 135, 122, 108, *93*, 79.

4a-Propyl-bicyclo[4.4.0]dec-1(8a)-en-2-one (**23**). 1.9 g Methylvinylketone were added portionwise over a period of 5 h to a mixture of 3.5 g 2-propylcyclohexanone (**22**) and 0.3 ml 3N ethanolic C_2H_5ONa solution which was kept under an argon atmosphere at –15°. *8a-Hydroxy-4a-propyl-bicyclo[4.4.0]-2-decanone* crystallized slowly from the reaction mixture which was refluxed for 2 h together with 50 ml aqueous 10% KOH solution. The work-up and chromatography in hexane/ethyl acetate 1:1 furnished 1.5 g **23** (29% yield). – UV. (hexane): 232 (11500). – IR.: 1620, 1680, 3040. – NMR.: 5.60/*s*, H–C(1). – MS.: 192 ($C_{13}H_{20}O^+$), 177, *150*, 135, 121, 107.

UV.-Irradiations. – *Preparative Photolyses.* a) *Irradiation of (E+Z)*-**6** *at 254 nm.* A solution of 1 g *(E+Z)*-**6** in 100 ml hexane (0.053M) was irradiated until a conversion of *ca.* 75% (VPC.: Apiezone L-200) was reached, accompanied by the formation of insoluble material. Chromatography in toluene/ethyl acetate 10:1 gave 250 mg *(E+Z)*-**6**, 100 mg *(E+Z)*-**8**, and a mixture (390 mg) of **9** and *(E)*-**10** which were separated by VPC. The yields based on converted *(E+Z)*-**6** were 13% *(E+Z)*-**8**, 41% **9**, and 11% *(E)*-**10**. *4a-(*E- *and* Z*-1-propenyl)-bicyclo[4.4.0]dec-8-en-2-one* (**8**). – IR.: 665, 705, 960, 1240, 1720. – NMR.: 1.5–2.4/*m*, 13 H, with *d* at 1.7, $J_{2,3}$ ~ 5, 3 H–C(3) of –CH=CH–CH_3; 2.9–3.4/*m*, 2 H–C(1); 4.9–5.95/*m*, H–C(1) and H–C(2) of –CH=CH–CH_3 and H–C(8). Treatment of *(E+Z)*-**8** with K_2CO_3 in C_2H_5OH at RT. gave quantitatively *(E+Z)*-**6**. *Tricyclo[4.4.3.0]tridec-12-en-3-one* (**9**). – UV. (hexane): 275 (68). – IR.: 700, 965, 1715, 3020. – NMR. ($CDCl_3$): 1.2–2.4/*m*, 11 H, with *AB*XY at 2.1 and 2.4, double resonance at 5.7 decouples to *AB*, J_{gem} = 16, 2 H–C(11); 5.62 and 5.72/AB*XY*, double resonance at 2.25 decouples to *XY*, $J_{12,13}$ = 5, H–C(12) and H–C(13), resp.). – For ^{13}C-NMR. see *Table 5.* – MS.: 190 ($C_{13}H_{18}O^+$), 162, 161, 148, 147, 133, *120*, 105, 91. – *2,4-Dinitrophenylhydrazone derivative of* **9**. – M.p. 90°. – MS.:

370 ($C_{19}H_{22}N_4O_4^+$). – *1-(E-1-Propenyl)-tricyclo[4.4.0.0^{2,6}]decan-3-one* (**10**). – UV. (hexane): 280 (55). – IR.: 975, 1180, 1715, 3020. – NMR. ($CDCl_3$): 1.3–2.4/*m*, 16 H, with ABX_3 at 1.7, $J_{1,3}$ = 1.5, $J_{2,3}$ = 6, 3 H–C(3) of –CH=CH–CH_3; 5.0 and 5.53/*AB*X_3, double resonance at 1.7 decouples to *AB*, $J_{1,2}$ = 14, H–C(1) and H–C(2) of –CH=CH–CH_3. – MS.: 190 ($C_{13}H_{18}O^+$), *175*, 162, 148, 133, 119, 105, 91.

b) *Irradiation of (E+Z)-***6** *at >300 nm.* 1 g *(E+Z)-***6** was irradiated in 100 ml ether (0.053M). After *ca.* 90% conversion the solution was concentrated i.V., and the residue was treated for 5 h with 5% NaOH in CH_3OH at 50° in order to reconvert *(E+Z)-***8** to starting material. The mixture was then extracted with toluene. The organic layer was washed with H_2O and taken to dryness. Chromatography in toluene/ethyl acetate 20:1 gave 550 mg *(E)-***10** (55% yield).

