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Photochemistry of two diphenyl β,γ-enones and a series of methyl- and phenyl-substituted α-phenyl ketones[§]

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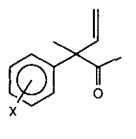
Abstract. The photochemistry of the diphenyl β,γ-enones **2** and **3** and the methyl- and phenyl-substituted α-phenyl ketones **4–9** has been studied, using mainly benzene as solvent. Irradiation of **2** with λ 300 nm leads to the 1,3-acyl shift (1,3-AS) product **17**, relatively small amounts of the decarbonylation products **15** and **16**, and the photo-oxidation products benzophenone (**18**) and the α,β-unsaturated aldehyde **19**. Direct irradiation of the 1,3-AS product **17** yields **15**, **16**, **18** and **19**, but no **2**.

Direct irradiation of **3** with λ 350 nm leads mainly to the formation of 1,3-AS products (*E*)- and (*Z*)-**22**, the decarbonylation products (*E*)- and (*Z*)-**20** and **21** and, in addition, a small amount of the *cis*-di-π-methane isomer **23**.

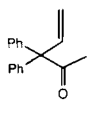
Direct irradiation of the substituted α-phenyl ketones **4**, **5**, **8** and **9** with λ 300 nm leads predominantly to the formation of the radical coupling products 2,3-butanedione and **24–27**, respectively, whereas **6** and **7** yield 1,2-diphenyl-1,2-ethanedione and the respective **24** and **25**. The acetone-sensitized irradiation of **4** leads to 4-phenyl-2-butanone (**33**) in addition to 2,3-butanedione and 1,2-diphenylethane (**24**).

Introduction

We have been interested for a number of years in the photochemistry of β,γ-enones[1,2]. The most general reactions displayed by these types of compounds are the 1,3-acyl shift (1,3-AS) isomerization, the oxa-di-π-methane (ODPM) rearrangement and (*E*)–(*Z*) isomerization[3]. The results of various investigations have led to the general conclusion that the ODPM rearrangement arises from the *T*(ππ*) state, which is usually the lowest triplet state[4-6]. The 1,3-AS proceeds from the excited *S*(*n*π*) state[7,8] or, at least for certain systems, might proceed from the excited *T*(*n*π*) state[9-13]. However, in acyclic systems, the excited triplet (ππ*) state deactivates efficiently by bond rotation and the resulting (*E*)–(*Z*) isomerization then dominates over the ODPM rearrangement[14,15].



1a X = H
1b X = *o*-MeO
1c X = *p*-MeO
1d X = *p*-CN



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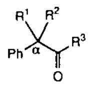
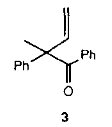


4 $R^1 = R^2 = H$, $R^3 = Me$
5 $R^1 = R^2 = R^3 = Me$
6 $R^1 = R^2 = H$, $R^3 = Ph$
7 $R^1 = R^2 = Me$, $R^3 = Ph$
8 $R^1 = H$, $R^2 = Ph$, $R^3 = Me$
9 $R^1 = R^3 = Me$, $R^2 = Ph$
14 $R^1 = R^3 = Me$, $R^2 = H$



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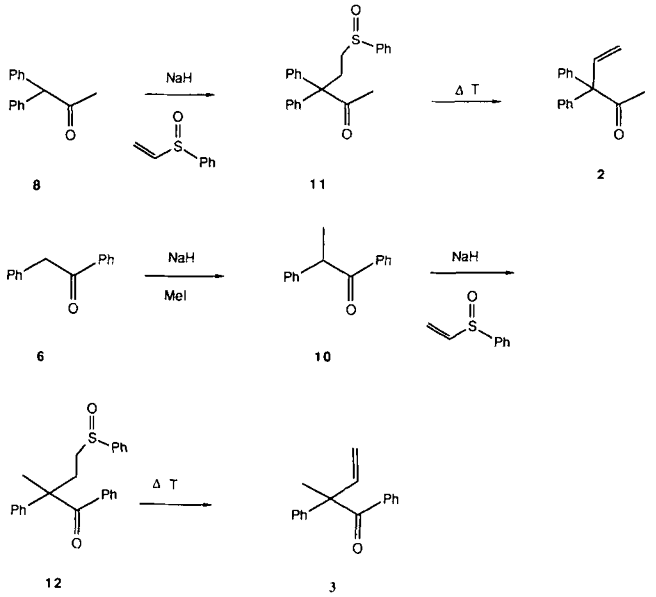
In a detailed study using acyclic β,γ-enones, *Van der Weerdt*[1] showed that the occurrence of the 1,3-AS and ODPM rearrangements – which are in competition with the (*E*)–(*Z*) isomerization – is strongly related to the degree and type of α-alkyl substitution. It appeared that the α-cleavage and the 1,3-AS are favoured by α-alkyl substitution and homoconjugation, whereas the ODPM rearrangement only occurs if the (*E*)–(*Z*) isomerization is retarded by bulky γ-substituents.

Extensive studies have shown that 3-phenyl- and 3-arylpropenes and derivatives thereof which may formally be considered to be 1,4-pentadienes, in which one "double" bond is contained in the phenyl and aryl ring, respectively, undergo the aryl-vinyl methane, also referred to as di-π-methane (DPM), rearrangement[16-19]. α-Methyl substitution and the presence of electron-delocalizing substituents at the phenyl group lead to an increase in the relative yield of the DPM product[18,19].

[§] Photochemistry of β,γ-enones 13. For part 12, see *M. J. C. M. Koppes* and *H. Cerfontain*, Recl. Trav. Chim. Pays-Bas **107**, 412 (1988).

*Table I UV-absorption data of the α-phenyl β,γ-enones **2** and **3**, the related α-phenyl ketones **8** and **6** and acetophenone (**13**) in cyclohexane.*

Solute	λ_{max} (nm)	ε ($l \cdot mol^{-1} \cdot cm^{-1}$)	Solute	λ_{max} (nm)	ε ($l \cdot mol^{-1} \cdot cm^{-1}$)
2	321	119	**8**	320	78
	309	310		310	115
	301	342		302	180
	292	333		292	184
	267	525		268	370
	262	570		262	570
	255	535		257	376
3	367	45	**6**	368	28
	348	152		352	85
	335	223		338	130
	324	242		327	133
	318	210		318	111
	246	1100		242	14000
13	368	11			
	347	32			
	335	43			
	325	48			



*Scheme 1. Synthesis of **2** and **3**.*

In order to obtain further insight into the mechanism of these interesting rearrangements, we have recently investigated a series of α-phenyl β,γ-enones (**1**) in which the carbonyl, vinyl and phenyl groups are all substituted at one (*i.e.* the central) carbon atom[20]. These systems are almost free of conformational and configurational constraints and allow competition between the ODPM and DPM rearrangements. Both the *p*-CN and *o*-MeO substituted substrates were found to rearrange to the *cis*- and *trans*-DPM products upon triplet-sensitized irradiation. However, no ODPM products were observed. As an extension to that study, we have investigated the photochemistry of the two phenyl-substituted α-phenyl β,γ-enones **2** and **3** and the related α-phenyl ketones **4**–**9**.

Results

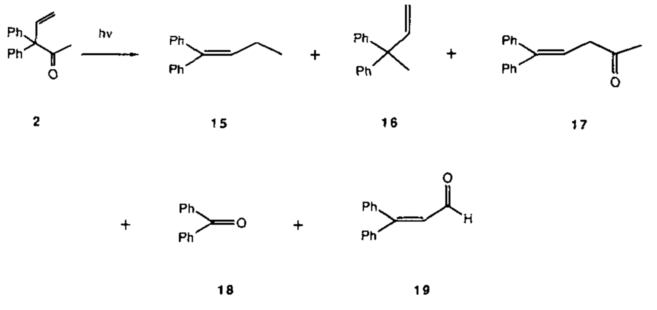
Synthesis of the photochemical reactants

The syntheses of **2** and **3** are outlined in Scheme 1. Since phenyl vinyl sulfoxide is a strong and aselective reagent[21], the blocking of one of the α-carbon hydrogens of 1,2-diphenylethanone (**6**) is necessary in order to avoid divinylation. The addition of the anion of **6** to methyl iodide afforded the monomethylated compound **10** in high yields. The addition of phenyl vinyl sulfoxide to **8** and **10** provided the sulfoxides **11** and **12**, respectively. The pyrolyses *in vacuo* of these sulfoxides gave **2** and **3** in addition to diphenyl disulfide.
The compounds **5**, **7** and **9** were synthesized by methylation of **4**, **6** and **8**, respectively.

