17. Specifically ($\pi \rightarrow \pi^*$)-Induced Cyclohexenone Reactions 6-Benzylbicyclo[4.4.0]dec-1-en-3-ones[1][2][2a]

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Summary

6-Benzylbicyclo[4.4.0]dec-1-en-3-one (**9**) and the 2-methyl homologue (**10**) underwent a ($\gamma \rightarrow \alpha$)-1,3-benzyl shift to the β,γ-unsaturated ketones **21** and **22**, respectively, when excited in the $\pi \rightarrow \pi^*$ absorption band. The quantum yield was *ca.* 0.1 at 254 nm for the formation of both products in alkane solvents. These reactions occur specifically from the $S_2(\pi,\pi^*)$ state in competition with its decay to the $S_1(n,\pi^*)$ and T states. The triplet reaction of **9**, initiated by $n \rightarrow \pi^*$ irradiation and by sensitization, was a double-bond shift to **20**, whereas no identifiable product was observed from **10** under these conditions. Direct and acetone-sensitized irradiations of **21** and **22** resulted in oxadi-π-methane rearrangements to mixtures of *syn*- and *anti*-**30** and *syn*- and *anti*-**31**, respectively.

Over the last years, organic photoreactions from upper excited states in solution have been reported in a number of examples[2]. Among these, appropriately 4-substituted 2-cyclohexenones, on $\pi \rightarrow \pi^*$ excitation, have been found to undergo such reactions, presumably from the $S_2(\pi,\pi^*)$ state. In the (*Z*)-propenyl enone **1** an intramolecular hydrogen transfer from the allylic methyl group to the enone α-carbon atom and cyclization to product **2** occurred with a quantum yield $\Phi_2 = 0.29$ at 245 nm [1]. A similar process (**3** → **4**) together with an overall ($\gamma \rightarrow \alpha$)-1,3-shift of the substituent (**3** → **5**) *via* a cleavage and alternate recombination sequence, was observed with the dimethoxymethyl enone **3** [3] *(Scheme 1)*. We now report that a 1,3-benzyl shift (**9** → **21** and **10** → **22**) was the exclusive reaction of the benzyl enones **9** and **10**, in which the hydrogen transfer/cyclization process is barred by geometric and energetic constraints.

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[1] Taken from the Doctoral Thesis of *R. Mariaca* (Université de Genève, 1978).

[2] *Cf.* [1] for a first reference to this work, and [2] for a recent review on upper excited-state reactions of, *inter alia*, α,β-unsaturated ketones.

[2a] The numbering given in [1] for the bicyclo[4.4.0]decane derivatives should be revised in accord with the IUPAC rules on nomenclature. *E.g.*, the title compounds in [1] should read '1-(*Z*-1-Propenyl)-bicyclo[4.4.0]dec-5-en-4-one and 1-(*Z*-1-Propenyl)-bicyclo[4.4.0]deca-5,7-dien-4-one'.

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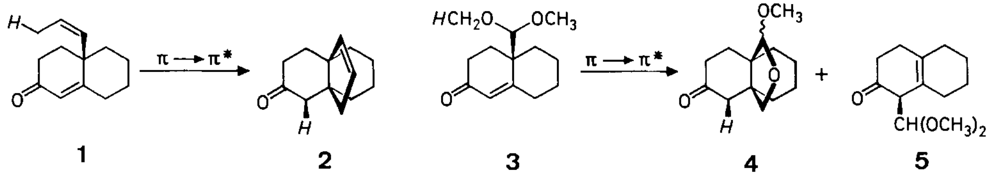
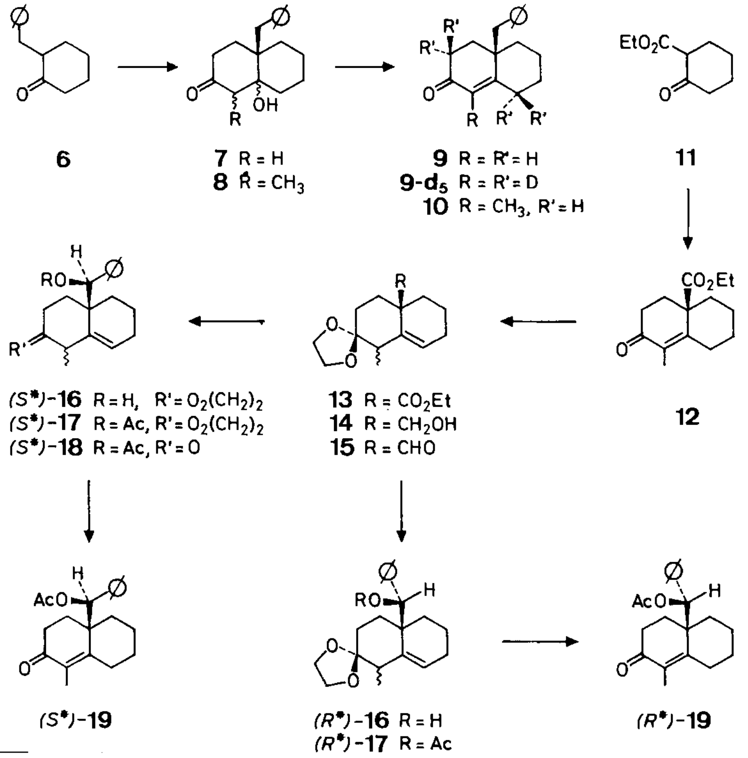
Scheme 1. *Specifically* $\pi \rightarrow \pi^*$ *induced reactions of the 6-(Z-1-propenyl)-* (**1**) *and 6-dimethoxymethyl-bicyclo[4.4.0]dec-1-en-3-ones* (**3**)[4])



Synthesis of compounds 9(-d$_5$), 10, (*R)- and (*S**)-19** *(Scheme 2).* - Sodium ethoxide-catalyzed annelation of 2-benzylcyclohexanone (**6**) with methyl and ethyl vinyl ketone gave the hydroxyketones **7** and **8**, respectively, which were dehydrated with sulfuric acid in dioxan to **9** and **10**, each in an overall yield of 34%. Base-catalyzed H/D exchange afforded **9-d$_5$**. The UV. absorption spectra showed the following maxima (in isooctane): 235 and 335 nm (ε = 11300 and 34) for **9**, 245 and 324 nm (ε = 18700 and 40) for **10**.

Scheme 2. *Synthesis of compounds* 9(-d$_5$), 10, (R*)- *and* (S*)-19[4])



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[4]) All chiral formula shown stand for racemic compounds. The configuration at C(6) being always the same, for simplification diastereoisomers are for simplicity designated *R** and *S** instead of 6*R**, 11*R** and 6*R**, 11*S** for example.

The preparation of the diastereoisomeric hydroxyketones **16** involved basecatalyzed annelation of **11** with ethyl vinyl ketone (→ **12**), acetalization with ethylene glycol and *p*-toluenesulfonic acid (→ **13**), reduction with lithium aluminium hydride (→ **14**), oxidation with pyridinium chromate (→ **15**), and reaction with phenyl lithium. (*R**)- and (*S**)-**16** were obtained in a 2.4:1 ratio and an overall yield of 33%. Separate acetylation of the two diastereoisomers to (*R**)- and (*S**)-**17** and subsequent hydrolysis of the acetals with *p*-toluenesulfonic acid in aqueous acetone at RT. gave the conjugated acetoxyenone (*R**)-**19** and the *β,γ*-unsaturated ketone (*S**)-**18**, respectively. Isomerization of the latter to (*S**)-**19** was achieved by treatment with aqueous hydrochloric acid.