c) *Irradiation of (E+Z)-***6-d$_1$** *at 254 nm.* Irradiation as in paragraph a: *13-Deuteriotricyclo[4.4.3.0]-tridec-12-en-3-one* (**9-d$_1$**) was isolated by VPC. – IR.: same as **9**. – NMR. ($CDCl_3$): only one olefinic H at 5.7/*t*, $J_{11,12}$ = 5, H–C(12). – MS.: 191 ($C_{13}H_{17}DO^+$), 149, 148, 134, *121*, 106, 92.

d) *Irradiation of (E+Z)-***6-d$_4$** *at 254 nm* (*cf.* paragraph a) gave after VPC. isolation exo-*2,11,11,12-tetradeuteriotricyclo[4.4.3.0]tridec-12-en-3-one* (**9-d$_4$**). – NMR.: 5.62 br. *s*, H–C(13). – MS.: 194 ($C_{13}H_{14}D_4O^+$), 166, 135, *122*. – Treatment of **9-d$_4$** with K_2CO_3 in C_2H_5OH at RT. removed one D [MS.: 193 ($C_{13}H_{15}D_3O^+$), *122*].

e) *Sensitization of* (E)- *and* (Z)-**10**. Samples of each isomer (20 mg)+200 mg acetophenone in 10 ml benzene were photolysed at > 340 nm and then directly chromatographed in toluene/ethyl acetate 20:1. In each case both isomers, *(E)*- and *(Z)*-**10**, were isolated and identified by VPC. coinjection and IR.

f) *Photolyse of (E+Z)-***17** *at 254 nm.* 200 mg were irradiated in 50 ml ether to full conversion. The insoluble products were filtered off. Chromatography in toluene/ethyl acetate 10:1 gave 60 mg *tricyclo-[4.4.3.0]trideca-9,12-dien-3-one* (**30**) (33% yield). – IR.: 720, 895, 1725, 3030, 3060. – NMR. ($CDCl_3$): 1.5–2.4/*m*, 12 H; 5.3–5.8/*m*, H–C(9, 10, 12, 13). – MS.: 188 ($C_{13}H_{16}O^+$), 160, 146, *120*.

g) *Irradiation of (E+Z)-***17** *at >300 nm* in ether gave only insoluble material.

h) *Irradiation of (E+Z)-***18** *at >300 nm.* After 50% conversion of 150 mg in 50 ml hexane and filtration in CH_2Cl_2 through neutral Al_2O_3 (act. III), chromatography with toluene/ethyl acetate 10:1 gave, besides 75 mg starting material, 7 mg *(Z)-***31** (5% yield) and 20 mg *(E)-***32** (13% yield).

1-(Z-1-Propenyl-tricyclo[4.4.0.0^{2,6}]dec-4-en-3-one (**31**). – IR.: 710, 1670, 1705, 3020. – NMR.: owing to insufficient amounts, the spectrum of a mixture of **31**+**32** was measured; 5.60+7.10/*AX*, $J_{4,5}$ = 6, H–C(4) and H–C(5).

3(or *4*)-(E-*1-Propenyl)-5,6,7,8-tetrahydro-1*(or *2*)*-naphthol* (**32**). – IR.: 970, 1595, 1610, 3020, 3610. – NMR. (see comments above for **31**): 5.8–6.4/*m*, H–C(1) and H–C(2) of –CH=CH–CH_3; 6.60+6.90/*AB*, *J* = 3, arom. H. – MS.: *188* ($C_{13}H_{16}O^+$), 173, 160, 145, 131.

