

## The Photochemical 1,5-Benzoyl Migration in 2,2-Diaryl-1,4,4-triphenyl-3-azabut-3-en-1-ones. A Novel Rearrangement in $\beta,\gamma$ -Unsaturated Enone Systems

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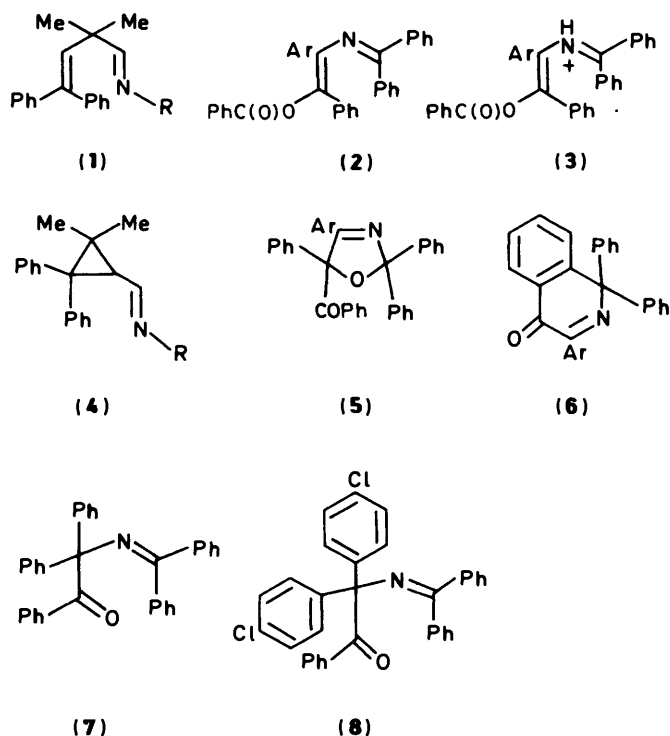
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The synthesis of 2,2-diphenyl- and 2,2-bis(*p*-chlorophenyl)-1,4,4-triphenyl-3-azabut-3-en-1-one is described. The photochemical reactivity of these compounds is described and interpreted in terms of 1,5-benzoyl migration, the terminus of which rearrangement is a phenyl ring. This type of reactivity is novel for  $\beta,\gamma$ -unsaturated systems.

The photochemistry of molecules containing the imine group has been a subject of study for many years. Many diverse reactions such as isomerization, rearrangement, cycloaddition, photoreduction, and photoalkylation have been reported and only in the last fifteen years or so have attempts been made to classify the reactions.<sup>1,2</sup>

In recent years we have been interested in the effect of the incorporation of an imine group on the photochemical reactivity of organic molecules. As a result we have observed the novel transformations of imines (1), (2), and (3) into the photoproducts (4)<sup>3</sup>, (5)<sup>4</sup>, and (6)<sup>5</sup> respectively. It is clear from these results that the incorporation of a nitrogen into the system has a profound effect on the course of the reaction. The behaviour of these molecules is substantially different from the reactions of  $\beta,\gamma$ -unsaturated enones to which the imines are structurally related.<sup>6</sup>

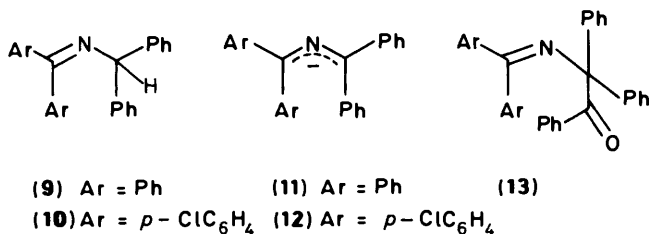


again closely related to the  $\beta,\gamma$ -unsaturated enones, and herein we report the details of our results.

