Photochemical Reaction of 2,4,4,6-Tetrasubstituted 1,4-Dihydropyridines in Deaerated Media: Photocolouration and Photorearrangement accompanying Dehydrogenation

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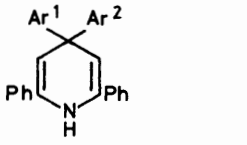
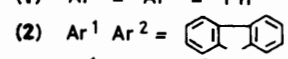
The photochemical colour change of 2,2,4,6-tetraphenyl-1,4-dihydropyridine (**1**) in deaerated solutions from colourless to violet, which has been reported as a photochromic phenomenon, was found to be an irreversible change and to give 2,3,4,6-tetraphenylpyridine (**7**) as a main product. Spiro-[2,6-diphenyl-1,4-dihydropyridine-4,9'-fluorene] (**2**), 4-*p*-bromophenyl-2,4,6-triphenyl-1,4-dihydropyridine (**3**), and 2,4,6-triphenyl-4-*p*-tolyl-1,4-dihydropyridine (**4**) also showed a similar photocolour change in deaerated solutions and gave 1,3-diphenyl-2-azatriphenylene (**8**), 3-*p*-bromophenyl-2,4,6-triphenylpyridine (**9**), and 2,3,6-triphenyl-4-*p*-tolylpyridine (**11**), respectively. These reactions proceed through di-π-methane rearrangement accompanying dehydrogenation. 4-Benzyl-2,4,6-triphenyl-1,4-dihydropyridine (**5**) and 4-benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine (**6**) showed very faint colouration on irradiation. Compound (**5**) gave 2,4,6-triphenylpyridine (**12**) produced by elimination of the benzyl group and a hydrogen. For a compound (**6**) products have not been isolated.

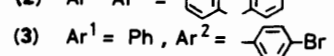
The photochemical colour change of 2,4,4,6-tetraphenyl-1,4-dihydropyridine (**1**) both in the solid state and in oxygen-free solutions has been reported as a photochromic phenomenon.[1,2] During the course of an investigation of the photochromism of (**1**) we found that the violet colour appearing upon irradiation did not fade in deaerated crystals at various temperatures and in deaerated solutions cooled in liquid nitrogen. At higher temperatures the colour of the solutions gradually faded even under irradiation, and 2,3,4,6-tetraphenylpyridine (**7**) was



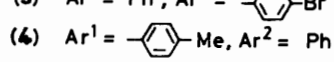
(**1**) $Ar^1 = Ar^2 = Ph$



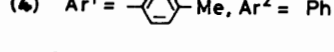
(**2**) $Ar^1\ Ar^2 =$

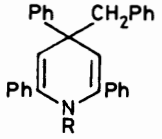


(**3**) $Ar^1 = Ph$, $Ar^2 =$



(**4**) $Ar^1 =$





(**5**) R = H

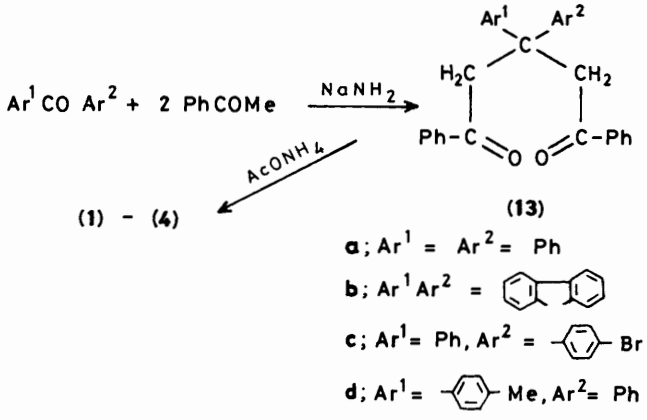
(**6**) R = Me

isolated.[3] Similar photocolouration and bleaching phenomena were observed on other dihydropyridines, spiro-[2,6-diphenyl-1,4-dihydropyridine-4,9'-fluorene] (**2**), 4-*p*-bromophenyl-2,4,6-triphenyl-1,4-dihydropyridine (**3**), 2,4,6-triphenyl-4-*p*-tolyl-1,4-dihydropyridine (**4**), 4-benzyl-2,4,6-triphenyl-1,4-dihydropyridine (**5**), and 4-benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine (**6**). This paper deals with a spectroscopic investigation of the photocoloured species and a mechanistic study of the formation of photoproducts which were isolated and identified.

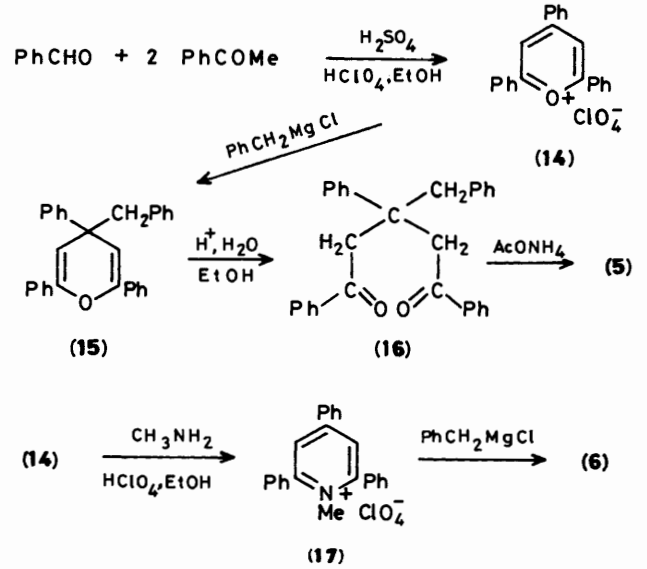
Results and Discussion

Compounds (**1**)—(**4**) were prepared by the method of Peres de Carvalho[1] as shown in Scheme 1, and compounds (**5**) and (**6**) were obtained from (**14**)[4] by the method of Dimroth,[5] as shown in Scheme 2.

