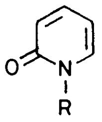
Structures of the Four Possible [4 + 4] Cycloaddition Products Formed on Photodimerization of *N*-Alkyl-2-pyridones

By **Yushin Nakamura,* Takeshi Kato,** and **Yutaka Morita,** Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02, Japan

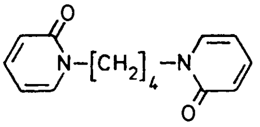
Photodimerization of *N*-methyl-2-pyridone (1a) in water gave exclusively the four [4 + 4] cycloaddition products [*trans,anti* (5a) (51%), *trans,syn* (6a) (0.6%), *cis,anti* (7a) (11.2%), and *cis,syn* (8a) (6.8%)]. In contrast, the reaction in non-aqueous solvents (benzene or ethanol), gave only the *anti*-dimers. The four dimers (5a)—(8a) were photostable, but showed remarkable differences in their thermal stability: (5a) and (6a) were unchanged when heated under reflux in $CHCl_3$, but (7a) and (8a) rearranged to give an unsymmetrical [2 + 2] dimer (9), and symmetrical [2 + 2] dimers (10) and (11), respectively; thus, structures (7a) and (8a) possess Cope systems. Structures were assigned on the basis of spectral evidence. Variation of the *N*-alkyl groups and of reagent concentrations had no influence on the relative yields of the dimers.

THE photochemistry of 2-pyridones was first described by Taylor.[1] The dimers isolated were assigned structures (2) on the basis of u.v. absorption, dipole moment, hydrogenation, epoxidation, and pyrolytic data. Ayer [2] and Paquette [3] later proposed the revised structure (5) on the basis of n.m.r. data, and this was confirmed by *X*-ray crystallography.[4] Corey reported that irradiation of 2-pyridone in low concentration gave the valence isomer (3; R = H).[5] Hammond described the photoreaction of neat *N*-methyl-2-pyridone (1a) to give two other new dimers, of which one was identified as the [2 + 2] dimer (4); the other was not identified.[6] Intramolecular photocycloisomerization of *N*,*N*-polymethylenebis-2-pyridones with sensitizer gives [2 + 2], [4 + 2], and [4 + 4] addition products.[7]

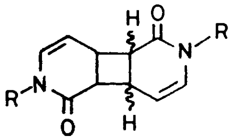


(1)

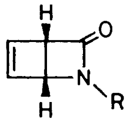
a ; R = Me
b ; R = Bu^n
c ; R = n - $C_{12}H_{25}$



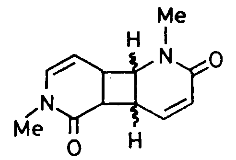
(1d)



(2)



(3)



(4)

We report here the structures of three new [4 + 4] dimers formed on the irradiation of *N*-methyl-2-pyridone (1a),[8] and a revised structural assignment for the product previously thought to have structure (4).

RESULTS AND DISCUSSION

Formation and Structures of the Photocyclodimerization Products from N-*Methyl-2-pyridone* (1a).—A solution of (1a) (0.5M) in water was irradiated with a 400 W high-pressure mercury arc in a Pyrex cell through which a fine stream of nitrogen was bubbled at 20 °C for 15 h. The products were chromatographed on silica gel to separate the known dimer (5a) (51%) and three new dimers [(6a) (0.6%), (7a) (11.2%), and (8a) (6.8%)], besides a trace of the valence isomer (3; R = Me) and 19% of unchanged (1a). All four dimers show features characteristic of [4 + 4] cycloaddition products, having i.r. absorptions at 1 660 (C=O) and 1 640sh cm^{-1} (non-conjugated C=C) and only end absorption in the u.v. spectrum. N.m.r. spectral data are in Table 1.