The configurational assignment of (*R**)- and (*S**)-**16** is based on IR. (CCl_4) and ^{1}H-NMR. data. The major isomer exhibited only one sharp hydroxyl IR. band at 3540 cm^{-1}, indicating a strong hydrogen bond between the hydroxyl and the *cis* acetal oxygen atoms. The minor isomer was characterized by bands for free and intermolecularly associated hydroxyl groups, at 3610 (sharp) and 3400-3600 cm^{-1} (broad). The band intensities of both spectra showed the appropriate responses upon dilution. A rotamerically frozen conformation for the hydrogen-bridged isomer should be sterically facilitated by the (*R**)-configuration of the hydroxyphenylmethyl carbon atom, with the aromatic ring pointing away from the bicyclodecene system. The NMR. shift differences between the benzylic and olefinic protons, $\Delta\delta(R^* - S^*) = -0.12$ and $+0.3$, respectively, are in agreement with this assignment. The upfield shift of the benzylic proton in (*R**)-**16** is attributed to diamagnetic shielding by the double bond. In the (*S**)-isomer, which has smaller rotational barriers, this effect is less pronounced and accompanied by a similar but stronger influence by the phenyl group on the olefinic proton.

$n \rightarrow \pi^*$ Irradiation and triplet sensitization of the 6-benzylbicyclo[4.4.0]hex-1-en-3-ones *9* and *10* (*Scheme 3*). - Irradiations of **9**, both directly at > 300 nm, and sensitized with acetophenone at > 340 nm, afforded isomer **20** as a single photoproduct. On standing and on treatment with base the double bond of **20** was shifted back to regenerate the *α,β*-unsaturated starting ketone. The formation of **20** represents a widely encountered photoreaction of conjugated cyclohexenones which results from hydrogen abstractions between triplet-excited (presumably $^3n,\pi^*$) and ground-state enones [4]. The appreciable variation of the quantum yields with solvent (*Table 1*) conforms with expectations concerning the influence of the solvent

Scheme 3. $n \rightarrow \pi^*$ *Irradiation (> 300 nm) and triplet sensitization of* **9**[4])

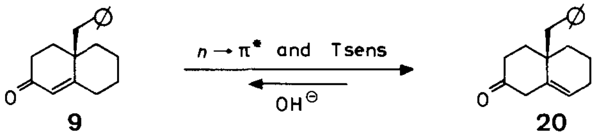


Table 1. $n \rightarrow \pi^*$ *Irradiation (366 nm) of* **9**: *quantum yields of conversion and product formation*

Solvent	Initial concentration	Final conversion of **9**	Quantum yields	
			Φ_{-9}[a])	Φ_{20}[b])
Benzene	0.036 M **9**	66%	0.037	0.019
Isooctane	0.033 M **9**	33%	0.013	0.007
t-Butyl alcohol	0.036 M **9**	20%	0.004	< 0.001

Experimental errors:

[a]) ±20%; limiting upper values.

[b]) ±20%; limiting lower values. - For further details see exper. part.

nature on the order of the energy levels of the α,β-enone $^3n,\pi^*$ and $^3\pi,\pi^*$ states, and on the thermal behaviour of the dienol intermediate and β,γ-enone product.

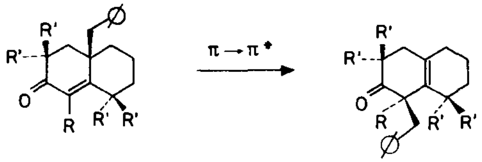
In similar irradiation and sensitization experiments with the methyl homologue **10** no double bond shift or other product could be detected apart from the formation of insoluble deposits.

$\pi\rightarrow\pi^*$ Irradiation of enones 9(-d$_5$), 10, and (*R)- and (*S**)-19** *(Scheme 4)*. - The irradiation of **9**, **9-d$_5$** and **10** at 254 nm yielded in each case a single identifiable product, the 1,3-benzyl-shifted compounds **21**, **21-d$_5$**, and **22**, respectively. The quantum yields for the formation of **21** and **22** were around 0.1 in alkane solvents and somewhat lower in methanol, and they proved independent of excitation wavelength within the $\pi\rightarrow\pi^*$ absorption range *(Table 2)*. While these reactions were also accompanied by the precipitation of some insoluble material, no trace of product **20** could be detected in the runs with **9**. It appears therefore that the upper excited-state (S_2) reaction competes here with $S_2\rightarrow S_1$ internal conversion and/or $S_2\rightarrow T$ intersystem crossing even more efficiently than in the previous examples [1] [3].

In striking contrast to the results with the benzylenone **10**, the acetoxyphenylmethyl analogues (*R**)- and (*S**)-**19** did not afford any photoproduct on irradiation at 254 nm.

The mechanism of the 1,3-benzyl shifts **9**→**21** and **10**→**22** remains unsolved. Formally similar 1,3-shifts of phenyl-substituted saturated carbon atoms have been observed previously in 2 cases. $n\rightarrow\pi^*$ Excitation of *endo*- and *exo*-**23** each gave the

Scheme 4. $\pi\rightarrow\pi^*$ *Irradiation of* **9**(-**d$_5$**) *and* **10**[4])



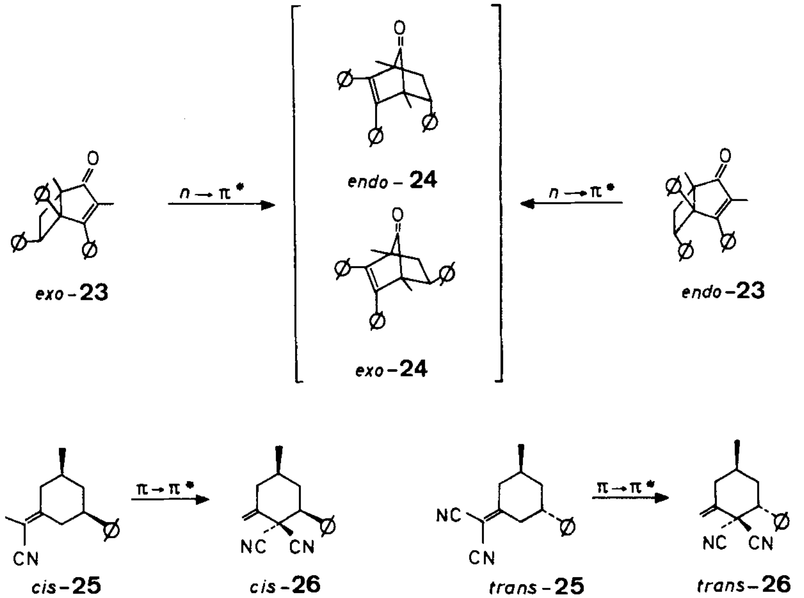
9	R = R' = H	**21**
9-d$_5$	R = R' = D	**21-d$_5$**
10	R = CH$_3$, R' = H	**22**

Table 2. $\pi\rightarrow\pi^*$ *Irradiation of* **9** *and* **10**: *quantum yields of conversion and product formation*

Starting ketone	Solvent	Excitation wavelength, nm	Quantum yields[a])	
			Φ_{-9}	Φ_{21}
0.033 M **9**	Isooctane	254	0.32	0.10
0.033 M **9**	Isooctane	265	0.32	0.09
0.0064 M **9**	Isooctane	254	0.35	0.13
0.0064 M **9**	Isooctane	265	0.36	0.09
0.021 M **9**	Methanol	254	0.27	0.06
0.021 M **9**	Methanol	265	0.24	0.05
			Φ_{-10}	Φ_{22}
0.080 M **10**	Hexane	254	0.28	0.13

[a]) Extrapolated to Φ at zero conversion; experimental error ±20%. - For further details see exper. part.

