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PHOTOCHEMISTRY OF β,γ-ENONES—VIII[1]

ON THE REMARKABLE PHOTOSTABILITY OF SOME $\beta,\gamma.\beta',\gamma'$-DIENONES AND THE 1,3-ACYL SHIFT PHOTOREACTIVITY OF TWO $\beta,\gamma.\gamma',\delta'$-DIENONES

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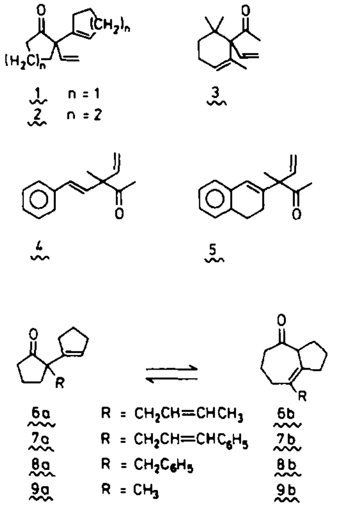
Abstract—The direct irradiation of the $\beta,\gamma.\beta',\gamma'$-dienones **1–5** and the $\beta,\gamma.\gamma',\delta'$-dienones ($E$)-**6a**, ($E$)-**7a** and **8a** at λ 300 nm has been studied. The $\beta,\gamma.\beta',\gamma'$-dienones **1–5** are remarkable photostable for $\lambda \geqslant 300$ nm, even upon prolonged irradiation, in contrast to simple β,γ-enones which upon irradiation exhibit α-cleavage, γ-hydrogen abstraction, (E)–(Z) isomerization and oxetane formation. The observed photostability of the $\beta,\gamma.\beta',\gamma'$-dienones is rationalized in terms of a rapid radiationless decay of the excited singlet state, enhanced by CT-interaction between the carbonyl ^{1}(n-π^*) state and the homoconjugated 1,4-diene moiety, which precludes fluorescence, photochemical reactions and intersystem crossing (ISC).

The $\beta,\gamma.\gamma',\delta'$-dienones ($E$)-**6a**, ($E$)-**7a** and **8a** exhibit only a 1,3-acyl shift (1,3-AS) without (E)–(Z) isomerization of the alkenyl moiety, to yield (E)-**6b**, (E)-**7b** and **8b**. It is concluded that the 1,3-AS proceeds from the ^{1}(n-π^*) state with a rate which is very large relative to the rate of ISC to the ^{3}(n-π^*) state, thus precluding any internal triplet energy transfer (ITET) from the ^{3}(n-π^*) to the ^{3}(π-π^*) state which would manifest itself by (E)–(Z) isomerization.

The sustained research on β,γ-enones in recent years is related to the complexity of the photochemistry of these bichromophoric systems. The overwhelmingly intriguing features which determine the pathways of energy conversion by luminescence, intersystem crossing, radiationless decay and photochemical reactions form an unremitting challenge for many photochemists. At the outset of the present work, the photochemistry of $\beta,\gamma.\beta',\gamma'$-dienones had only been examined fragmentarily. More thorough and detailed studies were still lacking probably due in part to the absence of a readily accessible synthetic route to theses dienones.[2]

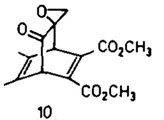
β,γ-Enones exhibit various types of photochemical reactions, such as oxetane formation, γ-hydrogen abstraction with formation of e.g. cyclobutanol derivatives, α-cleavage, ODPM rearrangements and (E)–(Z) isomerization. Recent reports from our laboratories[3] have shown that acyclic β,γ-enones upon direct irradiation in solution at λ 300 nm exhibit an efficient α-cleavage followed by a 1,3-acyl shift (1,3-AS) and decarbonylation. The 1,3-AS was shown to proceed at least in part via radical pair intermediates which are of singlet or triplet nature depending on the type of β,γ-enone.[3] Also some (E)–(Z) isomerization was observed, due to ISC of the carbonyl ^{1}(n-π^*) moiety and subsequent internal triplet energy transfer (ITET) to the alkenyl moiety. Usually this process is not efficient enough to afford an ODPM-rearrangement. Engel,[4a,b] Nakanishi,[4c] and Cerfontain[3] studied the effect of α-methyl substitution on the α-cleavage. The incipient allylic stabilization in the transition state leading to α-cleavage seems to determine the efficiency of the α-cleavage. Consequently we were highly interested in the photochemical properties of dienones, such as **1–5**, in which a highly stabilized radical pair would be formed upon α-cleavage.

In the literature a number of *rigid* $\beta,\gamma.\beta',\gamma'$-dienones are reported which exhibit photochemical reactivity.



Scheme 1. The dienones **1–8** studied by direct irradiation at λ 300 nm.

Becker and Ruge[5a] investigated the direct irradiation of several bicyclo[2.2.2]octadienones, such as **10**, at $\lambda > 290$ nm and observed fragmentation as result of α-cleavage with formation of benzene derivatives and ketenes. The direct irradiation of benzobarrelenone **11**[5b] leads to the formation of the α-cleavage products naphthalene and ketene, and further to the 1,3-AS isomer of **11** all in high yield. Ipaktschi showed photochemical reactivity of 7-isopropylidenebicyclo[2.2.1]hept-5-en-2-one **12** and its benzo analogue **13**.[6] Further Fuchs[7a] examined the formation of 2-oxabicyclo[3.2.2]nona-6,8-dien-2-one **14** upon direct irradiation of 2,3,8,9-tetrahydroinden-1-one resulting from a 1,3-AS which appears to be photoreversible, besides the formation of other acyl



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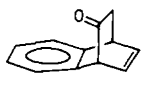

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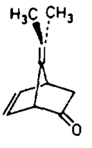

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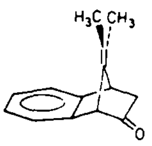

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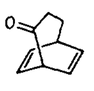

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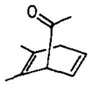

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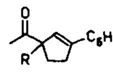
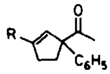
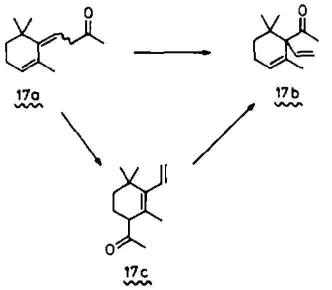
cleavage products such as benzene and 3-phenylpropanal. The related 1-acetyl-1,2-dimethylcyclohexa-2,4-diene **15** leads to the 1,3-AS isomer which conversion is photo-irreversible.[7b]





16a R = H 16c

16b R = CH$_3$ 16d



17a 17b 17c

With another type of $\beta,\gamma.\beta',\gamma'$-dienones, in which there is *no rigid* orientation of the carbonyl chromophore to be excited with respect to the diene system, the photochemistry appears to be fully inhibited, as will now be discussed. The methyl 3-phenylcyclopent-2-enyl ketones **16a** and **16b** upon direct irradiation at $\lambda > 290$ nm, are fully converted into their 1,3-AS isomers **16c** and **16d**, respectively.[8] However, it was shown that this reaction is *irreversible*, i.e. the methyl 1-phenylcyclopent-2-enyl ketones **16c** and **16d** proper fail to react *via* an intramolecular photochemical 1,3-AS. Only in the presence of **16a**, the 1,3-AS of **16c** occurs to some extent, but this inefficient process is induced by **16a** and thus intermolecular, as was established in experiments using substrates with deuterated acetyl groups.