i) *Irradiation of (E)-***21** *at 254 nm.* After 50% conversion of 2 g in 150 ml dioxan and chromatography with benzene/ether 3:1 1 g starting material which was strongly enriched with *(Z)-***21**, 400 mg *endo-(E)-***33** (20% yield), 40 mg *exo-(E)-***33** (2% yield) and 55 mg **34** (3% yield) were obtained. *5-Methyl*-endo-*6-(1-*E-*propenyl)-bicyclo[3.1.0]hexan-2-one* (**33**). – UV. (C_2H_5OH): 280 (70). – IR.: 900, 965, 1175, 1290, 1735. – NMR.: 1.35/*s*, H_3C–C(5); 1.71/*d* with allylic fine splitting, $J_{2,3(-CH=CH-CH_3)}$ = 6, 3 H–C(3) of –CH=CH–CH_3; 5.0–5.9/*AB*XY_3, double resonance at 1.71 decouples to *AB*X at 5.36/*d*×*d* ($J_{6,1(-CH=CH-CH_3)}$ = 5, $J_{1,2(-CH=CH-CH_3)}$ = 15)+5.80/*d*, H–C(1) and H–C(2) of –CH=CH–CH_3. With Eu(fod)$_3$: *d*, $J_{1,6}$ = 10, H–C(1); *d*×*d*, H–C(6); double resonance at H–C(6) decouples H–C(1) to *s* and H–C(1) of –CH=CH–CH_3 to *d*. – MS.: *150* ($C_{10}H_{14}O^+$), 135, 122, 93. *5-Methyl*-exo-*6-(1-*E-*propenyl)-bicyclo[3.1.0]hexan-2-one* (**33**). – IR.: 875, 900, 970, 1185, 1740. – NMR.: 1.33/*s*, H_3C–C(5); 1.70/*d* with allylic fine splitting, $J_{2,3(-CH=CH-CH_3)}$ = 6, 3 H–C(3) of –CH=CH–CH_3; 5.0–5.7/*AB*XY_3, double resonance at 1.70 decouples to *AB*X at 5.18/*d*×*d* ($J_{6,1(-CH=CH-CH_3)}$ = 8, $J_{1,2(-CH=CH-CH_3)}$ = 15)+5.66/*d*, H–C(1) and H–C(2) of –CH=CH–CH_3. With Eu(fod)$_3$: *d*, $J_{1,6}$ = 3, H–C(1); *d*×*d*, H–C(6); double resonance at H–C(1) of –CH=CH–CH_3 decouples H–C(6) to *d*. – MS.: 150 ($C_{10}H_{14}O^+$), 135, 108, *93*.

3-(E-1-Propenyl)-4-methyl-2-cyclohexenone (**34**). – UV. (isooctane): 266 (25000), 340 (50). – IR.: 890, 975, 1260, 1590, 1645, 1675, 3030. – NMR.: 1.25/*d*, *J* = 7, double resonance at 2.9 decouples to *s*. H_3C–C(4); 1.91/*d*, $J_{2,3(-CH=CH-CH_3)}$ = 5.5, 3 H–C(3) of –CH=CH–CH_3; 5.80/*s*, H–C(2); 6.0–6.5/*AB*X_3, double resonance at 1.9 decouples to *AB* at 6.12 and 6.31, $J_{1,2(-CH=CH-CH_3)}$ = 15.5, H–C(1) and H–C(2) of –CH=CH–CH_3. – MS.: *150* ($C_{10}H_{14}O^+$), 135, 122, 107.

j) *Irradiation of* **23** *at 254 nm.* 200 mg in 20 ml *t*-BuOH were photolysed to 80% conversion. Chromatography with toluene/ethyl acetate 10:1 gave 40 mg **23**, 40 mg **24** (20% yield), and 35 mg **25** (18% yield).

1-Propyltricyclo[4.4.0.0^{2,6}]decan-3-one (**24**). – IR.: 890, 920, 960, 1180, 1460, 1720. – NMR.: 0.95/*t*, J=6, H_3–C(3-propyl). – MS.: 192 ($C_{13}H_{20}O^+$), *150*, 149, 135, 121, 107.

4a-Propyl-bicyclo[4.4.0]dec-8-en-2-one (**25**). – NMR.: 2.75–3.05/*m*, 2 H–C(1); 5.4/br. *s*, H–C(8). Treatment of **25** with K_2CO_3 in C_2H_5OH at RT. gave quantitatively **23**.

Analytical Photolyses. – a) *Solvent-dependent Product Distribution from* **6**. 0.05M Solutions of *(E)*- and *(Z)*-**6** were irradiated; product analysis with capillary VPC., Carbowax 1540 (column 150°, injector and detector 200°). For further experimental details and results see 'General Remarks' and *Tables 1* and *4*.

b) *Sensitization of (Z)*-**6**. Irradiations at >340 nm of (i) 0.06M *(Z)*-**6** in benzene, (ii) 0.06M *(Z)*-**6**+0.5M acetophenone in benzene, (iii) 0.08M *(Z)*-**6** in *t*-BuOH, and (iv) 0.08M *(Z)*-**6**+0.5M acetophenone in *t*-BuOH were monitored by capillary VPC. (Carbowax 1540, 140°). In all runs, product mixtures similar to those summarized in *Table 1* (>300 nm) were formed, and **9** was not detectable. In experiments (ii) and (iv) at conversions of ≥50%, the formation of *(Z)*-**10** set in increasingly.

c) *Irradiation of (E+Z)*-**18** *at 254 nm.* TLC. analysis of the product mixture obtained from a photolysis at 254 nm showed the same composition as a similar run at >300 nm (both experiments in hexane solution).

d) *Quantum Yield Determinations.* The quantum yields were measured at 20° in degassed solutions [3 freeze-pump(10^{-5} Torr)-thaw cycles] using an electronically integrating actinometer [37]. The results are summarized in *Tables 2* and *3*. The product compositions were analysed by capillary VPC. (Carbowax 1540; column 150°, injector and detector 200°). The Φ values given in the *Tables* are averaged from 2–3 measurements.