### Results and Discussion

The synthesis of the azaenones (7) and (8) relies on the ability to prepare the imines (9) and (10). As it turns out these latter compounds can be readily prepared by the action of benzophenone and *p,p'*-dichlorobenzophenone with diphenylmethylamine under dehydrating conditions using zinc chloride-diphenylethylamine as a catalyst. These reactions provided the crystalline imines in high yield after reflux for many days. The identity of the imines (9) and (10) was readily established by microanalysis (in these cases the imines are not prone to hydrolysis as had been our experience with other imines<sup>3-5</sup>) and spectroscopy. The i.r. spectra showed the presence of a C=N absorption in the 1610–1620  $\text{cm}^{-1}$  region typical for such groups.<sup>8</sup> The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra show resonances at positions compatible with literature values.<sup>9,10</sup>

Both imines (9) and (10) react with NaH in hexamethylphosphoric triamide-tetrahydrofuran (HMPTA-THF) at 0 °C to give highly coloured solutions of the corresponding anions (11) and (12) which can then be quenched by the addition of benzoyl chloride. Conventional work-up yields the colourless crystalline azaenones (7) and (8) in good yield. The structure of enone (7) was verified by X-ray crystallography the results of which have been published elsewhere.<sup>11</sup> Conventional microanalysis and i.r. and n.m.r. spectroscopy were in accord with the proposed structure. This information was then used to confirm the structure of azaenone (8) since in this instance it is important to know at which C atom of the anion (12) the benzoylation



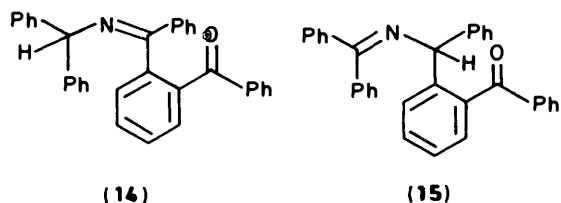
takes place. It can be argued, however, that the more likely site for the arylation is at the carbon bearing the chloroaryl groups. Structure proof for compound (8) comes from a comparison of the i.r., <sup>1</sup>H, and <sup>13</sup>C n.m.r. spectra of both compounds (7) and (8). Final confirmation comes from the acid hydrolysis of compound (8) where only benzophenone is obtained from the hydrolysis of the imine group in this

As an extension of our studies we have examined<sup>7</sup> the photochemical reactivity of the imines (7) and (8) which are

compound. The alternative arylation would have given the enone (13) which on hydrolysis would yield *p,p'*-dichlorobenzophenone, but no trace of this was detected. Thus definitive proof of arylation of the anion (12) yielding only imino ketone (8) had been obtained.

The u.v. spectra of both azaenones (7) and (8) show a principal maximum in the 250 nm region of the spectrum with a long tail to above 320 nm.