Also in the ionone chemistry[9] the 1,3-AS product **17b**, formed upon irradiation of *retro*-α-ionone **17a**, appears to be photostable, whereas the 1,5-AS product is photoreactive affording the 1,3-AS isomer. This result is in strong contrast with the photochemistry of dienone **14**, where the $\beta,\gamma.\delta,\varepsilon$-dienone formed by a 1,3-AS is the favoured isomer in the photostationary state.[7]

In order to gain more insight into the photochemistry of the $\beta,\gamma.\beta',\gamma'$-dienones we have investigated the direct irradiation of the dienones **1–5**. In addition we have examined the photochemistry of the three $\beta,\gamma.\gamma',\delta'$-dienones (*E*)-**6a**, (*E*)-**7a**, and **8a**.

RESULTS

UV studies. The UV spectra of the $\beta,\gamma.\beta',\gamma$-dienones **1–5** (see Fig. 1) are quite similar to those of alkyl substituted β,γ-enones[3a,d] in that the n-π^* transition is similarly disturbed by homoconjugation, as appears from their λ_{max} and ε_{max} (Table 1). The n-π^* character of the absorption at 302 nm of **1** is apparent from the 5 nm shift to shorter wavelength for ethanol as compared with cyclohexane as solvent. The intensities of the (n-π^*) absorptions of the $\beta,\gamma.\gamma',\delta'$-dienones (*E*)-**6a**, (*E*)-**7a** and **8a** are similar to those of the $\beta,\gamma.\beta',\gamma$-dienones **1–5** and greater than that of **9a** (*cf.* Tables 1 and 2). The enhanced (n-π^*) absorption is typical for γ,δ-enones (*cf.* Fig. 2) and illustrates significant interaction between the carbonyl and olefinic bond.[10]

Table 1. UV absorption data of the $\beta,\gamma.\beta'\gamma'$-dienones 1–5 and related compounds in cyclohexane.

Solute	λ_{max}(nm)	ε (l.mol^{-1}.cm^{-1})
1	302	136
2	288	91
3	288	67
4	293	1320
	284	1620
5	293	2290
	284	2730
cyclopentanone	300	18.5
cyclohexanone	288	15.5
styrene	289	635
	281	900
	245	14700
(*E*)-3,3-diethyl-5-phenylpent-4-en-2-one[3d]	294	2400
	285	2810
	253	20000

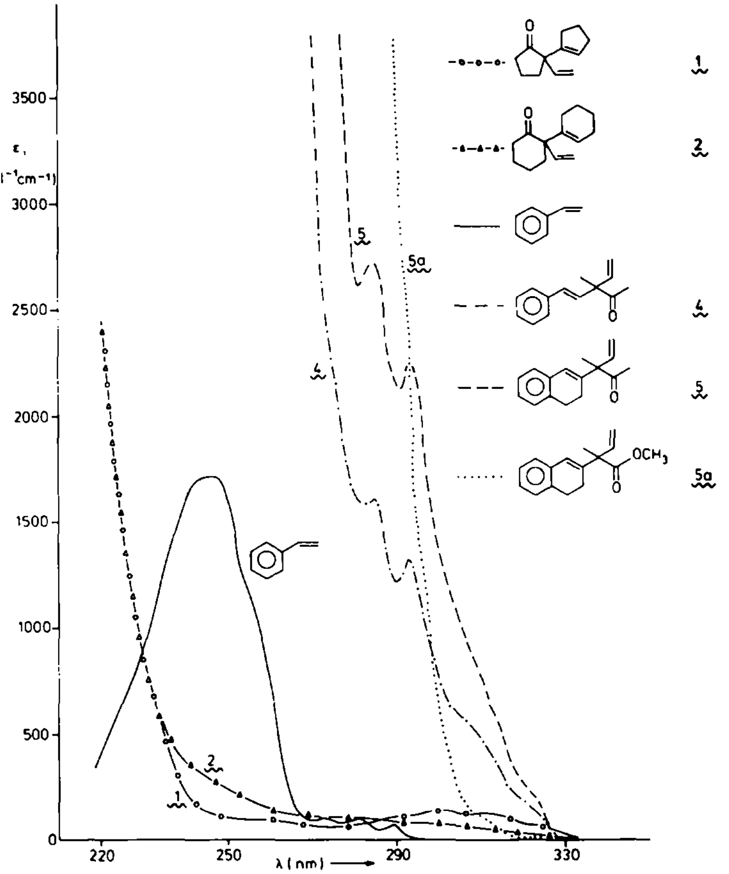


Fig. 1. UV spectra of $\beta,\gamma,\beta',\gamma'$-dienones and related compounds. The spectrum of **3** is very similar to that of **2**.

Table 2. UV absorption data of the $\beta,\gamma,\gamma',\delta'$-dienones (*E*)-**6a** (*E*)-**7a**, **8a**, the β,γ-enone **9a**, and cyclopentanone in cyclohexane

Solute	λ_{max}(nm)	ε (l.mol^{-1}.cm^{-1})
(*E*)-**6a**	327	71
	313	148
	302	160
	293	132
	253	409
(*E*)-**7a**	325 (no max)	88
	315	171
	303	317
	295	560
	287	700
8a	325 (no max)	96
	315	204
	303	228
	295 (no max)	200
	266	288
	260	349
	253	324
9a	325	53
	315	97
	303	133
	293	113
	255	156
Cyclopentanone	324	6.6
	312	14.6
	300	18.5
	289	18.0

Direct irradiation of the dienones **1–5**, (*E*)-**6a**, (*E*)-**7a**, and **8a**. The direct irradiation of the dienones **1–5** at λ 300 nm in cyclohexane, acetonitrile, and isopropyl alcohol as solvent was monitored with GLC, HPLC, TLC and ^{1}H-NMR. With **1–5** no product formation was observed. Even after prolonged irradiation of **1–3** no photoconversion was detected with GLC using an internal standard and with **4** and **5** the decomposition was only very slow (*ca.* 10% in 3 weeks). The $\beta,\gamma,\gamma',\delta'$-dienones (*E*)-**6a**, (*E*)-**7a**, and **8a** exhibit a 1,3-AS and eventually, after three days of irradiation a photostationary state of **a**/**b** was obtained of 0.66, 0.24, and 0.47 respectively *without* (*E*)–(*Z*) isomerization. The 1,3-acyl products were isolated with preparative GLC and their spectral data were in accordance with those of the 1,3-AS product of the enone **9a** (Experimental) for which the photostationary state ratio **a**/**b** is 1.38.[16]

Emission studies on **1–5**, (*E*)-**6a**, (*E*)-**7a**, *and* **8a**. Fluorescence studies employing solutions of **1–5** in cyclohexane have been carried out at room temperature on a Spex apparatus. Except for **2** which showed a very weak fluorescence at λ 395 nm no emission was observed. The fluorescence quantum yield of **2** was estimated to be less than one percent of that of cyclohexanone for which $\phi_{fl} = 1.7 \times 10^{-3}$.[11] The excitation spectrum at λ_{em} 400 nm showed a maximum at λ_{exc} = 305 nm which agrees well with the n-π^* absorption maximum of **2** at λ 300 nm. The fluorescence of (*E*)-**6a**, (*E*)-**7a**, **8a**, and **9a** was also examined with a Zeiss fluorometer, but in the region of