Transformations of Photoproducts. – *Hydrogenation of* (E)-**10**. A solution of 200 mg *(E)*-**10** and 100 mg $[(C_6H_5)_3P]_3RhCl$ in 20 ml benzene was stirred for 3 days in the dark at RT. under H_2. The reaction was monitored by GC. (Apiezon L, 180°). The solvent was evaporated i.V. and the crude product filtered in hexane through neutral Al_2O_3 (act. III). Chromatography with toluene/ethyl acetate 10:1 gave 90 mg of an unknown product (IR.: 1750) and 80 mg **24** [identification by IR., NMR., MS., GC. coinjection (Apiezon L, 180°), and TLC. (hexane/ether 2:1)].

2,2,4,4-Tetradeuteriotricyclo[4.4.3.0]tridec-12-en-3-one (**26**) was obtained by treatment of **9** with 5 mol/equiv. NaOH in refluxing dioxan/D_2O 1:1 for 5 h, extraction with ether, washing of the organic layer with D_2O and drying over $MgSO_4$. – MS.: *194* ($C_{13}H_{14}D_4O^+$, 78%), 193 (15%).

Tricyclo[4.4.3.0]tridecan-3-one (**27**). – a) The hydrogenation of 50 mg **9** in 20 ml ethyl acetate over 10% Pd/C gave, after chromatography with toluene/ethyl acetate 10:1, 40 mg **27**; m.p. 50°. – NMR.: 1.4–1.8/*m*, 16 H; 2.05–2.4/*m*, 4 H. – MS.: 192 ($C_{13}H_{20}O^+$), 174, 163, 150, *121*.

b) A similar hydrogenation of **30** gave again **27** [identification by IR., NMR., TLC. (hexane/ether 2:1), and VPC. coinjection (K 1540, 140°)].

Tricyclo[4.4.3.0]tridecane (**28**). 40 mg **27** were dissolved in 0.2 ml 85% $N_2H_4 \cdot H_2O$ and 2 ml diethylene glycol. After addition of 70 mg finely ground KOH the solution was heated under argon to 180° for 15 h. The reaction mixture was extracted with hexane and the extract washed with saturated NH_4Cl-solution and dried over $MgSO_4$. 20 mg **28** were obtained; m.p. 79°. – IR.: 1440, 1455, 1470, 2850, 2870, 2925. – NMR.: 1.15–1.7/*m*. – MS.: *178* ($C_{13}H_{22}^+$), 150, 135, 121. – M.p., IR. and NMR. data are in good agreement with those published for **28** [15].

Reduction of (Z)-**31**. 7 mg *(Z)*-**31** were reduced at 0° with $NaBH_4$ in CH_3OH/H_2O 1:1, and the crude product was oxidized with *Collins* reagent as described for **14**→**15**. 4 mg *(Z)*-**10** were obtained and identified by IR. (710, 1715) and GC. coinjection (Carbowax 1540, 150°).

endo-*2-Hydroxy-5-methyl-bicyclo[3.1.0]hexan*-endo-*6-carboxylic lactone* (**35**). After reduction of 90 mg *endo-(E)*-**33** with $NaBH_4$ in CH_3OH/H_2O 1:1 at 0°, the crude product was ozonized at −10° in CH_2Cl_2. The ozonide was oxidatively cleaved with H_2O_2 and HCO_2H. Chromatography with toluene/ethyl acetate 10:1 yielded 45 mg **35**. – IR.: 980, 1185, 1295, 1345, 1450, 1780. – NMR.: 1.30/*s*, H_3C–C(5); 2.04/*d* with fine coupling ($J_{1,2}<0.5$), $J_{1,6}=7$, H–C(1); 2.78/*d*×*d*, $J_{2,6}=5$, H–C(6); 4.98/*d* with fine coupling, H–C(2); double resonance at 2.04 decouples H–C(2) and H–C(6) to sharp *d*, at 2.78→*s* for H–C(1) and *s* with fine coupling for H–C(2), and at 4.98→*AX* for H–C(1) and H–C(6). – MS.: 138 ($C_8H_{10}O_2^+$), 123, 121, 109, *79*.

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