

Conformation Dependent Photochemistry of Dienes. Substituent Effects on the Photochemical Reactions of some 4-Acyloxy-2-azabuta-1,3-dienes

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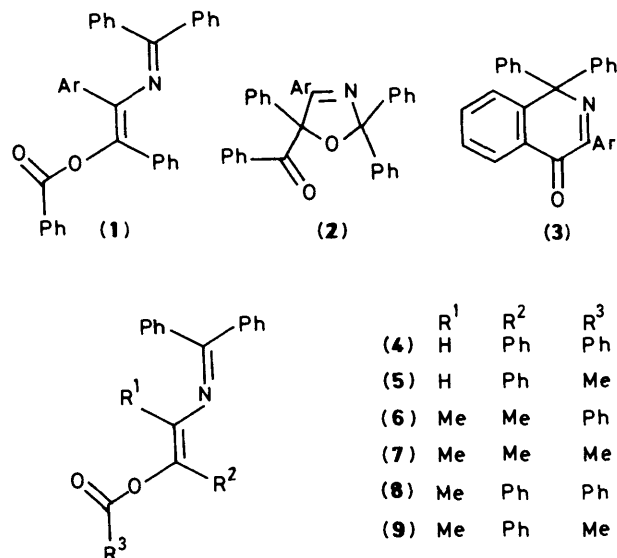
The photochemical behaviour of 4-acyloxy-2-azabuta-1,3-dienes is dependent upon the nature of the 3- and 4-substituents of the diene and also, in some cases, on the type of the 4-acyloxy group. Thus when the 3-position is unsubstituted and the 4-substituent is a phenyl the dienes undergo *trans-cis*-isomerization on direct irradiation independent of the type of 4-acyloxy group. When the 3-substituent is a methyl and when there is a 4-methyl or 4-phenyl group then the benzoates undergo 1,3-benzoyl migration on direct or diene quenched irradiation. The acetates (7) and (9) in this series are unreactive on direct irradiation but compound (7) undergoes *trans-cis*-isomerization on sensitized irradiation. The difference in behaviour of the dienes is associated with the twist around the C(3)-N bond of the diene skeleton.

Study of the photochemical behaviour of acyclic dienes has been somewhat neglected even although there has been a rapid growth in our understanding of photochemistry in general. Most of the studies on dienes have examined the photoreactions of simple dienes¹ or dienes with few substituents² in aprotic and protic media. The azadiene system has also been neglected although we have contributed to this field of study in our observations of the facile conversion of the highly substituted azadienes (1) into the 2,5-dihydro-oxazoles (2)³ and the synthesis of the isoquinolinones (3)⁴ by the photocyclization of protonated derivatives of the azadienes (1). The present report deals with aspects of the conformational-dependent photochemistry of variously substituted azadienes (4)–(9) where the outcome is controlled by the substitution pattern on the azadiene skeleton.

