Chemically Efficient Aza-Di-π-Methane Photoreactivity with Novel Stable Derivatives of β,γ-Unsaturated Carbonyl Compounds

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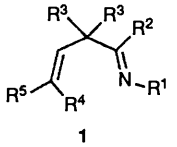
The syntheses of new stable derivatives of β,γ-unsaturated carbonyl compounds such as 2,2-dimethyl-4,4-diphenylbut-3-enal **6** and 3,3-dimethyl-5,5-diphenylpent-4-en-2-one **7** are described. The majority of these derivatives undergo efficient aza-di-π-methane rearrangement on short, acetophenone-sensitized, irradiation to afford the corresponding derivatives of the cyclopropane carbonyl compound in good to excellent yield; for example, the photoconversion of the oximino trifluoro acetate of the aldehyde **6** affords 2,2-dimethyl-3,3-diphenylcyclopropane-1-carbonitrile **16** in 80% yield. This is of synthetic value since β,γ-unsaturated nitriles do not undergo the aza-di-π-methane reaction. The study has also indicated some limits to the type of derivative that can be used. Thus with a methyl ketone derivative where the functional group can undergo SET from the triplet 1,1-diphenylvinyl moiety; an alternative fragmentation path can be operative in a novel reaction not seen previously in such systems.

The discovery of the aza-di-π-methane (ADPM) rearrangement has been the high point of our study of the photochemical reactivity of β,γ-unsaturated imines **1**.[1] This arose from a general investigation of the influence of nitrogen incorporation that gave rise to a number of new photochemical reactions.[2] Our studies have shown that the success of the aza-di-π-methane rearrangement, in terms of both chemical yield and photochemical efficiency, is dependent upon the suppression of electron transfer from the nitrogen of the imine moiety to the alkene component.[3] Thus there is a dependence for the success of the reaction upon the ionization potential of the nitrogen lone pair and as consequence the oxime **2**,[4] with a relatively low ionization potential is unreactive as is the corresponding oxime ether **3**.[5] The conversion of the oxime into the acetate introduces an electron withdrawing group which raises the ionization potential. This compound **4** was shown to be photochemically reactive in the ADPM rearrangement and affords the cyclopropane **5** in high yield.[6] This synthetic method, formation of the oxime acetate and irradiation, allows the transformation of



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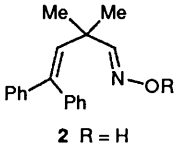
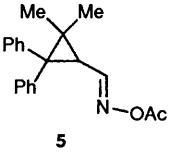


2 R = H
3 R = Me
4 R = Ac



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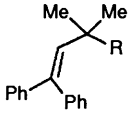
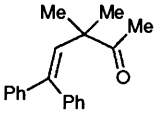


6 R = CHO
12 R = CN



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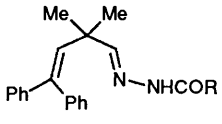
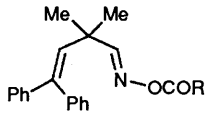
the β,γ-unsaturated aldehyde **6**, which has been demonstrated to undergo efficient photodecarbonylation rather than the oxa-di-π-methane rearrangement,[7] into the cyclopropane **5** *via* a stable C=N derivative. Subsequent studies by us have shown this approach to be applicable to a variety of β,γ-unsaturated aldehydes and ketones.[8] The increase of the efficiency of conversion of the oxime acetate derivative over the imines prompted a search for other stable derivatives which might be even more efficient than the oxime acetates. Furthermore, such an investigation could provide additional information on the participation of an intramolecular electron transfer. The present report details our findings with other stable derivatives of the aldehyde **6**, the subject of a preliminary account,[9] and results from the ketone **7** and illustrates the scope and efficiency of the aza-di-π-methane reaction.