UV studies

All the compounds exhibit vibrational fine structure in the UV spectra when cyclohexane is used as solvent. The $n\pi^*$ character of the absorption in the region 290–360 nm is apparent from the 5-nm shift to shorter wavelength when ethanol is used as solvent. For the compounds **3** and **6**, the absorption pattern in the region of 300–360 nm is analogous to that of acetophenone (**13**) (Table I), which may be considered as the parent chromophore. For **3** and **6**, the wavelengths of the $n\pi^*$ absorption maxima are quite similar; the intensities are higher for **3** than for **6**, indicating additional interaction between the vinyl, the benzoyl and the phenyl groups[22]. Similarly, the intensities of the absorption maxima of **2** are enhanced as compared with **8**.

The 0–0 bands of **2** and **3** correspond with an $S^1(n\pi^*)$ energy of 373 ± 3 and 398 ± 3 $kJ \cdot mol^{-1}$, respectively. Fluorescence has not been observed, preventing an independent confirmation of these values.



*Scheme 2. Photoproducts resulting from **2** upon direct irradiation λ 300 nm) in 2-propanol.*

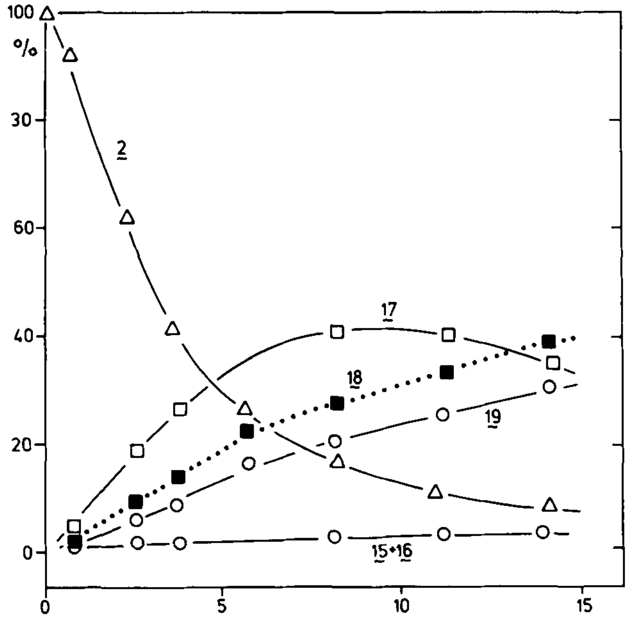


Fig. 1. Dependence of the composition of the reaction of **2** *(0.10 M) in 2-propanol on the irradiation (λ 300 nm) time.*

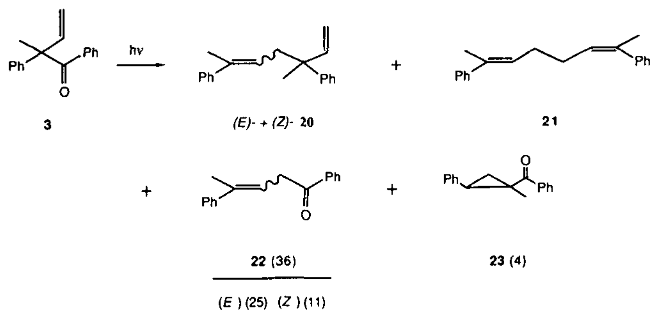
Direct irradiation

Upon direct irradiation (λ 300 nm) of **2** in 2-propanol, the main photoreaction is the 1,3-AS leading to **17**; in addition, four other products were isolated, *viz.* the decarbonylation products **15** and **16**, benzophenone (**18**) and the aldehyde **19** (Scheme 2). The dependence of the product composition on the irradiation time (Fig. 1) clearly shows that the compounds **15–19** are all primary products. The 1,3-AS was found to be irreversible, since, upon direct irradiation of the 1,3-AS product **17** proper, the photoproducts **15**, **16**, **18** and **19** were formed in a ratio very similar to that observed on starting with **2** as substrate, although no **2** was formed.

In order to investigate the mechanisms for the formation of **18** and **19**, irradiations were performed in both an atmosphere rich and poor in oxygen. In the atmosphere rich in oxygen, the formation of the products **18** and **19** dominated that of the 1,3-AS product **17**, whereas in an atmosphere of argon, the formation of both **18** and **19**, relative to **17**, was strongly suppressed. Addition of the triplet quencher 1,3-cyclohexadiene prohibited the formation of **18** and **19**, but not that of **17**; the addition of 2,4-dimethyl-1,3-pentadiene had no effect on the relative product formation. Essentially, the same results were obtained using the 1,3-AS product **17**. Upon its irradiation in the presence of 1,3-cyclohexadiene or in an atmosphere of argon, **18** and **19** were not formed. Finally, the irradiation of **2** was performed in an NMR tube and the photoconversion was followed directly by ^{1}H NMR. The spectra indicated the formation of all the isolated products, which illustrates that none of the products was formed thermally under the GLC conditions.

Upon direct irradiation (λ 350 nm) of **3** in benzene, a series of products was observed using GLC, of which only the main photoproducts were isolated. The main compounds formed are (*E*)- and (*Z*)-**20** and **21** and the 1,3-AS products (*E*)- and (*Z*)-**22**. In addition, a small amount of the cyclopropane derivative **23** was isolated. All these products, the structures and yields of which are shown in Scheme 3, are primary photoproducts.

On the basis of the information obtained from the ^{1}H NMR spectrum of the isolated cyclopropane product **23**, four structures, *viz.* those of the *cis*- and *trans*-ODPM isomers



Scheme 3. Photoproducts resulting from **3** *upon direct irradiation (λ 350 nm) in benzene. The sum of the yields of (E)- + (Z)-***20** *and* **21** *is 38%; the other yields are given in parentheses.*

and the *cis*- and *trans*-DPM isomers, may *a priori* be considered. The definitive structure of **23** has been assigned on the basis of ^{1}H NMR NOE difference and $Eu(fod)_3$-shift experiments (Fig. 2). Upon irradiation of the cyclopropane CH_3 group, the signals of two cyclopropane hydrogens H2 and H3b and the *ortho* hydrogens of COPh are observed. The appearance of the two cyclopropyl hydrogens indicates that the cyclopropane product is a *cis*-isomer. Complexation with added $Eu(fod)_3$ led to the strongest downfield shift for the other cyclopropyl hydrogen H3a. The observed signal of the *ortho* hydrogens of COPh, upon irradiation of the methyl group, indicates the close vicinity of these two groups, which is taken to suggest that the methyl group and benzoyl group are substituted at one and the same cyclopropane carbon. On the basis of these results, the cyclopropane product was assigned as the *cis*-DPM isomer **23**.

