

Novel Photochemical Rearrangement of 2,4,4,6-Tetraphenylpyridin-3(4H)-one to an Oxazole Derivative

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Irradiation of 2,4,4,6-tetraphenylpyridin-3(4H)-one **1** in solution and in the solid state gave 1,3,6,6-tetraphenyl-2-azabicyclo[3.1.0]hex-2-en-4-one **4** as a primary photoproduct, which underwent a novel photorearrangement to yield 5-(2,2-diphenylethenyl)-2,4-diphenyloxazole **3** along with 3-hydroxy-2,4,5,6-tetraphenylpyridine **2**: the structures of **3** and **4** were determined by X-ray structure analysis.

Previously one of the authors reported that 2,4,4,6-tetraphenylpyridin-3(4H)-one **1** was obtained by dye-sensitized photooxygenation of 2,4,4,6-tetraphenyl-1,4-dihydropyridine followed by thermal dehydration.¹ In contrast to 2-pyridones whose photochemical reactions have been extensively investigated, to our knowledge, no photochemical studies of 3-pyridones such as **1** have been reported. We have now observed that **1** undergoes photochemical rearrangement to give an unexpected oxazole derivative along with a hydroxypyridine.

When a benzene solution of **1** was irradiated ($\lambda > 400$ nm), the orange solution turned to yellow and then to colourless. After column chromatography of the reaction mixture two photoproducts were isolated. The major product (73%) was identified as 3-hydroxy-2,4,5,6-tetraphenylpyridine **2** on the basis of comparison of its spectral data with those reported in ref. 2. The structure of the minor product (m.p. 141–142°C;

19% yield) could not be assigned from its spectral data alone,[†] but it was determined as 5-(2,2-diphenylethenyl)-2,4-diphenyloxazole **3** by X-ray structure analysis (Fig. 1).[‡] Irradiation of **1** in ethanol gave a similar result.

In order to clarify the mechanism of the photorearrangement of **1** the progress of the reaction was monitored by ¹H NMR spectrometry. When **1** was irradiated in C₆D₆ for a few

[†] NMR data for **3**: δ (CDCl₃) 7.05 (1H, s, alkenic), 7.2–7.8 (20H, m, aromatic); δ 112.3 (=CH).

[‡] Crystal data for **3**: C₂₉H₂₁NO, monoclinic, space group *P2₁/n*, *a* = 23.549(3), *b* = 8.017(1), *c* = 11.579(2) Å, β = 100.35(1)°, *U* = 2150.6(5) Å³, *D_c* = 1.23 g cm⁻³, *F*(000) = 840, *Z* = 4, λ (Mo-K α) = 0.7107 Å, μ = 0.40 cm⁻¹. The structure was determined by direct methods and refined to *R* = 0.054 (*R_w* = 0.063) for 2262 observed reflections [*F_o*] > 3 σ (*F_o*)].

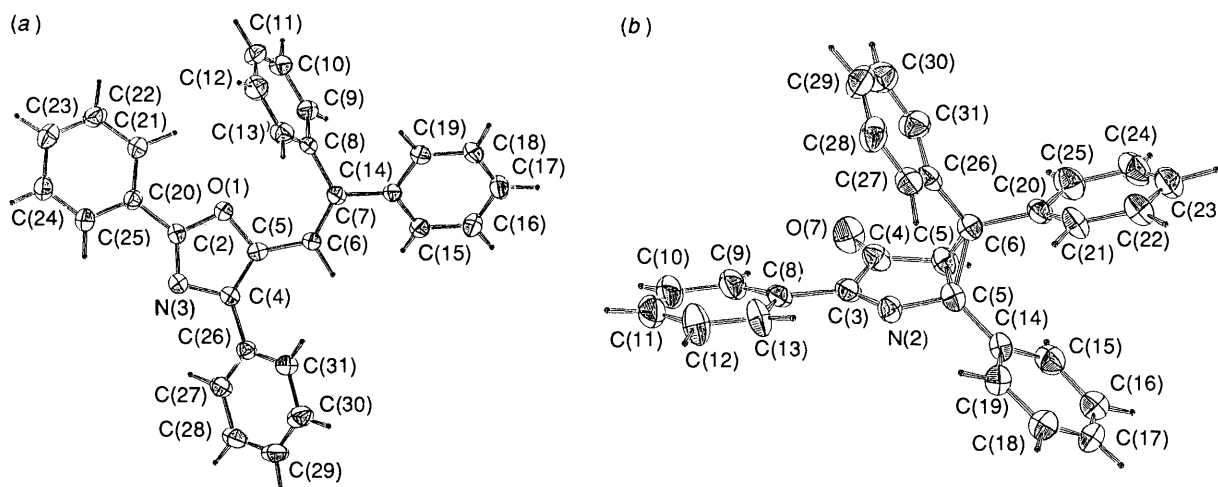
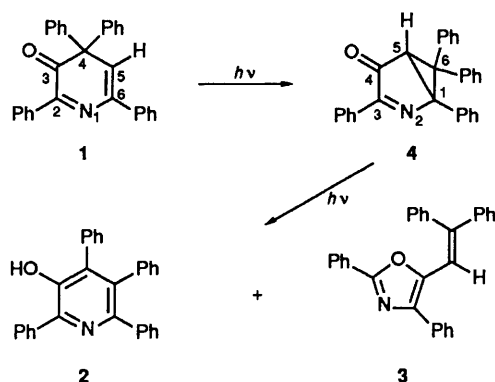


