New Results on the Triplet Photoreactivity of β,γ-Unsaturated Aldehydes: Diastereoselective Synthesis of Cyclopropanecarbaldehydes

Diego Armesto,* Maria J. Ortiz,* Antonia R. Agarrabeitia, Santiago Aparicio-Lara

Departamento de Quimica Organica I, Facultad de Ciencias Quimicas, Universidad Complutense, 28040-Madrid, Spain
Fax +34(91)3944103; E-mail: darmesto@eucmos.sim.ucm.es

Received 1 February 2001; revised 29 March 2001

Dedicated with admiration to Professor Howard E. Zimmerman on the occasion of his 75th birthday

Abstract: A comparative study on the triplet photoreactivity of a series of β,γ-unsaturated aldehydes and methyl ketones has been carried out. Aldehydes **14** and **20** were found to undergo the oxa-di-π-methane rearrangement yielding the corresponding cyclopropane carbaldehydes **15** and **21** diastereoselectively. Decarbonylations and 1,3-carbonyl migrations have been observed in some cases, although these reactions do not take place via a Norrish Type I mechanism.

Keywords: β,γ-unsaturated carbonyl compounds, oxa-di-π-methane rearrangement, decarbonylation, cyclopropanecarbaldehydes, 1,3-formyl migration.

The photochemical reactivity of β,γ-unsaturated carbonyl compounds has been the subject of extensive studies.[1] The results obtained from these efforts, conducted over a thirty year period, show that, in general, direct irradiation of β,γ-unsaturated ketones yields products resulting from 1,3-acyl migration, while triplet-sensitized reactions of these compounds afford cyclopropyl ketones by oxa-di-π-methane rearrangement (ODPM) pathways.[1] In addition, the results of numerous studies suggest that β,γ-unsaturated aldehydes undergo only decarbonylation to form alkenes both on direct and sensitized irradiation.[1a,b,d,e] There are only two examples of the occurrence of ODPM rearrangements on triplet sensitized irradiation of β,γ-unsaturated aldehydes. One is found in a report by Schaffner et al. in 1966[2] and the other by Zimmerman and Cassel in 1989.[3]

The combined results have led to a consensus opinion that β,γ-unsaturated aldehydes lack ODPM photoreactivity.[1b,d] Contrary to this common belief are our recent observations of efficient triplet ODPM rearrangement reactivity in members of a series of acyclic and cyclic β,γ-unsaturated aldehydes.[4] Based on these results, we proposed that β,γ-unsaturated aldehydes do indeed undergo efficient triplet ODPM rearrangement when the following criteria are met. First, the triplet energy of the sensitizer must be efficiently transferred to the β,γ-double bond in order to generate a $T_1(\pi\text{-}\pi^*)$ excited state of the substrate. Second, the biradical intermediates in the non-concerted ODPM pathway must be stabilized by conjugation with phenyl or vinyl groups.[4b] β,γ-Unsaturated aldehydes that do not meet these two requirements, like in most of the cases previously probed,[1e] undergo exclusive photodecarbonylation.

In this publication, we describe an extension of our studies on the photoreactivity of β,γ-unsaturated aldehydes. The current effort was aimed at determining the efficacy of our proposal about the factors governing ODPM reactivity of these substances and establishing the scope of the process.

In a previous study Schaffner and his co-workers [5] reported that aldehyde **1** does not undergo ODPM photorearrangement but rather on irradiation a decarbonylation to produce the alkenes **2a** and **2b**. If the proposals presented above are correct, it should be possible to transform **1** into a ODPM reactive substrate by introducing a substituent which would enable efficient triplet energy transfer to the C–C double bond and lead to stabilization of the biradical intermediates in the ODPM pathway. With this idea in mind, we prepared aldehyde **3**, a phenyl-substituted analog of **1**. Unfortunately, all synthetic attempts yielded an inseparable mixture of **3** and its endocyclic double bond isomer **4**. Nevertheless, a 1:1 mixture of **3** and **4** was irradiated using acetophenone as sensitizer. In spite of the complexity of the photomixture, ^{1}H NMR analysis suggested that the bicyclic aldehyde **5**, the product of ODPM rearrangement of the aldehyde **3**, was present in the crude photolysate (Figure).

In order to avoid synthetic problems, we prepared aldehyde **6**, a substrate in which isomerization of the C–C double bond to the endocyclic position is less likely. Contrary to our expectations, irradiation of **6**, by using *m*-methoxyacetophenone as sensitizer, led to formation of the diene **7** (38%), the product of photodecarbonylation. No ODPM product was formed in this process. The formation of **7** is reminiscent of a Norrish Type I process. However, in this case, homolytic bond fission does not occur in the carbonyl n-π* excited state, as is the case in normal Norrish Type I reactions.[1a–c] In addition, irradiation of the corresponding methyl ketone **9**, under the same conditions as used for **6**, afforded the product of 1,3-acyl migration, **10** (24%) (Figure). Again, no ODPM product was formed.

As far as we are aware, these observations are the first which show that the well known Norrish Type I reactions of β,γ-unsaturated carbonyl compounds can take place by excitation of the alkene moiety rather than the carbonyl group. The reason for this unusual reactivity may be that the T_1 (π-π*) excited states of **6** and **9** possess sufficient

Synthesis 2001, No. 8, 18 06 2001. Article Identifier:
1437-210X,E;2001,0,08,1149,1158,ftx,en;C01001SS.pdf.

ISSN 0039-7881

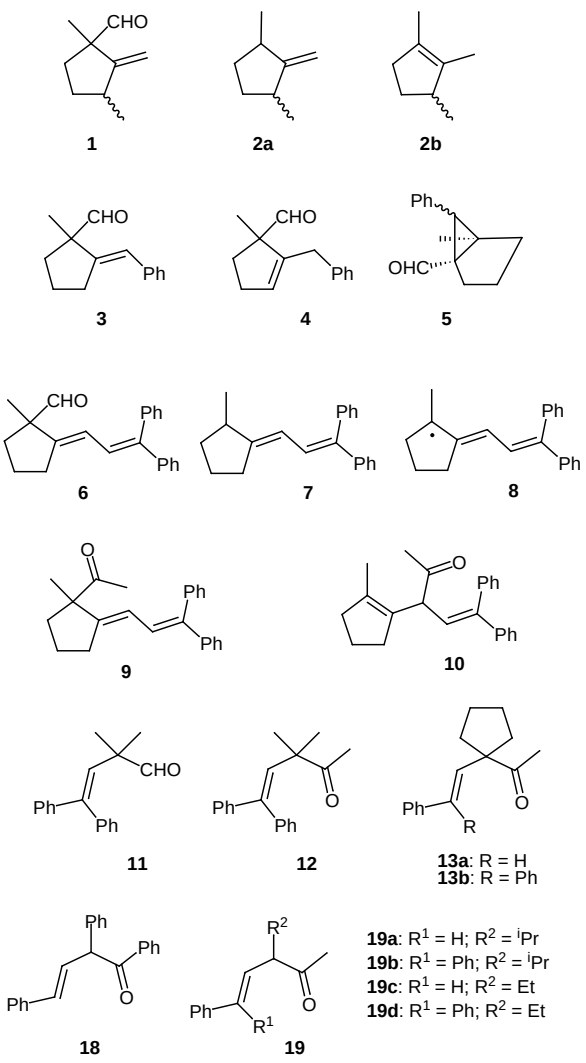
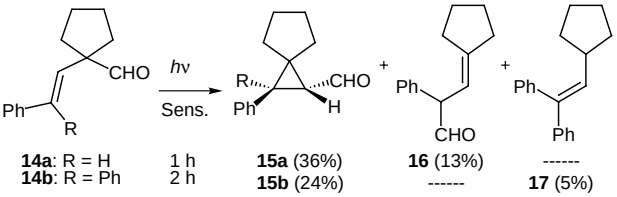


Figure Structures of compounds **1–13, 18** and **19**

energy to promote the homolytic bond fission at the allylic position to form the stabilized pentadienyl radical **8**. As a result photodecarbonylation competes favorably with the ODPM rearrangement.

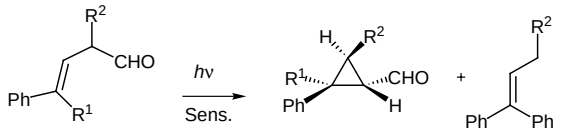
These unexpected results suggest a modification of the conclusions reached in our earlier studies. Specifically, the observations indicate that in order to detect ODPM photoreactivity in β,γ-unsaturated aldehydes, substituents should be present to stabilize intermediate biradicals in the rearrangement pathway, but not to enhance alternative reactions, such as allylic homolytic cleavage. Further studies will be necessary to confirm this hypothesis and to determine the scope of these new reactions.

Another intriguing observation made in our preliminary investigation is that β,γ-unsaturated aldehyde **11** undergoes photoinduced ODPM rearrangement while the analogous methyl ketone **12** does not react in this manner.[4b] This result suggests that other aldehydes with substitution patterns similar to those found in ODPM unreactive ketones might participate in this photorearrangement process. Previous studies have shown that methyl ketone **13a** is not an ODPM substrate.[6] The corresponding aldehyde **14a**, which has the same substitution pattern as **13a**, according to our postulates, should undergo the ODPM rearrangement. In order to test this proposal, aldehydes **14a** and **14b** were synthesized by a modification of the procedure used to prepare **13a**. *m*-Methoxyacetophenone triplet-sensitized irradiation (1 h) of **14a** leads to generation of the spirocyclic derivative **15a** (36%), as the *trans*-diastereoisomer, along with a mixture of starting material and **16**, a compound resulting from 1,3-formyl migration (Scheme 1). Irradiation (2 h) of the diphenyl analog **14b**, under the same conditions used for **14a** gives rise to the ODPM product **15b** (24%), the alkene **17** (5%) and recovered starting material (53%) (Scheme 1). The formation of the alkene **17** in the irradiation of **14b** might be due to the stabilization of the radical resulting from homolytic fission of the bond between the formyl group and the α-carbon, similarly to the reaction observed for compound **6**. In contrast, the methyl ketone derivative **13b** does not undergo the ODPM rearrangement; sensitized irradiation (17 h) of this substance provides recovered starting material (71%) and a complex mixture of products. These additional examples add further support to the proposal that β,γ-unsaturated aldehydes are more prone to undergo the ODPM rearrangement than the corresponding methyl ketones.



Scheme 1

The large number of studies carried out in the di-π-methane area have established that disubstitution at the central carbon of 1,4-diene substrates is an important structural requirement for efficient rearrangement.[1] In fact, there are only two examples in which β,γ-unsaturated ketones (**18**[7] and **19a**[6]), monosubstituted at α-position, undergo the ODPM rearrangement. The reactivity observed in these two substrates was attributed to the bulk of the substituent at C-2 that compensates for the absence of disubstitution at that α-position.[1e] In an attempt to establish the limits for ODPM reactivity of β,γ-unsaturated aldehydes, we have extended our studies to a series of β,γ-unsaturated aldehydes **20**, which are monosubstituted at C-2. Triplet-sensitized irradiation of **20** leads to formation of the corresponding cyclopropanecarbaldehydes **21** (Scheme 2). The diphenyl-substituted aldehydes **20b** and **20d** yielded, in addition to the ODPM products, the corresponding alkenes **22a** and **22b**, resulting from photodecarbonylation. The formation of these alkenes is probably due to stabilization of the radical, formed by allylic cleavage, by diphenyl-conjugation.