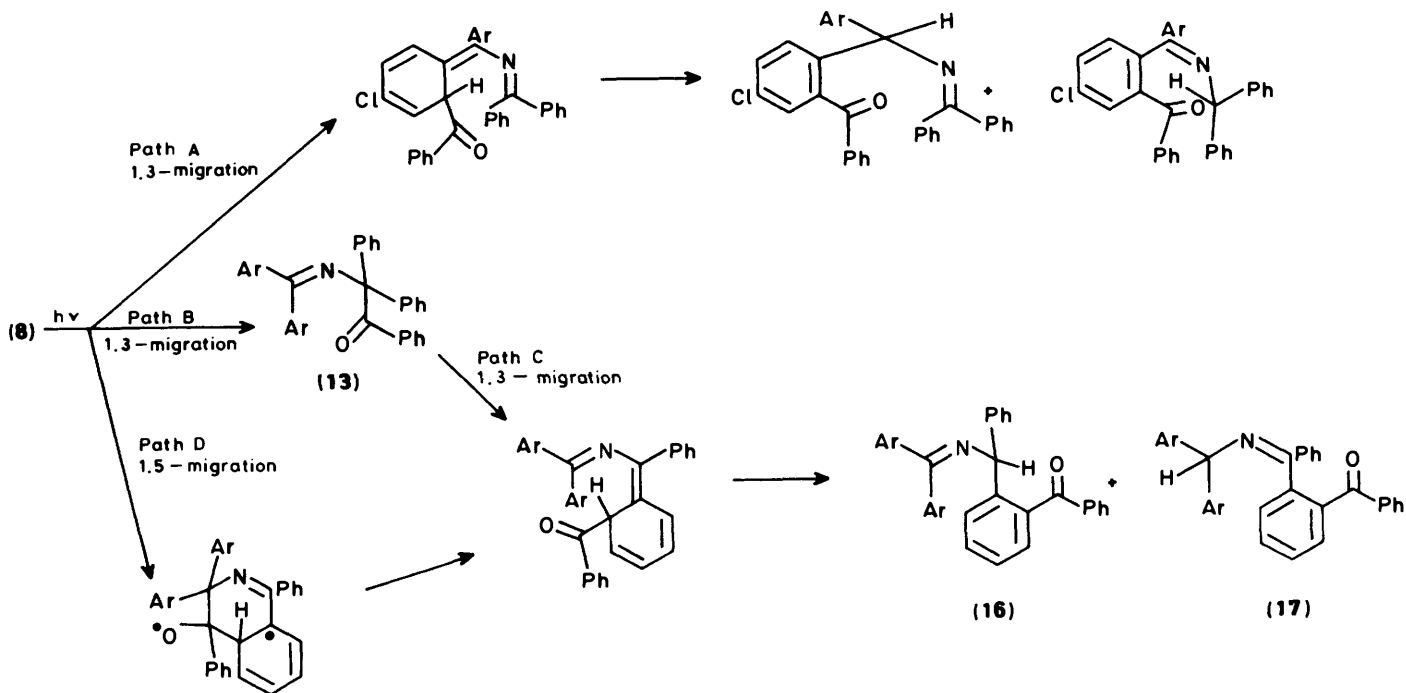
The direct irradiation of enone (7) using a Pyrex filter brought about a 67% conversion of starting material into principally two products obtained in an overall yield of 43% and in the ratio 1:1. Dark control experiments confirmed that the reaction was photochemical. Conventional chromatography on silica gel allowed the separation of the two crystalline photoproducts but also brought about some hydrolysis on the column substrate, yielding benzophenone and *o*-dibenzoylbenzene. The structure of the first product was determined by X-ray crystallography<sup>12</sup> and identified as the rearranged keto imine (14). The <sup>1</sup>H n.m.r. spectrum of keto imine (14) shows, apart from the aryl resonances, the methine hydrogen at  $\delta_H$  5.53. Acid hydrolysis followed by silica gel chromatography affords only *o*-dibenzoylbenzene, with diphenylmethyl amine adhering to the column. The other product (15) was clearly isomeric both with starting material and with product (14). This molecule showed <sup>1</sup>H n.m.r. resonances in the aryl region and a singlet at  $\delta_H$  5.41 attributable to the methine hydrogen. Final proof of this structure was obtained by the isolation of benzophenone as the sole mobile compound from chromatography of the acid-hydrolysis products of compound (15).



The formation of products (14) and (15) could arise by a variety of paths which are difficult to differentiate using only azaenone (7) because of the identical substitution at each end of the enone system. This problem can be surmounted using azaenone (8) which on irradiation is converted into analogous products (16) and (17). The identity of these products was established by the normal spectroscopic methods and also by comparison with photo products (14) and (15). A useful method of further confirmation is by acid hydrolysis which yielded *p,p'*-dichlorobenzophenone from (16) and *o*-dibenzoylbenzene from (17), as the only mobile components, from silica gel chromatography.

The Scheme illustrates all the possibilities which can apply to the rearrangement of both enones (7) and (8). It can be seen that the use of the chlorophenyl groups as a label allows the identification of the sole rearrangement path. Thus the absence of dichloro-*o*-dibenzoylbenzene as a hydrolysis product eliminates path A – the simple 1,3-migration. 1,3-Acyl migrations are common reactions of  $\beta,\gamma$ -unsaturated enones and arise, in the main, from the singlet excited state. However, it should also be borne in mind that while 1,3-acyl migrations occur along a carbon chain they have never been reported as involving an aryl group as the terminus for the migration.<sup>13</sup> It is also of interest that the rearrangement described by us occurs on acetophenone-sensitization and cyclo-octadiene quenching conditions. Path B can also be eliminated since the hydrolysis of recovered enone (8) yields only benzophenone. Thus the degenerate 1,3-route, a more common example of a 1,3-acyl migration,<sup>13</sup> and, therefore, the second 1,3-migration (path C), can also be discounted. As a consequence of the above only the 1,5-benzoyl migration, path D, appears to be applicable. 1,5-Acyl migrations are uncommon. However, some reports of such processes in acyclic dienone systems have been published.<sup>14,15</sup> As for the 1,3-acyl migration, phenyl groups have not been reported previously as the terminus for such a reaction.