Fig. 1 Molecular structures of (a) **3** and (b) **4**. The anisotropic ellipsoids enclose 30% probability.



Scheme 1

minutes a new singlet signal appeared at δ 3.62 accompanied by a decrease of the signal at δ 6.61 due to 5-H of **1**. On further irradiation the signal at δ 3.62 decreased and a new signal appeared at δ 5.08, which was assigned to the hydroxy proton of **2**. These spectral changes suggested that **2** was formed by two sequential photochemical reaction steps *via* a primary photoproduct which showed the characteristic ^1H NMR signal at δ 3.62. With longer wavelength ($\lambda > 450$ nm) irradiation of **1** this primary product was rather stable and could be isolated as yellow crystals. Its structure was assigned as 1,3,6,6-tetra-phenyl-2-azabicyclo[3.1.0]hex-2-en-4-one **4** based on spectral data \S and was confirmed by X-ray analysis. \P Irradiation of **4** in C_6D_6 ($\lambda > 400$ nm) gave **2** and **3** with a ratio of *ca.* 4 : 1. On the basis of these results it was confirmed that **1** was transformed to **4** in the first step and then **4** underwent secondary photochemical rearrangement to **2** and **3** (Scheme 1).

3-Pyridones such as **1** can be regarded as aza-analogues of cyclohexa-2,4-dienone. The observed rearrangement from **1**

to **4** can be considered to proceed *via* bond formation between C(3) and C(5) followed by migration of the benzhydryl group to C(6), a process which is closely similar to direct photoisomerization of cyclohexa-2,4-dienone to bicyclo[3.1.0]hexenone. 3,4 Formation of hydroxypyridine **2** from **4** is probably a similar type of reaction as the photorearrangement of bicyclohexenone to phenol derivatives, namely migration of one of the 6-phenyl groups to C(1) followed by keto-enol tautomerization. 5 On the other hand, transformation of **4** to oxazole **3** seems a new type of photochemical rearrangement, though some conjugated dienones have been reported to isomerize photochemically into furan derivatives. 6,7 Although a detailed mechanism for the formation of **3** from **4** is still unclear, the carbonyl oxygen may attack C(5) accompanied by cleavage of the three-membered ring.

The above photoisomerizations were also observed in the solid state. When crystals of **1** were irradiated ($\lambda > 400$ nm) in KBr pellets for 5 h, **1** was completely consumed and the reaction mixture containing **4**, **2** and **3** (1 : 1.1 : 1.9 based on its ^1H NMR spectrum) was obtained along with a small amount of an unidentified product **5**. Irradiation of crystals of **4** under similar conditions gave **2**, **3** and **5** (1 : 1 : 0.7) at *ca.* 20% conversion. The ratio of oxazole **3** to hydroxypyridine **2** tends to increase in the solid state compared with that observed in solutions, suggesting that restriction of atomic motions by the crystalline lattice will influence the product distribution of the photochemical reaction of **4**.

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\S Spectral data for **4**: UV; λ_{max} /nm (hexane) 410 (ϵ 700), 297 (ϵ 9200); IR ν/cm^{-1} (KBr) 1730 (C=O); ^1H NMR (C_6D_6) δ 3.62 (1H, s, 5-H), 6.7–7.5 (18H, m) and 8.20 (2H, m); ^{13}C NMR ($[\text{F}_0]$ acetone) δ 41.4 (CH), 70.2, 70.4, 166.3 (C=N) and 198.6 (C=O) in addition to signals due to the aromatic carbons.

\P Crystal data for **4**: $\text{C}_{29}\text{H}_{21}\text{NO}$, monoclinic, space group $C2/c$, $a = 35.938(12)$, $b = 6.636(2)$, $c = 19.092(15)$ Å, $\beta = 107.5(2)^\circ$, $U = 4342(2)$ Å 3 , $D_c = 1.22$ g cm $^{-3}$, $F(000) = 1680$, $Z = 8$, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 0.39$ cm $^{-1}$. $R = 0.074$ ($R_w = 0.078$) for 1389 observed reflections [$|F_0| > 2\sigma(|F_0|)$]. Atomic coordinates, bond lengths and angles, and thermal parameters for **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.