Because dihydropyridines (**1**)—(**5**) were very sensitive to oxygen especially in solution only compound (**1**) was recrystallised from benzene or acetone under nitrogen, and the others were used without recrystallisation to avoid oxygenation during manipulation. Compound (**6**) was not sensitive to oxygen.



Scheme 1.



Scheme 2.

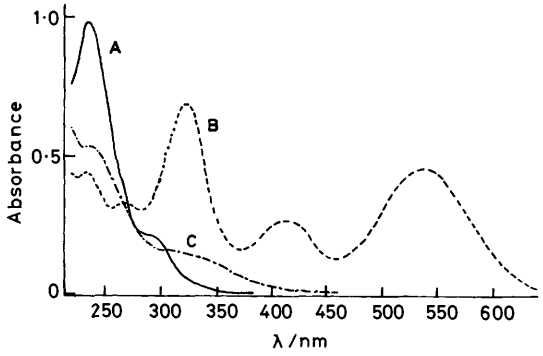


Figure 1. Variation of absorption spectra of compound (**1**) (2.7×10^{-4} mol dm^{-3}) in THF on irradiation at 20 °C: A, before irradiation; B, after 3 min irradiation; C, after 1 h irradiation, the violet colour was discharged

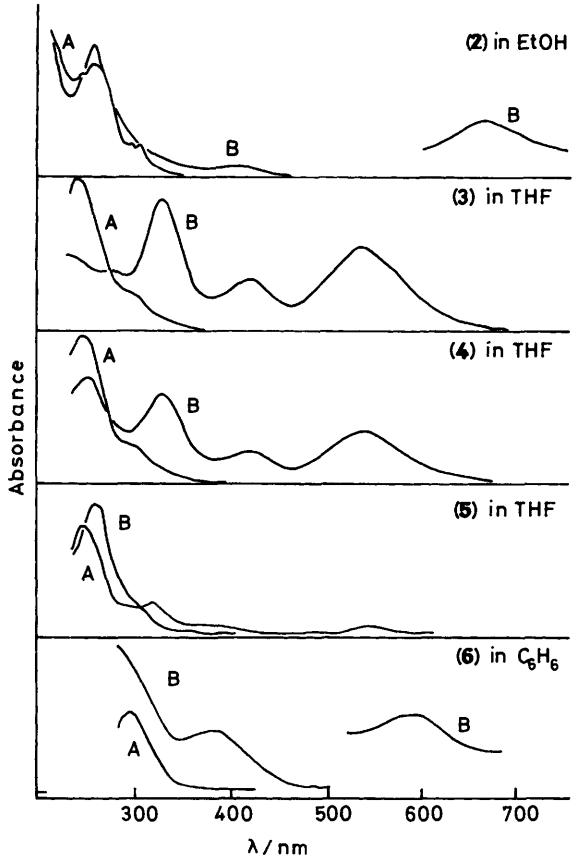


Figure 2. Absorption spectra of compounds (**2**)—(**6**): A, before and B, after irradiation in deaerated solutions at 20 °C

When deaerated solutions of (**1**) in THF, 2-methyltetrahydrofuran (MTHF), dioxane, acetone, benzene, and toluene were irradiated with u.v. light, the solutions became violet in colour. The coloured substance was stable at 77 K even in the dark, but at higher temperatures where solutions are fluid the colour gradually faded. The stability of the coloured substance at room temperature varied according to the kind of solvents. Cyclic ethers, THF, MTHF, and dioxane, were the best and acetone was moderate, but in aromatic hydrocarbons, benzene and toluene, the coloured substance was unstable, and in chloroform colouration did not occur. After repeated irradiation or continued irradiation, the solutions became

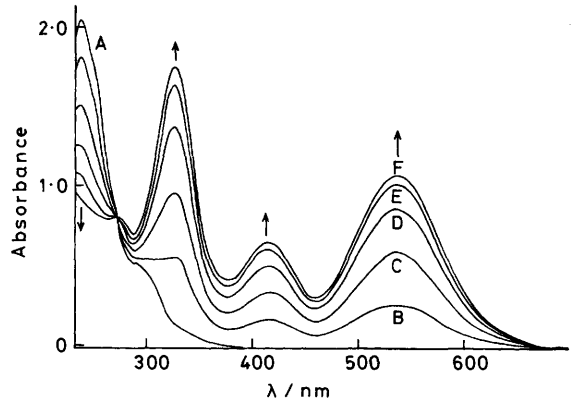


Figure 3. Variation of absorption spectra of compound (**3**) (4.67×10^{-5} mol dm^{-3}) in THF on irradiation at 20 °C: A, before irradiation; B, after 0.5 min irradiation; C, after 1 min irradiation; D, after 2 min irradiation; E, after 3 min irradiation; F, after 6 min irradiation