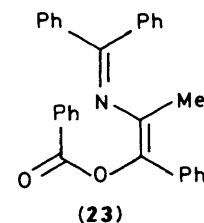
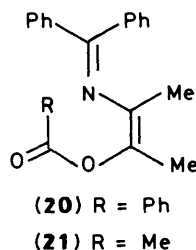
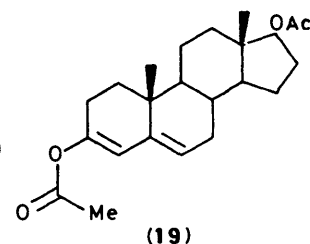
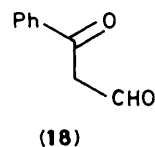
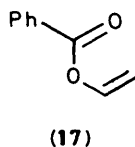
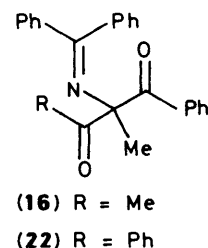
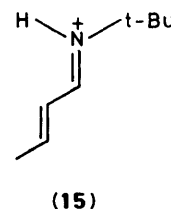
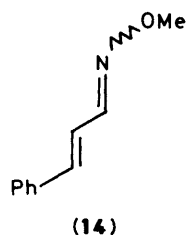
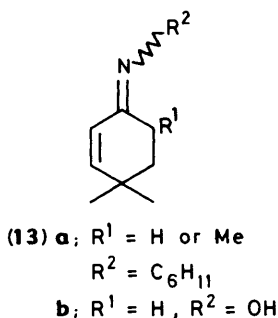
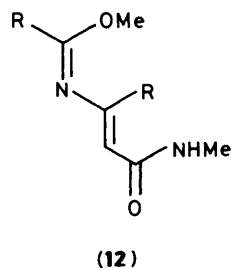
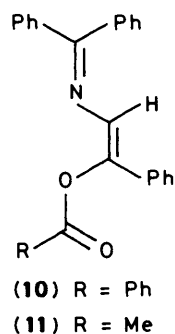
The synthesis of the azadienes (4)–(9) has been reported previously.⁵ All the dienes were obtained as single isomers and in line with our previous reasoning^{6,7} we propose that this is the *trans*-isomer illustrated in structures (4)–(9).

coefficient ($\epsilon = ca. 20\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) absorption in the 350 nm region. The second group, compounds (6)–(9), also shows an absorption in this region but in these cases the extinction coefficient is lower ($\epsilon = ca. 1\,300\text{--}2\,300$). The reason for this change in the $\pi\text{-}\pi^*$ band of the azadienes becomes obvious when molecular models of the dienes are constructed. It can be seen from these that the azadienes (4) and (5) are flat with full conjugation between the imine and the enol ester entities. When there is a 3-methyl substituent, (6)–(9), however, the azadiene skeleton can no longer be flat and so the overlap between the imine and the enol ester entities is decreased because of twisting around the C(3)-N bond. As a result of this feature the low-energy absorption is weaker and the u.v. absorption in the 250–300 nm region becomes important. Furthermore, with the 4-benzoyloxy compounds [azadienes (6) and (8)], the ester group has a substantial absorption above 280 nm. Since all the azadienes (4)–(9) have an absorption above 280 nm they were irradiated under identical conditions using Pyrex-filtered light from a 400 W Hg arc lamp in a conventional immersion well apparatus.

Direct or cyclo-octa-1,3-diene (COD)-quenched irradiation of the dienes (4) and (5) gave one photoproduct in each case which was separated from unchanged starting material by column chromatography. The photoproducts were shown by mass spectrometry to be isomeric with starting material and on the basis of this and ¹H n.m.r. spectroscopy they were identified as the *cis*-isomers (10) and (11). The ¹H n.m.r. spectra showed that the resonances for the vinylic hydrogen moves in both cases to higher field due to the shielding effect of the phenyl on C-4. The acetyloxy methyl group of diene (11) also exhibits a small upfield shift from its position in the corresponding *trans*-isomer (5). The behaviour exhibited by these two dienes (4) and (5) is much in line with that reported for other related systems. There are few direct comparisons available due to the paucity of information available on 2-azadienes.⁸ Takahashi *et al.*⁹ have reported *trans-cis*-isomerization of the azadienes (12) obtained from ring opening of Dewar pyrimides with methanol. In other closely related systems Margaretha¹⁰ has reported that the 1-azadienes (13a) undergo *E/Z* isomerization on $n\text{-}\pi^*$ excitation. Similar behaviour is, of course, typical for the photoisomerization of many substituted oximes such as (13b)¹¹ and (14).¹² Childs and Dickie¹³ have also described the photoisomerization of the protonated Schiff base (15) which in addition to isomerization around the C=N system also shows isomerization of the C=C moiety.