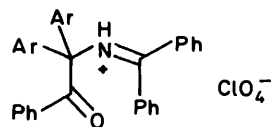
The Scheme shows the 1,5-migration in azaenones (7) and (8) as a biradical process. There is also the possibility that an electron transfer is involved. Previously we have demon-



Scheme

strated<sup>3-5</sup> that the incorporation of an imine group into a molecule can be responsible for photochemical reactivity different from that normally expected. Indeed it seems likely in some instances<sup>16</sup> that electron transfer may be involved as in the conversion of the azadienes (2) into the 3-oxazolines (5). The transfer of an electron from a nitrogen to a carbonyl group is a fairly common process and there are ample literature precedents for both the intra- and the inter-transfer.<sup>17</sup> Protonation of the nitrogen in the dienes (3) and irradiation yields the isoquinolinones (6).<sup>5</sup>

The possibility of electron-transfer involvement in the photoreaction of azaenone (8) was investigated. The azaenone (8) was dissolved in methylene dichloride and treated with perchloric acid, a process well known<sup>18</sup> to effect nitrogen protonation. This treatment forms the ion (18). A dark control



(18) Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>

experiment demonstrated that the azaenone (8) can be recovered quantitatively from such a reaction. Irradiation of solutions of the ion (18) followed by hydrolysis and flash chromatography on silica gel yielded benzophenone and *p,p'*-dichlorobenzophenone as the only mobile fragments. The absence of *o*-dibenzoylbenzene and dichloro-*o*-dibenzoylbenzene eliminates the operation of any of the paths A, C, and D in the Scheme. Thus only path B is operative and irradiation of the ion (18) yields only the degenerate 1,3-acyl rearranged product enone (13) in its protonated form.

This simple hydrolytic treatment only gives information concerning the position of the imine bond in compounds (8) and (13). An alternative work-up procedure, involving hydrolysis, diazotization, and lead tetra-acetate oxidation, showed that the amine portion of the hydrolysis had undergone no change.

From these experiments it seems that the role of the nitrogen in the rearrangement of compounds (7) and (8) is vital and that an electron-transfer step is involved. It is of interest to note that the reaction of the azaenone (7) can be brought about by both direct and sensitized irradiation and also in the presence of a quencher, each experiment being carried out under identical conditions. It is, therefore, probable that a triplet state is involved since the chromophore in the molecule which absorbs light above 300 nm is most likely to be the benzoyl group, the intersystem crossing efficiency to the triplet of which is normally unity.<sup>19</sup> The failure of the quencher to inhibit the reaction even at high concentration could again be construed as evidence for the involvement of an electron-transfer process. Substantiation of this comes from the fact that previous studies on the photochemistry of ketones<sup>20</sup> and esters<sup>21</sup> with nitrogen substituents have clearly demonstrated that intramolecular electron-transfer processes cannot be quenched.

## Experimental

M.p.s were determined on a Buchi 510D apparatus for open capillaries and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. <sup>1</sup>H N.m.r. spectra were obtained on a Varian T60A spectrometer, and <sup>13</sup>C spectra on a Varian FT80A spectrometer. Samples were dissolved in CDCl<sub>3</sub> and chemical shifts are recorded in p.p.m. downfield from internal Me<sub>4</sub>Si. Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas de Madrid. Mass spectra were performed on a Varian MAT 711

spectrometer. U.v.-visible spectra were recorded on a Perkin-Elmer I 24 spectrophotometer.

**Synthesis of Imines.—General procedure.** The imines were synthesized by reaction between equimolecular amounts of the amine and the ketone in dry toluene (100 ml). The reactions were catalysed by a zinc chloride—phenylethylamine complex. The mixtures were refluxed and the water formed during the reactions was removed by a Dean-Stark water separator. The solvent was then removed under reduced pressure and the crude product was crystallized from ethanol.