Upon direct irradiation (λ 300 nm) of **4**, **5**, **8** and **9**, after initial α-cleavage, the respective corresponding radical coupling products 2,3-butanedione and **24–27** were formed in greater than 98% yield (Scheme 4). In addition to the main photoproducts, a trace (< 1%) of the decarbonylation product *tert*-butylbenzene (**28**) was formed in the case of **5**, and in the case of **8**, small amounts (< 1%) of the decar-

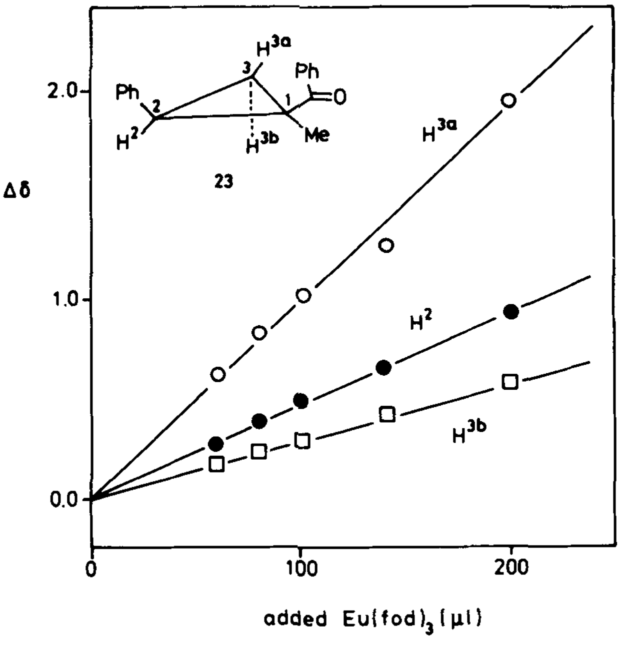
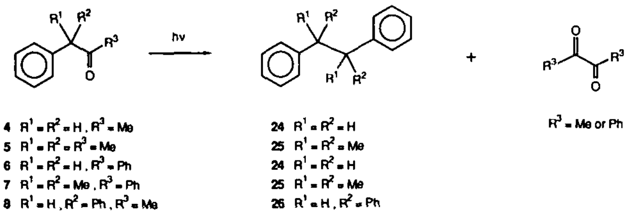


Fig. 2. Shift reagent study of the DPM isomer **23**. *Variation in the* ^{1}*H NMR chemical shift in ppm* versus *the amount of added shift reagent.*

bonylation products **29** and **30** and the pinacol **31**. Variation of the solvent had no effect on the product formation. However, upon direct irradiation (λ 350 nm) of **6** in the hydrogen donating solvent 2-propanol, the pinacol type of products *meso*- and *racemic*-**32** were obtained as the main photoproducts, in addition to some benzaldehyde and the radical coupling products 1,2-diphenyl-1,2-ethandione and **24**. The latter two compounds are the predominant products (>98%) observed on using benzene rather than 2-propanol as solvent. Irradiation (λ 350 nm) of **7** afforded predominantly the radical coupling product **25** and 1,2-diphenyl-1,2-ethanedione.

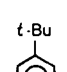


Scheme 4. Photoproducts of **4–9** *upon direct irradiation with λ 300 nm.*

Triplet-sensitized irradiation

Upon sensitized irradiation of **2** and **3** using triplet sensitizers with triplet energies in the range of 335–210 kJ · mol^{-1}, no photoproducts could be detected by TLC, GLC and ^{1}H NMR spectroscopy. After prolonged irradiation (> 10 days), decomposition of starting material and sensitizers was observed.

Upon acetone-sensitized irradiation of **4**, in addition to the photoproducts 2,3-butanedione and 1,2-diphenyl-1,2-ethanedione (**24**), which were also found upon direct irradiation, a third photoproduct, *viz.* 4-phenyl-2-butanone (**33**), was isolated. The ratio **24**/**33** was determined to be 1.28. Acetophenone failed to photosensitize **4**, since the only product then obtained was the pinacol of acetophenone (**34**). In the case of **8** and **9**, the triplet-sensitized irradiations yielded the same products as observed in the direct irradiations.



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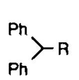
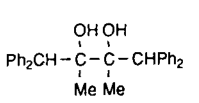
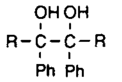


29 R = H
30 R = Me



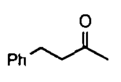
$$Ph_2CH-\overset{OH}{\underset{Me}{C}}-\overset{OH}{\underset{Me}{C}}-CHPh_2$$

31



$$R-\overset{OH}{\underset{Ph}{C}}-\overset{OH}{\underset{Ph}{C}}-R$$

32 R = PhH$_2$C
34 R = Me



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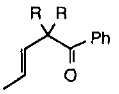
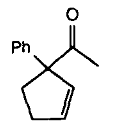


36 R = H
37 R = Me



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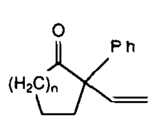
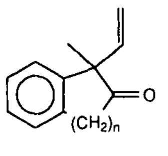
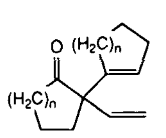


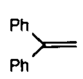
39 n = 1, 2



40 n = 1, 2



41 n = 1, 2



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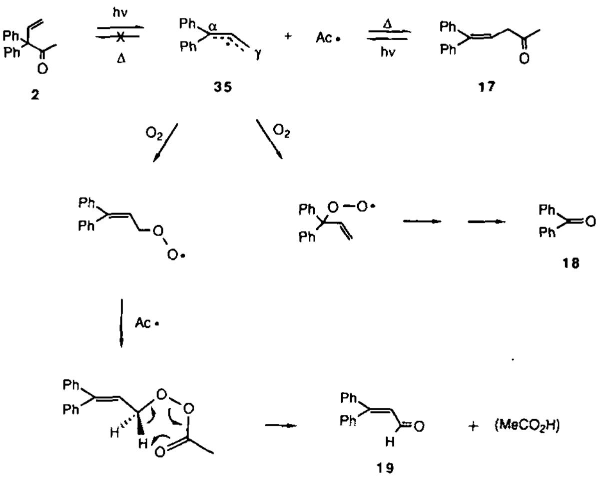
Discussion

The solution photochemistry of acyclic dibenzyl ketones has been extensively studied[23-25]. These types of compounds, upon direct irradiation, undergo decarbonylation to form radical coupling products and it has been suggested that a very short-lived triplet state is responsible, to a large extent, for the formation of these α-cleavage products, which resulted from coupling of free, as opposed to caged, benzylic radicals in solution.

Benzyl methyl ketone (**4**), upon direct irradiation in hexane, was reported[26] to give *p*-methylacetophenone (0.4%), the pinacol (11.2%) and 1,2-diphenylethane (**24**). The ratio of **24** to *p*-methylacetophenone decreases with increasing concentration of **4**. In 2-methyl-2-propanol as solvent, the pinacol formation was suppressed, but *o*-methylacetophenone was reported as an additional product. A mechanism involving α-cleavage, in-cage formation of acetophenone and diffusion out of cage with subsequent dibenzyl formation was suggested. Our present results are inconsistent with those reported[26]. Using solvents such as heptane, acetonitrile, 2-methyl-2-propanol or 2-propanol, the direct irradiation of **4** yielded the radical couping products 2,3-butanedione and 1,2-diphenylethane in yields >99% and we were unable to detect any pinacol type of product or methylacetophenones. Our results on the irradiation of **5**, **8** and **9** are similar to those of **4** in that the radical coupling products are formed in >98% yield. This clean and efficient photoreaction is apparently a very convenient and general method of preparing symmetrically substituted 1,2-diarylethanes, which are normally synthesized by reductive "homocoupling" of the corresponding benzylic halides[27]. The formation of **33**, upon irradiation of **4** in acetone with λ 300 nm, indicates the intermediacy of acetonyl radicals, most likely formed by reaction of free acetyl and – although less likely – of benzyl radicals[28] with acetone. The formation of the pinacol **34**, when acetophenone was used as addendum, illustrates the extremely high hydrogen donor ability of **4**.

The present results lead to the conclusion that the photochemistry of the studied α-phenyl ketones does not differ markedly from that of dibenzyl ketone in that they all proceed by initial α-cleavage, subsequent decarbonylation and coupling of the relatively long-living free radicals. The photochemistry of the ketones **6** and **7** has been previously reported[29-31] and our results are in complete accordance with these earlier reports.



