Photochemistry of Acylic βγ-Unsaturated Ketones. Part 4.[1] The Effect of α-Methyl Substitution with Some Hex-4-en-2-ones and 1-Phenylpent-3-en-1-ones [2]

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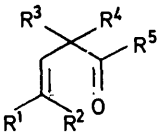
The photochemistry of the two hex-4-en-2-ones (1a and b), and the three 1-phenylpent-3-en-1-ones (1c—e) have been studied. Upon direct irradiation (1a) shows exclusively (*E*)–(*Z*) isomerization, whereas (1b) yields only α-cleavage products, illustrating competition between (*E*)–(*Z*) isomerization and α-cleavage for the hex-4-en-2-ones. Upon direct irradiation of (1c) no photochemical reaction is observed, but with (1d and e) products resulting from the α-cleavage reaction are obtained. Upon triplet sensitized irradiation (1a and b) yield the corresponding (*Z*)-isomers, but (1d) gives α-cleavage products. The difference in α-cleavage ability between (1a and c) on the one hand and (1b, d, and e) on the other upon direct irradiation is ascribed to the effect of α-methyl substitution. The difference in the photochemical behaviour of the hex-4-en-2-ones (1a and b) compared with that of the 1-phenylpent-3-en-1-ones (1c—e) is rationalized in terms of differences in the triplet state energy levels of the two types of βγ-enones.

βγ-UNSATURATED ketones (βγ-UKs) can exhibit a variety of light-induced reactions,[3] which are characteristic for each of the two π-moieties present in these compounds, *viz.* the alkene and the carbonyl. The carbonyl (*n*–π*) photoreactions are α-cleavage and hydrogen abstraction. The alkene (π–π*) photoreactions are (*E*)–(*Z*) isomerization and oxa-di-π-methane (ODPM) rearrangement. From the triplet excited state of alkenes the (*E*)–(*Z*) isomerization is a highly efficient process,[4] and the occurrence of this process may therefore serve as an indication of the presence of triplet excited alkenes. α-Cleavage occurs upon direct irradiation of some alkyl substituted hex-4-en-2-ones.[5,6] (*E*)-Hex-4-en-2-one (1a) exhibits (*E*)–(*Z*) isomerization upon direct irradiation,[7] but (*E*)-4-ethyl-3,3-dimethylhex-4-en-2-one yields the (*Z*)-isomer only upon triplet sensitized irradiation.[6b] There is no systematic study on the influence of α-methyl substituents on the photochemical behaviour of hex-4-en-2-ones [*viz.* α-cleavage and (*E*)–(*Z*) isomerization] and it was therefore decided to investigate the photochemistry of (1a and b).



(1)

a; $R^1 = R^5 = Me, R^2 = R^3 = R^4 = H$
b; $R^1 = R^3 = R^4 = R^5 = Me, R^2 = H$
c; $R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = Ph$
d; $R^1 = R^3 = R^4 = Me, R^2 = H, R^5 = Ph$
e; $R^1 = R^2 = R^3 = R^4 = Me, R^5 = Ph$
f; $R^1 = R^3 = R^4 = H, R^2 = R^5 = Me$
g; $R^1 = R^2 = R^3 = R^5 = Me, R^4 = H$
h; $R^1 = R^2 = R^3 = Me, R^4 = H, R^5 = Ph$
i; $R^1 = H, R^2 = R^3 = R^4 = R^5 = Me$

The α-cleavage of hex-4-en-2-ones occurs from the triplet excited (*n*–π*) state.[8] Upon triplet sensitized irradiation (*E*)-4-ethyl-3,3-dimethylhex-4-en-2-one yields only the (*Z*)-isomer,[6b] indicating that the triplet excited (π–π*) state has a lower energy than the triplet excited (*n*–π*) state. The triplet energies of the isolated chromophores (E_T 79—82 kcal mol^{-1} for acetone;[9] E_T 78 kcal mol^{-1} for the twisted triplet state of but-2-ene [9]) in fact indicate that the triplet (*n*–π*) level will have a higher energy content than the twisted triplet (π–π*) level.

It was thought of interest to study βγ-UKs in which the energy of the triplet (*n*–π*) state would be below that of the (π–π*) state, and to compare the photochemical behaviour of this type of compounds with that of the hex-4-en-2-ones. The 1-phenylpent-3-en-1-ones (1c—e) in which the carbonyl carries a phenyl group meet this requirement as the energy of their triplet excited (*n*–π*) state will be of the same value as that of acetophenone (E_T 74 kcal mol^{-1}).[9]

RESULTS

Direct Irradiation of Compounds (1a *and* b).—The photoproducts obtained upon irradiation (λ 310 nm) of (1a and b) in 2,2-dimethylbutane (DMB) are shown in Scheme 1.