Scheme 5[4])



same mixture of epimers, *endo*- and *exo*-**24** in a 1,3-shift *via* bond cleavage to a biradical intermediate capable of conformational equilibration prior to ring closure [5] *(Scheme 5)*. Although obviously different in the nature (electronic configuration and/or spin multiplicity) of the reactive excited state, the 1,3-shifts **3** → **5** and **23** → **24** are operationally similar [3c] and those in **9**/**10** → **21**/**22** may be of the same type, despite the failure to find escape products from the intermediate radical cage (*e.g.*, 1,2-diphenylethane).

On the other hand, the 1,3-rearrangements **25** → **26** proceeded stereospecifically and with retention of the configuration of the migrating benzylic carbon atom as required by orbital symmetry control in a photochemically allowed concerted process [6] [7]. These reactions have been attributed to the $^1\pi,\pi^*$ state (S_1 in these compounds) which, albeit in an oversimplified categorization, corresponds to the reactive S_2 state in **9** and **10**[5]).

Structural evidence for **21** *and* **22**. Both compounds exhibit UV. and IR. spectra characteristic of β,γ-unsaturated ketones of this type [**21**: $\lambda_{max} = 213$ ($\varepsilon = 4600$) and 280 nm (43), $\tilde{\nu}_{CO} = 1725$ cm^{-1}; **22**: $\lambda_{max} = 225$ ($\varepsilon = 2500$) and 285 nm (162), $\tilde{\nu}_{CO} = 1710$ cm^{-1}]. The complex NMR. pattern of the benzylic and ring A protons of **21**

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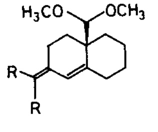
[5] The reactivities of $^1\pi,\pi^*$ states of α,β-unsaturated ketones and structurally related butadienoid compounds are not necessarily similar. For example, compounds **27** and **28** did not undergo any of the specifically $\pi \rightarrow \pi^*$-induced reactions of the related enone **3** [8].



27 R = H
28 R = CN

Scheme 6[4])

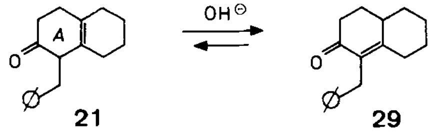


Table 3. ^{1}*H-NMR. Chemical shifts of* **21** *as a function of Eu(fod)$_3$ concentration*

^{1}H Signal	Chemical shift, δ[a]), in the presence of			$\Delta\delta/\Delta$Eu(fod)$_3$
	0 mg	12 mg	25 mg Eu(fod)$_3$	
H$_2$C (benz.)	2.95+2.80	4.50+3.84	6.28+5.00	0.137+0.089
HC(2)	2.80	4.77	6.90	0.164
H$_2$C(4)	2.20	4.00	6.00	0.154
H$_2$C(5)	1.80	2.50	3.20	0.054
2 HC (ar., *o*)	7.50	7.88	8.85	0.075
3 HC (ar., *m*+*p*)	7.20	7.92	7.65	0.020

[a]) CDCl$_3$ solution, RT.

could be resolved with the aid of the Eu(fod)$_3$ shift reagent and double-resonance experiments (see *Table 3*). Furthermore, the benzylic protons of **21-d$_5$** and **22** appeared as *AB* systems with $J = 14$ Hz at δ2.80/2.92 and 2.78/3.10, respectively, and a singlet at δ 1.25 confirmed the attachment of the methyl group of **22** to a tertiary carbon atom. Treatment with potassium carbonate in aqueous methanol equilibrated **21** with the α,β-unsaturated ketone **29** [UV.: $\lambda_{\text{max}} = 250$ nm ($\varepsilon = 10200$); IR.: $\tilde{\nu}_{\text{CO}} = 1680$ cm^{-1}; **21**:**29**$\sim$1:4] *(Scheme 6)*. The IR.-inactive tetrasubstituted double bond of **22** had a *Raman* frequency of 1670 cm^{-1}[6]).

Photorearrangement of the enones 21(-d$_5$) and 22 *(Scheme 7)*. - The photoproducts **21(-d$_5$)** and **22** were not photostable but underwent oxadi-π-methane rearrangements to the *syn-* and *anti*-tricyclodecanones **30(-d$_5$)** (*ca.* 1.5:1.0) and **31** (*ca.* 1.2:1.0) as is characteristic of triplet-excited β,γ-unsaturated ketones [9] [10]. Thus, *syn-* and *anti*-**30(-d$_5$)** appeared as additional photo-products in the 254 nm-irradiations of **9** and **9-d$_5$** at sufficiently large conversions to **21(-d$_5$)**. The epimers of **30** and **31** were formed, furthermore, when **21** and **22**, respectively, were directly irradiated at 254 nm in isooctane and when they were triplet-sensitized in acetone and 254 nm-light.

Population of the T_1 (π,π^*) state on direct irradiation of most β,γ-unsaturated ketones is negligible (*cf.* [11]), and triplet sensitization is normally necessary to obtain the oxadi-π-methane rearrangement products in more than trace amounts. Bicyclo[4.4.0]decenones such as **21** and **22** are among the relatively few systems which afford appreciable amounts of such products on direct irradiation [10]. The stereochemistry of the rearrangement and evidence in favour of a stepwise reaction path has been established for a bicyclononenone closely related to **21** and **22** [12].

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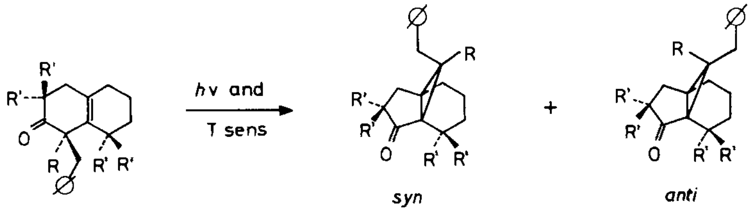
[6]) We thank Dr. *K. Seevogel*, *Max-Planck*-Institut für Kohlenforschung, Mülheim a.d. Ruhr, for measuring the laser *Raman* spectrum of **22**.