Results and Discussion

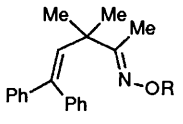
The derivatives **8**–**11** are readily prepared by conventional methods and afforded the desired compounds in high yield. The structures of the products **8** and **9** were readily confirmed by conventional spectroscopy and microanalysis. For example, the ^{1}H NMR spectra show the presence of protons on the alkene and the imine double bonds which have undergone the expected shifts from the positions in which they resonate in the parent aldehyde. Other spectroscopic data such as the IR absorption frequencies of the C=N and C=C groups also support the structural assignments as do the absorptions shown in the ^{13}C NMR spectra. The structures of products **10** and **11**, which are derived from ketone **7**, are substantiated by the normal spectroscopic and microanalytical methods. ^{13}C NMR spectroscopy is particularly useful with these compounds since the C=N is readily identifiable in the 160–175 ppm region. Among all the



8a R = NH_2
b R = Me
c R = Ph



9a R = CF_3
b R = Ph

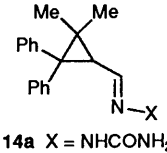


10 R = $COCF_3$
11 R = COPh
13 R = H

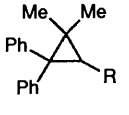
derivatives described only the trifluoroacetates show thermal instability. In the case of **9a** thermal elimination of trifluoroacetic acid affords the nitrile **12** while **10** undergoes facile hydrolysis to the oxime **13**. Thus care has to be taken in handling these compounds.

The irradiation of **8a**, as with all of the compounds, was carried out in an immersion well apparatus using acetophenone as sensitizer. After irradiation for 2 h work-up by flash chromatography afforded a mixture of starting material (52%) and a new product (40%). This new product was again readily identified by conventional techniques. Thus, the ^1H NMR spectrum showed a doublet corresponding to one hydrogen at δ 2.3 in accord with a hydrogen on a three-membered ring. The presence of the cyclopropyl ring was further confirmed by ^{13}C NMR spectroscopy. Thus, the compound was conclusively identified as the semicarbazone derivative **14a** of 2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde **15**. Similar photochemical reactivity, the formation of a cyclopropane, was shown by the other derivatives **8b** and **8c**. In the case of **8b** a different work-up procedure was used, that of hydrolysis of the photolysate, which allowed the isolation of aldehyde **15** in 71% rather than the acetylhydrazone derivative.

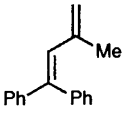
The photocyclization of the trifluoroacetate derivative **9a** is very efficient and irradiation for a mere 10 min affords the cyanocyclopropane **16** in 80% isolated yield. The photocyclization in this example is followed by an efficient thermal elimination of trifluoroacetic acid during the work-up procedure. This provides a new synthetic route to cyanocyclopropanes from derivatives of β,γ-unsaturated aldehydes. A direct path by the irradiation of β,γ-unsaturated nitriles fails because of their photochemical inertness previously established by us.[4] The transformation of the benzoate derivative **9b** is also efficient and gives the corresponding cyclopropane **14c** in 90% yield after 20 min irradiation.



14a X = $NHCONH_2$
b X = NHCOPh
c X = OCOPh



15 R = CHO
16 R = CN



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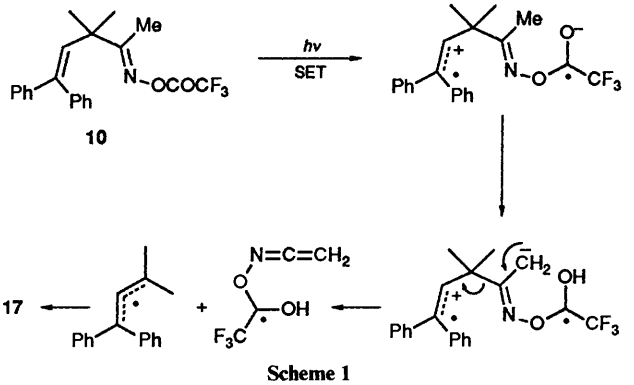
The results obtained from the derivatives **8** and **9** fall into distinct groups. The hydrazine derivatives **8** are all stable crystalline compounds which undergo the aza-di-π-methane rearrangement with reasonable efficiency with the semicarbazone being the least efficient. The cyclopropane derivatives formed from them can all be hydrolysed quantitatively to the cyclopropanecarbaldehyde **15** which, from a synthetic standpoint, is a considerable advantage. The other derivatives **9** are even more efficient with yields of 80–90% of cyclopropane after only 10–20 min irradiation. Perhaps the one drawback with these is the thermal instability of the trifluoroacetate **9a**. However, the benzoate **9b** is a stable crystalline derivative. In general, the hydrazine derivatives undergo cyclization less efficiently than the oxime derivatives. Previously we have demonstrated that the attachment of an electron withdrawing group to the imine nitrogen was essential for successful cyclization. The poorer efficiency observed with the hydrazine derivatives could be explained by the fact that amide groups have poorer electron withdrawing capacity than ester groups. However, the mechanism for the formation of the cyclopropane derivatives **14** from the sensitized irradiation of these new stable C=N derivatives is presumed to be analogous to that for the conversion of the oxime acetate **4**, namely, the well established triplet state ADPM process.[1,3,4]