The yellow azadienes (4)–(9) can be divided into two distinct categories based upon their u.v. characteristics. The first group, azadienes (4) and (5), shows a low-energy, high extinction



The direct or COD-quenched irradiation of the diene (6) gave a single colourless photoproduct in low yield (20%) as well as recovered starting material. Again mass spectrometry showed that the photoproduct was isomeric with starting material. However, the i.r. spectrum indicates that the product has two carbonyl groups (1 715 and 1 695 cm⁻¹) replacing the single ester carbonyl absorption (1 730 cm⁻¹) of the starting material.¹⁴ Furthermore, the ¹H n.m.r. spectrum of the product shows two methyl singlets, one as part of an acetyl function (δ 2.76) and the other on a saturated carbon (δ 1.56).¹⁵ The starting diene (6) also shows two methyl singlets in the ¹H n.m.r. spectrum but these appear at δ 1.51 and 1.93. On this evidence the structure of the photoproduct was assigned as the 1,3-benzoyl migrated compound (16). The ¹³C n.m.r. spectrum of (16) is in complete agreement with this assignment. 1,3-Benzoyl migrations are common in enol esters and are the result of excitation of the benzoyl ester entity.¹⁶ Thus in the simple benzoate (17), irradiation yields the 3-oxoaldehyde (18) in poor yield due to the light-absorbing properties of the enol form.¹⁷ In our examples enolisation is impossible and yields are consequently higher. In some cases, as in the diene acetate (19),¹⁶ both the 1,3- and the 1,5-migration products are obtained. There is little evidence that the 1,5-rearrangement product is the result of a primary photochemical event. It is likely that the 1,5-diketone arises by photorearrangement of the initially formed 1,3-product. We propose that concerted 1,5-migrations are unlikely to occur in our examples due to the deconjugation of the imine from the ester by the twist around the C(3)-N bond. Furthermore, the likelihood of the initial 1,3-diketone undergoing further photoreaction is small since the unconverted diene (6) will act as a light filter and minimize the chance of excitation of the diketone. The direct irradiation of the acetate (7) fails to yield a photoproduct in accord with the postulate that the principal absorbing moiety in diene (6) is the benzoyl function. In contrast acetophenone-sensitized irradiation of dienes (6) and (7) brings about *trans-cis*-isomerization in each case to afford the azadienes (20) and (21) respectively.

The pair of azadienes (8) and (9) also fits into this scheme. Thus while the azadiene (9) is unreactive on direct irradiation, the azadiene (8) is converted on direct or COD-quenched irradiation into the diketone (22) analogous to the diketone (16). Again the spectroscopic evidence and analytical data are in complete agreement with the proposed structure. The diene (8) is also reactive on acetophenone-sensitized irradiation and is converted into the *cis*-isomer (23). This behaviour is identical

with that of the diene (6). On sensitized irradiation the diene (9) fails to yield identifiable products.

From the foregoing it is clear that the twist around the C(3)-N bond has a considerable influence on the outcome of the irradiations. The X-ray structure determination of the azadiene (4) has shown it to be flat with full conjugation between the imine and the alkene moiety.¹⁸ With full conjugation of the diene the absorption above 280 nm is dominated by the π - π^* absorption of the diene and, not surprisingly, *trans-cis*-isomerization is the sole photochemical event as shown by dienes (4) and (5). The extreme situation, *i.e.* an angle of twist of 40°, has been determined in the crystal by Florencio *et al.*¹⁹ and is observed in the dienes (1), the photochemistry of which has already been described by us.³ The dienes (6) and (8) are presumed to be intermediate with an angle of twist around the C(3)-N bond of between 0 and 40°. As a result of this twist from planarity these dienes (6) and (8) have a reduced absorption at *ca.* 350 nm and the absorption of the benzoyl ester group tailing above 280 nm becomes the active chromophore. This excitation brings about the 1,3-benzoyl migration.