**N-Benzhydryldiphenylmethanimine (9).** Diphenylmethylamine (6.2 g, 0.034 mol) and benzophenone (6.1 g, 0.034 mol) were refluxed in toluene (100 ml) for 15 days. After conventional work-up the crude imine was crystallized to afford *imine* (9) (10.97 g, 95%), m.p. 150–152 °C; δ<sub>H</sub> (CDCl<sub>3</sub>) 7.15–7.68 (20 H, m, ArH) and 5.50 (1 H, s, benzhydryl); δ<sub>C</sub> (CDCl<sub>3</sub>) 169.33 (C=N), 145.04, 141.33, 138.00, 126.70–130.14 (aryl), and 70.00 (C-1); ν<sub>max</sub> (KBr) 1 620 cm<sup>-1</sup> (C=N); λ<sub>max</sub> (EtOH) 209 (ε 50 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) and 250 nm (21 800) (Found: C, 89.8; H, 3.1; N, 4.1. C<sub>26</sub>H<sub>21</sub>N requires C, 89.90; H, 3.20; N, 4.00%).

**N-Benzhydryl-*p,p'*-dichlorodiphenylmethanimine (10).** Diphenylmethylamine (4.78 g, 0.026 mol) and *p,p'*-dichlorobenzophenone (6.56 g, 0.026 mol) were refluxed in toluene (100 ml) for 18 days. The crude material obtained from conventional work-up was crystallized from ethanol to afford the *imine* (10) (7.03 g, 65%), m.p. 95–97 °C; δ<sub>H</sub> (CCl<sub>4</sub>) 6.90–7.71 (18 H, m, ArH) and 5.41 (1 H, s, benzhydryl); δ<sub>C</sub> (CDCl<sub>3</sub>) 164.63 (C=N), 144.55, 137.93, 136.58, 134.91, 126.91–129.96 (aryl), and 70.27 (C-1); ν<sub>max</sub> (KBr) 1 610 cm<sup>-1</sup> (C=N); λ<sub>max</sub> (EtOH) 209 (39 100) and 255 nm (21 000); (CH<sub>2</sub>Cl<sub>2</sub>) 231 (25 100) and 262.5 nm (30 800); *m/z* 415 (*M*<sup>+</sup>, 9%), 167 (100), 165 (23), and 105 (4) (Found: C, 75.0; H, 4.5; N, 3.3; Cl, 17.2. C<sub>26</sub>H<sub>19</sub>Cl<sub>2</sub>N requires C, 75.00; H, 4.60; N, 3.40; Cl, 17.10%).

**General Procedure for the Synthesis of Azaenones (7) and (8).**—Solutions of the imines were treated in HMPTA-THF (10:1) with NaH under nitrogen at room temperature. The highly coloured solutions of the carbanions were quenched by the dropwise addition of benzoyl chloride at 0 °C. The crude product was hydrolysed, and extracted with ether, and the extracts were dried over MgSO<sub>4</sub>. The solutions were filtered and the ether was removed under reduced pressure. The crude product was then crystallized from ethanol.

**1,2,2,4,4-Pentaphenyl-3-azabut-3-en-1-one (7).**—The imine (9) (1.53 g, 0.0044 mol) was treated with NaH (0.925 g, 80%) in HMPTA-THF (60 ml). The mixture was then treated with benzoyl chloride (3.09 g, 0.022 mol). After work-up the crude product was crystallized to afford *enone* (7) (1.27 g, 64%), m.p. 158–160 °C; δ<sub>H</sub> (CDCl<sub>3</sub>) 6.13–7.83 (m, ArH); δ<sub>C</sub> (CDCl<sub>3</sub>) 197.0 (C=O), 170.46 (C=N), 146.19, 135.81, 132.3–124.52 (m, aromatic), and 77.10 (C-2); ν<sub>max</sub> (KBr) 1 690, 1 675 (C=O), and 1 615 cm<sup>-1</sup> (C=N); λ<sub>max</sub> (EtOH) 222 (13 100) and 252 nm (13 200) (Found: C, 87.5; H, 5.5; N, 3.1. C<sub>33</sub>H<sub>25</sub>NO requires C, 87.80; H, 5.5; N, 3.1%).