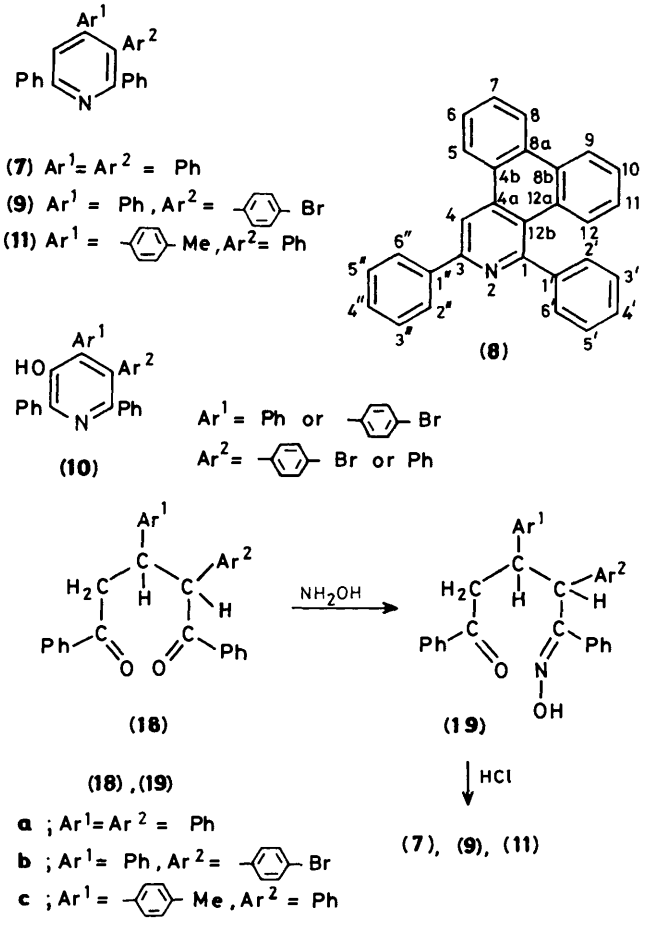
yellow. Variation of the absorption spectra of (**1**) measured in deaerated THF before and after irradiation and also after bleaching of the violet colour are shown in Figure 1. These spectral changes revealed that the fading of the colour did not correspond to a reverse change from a violet substance to colourless starting material (**1**). Dihydropyridines (**2**)—(**6**) also showed an irreversible photocolouration in deaerated solutions. Absorption spectra before and after irradiation are shown in Figure 2.

On the other hand, when deaerated solid solutions of compounds (**1**)—(**6**), which were obtained by cooling in liquid nitrogen in the dark, were irradiated, no colouration occurred.

As shown in Figure 3 variation of the absorption spectra of compound (**3**) obtained after repeated irradiation, which was accompanied by the photocolouration, showed that the intensity of the absorption due to the coloured species reached a maximum indicating an isosbestic point at 272 nm. This observation suggests that the coloured species is produced directly from the starting material on irradiation. On further irradiation the last spectrum in Figure 3 decreased with bleaching of the colour, with different isosbestic points. This fact indicated that the colouration was followed by an irreversible reaction. Comparison of the i.r. and n.m.r. spectra was also attempted before and after irradiation of (**1**)—(**6**). The i.r. spectra of the coloured compounds obtained in the solid state and the n.m.r. spectra obtained in deaerated solutions did not show any appreciable change because of the low concentration of the photocoloured species. Although the structures of the coloured species are still open to question, there is more than one reaction site in the molecule leading to colouration; the colour change occurred in fluid solution and in crystals at medium temperatures but not in solid solutions and crystals at liquid nitrogen temperature. The following observations suggested that the coloured products are not directly related to radical species. Measurements of e.s.r. spectra were carried out simultaneously with the formation of coloured species, in the deaerated solid state and in MTHF solution at room temperature and 77 K, but no e.s.r. absorption was observed. A yellow solution of (**1**) resulting from bleaching of the violet colour in benzene exhibited an e.s.r. absorption at room temperature, whose intensity gradually decreased in the dark and even under irradiation. The molecular structure of (**1**) was determined by an *X*-ray method[6] to establish the relationship between the structure and photocolouration. Although colourless crystals of (**1**) showed a colour change during irradiation with *X*-rays the crystal structure was retained.

In order to identify the products formed after bleaching of the

violet colour, irradiation of solutions of compound (**1**) in benzene and THF with u.v. light was carried out at *ca.* 20 °C under nitrogen. The reaction was monitored by t.l.c. and when the starting material (**1**) was completely consumed irradiation was stopped. Although four products were detected by t.l.c., only the major one was isolated, as colourless needles. Because the spectral properties were identical with those of an authentic sample synthesized separately by the method of Schmidt[7] shown in Scheme 3, the product was identified as 2,3,4,6-tetraphenylpyridine (**7**). Although in the photolysis of dihydropyridine (**2**) under nitrogen five products were detected on t.l.c. when the starting material was consumed, only the major product (**8**) was isolated. Compound (**8**) was established to be 1,3-diphenyl-2-azatriphenylene[8] on the basis of spectral properties, elemental analysis, and the molecular ion peak in the mass spectrum. The two-dimensional ^1H–^1H shift-correlation n.m.r. spectrum of (**8**) showing the presence of a spin system consisting of the nine protons on azatriphenylene supported the structural assignment. The measurement of ^1H–^{13}C and long-range ^1H–^{13}C ($^3J_{CH}$) shift-correlation 2D n.m.r. spectra of (**8**) was also carried out and the structure of the compound was further confirmed. In the photolysis of (**3**) under nitrogen formation of a complex mixture was observed on t.l.c. and two products, a major one (**9**) and a minor one (**10**), were isolated as colourless prisms and colourless columns, respectively. Elemental analysis, the molecular ion peak in the mass spectrum, and a positive Beilstein test gave the molecular formula $C_{29}H_{20}BrN$ for the major product (**9**). The i.r., u.v., and n.m.r. spectra of (**9**) were identical with those of 3-*p*-bromophenyl-2,4,6-triphenylpyridine which was prepared separately by the method of Schmidt[7] shown in Scheme 3.



Scheme 3.

These results revealed that (**9**) was formed by the migration of the *p*-bromophenyl group. The minor product (**10**) showed an absorption at 3 540 cm^{-1} in the i.r. spectrum, and a signal at δ 5.26 exchangeable with D_2O is well as those for aromatic protons in the n.m.r. spectrum. The positive Beilstein test and the high-resolution mass spectrum gave the molecular formula $C_{29}H_{20}BrNO$ for product (**10**). Comparison of these spectral properties with those of 2,4,5,6-tetraphenyl-3-hydroxypyridine,[9] which showed an absorption at 3 525 cm^{-1} in the i.r. spectrum and a peak at δ 5.12 (s, OH) in the n.m.r. spectrum, suggested that compound (**10**) was either 5-*p*-bromophenyl-2,4,6- or 4-*p*-bromophenyl-2,5,6-triphenyl-3-hydroxypyridine, although the regiochemistry was not defined. In the photolysis of (**4**) under nitrogen nine products were observed on t.l.c. when (**4**) was consumed. Only the major product was isolated as colourless needles and identified as 2,3,6-triphenyl-4-*p*-tolylpyridine (**11**) on the basis of spectral properties and comparison with a sample synthesized separately by a similar method to that of Schmidt.[7] These products (**7**)—(**9**) and (**11**) were formed probably through the same reaction pathway involving aryl-group migration accompanying dehydrogenation.