As far as we are aware this is the first observation of conformation-dependent diene photochemistry. The dienes described by us have the additional feature of the heteroatom. In other systems, namely the heavily substituted dienes (1),³ the lone pair on nitrogen does appear to influence the outcome of the reaction. In the dienes (1) the twist on the C(3)-N bond is such that the lone pair on the nitrogen is in a position to overlap with the enol ester moiety. This is quite different from the present series of dienes (4)-(9) where the twist, where it does occur, *i.e.* dienes (5)-(9), slightly decreases the level of conjugation between the imine and the enol ester group. The twist around the C(3)-N bond is not great enough to bring about overlap between the nitrogen lone pair and the enol ester group. Thus, in the present examples electron transfer is not

involved and the nitrogen atom does not appear to influence the outcome of the reactions.

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and are reported in wave numbers. U.v. spectra were recorded on a Perkin-Elmer I 24 spectrophotometer. ^1H and ^{13}C N.m.r. spectra were recorded on Varian T60 and Varian FT-80A spectrometers respectively. Samples were dissolved in CDCl_3 and chemical shifts are expressed in p.p.m. downfield from internal SiMe_4 . The mass spectra were recorded on a Varian MAT-711 spectrometer. Sodium hydride used was supplied by Merck, the weights quoted are those for pure NaH. Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas, Madrid.

Synthesis of Azadienes (4)–(9).—The azadienes (4)–(9) were prepared by the method described previously.⁵

General Procedure for Photolyses.—Irradiations were carried out in a conventional immersion well apparatus of 400 ml capacity using a Pyrex filtered 400 W Hg arc lamp. The diene (300 mg) was dissolved in purified methylene dichloride (380 ml). This solution was de-aerated in the apparatus by a stream of de-oxygenated nitrogen for 1 h prior to and during the irradiation. After the irradiation was complete the solvent was removed under reduced pressure and the sensitizer or quencher, if used, was removed by distillation. The residue was flash chromatographed²⁰ on silica gel (3 × 20 cm) using mixtures of ethyl acetate:hexane or benzene:hexane.

Irradiation of trans-4-Benzoyloxy-1,1,4-triphenyl-2-azabuta-1,3-diene (4).—Irradiation time: 1 h, chromatography using benzene-hexane (5:4) as eluant gave the following compounds: recovered starting azadiene (160 mg, 53%); benzophenone (trace); and *cis*-4-benzoyloxy-1,4,4-triphenyl-2-azabuta-1,3-diene (10) (60 mg, 20%) m.p. 118–120 °C as yellow crystals from ethanol; $\nu_{\text{max.}}$ (KBr) 1 730 and 1 620 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 235 (22 300) and 343 nm (19 500); δ_{H} 7.13–8.40 (20 H, m, aryl) and 7.07 (1 H, s, vinyl H); δ_{C} 166.79, 164.70, 145.88, 139.01, 135.80, 133.98, 133.23, and 124.57–130.28; m/z 403 (M^+ , 12%), 298 (34), 165 (14), 105 (100), and 77 (22) (Found: C, 83.40; H, 5.40; N, 3.20. $\text{C}_{28}\text{H}_{21}\text{NO}_2$ requires C, 83.37; H, 5.21; N, 3.47%).

Cyclo-octadiene-quenched irradiation of diene (4). The above reaction was repeated using cyclo-octadiene (3.4M) as quencher. This process gave the same spread of products as above. The *cis*-diene (10) was obtained in 23% yield.

Irradiation of trans-4-Acetyloxy-1,1,4-triphenyl-2-azabuta-1,3-diene (5).—Irradiation time: 55 min, chromatography using benzene-hexane (5:4) gave the following compounds: recovered starting azadiene (240 mg, 80%); benzophenone (trace); and *cis*-4-acetyloxy-1,4,4-triphenyl-2-azabuta-1,3-diene (11) (50 mg, 17%) as yellow crystals, m.p. 79–80 °C from ethanol; $\nu_{\text{max.}}$ (KBr) 1 748 and 1 620 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 344 (26 100) and 280 nm (16 100); m/z 341 (M^+), 282 (11), 182 (31), 105 (100), and 77 (48); δ_{H} 7.06–7.76 (15 H, m, aryl), 6.96 (1 H, s, vinyl H), and 2.33 (3 H, s, Me); δ_{C} 168.65, 167.10, 145.42, 139.21, 135.78, 133.83, 130.42, 124.42–128.98, and 20.67 (Found: C, 81.30; H, 5.70; N, 4.05. $\text{C}_{23}\text{H}_{19}\text{NO}_2$ requires C, 80.93; H, 5.57; N, 4.10%).

