Regiochemistry of the Intramolecular [2 + 2] Photocycloaddition of Enones to Vinyl Ethers as a Function of Chain Length

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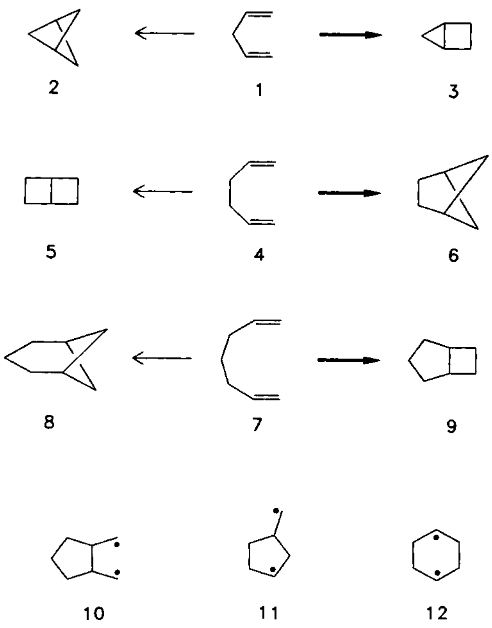
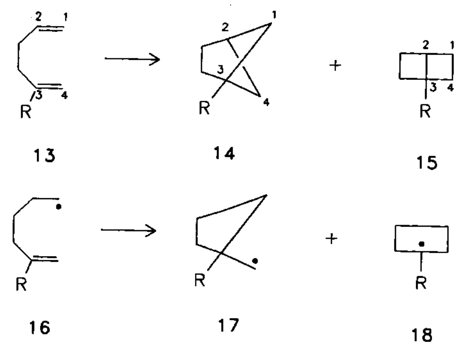
The intramolecular [2 + 2] cycloaddition of a cyclohexenone moiety bound to a vinyl ether fragment has been explored. The regiochemistry and the quantum yield of the reaction have been investigated as a function of the chain length n and the position of the methoxy group. It has been found that in those cases where the chain consists of three and four members the position of the methoxy group has no influence on the regiochemistry but on the quantum yield. Only head-to-head cycloaddition is observed. In the case of $n = 2$ both the regiochemistry and the quantum yield depend strongly on the position of the methoxy group. It is concluded that the main reason for the different behavior of $n = 2$ is due to a through-bond effect between the two olefinic units mediated by a C_2H_4 bridge.

The regiochemistry of the light-induced intramolecular [2 + 2] ring closure of acyclic nonconjugated dienes shows a remarkable dependence of the chain length[1]. Little or no further change has been observed when the double bonds are incorporated into more complex systems like trienes[2], tetraenes[3], α,β-unsaturated ketones[4,5] or esters[6]. Typically, the irradiation of 1,4-pentadiene (**1**) and 1,6-heptadiene (**7**) leads mainly to the 1,2-bridged cyclobutane derivatives **3** and **9**: 1,5-hexadiene (**4**), however, gives predominantly the cross cycloaddition product **6**. This observation has been rationalized by postulating a biradical pathway[1,2], assuming that the biradical of the 1,5-ring closure (e.g. **10** or **11**) is favored over other possible biradical intermediates like **12**. Various authors have called their attention to this "rule of five" and its broad validity[1,2,7–10].



A comparison of **10**–**12** shows that there should be other reasons than the thermodynamic stability of intermediate biradicals to account for the validity of this rule. By a series of experiments with carbonyl-substituted nonconjugated dienes, Wolff and Agosta have pointed out[10] that the postulation of the preferred formation of the fivemembered biradical during the photoreaction of 1,5-dienes (e.g. **13**) is reminiscent of the cyclization of 5-hexenyl radicals (**16**)[11]. In both cases steric factors are important; the yield of the product with a 1–4 bond increases with the size of the substituent at C-3.



As an alternative view of looking at these reactions it has been suggested that the regioselectivity of the intramolecular [2 + 2] cycloaddition is strongly influenced by the symmetry of the frontier orbitals[12]. On the assumption that a close proximity of both double bonds exists in the excited state it has been argued that the π/σ interaction influences the symmetry of the frontier orbitals. Based on a state correlation diagram[13] it has been inferred[12] that in the case of **4** for both modes of cycloaddition **a** and **b** an electronic activation energy of about the same value is needed. Since the transition state with parallel bond formation (**a**) is sterically more congested than that for the cross product (**b**), the latter should be more favored.

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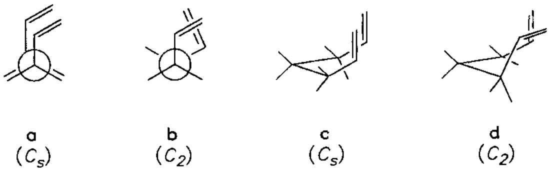
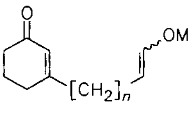
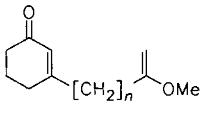
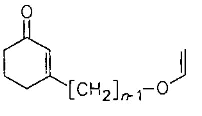


For 1,6-heptadiene (**7**) a similar correlation[12] yields no electronic contribution to the activation energy for the "parallel approach" (**c**) which leads to **9**. In the case of a C_2 transition state for **7** (**d**) a considerable electronic contribution is predicted. The propano bridge in **7** allows more flexibility in the transition states **c** and **d** than the ethano bridge in **4**, thus steric arguments, as discussed above for **4**, are less relevant for **7**.

Besides steric effects[14], the stability of intermediates and/or the symmetry of frontier orbitals as well as the polarization of the components in the excited state might also play a role[15]. This latter factor has been put forward to rationalize the photocycloaddition of enones to olefins and enol ethers[15–17]. However, the proposed oriented exciplex[15,16] has been questioned lately[18]. Since the methylene groups of the chain also contribute by their inductive and hyperconjugative effects to a polarization of the double bond, we have investigated the regiochemistry of the intramolecular [2 + 2] photocycloaddition of enones to enol ethers as a function of the chain length of compounds **19**-*n* – **21**-*n*[19].


19-*n*


20-*n*


21-*n*

The main reasons for choosing these models were:

a) the enone can be excited conveniently to the π,π^* triplet state exclusively[8,20],

b) the π,π^* triplet state of the enone fragment has been carefully studied[21],

c) the ether function in different positions of the chain should tell us something about the influence of polar effects, and

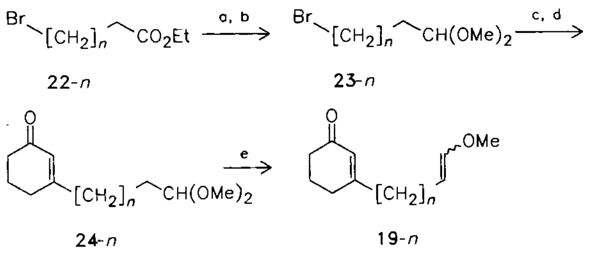
d) the results on **19**-*n* – **21**-*n* allow a direct comparison with the results of studies on molecules with related structures[10,22].

Synthesis of the Starting Materials

As the compounds **19**-*n* – **21**-*n* possess two functional groups which are closely related to each other we were limited in our synthetic procedures. The dienones **19**-*n* were synthesized according to Scheme 1.

The ω-bromoacetals **23**-*n*[23] were readily available from the corresponding esters[24] via the aldehydes[25]. The appropriate Grignard reagents[26,27] were coupled with 3-ethoxy-2-cyclohexenone to give **24**-*n*. Elimination of MeOH in the gas phase[23,28] yielded the corresponding vinyl ethers **19**-*n* in reasonable yields.

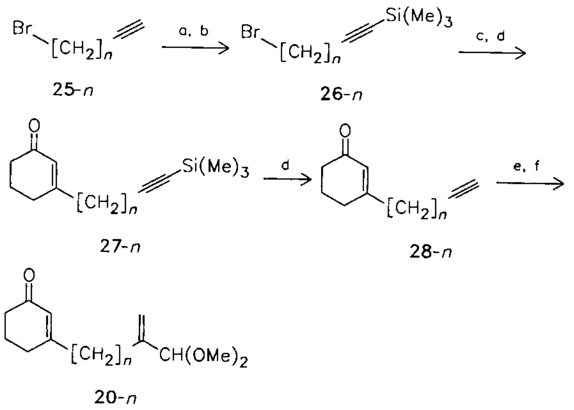
Scheme 1



a: DIBAH, −78°C, hexane. – b: $HC(OMe)_3$, TsOH, room temp. – c: Mg, THF, room temp. – d: 3-Ethoxycyclohexenone. – e: NaH_2PO_4, 250°C.

For the synthesis of **20**-*n* (Scheme 2) ω-bromo-1-trimethylsilyl-1-alkynes **26**-*n*[29] were coupled in a Grignard reaction with 3-ethoxy-2-cyclohexenone to yield **27**-*n*. Removal of the silyl group[30] gave **28**-*n* which was converted into the Markovnikov vinyl ether **20**-*n* by a methoxy mercuration/reductive demercuration[31,32].

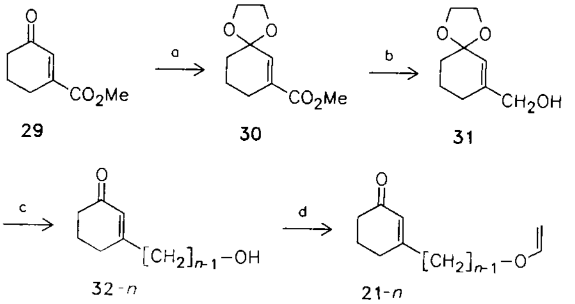
Scheme 2



a: BuLi, THF, −78°C. – b: Me_3SiCl, 0°C. – c: Mg, THF, room temp. – d: 3-Ethoxycyclohexenone, 0°C. – d: KF · 2 H_2O, THF/DMF, room temp. – e: $Hg(OAc)_2$, MeOH. – f: $NaBH_4$, NaOH.

The dienone **21**-2 was prepared from methyl 3-oxo-2-cyclohexenecarboxylate (**29**)[33] as shown in Scheme 3. After reduction[34,35] of the protected ketone **30** to the alcohol **31**, the latter was deprotonated and treated with ethyl vinyl ether[36] to yield **21**-2. Similarly, **21**-4 was prepared.

Scheme 3



a: $HOCH_2CH_2OH$, pyridinium tosylate, C_6H_6. – b: $LiAlH_4$, C_6H_6. – c: Pyridine tosylate, acetone. – d: $EtOCH=CH_2$, $Hg(OAc)_2$.

Photochemical Experiments

Compounds **19**-*n*—**21**-*n* were irradiated in cyclohexane solution (ca. 10^{-2} M) in a quartz tube at room temperature by using a 320-nm cut-off filter. The irradiation of pure *cis*-**19**-2 caused a *cis/trans* isomerization (see Figure 1a) and yielded three products (**33**, **34**, **35**) in a ratio of 45:28.5:26.5 (GC). The irradiation of the *trans* isomer (92% *trans*-**19**-2, 8% *cis*-**19**-2) yielded the same three products in the same ratio (Figure 1b). Controll experiments by GC at 120°C showed that **36** was not formed during irradiation. All three products could be separated. Flash chromatography afforded **35** and a mixture of **33** and **34**.

