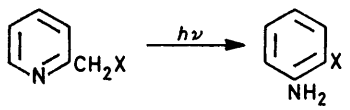
Photoisomerisation of Substituted 2-Methylpyridines to *ortho*-Substituted Anilines

By **Katsuhiko Takagi** and **Yoshiro Ogata,*** Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

2-Methylpyridines substituted in the side chain [2-$PyCH_2X$ (1) (X = CN, CO_2Me, or Ph)] photoisomerised to the corresponding anilines in moderate yields. The four ethyl methyl-2-pyridylacetates (3a—d) were prepared and irradiated. Except for the 6-methyl isomer (3d), they rearrange to ethyl methylanthranilates (4a—c) through exchange of the ring nitrogen atom with the side chain carbon. The photoreactivity of (3d) (6-Me) is low in contrast with the other acetates; the quantum yields ($\phi_{decomp.}$) for the disappearance of starting materials are: (3a) 0.25, (3b) 0.18, (3c) 0.09, and (3d) 0.006 7. The multiplicity of the reactive state is discussed.

PHOTOREACTIONS of aza-aromatic compounds include photoalkylation,[1,2] rearrangement *via* valence isomerisation,[3] and photoelimination.[4] Valence isomers of the benzvalene, prismane, and Dewar benzene types are responsible for the transformation of 2-methylpyridines into 3- of 4-methylpyridines,[3b,f] and of pyrimidines and pyridazines into pyrazines.[3a,g-i] A similar intermediate equivalent to a 1,4-bonded Dewar pyridine in which ring closure is not yet complete has been postulated for the photoalkylation of pyridines.[1a] We now describe details of a novel photoisomerisation of 2-pyridylacetonitrile to anthranilonitrile,[5] and related reactions.

Isomerisation of 2-Methylpyridines.—Irradiation of 2-pyridylacetonitrile (1a) in t-butyl alcohol–diethyl ether (1 : 1 v/v) under nitrogen gave anthranilonitrile (2a)



(1) (2)

a; X = CN b; X = CO_2Me c; X = Ph

(44%). Similarly, methyl 2-pyridylacetate (1b) and 2-benzylpyridine (1c) gave methyl anthranilate (2b) (31%) and *o*-aminobiphenyl (2c) (18%), respectively. Various amounts of decomposition occurred, producing an intractable deposit, especially with (1c).

Although the u.v. absorption of (1a) disappears as that of (2a) increases, no isosbestic point was observed, and an immediate increase of another absorption at *ca.* 280 nm implies other pathways to unknown products, which were not detected by g.l.c. up to 240 °C. Table 1 summarises the results of photoreactions of substituted 2-methylpyridines in various solvents. Methyl 4-pyridylacetate was easily photodecomposed, but (2b) was not formed.

TABLE 1

Solvent dependence of the isomerisation of substituted 2-methylpyridines (1a and c) [a]

	Solvent	% Conversion [b]	% Formation of (2) [b]	Quantum yield for product formation [c]
(1a)	Et_2O [d]	55.3	8.3	0.054
(1a)	Et_2O [e]			0.050
(1a)	Bu^tOH–Et_2O (1 : 1 v/v)	38.0	36.8	0.068
(1a)	MeCN	42.7	3.0	0.024
(1a)	PhH	10.9	22.9	*f*
(1a)	MeOH	65.2	5.2	*f*
(1a)	Bu^tOH	*f*	*f*	0.076
(1a)	$(CH_2Cl)_2$	*g*	0	0
(1c)	Bu^tOH–Et_2O (1 : 1 v/v)	66.7	18.0	*f*
(1c)	MeOH–HCl	60.0	*h*	*f*

[a] Concentration 3—7 × 10^{-4}M; irradiation conducted in a degassed sealed tube with a water-cooled merry-go-round apparatus. [b] Amounts of (1a) and (2a) estimated by g.l.c. [c] Quantum yield determined by ferrioxalate actinometry; yields were determined by u.v. spectrophotometry. [d] Dried over Na wire. [e] Saturated with water. [f] Not determined. [g] A large amount of polymeric material deposited. [h] 2-Benzyl-4-methylpyridine obtained (40%).

Isomerisation of Methyl-2-pyridylacetates.—Irradiation of the four ethyl methyl-2-pyridylacetates was studied to elucidate the course of the rearrangement. Ethyl 3-methyl-2-pyridylacetate (3a), irradiated in dilute solution in t-butyl alcohol–diethyl ether (1.2 × 10^{-2}M) for 20 h, gave ethyl 3-methylanthranilate (4a) (30%) (44% of reactant was recovered).

Irradiation of ethyl 4-methyl-2-pyridylacetate (3b) gave compounds (4a—d) and (3d). Their relative yields (g.l.c.) were (4a) 1.3, (4b) 7.9, (4c) 1.0, (4d) trace, and

[1] (*a*) T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, 1972, **94**, 8451; (*b*) F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, 1968, **33**, 1136.