20a: R^1 = H; R^2 = ^{i}Pr	40 min	**21a** (21%)	------
20b: R^1 = Ph; R^2 = ^{i}Pr	2.5 h	**21b** (23%)	**22a** (9%)
20c: R^1 = H; R^2 = Et	7.0 h	**21c** (22%)	------
20d: R^1 = Ph; R^2 = Et	7.0 h	**21d** (24%)	**22b** (25%)

Scheme 2

ODPM rearrangement of aldehydes **20** is stereoselective, yielding only one diastereoisomer of **21**. Stereochemical assignment to **21** was made by use of conventional spectroscopic methods in conjunction with comparisons to related compounds.[4] Specifically, in the ^{1}H NMR spectra of **21c**, the aldehydic hydrogen resonates as a doublet at $\delta = 9.35$ ($J = 4.8$ Hz), while cyclopropane H-1 appears at $\delta = 2.19$ as a quadruplet ($J = 5.0$ Hz). These data are consistent with a *trans* arrangement for these hydrogens. The appearance of cyclopropane hydrogen next to the phenyl at $\delta = 2.94$ as a doublet of doublets ($J = 9.6$, 5.1 Hz) suggests a *cis* arrangement between this hydrogen and the cyclopropane hydrogen next to the ethyl group and *trans* with respect to the hydrogen at C-1. These relative stereochemical assignments were confirmed by NOE experiments. Thus, irradiation at $\delta = 2.94$ results in the disappearance of the signal at $\delta = 2.19$ and the enhancement (6%) of the signal at $\delta = 1.80$ corresponding to the cyclopropane hydrogen next to the ethyl group. Furthermore, the signals at $\delta = 2.94$ and 1.80 disappear on irradiation of the signal at $\delta = 2.19$. These data permitted the assignment of **21c** as the 1*R*,2*S*,3*R*/1*S*,2*R*,3*S* diastereoisomer. The ODPM rearrangement of **20a** occurs with the same stereoselectivity, yielding the cyclopropylaldehyde **21a** as the 1*R*,2*S*,3*R*/1*S*,2*R*,3*S* diastereoisomer. Aldehydes **20b** and **20d** afford the cyclopropanes **21b** and **21d** in which the formyl group and the alkyl group are *trans* to each other. A similar diastereoselectivity has been observed for ODPM rearrangements of other aldehydes.[4]

The ODPM reactivity of aldehydes **20** is surprising since, as mentioned before, the only two ODPM reactive acyclic β,γ-unsaturated mono-C-2 substituted ketones are compounds **18** and **19a**, each containing bulky substituents at C-2. However, the observations made with **20c** and **20d**, each having ethyl groups at C-2, clearly demonstrates that the bulk of the C-2 substituent is not an important feature in determining the ODPM reactivity of β,γ-unsaturated aldehydes. However, it should be noted that the isopropyl substituted aldehydes **20a** and **20b** do react more efficiently, in qualitative terms, than **20c** and **20d**.

Substrates **19b–d** were synthesized in order to determine whether the aldehydes **20** are more reactive towards the ODPM than the corresponding methyl ketones (Figure). Compound (*E*)-**19c** does not undergo the ODPM rearrangement. Irradiation of this ketone under the same conditions used for **20** affords the corresponding diastereoisomer (*Z*)-**19c** in 50% yield and 25% of recovered starting material. Prolonged irradiation of **19b** and **19d** under these conditions afforded a complex mixture of highly polar materials (ca 20%) along with recovered starting material (ca 80%). These results confirm the postulate that β,γ-unsaturated aldehydes are better substrates for ODPM rearrangement. In this regard, there are questions that still remain to be answered. For instance, it is surprising that ketone **19a** is reported to be ODPM reactive while ketones **19b–d** do not undergo this rearrangement reaction.

In summary, our current studies have provided the first examples of reactions, similar to the well know Norrish Type I process, which take place in the triplet excited state of β,γ-unsaturated carbonyl compounds by excitation of the C–C double bond instead of the carbonyl group. In addition, a comparison of the photochemical reactivity of β,γ-unsaturated aldehydes and corresponding methyl ketones has shown that the ketones do not undergo the ODPM rearrangement while the corresponding aldehydes are reactive by this pathway. The results contrast with firmly established, but apparently incorrect, ideas about the reactivity of compounds in these families. Finally, ODPM rearrangement of mono-C-2 substituted aldehydes is surprising since there are only two precedents of ketones with this type of substitution that undergo this photoreaction. Furthermore, the photoreactions of these substances are stereoselective, yielding only one of the possible diastereoisomeric cyclopropanecarbaldehyde products. When combined, the results of the current effort broaden the synthetic potential of the ODPM rearrangement.

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Varian VXR-300S (^{1}H, 300 MHz; ^{13}C, 75 MHz), a Bruker AC-250F (^{1}H, 250 MHz; ^{13}C, 62 MHz) or a Bruker AC-200 (^{1}H, 200 MHz; ^{13}C, 50 MHz) spectrometer in $CDCl_3$ solution. *J* values are given in Hertz. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. Mass spectra were recorded on a HP 5989 A spectrometer. UV/visible spectra were recorded on a Perkin Elmer Lambda 3B in CH_2Cl_2 solutions. Column chromatography was performed using silica gel 60 (40–63 mm) from Merck. Commercially available starting materials and reagents were purchased from Aldrich.

Aldehyde **20b**[3] and ketones **13a**[8] and **19a**[8] were synthesized by the methods previously described.

β,γ-Unsaturated Aldehydes 14, 20a, 20c, 20d; General Procedures

These aldehydes were synthesized from the corresponding carboxylic acids by a procedure consisting of esterification, α-alkylation, reduction and oxidation, according to the following general procedures. When describing the experimental procedure below for individual products, a further reference to the general procedure is not always necessarily given.

Esterification of β,γ-Unsaturated Acids: To a solution of β,γ-unsaturated acid in anhyd CH_2Cl_2 was added anhyd MeOH and a few drops of H_2SO_4. The resulting mixture was refluxed for different times (for specific cases, see below). The organic layer was washed with H_2O, sat. aq $NaHCO_3$ solution, H_2O, dried ($MgSO_4$), filtered and evaporated to dryness. The β,γ-unsaturated esters were purified

by flash chromatography on silica gel using hexane–Et_2O (8:2) as eluent.

α-Alkylation of β,γ-Unsaturated Esters: To a solution of *i*-Pr_2NH in anhyd THF at –78°C under argon was added BuLi (1.6 M in hexane) dropwise. The mixture was stirred for 1 h, and then a solution of the corresponding β,γ-unsaturated ester (for specific cases, see below) in anhyd THF was added dropwise over 1 h. The resulting solution was stirred for an additional 10 min at –78°C, and then the corresponding halogen derivative was added dropwise. The solution was stirred for 18 h at r.t. before quenching with 5% aq NH_4Cl solution. The organic layer was washed with 5% aq HCl and H_2O, dried ($MgSO_4$), filtered and evaporated to dryness. The alkylated β,γ-unsaturated esters were purified by flash chromatography on silica gel using hexane–Et_2O as eluent.

Reduction of Esters: A solution of the corresponding ester (for specific cases, see below) in anhyd Et_2O was added slowly at 0°C to a suspension of $LiAlH_4$ in Et_2O. The resulting mixture was stirred at r.t. for 1 h. The residual $LiAlH_4$ was decomposed by addition of H_2O. The mixture was filtered and washed with Et_2O. The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. The alcohol was purified by flash chromatography on silica gel.

Oxidation of Alcohols to Aldehydes: A solution of the corresponding β,γ-unsaturated alcohols and PCC were allowed to react in CH_2Cl_2 at r.t. for different times (for specific cases, see below). The reaction mixture was filtered through silica gel and the solvent evaporated to give the desired aldehyde. The products were purified by flash chromatography on silica gel.

β,γ-Unsaturated Methyl Ketones 13b, 19b–d; General Procedures

These ketones were synthesized from β,γ-unsaturated aldehydes by reaction with MeMgI followed by oxidation of the corresponding alcohols. When describing the experimental procedure below for individual products, a further reference to the general procedure is not always necessarily given.

β,γ-Unsaturated Alcohols**:** To a solution of MeMgI in anhyd Et_2O under argon was added dropwise a solution of aldehyde (for specific cases, see below) in anhyd Et_2O. After refluxing for 1 h, the solution was cooled to 0°C, quenched with sat. aq NH_4Cl solution. The mixture was extracted with Et_2O and the organic layer was washed with H_2O, dried ($MgSO_4$), filtered and concentrated to dryness. The alcohols were purified by flash chromatography on silica gel.

Oxidation of Alcohols to Ketones: To a solution of the alcohol (for specific cases, see below) in Et_2O was added dropwise a solution of $K_2Cr_2O_7$, H_2SO_4 and H_2O (the temperature was maintained below 25°C). After the addition was complete, the solution was stirred at r.t. for different times (for specific cases, see below). Et_2O was added, the organics layers were separated, washed with H_2O, sat. aq $NaHCO_3$ solution and H_2O, dried ($MgSO_4$), filtered and evaporated under reduced pressure to give, after purification by flash chromatography on silica gel, the corresponding β,γ-unsaturated ketones.

(*E*)-2-(3,3-Diphenylprop-2-enylidene)-1-methylcyclopentane Carbaldehyde (6)

This compound was synthesized in three steps from ethyl 2-formylmethylidene-1-methylcyclopentanecarboxylate, obtained by the method previously described for the corresponding methyl ester.[9] To a stirred solution of diethyl diphenylmethylphosphonate[10] (2.5 g, 8.2 mmol) in anhyd DME (10 mL) under argon and at 0°C was added BuLi (3.3 mL, 2.5 M in hexane). The resulting solution was stirred for 1 h at 0°C, and ethyl 2-formylmethylidene-1-methylcyclopentanecarboxylate (1 g, 5.1 mmol) in DME (10 mL) was added. The reaction mixture was stirred at 0°C for 3 h before quenching with sat. aq NH_4Cl solution and extracted with Et_2O. The organic layer was washed with brine, H_2O, dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography using hexane–Et_2O (9:1) yielded ethyl (*E*)-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarboxylate (1.4 g, 79%) as an oil.

IR (neat): ν = 1724 cm^{-1}.