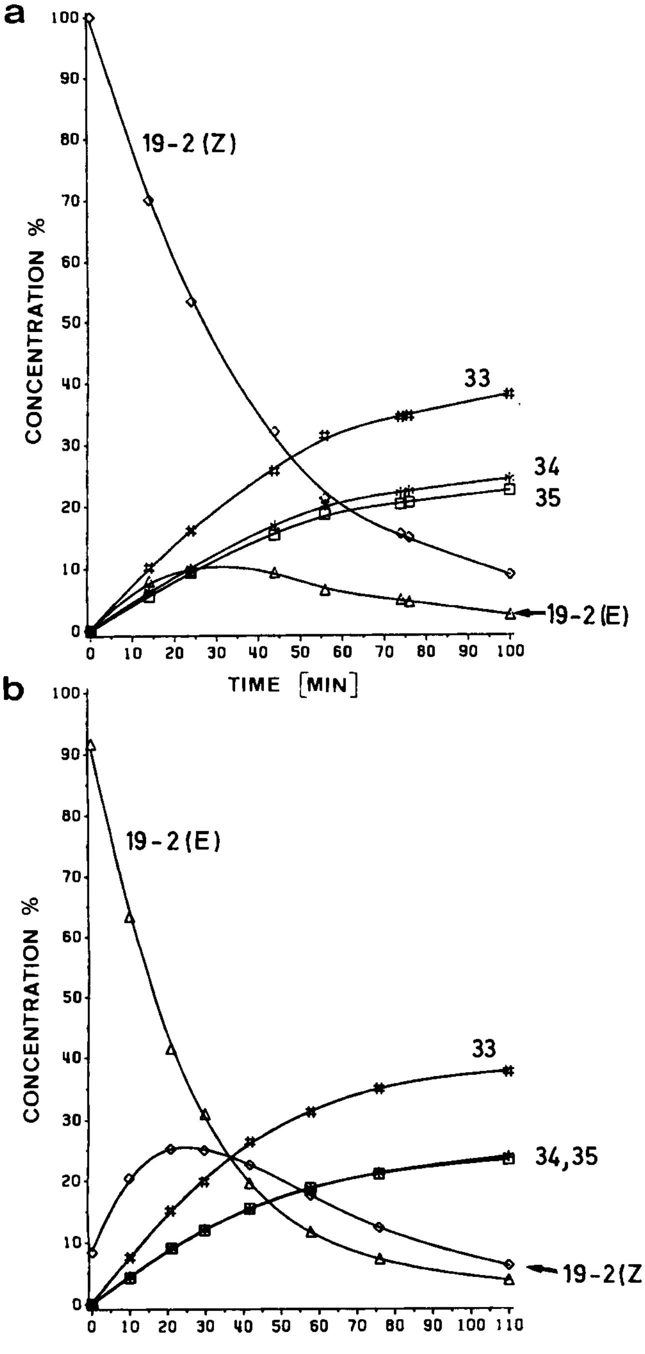
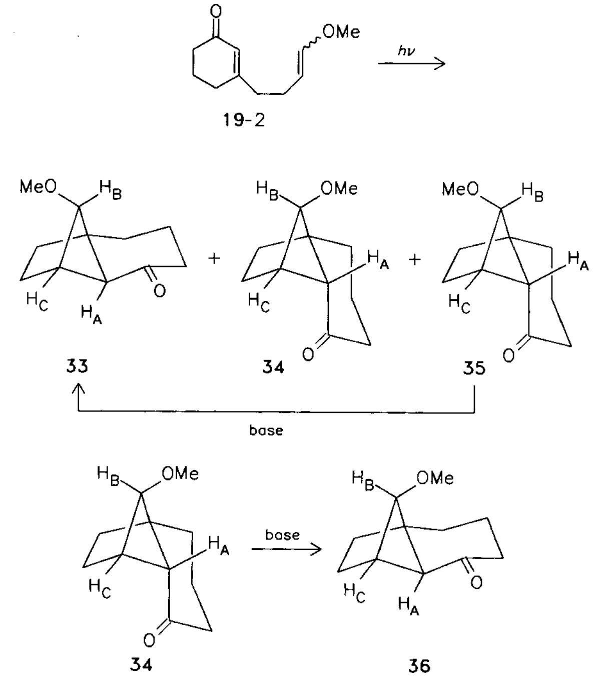


Figure 1. Product distribution followed by gas chromatography during the irradiation of *cis*-**19**-2 [≡ **19**-2(*Z*)] (a) and *trans*-**19**-2 [≡ **19**-2(*E*)]



The latter could be separated by preparative VPC. Treatment of all three products with K_2CO_3 in methanol converted **35** into **33** and **34** into **36**, but left **33** unchanged. The assignment of the structures is based on the ^{1}H-NMR spectra of **33**—**36** as well as on those of the corresponding dinitrophenylhydrazones. Looking at the spectra it is noticed that besides the complex multiplets and the singlet of the methoxy group there are three simple signals which can be singled out. These signals of **33**—**36** are listed in Table 1. We ascribe these signals to the three protons of the four-membered ring. A comparison of the measured coupling parametes for **36** with those of related bicyclo[2.2.0]- and bicyclo[2.1.1]hexane systems[37,38], reveals that the product belongs to the bicyclo[2.1.1]hexane system, because in the case of the bicyclo[2.2.0] system larger coupling parameters are expected. The expected strong coupling (W form) is found in **36**. The assignment of the ^{1}H-NMR spectra of **33**—**35** is based on chemical shift arguments.

The irradiation of *cis*- and *trans*-**19**-3,4 gives rise to a *cis/trans* isomerization as shown for **19**-3 in Figure 2. Further irradiation of both compounds leads to a mixture of **37**-3,4 and **38**-3,4 in the ratio of 1:1. In the case of **19**-3 and **19**-4

Table 1. ^{1}H-NMR data [chemical shifts δ (multiplicities)] of **33**—**36**; for the meaning of H_A, H_B, H_C see formulae

	δ_A	δ_B	δ_C
33	1.73 (s)	3.15 (s)	2.98 (br. s)
34	3.18 (s)	3.43 (s)	2.70 (d)
35	1.63 (s)	3.09 (t)	2.74 (t)
36	2.04 (d)[a]	3.46 (d)[a]	2.95 (s)

[a] $J_{A,B}$ = 4.7 Hz.

the mixture of the products (**37**-3, **38**-3 as well as **37**-4 and **38**-4) could be separated by MPLC. The obtained compounds were stable when treated with K_2CO_3 in methanol. Yet, traces of acids lead to an equilibration between **37** and **38** and to a rearrangement to the aldehyde **40** and the ketal **41**. The H-NMR data of **37** and **38** are listed in Table 2.

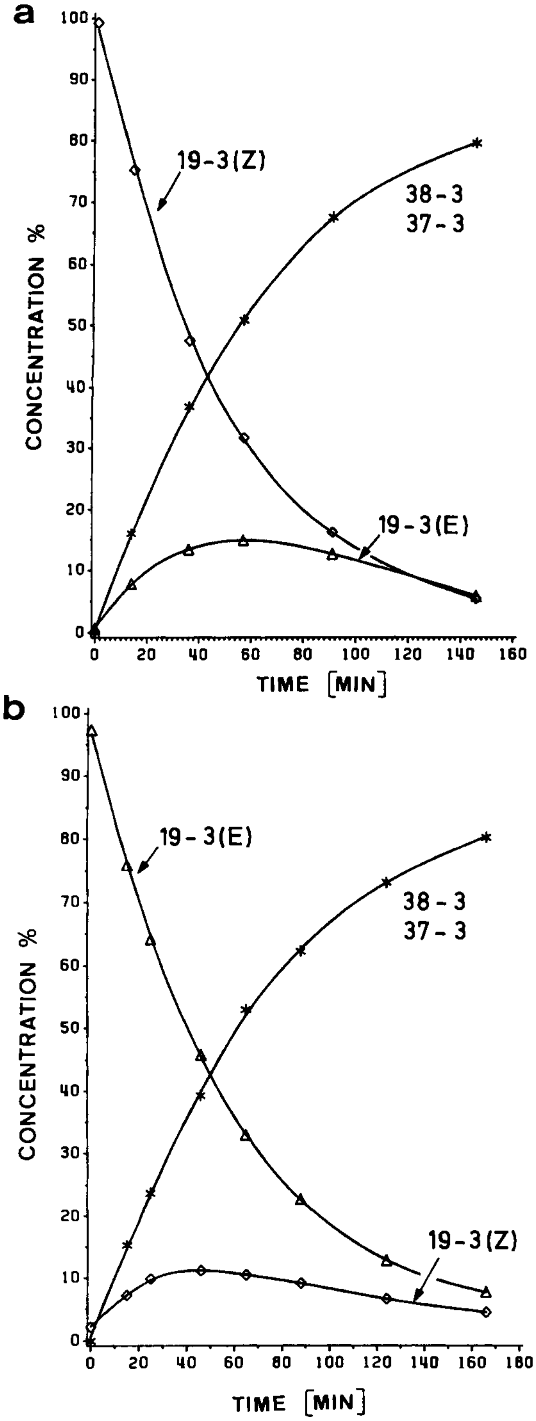
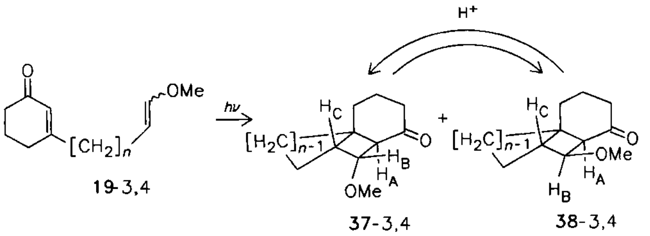
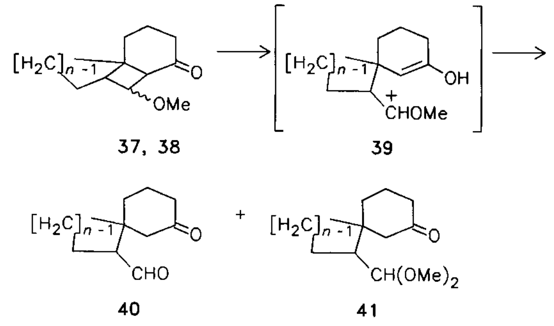


Figure 2. Product distribution followed by gas chromatography during the irradiation of *cis*-**19**-3 [≡**19**-3(*Z*)] (a) and *trans*-**19**-3 [≡**19**-3(*E*)]



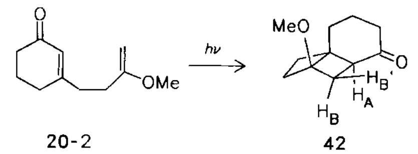


The structural assignment of the products is based on the ^{1}H-NMR data. Crucial for our assignment is the observation that H_B, which is geminal to the methoxy group, couples strongly with H_A and H_C and gives rise in the case of **37**-3 and **38**-3 to a doublet of doublets (see Table 2). This excludes the head-to-tail structural possibilities because in this case we would have expected at most a doublet as in **36**. The definitive assignment of the ^{1}H-NMR data to either **37** or **38** remains open, because in the case of a cyclobutane ring it is not possible to discriminate between a *cis* or *trans* configuration on the basis of the coupling constants alone[39,40]. This open question is indicated by braces in Table 2.

Table 2. ^{1}H-NMR data [chemical shifts δ (multiplicities) and coupling constants *J* in Hz] of the protons of the cyclobutane ring of **37**-3,4 and **38**-3,4; for the meaning of H_A, H_B, and H_C see formulae

	δ_A	δ_B	δ_C	$J_{A,B}$	$J_{B,C}$
37-3	2.50 (br. d)	3.78 (dd)	2.61 (t)	5.8	8.3
38-3	2.72 (d)	3.51 (dd)	2.40 (br. d)	8.8	3.0
37-4	2.88 (d)	4.07 (t)	2.23 (q)	7.2	ca. 7.5
38-4	2.71 (d)	3.89 (t)	2.31 (m)	8.3	8.2

The irradiation of **20**-2 yields only one product (**42**). Based on the large geminal and vicinal coupling constants (see Table 3) together with high δ values for H_A and H_B we assign a tricyclo$[4.4.0.0^{1,4}]$decane structure to **42**. A further hint to this structure is the fact that **42** shows no isomerization on treatment with dilute acids or with base.