Scheme 7. *Oxadi-π-methane rearrangement of* **21**(-d_5) *and* **22**[4]



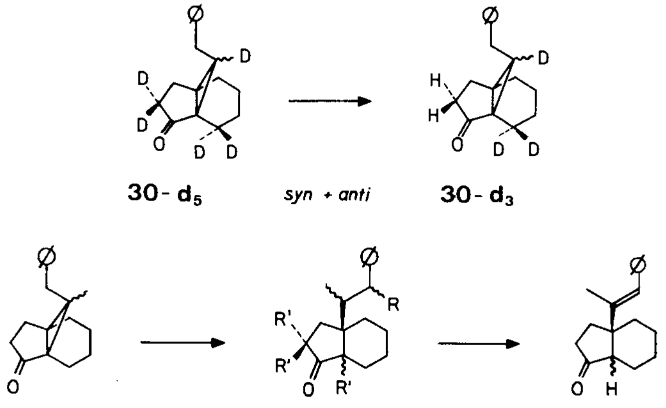
21	R = R' = H	**30**
21-d_5	R = R' = D	**30-d_5**
22	R = CH_3, R' = H	**31**

Structural evidence for syn- *and* anti-**30** (-d_5) *and* -**31**. The mixtures of **30** (-d_5) and **31** (IR.: $\tilde{\nu}_{CO}$ = 1725 and 1710 cm^{-1}, respectively) could not be separated into the *syn*- and *anti*-epimers. The composition was determined from the NMR. signal intensities of the A_2X system for the benzylic (δ 2.78 and 2.85; **30-d_5**: 2 singlets) and cyclopropyl protons (δ 1.60 and 1.62, J = 7 Hz) of **30**, and of the 2 singlets for the benzylic protons (δ 2.70 and 2.80) of **31**. The configurational assignments were made on the basis of the chemical shift differences of the benzylic protons, which were attributed to a deshielding effect by the magnetic anisotropy of the ketone group. A similar effect had been observed with the 9-dimethoxymethyl-tricyclo[3.3.1.$0^{1,5}$]-nonan-2-one epimers ($\Delta\delta$ = 0.19) [12].

In accordance with the 1,2-acyl shift which is included in the oxadi-π-methane rearrangement, one of the original 3 deuterium atoms in vicinal positions to the ketone group (C(2) and C(4) in **21-d_5**) was no longer exchangeable in **30-d_5**, and treatment of this sample with refluxing methanolic sodium hydroxide afforded **30-d_3** *(Scheme 8)*.

Further structural evidence was obtained from the following transformations of *syn*- and *anti*-**31**. Reductive opening of the 3-membered ring with lithium in liquid

Scheme 8[4]



30-d_5 **30-d_3**

31

32 R = R' = H
32-d_3 R = H, R' = D
33 R = Br, R' = H

34

ammonia and subsequent oxidation with pyridinium chromate gave **32** (IR.: $\tilde{\nu}_{CO} = 1735$ cm^{-1}). In the NMR. spectrum the methyl group appeared as a doublet at δ 0.70, $J = 6$ Hz, and the benzylic protons as the *AB* part of an *ABX* system at δ 2.40 and 3.10, $J_{AB} = 10$ Hz. Base-catalyzed H/D exchange converted **32** into **32-d$_3$**. Bromination of **32** with *N*-bromosuccinimide gave a mixture of *erythro-* and *threo*-diastereoisomers **33** (NMR.: doublets for the methyl group at δ 0.90 and 1.00, $J = 6$ Hz, and for the benzylic proton at δ 5.28 and 5.31, $J = 10$ Hz). Dehydrobromination with lithium carbonate and lithium chloride finally led to **34** which was characterized by a styrene-type UV. absorption ($\lambda_{max} = 241$ nm, $\varepsilon = 6100$), by a ketone IR. band at 1740 cm^{-1}, and in the NMR. by a doublet ($J < 1$ Hz) for the methyl group at δ 1.83 and a quadruplet for the olefinic proton at δ 6.28.

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Experimental Part

General Remarks. Unless otherwise specified, the usual work-up of crude reaction mixtures involved extraction with ether, washing of the organic layer with a saturated aqueous NaCl-solution to neutrality, drying ($MgSO_4$), and removal of the solvent in vacuum (i.V.) in a rotatory evaporator. Preparative chromatography was carried out on silica gel 60 *Merck* (0.05-0.20 nm) in columns with decreasing diameter. For thin-layer chromatograms (TLC.) *Merck* plates F_{254} (silicagel) were used. The spots were located by fluorescence and by treatment with either conc. H_2SO_4-, $KMnO_4$-, or I_2-solutions, and heating. *Merck* plates, 2mm, were used for preparative TLC. In vapor phase chromatography (VPC.) either capillary columns (150'×0.01", with OV-17) or packed columns (10'×⅜' and 10'×¼', with 2-5% SE-30 and 15% QF-1 on Chromosorb G-AW-DMCS) were used. Composition of the mixtures was determined by calibrated electronic integration. Melting points (m.p.) and boiling points are not corrected. - UV.: λ_{max} in nm, ε in parentheses. - IR.: $\tilde{\nu}_{max}$ in cm^{-1}; CCl_4. - ^{1}H-NMR.: 100 MHz; chemical shifts in δ and coupling constants (*J*) in Hz; br. = broad, *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *m* = other than first-order multiplet. - Mass spectra (MS.): base peak in italics.

UV. Irradiations. - Light source for 254 nm: ring-shaped Hg low-pressure lamps (Minerallight PCQX 1, *Ultraviolet Products Inc.*), magnetically stirred solutions in quartz tubes placed in the centre of the lamp rings. - *For > 300 nm and > 340 nm:* 250 W Hg high-pressure lamp *(Philips)* in a water-cooled *Pyrex* mantle which, for > 340 nm, was surrounded with an additional mantle of 1 cm inner path containing a filter solution of 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 and > 340 nm, analytical irradiations were carried out in a turn-table reactor with magnetically stirred sample tubes, and for preparative experiments the lamp housing was immersed in the magnetically stirred solution. Prior to all irradiations the solutions were flushed with argon.

Synthesis of 9(-d$_5$), 10, (*R)- and (*S**)-19** *(Scheme 2). - 6-Benzyl-1-hydroxybicyclo[4.4.0]decan-3-one* (**7**) [13]. A mixture of 12.52 g 2-benzylcyclohexanone (**6**) and 0.3 ml 3N ethanolic EtONa solution was stirred at −10° under N_2 while 5.4 g methyl vinyl ketone were added slowly. After stirring for 24 h at −10°, the work-up and crystallization from ether/hexane gave 7.4 g (43%) **7**, m.p. 130-132°. - IR.: 3610, 3460 (br.), 1720, 1610, 1500. - NMR. ($CDCl_3$): 2.7+3.3 (*AB*, $J = 14$, $H_2C-C(6)$); 7.0-7.4 (*m*, 5 ar. H). - MS.: 258 ($C_{17}H_{22}O_2^{+}$), *240*, 167, 92, *91*.

6-Benzyl-1-hydroxy-2-methylbicyclo[4.4.0]decan-3-one (**8**). The same procedure as above, with 60 g **6**, 5 ml EtONa solution, and 100 g ethyl vinyl ketone, gave 58 g (66%) crude **8** used without further purification.