For the photoreaction of (**5**) under nitrogen seven spots were detected on t.l.c. Only the major one was isolated, and was identified as 2,4,6-triphenylpyridine (**12**)[10] by comparison with a sample synthesized from (**14**) by the method of Dimroth.[5] For photolysis of the benzene solution of (**6**) under nitrogen a complex mixture (seven spots on t.l.c.) was obtained and the isolation and identification of the products were unsuccessful.

To reveal the reaction mechanism of the oxidative rearrangement of dihydropyridines (**1**)—(**4**) to the corresponding pyridine derivatives (**7**)—(**11**) variation of the n.m.r. spectra of the dihydropyridines with repeated irradiation in deaerated solutions was recorded. The yellow C_6D_6 solution of (**1**) obtained after bleaching of the violet colour showed a singlet peak at δ 3.11 accompanying significant decrease of the signal intensity at δ 5.25 assigned to 3- and 5-H on the dihydropyridine ring of (**1**). The intensity of the signal at δ 3.11 decreased gradually under prolonged irradiation, and after 50 h the spectrum was similar to that of compound (**7**) showing a singlet at δ 7.68 assigned to 5-H of the pyridine ring in (**7**). The time courses of n.m.r. variation of compounds (**2**) and (**3**) measured from time to time after repeated irradiations showed similar aspects to that of (**1**). Both the n.m.r. spectra of (**2**) in C_6D_6 and (**3**) in $(CD_3)_2CO$ obtained after bleaching of the colour appearing on irradiation showed a singlet at δ 2.81 and 2.83, respectively. These signals redisappeared and after *ca.* 4 h irradiation the n.m.r. spectra of (**2**) and (**3**) were similar to those of (**8**) and (**9**), respectively. The variation of the n.m.r. spectra of compound (**3**) is shown in Figure 4. In compound (**4**) the variation of the n.m.r. spectra under photolysis was complicated and many signals which are difficult to assign appeared in the range δ 1.5—3.0. This observation was in accord with the finding that many products were detected by t.l.c. and the pyridine derivative (**11**) was isolated only in 10% yield.

The n.m.r. signals at δ *ca.* 3 appeared at an early stage of irradiation of (**1**)—(**4**) suggesting the formation of 2-azabicyclo[3.1.0]hex-3-enes (**20**), which were derived probably *via* di-π-methane rearrangement of the 1,4-dihydropyridines. The formation of an intermediate containing a cyclopropyl moiety was supported by the fact that in the di-π-methane rearrangements of 4,4,5-triphenyl-2-cyclohexen-1-one and 1-methylene-4,4-diphenylcyclohex-2-ene n.m.r. signals at δ 1.7—3.4 for bicyclo products have been assigned to cyclopropyl hydrogens.[11,12] The intermediates (**20**) may be transformed into products (**7**)—(**11**) by dehydrogenation with the small amount of oxygen remaining in the reaction mixture. A proposed reaction pathway is outlined in Scheme 4. A tentative pathway for the formation of the minor product (**10**) from (**3**) involving

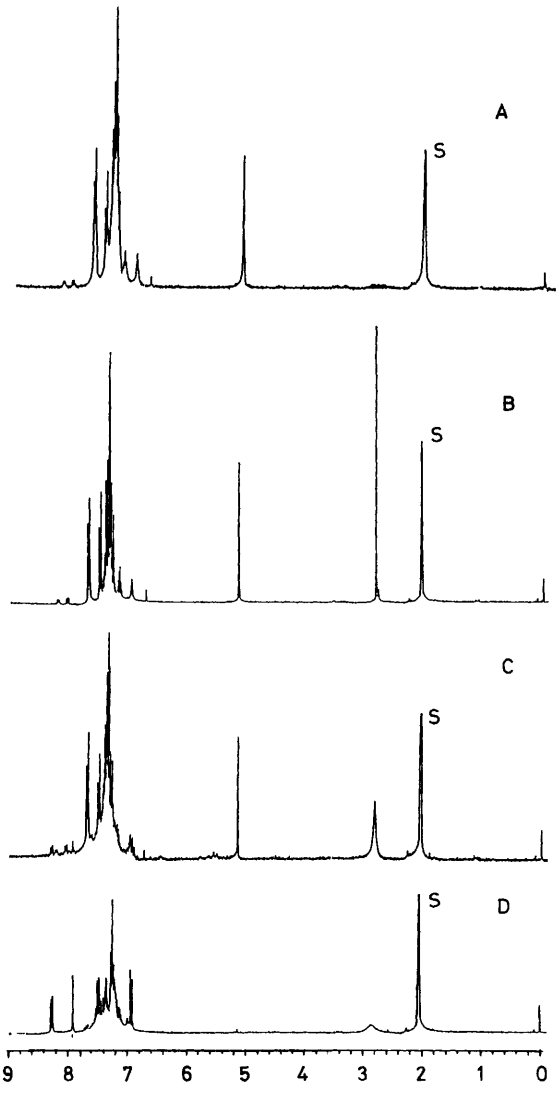
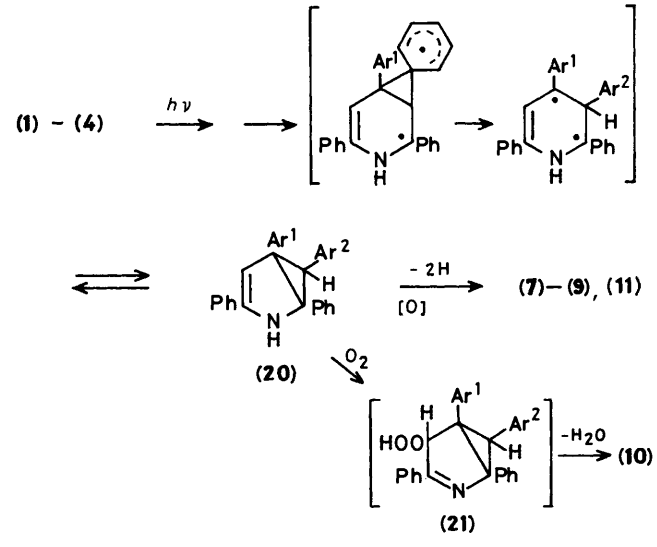