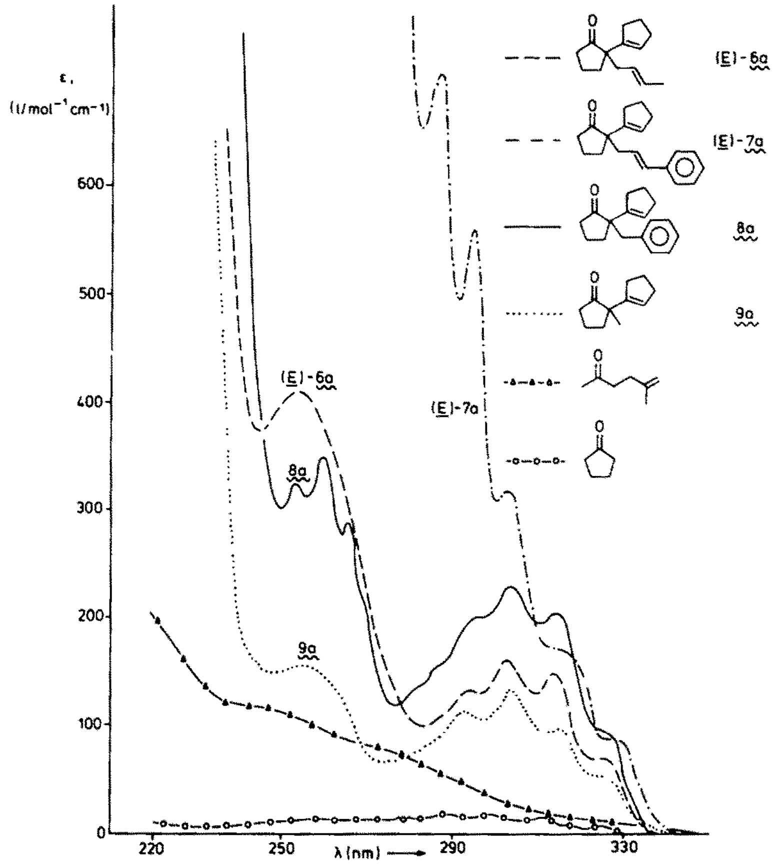


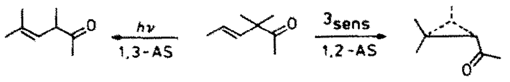
Fig. 2. UV spectra of the $\beta,\gamma.\gamma'\delta'$-dienones (*E*)-**6a**, (*E*)-**7a**, **8a**, and related compounds.

λ 380–450 nm no signals were detected. Cyclopentanone itself fluoresces very weakly at λ_{em} = 405 nm with $\phi_{fl} = 1.6 \times 10^{-3}$. With (*E*)-**6a**, (*E*)-**7a**, **8a**, and **9a** only a weak fluorescence was seen at λ = 329 nm, which is probably due to an impurity in the samples (*N.B.* previously, this weak fluorescence was ascribed to excimer fluorescence of the ketones).[12]

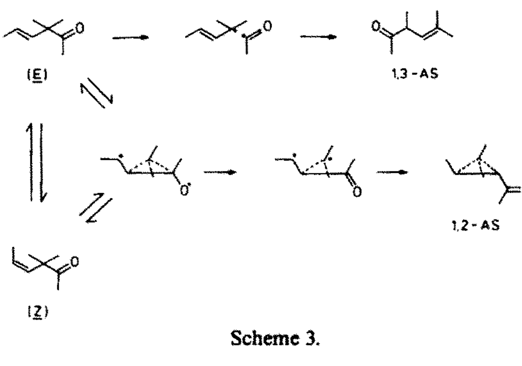
CIDNP studies of the $\beta,\gamma.\beta',\gamma'$-dienones **1–5** *and* **17b**. Certain β,γ-enones are known to react *via* radical pairs in the 1,3-AS rearrangement, as was illustrated by Schaffner[13] and Cerfontain[3b,d] on the basis of CIDNP studies. In order to gain more insight concerning the possibility of a *reversible* α-cleavage a CIDNP study has been performed on the $\beta,\gamma.\beta',\gamma'$-dienones **1–5** and **17b** during the direct irradiation at λ 300 nm with the objective to detect possible (bi)radical pairs. With none of the substrates in the various solvents studied (benzene, chloroform, acetonitrile, methanol and dichloromethane) any CIDNP signal was observed, not even after accumulation of 20 repeated scans (the reference samples di-t-butyl ketone and cycloheptanone both already exhibited strong signals after one scan!). Thus the photo-excited $\beta,\gamma.\beta',\gamma'$-dienones **1–5** and **17b** do not undergo an α-cleavage unless this process is very fast relative to the NMR time scale (10^{-7} sec).

DISCUSSION

The photostability of $\beta,\gamma.\beta',\gamma'$-dienones. Two types of particularly interesting rearrangements of β,γ-enones were frequently studied, *viz* the 1,3-AS and the 1,2-AS (Scheme 2). The latter is usually referred to as the oxa-di-π-methane (ODPM) rearrangement and is often accompanied by (*E*)–(*Z*) isomerization. The mechanisms of these two rearrangements are quite different as is illustrated in Scheme 3 for the situation where they proceed non-concertedly, i.e. *via* radicals (1,3-AS) and biradicals (1,2-AS). Both rearrangements are related to the nature of the preceding excited state. Thus the 1,3-AS can be ascribed to a (n-π*) state initiated cleavage and the ODPM rearrangement to an initial bridging of



Scheme 2.



Scheme 3.

the excited π-π^* state with the carbonyl carbon, forming a 1,4-biradical, followed by conversion into a 1,3-biradical with subsequent ring closure to yield the 1,2-AS product.[14] Recently the mechanism of the 1,3-AS has received considerable attention. At present, there is substantial evidence that it is not only the ^{1}(n-π^*) state that undergoes the 1,3-AS.[15] There are now a number of examples for which it is in fact more likely that the ^{3}(n-π^*) state is responsible for the 1,3-AS.[15a] Schuster[15b] observed a relationship between the increase in the quantum yield of the 1,3-AS and the decrease in the fluorescence quantum yield upon enhancing the rate of ISC by heavy atom perturbation with xenon. He further noted the absence of competition between the 1,3-AS and the fluorescence for several β,γ-enones.[15c] However, based on the absence of the heavy atom effect for a series of α-halogen substituted bicyclic enones Givens[15e] concluded that an enhancement in the rate of radiationless decay rather than in that of the ISC must be responsible for the singlet decay and thus for the low quantum yields of the 1,3-AS.