TABLE 1

Quantum yields of substrate disappearance and product formation for the direct irradiation (310 nm) of (1a, b, and d) in 2,2-dimethylbutane

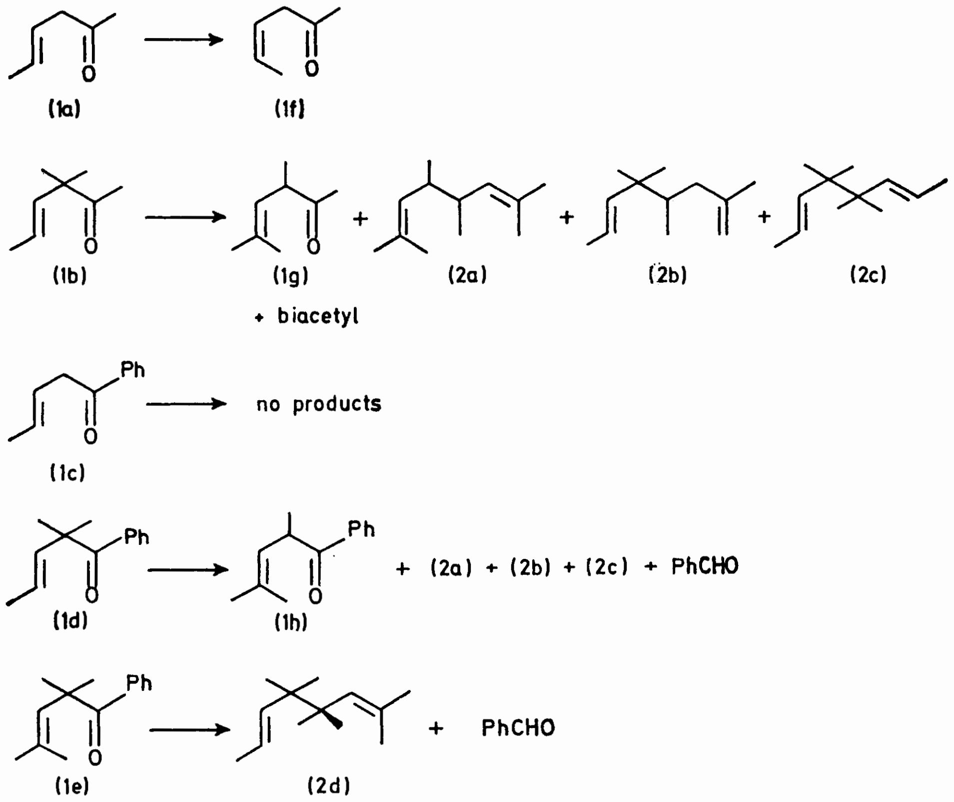
	φ			
Substrate	Ketone	Allyl recombinations	1,3-Acyl shift	*Z*-Isomer
(1a)	0.6 [a]			0.5 [a]
(1b)	0.64	0.16^{8}	0.16^{8}	
(1d)	0.39	0.02^{1}	0.08^{5}	
(1g)	0.38^{5}	0.09^{5}	0.05^{7}	

[a] The accuracy of this datum is low due to overlap of the g.l.c. peaks of the (*E*)- and (*Z*)-isomer.

With (1a) initially the (*Z*)-isomer (1f) is formed, but upon prolonged irradiation some products with a larger g.l.c. retention time are detected, as was also reported for (1a) by Morrison.[7]

Upon direct irradiation of (1b) α-cleavage products are formed, *viz.* the 1,3-acyl shift product (1g), the three octa-2,6-dienes (2a—c), formed in a 1 : 2 : 1 ratio as was also observed for (1g) as substrate,[5] and minute amounts of biacetyl. No (*Z*)-isomer could be detected amongst the photoproducts of (1b), illustrating the difference in photochemical behaviour between (1a and b). The quantum yields for substrate disappearance and product formation with (1a and b) are given in Table 1.