Figure 4. Variation of n.m.r. spectra of compound (**3**) in $(CD_3)_2CO$: A, before irradiation; B, after 2 min irradiation (violet colour was discharged); C, after 16 min irradiation; D, after 250 min irradiation. s = solvent



Scheme 4.

oxygenation of the bicyclic intermediate (**20**) to give a transient hydroperoxide (**21**) followed by decomposition of this to give (**10**) has been assumed as outlined in Scheme 4.

Variations of the n.m.r. spectra of compounds (**5**) and (**6**) obtained after repeated irradiations were also observed. In the n.m.r. spectrum of (**5**) in C_6D_6 obtained after 3 min irradiation, a singlet at δ 3.22 assigned to benzyl protons was missing. This easy elimination of the benzyl group corresponded to the finding that in the mass spectrum of (**5**) the molecular ion peak was not observed and there was a base peak at *m/z* 308 assignable to the fragment ion derived from the elimination of a benzyl group. In photolysis of 4-benzyl-2,4,6-triphenyl-4*H*-pyran, which has a similar structure to compound (**5**), benzyl group migration from the 4 to the 2 position has been reported to give the 2*H*-isomer.[5] However, in the photolysis of (**5**) a benzyl-migration product corresponding to the 2*H*-isomer was not detected. Because of the stability of 2,4,6-triphenylpyridine (**12**), elimination of the benzyl group was probably stimulated by the accompanying oxidative dehydrogenation. In the n.m.r. spectrum of (**6**) in C_6D_6 which was measured after the green colour was eradicated a singlet at δ 2.32 appeared. The signal redisappeared after further irradiation with a decrease of the benzyl proton signal at δ 3.1 and that of the olefinic protons at δ 5.05 and the appearance of many small signals over the range δ 2—8.5. These observations suggested the formation of an intermediate containing a cyclopropyl moiety at an early stage of the photoreaction of (**6**), and therefore it was supposed that dehydrogenation was prevented because of the presence of the NMe group; rearrangement products were not obtained.

Experimental

I.r. spectra were taken on a JASCO A-302 spectrometer as KBr disks. ^1H (270 MHz) and ^{13}C n.m.r. (67.8 MHz) spectra were recorded on a JEOL JNM-GX270 spectrometer with Me_4Si as internal standard. Measurements of u.v. spectra were carried out using a Shimadzu UV 240 spectrometer. E.s.r. spectra were recorded on a JES FE2XG spectrometer equipped with an ES-DVTI variable-temperature controller. Mass spectra were recorded on a Hitachi RMU 6MG or a JEOL DX-300 mass spectrometer. M.p.s were obtained with a Yanagimoto micro apparatus and are uncorrected.

2,4,4,6-Tetraphenyl-1,4-dihydropyridine (**1**)[1] was synthesized as stated in a previous report.[13]

9,9-*Diphenacylfluorene* (**13b**).—To an ethereal solution (20 cm^3) of fluoren-9-one (3.6 g) and acetophenone (4.8 g) was added freshly prepared sodium amide (1.2 g) in limited amounts and the mixture was stirred for *ca.* 10 h. After decomposition of the excess of sodium amide by the addition of water, the precipitated 9,9-diphenacylfluorene (**13b**) was filtered off and recrystallised from benzene–ethanol to give colourless prisms (78%), m.p. 210—212 °C; $\nu_{max.}$ 1 685 cm^{-1} (C=O).

Spiro-[2,6-*diphenyl*-1,4-*dihydropyridine*-4,9′-*fluorene*] (**2**).—To a solution of ammonium acetate (20 g) in acetic acid (20 cm^3) compound (**13b**) (0.3 g) was added and the resulting mixture was refluxed for 1.5 h under nitrogen. The mixture was cooled to room temperature and the precipitated product was immediately filtered off to give compound (**2**) as colourless needles (89%), m.p. 152—154 °C; $\nu_{max.}$ 3 400 cm^{-1} (NH); $\lambda_{max.}$(EtOH) 256, 292, and 304 nm (ε 30 000, 9 000, and 8 700 $dm^3\ mol^{-1}\ cm^{-1}$); δ($CDCl_3$) 4.62 (2 H, s, olefinic H), 5.4 (1 H, s, NH), and 7.24—8.02 (18 H, m, aromatic H); *m/z* 383 (83%, M^+), 382 (100), 306 (34), and 280 (27) (Found: C, 90.7; H, 5.6; N, 3.6. $C_{29}H_{21}N$ requires C, 90.8; H, 5.5; N, 3.65%).

3-p-*Bromophenyl*-1,3,5-*triphenylpentane*-1,5-*dione* (**13c**).—Acetophenone (4.8 g) and *p*-bromobenzophenone (5.2 g) were reacted in the presence of sodium amide (2.4 g) in ether using the method for the preparation of compound (**13b**). Compound (**13c**), colourless prisms from benzene–ethanol (37%), m.p. 127—129 °C; $\nu_{max.}$ 1 685 cm^{-1} (C=O).