Previously we have demonstrated that the imine and oxime acetate derivatives of **7** undergo the ADPM reaction inefficiently.[4,8] Indeed the ADPM reaction generally is inefficient with ketone derivatives.[4] Some of the new stable derivatives of **6**, the oximino trifluoroacetate and oximino benzoate, have been shown to be the most efficient in undergoing the ADPM rearrangement in the present study. Thus, to give enone **7** the best possible chance to undergo the ADPM process efficiently **7** was converted into **10** and **11** by conventional methods. However, irradiation of these under the normal sensitized conditions failed to yield products arising from ADPM rearrangement. While the benzoate **11** appeared to be inert on irradiation, the trifluoroacetate **10** affords the diene **17**, the identity of which was established by independent synthesis. A fragmentation reaction of this type has not been reported previously in 1-aza-1,4-diene derivatives and we have established that the process is photochemical since dark-control reactions yield only recovered starting material. There are several possible mechanisms which could be considered. However, our previous results have shown that under the sensitized conditions used the triplet energy is transferred to the 1,1-diphenylvinyl moiety. Normally such excitation results in bridging and rearrangement. This is apparently not the case in derivative **10** since no cyclopropane is obtained. It is also unlikely that the triplet energy is transferred to the trifluoroacetyl group since there is a considerable energy mismatch. We propose, therefore, that the fragmentation is brought about by a SET. Since trifluoroacetic acid is capable of bringing about one-electron oxidations[10] the SET in this example occurs to the trifluoroacetyl group from the 1,1-diphenylvinyl moiety. The involvement of such a step may be due to the greater electron accepting properties of the trifluoroacetyl group compared to the other subsituents used above. This electron transfer is followed by hydrogen abstraction from the proximate methyl group. The resultant radical cation/radical anion undergoes fragmentation and hydrogen abstraction as shown in Scheme 1. That the aldehyde



Scheme 1

derivative **9a** does not undergo fragmentation is presumably due to the absence of an abstractable acidic hydrogen. The failure of the benzoate **11** to undergo reaction was surprising and cannot be explained on the evidence available. Further studies are intended to clarify this situation.

The above results qualitatively demonstrate the efficiency of the ADPM rearrangement for the series of derivatives of the aldehyde **6**. The oxime esters benzoate **9b** and trifluoroacetate **9a**, are particularly efficient and the yields of product are similar but the length of irradiation changes dramatically from 30 min to 10 min. One of the most important advantages of the compounds used in this study is that the hydrazine derivatives **8** and the cyclopropanes derived from them are stable and crystalline and are obtained in high yield. The success with the derivatives **8** indicates that there is no adverse effect, apart from a slight decrease in efficiency, from the incorporation of a nitrogen adjacent to the imine nitrogen. This effect is evidence that the increased electron withdrawing ability of the acyl group increases the ionization potential of the oxime nitrogen lone pair which minimises the adverse intramolecular single electron transfer from the oxime to the alkene moiety which is respons-

ible for the quenching of the aza-di-π-methane process.[3] It is clear from these results that the ADPM rearrangement is not restricted to imines and oxime acetates but can be readily extended to other common derivatives of carbonyl compounds. The study has also indicated some limits to the type of derivative that can be used. Thus with a methyl ketone derivative where the functional group can undergo SET from the triplet 1,1-diphenylvinyl moiety an alternative fragmentation path can be operative in a novel reaction not seen previously in such systems.