Cyclo-octadiene-quenched irradiation of the diene (5).—The above experiment was repeated using cyclo-octadiene (2.55M) as quencher. This gave the same spread of products. The *cis*-diene (11) was obtained in 13% yield.

Irradiation of trans-4-Benzoyloxy-3-methyl-1,1-diphenyl-2-azapenta-1,3-diene (6).—Irradiation time: 15 min, chromatography using ethyl acetate-hexane (4:96) gave the following compounds: recovered starting azadiene (230 mg, 76%) and 3-benzoyl-3-methyl-5,5-diphenyl-4-azapent-4-en-2-one (16) (60 mg, 20%), as colourless crystals m.p. 135–137 °C from ethanol; $\nu_{\text{max.}}$ (KBr) 1 715, 1 685, and 1 615 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 237 (12 700), 274 (4 500), and 280 nm (4 400); δ_{H} 6.53–7.80 (15 H, m, aryl), 2.76 (3 H, s, Me), 1.56 (3 H, s, Me); δ_{C} 210.56, 196.01, 168.67, 140.59, 136.57, 134.44, 132.62, 127.66–130.62, 80.29, 26.13, and 13.24; m/z 355 (M^+), 312 (53), 250 (87), 207 (100), 165 (80), 105 (67), and 77 (27) (Found: C, 81.05; H, 6.2; N, 3.65. $\text{C}_{24}\text{H}_{21}\text{NO}_2$ requires C, 81.12; H, 5.91; N, 3.94%).

Cyclo-octadiene-quenched irradiation of the diene (6). Irradiation time: 15 min, cyclo-octadiene used 100 ml (807 mmol). This procedure afforded the 1,3-diketone (16) in 20% yield.

Acetophenone-sensitized irradiation of the diene (6). Irradiation time: 15 min, acetophenone used 45 ml (383 mmol), chromatography using ethyl acetate-hexane (4:96) gave the following compounds: recovered starting azadiene (210 mg, 73%) and *cis*-4-benzoyloxy-3-methyl-1,1-diphenyl-2-azapenta-1,3-diene (20) (90 mg, 30%) as a yellow oil which decomposed on attempted distillation; $\nu_{\text{max.}}$ (liq. film) 1 730 and 1 620 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 239 (15 900) and 348 nm (820); δ_{H} (CCl_4) 6.23–8.03 (15 H, m, aryl), 1.93 (3 H, s, Me), and 1.65 (3 H, s, Me); δ_{C} 167.38, 164.21, 139.23, 136.80, 133.19, 132.60, 127.22–131.97, 16.80, and 15.47; m/z 355 (M^+), 250 (77), 207 (100), 193 (5), 165 (58), 149 (17), 105 (70), 91 (5), and 77 (33). This diene was very unstable and gave unreliable microanalytical data.

Irradiation of trans-4-Acetyloxy-3-methyl-1,1-diphenyl-2-azapenta-1,3-diene (7).—This diene was irradiated for a variety of periods from 1–6 h. Each of the irradiations afforded only unchanged starting material.