Direct Irradiation of (1c—e).—The direct irradiation (λ 310 nm) of (1c) in DMB did not lead to any substrate conversion. In contrast (1d and e) then yield α-cleavage products (see Scheme 1). These are with (1d) the 1,3-acyl shift product (1h), the three octa-2,6-dienes (2a—c), and benzaldehyde, and with (1e) the octa-2,6-diene (2d) and benzaldehyde. The occurrence of only one allyl recombination product and the fact that no 1,3-acyl shift product is obtained with (1e), is due to the symmetry of the allyl radical formed upon α-cleavage. For (1d) the quantum yields for substrate disappearance and product formation are given in Table 1. At low conversion of (1d) (*ca.* 10%) the ratio (1h) : [(2a) + (2b) + (2c)] : PhCHO = 8 : 2 : 1, whereas at high conversion (*ca.* 80%) this ratio is 5 : 6 : 2. This indicates that the 1,3-acyl shift product (1h) also yields α-cleavage products. Eventually upon prolonged irradiation the octa-2,6-dienes (2a—c) are the only g.l.c. detectable volatile products.



SCHEME 1 Photoproducts upon direct irradiation (λ 310 nm) of the acylic βγ-unsaturated ketones (1a—e) in 2,2-dimethylbutane

The absence of any photoreactivity of (1c), even upon prolonged irradiation, is surprising. Direct irradiation (λ 360 nm) of (1c) in DMB in the presence of tri-n-butyltin hydride leads to the formation of the corresponding alcohol *viz.* 1-phenylpent-3-en-1-ol (3), indicating † that the (n–π^*) excited state of the substrate is in fact formed.

Triplet Sensitized Irradiation of (1a *and* b).—Upon acetone triplet sensitized irradiation of (1a and b) the corresponding (*Z*)-isomers (1f and i) are formed, but no α-cleavage products could be detected. These results indicate that the lowest triplet state of the βγ-UKs (1a and b) is of mainly π–π^* character.

Triplet Sensitized Irradiation of (1d).—Acetophenone triplet sensitized irradiation of (1d) yields the 1,3-acyl shift product (1h). It was not possible to establish the formation of the octa-2,6-dienes (2a—c) and benzaldehyde by the g.l.c. analysis applied as the peak of the sensitizer overlapped with those of these possible photoproducts. No (*Z*)-isomer of (1d) is formed under these conditions. From these results it is concluded that the lowest triplet state of (1d) is of mainly n–π^* character.

DISCUSSION

There is a striking difference in the photochemical behaviour of (1a and b) upon direct irradiation. With (1a), the (*Z*)-isomer is formed and hardly any α-cleavage products, but (1b) yields α-cleavage products and no (*Z*)-isomer. This difference cannot be ascribed to differences in the energy levels between the triplet n–π^* and π–π^* states as the triplet sensitization experiments pointed out that the lowest triplet state of both compounds is of π–π^* character. The diverse photochemical behaviour is ascribed to a very much lower rate of α-cleavage of (1a) as compared with (1b) as a result of the absence of the two α-methyl groups. The α-cleavage is thus accelerated by α-methyl substitution, leading to a reduction of the formation of the (*Z*)-isomer.

With (1g) [5] and (1b) the allyl and acyl radicals formed in the α-cleavage step are the same. This is reflected by

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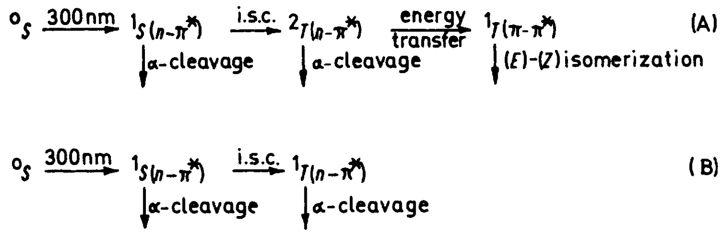
† Carbonyl compounds upon direct irradiation in the presence of good hydrogen atom donors are reduced to the corresponding alcohols by reaction of the triplet (n–π^*) excited state.[10]

the equality of the ratio between the quantum yields for the formation of the allyl recombination product and the substrate disappearance for the two substrates [0.25 for (1g) and 0.26 for (1b)]. The ratio between the quantum yields for 1,3-acyl shift product formation and substrate disappearance is 0.15 for (1g) and 0.26 for (1b). This indicates that the combination of the acetyl radical at the secondary site of the allyl radical is faster than at the tertiary site, which is in contrast to the relative reactivity of these two sites, observed for the recombination of these allyl radicals (see Results).