Experimental

Melting points were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer and band positions are reported in wavenumbers. NMR spectra were recorded on a Varian FT-300A spectrometer for protons and carbon with chemical shifts (δ) expressed in ppm downfield from internal Me_4Si and coupling constants J are given in Hz. UV–VIS spectra were recorded in methylene dichloride or ethanol solution using a Perkin-Elmer 550 spectrometer. The mass spectra were run at the University of Strathclyde using an AEI (Kratos) MS 9 mass spectrometer fitted with a Mass Spectrometry Services Solid State Console and a GEC 905 computer.

2,2-Dimethyl-4,4-diphenylbut-3-enal **6**[7] and 3,3-dimethyl-5,5-diphenylpent-4-en-2-one **7**[7] were prepared by the literature procedures. The oximes of **6**[4] and **7**[8] were prepared as described previously.

2,2-Dimethyl-4,4-diphenylbut-3-enal Semicarbazone **8a**.—The enal **6** (2 mmol), pyridine (2 mmol) and semicarbazide hydrochloride (2 mmol) were dissolved in ethanol (60 cm^3) and heated at reflux for 1 h. Conventional work-up afforded the desired product. The semicarbazone **8a** was obtained as a colourless crystalline compound (90%) from ethanol, m.p. 166–167 °C; ν_{max}(KBr)/cm^{-1} 3400–3300 (NH and NH_2), 1720 (C=O) and 1670 (C=N); δ_H($CDCl_3$) 1.2 (6 H, s, 2Me), 5.2 (2 H, br s, NH_2), 5.9 (1 H, s, vinyl H), 6.4 (1 H, s, imine H), 6.8–7.3 (10 H, m, aryl H) and 7.6 (1 H, br s, NH); δ_C($CDCl_3$) 27.3 (2Me), 40.1 (quaternary C), 126.8–142.6 (aryl and vinyl C), 150.1 (C=N) and 158.2 (C=O); λ_{max}(CH_2Cl_2)/nm 249 (ε/dm^3 mol^{-1} cm^{-1} 47 300); m/z 307 (M^+, 18%), 292 (10), 265 (31), 249 (22), 248 (100), 232 (30) and 97 (51) (Found: C, 74.3; H, 7.0; N, 13.9. $C_{19}H_{21}N_3O$ requires C, 74.30; H, 6.80; N, 13.60%).

2,2-Dimethyl-4,4-diphenylbut-3-enal Acetylhydrazone **8b**.—The enal **6** (500 mg, 2 mmol) and acetylhydrazine (2 mmol) were dissolved in ether (60 cm^3) and stirred at room temperature in the presence of $MgSO_4$ for 1 h. Conventional work-up afforded the desired product. The acetyl hydrazone **8b** was obtained as a colourless crystalline solid (600 mg, 98%) from ethanol–H_2O, m.p. 165–167 °C; ν_{max}(KBr)/cm^{-1} 3200, 3080 (NH and NH_2) and 1680 (C=O); δ_H($CDCl_3$) 1.2 (6 H, s, 2Me), 2.0 (3 H, s, MeCO), 6.0 (1 H, s, vinyl H), 6.6 (1 H, s, imine H), 7.1–7.3 (10 H, m, aryl H) and 8.6 (1 H, br s, NH); δ_C($CDCl_3$) 20.0 (MeCO), 27.3 (Me), 40.3 (quaternary C), 126.7–142.4 (aryl and vinyl C), 152.0 (C=N) and 172.9 (C=O); λ_{max}(ethanol)/nm 260 (4100); m/z 306 (M^+, 51%), 265 (63), 236 (36), 191 (52), 165 (43), 91 (58), 85 (100), 77 (30) and 43 (28) (Found: C,78.2; H, 7.0; N, 8.9. $C_{20}H_{22}N_2O$ requires C, 78.39; H, 7.18; N, 9.14%).