[2] (*a*) M. Ochiai and K. Morita, *Tetrahedron Letters*, 1967, 2349; (*b*) M. Natsume and M. Wada, *ibid.*, 1971, 4503; (*c*) S. Caplain, A. Castellano, J.-P. Catteau, and A. Lablache-Combier, *Tetrahedron*, 1971, **27**, 3541; (*d*) F. L. Minn, C. L. Trichilo, C. R. Hurt, and N. Filipescu, *J. Amer. Chem. Soc.*, 1970, **92**, 3600; see text for further related references.

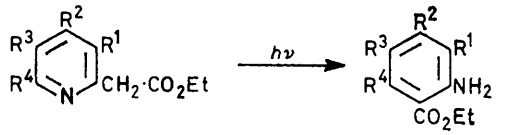
[3] (*a*) F. Lahmani and N. Ivanoff, *Tetrahedron Letters*, 1967, 3913; (*b*) W. Roebke, *J. Phys. Chem.*, 1970, **74**, 4198; (*c*) K. L. Wierzchowski and D. Shugar, *Photochem. and Photobiol.*, 1963, **2**, 377; (*d*) K.L. Wierzchowski, D. Shugar, and A. R. Katritzky, *J. Amer. Chem. Soc.*, 1963, **85**, 827; (*e*) D. W. Johnson, V. Austel, R. S. Feld, and D. M. Lemal, *ibid.*, 1970, **92**, 7505; (*f*) S. Caplain and A. Lablache-Combier, *Chem. Comm.*, 1970, 1247; (*g*) S. L. Bell, R. D. Chambers, M. Y. Gribble, and J. R. Maslakiewicz, *J.C.S. Perkin I*, 1973, 1716; (*h*) R. D. Chambers, J. A. MacBride, J. R. Maslakiewicz, and K. C. Srivastava, *ibid.*, 1975, 396; (*i*) R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *ibid.*, p. 1130, and references therein.

[4] (*a*) F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, 1969, **91**, 3103; (*b*) F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *ibid.*, 1970, **92**, 2745; (*c*) C. M. O'Donnell, G. A. Knesel, T. S. Spencer, and F. R. Stermitz, *J. Phys. Chem.*, 1970, **74**, 3555; (*d*) F. R. Stermitz, W. H. Huang, D. J. Blythin, A. Hoeft, D. K. Kim, and C. M. O'Donnell, *J. Heterocyclic Chem.*, 1972, **9**, 1289; (*e*) F. R. Stermitz and W. H. Huang, *J. Amer. Chem. Soc.*, 1971, **93**, 3427; (*f*) E. C. Alexander and R. J. Jackson, jun., *ibid.*, 1974, **96**, 5663.

[5] Preliminary report, Y. Ogata and K. Takagi, *J. Amer. Chem. Soc.*, 1974, **96**, 5933.

(3d) 3.2. Chromatography yielded compounds (4a—c). The major product was (4b). The products (4a—c) were identified by mass, i.r., and n.m.r. spectra. The photoisomer (4d) and the pyridylacetate (3d) were identified by comparison of g.l.c. retention times with those of authentic samples.[6,7]

Similarly, irradiation of ethyl 5-methyl-2-pyridylacetate (3c) gave ethyl 5-methylanthranilate (4c) (11%).



(3) (4)

a; R^1=Me, R^2=R^3=R^4=H b; R^1=H, R^2=Me, R^3=R^4=H
c; R^1=R^2=H, R^3=Me, R^4=H d; R^1=R^2=R^3=H, R^4=Me

However, ethyl 6-methyl-2-pyridylacetate (3d) was photochemically inert. Prolonged irradiation yielded only (4b) in 3% yield [instead of (4d)].

The ratio of products from (3b) remains nearly constant up to 61% conversion (Table 2). The results of a control experiment suggest that the major product (4b) cannot be a precursor of the minor products, (4a, c, and d), and (3d).

The quantum yields for disappearance of the four isomers (3a—d) are listed in Table 3. The photo-

TABLE 2

Dependence of conversion and product formation on irradiation time for the isomerisation of (3b) [a]

Time (h)	Conv. (%)	Formation (%) [b] (4a)	(4b)	(4c)	(3d)
3	26				
5	51	0.3	3.3	0.3	1.5
9	53	1.0	9.5	1.1	1.4
15	61	1.5	11.4	1.4	4.7

[a] Concentration of (3b) 7×10^{-5}M in Bu^tOH–Et_2O. [b] Measured by g.l.c. (acetophenone as internal standard).

reactivities are similar to that of (1b) except for (3d) (6-Me).