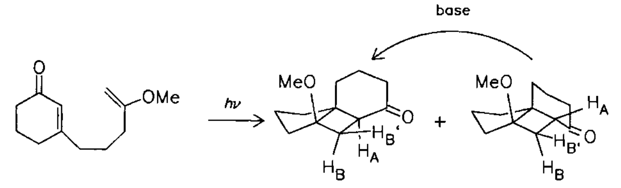


In the case of **20**-3 we isolated two products (**43**, **44**) in the ratio of 47:53. Compound **44** could be rearranged to **43** with K_2CO_3 in methanol. A comparison of the coupling constants obtained for **43** and **44** (Table 3) and those of bicyclo[2.2.0]- and bicyclo[2.1.1]hexan derivatives clearly

Table 3. ^{1}H-NMR data [chemical shifts δ (multiplicities) and coupling constants J in Hz] of the protons of the cyclobutane ring of **42**–**44**; for the meaning of H_A, H_B and $H_{B'}$ see formulae

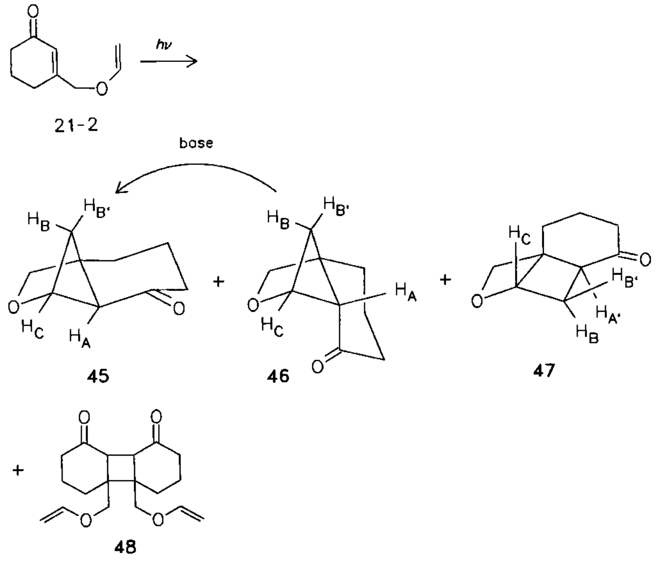
	δ_A	δ_B	$\delta_{B'}$	$J_{A,B}$	$J_{A,B'}$	$J_{B,B'}$
42	2.63 (m)		2.29 (ddd)	ca. 9	10.1	16.3
43	2.29 (dd)	2.25 (t)	2.13 (ddd)	10.4	7.3	11.7
44	3.31 (dd)	2.03 (dd)	1.91 (dd)	10.7	7.7	12.1

excludes the formation of the head-to-tail products. This and the experiment with base allows to assign the less strained *cis* arrangement to **43**. Also the measured coupling constants of the cyclobutane protons are in favor of the given structures.

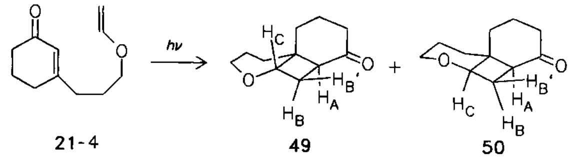


43-3 **43** **44**

In contrast to the previous examples we observe in the case of **21-2** a rather sluggish reaction. The formation of four products, **45**–**48**, in a ratio of 12:15:45:27 was observed. The spectroscopic (IR, ^{1}H NMR) investigation revealed only for **45**–**47** a tricyclic skeleton while **48** was found to be a photodimer. Furthermore, it was discovered that **46** could be converted into **45** when treating the former with K_2CO_3 in methanol, while **45** and **47** remained unchanged under these conditions.



From the four possible tricyclic structures three have been obtained. Two of them show *cis* and one *trans* connection. Based on the pattern of coupling constants for **47** as compared to the other two compounds (Table 4) we assign **47** to the head-to-head *cis* product, **45** to the head-to-tail *cis* product and **46** to the head-to-tail *trans* product. The coupling constants for $J_{B,B'}$ (Table 4) clearly point to the given structures. In **45** and **46** H_B and $H_{B'}$ are shifted upfield while in **47** the expected downfield shift is observed. We also notice a large coupling constant $J_{A,B'}$ for **45** due to the W arrangement.



21-4 **49** **50**

The photolysis of **21-4** yielded two products (**49**, **50**) in a ratio of 88:12 in a smooth reaction. Both compounds remained unchanged when treated with dilute acid or with K_2CO_3. The relative complicated ^{1}H-NMR spectra could be interpreted on the basis of the results obtained from decoupling experiments. The coupling constants and chemical shifts are listed in Table 4. From the three possible structures with a *cis* connection, the one originating from a head-to-tail ring closure can be ruled out due to the coupling constants and the splitting pattern (ddd or dt for head-to-head ring closure and dd at most for head-to-tail ring closure for H_B and $H_{B'}$). Striking features for **49** are the shift for H_C and the larger coupling constant $J_{B,C}$ in **50**. The final assignment is based on an NOE found for H_C and H_A in **50**.

Physical Measurements

The quantum yields of all photoreactions were determined (Table 5) by irradiation of a degassed 0.1 M solution (E = 0.9) in cyclohexane at λ = 366 nm. The intensity I_0 was determined according to Hatchard and Parker[41] using a potassium ferrioxalate actinometer. From the data listed in Table 5 it is evident that compounds **19-2**, **20-2** and **21-2** show smaller quantum yields than their congeners. The differences are larger in the **20** and **21** series.

To check whether the photoreactions proceed via the triplet state we have carried out sensiblization experiments with

Table 4. ^{1}H-NMR data [chemical shifts δ (multiplicities) and coupling constants J in Hz] of the protons of the cyclobutane ring of **45**–**47**, **49** and **50**; for the meaning of H_A, H_B, $H_{B'}$ and H_C see formulae

	δ_A	$\delta_{B'}$	δ_B	δ_C	$J_{B,B'}$	$J_{A,B}$	$J_{A,B'}$	$J_{B,C}$	$J_{B',C}$
45	2.47 (d)	1.90 (d)	1.45 (t)	4.72 (d)	ca. 8.5	9.4	–	–	
46	2.50 (s)	1.73 (dd)	1.78 (d)	4.76 (s)	7.4	–	–	–	
47	3.28 (dd)	2.52 (ddd)	2.85 (dd)	4.97 (d)	14.2	9.7	6.9	–	4.5
49	2.56 (dd)	2.34 (ddd)	2.48 (ddd)	3.97 (t)	11.6	10.0	4.6	6.2	7.0
50	2.36 (m)	2.64 (dt)	2.55 (dt)	3.20 (dd)	9.3	6.9	9.2	6.9	10.7

Table 5. Quantum yield ϕ and slope of a Stern-Volmer plot $k_q\tau_R$ of the photoreactions of **19**–**21**; for the meaning of ϕ_{AC}, ϕ_{BE}, τ_R, ϕ_I, ϕ_P and ϕ_Z see text

	ϕ	ϕ_{AC}	ϕ_{BE}	$k_q \cdot \tau_R$ [l/mol]	τ_R [s]	ϕ_I	ϕ_P	ϕ_Z
19-2	0.30	0.29	0.05	1.7	$2.4 \cdot 10^{-10}$	0.32	0.48	0.62
19-3	0.46	0.48	–	0.6	$0.9 \cdot 10^{-10}$	0.37	0.55	0.83
19-4	0.31	0.27	–	7.7	$11 \cdot 10^{-10}$	0.28	0.53	0.59
20-2	0.13	–	–	–	–	–	–	–
20-3	0.71	–	–	–	–	–	–	–
21-2	0.06	0.05	–	–	–	–	–	–
21-4	0.50	0.49	0.13	9.9	$18 \cdot 10^{-10}$	–	–	–

19-*n* and **21**-*n* using acetophenone (AC) and benzophenone (BE) as sensitizers in a concentration of 0.5 M assuming the total absorption of the light[42]. In the case of acetophenone (3rd column of Table 5) we obtained the same quantum yields as without sensitizer. With benzophenone (4th column of Table 5) we encountered significantly smaller values for the quantum yield. The product ratio was not changed by both sensitizers. This suggests that the nonsensitized reaction also occurs via a triplet state ($\phi_{ISC} = 1$)[43,44]. The smaller quantum yield for benzophenone can be rationalized if one assumes that the energy transfer from triplet benzophenone ($E^{BE} = 68.6$ kcal/mol)[42] to cyclohexenone is endothermic, while the energy transfer from triplet acetophenone ($E^{AC} = 73.8$ kcal/mol)[42] is exothermic. From these data and arguments it follows that the triplet energy of the cyclohexenone fragment in **19**-*n*–**21**-*n* should be close to 70 kcal/mol. This value is in line with that determined for a planar triplet of cyclohexenone[43].

To learn about the lifetime of the reactive triplet involved in our photoreactions we carried out quenching experiments in cyclohexane with **19**-*n* and **21**-4 using 1,3-pentadiene (piperylene) as quencher. (The triplet energy of piperylene has been determined to be 59 kcal/mol[42].) Again, we find no change in the product ratio with and without quencher, a result which is in line with the assumption of a triplet intermediate. The results obtained from a Stern-Volmer plot (see Figure 3) are listed in column 5 of Table 5. From the rate constant for diffusion of piperylene in cyclohexane at room temperature ($k_{diff} = 7 \times 10^9$ l/mol · s)[8] one can estimate the lifetime of the reactive triplet state (τ_R). The values are listed in Table 5. It is interesting to note that the compounds with shorter chains also show a shorter lifetime. The smaller values for **19**-3 compared to **19**-2 suggest a larger activation energy for **19**-2 than for **19**-3 which overcompensates the advantage of the shorter chain length.

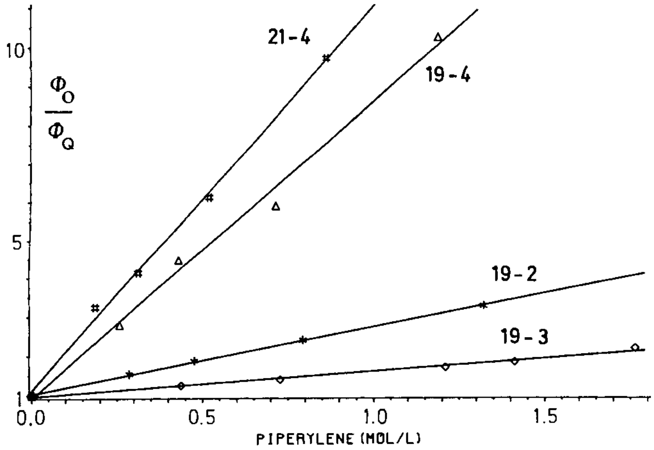


Figure 3. Ratio of the quantum yield without (ϕ_O) and with quencher (ϕ_Q) as a function of the concentration of the quencher (piperiylene) (Stern-Volmer plot) for **19**-2, **19**-3, **19**-4 and **21**-4

Analogous to Schröder, Wolff and Agosta[10c], we find a *cis/trans* isomerization in **19** (see Figures 1 and 2). The quantum yield of the isomerization (Φ_I) of **19**-2, **19**-3 and **19**-4 allows an estimation of the quantum yield of the formation of the (biradicaloid) intermediate *Z* (ϕ_Z) and the quantum yield of the part that is converted into the photoproducts (ϕ_P). On the assumption that the intermediates are either converted into the dienones or undergo ring closure to cyclobutane we obtain

$$\phi_Z = \phi + \phi_I$$

with

$$\phi_I = \phi_I^{cis \to trans} + \phi_I^{trans \to cis}$$

and

$$\phi_P = \frac{\phi}{\phi_Z}.$$

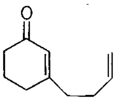
This leads to the values given in Table 5. Interestingly, ϕ_P is close to 0.5 for all three dienones. This means that only about half of the biradicals is transformed to cycloadducts. The values for ϕ_Z, however, differ considerably, they are larger for **19**-3 than for **19**-2 and **19**-4. This means that for the latter two a rather large percentage (40%) is deactivated before reaction to the intermediate. This might be interpreted by assuming a larger activation energy for the reaction of the triplet of the starting compound to the triplet of the intermediate for **19**-2 as compared to **19**-3. It can also be concluded from the stereochemistry of the products that bond formation occurs either at C_α (**19**-2) or C_β (**19**-3,4) first. The site of the second radical center seems to be more crucial: it is preferentially located at the carbon atom bearing the alkoxy group. The stereochemistry also shows that the biradicals leading to the products or to *cis/trans* isomerization must be the same. Otherwise the product distribution would be different when starting from *cis*- or *trans*-dienone.