The present results reveal that α-vinyl substitution of non-rigid β,γ-enones leads to substrates which are fully photostable for direct irradiation at λ 300 nm. This contrasts with the photochemistry of various types of β,γ-enones and rigid β,γ.β′,γ′-dienones.[14] Most remarkable is the absence of α-cleavage products with the dienones **1**,[16] **4**, and **5**,[3] as well as the absence of γ-hydrogen abstraction with the dienones **2**, **3**, and **5**,[4a,b,17] and further the lack of (*E*)-(*Z*) isomerization, established for dienone **4**[3] which is a very common reaction for β,γ-enones[3b–d] in which the carbon–carbon double bond is not a constraint in a too small ring. The latter result indicates that the low-lying ^{3}(π-π^*) is not populated at all.[18] The lack of population of—and thus of reaction from—the ^{3}(π-π^*) state may be the result from either the non-occurrence of ISC from the excited ^{1}(n-π^*) state or a too low rate of ITET from the upper ^{3}(n-π^*) state to the lower ^{3}(π-π^*) state compared with that of radiationless decay.

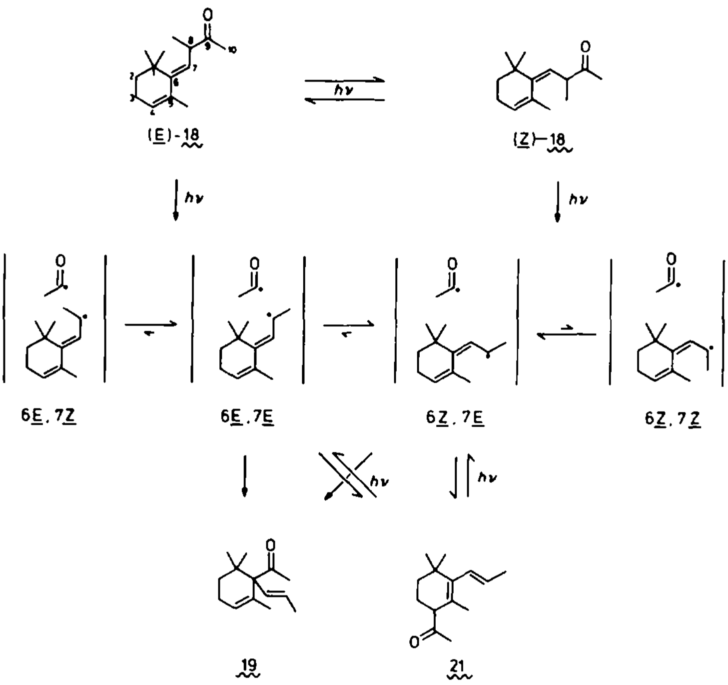
The fluorescence quantum yields of the β,γ.β′,γ′-dienones **1**–**5** are at most very small when compared with those of other types of β,γ-enones.[15b] This result suggests an efficient quenching of their ^{1}(n-π^*) state. In rigid β,γ.β′,γ′-dienones the excited ^{1}(n-π^*) chromophore leads efficiently to α-cleavage,[5–7] whereas our non-constrained dienones are photostable.[8,9]

Now the question arises which mechanism is responsible for the non-productive internal conversion of our type of β,γ.β′,γ′-dienones. There are in principle three mechanisms for radiationless decay which may intervene with the photoreactivity. The *first* mechanism consists of a normal [^{1}(n-π^*) $\rightarrow$ ^{3}(n-π^*)] ISC, followed by a rapid ITET to the vinyl group, and a subsequent degenerate (*E*)-(*Z*) isomerization. The *second* mechanism is based on the frequently encountered α-cleavage process in β,γ-enones, but which with the β,γ.β′,γ′-dienones would be a fast degenerate process. The *third* mechanism presumes intramolecular CT-interaction between the (n-π^*) state (singlet or triplet) and the homodiene system which strongly enhances the radiationless decay to the ground state.

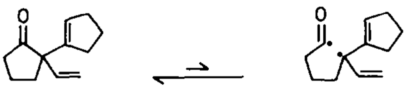
As to the *first* mechanism, the photostability of **4** would infer a selective degenerate (*E*)-(*Z*) isomerization of the vinyl group, since no (*E*)-(*Z*) isomerization of the styryl group is observed. This now is highly unlikely since the ITET from the ^{3}(n-π^*) state will be much more rapid to the styryl than the vinyl group, the former being strongly exothermic [$\Delta E \simeq E_T$ (acetone) $- E_T$ (styrene) $= 80$[19] $- 62$[19] $= 18$ kcal/mol] and the latter strongly endothermic [$\Delta E \simeq E_T$ (acetone) $- E_T$ (propene) 80[19]–99[20] $= -19$ kcal/mol].

It is of interest to elaborate the photochemistry of the ionones investigated by van Wageningen,[9a] who examined the direct irradiation at λ 300 nm of the *retro*-α-ionones **18**. Two products were formed, which were isolated by GLC, *viz* the (*E*)-isomers of the 1,3-AS and 1,5-AS products **19** and **21**, but not the corresponding (*Z*)-isomers. Further upon direct irradiation of the 1,3-AS product **19** proper at λ 300 nm no monomeric products were found.[21] Upon direct irradiation hex-4-en-2-one[22] exhibits a fast (*E*)-(*Z*) isomerization. Thus if **19** would not be photostable, then significant amounts of the (*Z*)-isomer **20** would have been formed. The mere isolation of the (*E*)-isomer **19** indicates that the eventual photostationary state—if (*E*)-(*Z*) isomerization occurs at all—is strongly in favour of **19**, with $[(\mathbf{19})/(\mathbf{20})]_{\text{pss}} \geqslant 25$. As to the explanation of the formation of the (*E*)-configurations of the 1,3-AS and 1,5-AS products, it should be recalled that the conversion of the related *retro*-α-ionone **17a** into the 1,3-AS and 1,5-AS isomers was concluded on the basis of a CIDNP study to proceed *via* singlet radical pairs.[9b] It is thought that the *retro*-α-ionone **18** also reacts *via* singlet radical pairs (*cf.* Scheme 4). For steric reasons the most stable dienyl radical resulting from the α-cleavage have the 7(*E*)-configuration, as appears from studies of molecular Catalin Stewart models (also in simple β,γ-enone photochemistry, the product formation was found to be determined by steric factors in the radical intermediates).[3d] Upon recombination of the dienyl and acetyl radicals the exclusively observed (*E*)-isomers of the 1,3-AS and 1,5-AS products **19** and **21** are formed. The 1,5-AS (*E*)-isomer **21** affords eventually the 1,3-AS (*E*)-isomer **19** again *via* the acetyl dienyl radical pair. The absence of formation of **20** (i.e. the (*Z*)-isomer of **19**) upon irradiation of **18** seems to rule out the possibility of radiationless decay *via* degenerate (*E*)-(*Z*) isomerization as explanation for the photostability of the β,γ.β′,γ′-dienones **1**–**5** and **17b**.