Mechanisms. We proposed previously the intermediacy of a valence isomer (Dewar pyridine), which is known to be formed in the photoreactions of pyridine.[8a,b] Two other isomers, (6) and (7), are conceivable, since they are also photoproducts of pyridines.[8c] Mechanisms involving the species (5)—(7) have been postulated for some rearrangements, *e.g.* pyrimidine to pyrazine,[3a] 2- to 4-methylpyridines,[3b,f] and pyridazine to pyrazine.[3g-i]

The observed rearrangements (1) ⟶ (2) and (3) ⟶ (4) appear to involve an exchange of ring nitrogen with methylene carbon, with the arrangement of the other ring carbons unchanged except in the case of (3d). This exceptional behaviour of (3d) may be caused by its low reactivity in comparison with (3a—c).

The most attractive mechanism involves ring opening and closure (Scheme 1). Although no evidence is available for the formation of the species (10) (diradical or zwitterion) by bond breaking of the 3,6-bonded Dewar pyridine (9), our observations suggest its intermediacy. One of products (11), formed by 1,4-bonding of (10), possesses a ring with the carbon arrangement 1,2,3,6,5,4, in which C-4 and C-6 have been exchanged. Another

TABLE 3

Quantum yields for product formation in direct,[a] sensitised,[b] and quenched [c] irradiations of compounds (1a and b) and (3a—d) in t-butyl alcohol–diethyl ether

	Additive (conc.)	Quantum yield of product formation
(1a)	None	0.068
(1a)	Aerated	0.063
(1a)	Flushed with O_2	0.068
(1a)	Penta-1,3-diene (0.03M)	0.060
(1a)	Penta-1,3-diene (0.15M)	0.033
(1a)	Acetophenone (0.2M)	0
(1a)	Propiophenone (0.2M)	0
(1b)	None	0.039 (0.17) [d]
(1b) [e]	Bu^nBr (0.75M)	0.039 (0.18) [d]
(3a)	None	(0.25) [d]
(3b)	None	(0.18) [d]
(3c)	None	(0.09) [d]
(3d)	None	(0.006 7) [d]

[a] A *ca.* 10^{-4}M-solution of a substrate was degassed and irradiated at 254 nm; the yield was measured by u.v. spectrophotometry at 324 nm for (1a) and 337 nm for (1b). [b] U.v. irradiation filtered by Pyrex (over 99% incident light 'absorbed' by the sensitiser); product analysis by g.l.c. [c] U.v. spectrophotometry used to estimate the yield; all reaction cells were degassed after addition of an appropriate quencher. [d] Figures in parentheses are quantum yields for decomposition of the substrates measured by g.l.c. [e] Concentration 0.5M.

(12), formed by 1,6-bonding, has a ring with the unchanged arrangement 1,2,3,4,5,6. Therefore, the starting material (8) having 4- or 6-Me will give two products, (11) with 4- (or 6-) Me and (12) with 4- (or 6-) Me, whereas (8) having 3- or 5-Me will give only one (11) = (12); this is indeed observed.

The only exception is (3b), which gave low yields of methyl-scrambled isomers (4a, c, and d) besides the major product (4b). Additionally, we note that recombination

(5) (6) (7)

is favoured at the carbon atom bearing no methyl group (which would sterically hinder the ring closure), *i.e.* (8) with 4-Me gives predominantly (12), and (8) with 6-Me gives mainly (11).

On the basis of this mechanism, isomerisation of (8) to (13) should also occur. This recombination was observed with (3b), but not with (3a or c): the arrangement of ring carbons in the product (13) should have involved exchange between C-4 and C-6, but not between C-3 and C-5. In the case of (3d), the isomerisation of (8) to (13) was not observed on account of the photostability of the substrate.

[6] T. Sandmeyer, *Helv. Chim. Acta*, 1919, **2**, 234 (*Chem. Abs.*, 1919, **13**, 1840).

[7] F. Mayer and R. Schulze, *Ber.*, 1925, **58**, 1465.