Table 6. Ratio of the head-to-head (h) to the head-to-tail (t) regioisomer and quantum yield ϕ for **19**–**21** as well as **51**–**54**

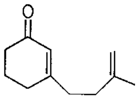
$n = 2$	h:t	ϕ	$n = 3$	h:t	ϕ	$n = 4$	h:t	ϕ
19-2	0:100	0.30	**19**-3	100:0	0.46	**19**-4	100:0	0.31
51	26:74	0.26	**53**	100:0	–	–	–	–
21-2	70:30	0.06	**54**	100:0	–	**21**-4	100:0	0.50
52	87:13	0.55	–	–	–	–	–	–
20-2	100:0	0.13	**20**-3	100:0	0.71	–	–	–

Discussion

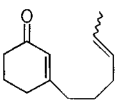
In Table 6 we have compared the ratio of the head-to-head (h) and head-to-tail (t) product with the quantum yield of **19**–**21** as well as of **51**–**54**.



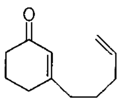
51[10a, c]



52[10a]



53[22a]



54[44]

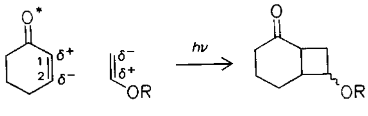
This comparison shows:

1) Compounds with $n = 3$ (**19**-3, **20**-3, **53** and **54**) are converted into the head-to-head products only. The product distribution is not influenced by the replacement of the acyclic double bond in the α- or β-position by a methoxy or methyl group. The quantum yield, however, is influenced by the substitution pattern. The quantum yield in **20**-3 (0.74) is higher than in **19**-3 (0.46).

2) Dienes with a four-membered chain between both units reveal the same regioselectivity as for compounds with $n = 3$. The quantum yield for $n = 4$ is lower than for the congeners with $n = 3$ and is also influenced by the substitution of the noncyclic double bond e.g. ϕ(**21**-4) > ϕ(**19**-4).

3) When $n = 2$, the regioselectivity is strongly dependent on the substituion of the enol ether double bond. In the case of **19**-2 the head-to-tail [2 + 2] cycloaddition is favored, and only tricyclo[5.2.1.$0^{1,6}$]decane is formed. Nevertheless, the quantum yield (0.30) is lower than in the case of **19**-3 (0.46), where also a methoxy group is in the α-position. Introduction of an electron-releasing group (**52**, **20**-2, **21**-2) into the β-position leads to an increase of the position of the head-to-head product, and a decrease in the quantum yield for the head-to-tail [2 + 2] cycloaddition drops to zero.

The results summarized in Tables 5 and 6 can be rationalized by assuming a polarization of the excited state of cyclohexenone as shown in **55** and of the enol ether moiety in the ground state as depicted in **56**. This polarization was proposed by Corey et al.[15] to rationalize the preferential formation of **57** in the intermolecular [2 + 2] cycloaddition reaction.

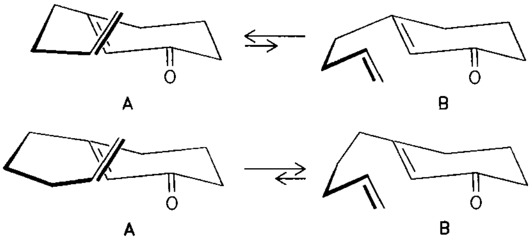


55 56 57

To find out the charge distribution in a twisted triplet π,π* state of an enone – the state which is involved in the [2 + 2]cycloaddition reaction[21] – model calculations on the n,π* and π,π* state of acrolein were carried out by means of the SINDO/1 procedure[45] using a 3 × 3 CI matrix. It was found[46] that there is essentially no difference of the net charges between the two carbon atoms in the α- and β-position relative to the CO group. This result is also not altered if the methylene group is twisted out of the molecular plane up to 70°.

These results together with the findings of Schuster, Turro et al.[18] prompted us to look for an alternative rationalization.

In the following we assume a stepwise mechanism for the ring closure. Nevertheless, the geometrical approach of the two double bonds will be influenced in the same way by π/σ interaction as discussed for a concerted process in the Introduction. Thus, if we extrapolate our results form the studies on 1,5-hexadiene and 1,6-heptadiene[12] to the present examples of **19**–**21**, we estimate for both modes of approach (**a** or **b**) to those compounds containing an ethano chain an electronic activation energy due to π/σ interaction. Steric effects should therefore be decisive, and **A** should be favored over conformer **B**.



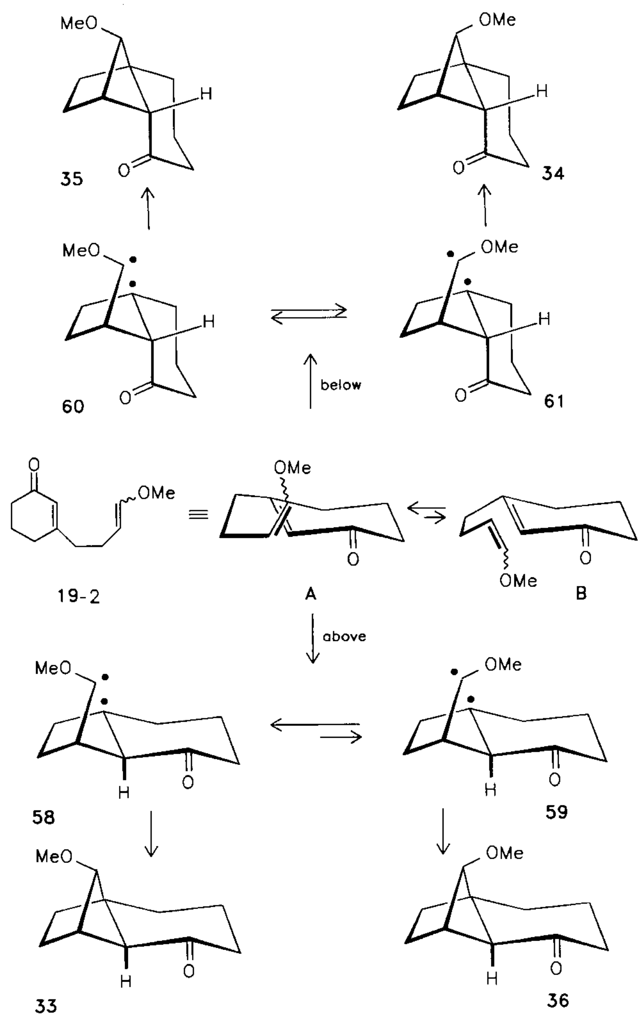
Conformation **B** should be electronically favored, if a propano chain connects the two π fragments. This assumption is based on the observation that the through-space effect of a propano chain increases the through-bond effect[47].

As an example we will discuss briefly the product distribution for **19**-2, and **19**-3, presented in Schemes 4 and 5 by assuming a stepwise process in which the most stable biradical is formed as an intermediate. Starting points are transition structures as shown above.

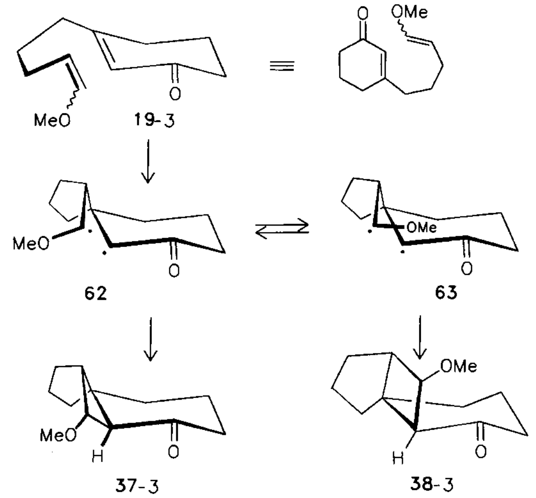
In the case that conformation **A** is preferred for **19**-2 the bond formation between C-β of the olefinic unit and C-α of the enone moiety should generate the most stable biradical. There are two modes of addition, from above and below the enone double bond. Thus, four biradicals **58**–**61** may be generated. For steric reasons, **59** should be less stable than **58**, **60** and **61**. A collapse yields **33**–**35**.

In the case of **19**-3 conformation **B** is the preferred one. The most stable radical is obtained by bond closure between C-β – C-β of both olefinic units (Scheme 5). This yields the two biradicals **62** and **63** which undergo bond closure to **37**-3 and **38**-3. In an analogous manner one can rationalize the

Scheme 4



Scheme 5



products obtained from the irradiation of **19**-4, **20**-2, **20**-3, **21**-2 and **21**-4.

Conclusion

Our results confirm the hypothesis that one of the main reasons for the "rule of five" is to be sought in the through-bond interaction. The absence of an electronic contribution to the activation energy for the C_S transition state with chains where $n = 3, 4$ determines the regioselectivity of the cycloaddition[12]; all electronic effects of the substituents are overruled. On the other hand in the case of compounds with $n = 2$, whose C_2 and C_S transition states are predicted to experience an electronic activation energy[12], the substitution of the vinyl ether double bond is decisive for the regiochemistry. In other words we expect for $n = 1, 3, 4$ a head-to-head [2 + 2] cycloaddition, only for $n = 2$ substitution and steric effects may favor formation of the head-to-tail product.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *BASF Aktiengesellschaft* for financial support. E. F. thanks the state of *Baden-Württemberg* for a graduate grant.

Experimental

General: Melting points (uncorrected): Dr. Tottoli (Büchi). – ^{1}H, ^{13}C NMR ($CDCl_3$, tetramethylsilane as an internal standard unless noted otherwise): 60 MHz: Varian EM 360; 90 MHz: Varian EM 390; 300 MHz: Bruker WM 300 (^{13}C: 75.46 MHz); 360 MHz: Bruker HX 360 (^{13}C: 90.55 MHz); 500 MHz: Bruker AM 500 (^{13}C: 125.76 MHz). – HR MS (70 eV): ZAB (Vacuum Generators). – IR (only the most prominent peaks are given): Beckman IR 4200, Bruker GC-FT-IR IFS-85. – UV/Vis (cyclohexane): Cary 17D (Varian). – Most of the compounds were purified by flash chromatography on silica gel (230–400 mesh). – Analytical VPC: Dani 6800 with flame detector and Shimadzu integrating recorder model C-3R4 with a 4 m × 2 mm column filled with 3% Carbowax-20M on 100/120 Chromosorb WHP; temp. program: initial temp. 170°C for 10 min, temp. rate 5°C/min, final temp. 200°C. – Preparative GC: Perkin-Elmer F21 with a 4 m × 12 mm column (15% Carbowax 20M on 80/100 Chromosorb WHP). – MPLC: 55 × 4.5 cm column filled with silica gel (Grace QR03, 60 Å – 15 μm) with a mixture of cyclohexane/ethyl acetate (9:1) as eluent. – Dienones and photoproducts are given in the order of VPC (**37** and **38**: MPLC) elution. Elemental analyses (Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg) and melting points of **33**–**36**, **42**, **43**, **44**, **49**, and **50** are given for the corresponding dinitrophenylhydrazones.

4-Bromobutanal Dimethyl Acetal (**23**-2): A solution of 61.2 g (314 mmol) of ethyl 4-bromobutyrate in 850 ml of dry hexane was stirred at −72°C under nitrogen. A 1 M solution of 420 ml of diisobutylaluminum hyride in heptane was added dropwise. After addition, stirring was continued for 3 h. The reaction mixture was acidified with 2 N HCl and allowed to warm up. The organic phase was washed with water and dried (Na_2SO_4). After most of the solvent had been removed, 80 ml of dry methanol, 100 ml of trimethyl formate and 0.3 g of *p*-toluenesulfonic acid were added, and the mixture was stirred for 30 h at room temp. A 3% solution of KOH (40 ml) in methanol was added, and the mixture was poured into 200 ml of saturated aqueous $NaHCO_3$ cooled by an ice bath. The aqueous phase was extracted with pentane, and the combined organic layers were washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and the solvent was evaporated. Distillation of the residue afforded 37.1 g (60%) of **23**-2; b.p. 83–84.5°C/17 mbar. – IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (s), 2830 (m), 1130 (s), 1070 (s). – ^{1}H NMR (60 MHz): δ = 4.33 [t, J = 5 Hz, 1H, C*H*(OCH_3)$_2$], 3.37 (t, J = 6 Hz, 2H, CH_2Br), 3.27 (s, 6H, OCH_3), 1.8 (m, 4H).