The ratios between the quantum yields for the 1,3-acyl shift product formation and substrate disappearance are about the same for (1b and d), *viz.* 0.26 and 0.22, respectively. This is not surprising as the only difference between (1b and d) is in the substituent at the carbonyl group [Me with (1b) *versus* Ph with (1d)]. The quantum yields proper for both the 1,3-acyl shift product formation and the substrate disappearance are however two times larger for (1b) than for (1d). Accordingly the lower energy content of the n–π^* excited state of the acetophenone part of (1d) (E_T 74 kcal mol^{-1}[9]) compared with that of the acetone part of (1b) (E_T 79—82 kcal mol^{-1}[9]) must be responsible for the lower degree of α-cleavage of (1d) compared with (1b). The same difference [as between (1b and d)] in the substituent at the carbonyl group exists between (1a and c), and again there is a large difference in α-cleavage ability of the two substrates [with (1a) some α-cleavage is found but this process is absent with (1c)]. Thus, on going from the excited state to the α-cleavage products the larger the exothermicity the higher the degree of α-cleavage. This photochemical behaviour is also apparent with the saturated carbonyl compounds, *e.g.* on comparing the photochemistry of phenyl t-butyl ketones with that of methyl t-butyl ketones.[11]

It is surprising that the degree of α-cleavage is at most very small with (1a and c),† but very substantial with methyl t-butyl ketone and phenyl t-butyl ketone,[11] since the allyl radical is somewhat more stable than the t-butyl radical [the bond dissociation energies of the $(CH_3)_3C$–H and CH_2=CH–CH_2–H bonds are 92 and 88 kcal mol^{-1}, respectively [12]]. The very low degree of α-cleavage with (1a and c) then infers that the incipient allylic stabilization in the transition state leading to α-cleavage is insufficient, and smaller than the incipient t-butyl stabilization.

The occurrence of (E)–(Z) isomerization upon triplet sensitization of (1a and b) illustrates that their lowest triplet excited state is of π–π^* character. CIDNP experiments with some methyl substituted hex-4-en-2-ones [8] showed that the α-cleavage is a reaction from the triplet excited (n–π^*) state. From the observation that no α-cleavage takes place upon triplet sensitization it must be concluded that the triplet (n–π^*) state (^2T) is of higher energy than the triplet (π–π^*) state (^1T). This energy content order of the triplet states of hex-4-en-2-ones is consistent with the triplet energies of the isolated π-moieties, since the triplet energy of acetone (n–π^*) is 80 kcal mol^{-1}[9] and that of the twisted state of but-2-ene (π–π^*) 78 kcal mol^{-1}.[9]



Interconversions of electronically excited states of two types of βγ-UKs and their photochemical reactions. (A), Hex-4-en-2-ones; (B), 1-phenylpent-3-en-1-ones

The photochemical and photophysical processes of the βγ-UKs can be understood by considering the alkene and carbonyl moieties in first approximation as isolated.‡ Direct irradiation [λ 310 nm (E 92 kcal mol^{-1})] of the hex-4-en-2-ones (1a and b) leads only to excitation of the carbonyl $^1S(n$–$\pi^*)$ state [$E_{S(n-\pi^*)}$ 88 and $E_{S(\pi-\pi^*)}$ 130 kcal mol^{-1}[9]], as shown schematically in the Figure. From this state intersystem crossing to $^2T(n$–$\pi^*)$ occurs which state exhibits α-cleavage, if the βγ-UK contains α-methyl substituents [as with (1b)], as was in fact established by CIDNP.[8] From $^2T(n$–$\pi^*)$ energy transfer to $^1T(\pi$–$\pi^*)$ § may occur which state exhibits (E)–(Z) isomerization [as observed with (1a)]. || This model of isolated π-moieties clearly explains the observation that no (E)–(Z) isomerization from $^1T(\pi$–$\pi^*)$ is observed with (1b), as the

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† With 5-methylhex-4-en-2-one Engel observed small amounts of products resulting from α-cleavage.[6b]

‡ In fact there is a weak interaction between the two π-moieties, as is apparent from the enhanced n–π^* absorption of the βγ-UKs relative to that of the saturated analogues.