**2,2-Bis-(*p*-chlorophenyl)-1,4,4-triphenyl-3-azabut-3-en-1-one (8).**—The imine (10) (2.84 g, 0.0068 mol) was treated with NaH (1.36 g, 0.034 mol; 80%) in HMPTA-THF (60 ml). The resultant solution was treated with benzoyl chloride (4.77 g, 0.034 mol). After conventional work-up the crude product was crystallized from ethanol to afford *enone* (8) (2.35 g, 66%), m.p. 220–221 °C; δ<sub>H</sub> (CDCl<sub>3</sub>) 6.13–7.70 (m, ArH); δ<sub>C</sub> (CDCl<sub>3</sub>) 196.84 (C=O), 169.68 (C=N), 144.37, 141.29, 136.75, 135.04, 127.23–132.62 (aryl), and 77.36 (C-2); ν<sub>max</sub> (KBr) 1 680 (C=O) and 1 605 cm<sup>-1</sup> (C=N); λ<sub>max</sub> (EtOH) 207 (49 000), 235 (23 100) and 251 nm (20 200); *m/z* 519 (*M*<sup>+</sup>), 414 (100%), 241 (10), 199 (22), and 165

(27) (Found: C, 75.9; H, 4.5; N, 2.4; Cl, 13.7.  $C_{33}H_{23}Cl_2NO$  requires C, 76.20; H, 4.40; N, 2.70; Cl, 13.70%).

**General Procedure for Irradiation of Enones (7) and (8).**—The photolyses were carried out using an immersion well apparatus in which the solutions of the compound (300 mg) in *t*-butyl alcohol (380 ml) were flushed with nitrogen prior to and during the irradiations. The solutions were irradiated through a Pyrex filter using a 400 watt Hg arc lamp for about 1 h. The solvent was then removed under reduced pressure and the crude photolysates were chromatographed on a column of silica gel with hexane—ether as the eluant.

**Irradiation of enone (7).** The solution was irradiated for 35 min.  $^1H$  N.m.r. spectroscopy of the crude product showed the presence of two compounds (ratio 1:1) in addition to unchanged starting material. This mixture was separated by column chromatography with hexane—ether (98:2) as eluant to give the following products: recovered starting material (100 mg); benzophenone (trace); *keto imine* (14) (60 mg, 20%, after crystallization), m.p. 114–115 °C; (from EtOH);  $\nu_{max}$  (KBr) 1 660 (C=O) and 1 615  $cm^{-1}$  (C=N);  $\lambda_{max}$  (EtOH) 210 (43 589) and 249 nm (25 641);  $\delta_H$  ( $CDCl_3$ ) 6.9–7.7 (24 H, m, ArH) and 5.53 (1 H, s, benzhydryl) (Found: C, 87.6; H, 5.4; N, 3.2.  $C_{33}H_{25}NO$  requires C, 87.80; H, 5.50; N, 3.10%). The structure of this *keto imine* was determined<sup>13</sup> using an ENRAF-Nonius CAD-4 diffractometer with a clear, colourless prismatic crystal. The results obtained were  $M_r = 451.6$ , monoclinic,  $P2_1/c$ ,  $a = 18.745(5)$ ,  $b = 9.9257(4)$ ,  $c = 14.261(5)$  Å,  $\beta = 91.64(2)^\circ$ ,  $V = 2 473(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.21$  mg  $m^{-3}$ ,  $\mu(Mo-K\alpha)$ ,  $\lambda = 0.716 09$  Å =  $0.067$  mm<sup>-1</sup>,  $F(000) = 952$ ,  $T = 295$  K, final  $R = 0.043$  and  $R_w = 0.047$  for 2 132 observed reflexions. The bond lengths and angles were normal; *keto imine* (15) (70 mg, 23%, after crystallization), m.p. 100 °C (decomp.) (from EtOH);  $\nu_{max}$  (KBr) 1 655 (C=O) and 1 615  $cm^{-1}$  (C=N);  $\lambda_{max}$  (EtOH) 208 (39 100) and 248 nm (24 600);  $m/z$  451 ( $M^+$ ), 346 (100%), 269 (14), 165 (45), 105 (5), and 77 (8);  $\delta_H$  ( $CDCl_3$ ) 6.9–7.7 (24 H, m, ArH) and 5.41 (1 H, s, benzhydryl) (Found: C, 87.8; H, 5.2; N, 2.9.  $C_{33}H_{25}NO$  requires C, 87.80; H, 5.50; N, 3.10%); and 1,2-dibenzoylbenzene (trace), formed by the hydrolysis of *keto imine* (14) on the silica gel.