Let us now consider the *second* mechanism (*cf* Scheme 5). Attempts to arrest a reversible α-cleavage of the dienones **1**–**5** all failed, as no CIDNP signals have been observed at all. As was pointed out by Seeman and Ziffer[23] this does not completely exclude the possibility of an intimate radical pair, but it then has to collapse very rapidly with respect to the NMR time scale. However, some other results also argue against the fast reversible α-cleavage explanation. Firstly, non-rigid β,γ.β′,γ′-dienones are photostable (see before), whereas bridged—i.e. rigid—β,γ.β′,γ′-dienones show photochemical α-cleavage[5–7a] and even yield strained cyclobutanones.[5b] Secondly, the fluorescence quantum yield of simple aliphatic ketones increases upon increasing the number of methyl groups at C_α which was explained in terms of a decrease in the vibrational deactivation induced by the C_α—H stretching vibration.[11,24] The fluorescence intensity of cyclic ketones also depends on the degree of α-methyl substitution.[11] A similar dependence of the fluorescence intensity on the degree of α-methyl substitution was reported for unsaturated β,γ-enones.[15b] The diminished radiationless decay *via* C_α—H stretching of



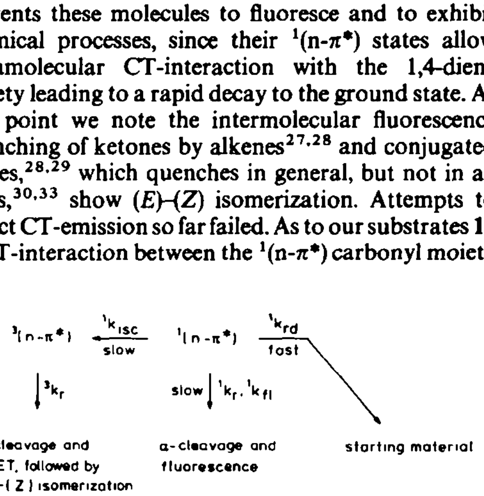
Scheme 4. Photochemistry (λ 300 nm) of the ionones **18** and **21**.



Scheme 5. Hypothetic reversible α-cleavage from the excited $^1(n\text{-}\pi^*)$ state of dienone **1**.

β,γ-enones upon increasing the degree of α-methyl substitution may also be related to the enhanced degree of α-cleavage. In that case the α-cleavage will be slower for hex-4-en-2-one than for t-butyl methyl ketone, as is in fact observed,[3c,22] whereas incipient radical stabilization in the transition state would predict the reverse [the bond dissociation energies for $CH_2{=}CHCH_2{-}H$ and $(CH_3)_3\,C{-}H$ being 88.6 and 92 kcal/mol respectively[19]].[25] Finally we note the similarity of the fluorescence intensities of acetone, 2-heptanone, (*E*)-hex-4-en-2-one and (*E*)-hept-6-en-2-one, whereas the γ,δ-enone (*E*)-hept-5-en-2-one exhibits no fluorescence.[26] Accordingly, we dismiss the possibility of radiationless decay *via* C_α—CO stretching in the β,γ.β′,γ′-dienones **1–5**. Although a (reversible) α-cleavage is not thought to be responsible for the photostability of **1–5** and thus for the absence of (*E*)-(*Z*) isomerization in dienone **4**, this mechanism satisfactorily explains the absence of (*E*)-(*Z*) isomerization of the β,γ.γ′,δ′-dienones (*E*)-**6a** and (*E*)-**7a** (see later).

Finally we will discuss the *third* mechanism in which the photostability is ascribed to a rapid internal conversion of the excited singlet state due to intramolecular CT-interaction (Scheme 6). The quenching of the $^1(n\text{-}\pi^*)$ state of ketones and α-diketones by "electron-rich" and "electron-poor" alkenes[27,28] and conjugated dienes[28,29] is usually ascribed to the formation of intermolecular CT-complexes which species allow a fast radiationless decay. There is a direct correlation between the efficiencies of various acyclic alkenes and conjugated dienes in quenching the fluorescence of ketones and α-diketones and their ionization potentials which observation is strongly indicative for an electron charge-transfer mechanism.[4b,28,30–32] The virtual absence of fluorescence of the β,γ.β′,γ′-dienones **1–5**, as compared with simple aliphatic ketones[24a] and β,γ-enones,[15c,26] indicates a rapid and (almost) complete deactivation of the $^1(n\text{-}\pi^*)$ state to the ground state. The β,γ.β′,γ′-dienones **1–5** can be considered as aliphatic ketones containing an intramolecular quencher which prevents these molecules to fluoresce and to exhibit chemical processes, since their $^1(n\text{-}\pi^*)$ states allow intramolecular CT-interaction with the 1,4-diene moiety leading to a rapid decay to the ground state. At this point we note the intermolecular fluorescence quenching of ketones by alkenes[27,28] and conjugated dienes,[28,29] which quenches in general, but not in all cases,[30,33] show (*E*)-(*Z*) isomerization. Attempts to detect CT-emission so far failed. As to our substrates **1–5**, CT-interaction between the $^1(n\text{-}\pi^*)$ carbonyl moiety



Scheme 6. Chemical and physical processes of the $^1(n\text{-}\pi^*)$ state of non-rigid β,γ.β′,γ′-dienones. The superscripts stand for the multiplicity of the excited state and the subscripts r, fl, rd, and isc for reaction, fluorescence, radiationless decay, and intersystem crossing respectively.

and the homodiene system allows an efficient route for radiationless decay. At most a limited twist of the alkenyl bond(s) which does not lead to (*E*)–(*Z*) isomerization may occur. The torsional vibration of the alkenyl double bond is thought to be enhanced upon CT-interaction with the carbonyl ^{1}(n-π) state in view of the reduced carbon–carbon bond strength of the alkenyl radical cation moiety[34] and this provides a route for rapid internal conversion of the excited singlet state.

It is interesting to note the photostability of the related α-phenyl-β,γ-enones **16c** and **16d**,[8] where a CT-interaction can again occur between the carbonyl ^{1}(n-π*) state and the homoconjugated 3-phenylcyclopentene system. This type of interaction is again thought responsible for the photostability, as it will lead to an enhanced rate of internal conversion, although the twist of the cyclopentene double bond will be restricted due to the limited size of the 5-membered ring.

Also the photoreactivity of bridged β,γ.β′,γ′-dienones **10–14** is readily explained. The geometric orientation of the exocyclic carbonyl group and the 1,4-diene in **10–14** is now such that the CT-interaction will be much less than with the non-constraint β,γ.β′,γ′-dienones **1–5**. Direct irradiation of **12** and **13** does yield the 1,3-AS isomers,[6] despite the possibility of decay via a degenerate (*E*)–(*Z*) isomerization.[35]

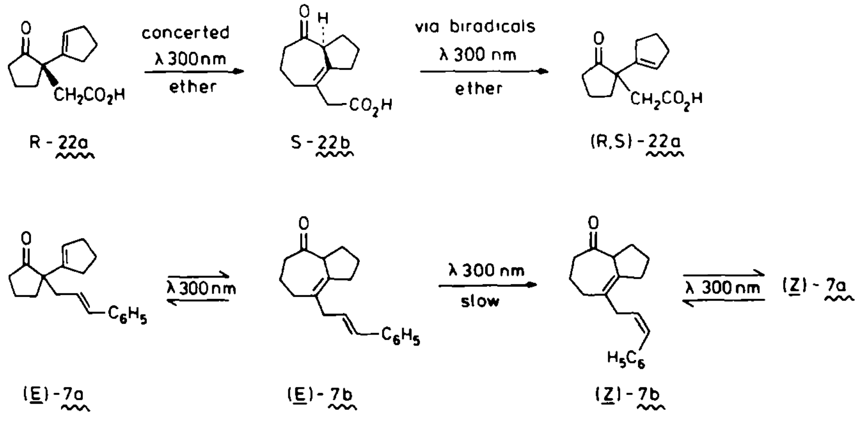
The photochemistry of β,γ.γ′,δ′-dienones. Upon direct irradiation the dienones (*E*)-**6a**, (*E*)-**7a** and **8a** show a 1,3-AS which process was reported previously for enone **9a**.[16] With (*E*)-**6a** and (*E*)-**7a** the (*E*)–(*Z*) isomerization is at most very slow relative to the reversible 1,3-AS. This may be explained in terms of a very fast α-cleavage of the ^{1}(n-π*) state with the resulting radical sites recombining to yield the 1,3-AS or the starting compound. Clearly no ISC to the ^{3}(n-π*) state takes place which would yield by a fast ITET the ^{3}(π-π*) state which would manifest itself by (*E*)–(*Z*) isomerization. In other words with (*E*)-**6a** and (*E*)-**7a**, the efficient α-cleavage from the ^{1}(n-π*) yielding the 1,3-AS product prevents the (*E*)–(*Z*) isomerization which is often encountered with the more simple γ,δ-enones.[11,26]