§ This energy transfer is non-vertical as the triplet excited carbonyl yields a twisted triplet excited alkene moiety.

|| By using the expression ' energy transfer ' instead of ' internal conversion ' the choice was made to describe the acyclic βγ-UKs as consisting of two isolated π-moieties. The consequence of the alternative, *i.e.* of considering these compounds as containing one homoconjugative chomophore would be that the $^1S(n$–$\pi^*)$ state could undergo two transitions *viz.* one to $^2T(n$–$\pi^*)$ and another to $^1T(\pi$–$\pi^*)$. The occurrence of (E)–(Z) isomerization upon direct irradiation of (1a) could then be explained by an $^1S(n$–$\pi^*) \longrightarrow {}^1T(\pi$–$\pi^*)$ transition. The absence of any (E)–(Z) isomerization with (1b) upon direct irradiation indicates that the $^1S(n$–$\pi^*) \longrightarrow {}^1T(\pi$–$\pi^*)$ transition does not occur with that substrate. We could not think of any apparent explanation why the latter transition would occur with (1a) and not with (1b). Accordingly the initial concept in which the βγ-UKs are described as consisting of two isolated π-moieties is preferred.

α-cleavage from $^{2}T(n-\pi^*)$ will be very fast due to the presence of two α-methyl groups and apparently fast relative to the $^{2}T \longrightarrow {}^{1}T$ conversion. With (1a) in the absence of α-methyl groups the α-cleavage is slow and allows the $^{2}T \longrightarrow {}^{1}T$ conversion to occur, and thus upon direct irradiation (*E*)-(*Z*) isomerization is observed.

The lowest triplet state of compounds (1c-e) is of $n-\pi^*$ character, as was concluded from the observation that triplet sensitization of (1d) yields the 1,3-acyl shift product. CIDNP studies on 3-benzoyl-3-methylcyclopentene, which like (1c—e) contains a benzoyl chromophore, revealed that the α-cleavage occurs from the triplet excited state.[13] This observation supports the explanation (see before) that the α-cleavage of (1c—e) is also a reaction from the triplet excited state. The absence of (*E*)-(*Z*) isomerization with these substrates can then be explained by considering the two π-moieties of the βγ-UK as isolated. Upon direct irradiation the $^{1}S(n-\pi^*)$ state is populated, and will have an energy content comparable to that of acetophenone (E_S 78 kcal mol^{-1} [9]). Intersystem crossing from $^{1}S(n-\pi^*)$ yields $^{1}T(n-\pi^*)$ which state exhibits α-cleavage. Energy transfer from $^{1}T(n-\pi^*)$ to $^{2}T(\pi-\pi^*)$ is apparently unlikely with these compounds, as it is exothermic by *ca.* 4 kcal mol^{-1}, and no (*E*)-(*Z*) isomerization is observed.*

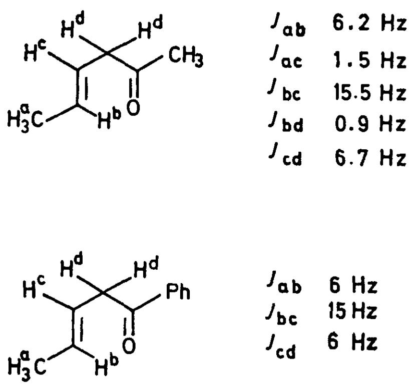
With the hex-4-en-2-ones and 1-phenylpent-3-en-1-ones no ODPM rearrangement is observed. The lowest triplet state of the 1-phenylpent-3-en-1-ones is of $n-\pi^*$ character, and since the ODPM rearrangement is a reaction from the triplet $\pi-\pi^*$ state, no ODPM rearrangement will occur. It is, however, surprising that the ODPM rearrangement does not occur with the hex-4-en-2-ones as their lowest excited triplet state is of $\pi-\pi^*$ character. For βγ-UKs in which the alkene moiety is, however, part of a small ring, the ODPM rearrangement is observed.[3c,14] With these compounds the triplet excited alkene moiety cannot deactivate by (*E*)-(*Z*) isomerization. As a result of the longer lifetime of the triplet $(\pi-\pi^*)$ state the molecule can reach the required conformation for the ODPM rearrangement in which there is overlap between the orbitals of the carbonyl carbon and the β-carbon atoms. For the acylic hex-4-en-2-ones the deactivation of the triplet $(\pi-\pi^*)$ state to the 'perpendicular', *i.e.* non-planar, triplet state, eventually leading to (*E*)-(*Z*) isomerization is apparently so fast that the ODPM rearrangement cannot compete with the formation of the 'perpendicular' triplet.†

In a previous paper [8] we have already used the concept of isolated chromophores in βγ-UKs. The present study further supports this description.