^1H NMR (200 MHz): δ = 1.14 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.25 (s, 3 H, CH_3), 1.49–1.58 (m, 1 H, CH_2), 1.71–1.97 (m, 2 H, CH_2), 2.35 (dt, 1 H, *J* = 12.1, 6.8 Hz, CH_2), 2.65 (t, 2 H, *J* = 6.2 Hz, CH_2), 4.05 (q, 2 H, *J* = 7.1 Hz, OCH_2), 6.12 (dt, 1 H, *J* = 11.4, 2.5 Hz, CH=C), 6.71 (d, 1 H, *J* = 11.4 Hz, CH=C), 7.11–7.43 (m, 10 H, ArH).

^{13}C NMR (50 MHz): δ = 14.2 (CH_3), 23.9 (CH_2), 24.7 (CH_3), 30.5 (CH_2), 38.7 (CH_2), 53.3 (quat. C), 60.7 (OCH_2), 120.4–143.0 (C=C and Ar-C), 151.9 (CO_2).

MS: *m/z* (%) = 346 (M^+, 61), 273 (100), 191 (23), 167 (14), 91 (25).

The above ester (1.4 g, 4 mmol) was reduced with $LiAlH_4$ (0.2 g, 4.8 mmol). Chromatography using hexane–Et_2O (8:2) yielded 1.1 g (89%) of (*E*)-2-(3,3-diphenylprop-2-enylidene)-1-hydroxymethyl-1-methylcyclopentane as a yellow oil.

IR (neat): ν = 3500–3200 cm^{-1}.

^1H NMR (200 MHz): δ = 0.99 (s, 3 H, CH_3), 1.32 (t, 1 H, *J* = 6.6, OH), 1.43–1.54 (m, 1 H, CH_2), 1.61–1.82 (m, 2 H, CH_2), 1.82–1.93 (m, 1 H, CH_2), 2.51–2.69 (m, 2 H, CH_2), 3.29–3.36 (m, 2 H, C*H*$_2$OH), 5.94 (dt, 1 H, *J* = 11.3, 2.4 Hz, CH=C), 6.74 (d, 1 H, *J* = 11.3 Hz, CH=C), 7.17–7.43 (m, 10 H, ArH).

^{13}C NMR (50 MHz): δ = 22.8 (CH_2), 23.7 (CH_3), 31.0 (CH_2), 36.9 (CH_2), 48.6 (quat. C), 69.3 (CH_2OH), 119.1, 125.6–130.7, 140.1, 140.8, 143.1, 153.7 (C=C and Ar-C).

MS: *m/z* (%) = 304 (M^+, 35), 273 (100), 191 (22), 167 (12), 91 (25).

(*E*)-2-(3,3-Diphenylprop-2-enylindene)-1-hydroxymethyl-1-methylcyclopentane (1.1 g, 3.6 mmol) was oxidized with PCC (1.7 g, 8.8 mmol) by stirring for 1 h. Chromatography using hexane–EtOAc (9:1) yielded 540 mg (50%) of **6** as an oil.

IR (neat): ν = 1718 cm^{-1}.

^1H NMR (200 MHz): δ = 1.14 (s, 3 H, CH_3), 1.42–1.60 (m, 1 H, CH_2), 1.75–1.89 (m, 2 H, CH_2), 2.19 (app dt, 1 H, *J* = 12.7, 6.6 Hz, CH_2), 2.61 (dq, 2 H, *J* = 7.4, 2.5 Hz, CH_2), 5.98 (dt, 1 H, *J* = 11.3, 2.5 Hz, CH=C), 6.72 (d, 1 H, *J* = 11.3 Hz, CH=C), 7.12–7.41 (m, 10 H, ArH), 9.23 (s, 1 H, CHO).

^{13}C NMR (50 MHz): δ = 20.6 (CH_3), 23.6 (CH_2), 31.6 (CH_2), 34.8 (CH_2), 58.3 (quat. C), 122.5–148.6 (C=C and Ar-C), 200.5 (CHO).

MS: *m/z* (%) = 273 (M^+ – 29, 2), 228 (27), 197 (100), 169 (24), 155 (24), 141 (28), 117 (19), 91 (42).

UV (CH_2Cl_2): λ_{max} = 245 nm (ε = 34040).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.42; H, 7.28. Found: C, 87.22; H, 7.20.

(*E*)-1-Acetyl-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentane (9)

This compound was synthesized in three steps from (*E*)-ethyl 2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarboxylate, obtained previously in the synthesis of aldehyde **6**. A solution of KOH (0.23 g, 0.2 mmol) and (*E*)-ethyl 2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarboxylate (0.5 g, 1.4 mmol) in absolute EtOH (18 mL) was refluxed for 24 h. The solvent was evaporated to dryness and the crude product was dissolved in H_2O. The solution was washed with Et_2O and the aqueous layer was acidified with a 20% HCl and extracted with Et_2O. The organic layers were dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography using hexane–Et_2O (7:3) yielded (*E*)-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarboxylic acid (240 mg, 54%) as a white solid; mp 137–138°C (hexane).

IR (KBr): ν = 3500–2500, 1690 cm^{-1}.

^{1}H NMR (300 MHz): δ = 1.28 (s, 3 H, CH_3), 1.53–2.01 (m, 3 H, 2 CH_2), 2.36 (dt, 1 H, *J* = 12.4, 6.2 Hz, CH_2), 2.63 (app dt 2 H, *J* = 7.2, 2.4 Hz, CH_2), 6.19 (dt, 1 H, *J* = 11.3, 2.4 Hz, CH=C), 6.69 (d, 1 H, *J* = 11.3 Hz, CH=C), 7.17–7.38 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 23.8 (CH_2), 24.1 (CH_3), 30.3 (CH_2), 38.7 (CH_2), 52.9 (quat. C), 121.0, 125.3–130.7, 139.5, 141.9, 143.0, 150.7 (C=C and Ar-C), 182.9 (CO_2).

MS: *m/z* (%) = 318 (M^+, 81), 273 (100), 218 (10), 191 (31), 165 (26), 91 (43), 81 (9), 77 (10), 55 (5).

A solution of (*E*)-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarboxylic acid (0.24 g, 0.7 mmol) and $SOCl_2$ (1 mL) was heated at reflux for 20 min. Removal of the residual $SOCl_2$ under reduced pressure yielded (*E*)-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarbonyl chloride (253 mg, 99%) as an oil, which was used without further purification.

IR (neat): ν = 1787 cm^{-1}.

^{1}H NMR (300 MHz): δ = 1.36 (s, 3 H, CH_3), 1.59–2.01 (m, 3 H, 2 CH_2), 2.43–2.58 (m, 1 H, CH_2), 2.62–2.79 (m, 2 H, CH_2), 6.14 (dt, 1 H, *J* = 11.4, 2.7 Hz, CH=C), 6.70 (d, 1 H, *J* = 11.4 Hz, C*H*=CPh_2), 7.20–7.42 (m, 10 H, ArH).

To a stirred suspension of CuI (171 mg, 0.9 mmol) in anhyd Et_2O (15 mL) under argon and at –40 °C was added MeLi (1 mL, 1.5 M in Et_2O). The mixture was stirred for 30 min, and *(E)*-2-(3,3-diphenylprop-2-enylidene)-1-methylcyclopentanecarbonyl chloride (253 mg, 0.75 mmol) in Et_2O (5 mL) was added. The reaction was kept at –40 °C for 30 min, allowed to warm at 0 °C, and stirred for 30 min before being quenched with a sat. aq NH_4Cl solution and extracted with Et_2O. The combined organic phases were dried, filtered, and concentrated to dryness. Flash chromatography using hexane–Et_2O (9:1) afforded the ketone **9** (210 mg, 89%) as an oil.

IR (neat): ν = 1787 cm^{-1}.

^{1}H NMR (300 MHz): δ = 1.12 (s, 3 H, CH_3), 1.47–1.54 (m, 1 H, CH_2), 1.73–1.90 (m, 2 H, CH_2), 2.06 (s, 3 H, CH_3CO), 2.12–2.58 (dt, 1 H, *J* = 11.7, 7.7 Hz, CH_2), 2.50–2.93 (m, 2 H, CH_2), 5,90 (dt, 1 H, *J* = 11.2, 2.5 Hz, CH=C), 6.72 (d, 1 H, *J* = 11.2 Hz, CH=C), 7.15–7.38 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 23.3 (CH_3), 23.7 (CH_2), 25.6 (CH_3), 30.7 (CH_2), 37.8 (CH_2), 60.2 (quat. C), 121.2, 125.2, 130.5, 139.6, 141.8, 142.7, 151.5 (C=C and Ar-C), 210.2 (CO).

MS: *m/z* (%) = 316 (M^+, 9), 273 (100), 191 (23), 165 (15), 91 (29), 77 (6), 55 (6).

UV (CH_2Cl_2): λ_{max} = 310 nm (∈ = 60189).

Anal. Calcd for $C_{23}H_{24}O$: C, 87.34; H, 7.59. Found: C, 87.20; H, 7.43.

(*E*)-1-(2-Phenylvinyl)-1-cyclopentanecarbaldehyde (14a)

trans-Styrylacetic acid (5 g, 30.9 mmol), MeOH (3 mL, 92.5 mmol) and H_2SO_4 (5 drops) were refluxed for 24 h to afford (*E*)-methyl 4-phenylbut-3-enoate;[8] yield: 4.83 g (89%).

i-Pr_2NH (1.7 mL, 12.75 mmol), BuLi (8 mL, 1.6 M in hexane), (*E*)-methyl 4-phenylbut-3-enoate (1.5 g, 8.5 mmol), and 1,4-dibromobutane (1 mL, 8.5 mmol) were used for the α-alkylation reaction. Chromatography using hexane–Et_2O (85:15) gave (*E*)-methyl 1-(2-phenylvinyl)-1-cyclopentanecarboxylate as a yellow oil; yield: 0.79 g (40%).

IR (neat): ν = 1740 cm^{-1}.

^{1}H NMR (300 MHz): δ = 1.61–1.75 (m, 4 H, 2 CH_2), 1.80–1.88 (m, 2 H, CH_2), 2.21–2.32 (m, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 6.40 (AB system, 2 H, *J* = 16.2 Hz, CH=CH), 7.19–7.39 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 24.0 (2 CH_2), 35.8 (2 CH_2), 52.3 (OCH_3), 56.5 (quat. C), 126.4–137.0 (C=C and Ar-C), 176.5 (CO_2).

MS: *m/z* (%) = 230 (M^+, 2), 171 (15), 129 (19), 117 (16), 91 (25), 71 (47), 57 (100).

(*E*)-Methyl 1-(2-phenylvinyl)-1-cyclopentanecarboxylate (0.6 g, 2.61 mmol) was reduced with $LiAlH_4$ (0.1 g, 2.61 mmol). Chromatography using hexane–Et_2O (8:2) yielded 0.39 g (73%) of (*E*)-1-hydroxymethyl-1-(2-phenylvinyl)cyclopentane as a yellow oil.

IR (neat): ν = 3620, 3450 cm^{-1}.

^{1}H NMR (250 MHz): δ = 1.60–1.76 (m, 9 H, 4 CH_2 and OH), 3.48 (br s, 2 H, C*H*$_2$OH), 6.24 (AB system, 2 H, *J* = 16.3 Hz, CH=CH), 7.17–7.39 (m, 5 H, ArH).