The absence of (*E*)–(*Z*) isomerization with (*E*)-**6a** and (*E*)-**7a** corroborates the mechanistic investigations of Givens on a chiral 2-cyclopent-1′-enylcyclopentanone (*cf* Scheme 7).[16] The 1,3-AS of (*R*)-**22a** is stereospecific with formation of the β,γ-enone (*S*)-**22b**. The detailed examination revealed that this conversion must be ascribed to a singlet rearrangement in a concerted fashion, i.e. a suprafacial 1,3-AS. The reverse photo 1,3-AS leads to an extensive loss of stereochemical integrity in the process of ring contraction [thus (*S*)-**22b** $\xrightarrow{h\nu}$ (*R*, *S*)-**22a**] which was explained in terms of "a biradical process with stereo-equilibration".[16]

The occurrence of some (*E*)–(*Z*) isomerization of (*E*)-**7b**, i.e. the 1,3-AS isomer of (*E*)-**7a**, upon prolonged irradiation (2 weeks) with λ 300 nm [which is also responsible for the formation of substantial amounts of the (*Z*)-**7a** isomer in the reaction mixture] leads to the conclusion that there is some ISC from the ^{1}(n-π*) state of (*E*)-**7b** to the ^{3}(n-π*) state which can exhibit α-cleavage leading to 1,3-AS and ITET leading to (*E*)–(*Z*) isomerization. The mechanism for the ring contraction of the dienones (*E*)-**6b** and (*E*)-**7b** thus differs significantly from the 1,3-AS of (*E*)-**6a** and (*E*)-**7a**; this result is in line with the photoracemization of enone (*R*)-**22a** observed by Givens.[16]

In order to establish the usefulness of intramolecular alkenyl moieties as sensors for short living ^{3}(n-π*) states of β,γ-enones, as appears from the occurrence of (*E*)–(*Z*) isomerization of the alkenyl group, further studies are in progress.

Comparison of the photoreactivities of β,γ-enones, β,γ.β′,γ′-dienones and β,γ.γ′,δ′-dienones. β,γ-Enones[3,4a–c] (e.g. **8**) and β,γ.γ′,δ′-dienones [e.g. (*E*)-**6a** and (*E*)-**7a**] upon direct irradiation with λ 300 nm are photoreactive, whereas non-constraint β,γ.β′,γ′-dienones (like **1–5**) are photostable. The photostability of the latter type of substrates was ascribed to an enhanced rate of internal conversion of the excited singlet state as result of an enhanced degree of CT-interaction, as compared with the former two types of substrates (see before). For the CT-interaction of a ^{1}(n-π*) carbonyl and a ground state alkene two types of interaction may be considered, *viz* the π (alkene) → n (n-π* carbonyl) and the π* (n-π* carbonyl) → π (alkene), of which the former has been proposed to apply to alkyl substituted ethenes.[31b] Now for the β,γ.β′,γ′-dienones the energy gap between the HOMO of the homoconjugated 1,4-diene and the highest n orbital of the carbonyl group will be smaller than that between the comparable MO's in a β,γ-enone and β,γ.γ′,δ′-dienones. This infers that the CT-interaction will be stronger with the



Scheme 7. Photochemistry of 2-cyclopent-1′-enylcyclopentanones.

$\beta,\gamma.\beta',\gamma'$-dienones **1–5** than the β,γ-enones and $\beta,\gamma.\gamma',\delta'$-dienones.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 257 grating IR spectrometer or a Perkin–Elmer 298 instrument using a neat film of purified oils or solns in CHCl$_3$. The ^{1}H-NMR spectra were recorded on either a Varian A60-D, a Varian XL 100-FT, or Bruker WM250 using TMS as internal standard. UV spectra were recorded on a Cary 14 spectrometer.

The fluorescence spectra were recorded with a Zeiss ZFM 4c spectrometer. The excitation wavelength was selected from the emission of a high-pressure Xenon arc (Osram XBO, 450 W, operated at 25 A direct current) by a Zeiss M4Q III monochromator. The fluorescence was detected at right angles by an EMI 9785 photomultiplier *via* a second motor-driven M4Q III monochromator. The signal was amplified by a Zeiss PMQ II amplifier and recorded on a Philips PM 8100 multirange recorder. The excitation spectra were recorded in order to check the emission signal of the samples. Some of the fluorescence spectra were also recorded with a SPEX-Fluorolog instrument. This instrument, in contrast to the former, provides options for on-line correction of both the excitation and emission spectra. Prior to obtaining the fluorescence measurements the compounds were carefully and repeatedly purified by distillation, gas–liquid chromatography, and/or liquid chromatography to ensure that the observed fluorescence is not due to impurities.

The GLC analyses were carried out on a Varian Model-3700 chromatograph and the semi-preparative GLC separations were conducted using a Varian Model-2700 chromatograph.

The mass spectra were obtained using a Varian MAT-711 double focussing mass spectrometer or a Varian AEI-MS-902 instrument, equipped with an all-glass heated inlet system at 15 and 70 eV.

The synthesis of the $\beta,\gamma.\beta',\gamma'$-dienones **1–5** and **17b** was described before.[1,2,9]

Preparation of the $\beta,\gamma.\gamma'\delta'$*-dienones* (E)-**6a**, (E)-**7a** *and* **8a**. To a soln of 1.38 g (33.5 mmol) t-BuOK (Aldrich) in 125 ml t-BuOH, 5 g (33.5 mmol) 2-cyclopentylidenecyclopentanone was added at room temp over a period of 30 min under N$_2$. After 4 hr, 1.05 eq. of the required alkyl halogenide, *viz* (*E*)-crotyl chloride (Fluka), (*E*)-cinnamyl bromide,[37] and benzyl bromide (Aldrich) for the preparation of respectively **6a**, **7a** and **8a**, was added at once. The soln was stirred overnight (it decolorized slowly after 30 min) to afford a milky white soln. The t-BuOH was removed under reduced pressure and the residue was dissolved upon addition of 200 ml of water and 100 ml of ether. The layers were separated and the aqueous layer was thoroughly extracted with ether. The combined ether extracts were washed with water and brine, dried on MgSO$_4$ and filtered. The ether was removed to afford the crude $\beta,\gamma.\gamma',\delta'$-dienones as a slightly yellow coloured product. Attempts to crystallize the resulting oils failed. The crude products were distilled under reduced pressure yielding 2.2 g (32%) colourless (*E*)-**6a**, b.p. 85° (0.02 mm Hg), 0.7 g (18%) slightly yellow (*E*)-**7a**, b.p. 135° (0.01 mm Hg), and 1.2 g (15%) **8a**, b.p. 105° (0.02 mm Hg). The distilled products contained some impurities which were removed using preparative GLC for (*E*)-**6a** on a copper column [$l = 1.5$ m, $\phi = 1/4$ in., Chromosorb W-AW (60–80 mesh), coated with 15% SE-30 at 195°], for (*E*)-**7a** on a copper column [$l = 2$ m, $\phi = 1/4$ in., Chromosorb W-AW (60–80 mesh), coated with 5% OV-101 at 260°], and for **8a** on a copper column [$l = 2$ m, $\phi = 1/4$ in., Chromosorb W-AW (60–80 mesh), coated with 10% DC-550 at 220°]. The carrier gas employed was helium at a flow rate of 60 ml/min.