**Irradiation of enone (8).** The solution was irradiated for 50 min. The crude photolysate was separated by flash column chromatography on silica gel (3 cm × 20 cm) with ether—hexane (2:98) as eluant. The following products were obtained: *keto imine* (16) (50 mg, 17%, after crystallization), m.p. 137–138 °C (from EtOH);  $\nu_{max}$  (KBr) 1 660 (C=O) and 1 620  $cm^{-1}$  (C=N);  $\lambda_{max}$  ( $CH_2Cl_2$ ) 231 (54 198) and 251 nm (46 759);  $\delta_H$  ( $CDCl_3$ ) 6.66–7.73 (22 H, m, ArH) and 5.41 (1 H, s, benzhydryl);  $m/z$  519 ( $M$ ), 270 (100%), 235 (42), 199 (10), and 165 (30) (Found: C, 76.3; H, 4.6; N, 2.5; Cl, 13.9.  $C_{33}H_{23}Cl_2NO$  requires C, 76.20; H, 4.40; N, 2.70; Cl, 13.70%); *keto imine* (17) (50 mg, 17%, after crystallization), m.p. 172–174 °C (from EtOH);  $\nu_{max}$  (KBr) 1 660 (C=O) and 1 620  $cm^{-1}$  (C=N);  $\lambda_{max}$  ( $CH_2Cl_2$ ) 256 nm (49 300);  $\delta_H$  ( $CDCl_3$ ) 6.55–8.06 (22 H, m, ArH) and 5.33 (1 H, s, benzhydryl);  $m/z$  519 ( $M$ ), 414 (100%), 269 (12), 199 (32), 165 (37), 105 (12), and 77 (13) (Found: C, 76.0; H, 4.4; N, 3.0; Cl, 14.0.  $C_{33}H_{23}Cl_2NO$  requires C, 76.20; H, 4.40; N, 2.70; Cl, 13.70%); recovered starting material (100 mg); *o*-dibenzoylbenzene (20 mg); *p,p'*-dichlorobenzophenone (20 mg); and benzophenone (40 mg).

**General Procedure for Hydrolysis.**—Hydrolyses were carried out on 10–20 mg samples of each product in THF solution (10 ml) to which sulphuric acid (1 ml; 50%) was added. The reaction mixture was stirred for 3 h at ambient temperature. The crude mixture was extracted into ether and the extract was washed successively with aqueous  $NaHCO_3$  and then water (until neutral), and was then dried ( $Na_2CO_3$ ). The mixture was

filtered and the solvent was removed under reduced pressure. The products obtained in this manner were identified by comparison with authentic samples.

**Hydrolysis of (8).** Hydrolysis of *keto imine* (8) (20 mg, 0.038 mmol) gave a yellow oil which slowly crystallized and was identified as benzophenone.

**Hydrolysis of (16).** Hydrolysis of *keto imine* (16) (10 mg, 0.019 mmol) afforded an oil which was identified as *o*-dibenzoylbenzene.

**Hydrolysis of (17).** Hydrolysis of *keto imine* (17) (10 mg, 0.019 mmol) for 4 h gave a mixture of compounds shown to be *p,p'*-dichlorobenzophenone and unchanged compound (17).

**Irradiation of 2,2-Bis-(*p*-chlorophenyl)-1,4,4-triphenyl-3-azabut-3-en-1-one Perchlorate (18).**—A solution containing the azaenone (8) (300 mg, 0.57 mmol) and perchloric acid (425 mg, 2.54 mmol; 60%) in benzene (380 ml) was purged with nitrogen for 2 h and then irradiated for 1 h in an immersion well apparatus with a 400 watt Hg arc lamp in conjunction with a Pyrex filter. The photolysate was neutralized with  $Na_2CO_3$  (270 mg, 2.54 mmol) and the solution was then concentrated under reduced pressure. The resultant oil was dissolved in  $CHCl_3$ , and the resulting solution was washed with saturated aqueous  $NaHCO_3$ , dried ( $Na_2SO_4$ ), filtered, and concentrated under reduced pressure. The residue was separated by flash chromatography on silica gel (3 cm × 15 cm) with ether—hexane (4:96) as eluant and gave benzophenone (40 mg, 40%) and *p,p'*-dichlorobenzophenone (60 mg, 41%), which were both identified by comparison with authentic samples.