^{13}C NMR (75 MHz): δ = 24.4 (2 CH_2), 34.3 (2 CH_2), 51.3 (quat. C), 69.0 (CH_2OH), 126.2–129.0, 136.1 (C=C and Ar-C).

MS: *m/z* (%) = 202 (M^+, 7), 171 (80), 129 (75), 115 (27), 91 (100), 77 (22).

(*E*)-1-Hydroxymethyl-1-(2-phenylvinyl)cyclopentane (0.386 g, 1.91 mmol) was oxidized with PCC (1.03 g, 4.78 mmol) by stirring for 3 h. Chromatography using hexane–Et_2O (9:1), yielded 0.3 g (78%) of aldehyde (*E*)-**14a** as an oil.

IR (neat): ν = 1730 cm^{-1}.

^{1}H NMR (250 MHz): δ = 1.59–1.74 (m, 6 H, 3 CH_2), 2.16–2.35 (m, 2 H, CH_2), 6.30 (AB system, 2 H, *J* = 16.4 Hz, CH=CH), 7.15–7.50 (m, 5 H, ArH), 9.46 (s, 1 H, CHO).

^{13}C NMR (62 MHz): δ = 24.6 (2 CH_2), 32.8 (2 CH_2), 61.2 (quat. C), 126.3–131.4, 136.8 (C=C and Ar-C), 201.3 (CHO).

MS: *m/z* (%) = 201 (M^+ + 1, 11), 171 (66), 141 (28), 128 (51), 105 (100), 91 (99), 77 (53), 55 (30).

UV (CH_2Cl_2): λ_{max} = 256 nm (ε = 17200).

1-(2,2-Diphenylvinyl)-1-cyclopentanecarbaldehyde (14b)

4,4-Diphenylbut-3-enoic acid[11] (2 g, 8.4 mmol) was esterified with MeOH (1 mL, 25 mmol) in the presence of H_2SO_4 (5 drops) by refluxing for 2.5 h to afford methyl 4,4-diphenylbut-3-enoate as a yellow oil; yield: 1.53 g (72%).

IR (neat): ν = 1750 cm^{-1}.

^{1}H NMR (300 MHz): δ = 3.16 (d, 2 H, *J* = 7.5 Hz, CH_2), 3.67 (s, 3 H, OCH_3), 6.25 (t, 1 H, *J* = 7.5 Hz, CH=C), 7.16–7.37 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 33.2 (CH_2), 51.9 (CH_3), 120.2–144.8 (C=C and Ar-C), 172.3 (CO_2).

i-Pr_2NH (1.2 mL, 8.9 mmol), BuLi (5.5 mL, 1.6 M in hexane), methyl 4,4-diphenylbut-3-enoate (1.5 g, 5.95 mmol) and 1,4-dibromobutane (0.7 mL, 5.95 mmol) were used for the α-alkylation reaction. Chromatography using hexane–Et_2O (85:15) yielded 2.15 g (94%) of methyl 2-(4-bromobutyl)-4,4-diphenylbut-3-enoate as a yellow oil.

^{1}H NMR (300 MHz): δ = 1.21–1.80 (m, 6 H, 3 CH_2), 3.15–3.25 (m, 1 H, CH), 3.31 (q, 2 H, *J* = 6.7 Hz, CH_2Br), 3.70 (s, 3 H, OCH_3), 6.10 (d, 1 H, *J* = 10.5 Hz, CH=C), 7.21–7.40 (m, 10 H, ArH).

The cyclization to the cyclopropane derivative was carrried out as follows: To a solution of *i*-Pr_2NH (0.9 mL, 6.11 mmol) in anhyd DME (25 mL) at –78 °C under argon was added dropwise BuLi (3.8 mL, 1.6 M in hexane). After the mixture was stirred for 20 min, a solution of methyl 2-(4-bromobutyl)-4,4-diphenylbut-3-enoate (2.15 g, 5.5 mmol) in anhyd DME (15 mL) was added dropwise over 30 min. The resulting solution was stirred for 2 h at 0 °C and 16 h at r.t. before quenching with 10% aq HCl. The organic layer was washed with 5% aq HCl and H_2O, dried ($MgSO_4$), filtered and evaporated to dryness. Flash chromatography on silica gel using hexane–EtOAc (95:5) yielded 1.62 g (96%) of methyl 1-(2,2-diphenylvinyl)-1-cyclopentanecarboxylate as a yellow oil.

IR (neat): ν = 1735 cm^{-1}.

^1H NMR (250 MHz): δ = 1.58–1.69 (m, 6 H, 3 CH_2), 2.21–2.26 (m, 2 H, CH_2), 3.36 (s, 3 H, OCH_3), 6.16 (s, 1 H, CH=C), 7.09–7.33 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 24.5 (2 CH_2), 39.1 (2 CH_2), 51.7 (OCH_3), 55.4 (quat. C), 127.3–134, 139.5, 142.0, 143.3 (C=C and Ar-C), 176.3 (CO_2).

MS: *m/z* (%) = 306 (M^+, 22), 247 (100), 205 (27), 169 (36), 141 (24), 117 (60), 91 (85), 77 (18), 51 (14).

Methyl 1-(2,2-diphenylvinyl)-1-cyclopentanecarboxylate (0.47 g, 1.5 mmol) was reduced with $LiAlH_4$ (63 mg, 1.65 mmol). Chromatography using hexane–EtOAc (8:2) yielded 0.31 g (75%) of 1-(2,2-diphenylvinyl)-1-hydroxymethylcyclopentane as a yellow oil.

IR (neat): ν = 3360 cm^{-1}.

^1H NMR (300 MHz): δ = 1.54–1.59 (m, 9 H, 4 CH_2 and OH), 3.27 (br s, 2 H, CH_2OH), 6.13 (s, 1 H, CH=C), 7.19–7.36 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 24.2 (2 CH_2), 36.5 (2 CH_2), 51.2 (quat. C), 68.4 (CH_2OH), 126.8–129.8, 135.9, 140.3, 141.9, 143.6, (C=C and Ar-C).

MS: *m/z* (%) = 278 (M^+, 5), 247 (100), 205 (22), 169 (37), 141 (24), 117 (60), 91 (92), 77 (20), 55 (25).

Oxidation of 1-(2,2-diphenylvinyl)-1-hydroxymethylcyclopentane (0.33 g, 1.19 mmol) was carried out with PCC (0.64 g, 2.96 mmol) by stirring for 1 h. Chromatography using hexane–EtOAc (8:2) yielded 0.26 g (80%) of aldehyde **14b** as an oil.

IR (neat): ν = 1730 cm^{-1}.

^1H NMR (250 MHz): δ = 1.20–1.35 (m, 2 H, CH_2), 1.50–1.75 (m, 4 H, 2 CH_2), 1.95–2.15 (m, 2 H, CH_2), 6.10 (s, 1 H, CH=C), 7.10–7.41 (m, 10 H, ArH), 9.20 (s, 1 H, CHO).

^{13}C NMR (62 MHz): δ = 25.2 (2 CH_2), 35.7 (2 CH_2), 60.4 (quat. C), 127.3–132.5, 139.4, 142.4, 144.1 (C=C and Ar-C), 199.5 (CHO).

MS: *m/z* (%) = 276 (M^+, 2), 259 (10), 247 (3), 207 (6), 171 (36), 141 (18), 129 (44), 91 (100), 77 (58), 55 (60).

UV (CH_2Cl_2): λ_{max} = 252 nm (ε = 41800).

1-Acetyl-1-(2,2-diphenylvinyl)cyclopentane (13b)

Mg (72 mg, 2.94 mmol), MeI (0.2 mL, 2.83 mmol) and aldehyde **14b** (0.263 g, 0.96 mmol) were used for the preparation of the α,β-unsaturated alcohol. Chromatography using hexane–Et_2O (8:2) yielded 90 mg (30%) of 1-(2,2-diphenylvinyl)-1-(1-hydroxyethyl)cyclopentane as a yellow oil.

IR (neat): ν = 3350 cm^{-1}.

^1H NMR (250 MHz): δ = 1.22 (d, 3 H, *J* = 6.4 Hz, CH_3), 1.41–2.70 (m, 8 H, 4 CH_2), 3.51 (br s, 1 H, OH), 3.70 (q, 1 H, *J* = 6.4 Hz, C*H*OH), 6.11 (s, 1 H, CH=C), 7.12–7.41 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 19.7 (CH_3), 24.5 (CH_2), 24.7 (CH_2), 35.0 (CH_2), 35.4 (CH_2), 54.9 (quat. C), 74.0 (CHOH), 126.1–129.9, 135.6, 140.6, 142.0, 144.4 (C=C and Ar-C).

MS: *m/z* (%) = 247 (M^+ – 45, 60), 205 (14), 167 (34), 112 (65), 91 (100), 71 (19).

1-(2,2-Diphenylvinyl)-1-(1-hydroxyethyl)cyclopentane (90 mg, 0.3 mmol) was oxidized with $K_2Cr_2O_7$ (90 mg, 0.3 mmol) in H_2SO_4 (2 mL) and H_2O (4 mL) by stirring for 5 min at r.t. Chromatography using hexane–Et_2O (9:1) yielded 57 mg (65%) of ketone **13b** as an oil.

IR (neat): ν = 1705 cm^{-1}.

^1H NMR (250 MHz): δ = 1.21–1.72 (m, 7 H, 4 CH_2), 2.00 (s, 3 H, CH_3CO), 2.00–2.13 (m, 1 H, CH_2), 6.20 (s, 1 H, CH=C), 6.95–7.25 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 25.0 (2 CH_2), 26.9 (CH_3), 37.8 (2 CH_2), 62.1 (quat. C), 126.4–134.5, 139.2, 143.3, 145.3 (C=C and Ar-C), 208.7 (CO).

MS: *m/z* (%) = 247 (M^+ – 43, 58), 205 (14), 178 (11), 167 (30), 165 (30), 112 (64), 91 (100), 77 (15), 71 (19), 51 (17).

UV (CH_2Cl_2): λ_{max} = 253 nm (ε = 10350).

(*E*)-2-Isopropyl-4-phenylbut-3-enal (20a)

i-Pr_2NH (0.8 mL, 6.1 mmol), BuLi (3.8 mL, 1.6 M in hexane), (*E*)-methyl 4-phenylbut-3-enoate[8] (0.789 g, 4.48 mmol), and *i*-PrI (0.9 mL, 8.96 mmol) were used for the α-alkylation. Chromatography using hexane–Et_2O (96:4) yielded 0.345 g (35%) of (*E*)-methyl 2-isopropyl-4-phenylbut-3-enoate as a yellow oil.

IR (neat): ν = 1730 cm^{-1}.