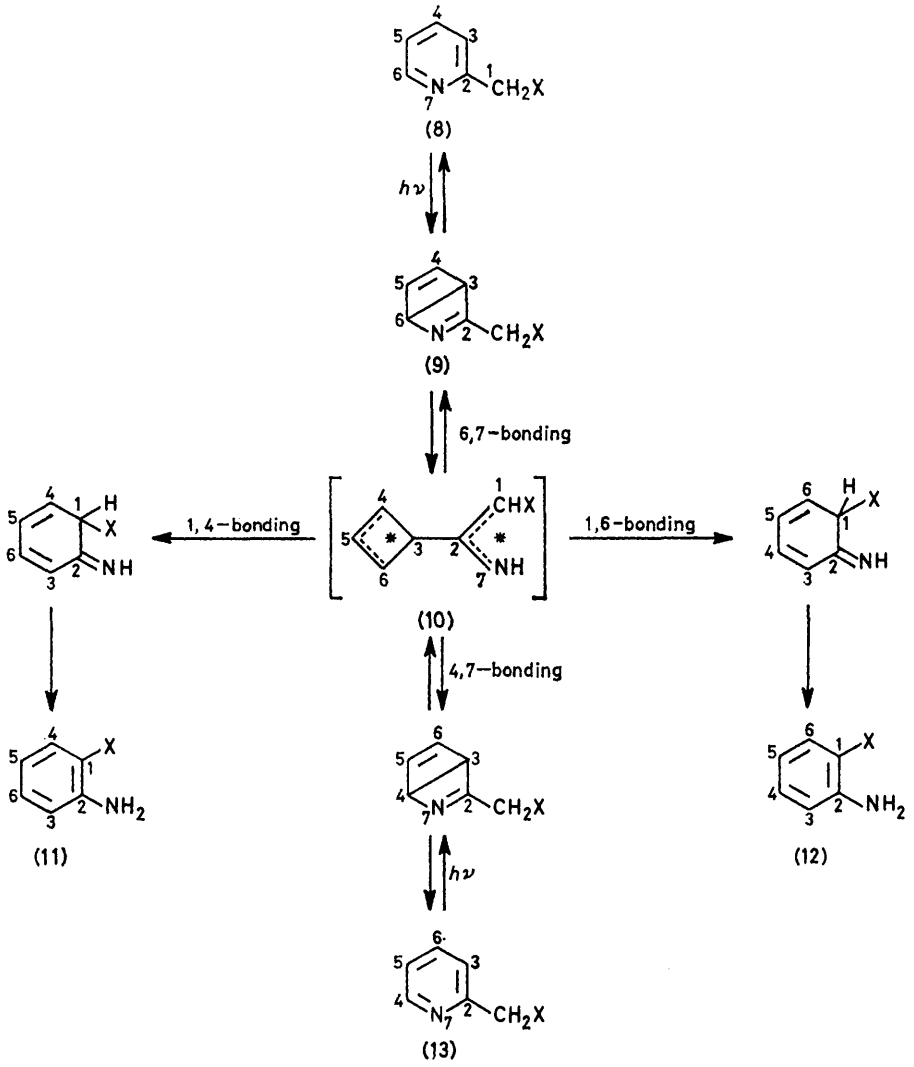
[8] (*a*) M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1580; (*b*) K. E. Wilzbach and J. G. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178; (*c*) L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *ibid.*, 1972, **94**, 3283.

Ring opening of (9) to (10) formally resembles the photoconversion of the 4,5-dimethyl-2-hydroxypyrylium ion into the 5,6-dimethyl-2-hydroxypyrylium ion.[9] A similar ring-opened intermediate has been postulated for the photochemical formation of β-methylglutaconic anhydride from triacetic acid lactone [10] and of hindered 2-pyridones from 4-pyridones.[11]

Another conceivable path (Scheme 2) for the rearrangement is that *via* 3,6-bonded Dewar pyridine (14) or its tautomer (15), which suffers a concerted thermal allowed [3,3] sigmatropic change and then gives (2) by rearomatisation. However, according to this Scheme (3b) should give (4d) but not (4b), which is not observed.

Pyridines can be photochemically hydrated *via* Dewar pyridines yielding aminopentadienals (16).[8,12] Recyclisation may yield the same products as observed in the present rearrangement (Scheme 3). However, this pathway is excluded, since irradiations of (1a) in completely dried and in water-saturated diethyl ether gave the same results (Table 1). Furthermore, Scheme 3 would yield (4d) from (3d), which is not observed.

The minor products (4a and c) from (3b) cannot be rationalised by Scheme 1, indicating the necessity of another pathway. The photoproduct ethyl 4-methylanthranilate (4b) is not converted into positional isomers such as (4a—d) under the same conditions as used with (3b). Further, the ratio of the products from (3b) remains nearly constant during irradiation (Table 2). Therefore, the isomerisation (3b) ⟶ (4a and c) is a result of the collapse of the original pyridine ring, but not of the benzene ring formed. Since (3a and c) are



SCHEME 1

[9] J. W. Pavlik and E. L. Clennan, *J. Amer. Chem. Soc.*, 1973, **95**, 1697.

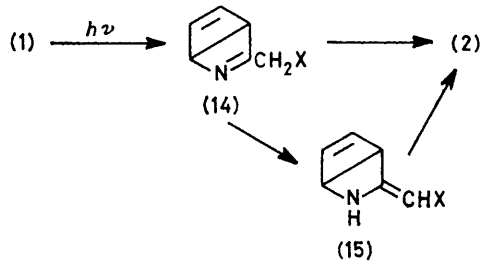
[10] C. T. Bedford, J. M. Forrester, and T. Money, *Canad. J. Chem.*, 1970, **48**, 2645.