Scheme 5. Mechanism of formation of **18** *and* **19** *from both* **2** *and* **17**.

The introduction of a vinyl group in **8**, as in **2**, strongly influences the photochemical behaviour. Compound **2** upon direct irradiation undergoes – in addition to photodecarbonylation – the irreversible 1,3-AS isomerization (see Scheme 2). The apparent irreversibility of the 1,3-AS of **2** may be explained in terms of prohibitive steric hindrance to the addition of the acetyl radical at the 1- as compared with the 3-position of the 1,1-diphenyl-2-propenyl radical[32]. For the formation of **18** and **19**, the presence of oxygen is essential. Since **2** and its 1,3-AS isomer **17** both yield the compounds **18** and **19** as primary products in essentially the same ratio, it is suggested (Scheme 5) that these products both result from the allyl radical **35** by addition of oxygen at the α- and the γ-position, respectively. The so formed peroxy radicals eventually provide benzophenone (**18**) and the aldehyde **19**, respectively. As to the formation of **19**, the γ-peroxy radical may first recombine with the acetyl radical, followed by dissociation of the resulting diphenylalkenyl peracetate into the aldehyde **19** and acetic acid; this acid, however, was not identifed among the photoproducts.

Related photo-oxidations have been reported for 1,2-diphenylethanone (**6**) and its 4′,4″-disubstituted derivatives[29-33], di- and tetraphenylethenes under conditions of 9,10-dicyanoanthracene sensitization[34], 1,1-dichloro-2,2-diarylethenes[35] and 9-(α-bromobenzylidene)fluorene[36], which yielded the corresponding benzaldehydes and/or benzoic acids, or diaryl ketones, and mechanisms for their formation have been suggested[31,34-36].

Compound **3**, upon direct irradiation, yields the radical coupling products **20** and **21** and, in addition, the 1,3-AS and the DPM products **22** and **23**, respectively (Scheme 3). The formation of the DPM product, upon direct irradiation, and the absence of any photochemical reactivity, upon triplet-sensitized irradiation, are highly remarkable, especially since DPM rearrangements were observed to occur for the reactants **1b** and **1d** upon triplet-sensitized irradiation[20]. Since the (O)DPM rearrangements normally proceed from a ($\pi\pi^*$) excited state, in contrast to the α-cleavage and 1,3-AS which arise from an excited ($n\pi^*$) state[3,37], the formation of the DPM product **23** probably results from a higher excited singlet state, the $S^2(\pi\pi^*)$, which may be populated in part by the "350"-nm irradiation employed, which in fact ranges from 410–305 nm. In this respect, it should again be noted that this DPM product is formed only in a relatively low yield (*cf.* Scheme 3).

On comparing the photochemistry of the β,γ-enones **3**, **36**[38] and **37**[38], it appears that the α-cleavage and 1,3-AS are relatively more favoured by α-vinyl than by α-methyl substitution, in agreement with the enhanced radical-stabilizing effect of the vinyl group. Secondly, the introduction of the α-vinyl group clearly diminishes the degree of ISC, since none of the products formed upon triplet-sensitized irradiation is obtained upon direct irradiation.

Finally, the presence of a vinyl group and/or a phenyl group at C(α), as in **2**, creates additional possibilities of radiationless decay for the triplet states, which might be ISC and/or degenerate (*E*)–(*Z*) isomerization of the vinyl group. In this respect, the stability, upon triplet photo-sensitization, of the related compounds **38**[4], **39**[39] and **40**[39] and the related α,α-divinyl compounds **41** is worthy of mention[2b]. For the latter compound, the photostability was ascribed to a rapid internal conversion due to CT complexation[2b].

Experimental

Materials

All synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride. Dichloromethane was distilled from P_2O_5. Benzene was distilled and stored over sodium wire. Flash column chromatography[40] was performed on a dry-packed column of Kieselgel 60 (Merck 230–400 Mesh ASTM). Melting points were determined on a Reichert hot-stage microscope and are uncorrected. NMR spectra were recorded on Varian A60-D (using Me_4Si as internal standard). Bruker WM-250 and Bruker AC-200 spectrometers in C^2HCl_3 solution. $Eu(fod)_3$ was purchased from Aldrich (gold label 97%). IR spectra were recorded on a Perkin Elmer 1310 apparatus, using chloroform as solvent. UV spectra were recorded on a Hewlett-Packard 8451-A diode array spectrometer. Mass spectra were obtained using a Varian MAT-711 spectrometer at 70 eV.

The fluorescence spectra were recorded on a Spex Fluorolog 2 equipped with 150 W Xe-lamp, MDI excitation and MD2 emission monochromator, SI emission detector R928 in photocounting mode.

Synthesis of photoreactants

3,3-Diphenyl-5-(phenylsulfinyl)-2-pentanone (**11**). To a solution of 50 ml benzene, containing 400 mg of NaH suspension, was added 20 g (95 mmol) of **8** dissolved in 100 ml benzene. After 2 h stirring, 17 g phenyl vinyl sulfoxide in 50 ml benzene was added dropwise to the solution over a period of 4 h. The mixture was stirred at room temperature overnight. The solution was then acidified with 1.0 M HCl to pH 1 and extracted with ether. The combined organic extracts were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, column chromatography using $EtOAc/CH_2Cl_2$ (1/9) as eluent afforded a very viscous oil. Yield 76%. ^1H NMR, 250 MHz (δ, ppm): 7.49–7.09 (m, 15H, 3 × Ph), 2.65–2.35 (m, 4H, CH_2CH_2), 1.94 (s, 3H, CH_3). IR, ν(cm^{-1}): 3060(w), 3000(m), 2940(w), 1710(s), 1600(w), 1570(m), 1490(m), 1480(m), 1445(s), 1355(s), 1085(m), 1045(s), 1020(s), 700(s). MS *m/z* (%): 362($M^{+\bullet}$, not seen), 237(100), 193(98), 178(32), 165(31), 137(32), 123(42), 115(81), 91(44). High-resolution mass spectrum, *m/z:* 237.1280; calcd. for $C_{12}H_{17}O$ ($M^{+\bullet}$–SOPh) *m/z:* 237.1279.

3,3-Diphenyl-1-penten-4-one (**2**). The sulfoxide **11** was heated at 180–200°C *in vacuo* (0.10 mm Hg). The pyrolysis resulted in the formation of **2** and diphenyl disulfide, which were distilled off at 120°C. Compound **2** was isolated by column chromatography using CH_2Cl_2/pentane (1/1) as eluent. Yield 32%. ^1H NMR, 250 MHz (δ, ppm): 7.38–7.12 (m, 10H, 2 × Ph), 6.77 (dd, *J* 18 and 10 Hz, 1H, $C\underline{H}{=}CH_2$), 5.42 (d, *J* 10 Hz, 1H, $CH{=}C\underline{H}_ZH_E$), 4.76 (d, *J* 18 Hz, 1H, $CH{=}C\underline{H}_EH_Z$), 2.18 (s, 3H, CH_3). IR, ν(cm^{-1}): 3080(w), 3060(w), 3000(w), 1710(s), 1630(w), 1600(w), 1490(s), 1440(s), 1350(s), 930(m), 700(s). MS, *m/z* (%): 236($M^{+\bullet}$, 26), 194(51), 193(100), 178(62), 115(85), 91(49), 65(10). High-resolution mass spectrum, *m/z:* 236.1191; calcd. for $C_{17}H_{16}O$, *m/z:* 236.1201.