^1H NMR (300 MHz): δ = 0.93 (d, 3 H, *J* = 6.9 Hz, CH_3), 0.96 (d, 3 H, *J* = 6.9 Hz, CH_3), 2.04–2.17 [m, 1 H, C*H*(CH_3)$_2$], 2.86 (t, 1 H, *J* = 9.6 Hz, CH), 3.69 (s, 3 H, OCH_3), 6.22 (dd, 1 H, *J* = 15.8, 9.6 Hz, PhCH=C*H*), 6.45 (d, 1 H, *J* = 15.8 Hz, PhC*H*=CH), 7.20–7.41 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 19.7 (CH_3), 20.6 (CH_3), 31.1 [*C*H(CH_3)$_2$], 51.5 (CH), 57.2 (OCH_3), 126.1–128.3, 132.8, 136.6 (C=C and Ar-C), 174 (CO_2).

MS: *m/z* (%) = 218 (M^+, 15), 159 (30), 144 (30), 128 (24), 115 (100), 91 (63), 71 (36), 57 (76).

(*E*)-Methyl 2-isopropyl-4-phenylbut-3-enoate (1 g, 4.6 mmol) was reduced with $LiAlH_4$ (0.175 g, 4.6 mmol). Chromatography using hexane–Et_2O (8:2) yielded 0.62 g (71%) of (*E*)-2-isopropyl-4-phenylbut-3-en-1-ol as a yellow oil.

IR (neat): ν = 3350 cm^{-1}.

^1H NMR (250 MHz): δ = 0.91 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.95 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.60 (br s, 1 H, OH), 1.73–1.83 [m, 1 H, C*H*(CH_3)$_2$], 2.12–2.24 (m, 1 H, CH), 3.50 (dd, 1 H, *J* = 10.5, 8.8 Hz, C*H*HOH), 3.71 (dd, 1 H, *J* = 10.5, 4.9 Hz, CH*H*OH), 6.01 (dd, 1 H, *J* = 15.9, 9.5 Hz, PhCH=C*H*), 6.50 (d, 1 H, *J* = 15.9 Hz, PhC*H*=CH), 7.30–7.40 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 19.8 (CH_3), 21.0 (CH_3), 29.2 [*C*H(CH_3)$_2$], 53.1 (CH), 64.3 (CH_2OH), 126.3–129.8, 133.6, 137.2 (C=C and Ar-C).

MS: *m/z* (%) = 190 (M^+, 8), 172 (5), 159 (23), 129 (56), 117 (55), 115 (30), 91 (100), 71 (38), 57 (80).

(*E*)-2-Isopropyl-4-phenylbut-3-en-1-ol (0.62 g, 3.26 mmol) was oxidized with PCC (1.76 g, 8.15 mmol) by stirring for 80 min. Chromatography using hexane–Et_2O (95:5) yielded 0.29 g (46%) of aldehyde (*E*)-**20a** as an oil.

IR (neat): ν = 1720 cm^{-1}.

^1H NMR (300 MHz): δ = 0.96 (d, 3 H, *J* = 6.9 Hz, CH_3), 1.00 (d, 3 H, *J* = 6.9 Hz, CH_3), 2.18–2.38 [m, 1 H, CH(CH_3)$_2$], 2.85–2.91 (m, 1 H, CH), 6.15 (dd, 1 H, *J* = 16.0, 9.1 Hz, PhCH=C*H*), 6.51 (d, 1 H, *J* = 16.0 Hz, PhC*H*=CH), 7.21–7.41 (m, 5 H, ArH), 9.60 (d, 1 H, *J* = 2.7 Hz, CHO).

^{13}C NMR (62 MHz): δ = 19.6 (CH_3), 20.9 (CH_3), 31.7 [*C*H(CH_3)$_2$], 63.6 (CH), 123.3, 126.4–128.7, 135.2, 136.8 (C=C and Ar-C), 201.8 (CHO).

MS: *m/z* (%) = 188 (M^+, 4), 159 (18), 131 (24), 105 (100), 91 (46), 77 (48), 51 (2).

UV (CH_2Cl_2): λ_{max} = 255 nm (ε = 16250).

(*E*)-2-Ethyl-4-phenylbut-3-enal (20c)

i-Pr_2NH (2.3 mL, 16.5 mmol), BuLi (10.3 mL, 1.6 M in hexane), (*E*)-methyl 4-phenylbut-3-enoate[8] (2.9 g, 16.5 mmol), and EtI (1 mL, 11.4 mmol) were used for the α-alkylation. Chromatography using hexane–Et_2O (99:1) yielded 1.42g (42%) of (*E*)-methyl 2-ethyl-4-phenylbut-3-enoate as a yellow oil.

IR (neat): ν = 1740 cm^{-1}.

^1H NMR (300 MHz): δ = 0.94 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.60–1.75 (m, 1 H, CH_2), 1.82–1.96 (m, 1 H, CH_2), 3.05–3.17 (m, 1 H, CH), 3.70 (s, 3 H, OCH_3), 6.22 (dd, 1 H, *J* = 15.9, 8.9 Hz, PhCH=C*H*), 6.44 (d, 1 H, *J* = 15.9 Hz, PhC*H*=CH), 7.30–7.38 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 11.8 (CH_3), 26.0 (CH_2), 51.3 (CH), 51.9 (OCH_3), 126.4–128.8, 132.4, 136.9 (C=C and Ar-C), 174.7 (CO_2).

MS: *m/z* (%) = 145 (M^+ – 59, 100), 130 (22), 115 (45), 103 (14), 91 (96), 77 (37), 51 (41).

(*E*)-Methyl 2-ethyl-4-phenylbut-3-enoate (0.74 g, 3.6 mmol) was reduced with $LiAlH_4$ (0.15 g, 4 mmol). Chromatography using hexane–Et_2O (8:2) yielded 0.46 g (71%) of (*E*)-2-ethyl-4-phenylbut-3-en-1-ol as a yellow oil.

IR (neat): ν = 3350 cm^{-1}.

^1H NMR (250 MHz): δ = 0.94 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.36–1.42 (m, 1 H, CH_2), 1.51–1.58 (m, 1 H, CH_2), 1.91 (br s, 1 H, OH), 2.28–2.32 (m, 1 H, CH), 3.50 (dd, 1 H, *J* = 10.6, 8.0 Hz, C*H*HOH), 3.61 (dd, 1 H, *J* = 10.6, 5.3 Hz, CH*H*OH), 5.90 (dd, 1 H, *J* = 15.9, 8.9 Hz, PhCH=C*H*), 6.51 (d, 1 H, *J* = 15.9 Hz, PhC*H*=CH), 7.20–7.41 (m, 5 H, ArH).

^{13}C NMR (75 MHz): δ = 11.6 (CH_3), 23.9 (CH_2), 48.0 (CH), 65.7 (CH_2OH), 126.0–128.4, 131.2, 132.4, 137.0 (C=C and Ar-C).

MS: *m/z* (%) = 176 (M^+, 10), 145 (61), 130 (9), 117 (30), 105 (26), 91 (78), 71 (44), 57 (100).

(*E*)-2-Ethyl-4-phenylbut-3-en-1-ol (0.66 g, 3.74 mmol) was oxidized with PCC (2 g, 9.3 mmol) were stirred for 50 min. Chromatography using hexane–Et_2O (95:5) yielded 0.52 g (80%) of aldehyde (*E*)-**20c** as an oil.

IR (neat): ν = 1730 cm^{-1}.

^1H NMR (250 MHz): δ = 0.97 (dt, 3 H, *J* = 7.5, 1.8 Hz, CH_3), 1.57–1.68 (m, 1 H, CH_2), 1.89–2.01 (m, 1 H, CH_2), 2.98–3.05 (m, 1 H, CH), 6.10 (dd, 1 H, *J* = 15.8, 8.7 Hz, PhCH=C*H*), 6.52 (d, 1 H, *J* = 15.8 Hz, PhC*H*=CH), 7.20–7.37 (m, 5 H, ArH), 9.63 (d, 1 H, *J* = 1.8 Hz, CHO).

^{13}C NMR (75 MHz): δ = 11.6 (CH_3), 22.3 (CH_2), 58.1 (CH), 124.6–128.7, 134.6 (C=C and Ar-C), 201.5 (CHO).

MS: *m/z* (%) = 174 (M^+, 19), 173 (33), 145 (100), 105 (35), 91 (79), 77 (44), 65 (23), 57 (62).

UV (CH_2Cl_2): λ_{max} = 254 nm (ε = 11000).

2-Ethyl-4,4-diphenylbut-3-enal (20d)

This compound was synthesized from methyl 4,4-diphenylbut-3-enoate obtained in the synthesis of aldehyde **14b.** According to the general procedure for alkylation, *i*-Pr_2NH (0.8 mL, 5.95 mmol), BuLi (3.7 mL, 1.6 M in hexane), methyl 4,4-diphenylbut-3-enoate (1.5 g, 5.95 mmol), and EtI (0.5 mL, 5.95 mmol) were used. Chromatography using hexane–Et_2O (9:1) yielded 1.1 g (66%) of methyl 2-ethyl-4,4-diphenylbut-3-enoate as a yellow oil.

IR (neat): ν = 1720 cm^{-1}.

^1H NMR (300 MHz): δ = 0.84 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.55–1.61 (m, 1 H, CH_2), 1.78–1.82 (m, 1 H, CH_2), 3.15–3.21 (m, 1 H, CH), 3.78 (s, 3 H, OCH_3), 6.10 (d, 1 H, *J* = 10.2 Hz, CH=C), 7.17–7.39 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 11.6 (CH_3), 26.5 (CH_2), 47.5 (CH), 51.8 (OCH_3), 126.6–129.8, 139.4, 141.9, 144.1 (C=C and Ar-C), 174.8 (CO_2).

MS: *m/z* (%) = 280 (M^+, 21), 221 (55), 191 (37), 179 (4), 143 (31), 91 (100), 77 (11), 51 (12).

According to the general procedure for reduction, methyl 2-ethyl-4,4-diphenylbut-3-enoate (0.762 g, 2.72 mmol) and $LiAlH_4$ (0.114 g, 2.99 mmol) were used. Chromatography using hexane–Et_2O (8:2) gave 0.493 g (72%) of 2-ethyl-4,4-diphenylbut-3-en-1-ol as a yellow oil.

IR (neat): ν = 3620, 3450 cm^{-1}.

^1H NMR (250 MHz): δ = 0.88 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.32–1.36 (m, 2 H, CH_2 and OH), 1.53–1.57 (m, 1 H, CH_2), 2.39–2.43 (m, 1 H, CH), 3.47–3.51 (m, 2 H, C*H*$_2$OH), 5.85 (d, 1 H, *J* = 10.5 Hz, CH=C), 7.19–7.38 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 11.7 (CH_3), 24.7 (CH_2), 43.9 (CH), 66.6 (CH_2OH), 127.0–130.7, 140.0, 142.0, 145.0 (C=C and Ar-C).

MS: *m/z* (%) = 252 (M^+, 7), 221 (52), 205 (8), 192 (4), 165 (11), 115 (16), 91 (100), 77 (13), 51 (89).