Acetophenone-sensitized irradiation of the diene (7). Irradiation time: 4 h, acetophenone used 22 ml (188 mmol), chromatography using ethyl acetate-hexane (5:95) gave the following compounds: recovered azadiene (7) (230 mg, 77%) and *cis*-4-acetyloxy-3-methyl-1,1-diphenyl-2-azapenta-1,3-diene (21) (20 mg, 7%) as a yellow oil; $\nu_{\text{max.}}$ (liq. film) 1 755 and 1 620 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 258 (18 300) and 349 nm (770); δ_{H} (CCl_4) 6.93–7.76 (10 H, m, aryl), 1.93 (3 H, s, Me), 1.8 (3 H, s, Me), 1.53 (3 H, s, Me); δ_{C} 168.84, 168.79, 139.39, 137.13, 130.21, 127.82–128.85, 20.69, 16.46, and 15.42; m/z 293 (M^+ , 12%), 250 (37), 234 (83), 207 (100), 193 (17), 174 (17), 165 (75), 148 (12), and 77 (29). This product decomposed on attempted distillation. It was also prone to hydrolysis and gave unreliable analytical data.

Irradiation of trans-4-Benzoyloxy-3-methyl-1,1,4-triphenyl-2-azabuta-1,3-diene (8).—Irradiation time: 30 min, chromatography using ethyl acetate-hexane (3:97) gave the following compounds: recovered starting azadiene (218 mg, 73%) and 2-benzoyl-2-methyl-1,4,4-triphenyl-3-azabut-3-en-1-one (22) (70 mg, 22%) as a colourless solid, m.p. 188–190 °C from ethanol; $\nu_{\text{max.}}$ (KBr) 1 700, 1 680, and 1 640 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 248 nm (24 800); δ_{H} 6.6–8.2 (20 H, m, aryl), 1.85 (3 H, s, Me); δ_{C} 198.56, 155.23, 140.37, 136.41, 134.70, 132.41, 130.62, 125.44–130.36, 79.58, and 25.08; m/z 417 (M^+ , 4%), 312 (100), 207 (35), 165 (54), 105 (89), 77 (25), and 51 (6) (Found: C, 83.55; H, 5.45; N, 3.05. $\text{C}_{29}\text{H}_{23}\text{NO}_2$ requires C, 83.45; H, 5.51; N, 3.35%).

Acetophenone-sensitized irradiation of the diene (8). Irradiation time: 30 min, acetophenone used 47 ml (392 mmol), chromatography using ethyl acetate-hexane (2.5:97.5) gave the following compounds: recovered starting azadiene (90 mg, 30%); benzophenone (10 mg); and *cis*-4-benzoyloxy-3-methyl-1,1,4-triphenylbuta-1,3-diene (23) (170 mg, 57%) as a yellow unstable oil; $\nu_{\text{max.}}$ 1 730 and 1 620 cm^{-1} ; $\lambda_{\text{max.}}$ (CH_2Cl_2) 233 (40 500) and 260 nm (29 000); δ_{H} 1.83 (3 H, s, Me), 6.36–8.23

(20 H, m, aryl); δ_c 167.66, 164.29, 138.89, 138.84, 136.63, 135.17, 132.72—125.79, and 17.80; m/z 417 (M^+ , 13%), 312 (60), 207 (20), 165 (36), 105 (100), and 77 (36). (This compound was unstable and gave unreliable microanalytical data.)

Irradiation of 4-Acetyloxy-3-methyl-1,1,4-triphenyl-2-azabuta-1,3-diene (9).—Irradiation time: 2 h, chromatography using ethyl acetate–hexane (3:97) gave the following compounds: recovered azadiene (100 mg, 33%); benzophenone (40 mg); and several minor unidentified products.

Acetophenone-sensitized irradiation of diene (9). Irradiation time: 2 h, acetophenone used: 36 ml (308 mmol), chromatography using ethyl acetate–hexane (3:97) gave the following compounds: recovered azadiene (100 mg, 33%); benzophenone (20 mg); and several unidentified products.

Acknowledgements

We gratefully acknowledge financial assistance from the British Council and the Comision Asesora de Investigacion Cientifica y Tecnica. (Grant PB 85-0040.)

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Received 24th November 1986; Paper 6/2247