4-p-*Bromophenyl*-2,4,6-*triphenyl*-1,4-*dihydropyridine* (**3**).—To a mixed solvent of acetic acid (10 cm^3) and methanol (50 cm^3) compound (**13c**) (0.6 g) and ammonium acetate (30 g) were added and the resultant mixture was refluxed for 2 h under nitrogen. After cooling to room temperature, precipitated (**3**) was filtered off as colourless prisms (80%), m.p. 154—155 °C; $\nu_{max.}$ 3 400 cm^{-1} (NH); $\lambda_{max.}$(EtOH) 236 and 287 nm (ε 33 000 and 5 800 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 5.10 (2 H, s, olefinic H), and 7.13—7.58 (19 H, m, aromatic H); *m/z* 465 (20%, M^+), 463 (23, M^+), 388 (51, $M^+ - 77$), 386 (51, $M^+ - 77$), and 308 (100) (Found: C, 74.7; H, 4.7; Br, 17.0; N, 3.1. $C_{29}H_{22}BrN$ requires C, 75.0; H, 4.8; Br, 17.2; N, 3.0%).

1,3,5-*Triphenyl*-3-p-*tolylpentane*-1,5-*dione* (**13d**).—Phenyl *p*-tolyl ketone (5.6 g) and acetophenone (6.9 g) were treated with sodium amide (2.3 g) in ether in a similar method to the preparation of compound (**13b**). After decomposition of the excess of sodium amide with water an oily brown product was obtained. Column chromatography of the crude product on activated alumina with light petroleum–ethyl acetate (12:1) as eluant gave (**13d**) as colourless needles (18%), m.p. 113—114 °C; $\nu_{max.}$ 1 685 cm^{-1} (C=O).

2,4,6-*Triphenyl*-4-p-*tolyl*-1,4-*dihydropyridine* (**4**).—To an ethanolic solution of ammonium acetate (15 g in 15 cm^3) was added compound (**13d**) (100 mg). After refluxing for 1 h under nitrogen the mixture was cooled to room temperature and the precipitate of (**4**) was filtered off as colourless prisms (73%), m.p. 162—163 °C; $\nu_{max.}$ 3 400 cm^{-1} (NH); $\lambda_{max.}$(EtOH) 240 and 288 nm (ε 24 000 and 5 600 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 2.33 (3 H, s, Me), 5.16 (2 H, s, olefinic H), and 7.05—8.04 (19 H, m, aromatic H); *m/z* 399 (38%, M^+), 322 (100), and 308 (81) (Found: C, 89.9; H, 6.2; N, 3.6. $C_{30}H_{25}N$ requires C, 90.2; H, 6.3; N, 3.5%).

2,4,6-*Triphenylpyrylium Perchlorate* (**14**).—According to the method of Wizinger *et al.*[4] compound (**14**) was prepared as yellow needles (26%), m.p. 296—299 °C (EtOH) (lit.,[4] 271 °C); $\nu_{max.}$ 1 090 cm^{-1} (ClO_4^-); $\lambda_{max.}$(EtOH) 354 and 406 nm (ε 16 900 and 12 700 dm^3 mol^{-1} cm^{-1}).

4-*Benzyl*-2,4,6-*triphenyl*-4H-*pyran* (**15**).—According to the method of Dimroth *et al.*[5] compound (**15**) was prepared from compound (**14**) and freshly prepared benzylmagnesium chloride in 48% yield. Compound (**15**), colourless prisms, m.p. 147—148 °C (EtOH) (lit.,[5] 143 °C).

3-*Benzyl*-1,3,5-*triphenylpentane*-1,5-*dione* (**16**).—According to the method of Dimroth *et al.*[5] compound (**15**) (1.0 g) was dissolved in ethanol (40 cm^3) containing hydrogen chloride and the mixture was refluxed for 10 min. Addition of water (40 cm^3) to the mixture resulted in an oily product being precipitated. Repeated washing with water followed by cooling of the oily product gave a colourless solid mass of (**16**), m.p. 89—90 °C.[5]

4-*Benzyl*-2,4,6-*triphenyl*-1,4-*dihydropyridine* (**5**).—To a solution of ammonium acetate (7 g) in a mixture of acetic acid (2.4 cm^3) and ethanol (2 cm^3) was added an ethanolic solution of compound (**16**) (0.7 g in 5 cm^3) and the resulting solution was refluxed for 2 h under nitrogen. Compound (**5**) was obtained as colourless needles in 70% yield, m.p. 126—128 °C; $\nu_{max.}$ 3 400 cm^{-1} (NH); $\lambda_{max.}$ 240 and 290 nm (ε 23 000 and 4 600 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 3.22 (2 H, s, CH_2Ph), 4.90 (2 H, s, olefinic H), and 7.10—7.55 (20 H, m, aromatic H); *m/z* 309 (98%), 308 (100), 230 (34), and 91 (51) (Found: C, 90.1; H, 6.2; N, 3.4. $C_{30}H_{25}N$ requires C, 90.2; H, 6.3; N, 3.5%).

1-*Methyl*-2,4,6-*triphenylpyridinium Perchlorate* (**17**).—According to the method of Wizinger *et al.*[4] compound (**17**) was obtained as colourless leaves by the reaction of compound (**14**) and methylamine in 90% yield, m.p. 219—220 °C (lit.,[4] 214—215 °C).

4-*Benzyl*-1-*methyl*-2,4,6-*triphenyl*-1,4-*dihydropyridine* (**6**).—According to the method of Dimroth *et al.*[5] compound (**6**) was obtained as colourless prisms by the reaction of compound (**17**) with freshly prepared benzylmagnesium chloride (72%), m.p. 146—147 °C (EtOH) (lit.,[5] 145—146 °C).

General Procedure of Photolysis for the Isolation of the Photoproducts (**7**)—(**12**).—All the reactions were performed on solutions (430 cm^3) irradiated by a 400 W high-pressure mercury lamp from inside the solution without a filter at 20 °C in a thermostatically controlled bath under nitrogen. Because of the sensitivity of compounds (**1**)—(**5**) to oxygen, purified nitrogen was flushed into the solvent for 1 h before dissolving the sample into the solvent. All the photochemical reactions were monitored by t.l.c. and when each starting material was completely consumed irradiation was stopped.