2-Ethyl-4,4-diphenylbut-3-en-1-ol (0.4 g, 1.59 mmol) was oxidized with PCC (0.85 g, 3.97 mmol) by stirring for 75 min. Chromatography using hexane–Et_2O (98:2) yielded 0.37 g (93%) of aldehyde **20d** as an oil.

IR (neat): ν = 1730 cm^{-1}.

^1H NMR (250 MHz): δ = 0.90 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.52–1.70 (m, 1 H, CH_2), 1.75–1.95 (m, 1 H, CH_2), 3.09–3.18 (m, 1 H, CH), 5.91 (d, *J* =10.2 Hz, CH=C), 7.20–7.40 (m, 10 H, ArH), 9.60 (d, 1 H, *J* = 1.8 Hz, CHO).

^{13}C NMR (62 MHz): δ = 11.5 (CH_3), 22.9 (CH_2), 55.0 (quat. C), 123.8–132.5, 139.5, 141.7, 146.8 (C=C, Ar-C), 201.6 (CHO).

MS: *m/z* (%) = 250 (M^+, 4), 221 (28), 205 (6), 143 (29), 105 (36), 91 (100), 77 (20), 51 (17).

UV (CH_2Cl_2): λ_{max} = 255 nm (ε = 14950).

3-Isopropyl-5,5-diphenylpent-4-en-2-one (19b)

Mg (0.13 g, 5.4 mmol), MeI (0.3 mL, 5.2 mmol) and aldehyde **20b** (0.47 g, 1.77 mmol) were reacted to form the alcohol. Chromatography using hexane–Et_2O (8:2) yielded 414 mg (83%) of 3-isopropyl-5,5-diphenylpent-4-en-2-ol as a 2:1 mixture of diastereoisomers **A** and **B**.

IR (neat): ν = 3600, 3450 cm^{-1}.

^1H NMR (250 MHz): δ = 0.85 (d, 1 H, *J* = 5.5 Hz, CH_3, isomer **B**), 0.87 (d, 2 H, *J* = 5.5 Hz, CH_3, isomer **A**), 0.94 (d, 2 H, *J* = 5.5 Hz, CH_3, isomer **A**), 0.96 (d, 1 H, *J* = 5.5 Hz, CH_3, isomer **B**), 1.15 (d, 2 H, *J* = 6.0 Hz, C*H*$_3$CHOH, isomer **A**), 1.21 (d, 1 H, *J* = 6.9 Hz, C*H*$_3$CHOH, isomer **B**), 1.80–2.00 [m, 0.66 H, C*H*$(CH_3)_2$, isomer **A**], 2.19–2.23 [m, 0.33 H, C*H*$(CH_3)_2$, isomer **B**], 3.46–3.50 (m, 1 H, CH), 3.80–4.00 (m, 1 H, C*H*OH), 5.90 (d, 0.33 H, *J* =11.0 Hz, CH=C, isomer **B**), 6.08 (d, 0.66 H, *J* = 11.0 Hz, CH=C, isomer **A**), 7.21–7.40 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 18.9, 19.5, 21.1, 21.5, 21.6, 21.8 (3 CH_3), 29.0 [*C*H$(CH_3)_2$, isomer **B**], 29.4 [*C*H$(CH_3)_2$, isomer **A**], 52.1 (CH, isomer **B**), 52.3 (CH, isomer **A**), 68.6 (CHOH, isomer **A**), 68.8 (CHOH, isomer **B**), 125.9–130.2, 140.3, 145.4 (C=C and Ar-C).

MS: *m/z* (%) = 235 (M^+ – 45, 82), 192 (18), 179 (6), 165 (24), 105 (74), 91 (100), 51 (20).

3-Isopropyl-5,5-diphenylpent-4-en-2-ol (0.41 g, 1.48 mmol) was oxidized with $K_2Cr_2O_7$ (0.43 g, 1.47 mmol) in H_2SO_4 (4 mL) and H_2O (8 mL) by stirring for 1 h. Chromatography using hexane–Et_2O (8:2) afforded 262 mg (64%) of ketone **19b** as an oil.

IR (neat): ν = 1720 cm^{-1}.

^1H NMR (300 MHz): δ = 0.83 (d, 3 H, *J* = 6.6 Hz, CH_3), 0.93 (d, 3 H, *J* = 6.6 Hz, CH_3), 2.07 (s, 3 H, CH_3CO), 2.08–2.13 [m, 1 H, C*H*$(CH_3)_2$], 3.01 (app t, 1 H, *J* = 7.0 Hz, CH), 6.02 (d, 1 H, *J* = 10.8 Hz, CH=C), 7.14–7.41 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 20.3 (CH_3), 21.0 (CH_3), 30.1 [*C*H$(CH_3)_2$], 31.0 (CH_3CO), 61.1 (CH), 125.9–132.5, 139.7, 141.9, 145.1 (C=C and Ar-C), 209.9 (CO).

MS: *m/z* (%) = 278 (M^+, 4), 235 (82), 219 (6), 205 (9), 193 (17), 179 (6), 157 (31), 129 (13), 115 (34), 105 (75), 91 (100), 77 (31), 51 (20).

UV (CH_2Cl_2): λ_{max} = 254 nm (ε = 13600).

(*E*)-3-Ethyl-5-phenylpent-4-en-2-one (19c)

According to general procedure, Mg (0.18 g, 7.4 mmol), MeI (0.5 mL, 7.4 mmol) and aldehyde (*E*)-**20c** (0.43 g, 2.47 mmol) were reacted to give the alcohol. Chromatography using hexane–EtOAc (85:15) gave 290 mg (62%) of (*E*)-3-ethyl-5-phenylpent-4-en-2-ol as a 3:2 mixture of diastereoisomers **A** and **B**.

IR (neat): ν = 3400 cm^{-1}.

^1H NMR (250 MHz): δ = 0.91 (m, 3 H, CH_3), 1.16 (d, 1.2 H, *J* = 6.3 Hz, C*H*$_3$CHOH, isomer **B**), 1.21 (d, 1.8 H, *J* = 6.3 Hz, C*H*$_3$CHOH, isomer **A**), 1.29–1.42 (m, 1 H, CH_2), 1.57–1.80 (m, 1 H, CH_2), 1.95–2.34 (m, 1 H, CH), 3.70–3.76 (m, 1 H, C*H*OH), 6.00 (dd, 0.4 H, *J* = 15.9, 21.6 Hz, PhCH=C*H*, isomer **B**), 6.01 (dd, 0.6 H, *J* = 15.6, 3.0 Hz, PhCH=C*H*, isomer **A**), 6.44 (d, 0.4 H, *J* = 15.9 Hz, PhC*H*=CH, isomer **B**), 6.46 (d, 0.6 H, *J* = 15.6 Hz, PhC*H*=CH, isomer **A**), 7.24–7.39 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 12.2 (CH_3), 20.4 (*C*H$_3$CHOH, isomer **B**), 20.9 (*C*H$_3$CHOH, isomer **A**), 24.0 (CH_2, isomer **B**), 24.1 (CH_2, isomer **A**), 53.0 (CH, isomer **B**), 53.5 (CH, isomer **A**), 70.2 (CHOH, isomer **A**), 70.5 (CHOH, isomer **B**), 125.5–132.2, 132.9, 137.4, 133.5, 136.6, 137.3 (C=C and Ar-C).

MS: *m/z* (%) = 190 (M^+, 4), 145 (54), 105 (84), 117 (80), 57 (94), 77 (37), 91 (100).

Oxidation of (*E*)-3-ethyl-5-phenylpent-4-en-2-ol (0.25 g, 1.3 mmol) was carried out with $K_2Cr_2O_7$ (0.38 g, 1.3 mmol) in H_2SO_4 (4 mL) and H_2O (8 mL) by stirring for 50 min. Chromatography using hexane–Et_2O (8:2) furnished 130 mg (53%) of ketone (*E*)-**19c** as an oil.

IR (neat): ν = 1710 cm^{-1}.

^1H NMR (300 MHz): δ = 0.91 (dt, 3 H, *J* = 7.5, 1.2 Hz, CH_3), 1.55–1.62 (m, 1 H, CH_2), 1.80–1.90 (m, 1 H, CH_2), 2.18 (s, 3 H, CH_3CO), 3.16 (app q, 1 H, *J* = 8.2 Hz, CH), 6.10 (dd, 1 H, *J* = 15.9, 9.6 Hz, PhCH=C*H*), 6.50 (d, 1 H, *J* = 15.9 Hz, PhC*H*=CH), 7.15–7.39 (m, 5 H, ArH).

^{13}C NMR (62 MHz): δ = 11.8 (CH_3), 24.5 (CH_3CO), 28.9 (CH_2), 59.4 (CH), 126.1–129.0, 133.3, 136.9 (C=C and Ar-C), 209.5 (CO).

MS *m/z* (%) = 187 (M^+ – 1, 5), 145 (17), 129 (16), 105 (100), 91 (43), 77 (80), 51 (51).

UV (CH_2Cl_2): λ_{max} = 251 nm (∈ = 13100).

3-Ethyl-5,5-diphenylpent-4-en-2-one (19d)

Mg (0.1 g, 4.4 mmol), MeI (0.3 mL, 4.4 mmol) and aldehyde **20d** (0.37 g, 1.48 mmol) were reacted to form the alcohol. Chromatography using hexane–Et_2O (8:2) yielded 350 mg (89%) of 3-ethyl-5,5-diphenylpent-4-en-2-ol as a 1:1 mixture of diastereoisomers **A** and **B**.

IR (neat): ν = 3350 cm^{-1}.

^1H NMR (250 MHz): δ = 0.87 (t, 1.5 H, *J* = 7.5 Hz, CH_3), 0.88 (t, 1.5 H, *J* = 7.5 Hz, CH_3), 1.15 (d, 1.5 H, *J* = 6.3 Hz, C*H*$_3$CHOH), 1.18 (d, 1.5 H, *J* = 6.3 Hz, C*H*$_3$CHOH), 1.33–1.37 (m, 1 H, CH_2), 1.50–1.70 (m, 1 H, CH_2), 2.10–2.30 (m, 1 H, CH), 3.73–3.77 (m, 1 H, C*H*OH), 5.88 (d, 0.5 H, *J* = 10.8 Hz, CH=C), 5.91 (d, 0.5 H, *J* = 10.5 Hz, CH=C), 7.18–7.36 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 12.1 (CH_3), 12.3 (CH_3), 21.0 (*C*H$_3$CHOH), 21.2 (*C*H$_3$CHOH), 24.6 (CH_2), 24.7 (CH_2), 48.3 (CH), 48.5 (CH), 70.6 (CHOH), 71.2 (CHOH), 126.0–131.0, 140.4, 144.9 (C=C and Ar-C).

MS: *m/z* (%) = 266 (M^+, 6), 221 (64), 191 (18), 143 (34), 105 (66), 91 (100), 57 (24).