1,2-Diphenyl-1-propanone (**10**). To a solution of 2.45 g NaH suspension in 100 ml THF, 9.95 g (50 mmol) 1,2-diphenylethanone (**6**) in 40 ml THF was added dropwise at room temperature. After 1 h stirring, the resulting solution was added using a syringe to a solution of 35 ml methyl iodide in 40 ml THF. The solution, which discoloured immediately, was stirred for $\frac{1}{4}$ h and then quenched by the addition of 25 ml of water. Extraction by ether, washing of the combined organic layers with water and brine, drying over $MgSO_4$ and removal of the ether *in vacuo* afforded, after recrystallization, white crystals. M.p. 50°C (lit.[41] 53°C). Yield 87%. ^1H NMR, 250 MHz (δ, ppm): 7.94–7.90 (m, 2H, $COPh_{ortho}$), 7.47–7.15 (m, 8H, C_6H_3 + Ph), 4.67 (q, *J* 7 Hz, 1H, $C\underline{H}CH_3$), 1.52 (d, *J* 7 Hz, 3H, $C\underline{H}_3CH$).

1,2-Diphenyl-2-methyl-4-(phenylsulfinyl)-1-butanone (**12**). This compound was obtained from **10** as described for **11**. Yield 65%. ^1H NMR, 60 MHz (δ, ppm): 7.6–7.1 (m, 10H, 2 × Ph), 2.9–2.7 (m, 2H, CH_2SO), 2.4–2.2 (m, 2H, $C\underline{H}_2CH_2SO$), 1.6 (s, 3H, CH_3).

1,2-Diphenyl-2-methyl-3-buten-1-one (**3**). This compound was obtained by pyrolysis of the sulfoxide **12** as described for the preparation of **2**. The product **3** was isolated by column chromatography using CH_2Cl_2/pentane (5/95) as eluent. Yield 38%. ^1H NMR, 250 MHz (δ, ppm): 7.54–7.50 (m, 2H, $COPh_{ortho}$), 7.39–7.18 (m, 8H, C_6H_3 + Ph), 6.60 (dd, *J* 17 and 11 Hz, 1H, $C\underline{H}{=}CH_2$), 5.28 (d, *J* 11 Hz, 1H, $CH{=}C\underline{H}_ZH_E$), 5.15 (d, *J* 17 Hz, 1H, $CH{=}C\underline{H}_EH_Z$), 1.93 (s, 3H, CH_3). IR, ν(cm^{-1}): 3080(w), 3060(w), 2980(w), 1670(s), 1590(m), 1440(m), 1400(w), 1360(w), 950(m), 935(m), 690(s). MS, *m/z* (%): 236($M^{+\bullet}$, 14), 148(33), 115(11), 105(100), 91(19), 77(34), 51(12). High-resolution mass spectrum, *m/z:* 236.1197; calcd. for $C_{17}H_{16}O$, *m/z:* 236.1201.

3-Phenyl-2-butanone (**14**). This compound was obtained from benzyl methyl ketone (**4**) as described for **10**. Yield 92%. ^{1}H NMR, 60 MHz (δ, ppm): 7.4–7.2 (m, 5H, Ph), 3.7 (q, *J* 7 Hz, 1H, $C\underline{H}CH_3$), 2.0 (s, 3H, $COCH_3$), 1.4 (d, *J* 7 Hz, 3H, $C\underline{H}_3CH$).

3-Methyl-3-phenyl-2-butanone (**5**). This compound was obtained from **14** as described for **10**. Distillation (0.5 mm Hg/61°C) yielded a slightly yellow oil. Yield 75%. ^{1}H NMR, 60 MHz (δ, ppm): 7.4–7.2 (m, 5H, Ph), 2.0 (s, 3H, $COCH_3$), 1.5 [s, 6H, $(CH_3)_2$]. IR, ν(cm^{-1}): 3060(w), 3040(w), 3000(m), 1720(s), 1610(w), 1510(m), 1480(m), 1460(m), 1400(w), 1380(m), 1370(m), 1140(m), 710(s). High-resolution mass spectrum, *m/z:* 162.1036; calcd. for $C_{11}H_{14}O$, *m/z:* 162.1044.

1,2-Diphenyl-2-methyl-1-propanone (**7**). This compound was obtained from **10** as described for **5**. Distillation (0.5 mm Hg/90°C) yielded a slightly yellow oil. ^{1}H NMR, 250 MHz (δ, ppm): 7.49–7.45 (m, 2H, $COPh_{ortho}$), 7.37–7.17 (m, 8H, C_6H_3 + Ph), 1.59 [s, 6H, $C(CH_3)_2$].

3,3-Diphenyl-2-butanone (**9**). This compound was obtained from **8** as described for **10**. Distillation (0.1 mm Hg/112°C) afforded a slightly yellow oil. Yield 97%. ^{1}H NMR, 60 MHz (δ, ppm): 7.4–7.2 (m, 10H, 2 × Ph), 2.1 (s, 3H, $COCH_3$), 1.9 (s, 3H, CCH_3).

Irradiation procedures

All solutions were purged with nitrogen for 10 min prior to the irradiation. For direct irradiation at λ 300 and 350 nm, pyrex vessels were used employing a Rayonet RPR-208 photoreactor equipped with eight RUL-3000 and RUL-3500 lamps, respectively. Sensitized irradiations were performed at the appropriate wavelength such as to excite selectively (>98%) the sensitizer. The reactions were monitored by GLC (Varian 3700, stainless steel column, 4 m, 1/8 inch, 3% OV-225 on Chromosorb W-(AW), 80–100 Mesh, He 30 ml/min). The GLC peak areas were determined using a Varian CDS-111C digital integrator. After the irradiation, the photolyzate was eluted by flash chromatography over a kieselgel column, using mixtures of hexane, dichloromethane and ethyl acetate as eluent. Of the various mixtures thus obtained, the photoproducts were separated and purified by preparative GLC [Varian 2720, copper column, 2 m, 1/4 inch, 10% OV-225 on Chromosorb W-(AW), 40–60 Mesh, He 100 ml/min]. The triplet sensitizers used came from a photosensitizer and quencher kit (Baker). An oxygen-rich atmosphere during irradiation was achieved by bubbling oxygen through the solution; the same procedure was followed using argon instead of oxygen to create an inert atmosphere. The products were identified on the basis of their spectral data or by comparison with reported spectral data. The quenchers 1,3-cyclohexadiene and 2,4-dimethyl-1,3-pentadiene were purchased from Aldrich.

Direct irradiation of 3,3-diphenyl-1-penten-4-one (**2**). A solution of 1.0 g of **2** in 250 ml of benzene was irradiated (λ 300 nm) for 4 days. Work-up of the photolyzate as described afforded the pure compounds **15–19**.

15. ^{1}H NMR, 250 MHz (δ, ppm): 7.60–7.16 (m, 10H, 2 × Ph), 6.07 (t, *J* 7 Hz, 1H, olef.), 2.21 (quintet, *J* 7 Hz, 2H, CH_2), 1.04 (t, *J* 7 Hz, 3H, CH_3). MS-FID, *m/z:* 208($M^{+\bullet}$).

16. ^{1}H NMR, 250 MHz (δ, ppm): 7.62–7.21 (m, 10H, Ph × 2), 6.41 (dd, *J* 17 and 11 Hz, 1H, $C\underline{H}{=}CH_2$), 5.18 (dd, *J* 11 and 1 Hz, 1H, $CH{=}C\underline{H}_ZH_E$), 4.92 (dd, *J* 17 and 1 Hz, 1H, $CH{=}C\underline{H}_EH_Z$), 1.79 (s, 3H, CH_3). MS-FID, *m/z:* 208($M^{+\bullet}$).

17. ^{1}H NMR, 250 MHz (δ, ppm): 7.38–7.12 (m, 10H, 2 × Ph), 6.26 (t, *J* 7 Hz, 1H, olef.), 3.24 (d, *J* 7 Hz, 2H, CH_2), 2.11 (s, 3H, CH_3O). IR, ν(cm^{-1}): 3080(w), 3060(w), 3005(w), 1710(s), 1650(m), 1595(m), 1490(m), 1440(m), 1355(m) 1160(m), 690(s). MS, *m/z* (%): 236($M^{+\bullet}$, 26), 207(25), 206(27), 193(100), 178(35), 165(28), 115(91), 105(38), 91(17), 77(18). High-resolution mass spectrum, *m/z:* 236.1190, calcd. for $C_{17}H_{14}O$, *m/z:* 236.1201.