6-Benzylbicyclo[4.4.0]dec-1-en-3-one (**9**). A solution of 7.4 g **7** in 35 ml 2N H_2SO_4 and 50 ml dioxan was stirred at RT. for 48 h. After the work-up, chromatography in ether/hexane 2:1 gave 5.5 g (80%) **9**; m.p. 77° (from ether). - UV. (isooctane): 235 (11300), 335 (34). - IR.: 1680, 1620, 1500. - NMR. ($CDCl_3$): 2.95+3.02 (*AB*, $J = 14$, $H_2C-C(6)$); 5.91 (br. *s*, HC(2)); 7.1-7.6 (*m*, 5 ar. H). - MS.: 240 (M^{+}), 212, 149, 148, 131, *91*.

$C_{17}H_{20}O$ (240.34) Calc. C 76.68 H 7.99% Found C 76.70 H 7.98%

6-Benzyl-2,4,4,10,10-pentadeuteriobicyclo[4.4.0]dec-1-en-3-one (**9-d$_5$**). A mixture of 240 mg **9** in 10 ml dioxan, 10 ml D_2O, and 100 mg of a 40% NaOD/D_2O solution was refluxed for 2 h. Extraction with ether, washing of the organic layer with D_2O (2 × 10 ml), drying ($MgSO_4$), and crystallization of the crude product from ether gave **9-d$_5$** with UV. and NMR. [except for signals of $H_2C(4)$ and $H_2C(10)$ at 2.25–2.95 and HC(2) at 5.91] identical with those of **9**. - MS.: 245 ($C_{17}H_{15}D_5O^+$); $d_5 = 60\%$, $d_4 = 26\%$, $d_3 = 7\%$, 154, 153, *91*.

6-Benzyl-2-methylbicyclo[4.4.0]dec-1-en-3-one (**10**). Dehydration of 58 g **8** was effected for 8 h with 10 g *p*-toluenesulfonic acid in 500 ml refluxing toluene. After washing with aqueous $NaHCO_3$ solution and work-up, the crude product was chromatographed with toluene/ether 9:1; 43 g (78%) **10** were obtained. - UV. (isooctane): 245 (18700), 324 (40). - IR.: 1680, 1610, 1500. - NMR. (CCl_4): 2.75 (*s*, $H_3C-C(2)$); 2.80+2.96 (*AB*, *J* = 14, $H_2C-C(6)$); 6.8–7.4 (*m*, 5 ar. H). - MS.: 254 ($C_{18}H_{23}O^+$), *163*, 92, 91.

Ethyl 2-methyl-3-oxobicyclo[4.4.0]dec-1-ene-6-carboxylate (**12**)[7]. To a solution of 8 g (110 mmol) ethyl vinyl ketone and 15 g (120 mmol) ethyl 2-oxocyclohexanecarboxylate (**11**) in 100 ml abs. EtOH, 6 ml of an ethanolic 0.5 M EtONa solution were added dropwise. After stirring for 2 h at RT., another 15 ml of the EtONa solution were added and stirring was continued for 48 h. The mixture was extracted with CH_2Cl_2 and worked up. Distillation at 114°/0.1 Torr gave 15 g (70%) **12**. - IR.: 1735, 1685, 1680, 1235, 1190. - NMR. (CCl_4): 1.25 (*t*)+4.13 (*qa*, *J* = 7, H_5C_2-O); 1.73 (*s*, $H_3C-C(2)$). - MS.: 236 ($C_{14}H_{20}O_3^+$), 221, *163*, 162, 147, 135, 107, 105, 93, 91.

Ethyl 3,3-ethylenedioxy-2-methylbicyclo[4.4.0]dec-1(10)-ene-6-carboxylate (**13**)[7]. A solution of 7.4 g (33 mmol) **12**, 20 g (32 mmol) ethylene glycol (dried over K_2SO_4) and 600 mg *p*-toluenesulfonic acid was refluxed in 500 ml dry toluene for 120 h, reaching a 90% conversion (VPC., SE-30, 220°). After work-up, the crude product was first filtered in CH_2Cl_2 through neutral Al_2O_3 (act. I) and then chromatographed in benzene/ether 9:1. 7.5 g (85%) **13** were obtained. - IR.: 1730, 1260, 1236, 1205, 1160, 1110, 1090. - NMR. (CCl_4): 0.90 (*d*, *J* = 6, $H_3C-C(2)$); 1.18 (*t*)+4.02 (*qa*, *J* = 7, H_5C_2-O); 3.75 (*s*, 2 H_2C-O); 5.4 (*m*, HC(10)). - MS.: 280 ($C_{16}H_{24}O_4^+$), 252, 230, 207, 163, 161, 145, 135, 105, *99*, 91.

(3,3-Ethylenedioxy-2-methylbicyclo[4.4.0]dec-1(10)-en-6-yl)methanol (**14**)[7]. A mixture of 1.3 g (50 mmol) **13** and 1.1 g (30 mmol) $LiAlH_4$ was stirred overnight at RT. in 100 ml abs. ether, followed by reflux for 4 h. The excess hydride was destroyed with sat. aqueous NH_4Cl-solution before work-up, which yielded crystalline **14**, m.p. 84–86°. - IR.: 3700, 3360 (br.), 1112, 1080, 1055, 1030. - NMR. (CCl_4): 0.90 (*d*, *J* = 7, $H_3C-C(2)$); 3.46 (*s*, $H_2C-C(6)$); 3.61 (*s*, 2 H_2C-O); 5.5 (br., HC(10)). - MS.: 238 ($C_{14}H_{22}O_3^+$), 208, 194, 163, 146, *99*.

3,3-Ethylenedioxy-2-methylbicyclo[4.4.0]dec-1(10)ene-6-carbaldehyde (**15**)[7]. Protions of CrO_3 (altogether 3.5 g, 35 mmol) were added to a stirred mixture of 200 ml CH_2Cl_2 and 4.3 g (64 mmol) pyridine at 0°, followed after 30 min by a solution of 1.0 g (4 mmol) **14** in 20 ml CH_2Cl_2. The mixture was stirred for another 2 h at RT., then taken up in 1 l ether and filtered through *Celite*. The filtrate was concentrated i.V. and pyridine was removed by azeotropic distillation with toluene. Filtration through neutral Al_2O_3 (act. III) in CH_2Cl_2 and chromatography in benzene/acetate 4:1 afforded 700 mg (70%) **15**. - IR.: 2790, 1715, 1125, 1085, 1070. - NMR. (CCl_4): 0.90 (*d*, *J* = 6, $H_3C-C(2)$); 3.70 (*s*, 2 H_2C-O); 5.50 (br., HC(10)); 9.40 (*s*, $HC-C(6)$). - MS.: 236 ($C_{14}H_{20}O_3^+$), 222, 208, 206, 149, 107, 105, *99*.

(R*)- *and* (S*)-*(3,3-Ethylenedioxy-2-methylbicyclo[4.4.0]dec-1(10)-en-6-yl)phenylmethanol* (**16**)[7]. A solution of 117 mg (0.5 mmol) **15** in 50 ml abs. ether was added dropwise to 0.5 ml (10 mmol) of a 2 M hexane solution of phenyl lithium at −80° under argon. After 2 h the solution was brought to −10°, poured into sat. aqueous NH_4Cl-solution and worked up. Chromatography in ether/hexane 2:1 gave 6.5 mg starting material (**15**), 62 mg (39%) (*R**)-**16**, and 25 mg (16%) (*S**)-**16**.