3-Ethyl-5,5-diphenylpent-4-en-2-ol (0.16 g, 0.6 mmol) was oxidized with $K_2Cr_2O_7$ (0.2 g, 0.6 mmol) in H_2SO_4 (2 mL) and H_2O (4 mL) by stirring for 1 h. Chromatography using hexane–Et_2O (8:2) yielded 100 mg (62%) of ketone **19d** as an oil.

IR (neat): ν = 1710 cm^{-1}.

^1H NMR (250 MHz): δ = 0.87 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.50–1.67 (m, 1 H, CH_2), 1.71–1.87 (m, 1 H, CH_2), 2.08 (s, 3 H, CH_3CO), 3.15–3.25 (m, 1 H, CH), 5.97 (d, 1 H, *J* = 10.8 Hz, CH=C), 7.16–7.61 (m, 10 H, ArH).

^{13}C NMR (62 MHz): δ = 11.8 (CH_3), 25.2 (CH_2), 29.4 (*C*H$_3$CO), 55.4 (CH), 127.0–132.5, 139.7, 141.8, 144.9 (C=C and Ar-C), 209.7 (CO).

MS: *m/z* (%) = 264 (M^+, 3), 221 (66), 206 (2), 191 (18), 165 (27), 143 (34), 128 (21), 105 (66), 91 (100), 77 (39), 51 (24).

UV (CH_2Cl_2): λ_{max} = 253 nm (ε = 14350).

Preparative Photolyses; General Procedure

The photolyses were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. Solutions of the compound to be photolyzed and the sensitizer (acetophenone or *m*-methoxyacetophenone) in anhyd CH_2Cl_2 (450 mL) were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent was evaporated under reduced pressure and the sensitizer was removed by vacuum distillation (acetophenone at 30°C/0.3 Torr, *m*-methoxyacetophenone at 50°C/0.3 Torr). The products were separated by flash chromatography on silica gel.

Irradiation of **6**

Compound **6** (200 mg, 0.7 mmol) and *m*-methoxyacetophenone (2.16 g, 14 mmol) were irradiated for 20 min. Chromatography using hexane–Et_2O (95:5) as eluent gave 70 mg (38%) of **7** as a yellow oil and 77 mg (39%) of **6**. Further elution with Et_2O afforded 53 mg of a highly polar material.

IR (neat): ν = 1635, 1596 cm^{-1}.

^1H NMR (300 MHz): δ = 0.97 (d, 3 H, *J* = 6.8 Hz, CH_3), 1.74–1.97 (m, 2 H, CH_2), 2.20–2.60 (m, 5 H, 2 CH_2 and CH), 5.97 (dt, 1 H, *J* = 11.5, 2.4 Hz, CH=C), 6.76 (d, 1 H, *J* = 11.5 Hz, C*H*=CPh$_2$), 7.16–7.41 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 18.9 (CH_3), 24.1 (CH_2), 30.0 (CH_2), 35.2 (CH_2), 39.8 (CH), 117.8, 126.0–130.6, 140.2, 145.0, 154.9 (C=C and Ar-C).

MS: *m/z* (%) = 274 (M^+, 100), 197 (40), 192 (43), 91 (53), 77 (32), 55 (21).

Anal. Calcd for $C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.85; H, 8.00.

Irradiation of **9**

Compound **9** (177 mg, 0.6 mmol) and *m*-methoxyacetophenone (2.9 g, 19 mmol) were irradiated for 3 h. Chromatography using hexane–Et_2O (95:5) as eluent gave 43 mg (24%) of **10** as a yellow oil and 88 mg (50%) of **9**. Further elution with Et_2O afforded 28 mg of a highly polar material.

IR (neat): ν = 1710, 1596 cm^{-1}.

^1H NMR (300 MHz): δ = 1.43 (br s, 3 H, CH_3), 1.64–1.82 (m, 2 H, CH_2), 2.00 (s, 3 H, CH_3CO), 2.12–2.34 (m, 4 H, 2 CH_2), 4.20 (d, 1 H, *J* = 9.7 Hz, CH), 6.49 (d, 1 H, *J* = 9.7 Hz, CH=C), 7.02–7.41 (m, 10 H, ArH).

^{13}C NMR (75 MHz): δ = 14.0 (CH_3), 21.7 (CH_2), 28.5 (CH_3CO), 33.0 (CH_2), 38.3 (CH_2), 53.7 (CH), 122.0–143.0 (C=C and Ar-C), 207.1 (CO).

MS: *m/z* (%) = 273 (M^+ – 43, 100), 191 (26), 165 (19), 91 (32), 77 (8), 55 (5).

Irradiation of (*E*)-**14a**
Compound (*E*)-**14a** (300 mg, 1.5 mmol) and *m*-methoxyacetophenone (2.16 g, 14.4 mmol) were irradiated for 1 h. Chromatography using pentane–Et_2O (85:15) as eluent gave 161 mg (51%) of an inseparable mixture of **14a** (as a 2:1 mixture of *Z*:*E*-isomers) and aldehyde **16** in a 3:1 ratio and 109 mg (36%) of *trans*-cyclopropanecarbaldehyde (**15a**) as a yellow oil. Further elution with Et_2O afforded 27 mg of a highly polar material.

16 and 14a
^1H NMR (300 MHz): δ = 1.50–1.74 (m, 8 H, 4 CH_2), 2.12–2.34 (m, 4 H, 4 CH_2), 4.29 (d, 0.25 H, *J* = 7.5 Hz, CH=C, **16**), 5.70 (br s, 0.25 H, PhC*H*, **16**), 5.71 (d, 0.5 H, *J* = 12 Hz, PhCH=C*H*, *Z*-isomer), 6.30 (AB system, 0.5 H, *J* = 16.5 Hz, PhC*H*=C*H*, *E*-isomer), 6.65 (d, 0.5 H, *J* = 12.0 Hz, PhC*H*=CH, *Z*-isomer), 7.00–7.40 (m, 5 H, ArH), 9.26 (s, 0.5 H, CHO, *Z*-isomer), 9.46 (s, 0.25 H, CHO, *E*-isomer), 9.57 (d, 0.25 H, *J* = 2.7 Hz, CHO, **16**).

15a
IR (neat): ν = 1710 cm^{-1}.

^1H NMR (300 MHz): δ = 1.43–1.75 (m, 6 H, 3 CH_2), 1.90–1.94 (m, 2 H, CH_2), 2.37 (app t, 1 H, *J* = 5.4 Hz, C*H*CHO), 2.95 (d, 1 H, *J* = 5.4 Hz, PhC*H*), 7.10–7.30 (m, 5 H, ArH), 9.43 (d, 1 H, *J* = 5.7 Hz, CHO).

^{13}C NMR (62 MHz): δ = 25.0 (CH_2), 26.0 (CH_2), 31.0 (CH_2), 32.9 (CH_2), 39.0 (CH), 41.0 (CH), 126.5, 127.9, 128.2, 136.6 (Ar-C), 200.7 (CHO).

Anal. Calcd for $C_{14}H_{16}O_2$ (acid): C, 77.78; H, 7.41. Found: C, 77.68; H, 7.30.[12]

Irradiation of **14b**
Compound **14b** (261 mg, 0.94 mmol) and *m*-methoxyacetophenone (2 g, 13.3 mmol) were irradiated for 2 h. Chromatography using pentane–Et_2O (8:2) as eluent gave 12 mg (5%) of **17**[13] as a yellow oil, 138 mg (53%) of **14b**, and 62 mg (24%) of **15b** as a yellow oil. Further elution with Et_2O afforded 39 mg of a highly polar material.

IR (neat): ν = 1715 cm^{-1}.

^1H NMR (300 MHz): δ = 1.69–1.84 (m, 8 H, 4 CH_2), 2.48 (d, 1 H, *J* = 7.2 Hz, C*H*CHO), 7.20–7.80 (m, 10 H, ArH), 9.02 (d, 1 H, *J* = 7.2 Hz, CHO).

^{13}C NMR (75 MHz): δ = 24.0 (CH_2), 25.8 (CH_2), 29.4 (CH_2), 34.3 (CH_2), 43.7 (CH), 43.9 (quat. C), 50.6 (CPh_2), 126.4–130.2, 139.2, 139.6, 142.2, 143.0 (Ar-C), 202.4 (CHO).

MS: *m/z* (%) = 247 (M^+ – 29, 6), 171 (26), 129 (4), 105 (100), 91 (14), 77 (64), 51 (31).

Anal. Calcd for $C_{20}H_{20}O_2$ (acid): C, 82.19; H, 6.85. Found: C, 82.10; H, 6.75.[12]

Irradiation of (*E*)-**20a**
Compound (*E*)-**20a** (285 mg, 1.5 mmol) and *m*-methoxyacetophenone (1.3 g, 8.7 mmol) were irradiated for 40 min. Chromatography using pentane–Et_2O (95:5) as eluent gave 199 mg (21%) of aldehyde **20a**, as a 1:1 mixture of *Z*:*E*-isomers; yellow oil. An amount of 61 mg (21%) of the yellow oil was identified as the 1*R*,2*S*,3*R*/1*S*,2*R*,3*S* diastereoisomer of cyclopropanecarbaldehyde **21a**. Further elution with Et_2O afforded 14 mg of a highly polar material.

^1H NMR (300 MHz): δ = 0.92 (d, 1.5 H, *J* = 6.6 Hz, CH_3, *E*-isomer), 0.94 (d, 1.5 H, *J* = 6.6 Hz, CH_3, *E*-isomer), 0.96 (d, 1.5 H, *J* = 6.6 Hz, CH_3, *Z*-isomer), 1.01 (d, 1.5 H, *J* = 6.6 Hz, CH_3, *Z*-isomer), 2.40–2.60 [m, 0.5 H, C*H*(CH_3)$_2$, *E*-isomer], 2.65–2.75 [m, 0.5 H, C*H*(CH_3)$_2$, *Z*-isomer), 2.90–2.98 (m, 0.5 H, CH, *E*-isomer), 3.20–3.30 (m, 0.5 H, CH, *Z*-isomer), 5.60 (t, 0.5 H, *J* = 11.7 Hz, PhCH=C*H*, *Z*-isomer), 6.17 (dd, 0.5 H, *J* = 16.0, 9.3 Hz, PhCH=C*H*, *E*-isomer), 6.50 (d, 0.5 H, *J* = 16.0 Hz, PhC*H*=CH, *E*-isomer), 6.80 (d, 0.5 H, *J* = 11.4 Hz, PhC*H*=CH, *Z*-isomer), 7.01–7.40 (m, 5 H, ArH), 9.55 (s, 1 H, CHO, *Z*-isomer), 9.60 (s, 1 H, CHO, *E*-isomer).

21a
IR (neat): ν = 1690 cm^{-1}.

^1H NMR (300 MHz): δ = 0.82 (d, 3 H, *J* = 6.3 Hz, CH_3), 1.02 (d, 3 H, *J* = 6.3 Hz, CH_3), 1.15–1.25 [m, 1 H, C*H*(CH_3)$_2$], 1.60–1.70 (m, 1 H, CH), 2.30 (q, 1 H, *J* = 5.1 Hz, C*H*CHO), 2.95 (dd, 1 H, *J* = 9.5, 5.1 Hz, C*H*Ph), 7.20–7.40 (m, 5 H, ArH), 9.34 (d, 1 H, *J* = 5.1 Hz, CHO).