19. ^{1}H NMR, 250 MHz (δ, ppm): 9.51 (d, *J* 8 Hz, 1H, CHO), 7.46–7.23 (m, 10H, 2 × Ph), 6.58 (d, *J* 8 Hz, 1H, olef.). IR, ν(cm^{-1}): 3080(w), 3000(w), 2850(m), 1655(s), 1590(m), 1570(w), 1445(m), 1130(m), 905(s), 690(m). High-resolution mass spectrum, *m/z:* 208.0878; calcd. for $C_{15}H_{12}O$, *m/z:* 208.0888.

Direct irradiation of 1,2-diphenyl-2-methyl-3-buten-1-one (**3**). A solution of 1.5 g of **3** was dissolved in 300 ml of benzene and irradiated (λ 350 nm) for 5 h. Work-up of the photolyzate as previously described afforded the pure compounds (*E*)- and (*Z*)-**20**, **21**, (*E*)- and (*Z*)-**22** and **23** in the yields shown in Scheme 3.

(*E*)-**20**. ^{1}H NMR, 250 MHz (δ, ppm): 7.39–7.17 (m, 10H, 2 × Ph), 6.11 (dd, *J* 18 and 11 Hz, 1H, $C\underline{H}{=}CH_2$), 5.67 (dt, *J* 7 Hz, 1H, $=C\underline{H}CH_2$), 5.14 (dd, *J* 11 and 1 Hz, 1H, $CH{=}C\underline{H}_ZH_E$), 5.10 (dd, *J* 10 and 1 Hz, 1H, $CH{=}C\underline{H}_EH_Z$), 2.75–2.59 (m, 2H, CH_2), 1.97 (s, 3H, $C\underline{H}_3C{=}$), 1.43 (s, 3H, CH_3CPh). MS-FID, *m/z:* 262($M^{+\bullet}$).

(*Z*)-**20**. ^{1}H NMR, 250 MHz (δ, ppm): 7.34–7.08 (m, 10H, 2 × Ph), 5.97 (dd, *J* 18 and 10 Hz, 1H, $C\underline{H}{=}CH_2$), 5.30 (t, *J* 6 Hz, 1H, $=C\underline{H}CH_2$), 5.05 (dd, *J* 10 and 1 Hz, 1H, $CH{=}C\underline{H}_ZH_E$), 4.96 (dd, *J* 18 and 1 Hz, H, $CH{=}C\underline{H}_EH_Z$), 2.44 (t, *J* 6 Hz, 2H, CH_2), 1.94 (d, *J* 1 Hz, 3H, $CH_3C{=}$), 1.27 (s, 3H, CH_3CPh). IR, ν(cm^{-1}): 3080(w), 3060(w), 3000(w), 2960(w), 2930(w), 2870(w), 2850(w), 1600(m), 1480(m). 1370(m), 910(s), 700(s). MS, *m/z* (%): 262($M^{+\bullet}$, 2), 131(100), 115(19), 91(22), 77(8). High-resolution mass spectrum, *m/z:* 262.1706; calcd. for $C_{20}H_{22}$, *m/z:* 262.1721.

21. ^{1}H NMR, 250 MHz (δ, ppm): 7.39–7.15 (m, 10H, 2 × Ph), 5.71 (dt, *J* 7 and 1 Hz, 1H, $C\underline{H}_E{=}CCH_3$), 5.16 (dt, *J* 7 and 1 Hz, 1H, $C\underline{H}_Z{=}CCH_3$), 2.22–2.08 (m, 4H, CH_2CH_2), 2.03 (d, *J* 1 Hz, 3H, $C\underline{H}_3C{=}CH_E$), 1.98 (d, *J* 1 Hz, 3H, $C\underline{H}_3C{=}CH_Z$). MS-FID, *m/z:* 262($M^{+\bullet}$).

(*E*)-**22**. ^{1}H NMR, 250 MHz (δ, ppm): 8.04–7.98 (m, 2H, $COPh_{ortho}$), 7.51–7.21 (m, 8H, C_6H_3 + Ph), 6.10 (dt, *J* 7 and 1 Hz, 1H, olef.), 3.90 (d, *J* 7 Hz, 2H, CH_2), 2.21 (d, *J* 1 Hz, 3H, CH_3). IR, ν(cm^{-1}): 3080(w), 3060(w), 3005(m), 2975(m), 1680(s), 1595(m), 1575(m), 1490(m), 1325(w), 1260(w), 905(m), 690(s). MS, *m/z* (%): 236($M^{+\bullet}$, 8), 131(17), 105(100), 91(18), 77(57), 51(21). High-resolution mass spectrum, *m/z:* 236.1199; calcd. for $C_{17}H_{16}O$, *m/z:* 236.1201.

(*Z*)-**22**. ^{1}H NMR, 250 MHz (δ, ppm): 7.87–7.81 (m, 2H, $COPh_{ortho}$), 7.71–7.42 (m, 8H, C_6H_3 + Ph), 5.81 (dt, *J* 7 and 1 Hz, 1H, olef.), 3.67 (d, *J* 7 Hz, 2H, CH_2), 2.31 (d, *J* 1 Hz, 3H, CH_3). MS-FID, *m/z:* 236 ($M^{+\bullet}$).

23 (for the numbering see Fig. 6.2). ^{1}H NMR, 250 MHz (δ, ppm): 7.96–7.92 (m, 2H, $COPh_{ortho}$), 7.55–7.12 (m, 8H, C_6H_3 + Ph), 2.93 (dd, *J* 7 and 5 Hz, 1H, H^2), 2.21 (dd, *J* 5 and 4 Hz, 1H, H^{3a}), 1.66 (s, 3H, CH_3), 1.29 (dd, *J* 7 and 4 Hz, 1H, H^{3b}). ^{13}C NMR, 250 MHz (δ, ppm) (*cf.* Fig. 6.2): 21(C3), 28(CH_3), 33(C2), 36(C1), 125–129 (12 × C_{Ph}), 196(CO). IR, ν(cm^{-1}): 3000(w), 2960(m), 2920(m), 2850(w), 1660(s), 1595(m), 1575(m), 1445(s), 1260(s), 980(s), 690(s). MS, *m/z* (%): 236($M^{+\bullet}$, 18), 231(42), 105(100), 91(14), 77(38). High-resolution mass spectrum, *m/z:* 236.1209; calcd. for $C_{15}H_{17}O$, *m/z:* 236.1201.

Direct irradiation of benzyl methyl ketone (**4**). A solution of 3 g of **4** was dissolved in 300 ml of acetonitrile and irradiated (λ 300 nm) for 2 days. Work-up of the photolyzate afforded only the bibenzyl (**24**). When the reaction was performed in acetone, 4-phenyl-2-butanone (**33**) was also obtained, the **24**/**33** ratio being 1.28.

24. ^{1}H NMR, 250 MHz (δ, ppm): 7.42–7.31 (m, 10H, 2 × Ph), 2.94 (s, 4H, CH_2CH_2). IR, ν(cm^{-1}): 3080(w), 3060(w), 3000(m), 2940(m), 2920(m), 2860(m), 1710(w), 1600(s), 1490(s), 1020(m), 700(s). MS, *m/z* (%): 182($M^{+\bullet}$, 18), 191(100). High-resolution mass spectrum, *m/z:* 182.1091; calcd. for $C_{14}H_{14}$, *m/z:* 182.1090. M.p. 50°C (lit.[42] 53°C).

33. ^{1}H NMR, 250 MHz (δ, ppm): 7.32–7.16 (m, 5H, Ph), 2.88 (m, 2H, CH_2), 2.78 (m, 2H, CH_2), 2.14 (s, 3H, CH_3). IR ν(cm^{-1}): 3080(w), 3060(w), 3000(m), 2960(m), 2940(m), 1710(s), 1600(m), 1495(m), 1460(s), 1405(m), 1370(m), 1360(m), 1160(m), 690(s). MS-FID, *m/z:* 170($M^{+\bullet}$).