3-(4,4-Dimethoxybutyl)-2-cyclohexen-1-one (**24**-2): From 19.7 g (100 mmol) of **23**-2 and 7.00 g (304 mmol) of magnesium in 50 ml of dry tetrahydrofuran the Grignard reagent was prepared according to the Ponaras procedure[26,27] and the mixture cooled to 0°C. A solution of 12.7 g (90.0 mmol) of 3-ethoxy-2-cyclohexen-1-one in 40 ml of dry tetrahydrofuran was added dropwise below 5°C. After stirring for 3 h at room temp., the reaction mixture was poured onto ice, neutralized with 5% HCl and extracted with ether. The organic phase was dried with Na_2SO_4, and the solvent was removed. Distillation of the residue afforded a fraction of **24**-2 boiling at 108–110°C/10^{-2} Torr that still contained some 3-ethoxycyclohexenone and vinyl ether **19**-2 but was pure enough to be used for further reactions. Pure **24**-2 (6.10 g, 28%) was obtained by subsequent flash chromatography [ether/petroleum ether (1:1)]. – IR (film): $\tilde{\nu}$ = 1665 cm^{-1} (s), 1625 (m). – ^1H NMR (60 MHz): δ = 5.87 (s, 1H, =CHCO), 4.37 [t, J = 4 Hz, 1H, C*H*$(OCH_3)_2$], 3.27 (s, 6H, OCH_3), 2.3 (m, 8H), 1.65 (m, 4H).

$C_{12}H_{20}O_3$ (212.28) Calcd. C 67.89 H 9.50
Found C 67.67 H 9.70

3-(4-Methoxy-3-butenyl)-2-cyclohexen-1-one (**19**-2): 3.80 g (18.8 mmol) of **24**-2 was evaporated at 10^{-2} Torr and brought into contact with sodium phosphate kept at 220–270°C. The products were trapped in a flask cooled with liquid nitrogen containing a few milliliters of pentane and 5% of aqueous K_2CO_3. After warming up at atmospheric pressure, the mixture was extracted with pentane, and the organic phase was dried with Na_2SO_4. Evaporation of the solvent and purification of the residue by column chromatography using ether/petroleum ether (1:2) as eluent afforded 1.90 g (56%) of a mixture of *cis*- and *trans*-vinyl ether **19**-2.

3-[(Z)-4-Methoxy-3-butenyl]-2-cyclohexen-1-one (*cis*-**19**-2): IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s), 1620 (m). – ^1H NMR (60 MHz): δ = 5.97 (d, J = 6 Hz, 1H, =CHO), 5.87 (s, 1H, =CHCO), 4.3 (m, 1H, =C*H*CH_2), 3.6 (s, 3H, OCH_3), 1.8–2.55 (m, 10H). – UV: λ_{max} (ε) = 222 nm (14840), 323 (41).

3-[(E)-4-Methoxy-3-butenyl]-2-cyclohexen-1-one (*trans*-**19**-2): IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (s), 1620 (s). – ^1H NMR (60 MHz): δ = 6.38 (d, J = 13 Hz, 1H, =CHO), 5.9 (s, 1H, =CHCO), 4.7 (m, 1H, =C*H*CH_2), 3.5 (s, 3H, OCH_3), 1.85–2.60 (m, 10H). – UV: λ_{max} (ε) = 222 nm (13590), 335 (32).

$C_{11}H_{16}O_2$ (180.24) Calcd. C 73.30 H 8.95
Found C 73.08 H 9.17

5-Bromopentanal Dimethyl Acetal (**23**-3): The amount of 32.0 g (153 mmol) of ethyl 5-bromovalerate was converted into the dimethyl acetal **23**-3 as described for **23**-2 to yield 22.5 g (70%) of **23**-3; b.p. 99–101°C/16 mbar. – IR (film): $\tilde{\nu}$ = 1120 cm^{-1} (s), 1070 (s), 1050 (s). – ^1H NMR (60 MHz): δ = 4.32 [t, J = 5 Hz, 1H, C*H*$(OCH_3)_2$], 3.4 (t, J = 6 Hz, 2H, CH_2Br), 3.3 (s, 6H, OCH_3), 1.85 (m, 2H), 1.6 (m, 4H).

3-(5,5-Dimethoxypentyl)-2-cyclohexen-1-one (**24**-3): Prepared from 21.1 g (100 mmol) of **23**-3 according to the synthesis of **24**-2. Distillation of the crude product followed by chromatographic purification afforded 5.20 g (23%) of **24**-3; b.p. 114–116°C/10^{-2} Torr. – IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (s), 1625 (m). – ^1H NMR (60 MHz): δ = 5.9 (s, 1H, =CHCO), 4.35 [t, J = 5 Hz, 1H, C*H*$(OCH_3)_2$], 3.4 (s, 6H, OCH_3), 1.9–2.5 (m, 8H), 1.3–1.75 (m, 6H).

$C_{13}H_{22}O_3$ (226.31) Calcd. C 68.99 H 9.80
Found C 68.77 H 9.63

3-(5-Methoxy-4-pentenyl)-2-cyclohexen-1-one (**19**-3): The conversion of 4.50 g (19.9 mmol) of **24**-3 into **19**-3 was carried out as described for **19**-2 and yielded 2.70 g (70%) of **19**-3.

3-[(Z)-5-Methoxy-4-pentenyl]-2-cyclohexen-1-one (*cis*-**19**-3): IR (film): $\tilde{\nu}$ = 1665 cm^{-1} (s), 1620 (m). – ^1H NMR (60 MHz): δ = 5.8 (br. s, 2H, =CHCO, =CHO), 4.3 (q, J = 7 Hz, 1H, =C*H*CH_2), 3.58 (s, 3H, OCH_3), 1.3–2.5 (m, 12H). – UV: λ_{max} (ε) = 226 nm (15350), 324 (37).

3-[(E)-5-Methoxy-4-pentenyl]-2-cyclohexen-1-one (*trans*-**19**-3): IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s), 1615 (m). – ^1H NMR (60 MHz): δ = 6.2 (d, J = 13 Hz, 1H, =CHO), 5.8 (s, 1H, =CHCO), 4.7 (dt, J = 13 Hz, J = 7 Hz, 1H, =C*H*CH_2), 3.45 (s, 3H, CH_3O), 1.4–2.4 (m, 12H). – UV: λ_{max} (ε) = 227 nm (14460), 323 (38).

$C_{12}H_{18}O_2$ (194.26) Calcd. C 74.19 H 9.34
Found C 74.46 H 9.10

6-Bromohexanal Dimethyl Acetal (**23**-4): 49.7 g (222 mmol) of ethyl 6-bromocaproate was converted into the dimethyl acetal **23**-4 as described for **23**-2 to yield 34.0 g (68%) of **23**-4; b.p. 111–113/16 mbar. – IR (film): $\tilde{\nu}$ = 1120 cm^{-1} (s), 1070 (s), 1050 (s). – ^1H NMR (60 MHz): δ = 4.35 [t, J = 5 Hz, 1H, $CH(OCH_3)_2$], 3.4 (t, J = 6 Hz, 2H, CH_2Br), 3.3 (s, 6H, OCH_3), 1.3–2.1 (m, 8H).

3-(6,6-Dimethoxyhexyl)-2-cyclohexen-1-one (**24**-4): Prepared from 22.5 g (100 mmol) of **23**-4 by using the same procedure as for the synthesis of **24**-2. Distillation of the crude product followed by chromatographic purification afforded 8.00 g (33%) of **24**-4; b.p. 146–149°C/5 × 10^{-2} Torr. – IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s), 1620 (m). – ^1H NMR (60 MHz): δ = 5.78 (s, 1H, =CHCO), 4.28 [t, J = 5 Hz, 1H, $CH(OCH_3)_2$], 3.25 (s, 6H, OCH_3), 1.7–2.4 (m, 8H), 1.25–1.65 (m, 8H).

$C_{14}H_{24}O_3$ (240.33) Calcd. C 69.96 H 10.07
Found C 70.25 H 10.05

3-(6-Methoxy-5-hexenyl)-2-cyclohexen-1-one (**19**-4): 5.60 g (23.3 mmol) of **24**-4 was converted into **19**-4 as described for **19**-2 and yielded 2.50 g (52%) of **19**-4.

3-[(Z)-6-Methoxy-5-hexenyl]-2-cyclohexen-1-one (*cis*-**19**-4): IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s), 1620 (s). – ^1H NMR (60 MHz): δ = 5.75 (br. s, 2H, =C*H*CO, =C*H*CH_2), 4.2 (q, J = 7 Hz, 1H), 3.45 (s, 3H, OCH_3), 1.1–2.5 (m, 14H). – UV: λ_{max} (ε) = 225 nm (16460), 335 (37).

3-[(E)-6-Methoxy-5-hexenyl]-2-cyclohexen-1-one (*trans* **19**-4): IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s), 1625 (s). – ^1H NMR (60 MHz): δ = 6.38 (d, J = 13 Hz, 1H, =CHO), 5.95 (s, 1H, =CHCO), 4.75 (dt, J = 13 Hz, J = 7 Hz, 1H, =C*H*CH_2), 3.55 (s, 3H, OCH_3), 1.7–2.6 (m, 10H), 1.3–1.7 (m, 4H). – UV: λ_{max} (ε) = 224 nm (16960), 335 (40).

$C_{13}H_{20}O_2$ (208.29) Calcd. C 74.96 H 9.68
Found C 75.06 H 9.88

4-Bromo-1-trimethylsilyl-1-butyne (**26**-2): A solution of 17.4 g (131 mmol) of **25**-2 in 500 ml of dry tetrahydrofuran was stirred at –70°C under argon; 80.0 ml (128 mmol) of 1.6 N *n*-butyllithium in *n*-hexane was added slowly, and the solution was stirred for another hour. The reaction mixture was allowed to warm up to 0°C, and 30.0 ml (236 mmol) of chlorotrimethylsilane was added below 3°C. The mixture was stirred for 20 h at room temp., and poured into 300 ml of saturated aqueous NH_4Cl cooled with an ice bath. The aqueous layer was extracted with ether, the combined organic layers were subsequently washed with water and brine and dried with Na_2SO_4. After evaporation of the solvents, the residue was distilled to yield 23.7 g (88%) of **26**-2; b.p. 71–73°C/16 mbar. – ^1H NMR (60 MHz; external standard: TMS): δ = 3.55 (t, J = 7 Hz, 2H, CH_2Br), 3.9 (t, J = 7 Hz, 2H, CH_2), 0.25 [s, 9H, $Si(CH_3)_3$].

3-(4-Trimethylsilyl-3-butynyl)-2-cyclohexen-1-one (**27**-2): Prepared from 20.5 g (100 mmol) of **26**-2 according to the synthesis of **24**-2. Purification of the product by column chromatography [ether/petroleum ether (1:4)] gave 14.2 g (64%) of **27**-2. – IR (film): $\tilde{\nu}$ = 2170 cm^{-1} (s), 1670 (s), 1630 (m). – ^1H NMR (90 MHz; standard: $CDCl_3$): δ = 5.82 (s, 1H, =CHCO), 2.35 (s, 4H), 2.25 (m, 4H), 1.9 (m, 2H), 0.05 [s, 9H, $Si(CH_3)_3$].