EXPERIMENTAL

Synthesis of the βγ-Unsaturated Ketones.—(E)-*Hex*-4-*en*-2-*one* (1a).—The βγ-UK was prepared by reaction of methyllithium with pent-3-enoic acid in a yield of 70%.[5,16] The crude product was purified by g.l.c. (see Table 2). The ^{1}H n.m.r. and i.r. data were in accordance with those reported in the literature.[17] In order to elucidate the conformation of (1a) (*E* or *Z*), Eu(fod)$_3$ was added to enlarge the ^{1}H n.m.r. chemical shifts, and the coupling constants in Scheme 2 were obtained. These data clearly reveal that the *E*-isomer was obtained. Double resonance experiments in the presence of Eu(fod)$_3$ furnished additional evidence for the correct structure of this compound: irradiation at the methyl absorption attached to the double bond leads to the formation of a doublet at δ 5.6. Irradiation at the methylene absorption leads to the formation of a doublet at δ 5.8.

(E)-3,3-*Dimethylhex*-4-*en*-2-*one* (1b) *and* 3-*methylhex*-3-*en*-2-*one*. The βγ-UK was prepared by the reaction of (1a) with methyl iodide using potassium t-butoxide as base.[5] The crude mixture was purified by g.l.c. (see Table 2). Ketone (1b) had δ 5.4 (2 H, m), 1.93 (3 H, s), 1.55 (3 H, m), and 1.07 (6 H, m); $\nu_{max.}$ (liquid capillary) 3 050, 2 990, 2 960, 2 890, 1 710, 1 475, 1 465, 1 455, 1 390, 1 360, 1 250, 1 225, 1 130, and 980 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 289 nm (ε 66). 3-Methylhex-3-en-2-one had δ 6.42 (1 H, t, *J* 7 Hz), 2.15 (2 H, m), 2.15 (3 H, s), 1.65 (3 H, s), and 1.01 (3 H, t, *J* 7 Hz); $\nu_{max.}$ (liquid capillary) 2 990, 2 950, 2 890, 1 670, 1 650, 1 465, 1 440, 1 400, 1 375, 1 355, 1 315, 1 285, 1 260, 1 150, 1 100, 1 050, 1 000, 940, and 870 cm^{-1}.



SCHEME 2

(E)-1-*Phenylpent*-3-*en*-1-*one* (1c). The βγ-UK was prepared by the reaction of phenyl-lithium [18] with pent-3-enoic acid.[5,16] The crude product (40%) was distilled *in vacuo*, b.p. 81—83° at 0.7 mmHg. The βγ-UK was further purified by g.l.c. (see Table 2), δ 7.9 (2 H, m), 7.4 (3 H, m), 5.6 (2 H, m), 3.55 (2 H, m), and 1.65 (3 H, m); $\nu_{max.}$ (liquid capillary) 3 080, 3 045, 2 980, 2 955, 2 935, 2 900, 2 870, 1 685, 1 625, 1 600, 1 580, 1 480, 1 450, 1 410, 1 385, 1 350, 1 280, 1 220, 1 190, 1 115, 1 080, 1 025, 1 010, 975, 935, 765, 750, and 700 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 337 (ε 32), 325 (33), and 241 nm (6 250).

On the basis of the ^{1}H n.m.r. spectral data it was not clear whether the *E*- or *Z*-isomer was obtained. The ^{1}H n.m.r. spectrum of the βγ-UK in the presence of added Eu(fod)$_3$ showed that the two vinyl protons had become magnetically unequivalent; the coupling constants in Scheme 2 were obtained. At δ 6.5 a double triplet and at δ 6.1 a double quartet was observed, indicating, that H^c is closer to the

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* Upon considering the βγ-UK as one chromophore two transitions are feasible, *viz.* from $^{1}S(n-\pi^*)$ to $^{2}T(\pi-\pi^*)$ and to $^{1}T(n-\pi^*)$. As it is not clear why only the latter transition occurs and not the former, the simpler description of the βγ-UK as consisting of two isolated chromophores remains the preferred one.

‡ An analogous behaviour was observed with the di-π-methane (DPM) rearrangement of acyclic 1,4-dienes.[15] These dienes only exhibit the DPM rearrangement from the singlet excited state, as the triplet excited state deactivates by rotation to the perpendicular triplet state (the so-called free rotor effect).

carbonyl group than H^b. Based on the coupling constant J_{bc} it is clear that the *E*-isomer was obtained.