[11] N. Ishibe and J. Masui, *J. Amer. Chem. Soc.*, 1974, **96**, 1152.

[12] (*a*) H. Freytag, *Ber.*, 1936, **69**, 32; (*b*) D. Abelson, E. Parthé, K. W. Lee, and A. Boyle, *Biochem. J.*, 1965, **96**, 840.

known to yield (4a and c), respectively, there is a probable intervention of (3a or c) in the photorearrangement of (3b) to (4a or c). Tentatively, the formation of (4a and c) from (3b) is explicable by a pathway involving prismane-like (6A) and/or benzvalene-like (7A) intermediates.

Attempts to extend the application of this rearrangement were unsuccessful: the corresponding anilines were not detected in the photoreactions of 2-methylpyridine

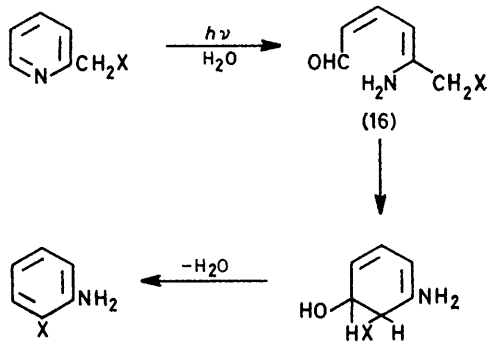


SCHEME 2

(1; X = H), 2-pyridylacetone (1; X = COMe), and 2-chloromethylpyridine (1; X = Cl).[13]

Solvent Effects.—Solvents used affect the yields as shown in Table 1, which suggests that the isomerisation is promoted in hydroxylic solvents bearing no α-hydrogen atom. An appreciable amount of polymeric material was obtained in some solvents (Table 1).

In alcohols bearing α-hydrogen, there is a possibility of formation of an 1 : 1 adduct of (1) with the solvents.[1a] An elimination product from such an adduct was isolated in the case of 2-benzylpyridine (1c), *i.e.* irradiation of (1c) in methanolic hydrochloric acid yielded a methylated product, 2-benzyl-4-methylpyridine (40%). However

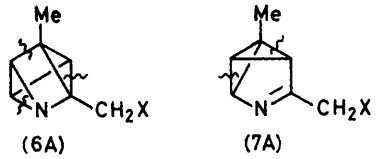


SCHEME 3

no isomerisation product such as (2c) was formed in this reaction.

Multiplicity and Photo-primary Processes.—Sensitisation with triplet sensitisers was not observed for the rearrangement of (1a). Triplet energy was transferred from neither acetophenone (E_T 73.6 kcal mol^{-1}) nor propiophenone (E_T 74.8 kcal mol^{-1}) to (1a) (E_T *ca.* 84 kcal mol^{-1} based on its phosphorescence spectrum [14]). Further, no quenching by molecular oxygen and the absence of an effect due to addition of n-butyl bromide was observed (Table 3). An attempt to quench with penta-1,3-diene was frustrated by its strong singlet quenching as evidenced by a decrease of fluorescence [$\lambda_{max.}$ (MeOH) 390 nm] on addition of the quencher. However the reaction was scarcely affected by penta-1,3-diene at concentrations below 0.05M, suggesting quenching by a singlet. There remains a possibility that a triplet quencher would not intercept a triplet reaction of pyridine compounds because of the short triplet lifetime of these species.

Finally, the source of the observed differences in the photoreactivity of the pyridylacetates (3) is still obscure. A common intermediate (10) may be formed from (3b or d) in spite of their large difference in reactivity. A weak, broad fluorescence was observed from (1a and b) and (3a—c) in t-butyl alcohol–diethyl ether, with emission maxima at *ca.* 390 nm, whereas no fluorescence was



observed with (3d) under the same conditions. The photostability of (3d) may be related to its lack of fluorescence.

EXPERIMENTAL

M.p.s were measured on a hot-stage (Yanagimoto micro-apparatus) and are corrected. I.r. spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer, u.v. spectra with a Hitachi 124 spectrophotometer, n.m.r. spectra with a JEOL C60 HL instrument, and mass spectra with a Hitachi RMS 4 spectrometer. G.l.c. was performed with a Yanaco GCG-550F gas chromatograph with a flame ionisation detector (columns of 5% SE-30 on Chromosorb and of 5% PEG-20M on Chamelite CS).