(*R**)-**16**. - M.p. 130–131°. - IR.: 3610, 3400–3600 (br.), 1600, 1500, 1090, 1050. On tenfold dilution, the relative band intensities increased at 3610 and decreased at 3400–3600. - NMR. ($CDCl_3$): 1.08 (*d*, *J* = 6, $H_3C-C(2)$); 2.8 (*m*, HC(2)); 3.92 (*s*, 2 H_2C-O); 5.18 (*s*, $HC-C(6)$); 5.90 (br. *s*, HC(10)); 7.0–7.4 (*m*, 5 ar. H). - MS.: 314 ($C_{20}H_{26}O_3^+$), *208*, 179, 146, 99, 86, 73.

(*S**)-**16**. - M.p. 170–172°. - IR.: 3540, 1600, 1500, 1450, 1090. On tenfold dilution, the relative band intensity at 3540 did not change. - NMR. ($CDCl_3$): 1.0 (*d*, *J* = 6, $H_3C-C(2)$); 3.83 (*s*, 2 H_2C-O); 3.10

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[7] Contrary to IUPAC rules, we retain the same numbering for all octalones, the oxo function (or its derivatives) remains at C(3).

(br. *m*, HC(2)); 5.30 (*s*, HC–C(6)); 5.60 (br. *s*, HC(10)); 7.0–7.4 (*m*, 5 ar. H). Double resonance at 1.0 decoupled 3.10 to br. *d*, $J = 2$. - MS.: same as for (*R**)-**16**.

$C_{20}H_{26}O_3$ (314.41) Calc. C 76.44 H 8.38% Found C 76.43 H 8.28%

(R*)- *and* (S*)-*(3,3-Ethylenedioxy-2-methylbicyclo[4.4.0]dec-1(10)-en-6-yl)phenylmethyl acetates* (**17**)7). (*R**)- and (*S**)-**16** were acetylated in pyridine/acetic anhydride 1:1 at RT. overnight. The work-up including azeotropic removal of pyridine with toluene, gave (*R**)- and (*S**)-**17** in 60% and 65% yield, respectively.

(*R**)-**17**. - IR.: 1745, 1600, 1500, 1200, 1190, 1155, 1130, 1080, 1025. - NMR. (CCl_4): 0.85 (*d*, $J = 7$, H_3C–C(2)); 1.85 (*s*, H_3C–OCO); 2.6 (br., HC(2)); 3.82 (br. *s*, 2 H_2C–O); 5.6 (br. *m*, HC(10)); 6.24 (*s*, HC–C(6)); 6.6–7.4 (*m*, 5 ar. H). - MS.: 356 ($C_{22}H_{28}O_4^{+}$), 296, 257, 207, 108, *99*.

(*S**)-**17**. - IR.: 1745, 1600, 1500, 1200, 1190, 1155, 1120, 1080, 1025. - NMR. (CCl_4): 0.98 (*d*, $J = 7$, H_3C–C(2)); 2.06 (*s*, H_3C–OCO); 3.0 (br., HC(2)); 3.82 (br. *s*, 2 H_2C–O); 5.5 (br., HC(10)); 6.35 (*s*, HC–C(6)); 6.6–7.4 (*m*, 5 ar. H). - MS.: same as for (*R**)-**17**.

Hydrolysis of (R*)- *and* (S*)-**17**. The 2 compounds were treated each with 100 mg *p*-toluenesulfonic acid in 5 ml acetone and 2 ml H_2O at RT. for 2 h. After work-up, 40 mg (R*)-*6-acetoxyphenylmethyl-2-methylbicyclo[4.4.0]dec-1-en-3-one* (**19**) were obtained from 50 mg (*R**)-**17**, and 45 mg (*S**)-*6-acetoxyphenylmethyl-2-methylbicyclo[4.4.0]dec-1(10)-en-3-one* (**18**) from 60 mg (*S**)-**17**.

(*R**)-**19**. - UV. (MeOH): 259 (13800), 290 (30). - IR.: 1745, 1680, 1625, 1500, 1230, 1030. - NMR. (CCl_4): 1.75 (*s*, H_3C–C(2)); 2.13 (*s*, H_3C–OCO); 6.30 (*s*, HC–C(6)); 6.8–7.3 (*m*, 5 ar. H). - MS.: 312 ($C_{20}H_{24}O_3^{+}$), 244, 243, 206, *164*, 149, 107, 91.

(*S**)-**18**. - UV. (MeOH): 210 (3200), 300 (shoulder, 300). - IR.: 1740, 1725, 1230, 1050, 1025. - NMR. (CCl_4): 1.16 (*d*, $J = 7$, H_3C–C(2)); 2.08 (*s*, H_3C–OCO); 3.6 (*m*, HC(2)); 5.6 (br., HC(10)); 6.36 (*s*, HC–C(6)); 7.25 (*s*, 5 ar. H). - MS.: 312 ($C_{20}H_{24}O_3^{+}$), 252, 206, *164*, 149, 146, 107, 91.

(S*)-*10-Acetoxyphenylmethyl-2-methylbicyclo[4.4.0]dec-1-en-3-one* (**19**). Treatment of 200 mg (*S**)-**18** with 25 mg 2N HCl in 2 ml acetone at RT. yielded, after work-up, 67 mg (34%) (*S**)-**19**. - UV. and MS. same as for (*R**)-**19**. - IR.: 1745, 1650, 1630, 1230, 1050. - NMR. ($CDCl_3$): 1.75 (*s*, H_3C–C(2)); 1.82 (*s*, H_3C–OCO); 6.32 (*s*, HC–C(6)); 7.3–7.5 (br., 5 ar. H).

$C_{20}H_{24}O_3$ (312.39) Calc. C 76.70 H 7.98% Found C 76.44 H 7.99%

UV.-Irradiations *(Schemes 3, 4, and 7)*. - *Preparative irradiations.* a) *Irradiation of* **9** *at* > *300 nm.* A solution of 200 mg **9** in 25 ml isooctane (0.033M) was irradiated for 36 h. The solvent was evaporated i.V. and the residue was chromatographed in benzene/ethyl acetate 9:1. 36 mg (18%) *6-benzylbicyclo[4.4.0]dec-1(10)-en-3-one* (**20**) were obtained. - UV. (MeOH): 210 (2350), 295 (shoulder, 300). - IR.: 1715, 1680, 1630, 1500. - NMR.: 2.80+2.90 (*AB*; $J = 14$, H_2C–C(6)); 5.4 (br. *s*, HC(10)). - MS.: 240 ($C_{17}H_{20}O^{+}$), 212, 149, 148, 121, *91*.