Direct irradiation of 3-methyl-3-phenyl-2-butanone (**5**). A solution of 3 g of **5** in 300 ml of benzene was irradiated (λ 300 nm) for 2 days. Work-up of the polyzate afforded **25** and a trace of *tert*-butylbenzene (**28**).

25. ^{1}H NMR, 250 MHz (δ, ppm); 7.24–7.03 (m, 10H, 2 × Ph), 1.29 (s, 12H, 4 × CH_3). IR, ν(cm^{-1}): 3080(w), 3060(w), 2980(s), 1600(w), 1480(m), 1460(m), 1440(m), 1370(s), 1140(m), 1020(m), 780(s). MS, *m/z* (%): 238($M^{+\bullet}$ not seen), 119(100), 103(11), 99(44), 79(10), 77(11), 43(13), 41(15). High-resolution mass spectrum, *m/z:* 119.0796; calcd. for $M^{+\bullet}$–C_9H_{11}, *m/z:* 119.0797. M.p. 115°C (lit.[43] 115°C).

Direct irradiation of 1,2-diphenylethanone (**6**). 3 g of **6** in 300 ml of benzene was irradiated (λ 350 nm) for 3 days. Work-up of the photolyzate afforded **24**. When the irradiation was performed in 2-propanol, in addition to a small amount of **24**, the pinacols *(meso)*- and *(racemic)*-**32** were isolated as the predominant products.
(meso)-**32**. ^{1}H NMR, 250 MHz (δ, ppm): 7.43–7.03 (m, 20H, 4 × Ph), 3.69 (AB-system, *J* 14 Hz, 2H, $2 \times C\underline{H}_A H_B$), 2.97 (AB-system, *J* 14 Hz, 2H, $2 \times CH_A\underline{H}_B$), 2.24 (s, 2H, 2 × OH). IR, ν(cm^{-1}): 3575(m), 3080(w), 3060(m), 3000(w), 1600(s), 1490(s), 1440(s), 1060(m), 700(s). MS, *m/z* (%): 394($M^{+\bullet}$, not seen), 197(84), 120(8), 105(100), 91(27), 77(36), 65(6). High-resolution mass spectrum, *m/z*: 197.0968; calcd. for $M^{+\bullet}$-$C_{14}H_{13}O$, *m/z*: 197.0966.
(racemic)-**32**. ^{1}H NMR, 250 MHz (δ, ppm): 7.42–7.05 (m, 20H, 4 × Ph), 3.48 (AB-system, *J* 14 Hz, 2H, $2 \times C\underline{H}_A H_B$), 3.00 (AB-system, *J* 14 Hz, 2H, $2 \times CH_A\underline{H}_B$), 2.85 (s, 2H, 2 × OH). IR, ν(cm^{-1}): 3560(w), 3090(m), 3060(w), 3000(m), 1600(m), 1490(s), 1440(s), 1380(w), 700(s). MS *m/z* (%): 394($M^{+\bullet}$, not seen), 197(100), 120(9), 105(96), 91(32), 77(28). High-resolution mass spectrum, *m/z*: 197.0971; calcd. for $M^{+\bullet}$-$C_{14}H_{13}O$, *m/z*: 197.0966.

Direct irradiation of 1,2-diphenyl-2-methyl-1-propanone (**7**). A solution of 3 g of **7** was dissolved in benzene and irradiated (λ 350 nm) for 3 days. Work-up of the photolyzate afforded **25** as the predominant product (> 96%) in addition to benzil.

Direct irradiation of 1,1-diphenylacetone (**8**). A solution of 2.5 g of **8** was dissolved in 250 ml of benzene and irradiated for 2 days. Work-up of the photolyzate as previously described afforded **26** and a trace of **29**, **30** and **31**.
26. ^{1}H NMR, 60 MHz (δ, ppm): 7.4–6.9 (m, 20H, 4 × Ph), 4.7 (s, 2H, 2 × CH). IR, ν(cm^{-1}): 3090(w), 3060(w), 3000(w), 1600(m), 1490(s), 1070(s), 1020(s), 690(s), 605(s). MS, *m/z* (%): 334($M^{+\bullet}$, 11), 167(100), 152(63), 139(7), 115(13). High-resolution mass spectrum, *m/z*: 334.1723; calcd. for $C_{26}H_{22}$, *m/z*: 334.1722. M.p. 208°C (lit.[44] 208–209°C).
29. ^{1}H NMR, 250 MHz (δ, pm): 7.53–7.13 (m, 10H, 2 × Ph), 4.14 (q, *J* 7 Hz, 1H, $C\underline{H}CH_3$), 1.64 (d, *J* 7 Hz, 3H, $C\underline{H}_3CH$). MS-FID, *m/z*: 182($M^{+\bullet}$).
30. MS-FID, *m/z*: 168($M^{+\bullet}$).
31. ^{1}H NMR, 250 MHz (δ, ppm): 7.58–7.16 (m, 20H, 4 × Ph), 4.23 (s, 1H, CH), 4.06 (s, 1H, CH), 2.21 (s, 1H, OH), 2.15 (s, 1H, OH), 1.39 (s, 3H, CH_3), 1.33 (s, 3H, CH_3). IR, ν(cm^{-1}): 3470(m), 3090(w), 3060(w), 3000(w), 2930(m), 1600(w), 1490(s), 1450(s), 1355(s), 905(s), 695(s). MS, *m/z* (%): 422($M^{+\bullet}$, not seen), 211(100), 195(14), 133(44), 105(38), 59(58), 43(29). High-resolution mass spectrum, *m/z*: 211.1131; calcd. for $M^{+\bullet}$-$C_{15}H_{15}O$, *m/z*: 211.1123.

Direct irradiation of 3,3-diphenyl-2-butanone (**9**). A solution of 2 g of **9** was dissolved in 250 ml of benzene and irradiated for 3 days. Work-up of the photolyzate as previously described afforded **27**.
27. ^{1}H NMR, 60 MHz (δ, ppm): 7.4–6.9 (m, 20H, 4 × Ph), 2.1 (s, 6H, 2 × CH_3). IR, ν(cm^{-1}): 3100(w), 3060(w), 3005(s), 1600(m), 1495(s), 1440(s), 1385(s), 1030(s), 700(s). MS, *m/z* (%): 362($M^{+\bullet}$, not seen), 181(100), 165(97), 152(28), 105(57), 89(23), 77(69), 51(50). High-resolution mass spectrum, *m/z*: 181.1010; calcd. for $M^{+\bullet}$-$C_{14}H_{13}$, *m/z*: 181.1017. M.p. 122°C (lit.[45] 122°C). The product **27** was found to be thermally unstable[45]. Under the GLC conditions, the resulting 1,1-diphenylethyl radical disproportionates to 1,1-diphenylethane (**30**) and 1,1-diphenylethene (**42**).
42. ^{1}H NMR, 250 MHz (δ, ppm): 7.53–7.18 (m, 10H, 2 × Ph), 5.45 (s, 2H, CH_2). MS-FID, *m/z*: 180($M^{+\bullet}$).

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References and Notes

[1a] *A. J. A. van der Weerdt* and *H. Cerfontain*, J. Chem. Soc. Perkin Trans. II 1357 (1977); *A. J. A. van der Weerdt*, *H. Cerfontain*, *J. P. M. van der Ploeg* and *J. A. den Hollander*, J. Chem. Soc. Perkin Trans. II 155 (1978);

[b] *A. J. A. van der Weerdt*, Thesis (in English), University of Amsterdam, 1978.

[2a] *R. H. van der Veen*, *C. Kruk* and *H. Cerfontain*, J. Am. Chem. Soc. **105**, 4367 (1983); *R. H. van der Veen* and *H. Cerfontain*, Tetrahedron **41**, 585 (1985);

[b] *R. H. van der Veen*, Thesis (in English), University of Amsterdam, 1985.