2 - (*Cyclopent* - 1′ - *enyl*) - 2 - [(E) - *but* - 2″ - *en* - 1″ - *yl*]*cyclopentanone* (E)-**6a**. ^{1}H-NMR (CDCl$_3$)-100 MHz (δ in ppm): 5.6–5.0 (m, 2H, olef.), 5.50 (br. t, 1H, olef.), 2.5–1.5 (m, 17H, aliph.); IR (liq. cap.): 3065 (m), 3040 (m), 2960 (s), 2900 (s), 2855 (s), 1735 (s), 1640 (m), 1470 (m), 1450 (s), 1440 (m), 1410 (m), 1380 (w), 1155 (s), 970 (s) cm^{-1}.

2-(*Cyclopent*-1′-*enyl*)-2-[(E) - 3″- *phenylprop* - 2″- *en* - 1″-*yl*] *cyclopentanone* (E)-**7a**. ^{1}H-NMR (CDCl$_3$)-250 MHz (δ in ppm): 7.35–7.14 (m, 5H, arom.), 6.37 (d, J = 17 Hz, 1H, olef.), 6.02 (dt, J = 17, 7 Hz, 1H, olef.), 5.53 (m, 1H, olef.), 2.57 (ddd, J = 14, 7, 2 Hz, 1H, HC$\underline{\text{H}}$—CH=CH), 2.37 (ddd, J = 14, 7, 2 Hz, 1H, $\underline{\text{H}}$CH—CH=CH); IR (liq. cap.); 3100 (w), 3070 (m), 3040 (m), 2960 (s), 2900 (s), 2855 (s), 1735 (s), 1640 (s), 1600 (m), 1560 (w), 1500 (m), 1450 (m), 1405 (m), 1150 (s), 970 (s), 740 (s), 690 (s) cm^{-1}.

2 - (*Cyclopent* - 1′ - *enyl*) - 2 - *benzylcyclopentanone* **8a**. ^{1}H-NMR (CDCl$_3$)-100 MHz (δ in ppm): 7.3–7.0 (m, 5H, arom.), 5.05 (m, 1H, olef.), 2.87 (d, J = 14 Hz, 1H, HC$\underline{\text{H}}$—Ph), 2.71 (d, J = 14 Hz, 1H, $\underline{\text{H}}$CH—Ph), 2.5–1.5 (m, 12H, aliph.); IR (liq. cap.): 3080 (m), 3060 (m), 3025 (m), 2960 (s), 2880 (s), 2845 (m), 1735 (s), 1600 (m), 1490 (m), 1450 (m), 1400 (m), 1150 (m), 1040 (m), 1030 (m), 760 (m), 740 (m), 700 (s) cm^{-1}.

The ^{1}H-NMR and IR absorptions of the ring systems of (*E*)-**6a**, (*E*)-**7a**, and **8a** are similar to those of the enone **9a** (see below).

2 - (*Cyclopent*-1′-*enyl*)-2-*methylcyclopentanone* **9a**.[16] ^{1}H-NMR (CDCl$_3$)-100 MHz (δ in ppm): 5.40 (m, 1H, olef.), 2.4–2.0 (m, 7H, aliph.), 2.0–1.5 (m, 5H, aliph.), 1.10 (s, 3H, CH$_3$); IR (liq. cap.): 3050 (w), 2960 (s), 2930 (s), 2900 (m), 2860 (m), 2840 (m), 1735 (s), 1450 (m), 1400 (m), 1365 (w), 1325 (w), 1150 (m), 1050 (m), 950 (m), 930 (m), cm^{-1}.

General procedure for the direct irradiation. A soln of the appropriate dienone [**1–5**, (*E*)-**6a**, (*E*)-**7a**, and **8a**] in cyclohexane was irradiated at λ 300 nm in a Rayonet RPR-208 photoreactor, equipped with eight RUL 3000 lamps using pyrex vessels. The dienones **1**, **4** and **5** were also irradiated at the same wavelength in acetonitrile and MeOH as solvent. Prior to the irradiation the solns were purged with dry N$_2$ for 15 min. Analysis by GLC, HPLC and TLC during the irradiaiton, usually with an internal standard, revealed that no products had been formed. The dienones **1–3** appeared to be fully photostable over a period of 3 weeks, whereas the dienones **4** and **5** decomposed very slowly (*ca* 10% in 1 week) yielding only polymeric products. The enone **9a** afforded one single product, *viz* the 1,3-AS isomer **9b** as described.[16] After 3 days a photostationary state was reached with $[[\mathbf{9a}]/[\mathbf{9b}]]_{pss} = 1.38$. Removal of the solvent and subsequent GLC purification afforded a colourless liquid. The formation of the 1,3-AS isomer **9b** is easily illustrated by the new absorption at 3.92 ppm due to the C—H between the carbonyl and olefinic bond, and the absence of the olefinic proton at 5.40 ppm. Further in the IR spectrum the olefinic C—H of **9a** at 3.28μ is absent for **9b**, and the C=O band at 5.80μ for **9a** is observed for **9b** at 5.87μ.

2-*Methylbicyclo*[5.3.0]*dec*-1-*en*-6-*one* **9b**.[16] ^{1}H-NMR (CDCl$_3$)-250 MHz (δ in ppm): 3.92 (br. s, 1H, aliph.), 2.5–1.5 (m, 12H, aliph.), 1.64 (s, 3H, CH$_3$). IR (liq. cap.): 2950 (s), 2870 (m), 2830 (m), 1710 (s), 1450 (m), 1430 (m), 1335 (w), 1250 (w) cm^{-1}.

Irradiation of dienone (*E*)-**6a** yielded one very predominant product, *viz* the 1,3-AS isomer (*E*)-**6b**. No trace of (*E*)-**6a** and (*E*)-**6b** could be detected by GLC on an OV-101, SE-30, DC-550 and Carbowax-20 M type of column. The ^{1}H-NMR spectrum of (*E*)-**6b** has an olefinic pattern which is very reminiscent to that of (*E*)-crotyl chloride. Further the IR absorption of (*E*)-**6b** at 10.41μ is characteristic for the (*E*)-configuration of alkenes;[38] it is also seen with (*E*)-hex-4-en-2-one (10.36μ)[22] and (*E*)-hept-5-en-2-one (10.33μ).[26] The related characteristic absorption for the (*Z*)-configuration at *ca* 14.4μ [for (*Z*)-hex-4-en-2-one at 14.8μ[22] and (*Z*)-hept-5-en-2-one at 14.38μ[26]] was absent. After prolonged irradiation the starting compound (*E*)-**6a** also fully maintained the (*E*)-configuration, as was apparent from the presence of the 10.41μ absorption and the absence of any absorption at *ca* 14.4μ.