Isolation of 2,3,4,6-*Tetraphenylpyridine* (**7**).—A benzene solution of compound (**1**) (250 mg) was irradiated for 2 h. The reaction mixture was concentrated *in vacuo*. The residue was chromatographed on silica gel with benzene as eluant under nitrogen and then recrystallised from ethanol to give colourless prisms of compound (**7**) in 50% yield, m.p. 189—190 °C; $\lambda_{max.}$(EtOH) 248 and 305 nm (ε 12 000 and 4 400 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 6.70—8.19 (20 H, m, aromatic H) and 7.77 (1 H, s, 5-H on the pyridine ring).

Isolation of 1,3-*Diphenyl*-2-*azatriphenylene* (**8**).—A solution of compound (**2**) (107 mg) in ethanol was irradiated for 1.5 h. Evaporation of the solvent gave crystals, which were recrystallised from acetone to give compound (**8**) (50%), colourless needles, m.p. 236—237 °C (lit.,[7] 223—225 °C); $\lambda_{max.}$(EtOH) 276, 310, and 361 nm (ε 50 000, 21 000, and 4 400 dm^3 mol^{-1} cm^{-1}); δ_H($CDCl_3$–C_6D_6 55:45 v/v) 6.97 (1 H, ddd, $J_{11\text{-}H,12\text{-}H}$ 8.3, $J_{11\text{-}H,10\text{-}H}$ 7.0, $J_{11\text{-}H,9\text{-}H}$ 1.2 Hz, 11-H), 7.33 (5 H, m, 10-, 3′-, 4′-, 5′-, and 4″-H), 7.43 (2 H, t-like, *J ca.* 7 Hz, 3″- and 5″-H), 7.52 (1 H, m, 6-H), 7.57 (1 H, m, 7-H), 7.67 (2 H, m, 2′- and 6′-H), 7.86 (1 H, dd, $J_{12\text{-}H,11\text{-}H}$ 8.3, $J_{12\text{-}H,10\text{-}H}$ 3.0 Hz, 12-H; long-range spin coupling with 9-H), 8.26 (2 H, d, *J* 7.1 Hz, 2″- and 6″-H), 8.34 (1 H, dd, $J_{9\text{-}H,10\text{-}H}$ 7.8, $J_{9\text{-}H,11\text{-}H}$ 1.2 Hz, 9-H), 8.42 (1 H, dd, $J_{8\text{-}H,7\text{-}H}$ 7.8, $J_{8\text{-}H,6\text{-}H}$ 1.5 Hz, 8-H; long-range spin coupling with 5- and 9-H), 8.49 (1 H, dd, $J_{5\text{-}H,6\text{-}H}$ 7.8, $J_{5\text{-}H,7\text{-}H}$ 1.0 Hz, 5-H; long-range spin coupling with 4- and 8-H), and 8.57 (1 H, s, 4-H); long-range spin coupling was observed between 4-H (δ 8.70) and 2″- and 6″-H (δ 8.27) in the spectrum measured in $CDCl_3$ at 50 °C; δ_C($CDCl_3$–C_6D_6 55:45 v/v) 110.72 (4-C), 122.94 (12b-C), 123.34 (9-C), 123.47 (8-C), 124.16 (5-C), 125.78 (11-C), 127.28 (4′-C), 127.39 (2″- and 6″-C), 127.60 (6-C), 128.39 (10-C), 128.44 (4b-C), 128.82 (3′- and 5′-C), 128.88 (3″- and 5″-C), 128.98 (4″-C), 129.07 (12a-C), 129.25 (7-C), 129.67 (12-C), 129.93 (2′- and 6′-C), 131.02 (8b-C), 131.93 (8a-C), 138.57 (4a-C), 139.49 (1″-C), 144.37 (1′-C), 152.35 (3-C), and 158.38 (1-C): the following long-range spin couplings $^3J_{HC}$ were observed, 4-H/4b-C, 4-H/12b-C, 5-H/8a-C, 5-H/7-C, 8-H/6-C, 8-H/4b-C, 9-H/11-C, 9-H/12a-C, 12-H/12b-C, 2″,6″-H/4″-C, 2″,6″-H/3-C, and 3″-H/1″-C; *m/z* 381 (99%, M^+), 380 (100), and 302 (20) (Found: C, 91.4; H, 5.0; N, 3.7. $C_{29}H_{19}N$ requires C, 91.3; H, 5.0; N, 3.7%).

Isolation of 3-p-*Bromophenyl*-2,4,6-*triphenylpyridine* (**9**) *and* 5-p-*Bromophenyl*-2,4,6- *or* 4-p-*Bromophenyl*-2,5,6-*triphenyl*-3-*hydroxypyridine* (**10**).—An ethanolic solution of compound (**3**) (250 mg) was irradiated for 80 min. After the mixture was concentrated *in vacuo* a crystalline product which was found to be a mixture of two products [t.l.c. (benzene) R_F 0.69 and 0.43] separated out. The mixture was chromatographed on silica gel with benzene as eluant to give colourless prisms (major, less polar) (**9**) and colourless solid (minor, more polar) (**10**). Each product (**9**) and (**10**) was then recrystallised from acetone. Compound (**9**) (30%), m.p. 220—221 °C; $\lambda_{max.}$(EtOH) 248, 277 (sh), and 300 (sh) nm (ε 39 000, 20 000, and 13 000 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 6.77—8.18 (19 H, m, aromatic H) and 7.76 (1 H, s, 5-H on the pyridine ring); *m/z* 463 (65%, M^+), 462 (100, $M^+ + 1$), 461 (65, M^+), and 460 (98, $M^+ - 1$). Compound (**10**) (2%) had m.p. 240—242 °C; $\nu_{max.}$ 3 540 cm^{-1}; δ($CDCl_3$) 5.26 (1 H, s, OH) and 6.74—8.11 (19 H, m, aromatic H); *m/z* 479 (74%, M^+), 478 (100, $M^+ - 1$), 477 (83, M^+), and 476 (87, M^+).