Materials.—Substituted and unsubstituted 2-pyridylacetates were prepared by treating the corresponding 2-pyridylmethyl-lithium with carbon dioxide followed by addition of an appropriate alcohol saturated with dry hydrogen chloride. Methyl 2-pyridylacetate (1b) [15] had b.p. 133—137° at 27 mmHg; ethyl 3-methyl-2-pyridylacetate (3a) [16] had b.p. 124—126° at 8 mmHg, δ (CCl_4) 2.25 (3 H, s); ethyl 4-methyl-2-pyridylacetate (3b) [17] had b.p. 116—119° at 4 mmHg, δ (CCl_4) 2.25 (3 H, s); ethyl 5-methyl-2-pyridylacetate (3c) [16] had b.p. 95—100° at 1—2 mmHg, δ (CCl_4) 2.2 (3 H, s); ethyl 6-methyl-2-pyridylacetate (3d),[18] had b.p. 101—103° at 1 mmHg, δ (CCl_4) 2.45 (3 H, s). 2-Pyridylacetonitrile (1a) [19] was prepared by dehydration of 2-pyridylacetamide; b.p. 130—133° at 5 mmHg.

[13] (*a*) E. Matsumura, *Nippon Kagaku Zasshi*, 1953, **74**, 363; (*b*) J. F. Vozza, *J. Org. Chem.*, 1962, **27**, 3856.
[14] (*a*) D. F. Evans, *J. Chem. Soc.*, 1959, 2753; (*b*) R. J. Hoover and M. Kasha, *J. Amer. Chem. Soc.*, 1969, **91**, 6508.
[15] R. B. Woodward and E. C. Kornfeld, *Org. Synth.*, Coll. Vol. III, 1955, p. 413.
[16] J. Izdebski, *Roczniki Chem.*, 1965, **39**, 1625 (*Chem. Abs.*, 1966, **64**, 17536b).
[17] (*a*) E. M. Kaiser, G. J. Bartling, W. R. Thomas, S. B. Nichols, and D. R. Nash, *J. Org. Chem.*, 1973, **38**, 71; (*b*) G. R. Clemo, N. Fletcher, and R. Rapper, *J. Chem. Soc.*, 1950, 1140.
[18] G. R. Clemo, B. W. Fox, and R. Rapper, *J. Chem. Soc.*, 1954, 2693.
[19] N. Sperber, D. Papa, E. Schwenk, M. Scherlock, and R. Fricano, *J. Amer. Chem. Soc.*, 1951, **73**, 5742.

All these synthesised materials were purified by chromatography on Florisil (benzene as eluant). 2-Benzylpyridine (1c) was of commercial guaranteed grade and was not further purified. Methyl 4-pyridylacetate was similarly prepared from 4-methylpyridine; b.p. 132—137° at 18 mmHg [lit.,[20] 115—120 at 0.5—1.5 mmHg].

Irradiation of 2-*Pyridylacetonitrile* (1a); *Product Isolation.*—A solution of 2-pyridylacetonitrile (1a) (0.323 g, 3.4×10^{-2} mol) in t-butyl alcohol–diethyl ether (1 : 1 v/v; 400 ml) was purged with nitrogen, then irradiated under nitrogen for 14.5 h (300 W Halos high-pressure mercury lamp in water-cooled immersion well). The solution was evaporated and the residue was chromatographed on a 100 × 2 cm column slurry of Florisil in light petroleum, and eluted with light petroleum (10 g fractions). The eluate up to 500 ml contained 0.143 g (44.3%) of crystalline material, m.p. 45—47°, characterised as anthranilonitrile (m.p. 47—48°),[21] $\nu_{max.}$ (KBr) 3 450, 3 350, 2 200, 1 620, 1 580, and 745 cm^{-1}; $\lambda_{max.}$ (MeOH) 247 (ε 6 600) and 324 nm (3 800); M^+ 118; δ (CCl_4) 7.3—7.4 (4 H, m) and 4.5 (2 H, s).

Irradiation of Methyl 2-*Pyridylacetate* (1b); *Product Isolation.*—A solution of methyl 2-pyridylacetate (1b) (1.01 g) in t-butyl alcohol–diethyl ether (500 ml) was irradiated under nitrogen. After 1 h, a blue fluorescence appeared, indicative of the formation of methyl anthranilate (2b). The mixture was evaporated and the residue separated on a column slurry of Florisil in benzene. Elution with benzene gave a pale yellow liquid (2b) (127 mg) with blue fluorescence; $\nu_{max.}$ (film) 3 460, 3 360, 2 930, 1 690, 1 620, and 750 cm^{-1}; $\lambda_{max.}$ (MeOH) 248 (ε 6 640) and 337 nm (4 600); M^+ 151; δ (CCl_4) 7.65 (1 H, m), 7.10 (1 H, m), 6.50 (2 H, m), 4.67 (2 H, s, NH_2), and 3.75 (3 H, s, OCH_3), identical with authentic material. Elution with benzene containing 10% acetone gave the pyridylacetate (1b) (358 mg).