2-[(E)-1′-*But*-2′-*enyl*]*bicyclo*[5.3.0.]*dec*-1-*en*-6-*one*(E)-**6b**. ^{1}H-NMR (CDCl$_3$)-250 MHz (δ in ppm): 5.40–5.33 (m, 2H, olef.), 3.92 (m, 1H, aliph.), 2.61 (m, 2H, bisallylic CH$_2$), 2.53–2.30 (m, 3H, aliph.), 2.25–2.00 (m, 5H, aliph.), 1.80–1.45

(m, 4H, aliph.), 1.61 (d, J = 7 Hz, 3H, allylic CH_3); IR (liq. cap.): 3010 (m), 2950 (s), 2870 (s), 2830 (m), 1705 (s), 1445 (m), 1430 (m), 1330 (m), 960 (s) cm^{-1}.

Dienone (*E*)-**7a** upon irradiation at λ 300 nm afforded only one product. After three days of irradiation the solvent of the irradiated mixture was removed under reduced pressure and both the starting compound as well as the 1,3-AS isomer were isolated by preparative GLC using the conditions described for the preparation of (*E*)-**7a** (see before). Both the dienone **7a** and its slightly yellow coloured 1,3-AS isomer **7b** had the (*E*)-configuration, as appeared from the ^1H-NMR vinylic hydrogen coupling constants of 17 and 15 Hz, respectively. The olefinic pattern was very similar to that of (*E*)-cinnamyl bromide. The IR of dienone **7a** and its 1,3-AS isomer **7b** both exhibit the olefinic absorption which is characteristic for the (*E*)-configuration, *viz* at 10.34 and 10.38μ respectively.

(*Z*)-**7a** was obtained by the sensitized irradiation (λ 360 nm) of (*E*)-**7a** using *m*-methoxyacetophenone as triplet sensitizer; it was isolated by preparative GLC, as described for (*E*)-**7a** (see before). The (*Z*)-configuration is apparent from the specific ^1H-NMR coupling constant (J = 12.5 Hz). The IR spectrum of the (*Z*)-isomer is very similar to that of the (*E*)-isomer, except that the 10.35μ absorption is absent and replaced by an absorption at 14.3μ (see later).

After prolonged irradiation of the photostationary state of (*E*)-**7a** and (*E*)-**7b** increasing amounts of the corresponding (*Z*)-isomers [(*Z*)-**7a** and (*Z*)-**7b**] become apparent, *ca* 15 and 30% after 1 and 2 weeks of irradiation respectively. The separation of the (*E*)- and (*Z*)-isomers of the 1,3-AS product **7b** failed. According to the IR and ^1H-NMR spectra the (*Z*)-**7a** eventually obtained by prolonged direct irradiation of (*E*)-**7a** proved to be identical with the compound obtained upon sensitized irradiation (see before).

2-[(E)-3′-*Phenylprop-2′-en-1′-yl*]*bicyclo*[5.3.0]*dec-1-en-6-one* (E)-**7b**. ^1H-NMR ($CDCl_3$)-250 MHz (δ in ppm): 7.35–7.15 (m, 5H, arom.), 6.41 (d, J = 15 Hz, 1H, C=CHPh), 6.10 (dt, J = 15, 7 Hz, 1H, CH_2—C$\underline{H}$=C), 3.96 (br. t, 1H, aliph.), 2.75–1.50 (m, 14H, aliph.); IR (liq. cap.): 3080 (w), 3060 (w), 3020 (m), 2950 (m), 2870 (m), 2850 (m), 1705 (s), 1670 (s), 1600 (m), 1495 (m), 1430 (m), 1175 (w), 965 (m), 695 (s) cm^{-1}.

2-(*Cyclopent-1′-enyl*)-2-[(Z)-3″-*phenylprop-2″-en-1″-yl*]*cyclopentanone* (*Z*)-**7a**. ^1H-NMR ($CDCl_3$)-250 MHz (δ in ppm): 7.37–7.14 (m, 5H, arom.), 6.48 (d, J = 11 Hz, 1H, CH=C$\underline{H}$Ph), 5.55 (m, 1H, C=C$\underline{H}$—CH_2CH_2), 5.50 (dt, J = 11, 7 Hz, C$\underline{H}$=CHPh), 2.77 (ddd, J = 16, 7, 1.5 Hz, 1H, HC$\underline{H}$—CH=), 2.44 (ddd, J = 16, 7, 1.5 Hz, 1H, $\underline{H}$CH—CH=), 2.38–2.05 (m, 7H, aliph.), 1.92–1.77 (m, 5H, aliph.); IR (liq. cap.): 3080 (w), 3055 (m), 3020 (m), 2955 (s), 2890 (m), 2865 (m), 2850 (m), 1735 (s), 1640 (m), 1600 (w), 1495 (m), 1465 (w), 1445 (m), 1405 (m), 1150 (m), 775 (s), 695 (s) cm^{-1}.

Irradiation of **8a** at λ 300 nm afforded predominantly **8b** with in addition a very minor product which was not isolated.

2-*Benzylbicyclo*[5.3.0]*dec-1-en-6-one* **8b**. ^1H-NMR ($CDCl_3$)-250 MHz (δ in ppm): 7.31–7.03 (m, 5H, arom.), 4.00 (br. t, 1H, C(7)H), 3.34 (s, 2H, C$\underline{H}_2$Ph), 2.65–1.50 (m, 12H, aliph.); IR ($CHCl_3$): 3080 (w), 3060 (m), 3030 (m), 3000 (m), 2950 (s), 2930 (s), 2870 (m), 2850 (m), 1700 (s), 1650 (m), 1600 (w), 1490 (m), 1450 (m), 1335 (m), 1140 (m), 695 (s) cm^{-1}.

CIDNP experiments. The CIDNP studies were carried out in Groningen with a Varian XL-100 ^1H-NMR instrument with a home-made probe. The radiation source was a high-pressure mercury lamp (Phillips, SP 1000W) in a lamphouse with a quartz window. The light was guided into the probe on the spinning NMR tube with a polished quartz stave (l = 40 cm, ϕ = 8 mm) and filtered through an aqueous $NiSO_4$ soln (80 g/l) with a pathlength of 50 mm in order to limit the radiation to the wavelength region of 230–350 nm. Pyrex vessels were used to cut off the radiation of 230–290 nm. The selected program parameters were 4s for the aquisition time (AT), 33 μs for the pulse width (PW), 10s for the pulse delay (PD), 5s for the irradiation period (IP) and 0.1s for the radiation delay (RD). The CIDNP difference spectrum was obtained with the following program: [PD-IP-RD-PW-(+AT)-PD-PW-(AT)]. The concentrations of the irradiated solns of the dienones **1**–**5** were 0.04–0.10 mol/l.

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