2,2-Dimethyl-4,4-diphenylbut-3-enal Benzoylhydrazone **8c**.—The enal **6** (500 mg, 2 mmol) and benzoylhydrazine (2 mmol) were dissolved in ether (100 cm^3) and stirred at room temperature in the presence of $MgSO_4$ for 1 h. Conventional work-up afforded the desired product. The benzoylhydrazone **8c** was obtained as a colourless crystalline solid (730 mg, 99%) from ethanol–H_2O, m.p. 130–131 °C; ν_{max}(KBr)/cm^{-1} 3240 (NH), 1655 (C=O) and 1625 (C=N); δ_H($CDCl_3$) 1.2 (6 H, s, 2Me), 6.0 (1 H, s, vinyl H), 6.8 (1 H, s, imine H), 7.0–7.7 (15 H, m, aryl H) and 8.1 (1 H, s, NH); δ_C($CDCl_3$) 28.0 (2Me), 40.8 (quaternary C), 125.0–142.4 (aryl and vinyl C), 156.3 (C=N) and 163.0 (C=O); λ_{max}(ethanol)/nm 257 (20 800); m/z 368 (M^+, 1%), 147 (100), 105 (45), 91 (9), 77 (26) and 51 (5) (Found: C, 81.2; H, 6.6; N, 7.4. $C_{25}H_{24}N_2O$ requires C, 81.50; H, 6.65; N, 7.60%).

Method for the Synthesis of Trifluoroacetate Derivatives of Oximes **2** *and* **13**.—The corresponding oxime (18 mmol) and pyridine (18 mmol) were dissolved in diethyl ether (anhydrous) (60 cm^3) and cooled to −60 °C under an atmosphere of argon. An equimolecular amount of trifluroacetic anhydride was added dropwise. The mixture was kept at 0 °C for 2 h and then was poured into hydrochloric acid (10% in water) and extracted with diethyl ether. The organic layer was washed with a saturated aqueous $NaHCO_3$ and water and dried over $MgSO_4$. The desiccant was removed by filtration and the solvent removed by evaporation under reduced pressure.

2,2-Dimethyl-4,4-diphenylbut-3-enal O-trifluoroacetyloxime **9a**. This compound was obtained as an unstable colourless oil (620 mg, 98%) and was used without further purification; ν_{max} (liq. film)/cm^{-1} 1820 (C=O), 1240, 1180 and 1140; δ_H($CDCl_3$) 1.2 (6 H, s, 2Me), 5.9 (1 H, s, vinyl H) and 7.0–7.2 (11 H, m, aryl H and CH=N); δ_C($CDCl_3$) 26.8 (2Me), 40.1 (quaternary C), 115.0 (CF_3), 126.7–142.0 (aryl and vinyl C), 158.0 (C=O) and 166.8 (C=N); λ_{max}(CH_2Cl_2)/nm 247 (8200).

3,3-Dimethyl-5,5-diphenylpent-4-en-2-one O-trifluoroacetyloxime **10**. This compound was obtained as an unstable colourless oil (620 mg, 94%) and was used without further purification; ν_{max}(liq. film)/cm^{-1} 1800 (C=O), 1210, 1160 and 1110; δ_H ($CDCl_3$) 1.3 (6 H, s, 2Me), 1.7 (3 H, s, Me), 6.0 (1 H, s, vinyl H) and 7.1–7.3 (10 H, m, aryl H); δ_C($CDCl_3$) 14.5 (MeCO), 26.5 (2Me), 44.2 (quaternary C), 114.0 (CF_3), 126.9–142.8 (aryl and vinyl C), 153.9 (C=O) and 173.7 (C=N); λ_{max}(ethanol)/nm 236 (2100).