[3] *D. I. Schuster* in "Rearrangements in ground and excited states", Vol. 3, *P. de Mayo*, ed., Academic Press, New York, 1980, pp. 167–297.

[4] *H. U. Gonzenbach*, *I. M. Tegmo-Larson*, *J. P. Grosaude* and *K. Schaffner*, Helv. Chim. Acta **60**, 1091 (1977).

[5] *P. S. Engel*, *M. A. Schexnayder*, *W. V. Phillips*, *H. Ziffer* and *J. I. Seeman*, Tetrahedron Lett. 1157 (1975).

[6] *W. G. Dauben*, *M. S. Kellogg*, *J. I. Seeman* and *W. A. Spitzer*, J. Am. Chem. Soc. **92**, 1786 (1970); *W. G. Dauben*, *G. Lodder* and *J. D. Robbins*, *ibid.* **98**, 3030 (1976).

[7] *E. Baggiolini*, *K. Schaffner* and *O. Jeger*, J. Chem. Soc., Chem. Commun. 1103 (1963).

[8] *H. Hart*, *R. K. Murray* and *G. D. Appleyard*, Tetrahedron Lett. 4785 (1969); *J. Ipaktschi*, *ibid.* 2153 (1969); *J. Ipaktschi*, Chem. Ber. **105**, 1840 (1972).

[9] *J. C. Dalton*, *M. Chen* and *J. J. Snyder*, J. Am. Chem. Soc. **98**, 5023 (1976).

[10] *D. I. Schuster*, *J. Eriksen*, *P. S. Engel* and *M. A. Schexnayder*, J. Am. Chem. Soc. **98**, 5025 (1976).

[11] *S. D. Parker* and *N. A. J. Rogers*, Tetrahedron Lett. 4389 (1976).

[12] *M. J. Mirbach*, *A. Henne* and *K. Schaffner*, J. Am. Chem. Soc. **100**, 7127 (1978).

[13] *A. Henne*, *N. D. Y. Siew* and *K. Schaffner*, J. Am. Chem. Soc. **101**, 3671 (1979).

[14] *P. S. Engel* and *M. A. Schexnayder*, J. Am. Chem. Soc. **97**, 145 (1975); *P. S. Engel*, *M. A. Schexnayder*, *H. Ziffer* and *J. I. Seeman*, J. Am. Chem. Soc. **96**, 924 (1974).

[15] *R. S. Givens*, *W. K. Chae* and *B. Matuszewski*, J. Am. Chem. Soc. **104**, 2456 (1982).

[16] *W. G. Griffin*, *J. Covell*, *R. C. Petterson*, *R. M. Dodson* and *G. Klose*, J. Am. Chem. Soc. **87**, 1410 (1965).

[17] *S. S. Hixson*, J. Am. Chem. Soc. **94**, 2507 (1972).

[18] *H. E. Zimmerman* and *R. L. Swafford*, J. Org. Chem. **49**, 3069 (1984).

[19] *H. E. Zimmerman*, *M. G. Steinmetz* and *C. L. Kreil*, J. Am. Chem. Soc. **100**, 4146 (1978).

[20] *M. J. C. M. Koppes*, *P. C. J. Beentjes* and *H. Cerfontain*, Recl. Trav. Chim. Pays-Bas **107**, 313 (1986).

[21] *R. H. van der Veen* and *H. Cerfontain*, J. Chem. Soc. Perkin Trans. I 661 (1985).

[22] *H. Labhart* and *J. Wagniere*, Helv. Chim. Acta **42**, 2219 (1959).

[23] *P. S. Engel*, J. Am. Chem. Soc. **92**, 6074 (1970).

[24] *W. K. Robbins* and *R. H. Eastman*, J. Am. Chem. Soc. **92**, 6076 (1970).

[25] *F. D. Lewis* and *J. G. Magyar*, J. Am. Chem. Soc. **95**, 5973 (1973).

[26] *Y. Ogata*, *K. Takagi* and *Y. Izawa*, Tetrahedron **24**, 1617 (1968).

[27] *S. Inaba*, *H. Matsumoto* and *R. D. Rieke*, J. Org. Chem. **49**, 2093 (1984); *G. A. Olah*, *T.-L. Ho*, *G. K. S. Prakash* and *B. G. B. Gupta*, Synthesis 607 (1977); *T.-L. Ho* and *G. A. Olah*, Synthesis 170 (1977); *Y. Okude*, *T. Hiyama* and *H. Nozaki*, Tetrahedron Lett. 3829 (1977); *Y. Fujiwara*, *R. Ishikawa* and *S. Teranskhi*, Bull. Chem. Soc. Jpn. **51**, 589 (1978); *I. Haskimoto*, *N. Tsuruta*, *M. Ryang* and *S. Tsutsumi*, J. Org. Chem. **35**, 3748 (1970); *Y. Yamada* and *D. Momose*, Chem. Lett. 1277 (1981).

[28] The bond dissociation energy Δ*H* is ≈ 10 kJ/mol greater for the Ac–H than for the $PhCH_2$–H bond. See, for example, *T. H. Lowry* and *K. Schueller Richardson*, "Mechanism and theory in organic chemistry", 3rd Edition, Harper and Row Publishers, New York, 1987, p. 161.

[29] *H.-G. Heine*, Tetrahedron Lett. 3411 (1972).

[30] *S. S. Jenkins*, J. Am. Chem. Soc. **57**, 2733 (1935).

[31] *J. Kenyon*, *A. Rassoul* and *G. Soliman*, J. Chem. Soc. 1774 (1956).

[32] *Cf.*, for example, *H. Lankamp, W. Th. Nauta* and *C. McLean*. Tetrahedron Lett. 249 (1968); *F. Popp, F. Bickelhaupt* and *C. McLean*, Chem. Phys. Lett. **55**, 327 (1978).

[33] 2-Methyl-1,2-diphenyl-1-propanone (**7**) and its 4′,4″ derivatives, which are devoid of α-hydrogens, do not yield photo-oxidation products[31] and it was therefore concluded that, for the oxidation of these types of ketones, the presence of the *two* α-hydrogens (as in **6**) is a prerequisite for the formation of the peroxy radical intermediate.

[34] *J. Erikson* and *C. S. Foote*, J. Am. Chem. Soc. **102**, 6083 (1980).

[35] *B. W. Petersen* and *C. L. Pedersen*, Acta Chem. Scand. B **34**, 523 (1980).

[36] *J. M. Verbeek, J. Cornelisse* and *G. Lodder*, Tetrahedron Lett. **42**, 5679 (1986).

[37] *K. N. Houk*, Chem. Rev. **1**, 1 (1976).

[38] Ref. 1b, p. 29–34.

[39] *M. J. C. M. Koppes* and *H. Cerfontain*, Recl. Trav. Chim. Pays-Bas **107**, 412, 549 (1988).

[40] *W. C. Still, M. Kahn* and *A. Mitra*, J. Org. Chem. **43**, 2923 (1978).

[41] *V. Meyer* and *L. Oelkers*, Chem. Ber. **21**, 1295 (1888).

[42] *K. M. Johnston* and *G. H. Williams*, J. Chem. Soc. 1168 (1960); *V. K. Schwetlick, W. Geyer* and *H. Hartmann*, J. Prakt. Chem. **30**, 256 (1965).

[43] *W. H. Zartman* and *H. Adkins*, J. Am. Chem. Soc. **54**, 1668 (1932).

[44] *E. Müller* and *G. Röscheisen*, Chem. Ber. **90**, 543 (1957).

[45] *K. Ziegler, A. Seib, K. Knoevenagel, P. Herte* and *F. Andreas*, Ann. **551**, 150 (1942); *L. R. Mahoney*, J. Am. Chem. Soc. **88**, 3035 (1966).