Irradiation of 2-*Benzylpyridine* (1c); *Product Isolation.*—A solution of 2-benzylpyridine (1c) (1.02 g) in t-butyl alcohol–diethyl ether (500 ml) was irradiated similarly for 43 h. The solvent was removed and the residue was chromatographed on a column slurry of Florisil in light petroleum. Benzene (1 l) eluted a pale yellow liquid (128.4 mg, 18%), which on treatment with hydrochloric acid followed by neutralisation with aqueous sodium hydroxide and then extraction with benzene gave crystalline 2-aminobiphenyl (2c) (m.p. and mixed m.p. 46—48°), identical (g.l.c. and spectral properties) with an authentic sample; $\nu_{max.}$ 3 450, 3 360, and 1 620 cm^{-1}. Acetone eluted starting material (1c) (304 mg).

Irradiation of 2-*Benzylpyridine* (1c) *in Methanolic Hydrochloric Acid; Product Isolation.*—A solution of (1c) in methanol (500 ml) containing concentrated hydrochloric acid (5 ml) was irradiated for 17 h, neutralised (1N-NaOH), and evaporated. The residue was chromatographed on a column slurry of Florisil in benzene–ethyl acetate to give 2-benzyl-4-methylpyridine as a pale yellow oil (40%) which gave a single peak in g.l.c.; δ (CCl_4) 8.40 (1 H, d), 7.13 (5 H, s), 3.98 (2 H, s), and 2.12 (3 H, s).

Irradiation of Ethyl 3-*Methyl*-2-*pyridylacetate* (3a); *Product Isolation.*—A solution of ethyl 3-methyl-2-pyridylacetate (3a) (0.63 g) in t-butyl alcohol–diethyl ether was irradiated under nitrogen for 27 h. Blue fluorescence ($\lambda_{max.}$ 410 nm) appeared after 30 min. Irradiation was continued to *ca.* 50% conversion (monitored by g.l.c.). The product was chromatographed on Florisil in benzene to give a liquid (103.4 mg, 29.6%), characterised as ethyl 3-methylanthranilate (4a), M^+ 179, $\nu_{max.}$ 3 460, 3 360, 1 680, 1 242, and 1 084 cm^{-1}; δ (CCl_4) 7.65 (1 H, dd, *J* 1 and 9 Hz), 7.01 (1 H, dd, *J* 1 and 9 Hz), 6.42 (1 H, t, *J* 9 Hz), 5.65br (2 H, s, NH_2), 4.24 (2 H, q, OCH_2), 2.10 (3 H, s, CH_3), and 1.36 (3 H, t, CH_3), and unchanged (3a) (44%), identified by g.l.c.

Irradiation of Ethyl 4-*Methyl*-2-*pyridylacetate* (3b); *Product Isolation.*—A solution of ethyl 4-methyl-2-pyridylacetate (3b) (1.00 g) in t-butyl alchol–diethyl ether (400 ml) was irradiated under nitrogen for 28 h (blue fluorescence), then evaporated. The residue was chromatographed on a column slurry of Florisil in benzene (g.l.c. showed six components) to give (i) a liquid (30 mg), characterised as ethyl 3-methylanthranilate (4a), $\nu_{max.}$ (film) 3 640, 3 360, 1 680, 1 610, 1 242, 1 084, 800, and 750 cm^{-1}; δ (CCl_4) 7.64 (1 H, dd, *J* 1 and 9 Hz), 6.45 (1 H, t, *J* 9 Hz), 5.6br (2 H, s, NH_2), 4.24 (2 H, q, OCH_2), 2.10 (3 H, s, CH_3), and 1.36 (3 H, t, CH_3); $\lambda_{max.}$ (MeOH) 245 and 335 nm; M^+ 179; (ii) a liquid (50 mg), identified as ethyl 4-methylanthraniliate (4b), $\nu_{max.}$ (film) 3 450, 3 350, 1 680, 1 620, 1 250, 1 100, 855, and 770 cm^{-1}; δ (CCl_4) 7.63 (1 H, d, *J* 9 Hz), 6.35 (2 H, m), 5.64br (2 H, s, NH_2), 4.25 (2 H, q, OCH_2), 2.25 (3 H, s, CH_3), and 1.36 (3 H, s, CH_3); $\lambda_{max.}$ (MeOH) 251 and 335 nm; M^+ 179, identical (spectral properties and g.l.c.) with an authentic sample;[11] and (iii) a liquid (30 mg) mixture of *ca.* 70% of ethyl 5-methylanthranilate (4c) and *ca.* 30% of (4b); $\nu_{max.}$ 3 450, 3 350, 1 680, 1 620, 1 240, 1 090, 855, 810, and 790 m^{-1}; δ (CCl_4) 7.55 (1 H, complex), 6.95 (1 H, dd, *J* 8—9 and 1.5 Hz), 6.41 (1 H, complex d, *J* 8—9 Hz), 5.6br (2 H, s, NH_2), 4.25 (2 H, q, OCH_2), 2.20 (3 H, s, CH_3), and 1.36 (3 H, t, CH_3); M^+ 179. The other three components [(3b), (4d), and (3d)] were not separated by chromatography, but were identified by comparing their g.l.c. retention times with those of the authentic samples [6,7] on two different columns (PEG 20M and SE-30). The product ratios were estimated from g.l.c. to be 7.9 : 1.3 : 1.0 : trace : 3.2 [(4b) : (4a) : (4c) : (4d) : (3d)].