$C_{13}H_{20}OSi$ (220.39) Calcd. C 70.85 H 9.14
Found C 70.83 H 8.89

3-(3-Butynyl)-2-cyclohexen-1-one (**28**-2): A solution of 13.7 g (62.0 mmol) of **27**-2 in 40 ml of dry tetrahydrofuran/dimethylformamide (4:6) was treated with 10.0 g (106 mmol) of KF · H_2O for 48 h at room temp. After addition of 30 ml of water, the mixture was extracted with ether. The organic phase was washed with brine and dried (Na_2SO_4). After removal of the solvents, **28**-2 was purified by column chromatography. Elution with ethyl acetate/petroleum ether (1:10) afforded 9.00 g (98%) of **28**-2. – IR (film): $\tilde{\nu}$ = 2110 cm^{-1} (w), 1670 (s), 1630 (s). – ^{1}H NMR (90 MHz): δ = 5.9 (s, 1H, =CHCO), 2.35 (m, 8H), 2.0 (m, 3H).

$C_{10}H_{12}O$ (148.20) Calcd. C 81.04 H 8.16
Found C 80.83 H 8.19

3-(3-Methoxy-3-butenyl)-2-cyclohexen-1-one (**20**-2): A mixture of 14.4 g (45.0 mmol) of $Hg(OAc)_2$ and 100 ml of dry methanol was stirred for 5 min under nitrogen, then cooled in an ice bath, and 6.40 g (43.0 mmol) of **28**-2 was added dropwise. The ice bath was removed, and the mixture was stirred for 30 min. After cooling in ice again, 100 ml of pentane was added followed immediately by 1.00 g (26.0 mmol) of $NaBH_4$ dissolved in 26 ml of 3 N NaOH. Sodium chloride was added to saturate the mixture, the ice bath was removed and the mixture was stirred for 20 min. The organic layer was separated, and the aqueous phase was extracted with pentane. The combined extracts were dried with Na_2SO_4 followed by $MgSO_4$, and the solvent was evaporated. Purification of the residue by column chromatography [ether/petroleum ether (1:2)] gave 3.00 g (39%) of **20**-2. – IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (s), 1630 (m). – ^{1}H NMR (90 MHz): δ = 5.85 (m, 1H, =CHCO), 3.88 (s, 2H, =CH_2), 3.5 (s, 3H, OCH_3), 2.32 (m, 8H), 2.0 (m, 2H). – UV: λ_{max} (ε) = 225 nm (13080), 324 (32).

$C_{11}H_{16}O_2$ (180.24) Calcd. C 73.30 H 8.95
Found C 73.26 H 8.71

5-Bromo-1-trimethylsilyl-1-pentyne (**26**-3): 38.6 g (263 mmol) of 5-bromo-1-pentyne (**25**-3) was converted into **26**-3 as described for **26**-2 to yield 45.9 g (80%) of **26**-3; b.p. 85–90°C/16 mbar. – ^{1}H NMR (60 MHz; external standard: TMS): δ = 3.55 (t, J = 6 Hz, 2H, CH_2Br), 1.8–2.6 (m, 4H, $[CH_2]_2$), 0.25 [s, 9H, $Si(CH_3)_3$].

3-(5-Trimethylsilyl-4-pentynyl)-2-cyclohexen-1-one (**27**-3): Prepared from 21.9 g (100 mmol) of **26**-3 according to the synthesis of **24**-2. Distillation of the residue gave 14.7 g (63%) of **27**-3; b.p. 106–109°C/2 · 10^{-2} Torr. – IR (film): $\tilde{\nu}$ = 2165 cm^{-1} (m), 1670 (s), 1625 (m). – ^{1}H NMR (90 MHz; standard: $CDCl_3$): δ = 5.8 (t, J = 1 Hz, 1H, =CHCO), 1.5–2.4 (m, 12H), 0.05 [s, 9H, $Si(CH_3)_3$].

$C_{14}H_{22}OSi$ (234.42) Calcd. C 71.73 H 9.46
Found C 71.62 H 9.20

3-(4-Pentynyl)-2-cyclohexen-1-one (**28**-3): Prepared from 14.4 g (61.5 mmol) of **27**-3 by using the same procedure as for the synthesis of **28**-2. The crude product was distilled to yield 10.4 g (91%) of **28**-3; b.p. 89–91°C/7 · 10^{-2} Torr. – IR (film): $\tilde{\nu}$ = 2110 cm^{-1} (w), 1670 (s), 1625 (m). – ^{1}H NMR (90 MHz): δ = 5.85 (t, J = 1.3 Hz, 1H, =CHCO), 1.5–2.45 (m, 13H).

$C_{11}H_{14}O$ (162.22) Calcd. C 81.44 H 8.70
Found C 81.49 H 8.94

3-(4-Methoxy-4-pentenyl)-2-cyclohexen-1-one (**20**-3): The conversion of 6.50 g (40.0 mmol) of **28**-3 into **20**-3 was carried out as described for **20**-2 and gave 3.10 g (40%) of **20**-3. – IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (s), 1630 (s). – ^{1}H NMR (90 MHz): δ = 5.85 (t, J = 1.3 Hz, 1H, =CHCO), 3.85 (s, 2H, =CH_2), 3.55 (s, 3H, OCH_3), 1.6–2.4 (m, 12H). – UV: λ_{max} (ε) = 225 nm (15660), 337 (33).

$C_{12}H_{18}O_2$ (194.26) Calcd. C 74.19 H 9.34
Found C 74.35 H 9.59

Methyl 3,3-Ethylenedioxy-1-cyclohexenecarboxylate (**30**): 30.0 g (480 mmol) of ethanediol and 1.60 g (6.00 mmol) of pyridinium tosylate were added to a solution of 15.8 g (103 mmol) of **29** in 600 ml of benzene. The mixture was refluxed for 18 h with water separation by a Dean-Stark trap. After removal of the solvents in vacuo, ether was added to the residue. The solution was washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and the solvents were evaporated. Distillation of the residue gave 18.3 g (90%) of **30**; b.p. 149–150°C/16 Torr. – IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (s), 1650 (m). – ^{1}H NMR (60 MHz): δ = 6.6 (br. s, 1H, =CHCO), 4.0 (s, 4H, OCH_2CH_2O), 3.75 (s, 3H, OCH_3), 2.25 (m, 2H), 1.8 (m, 4H).

$C_{10}H_{14}O_4$ (198.21) Calcd. C 60.59 H 7.12
Found C 60.72 H 7.14

3-Hydroxymethyl-2-cyclohexen-1-one Ethylene Ketal (**31**) *and 2-(3-Hydroxymethyl-1-cyclohexenyloxy)ethanol:* A solution of 36.5 g (180 mmol) of **30** in 100 ml of benzene was added dropwise with stirring to a mixture of 8.00 g (210 mmol) of $LiAlH_4$ in 450 ml of benzene. The reaction mixture was heated very carefully to 70–75°C and kept at this temperature for 20 h. It was cooled to 0°C and hydrolyzed with 8 ml of water, 8 ml of 15% aqueous NaOH and 24 ml of water. The precipitate was filtered off by suction and thoroughly extracted with ether. The combined organic layers were dried (Na_2SO_4), and the solvents were evaporated. Two products were separated by column chromatography. Elution with hexane/ethyl acetate (2:3) yielded 10.2 g (33%) of **31** and 10.8 g (35%) of 2-(3-hydroxymethyl-1-cyclohexenyloxy)ethanol.

31: IR (film): $\tilde{\nu}$ = 1175 cm^{-1} (s), 1090 (s), 1070 (s), 1030 (s). – ^{1}H NMR (60 MHz): δ = 5.8 (br. s, 1H, =CHCO), 3.92 (s, 3H, CH_2OH), 3.6 (s, 4H, OCH_2CH_2O), 1.7–2.1 (m, 6H).

$C_9H_{14}O_3$ (170.20) Calcd. C 63.51 H 8.29
Found C 63.51 H 7.96

2-(3-Hydroxymethyl-1-cyclohexenyloxy)ethanol: IR (film): $\tilde{\nu}$ = 1665 cm^{-1} (s), 1185 (s). – ^{1}H NMR (500 MHz): δ = 4.59 (t, J = 1.3 Hz, 1H, =CH), 3.83 (m, 2H, CH_2O), 3.79 (m, 2H, CH_2O), 3.51 (dd, J = 6.6 Hz, J = 10.3 Hz, 1H, $CHCH_2OH$), 3.47 (dd, J = 6.0 Hz, J = 10.3 Hz, 1H, $CHCH_2OH$), 2.75 (br. s, 1H, OH), 2.40 (m, 1H), 2.33 (br. s, 1H, OH), 2.09 (m, 2H), 1.82 (m, 1H), 1.74 (m, 1H), 1.62 (m, 1H), 1.30 (m, 1H). – ^{13}C NMR (125.76 MHz): δ = 156.41 (s), 95.33 (d), 67.63 (t), 67.58 (t), 61.24 (t), 37.33 (d), 27.93 (t), 25.60 (t), 21.08 (t).

$C_9H_{16}O_3$ (172.22) Calcd. C 62.76 H 9.36
Found C 62.90 H 9.25

3-Hydroxymethyl-2-cyclohexen-1-one (**32**-2): A solution of 8.00 g (49.0 mmol) of **31** and 3.70 g (14.7 mmol) of pyridinium tosylate in 400 ml of wet acetone was refluxed for 3.5 h. After evaporation of the solvent, ether was added to the residue. The solution was washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and the solvent was removed. The remaining crude product was chromatographed. Elution with hexane/ethyl acetate (1:2) afforded 4.00 g (65%) of **32**-2. – IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (s). – ^{1}H NMR (60 MHz): δ = 6.1 (m, 1H, =CHCO), 4.67 (t, J = 5 Hz, 1H, OH), 4.3 (d, J = 5 Hz, 2H, CH_2OH), 1.8–2.6 (m, 6H).

$C_7H_{10}O_2$ (126.15) Calcd. C 66.64 H 7.99
Found C 66.69 H 8.18

3-(Vinyloxymethyl)-2-cyclohexen-1-one (**21**-2): A solution of 3.60 g (28.0 mmol) of **32** in 60 ml of freshly distilled ethyl vinyl ether was treated at reflux with 1.5 g of $\mathrm{Hg(OAc)_2}$. After a period of 2 h and 4 h, respectively, 40 ml of ethyl vinyl ether and 1 g of $\mathrm{Hg(OAc)_2}$ were added, and the mixture was refluxed for another 12 h. After cooling the latter in an ice bath, 50 ml of a 10% K_2CO_3 solution was added. The aqueous layer was extracted with ether, the combined organic layers were dried (K_2CO_3), and the solvents were evaporated. The crude product was purified by column chromatography [ether/petroleum ether (1:1)] to yield 3.10 g (73%) of **21**-2. – IR (film): $\tilde{\nu}$ = 1670 $\mathrm{cm^{-1}}$ (s), 1635 (s), 1615 (s). – ^{1}H NMR (60 MHz): δ = 6.45 (dd, J = 7 Hz, J = 14 Hz, 1 H, =CHO), 6.02 (br. s, 1 H, =CHCO), 4.4 (s, 2 H, CH_2O), 4.15 (m, 2 H, $=CH_2$), 1.8–2.5 (m, 6 H). – UV: λ_{max} (ε) = 220 nm (14660), 338 (26).

$C_9H_{12}O_2$ (152.19) Calcd. C 71.02 H 7.95
Found C 71.00 H 7.81

3-(3-Vinyloxypropyl)-2-cyclohexen-1-one (**21**-4): 6.16 g (40.0 mmol) of **32**-4 was converted into **21**-4 (4.50 g, 62%) by using the same method as described for **21**-2. – IR (film): $\tilde{\nu}$ = 1665 $\mathrm{cm^{-1}}$ (s), 1615 (s). – ^{1}H NMR (60 MHz): δ = 6.65 (dd, J = 7 Hz, J = 14 Hz, 1 H, =CHO), 5.95 (s, 1 H, =CHCO), 4.25 (dd, J = 2 Hz, J = 14 Hz, 1 H, $=CH_2$), 4.1 (dd, J = 2 Hz, J = 7 Hz, 1 H, $=CH_2$), 3.75 (t, J = 6 Hz, 2 H, CH_2O), 1.7–2.6 (m, 10 H). – UV: λ_{max} (ε) = 225 nm (15660), 325 (32).