(E)-2,2-*Dimethyl*-1-*phenylpent*-3-*en*-1-*one* (1d). The βγ-UK was prepared by reaction of the conjugate base of (1c) [obtained from (1c) and potassium t-butoxide as base] with methyl iodide.[5] The crude product was purified by g.l.c. (see Table 2), δ 7.75 (2 H, m), 7.3 (3 H, m), 5.68 (1 H, d, *J* 16 Hz), 5.51 (1 H, d q, J_d 16, J_q 6 Hz), 1.69 (3 H, d, *J* 6 Hz), and 1.25 (6 H, s); $\nu_{max.}$ (liquid capillary) 3 070, 2 980, 2 940, 1 680, 1 600, 1 480, 1 450, 1 390, 1 370, 1 255, 1 175, 1 160, 1 135, 1 080, 975, 780, 740, and 705 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 241 nm (ε 10 600).

4-*Methyl*-1-*phenylpent*-3-*en*-1-*one*. The βγ-UK was prepared by reaction of phenyl-lithium with 4-methylpent-3-enoic acid.[5] An attempt to distill the crude product failed due to polymerization. The purification was therefore carried out by chromatography (silica gel–benzene) to give the product in 13% yield, δ ($CDCl_3$) 8.0 (2 H, m), 7.5 (3 H, m), 5.46br (1 H, t, *J* 7 Hz), 3.68br (2 H, d, *J* 7 Hz), and 1.71 (6 H, m); $\nu_{max.}$ (CCl_4) 3 100, 3 000, 2 940, 1 680, 1 630, 1 600, 1 580, 1 450, 1 380, 1 360, 1 320, 1 300, 1 275, 1 200, 1 175, 1 140, and 1 100 cm^{-1}.

2,4-*Dimethyl*-1-*phenylpent*-3-*en*-1-*one* (1h) *and* 2,2,4-*trimethyl*-1-*phenylpent*-3-*en*-1-*one* (1e). The βγ-UKs were prepared by the reaction of 4-methyl-1-phenylpent-3-en-1-one with methyl iodide using potassium t-butoxide as base.[5] The crude product was purified by g.l.c. (see Table 2). Ketone (1h) had δ ($CDCl_3$) 8.0 (2 H, m), 7.4 (3 H, m), 5.23br (1 H, d, *J* 10 Hz), 4.27 (1 H, d q, J_d 10, J_q 7 Hz), 1.72 (6 H, m), and 1.23 (3 H, d, *J* 7 Hz); $\nu_{max.}$ (CCl_4) 3 100, 3 000, 2 940, 2 860, 1 680, 1 600, 1 580, 1 450, 1 380, 1 325, 1 300, 1 260, 1 215, and 1 175 cm^{-1}. Ketone (1e) had δ ($CDCl_3$) 8.0 (2 H, m), 7.4 (3 H, m), 5.60br (1 H, s), 1.33br (3 H, s), and 1.35 (9 H, s); $\nu_{max.}$ (CCl_4) 3 100, 3 000, 2 940, 2 870, 1 675, 1 600, 1 580, 1 470, 1 450, 1 390, 1 380, 1 365, 1 315, 1 255, 1 225, 1 150, and 1 120 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 325 (ε 120) and 239 nm (10 400) (Found: C, 83.0; H, 8.9. Calc. for $C_{14}H_{18}O$: C, 83.1; H, 9.0%).

TABLE 2

G.l.c. conditions for the isolation of the βγ-unsaturated ketones

Ketone	Column	Temperature (°C)
(1a, b)	A	90
(1c, d)	A	180
(1e)	B	150

A, 5 m × 3/8 in, 10% SE–30; B, 3 m × 1/4 in, GE–XE–60.

Photochemical Experiments.—The irradiations were carried out in a Rayonet RPR-208 photoreactor equipped with eight RUL 3000 or 3500 lamps at room temperature. The solutions of the βγ-UKs (0.05—0.14M), contained in Pyrex tubes closed with a septum were saturated with nitrogen prior to the irradiation. The amounts of product formation and substrate disappearance were determined from the g.l.c. peak areas. With the quantitative experiments the substrate conversion was 25% and internal g.l.c. standards (*cf.* Table 3) were used. The deviation between duplicate experiments was found to be ⩽ 10%.

Quantum Yield Determinations.—The quantum yields were determined by valerophenone actinometry,[19] using a merry-go-round arrangement and a potassium chromate filter [9] to isolate the 310 nm group of lines. The solutions of the ketones were carefully saturated with nitrogen, to remove the oxygen.