On standing and on treatment with K_2CO_3/MeOH, **20** isomerized back to starting material **9**.

b) *Irradiation of* **9** *at 254 nm.* A solution of 200 mg **9** in 200 ml isooctane (0.004M) was irradiated to full conversion (1.5 h; VPC., SE-30, and TLC., ether/hexane 2:1). The solution was decanted from a white deposit and evaporated. The crude product was chromatographed in ether/hexane 2:1, affording 40 mg (20%) *2-benzylbicyclo[4.4.0]dec-1(6)-en-3-one* (**21**) and 20 mg (10%) of a 1.5:1.0 mixture (VPC.: SE-30) of syn- *and* anti-*10-benzyltricyclo[4.3.1.0^{1,6}]decan-7-ones* (**30**).

21. - UV. (MeOH): 213 (4600), 248 (1250), 280 (43). - IR.: 1725, 1500. - NMR.: $J_{benz,benz} = 14$, $J_{1,benz} = 6$; see *Table 3*. - MS.: 240 ($C_{17}H_{20}O^{+}$), 212, 149, 148, 121, 107, *91*.

Mixture of *syn*- and *anti*-**30**. - IR.: 1725, 1500. - NMR. ($CDCl_3$): 1.60+1.62 (2 *t*, $J = 7$, HC(10)); 2.76+2.85 (2 *d*, $J = 7$, H_2C–C(10)); 7.0–7.5 (*m*, 5 ar. H). Double resonance at 2.76 decoupled the signals 1.60 and 1.62 to 2 *s*, and at 1.60 the signals 2.76 and 2.85 to 2 *s*. - MS.: 240 ($C_{17}H_{20}O^{+}$), 149, 148, 107, *91*.

c) *Irradiation of* **9-d$_5$** *at 254 nm.* A solution of 150 mg **9-d$_5$** in 15 ml isooctane (0.04M) was irradiated to 90% conversion. Chromatography (ether/hexane 2.1) gave 30 mg (20%) *2-benzyl-2,4,4,10,10-pentadeuteriobicyclo[4.4.0]dec-1(6)-en-3-one* (**21-d$_5$**) and 32 mg (21%) of syn- *and* anti-*10-benzyl-5,5,8,8,10-pentadeuteriotricyclo[4.3.1.0.^{1,6}]decan-7-ones* (**30-d$_5$**).

21-d$_5$. - IR.: several bands at 2100–2240, 1725, 1500. - NMR. ($CDCl_3$): 2.80+2.92 (*AB*, $J = 14$, H_2C–C(2)); 7.0–7.5 (*m*, 5 ar. H). - MS.: 245 ($C_{17}H_{15}D_5O^{+}$; $d_5 = 60\%$, $d_4 = 26\%$, $d_3 = 7\%$).

Mixture of *syn*- and *anti*-**30-d$_5$**. - IR.: several bands at 2100–2200, 1725, 1500. - NMR. ($CDCl_3$): 2.78+2.85 (2 *s*, H_2C–C(10)); 7.0–7.5 (*m*, 5 ar. H). - MS.: 245 ($C_{17}H_{15}D_5O^{+}$; $d_5 = 60\%$, $d_4 = 26\%$, $d_3 = 7\%$).

Treatment of the mixture of *syn*- and *anti*-**30-d**$_5$ with refluxing 20% methanolic KOH gave, after work-up and chromatographic purification, syn- and anti-*10-benzyl-5,5,10-trideuteriotricyclo[4.3.1.0*^{1,6}*]decan-7-ones* (**30-d**$_3$). - MS.: 243 ($C_{17}H_{17}D_3O^+$; d_3 = 85%, d_2 = 14%).

d) *Irradiation of* **10** *at 254 nm.* A solution of 1.0 g **10** in 100 ml isooctane (0.036M) was irradiated for 1.5 h, then concentrated i.V. Chromatography of the residue in benzene/ethyl acetate 9:1 gave 500 mg (50%) starting material (**10**) and 300 mg (30%) *2-benzyl-2-methylbicyclo[4.4.0]dec-1(6)-en-3-one* (**22**). - UV. (hexane): 225 (2500), 247 (1030), 252 (944), 256 (790), 265 (571), 285 (162). - IR.: 1710, 1600, 1490, 1445. - Laser-Raman[6]): 1712 (ρ = 0.46), 1670 (0.22), 1608 (0.67), 1586 (0.83). - NMR. ($CDCl_3$): 1.25 (*s*, $H_3C-C(2)$); 2.78+3.10 (*AB*, J = 14, $H_2C-C(2)$); 6.9-7.5 (*m*, 5 ar. H). - MS.: 254 ($C_{18}H_{22}O^+$), 163, 162, 135, 121, 91.

e) *Sensitization of* **22**. A solution of 222 mg **22** in 200 ml acetone (0.004M) was irradiated at 254 nm to full conversion (3 h). Chromatography gave 94 mg (42%) of a 1.2:1.0 mixture of syn- and anti-*10-benzyl-10-methyltricyclo[4.3.1.0*^{1,6}*]decan-7-ones* (**31**). - UV. (MeOH): 244 (1070), 258 (610), 264 (470), 290 (268). - IR.: 1710, 1600, 1490, 1445. - NMR. (CCl_4): 0.98 (*s*, $H_3C-C(10)$); 2.70+2.80 (2 *s*, $H_2C-C(10)$); 7.0-7.5 (*m*, 5 ar. H).

Analytical irradiations. a) *Irradiations of* **9** *and* **10** *at* > *300 nm.* Isooctane solutions (0.042M) were irradiated for 60 h. In addition to some insoluble deposits, **20** was found as the only product from **9**, whereas no soluble product of **10** was detected (VPC.: SE-30, 240°; TLC.: ether/hexane 2:1). Similar results with **9** and **10** were also obtained in benzene and *t*-butyl alcohol.

b) *Irradiation of* **9** *and* **10** *at 254 nm.* After full conversion of both samples (0.040M in isooctane), insoluble deposits in both tubes and products **21**+*syn*- and *anti*-**30** (from **9**) and **22** (from **10**) had been formed (VPC. and TLC.: see a).

c) *Sensitization of* **9** *and* **10**. The following solutions were irradiated at > 340 nm: (i) 0.04M **9** in benzene, (ii) 0.04M **9**+0.5M acetophenone in benzene, (iii) 0.06M **9**+0.5M acetophenone in *t*-butyl alcohol, (iv) 0.03M **10**+0.5M acetophenone in benzene, and (v) 0.03M **10**+0.5M acetophenone in *t*-butyl alcohol. In runs (i)-(iii), **20** was formed as the only soluble product. Despite appreciable disappearance of **10** in runs (iv) and (v), no product was detectable by VPC. (see a).

d) *Direct irradiations and sensitization of* **21** *and* **22**. Isooctane and acetone solutions of **21** and **22** (0.024M) were irradiated at 254 nm to full conversion. The solvents were evaporated i.V. and the residue was analyzed by NMR. ($CDCl_3$): *syn*- and *anti*-**30** (from **21**) and *syn*- and *anti*-**31** (from **22**).

e) *Irradiation of* (R*)- *and* (S*)-**19** *at 254 nm.* Solutions in MeOH and isooctane (0.005M) were irradiated for prolonged periods. The compounds remained unchanged (TLC.; IR. after evaporation of the solvent).

f) *Quantum yield determinations.* The Φ values were measured at 25° using argon-flushed solutions and an electronically integrating actinometer [14]. In each run, the numbers of absorbed quanta (milli-Einsteins) were determined at several conversions. The concentrations of starting material and product were measured by VPC. (OV-17 for **9** and **21** at 254 and 265 nm, SE-30 for **10** and **22**; see *Table 2*) and by NMR. integration of the olefinic protons at C(1) (of **9**) and C(8) (of **20**) after evaporation of the sample solvents (at 366 nm; see *Table 1*).