$C_{11}H_{16}O_2$ (180.24) Calcd. C 73.30 H 8.95
Found C 73.20 H 8.87

General Procedure for Photochemical Reactions: Irradiation reactions were carried out in a cylindrical vessel (500 ml, Pyrex filter) by using either a Hanovia 450-W or Philips HPK 125-W medium-pressure Hg lamp; $1-5 \cdot 10^{-2}$ M solutions of the dienones in cyclohexane were purged with nitrogen and irradiated until conversion was almost complete. The reactions were monitored by analytical VPC. Subsequently, the solvent was evaporated. Analytically pure samples were obtained as indicated.

Photolysis of **19**-2: Flash chromatography using ether/petroleum ether (2:3) afforded **35** and a mixed fraction containing **33** and **34**. The latter were separated by preparative VPC (200 °C).

10-Methoxytricyclo[5.2.1.0^{1,6}]decan-5-one **33**: IR (film): $\tilde{\nu}$ = 1710 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (360 MHz): δ = 3.20 (s, 3 H), 3.15 (s, 1 H), 2.98 (br. s, 1 H), 2.33 (dt, J = 13.6 Hz, J = 3.2 Hz, 1 H), 2.19 (dt, J = 5.4 Hz, J = 13.5 Hz, 1 H), 2.06 (m, 1 H), 1.78–1.95 (m, 3 H), 1.73 (s, 1 H), 1.49–1.69 (m, 3 H), 1.43 (dt, J = 3.0 Hz, J = 9.6 Hz, 1 H). – ^{13}C NMR (75.46 MHz): δ = 211.2 (s), 74.9 (d), 56.9 (s), 55.1 (q), 51.3 (d), 42.7 (d), 40.6 (t), 27.9 (t), 24.9 (t), 24.0 (t), 21.8 (t).
2,4-Dinitrophenylhydrazone of **33**: m.p. 180–181 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.51 H 5.31 N 15.36

10-Methoxytricyclo[5.2.1.0^{1,6}]decan-5-one **34**: IR (FT-IR): $\tilde{\nu}$ = 1736 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (360 MHz): δ = 3.43 (s, 1 H), 3.37 (s, 3 H), 3.18 (s, 1 H), 2.70 (d, J = 1.4 Hz, 1 H), 2.25 (m, 1 H), 2.14 (m, 4 H), 1.90 (m, 1 H), 1.55–1.63 (m, 2 H), 1.34–1.50 (m, 2 H). – ^{13}C NMR (75.46 MHz): δ = 210.3 (s), 89.8 (d), 59.4 (s), 57.3 (q), 54.0 (d), 44.3 (d), 39.7 (t), 25.6 (t), 25.0 (t), 23.8 (t), 19.7 (t).
2,4-Dinitrophenylhydrazone of **34**: m.p. 156–157.5 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.61 H 5.68 N 15.58

10-Methoxytricyclo[5.2.1.0^{1,6}]decan-5-one **35**: m.p. 36–37 °C. – IR (film): $\tilde{\nu}$ = 1720 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (360 MHz): δ = 3.24 (s, 3 H), 3.09 (t, J = 1.0 Hz, 1 H), 2.74 (t, J = 1.3 Hz, 1 H), 2.33 (dt, J = 13.6 Hz, J = 3.2 Hz, 1 H), 2.0–2.24 (m, 4 H), 1.92 (m, 1 H), 1.82 (m, 1 H), 1.39–1.50 (m, 2 H), 1.63 (s, 1 H), 1.57 (m, 1 H). – ^{13}C NMR (90.55 MHz): δ = 195.3 (s), 82.0 (d), 59.5 (s), 56.0 (q), 48.3 (d), 43.3 (d), 40.7 (t), 27.3 (t), 26.4 (t), 22.8 (t), 19.3 (t).
2,4-Dinitrophenylhydrazone of **35**: m.p. 142.5–144 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.63 H 5.30 N 15.33

Photolysis of **19**-3: Flash chromatography [ether/petroleum ether (1:3)] afforded two fractions containing mainly **37**-3 and **38**-3. Both products were isolated from these fractions by further MPLC (27 ml/min; λ = 290 nm).

6-Methoxytricyclo[5.4.0.0^{1,5}]undecan-8-one **37**-3: IR (cyclohexane): $\tilde{\nu}$ = 1680 $\mathrm{cm^{-1}}$ (s), 1095 (m). – ^{1}H NMR (300 MHz): δ = 3.78 (dd, J = 5.9 Hz, J = 8.4 Hz, 1 H), 3.27 (s, 3 H), 2.61 (t, J = 8.2 Hz, 1 H), 2.50 (br. d, J = 5.7 Hz, 1 H), 1.30–2.25 (m, 12 H).

$C_{12}H_{18}O_2$ Calcd. 194.1307 Found 194.1293 (HR MS)

6-Methoxytricyclo[5.4.0.0^{1,5}]undecan-8-one **38**-3: IR (film): $\tilde{\nu}$ = 1695 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (500 MHz): δ = 3.51 (dd, J = 2.9 Hz, J = 8.8 Hz, 1 H), 3.23 (s, 3 H), 2.72 (d, J = 8.7 Hz, 1 H), 2.50 (m, 1 H), 2.40 (d, J = 3.1 Hz, 1 H), 2.15 (tq, J = 3.6 Hz, J = 12.7 Hz, 1 H), 2.07 (dd, J = 5.3 Hz, J = 7.6 Hz, 1 H), 1.91 (m, 1 H), 1.82 (m, 1 H), 1.54–1.65 (m, 6 H), 1.35 (m, 1 H).

$C_{12}H_{18}O_2$ Calcd. 194.1307 Found 194.1294 (HR MS)

Photolysis of **19**-4: The compounds **37**-4 and **38**-4 were purified as described for **37**-3 and **38**-3 (30 ml/min; λ = 290 nm).

7-Methoxytricyclo[6.4.0.0^{1,6}]dodecan-9-one **37**-4: IR (film): $\tilde{\nu}$ = 1695 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (500 MHz): δ = 4.07 (t, J = 7.2 Hz, 1 H), 3.24 (s, 3 H), 2.88 (d, J = 7.2 Hz, 1 H), 2.38 (m, 2 H), 2.23 (q, J = 8 Hz, 1 H), 1.91 (m, 1 H), 1.56–1.81 (m, 8 H), 1.35 (qt, J_q = 5.5 Hz, 1 H), 1.08–1.19 (m, 2 H).

$C_{13}H_{20}O_2$ Calcd. 208.1463 Found 208.1474 (HR MS)

7-Methoxytricyclo[6.4.0.0^{1,6}]dodecan-9-one **38**-4: IR (film): $\tilde{\nu}$ = 1690 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (360 MHz): δ = 3.89 (t, J = 8.2 Hz, 1 H), 3.38 (s, 3 H), 2.71 (d, J = 8.3 Hz, 1 H), 2.43 (dt, J = 17.0 Hz, J = 4.4 Hz, 1 H), 2.31 (m, 1 H), 2.10 (ddd, J = 5.9 Hz, J = 10.4 Hz, J = 17.0 Hz, 1 H), 1.24–1.99 (m, 12 H).

$C_{13}H_{20}O_2$ Calcd. 208.1463 Found 208.1469 (HR MS)

Photolysis of **20**-2: The photolysis of **20**-2 afforded **42** as the only product which was separated from **20**-2 by column chromatography [ether/petroleum ether (1:2)].

4-Methoxytricyclo[4.4.0.0^{1,4}]decan-7-one (**42**): IR (film): $\tilde{\nu}$ = 1710 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (500 MHz): δ = 3.11 (s, 3 H), 2.63 (m, 2 H), 2.47 (ddt, J = 1.4 Hz, J = 16.2 Hz, J = 4.0 Hz, 1 H), 2.29 (ddd, J = 2.4 Hz, J = 10.1 Hz, J = 16.3 Hz, 1 H), 2.24 (ddd, J = 2.5 Hz, J = 6.4 Hz, J = 12.3 Hz, 1 H), 2.16 (m, 2 H), 2.105 (ddt, J = 1.2 Hz, J = 14.4 Hz, J = 4 Hz, 1 H), 2.23 (dt, J = 5.7 Hz, J = 12.2 Hz, 1 H), 1.96–1.86 (m, 3 H), 1.425 (dd, J = 14.4 Hz, J = 16.7 Hz, 1 H). – From **42** two 2,4-dinitrophenylhydrazones were isolated.

a) m.p. 178–180 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.91 H 5.64 N 15.41

b) m.p. 150–152 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.50 H 5.68 N 15.47

Photolysis of **20**-3: The two photoproducts **43** and **44** were isolated by flash chromatography [ether/petroleum ether (1:2)].

5-Methoxytricyclo[5.4.0.0^{1,5}]undecan-8-one (**43**): IR (film): $\tilde{\nu}$ = 1715 $\mathrm{cm^{-1}}$ (s). – ^{1}H NMR (500 MHz): δ = 3.16 (s, 3 H), 2.49 (m, 1 H), 2.29 (dd, J = 7.3 Hz, J = 10.4 Hz, 1 H), 2.25 (t, J = 10.5/

11.7 Hz, 1 H), 2.19 (m, 2 H), 2.13 (ddd, J = 2.1 Hz, J = 7.3 Hz, J = 11.6 Hz, 1 H), 1.92 – 2.02 (m, 2 H), 1.85 (m, 2 H), 1.62 – 1.78 (m, 3 H), 1.55 (m, 1 H), 1.41 (m, 1 H). – From **43** two 2,4-dinitrophenylhydrazones were isolated.
a) m.p. 185 – 187 °C.

$C_{18}H_{22}N_4O_5$ (374.39) Calcd. C 57.74 H 5.92 N 14.97
Found C 57.80 H 5.93 N 14.85

b) m.p. 161 – 162 °C.

$C_{18}H_{22}N_4O_5$ (374.39) Calcd. C 57.74 H 5.92 N 14.97
Found C 57.78 H 5.89 N 14.84

5-Methoxytricyclo[5.4.0.0^{1,5}]undecan-8-one (**44**): IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (s). – ^{1}H NMR (500 MHz): δ = 3.31 (s, 3 H and dd, J = 7.9 Hz, J = 10.5 Hz, 1 H), 2.32 (m, 1 H), 2.17 – 2.11 (m, 2 H), 2.03 (dd, J = 10.9 Hz, J = 12.1 Hz, 1 H), 1.98 (m, 2 H), 1.91 (dd, J = 7.6 Hz, J = 12.2 Hz, 1 H), 1.86 – 1.66 (m, 5 H), 1.55 (m, 1 H), 1.47 (m, 1 H).

$C_{12}H_{18}O_2$ (194.26) Calcd. C 74.19 H 9.34
Found C 73.94 H 9.66

2,4-Dinitrophenylhydrazone of **44**: m.p. 149 – 150 °C.

$C_{18}H_{22}N_4O_5$ (374.39) Calcd. C 57.74 H 5.92 N 14.97
Found C 57.67 H 5.94 N 14.78

Photolysis of **21**-2: Flash chromatography [ether/petroleum ether (1:3)] afforded four products.

8-Oxatricyclo[5.2.1.0^{1,6}]decan-5-one **45**: IR (film): $\tilde{\nu}$ = 1705 cm^{-1} (s). – ^{1}H NMR (360 MHz): δ = 4.72 (d, J = 0.7 Hz, 1 H), 3.77 (d, J = 5.7 Hz, 1 H), 3.71 (dd, J = 0.8 Hz, J = 5.7 Hz, 1 H), 2.47 (d, J = 9.4 Hz, 1 H), 2.4 (m, 1 H), 2.13 – 2.27 (m, 2 H), 1.77 – 1.97 (m, 3 H), 1.9 (d, J = 8.0 Hz, 1 H), 1.45 (t, J = 8.9 Hz, 1 H).

$C_9H_{12}O_2$ (152.19) Calcd. C 71.02 H 7.95
Found C 70.88 H 7.76

8-Oxatricyclo[5.2.1.0^{1,6}]decan-5-one **46**: IR (film): $\tilde{\nu}$ = 1720 cm^{-1} (s). – ^{1}H NMR (360 MHz): δ = 4.76 (s, 1 H), 3.58 (d, J = 7 Hz, 1 H), 3.56 (d, J = 7 Hz, 1 H), 2.5 (s, 1 H), 2.3 – 2.25 (m, 2 H), 2.0 – 2.17 (m, 4 H), 1.78 (d, J = 7.4 Hz, 1 H), 1.73 (dd, J = 1.7 Hz, J = 7.4 Hz, 1 H).