Triplet Sensitization.—The concentration of (1a and b) in acetone as solvent and photosensitizer using λ 310 nm was 7 × 10^{-3}M. With the acetophenone sensitized irradiation of (1d) using λ 360 nm the concentration of the βγ-UK in neat acetophenone was 0.03M.

Analysis, Product Isolation, and Identification.—After irradiation the solutions were concentrated by rotary evaporation and the components of the residue were isolated by (preparative) g.l.c. (*cf.* Table 3) using a Varian 2720–1 gas chromatograph. For the columns copper tubing was used, containing the coated Chromosorb W-AW (60—80 mesh). The carrier gas employed was helium. G.l.c. peak areas were measured using the Varian CDS-111-C electronic integrator. The ^{1}H n.m.r. spectra of the βγ-UKs and the photoproducts were recorded with a Varian HA-100 or XL-100-15FT spectrometer. The ^{1}H n.m.r. spectra of the other compounds were recorded with a Varian A-60-D spectrometer. The solvent used for the ^{1}H n.m.r. spectra was CCl_4 using tetramethylsilane as internal reference. I.r. spectra were taken on a Perkin-Elmer 257 spectrometer. U.v. spectra were run on a Cary 14 instrument. The mass spectra were recorded with a Varian AEI-MS-902 or a MAT-711 mass spectrometer equipped with an all-glass heated inlet system. The structural assignment of the products was based on their spectral data.

TABLE 3

G.l.c. conditions for the isolation and quantum yield determinations of the photoproducts

Ketone	Column	Temperature (°C)	Internal standard
(1a, b)	A	80 + 2 min^{-1}	*p*-Dichlorobenzene
(1c, d)	B	100 + 4 min^{-1} to 200	tridecane
(1e)	C	80 + 6 min^{-1} to 180	

A, 5 m × 1/4 in, 10% Repoplex–400; B, 5 m × 1/4 in, 10% SE–30; C, 1/4 in, 10% GE–XE–60.

(*Z*)-Hex-4-en-2-one (1f) had δ ($CDCl_3$) 5.6 (2 H, m), 3.15 (2 H, d, *J* 6 Hz), 2.12 (3 H, s,), and 1.59 (3 H, d, *J* 6 Hz). By the addition of Eu(fod)$_3$ to the n.m.r. sample and subsequent double resonance experiments (upon irradiation at the alkene methyl group to saturation one of the vinyl absorptions simplified to a doublet with *J* 11 Hz) it was evident that the *Z*-isomer was obtained. 3,5-Dimethylhex-4-en-2-one (1g), 2,4,5,7-tetramethylocta-2,6-diene (2a), 2,4,5,5-tetramethylocta-2,6-diene (2b), 4,4,5,5-tetramethylocta-2,6-diene (2c), and 2,4,4,5,5,7-hexamethylocta-2,6-diene (2d) give spectra identical with those reported previously.[5] 2,4-Dimethyl-1-phenylpent-3-en-1-one (1h) gave spectral data identical with those of one of the products obtained by methylation of 4-methyl-1-phenylpent-3-en-1-one (1c). (*Z*)-3,3-Dimethylhex-4-en-2-one (1i) had δ 5.50 (2 H, m), 2.00 (3 H, s), 1.70 (3 H, m), and 1.18 (6 H, s). (*E*)-1-Phenylpent-3-en-1-ol (4). The presence of the alcohol, obtained upon irradiation of (*E*)-1-phenylpent-3-en-1-one in the presence of Bu_3SnH, was demonstrated by comparing the retention time of the photoproduct with that of an authentic sample prepared by reduction of the βγ-UK (1c) with lithium aluminium hydride.[20] The product was purified by g.l.c. (column B, Table 2, 150°), δ 7.2 (5 H, m), 5.35 (2 H, m), 4.50 (1 H, t, *J* 7 Hz), 2.28 (2 H, m), 1.82 (1 H, s), 1.59 (3 H, d, *J* 5 Hz); $\nu_{max.}$ (liquid capillary) 3 400, 3 100, 3 080, 3 040, 2 980, 2 950, 2 930, 2 870, 1 610, 1 500, 1 460, 1 445, 1 385, 1 200, and 1 120 cm^{-1}.

This work was carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) and with financial support from the Netherlands Organization for Advancement of Pure Research (Z.W.O.).

[9/378 *Received*, 8*th March*, 1979]

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