^{13}C NMR (75 MHz): δ = 21.4 (CH_3), 22.6 (CH_3), 24.1 [*C*H(CH_3)$_2$], 26.6 (CH), 32.7 (*C*HPh), 38.4 (*C*HCHO), 126.4–128.4, 135.1, 135.6 (Ar-C), 200.6 (CHO).

Anal. Calcd for $C_{13}H_{16}O_2$ (acid): C, 76.47; H, 7.84. Found: C, 76.35; H, 7.80.[12]

Irradiation of **20b**
Compound **20b** (300 mg, 1.14 mmol) and *m*-methoxyacetophenone (5.65 g, 37.4 mmol) were irradiated for 2.5 h. Chromatography using pentane–Et_2O (95:5) as eluent afforded 23 mg (9%) of **22a**[14] as a yellow oil, 137 mg (46%) of starting material (**20b**) and 69 mg (23%) of *trans*-cyclopropanecarbaldehyde **21b** as an oil. Further elution with Et_2O afforded 66 mg of a highly polar material.

IR (neat): ν = 1700 cm^{-1}.

^1H NMR (300 MHz): δ = 0.97 (d, 3 H, *J* = 5.7 Hz, CH_3), 1.21 (d, 3 H, *J* = 5.7 Hz, CH_3), 1.50–1.70 [m, 1 H, C*H*(CH_3)$_2$], 2.20–2.30 (m, 1 H, CH), 2.42–2.58 (m, 1 H, C*H*CHO), 7.19–7.34 (m, 10 H, ArH), 8.57 (d, 1 H, *J* = 6.6 Hz, CHO).

^{13}C NMR (75 MHz): δ = 21.8 (CH_3), 22.2 (CH_3), 27.6 (CH), 30.3 (CH), 39.6 (CH), 47.8 (quat. C), 126.6–130.9, 140.7, 141.8 (Ar-C), 201.1 (CO).

Anal. Calcd for $C_{19}H_{20}O_2$ (acid): C, 81.43; H, 7.14. Found: C, 81.36; H, 7.07.[12]

Irradiation of (*E*)-**20c**
Compound (*E*)-**20c** (520 mg, 3 mmol) and acetophenone (3 g, 25 mmol) were irradiated for 7 h. Chromatography using pentane–Et_2O (98:2) as eluent gave 295 mg (57%) of (*Z*)-**20c** as a yellow oil. An amount of 115 mg (22%) of a yellow oil was identified as the 1*R*,2*S*,3*R*/1*S*,2*R*,3*S* diastereoisomer of cyclopropanecarbaldehyde **21c**. Further elution with Et_2O afforded 99 mg of a highly polar material.

(*Z*)-**20c**
^1H NMR (300 MHz): δ = 0.90 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.61 (m, 1 H, CH_2), 1.85 (m, 1 H, CH_2), 3.40 (m, 1 H, CH), 5.50 (app t, 1 H, *J* = 11.4 Hz, PhCH=C*H*), 6.81 (d, 1 H, *J* = 11.4 Hz, PhC*H*=CH), 7.25–7.40 (m, 5 H, ArH), 9.60 (d, 1 H, *J* = 2.7 Hz, CHO).

21c
IR (neat): ν = 1690 cm^{-1}.

^{1}H NMR (300 MHz): δ = 0.80 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.00–1.20 (m, 1 H, CH_2), 1.21–1.41 (m, 1 H, CH_2), 1.70–1.90 (m, 1 H, C*H*Et), 2.19 (q, 1 H, *J* = 5.0 Hz, C*H*CHO), 2.94 (dd, 1 H, *J* = 9.6, 5.1 Hz, C*H*Ph), 7.20–7.41 (m, 5 H, ArH), 9.35 (d, 1 H, *J* = 4.8 Hz, CHO).

^{13}C NMR (62 MHz): δ = 13.4 (CH_3), 20.8 (CH_2), 31.3 (*C*HEt), 31.9 (*C*HPh), 35.5 (*C*HCHO), 126.9, 128.4, 129.0, 135.6 (Ar-C), 200.6 (CHO).

MS: *m/z* (%) = 173 (M^+ – 1, 12), 145 (26), 129 (4), 105 (100), 91 (18), 77 (64), 51 (28).

Anal. Calcd for $C_{12}H_{14}O_2$ (acid): C, 75.78; H, 7.37. Found: C, 75.57; H, 7.20.[12]

Irradiation of **20d**

Compound **20d** (300 mg, 1.2 mmol) and *m*-methoxyacetophenone (1 g, 6.7 mmol) were irradiated for 7 h. Chromatography using pentane–Et_2O (95:5) as eluent gave 66 mg (25%) of **22b**[15] as a yellow oil, 120 mg (40%) of **20d** and 72 mg (24%) of *trans*-cyclopropanecarbaldehyde (**21d**) as a yellow oil. Further elution with Et_2O afforded 18 mg of a highly polar material.

IR (neat): ν = 1690 cm^{-1}.

^{1}H NMR (300 MHz): δ = 0.91 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.70–190 (m, 2 H, CH_2), 2.38 (t, 1 H, *J* = 6.0 Hz, C*H*Et), 2.47 (q, 1 H, *J* = 6.0 Hz, C*H*CHO), 7.18–7.82 (m, 10 H, ArH), 8.60 (d, 1 H, *J* = 6.6 Hz, CHO).

^{13}C NMR (75 MHz): δ = 13.4 (CH_3), 22.5 (CH_2), 33.1 (*C*HEt), 40.7 (*C*HCHO), 46.9 (quat. C), 126.4–129.9, 132.0, 137.6, 140.6 (ArH), 201.1 (CHO).

MS: *m/z* (%) = 250 (M^+, 4), 221 (12), 173 (14), 143 (18), 129 (4), 105 (100), 77 (64), 51 (26).

Anal. Calcd for $C_{18}H_{18}O_2$ (acid): C, 81.20; H, 6.76. Found: C, 81.00; H, 6.86.[12]

Irradiation of **13b**

Compound **13b** (50 mg, 0.17 mmol) and *m*-methoxyacetophenone (0.5 g, 3.3 mmol) were irradiated for 17 h. Chromatography using hexane–Et_2O (9:1) as eluent gave 36 mg (71%) of recovered starting material. Further elution with Et_2O afforded 14 mg of a highly polar material.

Irradiation of **19b**

Compound **19b** (216 mg, 0.78 mmol) and *m*-methoxyacetophenone (1 g, 6.6 mmol) were irradiated for 12 h. Chromatography using hexane–Et_2O (9.1) as eluent gave 180 mg (83%) of recovered starting material. Further elution with Et_2O afforded 35 mg of highly polar material.

Irradiation of (*E*)-**19c**

Compound (*E*)-**19c** (40 mg, 0.21 mmol) and *m*-methoxyacetophenone (296 mg, 2 mmol) were irradiated for 30 h. Chromatography using hexane–Et_2O (9:1) as eluent gave 20 mg (50%) of (*Z*)-**19c** and 10 mg (25%) of recovered starting material. Further elution with Et_2O afforded 9 mg of a highly polar material.

^{1}H NMR (300 MHz): δ = 0.87 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.55–1.62 (m, 1 H, CH_2), 1.76–1.80 (m, 1 H, CH_2), 2.15 (s, 3 H, CH_3CO), 3.50–3.61 (m, 1 H, CH), 5.56 (app t, 1 H, *J* = 10.8 Hz, PhCH=C*H*), 6.66 (d, 1 H, *J* = 10.8 Hz, PhC*H*=CH), 7.24–7.36 (m, 5 H, ArH).

Irradiation of **19d**

Compound **19d** (40 mg, 0.15 mmol) and *m*-methoxyacetophenone (215 mg, 1.43 mmol) were irradiated for 31 h. Chromatography using hexane–Et_2O (9:1) as eluent gave 30 mg (75%) of recovered starting material. Further elution with Et_2O afforded 9 mg of a highly polar material.

Acknowledgments

S. A-L. thanks the Ministerio de Educacion y Ciencia for a postgraduate fellowship. We thank the Direccion General de Investigacion Cientifica y Tecnica (grant no. PB 97/0235) for financial support. We acknowledge the support provided by the Centro de Resonancia Magnetica, the Centro de Microanalisis and the Servicio de Espectrometria de Masas of the Universidad Complutense.

References

(1) For reviews see: (a) Dauben, G. W.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73. (b) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (c) Schuster, D. I. *Rearrangements in Ground and Excited States*, Vol. 3; deMayo, P., Ed.; Academic Press: New York, **1980**, 167. (d) Demuth, M. *Org. Photochem.*, Vol.11; Padwa, A., Ed.; Marcel Dekker: New York, **1991**, 37. (e) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065.
(2) (a) Poel, D. E.; Wehrli, H.; Schaffner, K.; Jeger, O. *Chimia* **1966**, *20*, 110. (b) Pfenninger, E.; Poel, D. E.; Berse, C.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1968**, *51*, 772.
(3) Zimmerman, H. E.; Cassel, J. M. *J. Org. Chem.* **1989**, *54*, 3800.
(4) (a) Armesto, D.; Ortiz, M. J.; Romano, S. *Tetrahedron Lett.* **1995**, *36*, 965. (b) Armesto, D.; Ortiz, M. J.; Romano, S.; Agarrabeitia, A. R.; Gallego, M. G.; Ramos, A. *J. Org. Chem.* **1996**, *61*, 1459.
(5) Baggiolini, E.; Hamlow, H. P.; Schaffner, K. *J. Am. Chem. Soc.* **1970**, *92*, 4906.
(6) van der Weerdt, A. J. A.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 247.
(7) Tenney, L. P.; Boykin, D. W. Jr.; Lutz, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 1835.
(8) van der Weerdt, A. J. A.; Cerfontain, H. *Tetrahedron* **1981**, *37*, 2121.
(9) Dauben, W. G.; Warshawsky, A. M. *J. Org. Chem.* **1990**, *55*, 3075.
(10) Zimmerman, H. E.; Khun, R. T. *Tetrahedron* **1978**, *34*, 1775.
(11) Johnson, W. S.; Petersen, J. W.; Schneider, W. P. *J. Am. Chem. Soc.* **1947**, *69*, 74.
(12) Aldehydes **15a–b** and **21a–d** undergo spontaneous oxidation in the presence of atmospheric oxygen. The combustion analyses quoted correspond to the carboxylic acids resulting from oxidation.
(13) Stetter, H.; Kiehs, K. *Chem.Ber.* **1965**, *98*, 1181.
(14) Schorigin, P. *Ber. Dtsch. Chem. Ges.* **1907**, *41*, 2711.
(15) Serijan, K. T.; Wise, H. P. *J. Am. Chem. Soc.* **1951**, *73*, 5191.