$C_9H_{12}O_2$ (152.19) Calcd. C 71.02 H 7.95
Found C 70.96 H 7.98

3-Oxatricyclo[4.4.0.0^{1,4}]decan-7-one **47**: IR (film): $\tilde{\nu}$ = 1700 cm^{-1} (s). – ^{1}H NMR (500 MHz): δ = 4.97 (d, J = 4.5 Hz, 1 H), 4.81 (d, J = 6.2 Hz, 1 H), 4.78 (d, J = 6.4 Hz, 1 H), 3.28 (dd, J = 6.9 Hz, J = 9.8 Hz, 1 H), 2.85 (dd, J = 9.6 Hz, J = 14.2 Hz, 1 H), 2.52 (m, 2 H), 2.17 (ddd, J = 5.4 Hz, J = 13.2 Hz, J = 16.4 Hz, 1 H), 2.105 (ddt, J = 1.3 Hz, J = 14.3 Hz, J = 3.5 Hz, 1 H), 1.995 (dddd, J = 3.8 Hz, J = 4.1 Hz, J = 5.3 Hz, J = 13.6 Hz, 1 H), 1.70 (tq, J = 3.5 Hz, J = 13.1 Hz, 1 H), 1.495 (dt, J = 4.0 Hz, J = 13.5 Hz, 1 H).

$C_9H_{12}O_2$ (152.19) Calcd. C 71.02 H 7.95
Found C 70.98 H 7.65

Dimer **48**: FT IR: $\tilde{\nu}$ = 1740 cm^{-1} (s), 1690 (s). – ^{1}H NMR (360 MHz): δ = 6.33 (dd, J = 6.7 Hz, J = 14.2 Hz, 2 H), 4.22 (dd, J = 1.9 Hz, J = 14.2 Hz, 2 H), 4.06 (dd, J = 1.9 Hz, J = 14.2 Hz, 2 H), 3.65 (d, J = 10.0 Hz, 2 H), 3.57 (d, J = 10.0 Hz, 2 H), 2.97 (s, 2 H), 2.36 (m, 2 H), 2.22 (dt, J = 18.4 Hz, J = 5.1 Hz, 2 H), 2.04 (m, 4 H), 1.70 (m, 4 H). – MS: m/z (%) = 305 (4) [M$^+$ + 1]. – Satisfactory analytical values could not be obtained for this compound.

Photolysis of **21**-4: The two [2 + 2] cycloadducts were separated by column chromatography [ether/petroleum ether (1:3)].

5-Oxatricyclo[6.4.0.0^{1,6}]dodecan-9-one **49**: IR (film): $\tilde{\nu}$ = 1700 cm^{-1} (s). – ^{1}H NMR (500 MHz): δ = 3.97 (t, J = 6.6 Hz, 1 H), 3.76 (ddd, J = 4.3 Hz, J = 7.6 Hz, J = 11.5 Hz, 1 H), 3.53 (dt, J = 4.7 Hz, J = 11.4 Hz, 1 H), 2.56 (dd, J = 4.6 Hz, J = 10.0 Hz, 1 H), 2.48 (ddd, J = 6.2 Hz, J = 10.0 Hz, J = 11.7 Hz, 1 H), 2.41 (dt, J = 5.6 Hz, J = 14.7 Hz, 1 H), 2.34 (ddd, J = 4.6 Hz, J = 7.0 Hz, J = 11.6 Hz, 1 H), 2.25 (ddd, J = 5.3 Hz, J = 9.8 Hz, J = 15.1 Hz, 1 H), 1.91 (m, 4 H), 1.7 (dt, J = 13.7 Hz, J = 5.2 Hz, 1 H), 1.6 (m, 2 H), 1.46 (ddd, J = 4.0 Hz, J = 6.7 Hz, J = 13.2 Hz, 1 H). – Two isomeric 2,4-dinitrophenylhydrazones of **49** were obtained.
a) m.p. 129.5 – 131.5 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.97 H 5.40 N 15.28

b) m.p. 168.5 – 169.5 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.91 H 5.63 N 15.51

5-Oxatricyclo[6.4.0.0^{1,6}]dodecan-9-one **50**: IR (film): $\tilde{\nu}$ = 1695 cm^{-1} (s), 1055 (m). – ^{1}H NMR (500 MHz): δ = 4.02 (dd, J = 6.2 Hz, J = 11.6 Hz, 1 H), 3.74 (dt, J = 3.6 Hz, J = 12.3 Hz, 1 H), 3.20 (dd, J = 7.0 Hz, J = 10.8 Hz, 1 H), 2.64 (dt, J = 10.7 Hz, J = 9.2 Hz, 1 H), 2.55 (dt, J = 9.4 Hz, J = 6.9 Hz, 1 H), 2.46 (ddd, J = 5.7 Hz, J = 13.5 Hz, J = 16.6 Hz, 1 H), 2.36 (m, 2 H), 2.08 – 2.0 (m, 2 H), 1.97 (dd, J = 1.4 Hz, J = 15.0 Hz, 1 H), 1.87 (br. d, J = 15 Hz, 1 H), 1.80 (ddd, J = 1.6 Hz, J = 5.2 Hz, J = 12.1 Hz, 1 H), 1.67 (m, 2 H), 1.45 (br. d, J = 10.9 Hz, 1 H).
2,4-Dinitrophenylhydrazone of **50**: m.p. 204 – 205 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.91 H 5.56 N 15.25

Isomerization of **34** *and* **46**: 50 mg of **34** and **46**, respectively, were dissolved in 3 ml of methanol and treated with 30 mg of K_2CO_3 for several days at room temp. Some water was added, and the ketone was extracted with ether. The ethereal extract was dried with Na_2SO_4. The solvent was evaporated, and the products **36** and **45** were purified by column chromatography.

10-Methoxytricyclo[5.2.1.0^{1,6}]decan-5-one (**36**): FT IR: $\tilde{\nu}$ = 1730 cm^{-1} (s). – ^{1}H NMR (360 MHz): δ = 3.46 (d, J = 4.8 Hz, 1 H), 3.13 (s, 3 H), 2.95 (s, 1 H), 2.38 (dt, J = 14.6 Hz, J = 4.0 Hz, 1 H), 2.30 (m, 1 H), 2.12 (m, 1 H), 2.04 (d, J = 4.7 Hz, 1 H), 1.74 – 1.88 (m, 2 H), 1.55 – 1.72 (m, 5 H).
2,4-Dinitrophenylhydrazone of **36**: m.p. 148 – 150 °C.

$C_{17}H_{20}N_4O_5$ (360.37) Calcd. C 56.66 H 5.59 N 15.55
Found C 56.36 H 5.63 N 15.15

Solvolysis of **37**-3,4 *and* **38**-3,4: 1.5 ml of 1 N HCl was added to a solution of 50 mg of the photoproduct in 15 ml of cyclohexane, and the mixture was stirred for 30 min. It was neutralized with saturated aqueous $NaHCO_3$, and the products were extracted with ether. The organic extract was dried (Na_2SO_4) and the solvents removed. Purification of the residue by column chromatography [ether/petroleum ether (1:3)] afforded **40**-4 and **41**-3,4, respectively.

7-Oxospiro[4.5]decylcarbaldehyd Dimethyl Acetal (**41**-3): IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (s). – ^{1}H NMR (90 MHz): δ = 4.2 [d, J = 8 Hz, 1 H, $CH(OCH_3)_2$], 3.35 (s, 3 H, OCH_3), 3.3 (s, 3 H, OCH_3), 1.4 – 2.4 (m, 15 H).

$C_{13}H_{22}O_3$ Calcd. 226.31 Found 225.15 [M$^+$ – 1] (HR MS)

8-Oxospiro[5.5]decylcarbaldehyd Dimethyl Acetal (**41**-4): IR (film): $\tilde{\nu}$ = 1705 cm^{-1} (s). – ^{1}H NMR (90 MHz): δ = 4.4 [d, J = 2 Hz, 1 H, $CH(OCH_3)_2$], 3.35 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 1.1 – 2.5 (m, 17 H).

$C_{14}H_{24}O_3$ Calcd. 240.33 Found 209.15 [M$^+$ – CH_3O] (HR MS)

8-Oxospiro[5.5]decylcarbladehyde (**40**-4): IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (s). – ^{1}H NMR (90 MHz): δ = 9.9 (d, J = 3 Hz, 1 H, CHO), 1.1 – 2.6 (m, 17 H).

$C_{12}H_{18}O_2$ Calcd. 194.26 Found 194.13 (HR MS)

Measurement of Quantum Yields: Solutions 0.1 M of the dienones in cyclohexane were degassed by the freeze-thaw method and irradiated to 0.5–12% conversion by using a 366-nm interference filter and the potassium ferrioxalate actinometer developed by Hatachard and Parker[41]. The reactions were monitored by analytical VPC. The sensitization experiments were performed in the same concentration range at a concentration of 0.5 M of acetophenone. In the quenching experiments the solutions contained freshly distilled piperylene in a concentration range of 0.2–1.8 M. The accuracy of the quantum yields given in Table 5 is estimated to be ±3%.

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(*cis*)-**19**-2: 121056-69-7 / (*trans*)-**19**-2: 121056-70-0 / (*cis*)-**19**-3: 141462-55-7 / (*trans*)-**19**-3: 141462-56-8 / (*cis*)-**19**-4: 141462-57-9 / (*trans*)-**19**-4: 141462-58-0 / **20**-2: 121056-72-2 / **20**-3: 121056-73-3 / **21**-2: 121056-74-4 / **21**-4: 121056-75-5 / **22**-2: 2969-81-5 / **22**-3: 14660-52-7 / **22**-4: 25542-62-5 / **23**-2: 24157-02-6 / **23**-3: 78643-42-2 / **23**-4: 78633-23-5 / **24**-2: 141462-68-2 / **24**-3: 141462-69-3 / **24**-4: 141462-70-6 / **25**-2: 38771-21-0 / **26**-2: 69361-41-7 / **26**-3: 66927-74-0 / **27**-2: 141462-71-7 / **27**-3: 141462-72-8 / **28**-2: 141462-73-9 / **28**-3: 136408-25-8 / **29**: 54396-74-6 / **30**: 141462-74-0 / **31**: 141462-75-1 / **32**-2: 76320-22-4 / **32**-4: 61589-86-4 / **33**: 121056-76-6 / **33** (=NNHDNP): 141462-64-8 / **34**: 121123-99-7 / **34** (=NNHDNP): 141552-64-9 / **35**: 121124-00-3 / **35** (=NNHDNP): 141552-65-0 / **36a**: 141552-63-8 / **36** (=NNHDNP): 141552-71-8 / **37**-3: 121056-77-7 / **37**-4: 121056-78-8 / **38**-3: 121124-01-4 / **38**-4: 121124-02-5 / **40**-4: 141462-63-7 / **41**-3: 141462-61-5 / **41**-4: 141462-62-6 / **42**: 121056-79-9 / **42** [(*E*) =NNHDNP]: 141462-65-9 / **42** [(*Z*) =NNHDNP]: 141552-66-1 / **43**: 121056-80-2 / **43** [(*E*) =NNHDNP]: 141462-66-0 / **43** [(*Z*) =NNHDNP]: 141552-67-2 / **44**: 121124-03-6 / **44** [=NNHDNP]: 141552-68-3 / **45**: 121056-81-3 / **46**: 121056-82-4 / **47**: 121056-83-5 / **48**: 141462-60-4 / **49**: 121056-84-6 / **49** [(*E*) =NNHDNP]: 141462-67-1 / **49** [(*Z*) =NNHDNP]: 141552-69-4 / **50**: 121124-04-7 / **50** (=NNHDNP): 141552-70-7 / 2-(3-hydroxymethyl-1-cyclohexenyloxy)ethanol: 141462-59-1 / 3-ethoxy-2-cyclohexen-1-one: 5323-87-5