Isolation of 2,3,6-*Triphenyl*-4-p-*tolylpyridine* (**11**).—A solution of compound (**4**) (129 mg) in ethanol was irradiated for 75 min. The mixture was concentrated *in vacuo* and the resultant solution was then cooled to separate out colourless crystals of (**11**) in 10% yield, m.p. 189—191 °C (EtOH); $\lambda_{max.}$(EtOH) 254 and 296 nm (ε 24 000 and 8 600 dm^3 mol^{-1} cm^{-1}); δ($CDCl_3$) 2.31 (3 H, s, Me), 6.94—8.17 (19 H, m, aromatic H), and 7.76 (1 H, s, 5-H on the pyridine ring); *m/z* 397 (56%, M^+) and 396 (100, $M^+ - 1$).

Isolation of 2,4,6-*Triphenylpyridine* (**12**).—A solution of compound (**5**) (100 mg) in ethanol was irradiated for 100 min. After evaporation of the solvent *in vacuo* colourless prisms of (**12**) separated out in 34% yield, m.p. 140—141 °C (lit.,[10] 138—139 °C); δ($CDCl_3$) 7.45—8.23 (15 H, m, aromatic H) and 7.90 (2 H, s, 3- and 5-H on the pyridine ring).

Independent Synthesis of Compounds (**7**), (**9**), *and* (**11**).—Compound (**7**) was prepared from benzyl phenyl ketone and phenyl styryl ketone through 1,2,3,5-tetraphenylpentane-1,5-dione (**18a**), then 1,3,4,5-tetraphenyl-5-hydroxyiminopentan-1-one (**19a**). Compound (**7**) had m.p. 187—189 °C (EtOH) (lit.,[7] 179 °C).

Compound (**9**) was prepared as follows. Sodium (0.3 g) was dissolved in ethanol (78 cm^3) and to the solution *p*-bromobenzyl phenyl ketone (3.3 g) and phenyl styryl ketone (2.5 g) were added and the mixture was stirred until a solid product was precipitated. Filtration and recrystallisation from ethanol of the product gave 2-*p*-bromophenyl-1,3,5-triphenylpentane-1,5-dione (**18b**), in 85% yield, m.p. 158—160 °C. To a solution of compound (**18b**) (513 mg) in ethanol–H_2O (1:1; 30 cm^3) were added hydroxylamine hydrochloride (150 mg) and sodium acetate trihydrate (235 mg) and the mixture was heated under reflux for 6 h. 4-*p*-Bromophenyl-5-hydroxyimino-1,3,5-triphenylpentan-1-one (**19b**) was collected by filtration in 81% yield, m.p. 232—234 °C. Into a solution of compound (**19b**) (0.3 g) in ethanol (15 cm^3) was bubbled dry hydrogen chloride until compound (**19b**) was dissolved. After the mixture was heated at 80 °C for 5 h, the solvent was evaporated off and to the residue was added an aqueous solution of potassium hydroxide to give a faintly alkaline mixture. From the resultant solution a product was precipitated. The filtered product was chromatographed on dry silica gel using benzene as eluant and then recrystallised from acetone to give 3-*p*-bromophenyl-2,4,6-triphenylpyridine (**9**) (38%), colourless prisms, m.p. 221—222 °C (Found: C, 75.2; H, 4.3; Br, 17.3; N, 3.0. $C_{29}H_{20}BrN$ requires C, 75.35; H, 4.35; Br, 17.3; N, 3.0%).

Compound (**11**) was obtained as follows. Sodium (0.21 g) was dissolved in ethanol (6 cm^3) and to the resultant solution were added benzyl phenyl ketone (1.8 g) and *p*-methylstyryl phenyl ketone (2.1 g) and the mixture was stirred until a solid product was precipitated. Filtration and recrystallisation from ethanol of the product gave 1,2,5-triphenyl-3-*p*-tolylpentane-1,5-dione (**18c**) (90%), m.p. 184—186 °C. To an ethanol solution of compound (**18c**) (1.0 g) in EtOH–H_2O (1:1, 20 cm^3) were added hydroxylamine hydrochloride (1.0 g) and sodium acetate trihydrate (2.5 g) and the mixture was refluxed for 6 h. Crude 5-hydroxyimino-1,2,5-triphenyl-3-*p*-tolylpentan-1-one (**19c**) was collected by filtration and chromatographed on dry silica gel using ethyl acetate–light petroleum (1:5) as eluant and then the product was recrystallised from ethanol (20%), m.p. 223—227 °C. Into a solution of compound (**19c**) (0.6 g) in ethanol (20 cm^3) was bubbled dry hydrogen chloride until (**19c**) was dissolved. The solution was removed by decantation and the residue was evaporated to dryness on a water-bath. The solid residue was recrystallised from ethanol to give 2,3,6-triphenyl-4-*p*-tolylpyridine (**11**) as colourless needles (10%), m.p. 192—193 °C (Found: C, 90.2; H, 5.8; N, 3.4. $C_{30}H_{23}N$ requires C, 90.6; H, 5.8; N, 3.5%).

Independent Synthesis of Compound (**12**).—2,4,6-Triphenylpyrylium perchlorate[4] (**14**) (50 mg) and ammonium acetate (80 mg) were heated at 60—70 °C in ethanol (10 cm^3) for 30 min. The resultant solution was evaporated off and the residue was recrystallised from ethanol to give 2,4,6-triphenylpyridine (**12**) as colourless needles, m.p. 140—141 °C (lit.,[10] 138—139 °C).

General Procedures for Following up Photoreactions by N.m.r. Spectroscopy.—Sample solutions were deaerated, filled with nitrogen, and then sealed just before the measurements. Irradation was carried out with 100-W high-pressure mercury lamp each spectrum was obtained immediately after irradation.

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