Method for the Synthesis of Benzoate Derivatives of Oximes **2** *and* **13**.—The corresponding oxime was dissolved in pyridine (2 cm^3) and cooled to 0 °C. An equimolecular amount of benzoyl chloride was added dropwise. The mixture was stirred at room temperature for 2 h and then was poured into sulfuric acid (10% in water) and extracted with diethyl ether. The organic layer was washed with a saturated solution of $NaHCO_3$ and water and dried over $MgSO_4$. The desiccant was removed by filtration and the solvent removed by evaporation under reduced pressure. The products were purified by chromatography on silica gel using hexane–diethyl ether (9:1) as eluent.

2,2-Dimethyl-4,4-diphenylbut-3-enal O-benzoyloxime **9b**. This compound was synthesized using oxime **2** (1.8 mmol) which yielded the desired product as a colourless crystalline solid (650 mg, 97%) from hexane, m.p. 40–42 °C; ν_{max}(KBr)/cm^{-1} 1750 (C=O), 1270, 1100 and 1080; δ_H($CDCl_3$) 1.4 (6 H, s, 2Me), 6.0 (1 H, s, vinyl H) and 7.1–7.9 (15 H, m, aryl H and CH=N); δ_C($CDCl_3$) 27.0 (2Me), 39.9 (quaternary C), 126.8–142.1 (aryl and vinyl C), 164.2 (C=N) and 171.4 (C=O); λ_{max}(ethanol)/nm 245 (21 000); m/z 369 (M^+, 1%), 246 (26), 232 (41), 204 (100) and 98 (20) (Found: C, 81.9; H, 6.4; N, 7.6. $C_{25}H_{23}NO_2$ requires C, 81.70; H, 6.30; N, 7.60%).

3,3-Dimethyl-5,5-diphenylpent-4-en-2-one O-benzoyloxime **11**. This compound was synthesized using oxime **13** (3.5 mmol) which yielded the desired product as a colourless crystalline solid (1.3 g, 93%) from hexane, m.p. 79–81 °C; ν_{max}(KBr)/cm^{-1} 1745 (C=O), 1250, 1230 and 1060; δ_H($CDCl_3$) 1.4 (6 H, s, 2Me), 1.7 (3 H, s, Me), 6.0 (1 H, s, vinyl H) and 7.1–8.1 (15 H, m, aryl H and CH=N); δ_C($CDCl_3$) 14.3 (MeCO), 27.5 (2 Me), 44.2 (quaternary C), 127.1–143.3 (aryl and vinyl C), 163.4 (C=N) and

170.7 (C=O); λ_{max}(ethanol)/nm 236 (21 000); *m/z* 383 (M^+, 28%), 263 (46), 239 (17), 221 (28), 220 (70), 204 (20), 128 (18), 122 (53), 105 (100) and 91 (41) (Found: C, 81.3; H, 6.5; N, 3.6. $C_{26}H_{25}NO_2$ requires C, 81.46; H, 6.52; N, 3.65%).

Preparative Photolyses.—The photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. Solutions of the compounds and acetophenone in anhydrous benzene (280 cm^3) were purged with argon for 1 h and irradiated under a positive pressure of argon for the times shown. After completion of the irradiation the solvent was removed under reduced pressure and the products were separated by chromatography.

Irradiation of the semicarbazone **8a**. This compound (250 mg, 0.81 mmol) and acetophenone (7 g) were irradiated for 2 h. Chromatography using ethyl acetate–benzene (9:1) afforded the *2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde semicarbazone* **14a** as a colourless crystalline compound (100 mg, 40%); m.p. 122–124 °C; ν_{max}(KBr)/cm^{-1} 3550–3380 (NH and NH_2), 1700 (C=O) and 1620 (C=N); δ_H($CDCl_3$) 1.1 (3 H, s, Me), 1.3 (3 H, s, Me), 2.3 (1 H, d, *J* 8, cyclopropyl H), 5.5 (2 H, br s, NH_2), 6.7 (1 H, d, *J* 8, imine H), 6.8–7.3 (10 H, m, aryl H) and 8.8 (1 H, br s, NH); δ_C($CDCl_3$) 15.1 (Me), 20.5 (Me), 29.5 (cyclopropyl C-2), 36.2 (cyclopropyl C-1), 47.0 (cyclopropyl C-3), 126.1–144.3 (aryl C), 144.8 (C=N) and 157.2 (C=O); *m/z* 307 (M^+, 9%), 289 (6), 248 (100), 217 (18), 191 (23), 165 (26), 115 (14), 91 (21) and 77 (7) (Found: C, 74.6; H, 7.0; N, 13.8. $C_{19}H_{21}N_3O$ requires C, 74.30; H, 6.80; N, 13.60%). Starting material **8a** (130 mg, 52%).