**Protonation of Azaenone (8).**—Perchloric acid (17 mg, 0.1 mmol; 60%) was added to a solution of azaenone (8) (10 mg, 0.019 mmol) in methylene dichloride (25 ml). The solution was stirred for 15 min at room temperature by which time a red colour had developed. The u.v.—visible spectrum showed that a new absorption had developed at 293 nm (20 163). This solution was kept for a further 1 h and was then neutralized by the addition of aqueous  $Na_2CO_3$ . After conventional work-up the starting enone (8) was recovered quantitatively.

**Irradiation of Perchlorate (18) followed by Diazotization.**—The azaenone (8) (400 mg, 0.77 mmol) was treated with perchloric acid (644 mg, 3.85 mmol; 60%) and the mixture, in methylene dichloride (380 ml), was irradiated for 20 min. Some of the solvent (300 ml) was removed under reduced pressure and the resultant solution was hydrolysed by the addition of sulphuric acid (50 ml; 50%). The mixture was stirred at ambient temperatures for 1 h. The hydrolysed solution was then cooled in an ice-bath to 0 °C and then conc. aqueous  $NaNO_2$  (100 mg, 1.44 mmol) was added. The solution was stirred for 1 h during which time the temperature was allowed to rise to ambient. The solution was then heated for 20 min, neutralized, and the organic layer was washed with aqueous  $Na_2CO_3$ , dried ( $MgSO_4$ ), and filtered, and the solvent was removed under reduced pressure. The resultant oil was flash chromatographed on silica gel (3 cm × 20 cm) with ether—hexane (4:96) as eluant. This gave benzophenone (70 mg, 50%), *p,p'*-dichlorobenzophenone (60 mg, 32%), and a mixture of alcohols (190 mg, 76%, in the ratio 97:3).

The aforementioned mixture of alcohols (90 mg) was dissolved in methylene dichloride (25 ml), and lead tetra-acetate (124 mg, 0.279 mmol) was added in small portions during 30 min. After the completion of the addition the solution was stirred for a further 1 h at room temperature. The precipitated lead salts were removed by filtration and the filtrate was washed with saturated aqueous  $NaHCO_3$ , dried ( $MgSO_4$ ), filtered, and evaporated to dryness under reduced pressure. The resultant oil was flash chromatographed on silica gel (3 cm × 20 cm) with

ether-hexane (3:97) as eluant. This gave the following: *p,p'*-dichlorobenzophenone (20 mg, 64%), benzoic acid (10 mg, 29%), and benzophenone (10 mg, 35%), all of which were identified by comparison with authentic samples.

**Irradiation of Azaenone (7) with Cyclo-octadiene.**—The azaenone (7) (450 mg, 1.0 mmol) and cyclo-octadiene (22.6 g, 0.21 mmol) were dissolved in *t*-butyl alcohol (374 ml). This solution was purged with nitrogen and then irradiated for 35 min. The solvent was removed under reduced pressure and the resultant crude material was chromatographed to afford the azaenone (7) (110 mg, 24%), keto imine (14) (65 mg, 22%), keto imine (15) (80 mg, 26%), *o*-dibenzoylbenzene (16 mg, 11%), and benzophenone (20 mg, 22%).

**Acetophenone-sensitized Irradiation of Azaenone (7).**—The azaenone (7) (300 mg, 0.67 mmol) and acetophenone (11.5 g, 95.76 mmol) were dissolved in *t*-butyl alcohol (380 ml) and the solution was purged with nitrogen for 30 min prior to irradiation for 35 min through a Pyrex filter. The solvent was removed under reduced pressure and the acetophenone was removed by distillation. The crude material was separated by chromatography on silica gel to afford unchanged azaenone (7) (110 mg, 36%), keto imine (14) (70 mg, 23%), keto imine (15) (80 mg, 26%), and traces of both *o*-dibenzoylbenzene and benzophenone.

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