Irradiation of Ethyl 5-*Methyl*-2-*pyridylacetate* (3c).—A solution of ethyl 5-methyl-2-pyridylacetate (3c) (70 mg) in t-butyl alcohol–diethyl ether (150 ml) was irradiated as for (3a). Blue fluorescence appeared after 3 h and irradiation was continued to 50% conversion. The solution was evaporated and the residue analysed by g.l.c. (on PEG 20M and SE-30). The mixture contained only one [ethyl 5-methylanthranilate (4c)] of the anthranilates (4a—d), identical (retention time) with the sample from (3b).

Irradiation of Ethyl 6-*Methyl*-2-*pyridylacetate* (3d).—A solution of ethyl 6-methyl-2-pyridylacetate (3d) (0.4 g) in t-butyl alcohol–diethyl ether (500 ml) was irradiated under nitrogen, but no fluorescence appeared. G.l.c. analysis showed almost no loss of (3d), with traces of two components which were not separated. One was identified as (4b) (g.l.c. retention time). The other was not one of the anthranilates (4a—d).

Measurement of Quantum Yields.—The quantum yields for the consumption of substrate were measured by irradiating 10 ml of a 1—2 × 10^{-2}M-solution in quartz tubes (40 × 10 mm thickness); the quantum yields for the product formation were measured by irradiating 4 ml of a 1—3 × 10^{-4}M-solution in quartz tubes (10 mm thickness) with u.v. light concentrated through three quartz lenses (253.7 nm Halos HIL 30 W lamp). The samples were degassed by three freeze–thaw cycles (10^{-3} mmHg) and sealed off. Light intensities were measured with a potassium ferrioxalate

[20] H. Zimmer and D. K. George, *Chem. Ber.*, 1956, **89**, 2285.

[21] J. Pinnow and C. Sämann, *Ber.*, 1896, **29**, 624.

actinometer.[22] The conversions were limited to below 10%, to minimise absorption of incident light by the products. Data for the individual runs are as follows [substrate (quantity used), energy absorbed by solution, quantity of corresponding aniline formed (or pyridine decomposed), quantum yield]: (1a) (1.60 μmol), 2.30×10^{-6} einstein, 0.125 μmol [formation of (2a)], ϕ 0.006 7; (1b) (0.708 μmol), 1.36×10^{-6} einstein, 0.042 5 μmol [formation of (2b)], ϕ 0.003 9; (1b) (0.125 mmol), 47.8×10^{-6} einstein, 6.5 μmol [decomposition of (1b)], ϕ 0.17; (3b) (0.104 mmol), 41.7×10^{-6} einstein, 6.0 μmol [decomposition of (3b)], ϕ 0.18.

The quantum yields for decomposition of other acetates (3a and c) were measured by using (3b) as a standard actinometer with a merry-go-round apparatus, with consumptions of substrate below 10%. The conversions of substrates were determined by g.l.c. (propiophenone or acetophenone as internal standard) and the concentrations of the products were determined by u.v. spectrophotometry at 324 nm for (1a) and 337 nm for (1b).

Emission Spectra.—The fluorescence spectra were recorded with a Hitachi MPF-2A fluorescence spectrophotometer and the phosphorescence spectra on the same apparatus with phosphorescence attachments. The emission spectra were measured in methanol or t-butyl alcohol–diethyl ether containing $1—3 \times 10^{-4}$M-substrate. No interference due to emission of solvents was observed.

Quenching.—A solution containing a given concentration ($1—4 \times 10^{-4}$M) of a substrate and a suitable concentration of penta-1,3-diene was placed in a 10 mm optical cell, degassed by three freeze–thaw cycles on a vacuum line, and sealed off. A similar solution saturated with oxygen or air was also sealed off. The tubes were irradiated with a Halos 300 W high pressure mercury lamp. The products were analysed by u.v. spectrophotometry.

Sensitising.—The u.v. irradiation was carried out for 6 h in the presence of a sensitiser and substrate in a molar ratio of 10 : 1 through a Pyrex filter which transmits light of wavelength longer than 300 nm, thus enabling sensitisers to absorb over 99% of incident light.

We thank Professor I. Kamiya and Dr. K. Aoki for their aid in measurement of emission spectra.

[6/1602 *Received*, 16*th August*, 1976]

[22] C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **234**, 518.