Irradiation of acetylhydrazone **8b**. This compound (268 mg, 0.8 mmol) and acetophenone (12 g) were irradiated for 2 h. In this instance the photolysate was hydrolysed using sulfuric acid (10% in water) in THF at room temperature. The resultant mixture of aldehydes was separated by column chromatography using hexane as eluent. This gave *aldehyde* **6** (55 mg, 25%) and *cyclopropanecarbaldehyde* **15** (155 gm, 71%).

Irradiation of benzoylhydrazone **8c**. This compound (300 mg, 0.81 mmol) and acetophenone (20 g) were irradiated for 30 min. Chromatography using hexane–ethyl acetate (7:3) afforded starting material **8c** (200 mg, 66%) and the derivative of *2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde benzoylhydrazone* **14b** as a colourless crystalline compound (60 mg, 20%) from ethanol m.p. 98–100 °C; ν_{max}(KBr)/cm^{-1} 3220 (NH), 1645 (C=O) and 1610 (C=N); δ_H($CDCl_3$) 1.0 (3 H, s, Me), 1.2, (3 H, s, Me), 2.5 (1 H,d, *J* 7.5, cyclopropyl H), 6.9 (1 H, d, *J* 7.5, imine H), 7.0–7.7 (15 H, m, aryl H) and 9.2 (1 H, br s, NH); δ_H($CDCl_3$) 20.6 (Me), 25.4 (Me), 29.4 (cyclopropyl C-2), 36.0 (cyclopropyl C-1), 47.8 (cyclopropyl C-3), 126.2–143.8 (aryl and vinyl C), 152.1 (C=N) and 163.5 (C=O); *m/z* 368 (M^+), 248 (76), 232 (38), 191 (25), 165 (20) 147 (31), 105 (100), 77 (48) and 51 (11) (Found: C, 81.7; H, 6.8; N, 7.5. $C_{25}H_{24}N_2O$ requires C, 81.50; H, 6.65; N, 7.60%).

Irradiation of trifluoroacetate **9a**. This compound (300 mg, 0.85 mmol) and acetophenone (5 g) were irradiated for 10 min. Chromatography using hexane–diethyl ether (9:1) afforded *2,2-dimethyl-4,4-diphenylbut-3-enonitrile* **12** (30 mg, 14%) and *2,2-dimethyl-3,3-diphenylcyclopropanecarbonitrile* **16** (170 mg, 80%) that were identified by comparison with authentic samples.[8]

Irradiation of benzoate **9b**. This compound (310 mg, 0.84 mmol) and acetophenone (1.8 g) were irradiated for 20 min. Chromatography using hexane–diethyl ether (9:1) afforded starting material (10 mg, 0.3%) and *2,2-dimethyl-3,3-diphenylcyclopropanecarbaldehyde O-benzoyloxime* **14c** (280 mg, 90%) as a colourless crystalline solid from hexane; m.p. 110–114 °C; ν_{max}(KBr)/cm^{-1} 1745 (C=O), 1620 (C=N), 1250 and 1060; δ_H($CDCl_3$) 1.1 (3 H, s, Me), 1.3 (3 H, s, Me), 2.6 (1 H, d, *J* 9, cyclopropyl H) and 7.1–8.1 (16 H, m, aryl H and CH=N); δ_C($CDCl_3$) 20.6 (Me), 25.3 (Me), 29.8 (cyclopropyl C-2), 33.3 (cyclopropyl C-1), 48.3 (cyclopropyl C-3), 126.3–133.1 (aryl and vinyl C), 143.4 (C=N) and 160.4 (C=O); *m/z* 369 (M^+, 1%), 246 (100), 232 (77), 121 (68), 105 (86) and 77 (45) (Found: C, 81.5; H, 6.5; N, 7.8. $C_{25}H_{23}N_2O$ requires C, 81.30; H, 6.20; N, 7.60%).