Transformation of photo-products *(Schemes 6* and *8).* - *2-Benzylbicyclo[4.4.0]dec-1(6)-en-3-one* (**29**). At RT. 100 mg **21** were treated with aqueous-methanolic K_2CO_3. A stationary equilibrium was reached after 80% conversion (VPC.). Work-up and chromatography in ether/hexane 2:1 gave 80 mg (80%) **29**. - UV. (MeOH): 250 (10200). - IR.: 1680, 1600, 1500. - NMR. (CCl_4): 3.6 (br. *s*, $H_2C-C(2)$); 6.8-7.2 (br., 5 ar. H). - MS.: 240 ($C_{17}H_{20}O^+$), 212, 149, 148, 131, *91*.

1-(1-Methyl-2-phenylethyl)bicyclo[4.3.0]nonan-7-one (**32**). A solution of 90 mg (0.35 mmol) *syn*- and *anti*-**31** in 5 ml abs. ether was added dropwise at -80° to 80 mg (11 mmol) Li dissolved in 10 ml liquid NH_3. After stirring for 2 h, NH_3 was removed by warming to RT., solid NH_4Cl was added, and the mixture was extracted with CH_2Cl_2. The work-up was followed by oxidation of the crude product (74 mg) in a solution of 280 mg (2.8 mmol) CrO_3 and 400 mg (5.6 mmol) pyridine in CH_2Cl_2 for 2 h. The mixture was taken up in 400 ml ether and filtered through *Celite*. The filtrate was concentrated i.V., and the pyridine was azeotropically removed with toluene. Filtration of the residue in CH_2Cl_2 through neutral Al_2O_3 (act. III) and separation in benzene/ethyl acetate 9:1 by prep. TCL. gave 37 mg (41%) **32**. - IR.: 1735, 1600, 1500. - NMR. (CCl_4): 0.70 (*d*, J = 6, $H_3C-C(1')$); 2.40+3.10 (*ABX*, J_{AB} = 10, $H_2C(2')$); 6.7-7.3 (*m*, 5 ar. H). - MS.: 256 ($C_{18}H_{24}O^+$), 165, 150, 137, *91*.

1-(1-Methyl-2-phenylethyl)-6,8,8-trideuteriobicyclo[4.3.0]nonan-7-one (**32-d$_3$**) was obtained from **32** as described for **9**→**9-d$_5$**. - MS.: 259 ($C_{18}H_{21}D_3O^+$; $d_3 = 6\%$, $d_2 = 30\%$, $d_1 = 5\%$).

1-(2-Bromo-1-methyl-2-phenylethyl)bicyclo[4.3.0]nonan-7-one (**33**). *N*-Bromosuccinimide (266 mg, 1.5 mmol) and 10 mg benzoyl peroxide were added to a solution of 37 mg (0.14 mmol) **32** in 50 ml CCl_4, which was then warmed until the bromination started. After refluxing for 1 h, the mixture was filtered, the filtrate was concentrated i.V., and the residue was chromatographed in benzene by prep. TLC. 48 mg (100%) of a *ca.* 1:1 *erythro/threo*-mixture of **33** were obtained. - IR.: 1740, 1600, 1500. - NMR. (CCl_4): 0.90+1.00 (2 *d*, $J = 6$, $H_3C-C(1')$); 5.28+5.31 (2 *d*, $J = 10$, HC(2')); 6.8-7.1 (*m*, 5 ar. H). - MS.: 338/336 ($C_{18}H_{23}OBr^+$), *257*, 255, 167, 165, 139, 135.

*1-(*E*-1-Methyl-2-phenylethenyl)bicyclo[4.3.0]nonan-7-one* (**34**). LiCl (18 mg, 0.42 mmol) and $LiCO_3$ (30 mg, 0.40 mmol) were added to a solution of 48 mg (0.14 mmol) **33** (*ca.* 1:1 *erthro/threo*-mixture) in freshly distilled hexamethylphosphotriamide [15]. The mixture was heated to 110° for 12 h and then extracted with ether. The organic layer was washed with aqueous HCl- and $NaHCO_3$-solution, and finally H_2O, then dried over Mg_2SO_4 and concentrated yield 30 mg (84%) **34**. - UV. (MeOH): 241 (6100). - IR.: 1740, 1630, 1600, 1500. - NMR. (CCl_4): 1.83 (*d*, $J < 1$, $H_3C-C(1')$); 6.28 (*qa*, $J < 1$, HC(2')); 6.8-7.2 (*m*, 5 ar. H). - MS.: 254 ($C_{18}H_{22}O^+$), 239, 152, *91*.

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REFERENCES

[1] *F. Nobs, U. Burger & K. Schaffner*, Helv. *60*, 1607 (1977).

[2] *N.J. Turro, V. Ramamurthy, W. Cherry & W. Farneth*, Chem. Rev. *78*, 125 (1978).

[3] a) *J. Gloor & K. Schaffner*, Helv. *57*, 1815 (1974); b) *M. Karvás, F. Marti, H. Wehrli, K. Schaffner & O. Jeger*, ibid. *57*, 1851 (1974); c) *J. Gloor & K. Schaffner*, J. Amer. chem. Soc. *97*, 4776 (1975).

[4] *D. Belluš, D.R. Kearns & K. Schaffner*, Helv. *52*, 971 (1969); *P. Margaretha & K. Schaffner*, ibid. *55*, 2884 (1973).

[5] *L.S. Besford, R.C. Cookson & J. Cooper*, J. chem. Soc. (C) *1967*, 1385.

[6] *R.C. Cookson, J. Hudec & M. Sharma*, Chem. Commun. *1971*, 108; *M. Sharma*, J. Amer. chem. Soc. *97*, 1153 (1975).

[7] *Cf.* also *F.C. Brown, R.C. Cookson & J. Hudec*, Tetrahedron *24*, 3955 (1968).

[8] *R. Mariaca & K. Schaffner*, unpublished results.

[9] *Cf. S.S. Hixson, P.S. Mariano & H.E. Zimmerman*, Chem. Rev. *73*, 531 (1973); *W.G. Dauben, G. Lodder & J. Ipaktschi*, Fortschr. chem. Forsch. *54*, 73 (1975).

[10] *Cf. K.N. Houk*, Chem. Rev. *76*, 1 (1976).

[11] *M.J. Mirbach, A. Henne & K. Schaffner*, J. Amer. chem. Soc. *100*, 7127 (1978).

[12] *B. Winter & K. Schaffner*, J. Amer. chem. Soc. *98*, 2022 (1976).

[13] *Cf. J.A. Marshall & W.I. Fanta*, J. org. Chemistry *29*, 2501 (1964).

[14] *W. Amrein, J. Gloor & K. Schaffner*, Chimia *28*, 185 (1974).

[15] *Cf. J.F. Normant & H. Deshayes*, Bull. soc. chim. France *1967*, 2455.