Irradiation of trifluoroacetate **10**. This compound (343 mg, 0.9 mmol) and acetophenone (9 g) were irradiated for 2 h. Chromatography using hexane–diethyl ether (9:1) afforded *oxime* **10** (134 mg, 50%) and *3-methyl-1,1-diphenylbuta-1,3-diene* **17** (83.7 mg, 40%) as a colourless oil. Proof of identity for this compound was obtained by an independent synthesis as follows.

Synthesis of 3-Methyl-1,1-diphenylbuta-1,3-diene **17**. 4,4-Diphenylbut-3-en-2-ol was synthesized from β-phenylcinnamaldehyde (1 g, 4.8 mmol) by reaction with methylmagnesium iodide (14 mmol) in diethyl ether (30 cm^3, anhydrous). The mixture was refluxed for 3 h and hydrolysed by addition of saturated aqueous ammonium chloride. Conventional work-up followed by column chromatography on silica gel using hexane–diethyl ether (9:1) as eluent yielded 4,4-diphenylbut-3-en-2-ol (1.02 g, 95%) as a pale yellow oil;[11] ν_{max}(liq. film)/cm^{-1} 3340 (OH) and 1670 (C=C); δ_H($CDCl_3$) 1.2 (3 H, d, *J* 9, Me), 4.3 (1 H, m, C*H*OH), 6.0 (1 H, d, *J* 9, CH) and 7.1–7.3 (10 H, m, aryl H); δ_C($CDCl_3$) 23.6 (Me), 65.6 (CH–OH) and 127.3–142.2 (aryl C and C=C).

4,4-Diphenylbut-3-en-2-one was prepared from 4,4-diphenylbut-3-en-2-ol (220 mg, 0.98 mmol) by oxidation with MnO_2 (2.5 g, 28 mmol) in methylene dichloride (100 cm^3) at room temperature for 3 h. The MnO_2 was removed by filtration and the solvent evaporated under reduced pressure. The oily residue was chromatographed on silica gel using hexane–diethyl ether (9:1) as eluent yielding the ketone as a pale yellow oil (155 mg, 71%).[12]

2-Methyl-4,4-diphenylbut-3-en-2-ol was synthesized from 4,4-diphenylbut-3-en-2-one (96 mg, 0.43 mmol) by reaction with methyllithium (0.4 cm^3, 0.56 mmol) in diethyl ether (60 cm^3), anhydrous) at −70 °C under argon. The mixture was stirred at room temperature for 90 min. Conventional work-up gave a colourless oil (121 mg, 93%).[13]

1,1-Diphenyl-3-methylbuta-1,3-diene **17** was synthesized from 2-methyl-4,4-diphenylbut-3-en-2-ol (200 mg, 0.84 mmol) by dehydration using sulfuric acid (10 cm^3, 15% in water) in THF (30 cm^3) by stirring at room temperature for 4 h. Conventional work-up gave the *diene* **17** as a yellow oil (170 mg, 92%); ν_{max}(liq. film)/cm^{-1} 1600, 1480 and 1440; δ_H($CDCl_3$) 1.4 (3 H, s, Me), 4.9 (1 H, s, CH_2), 5.0 (1 H, s, CH_2), 6.6 (1 H, s, vinyl H) and 7.1–7.3 (10 H, m, aryl H); δ_C($CDCl_3$) 21.9 (2Me), 119.0 (C=C) and 127.0–143.1 (aryl C).

Irradiation of benzoate **11**. This compound (300 mg, 2.7 mmol) and acetophenone (2.8 g) were irradiated for 21 h. Chromatography using hexane–ethyl acetate (7:3) afforded starting material **11** only.

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