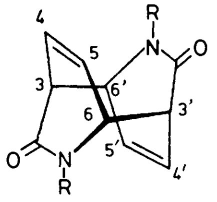
TABLE 1

N.m.r. spectral data for [4 + 4] dimers (5a)—(8a)

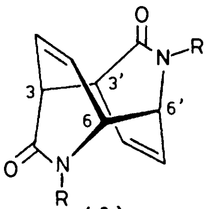
Compd.	3,3′-H	4,4′-H	5,5′-H	6,6′-H	N-CH_3
(5a)	3.58 ^{a} ddd *J* 10, 5, 2	6.17 ddd *J* 8, 5, 2	6.63 ddd *J* 8, 5, 2	3.96 ^{a} ddd *J* 10, 5, 2	2.75 s
(6a)	3.43 ^{a} m	6.42 m	6.42 m	4.08 ^{a} m	2.83 s
(7a)	3.63 ^{b} m	6.17 m	6.17 m	4.10 ^{b} m	2.93 s
(8a)	3.60 ^{b} m	5.90 m	6.50 m	4.08 ^{b} m	2.93 s
(8d) ^{c}	3.62 ^{b} m	5.92 m	6.59 m	4.06 ^{b} m	

^{a} Changes to doublet (*J* 10 Hz) on irradiation of 4,4′-H or 5,5′-H. ^{b} Changes to singlet on irradiation of the 4,4′-H or 5,5′-H. ^{c} Ref. 7.

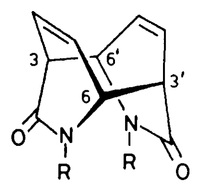
The four dimers show remarkable differences in thermal stability: (5a) and (6a) remain unchanged when heated under reflux in $CHCl_3$ but (7a) and (8a) rearranged. Compound (7a) rearranged to give only the oily product (9), in 84% yield, while (8a) gave (10) and (11) in the ratio 45 : 55. Compounds (5a)—(8a) all showed photostability: irradiation under the conditions as used for their preparation gave no change. On irradiation at 40 °C under otherwise identical conditions, (5a) and (6a) still remained unchanged, but (7a) was partially converted into (9), and (8a) was partially converted into (10) and (11). The rearrangement product (9) exhibits α,β-unsaturated amide absorption in the i.r. spectrum [1 665 (C=O) and 1 610s cm^{-1} (C=C)] and u.v. absorption at $\lambda_{max.}$ 262 nm (ε 3 210). In the n.m.r. spectrum, two distinct *N*-methyl singlets at δ 2.95 and 2.98 indicate that it is not a symmetrical dimer, ruling out [4 + 4] cycloadducts. Compound (10) shows strong enamide absorptions at 1 665 cm^{-1} in the i.r. and at $\lambda_{max.}$ 263 nm (ε 7 330) in the u.v. Compound (11) shows α,β-unsaturated amide absorptions at 1 670 (C=O) and 1 615s cm^{-1} (C=C) in the i.r., and at $\lambda_{max.}$ 257 nm (ε 2 230) in the u.v.



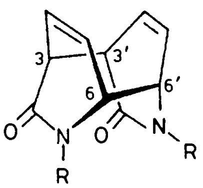
(5)
trans,anti



(6)
trans,syn



(7)
cis,anti



(8)
cis,syn

a; R = Me b; R = Bu^n c; R = n-$C_{12}H_{25}$

In view of the strong similarities between the spectra of compounds (9)—(11) and those of the intramolecular cycloaddition products (12) and (13),[7] we conclude that (9)—(11) have the structures shown. N.m.r. spectral data for (9)—(13) are in Table 2.

The structure of compound (9) is unsymmetrical, being composed of the partial structures (A) and (B). Its n.m.r. spectrum shows the olefinic H-5 and H-6 signals of unit (A), as in (12), at δ 4.77 and 6.02 (*J* 8 Hz). The H-3′ and H-4′ signals of unit (B), as in (13), appear at δ 5.83 and 6.40 (*J* 10 Hz). The C-4′ and C-5 protons are further coupled with the cyclobutane protons. The n.m.r. spectra of (10) and (11) show that they have symmetrical structures [(AA) and (BB), respectively]. The olefinic H-5 and H-6 (or H-5′ and H-6′) signals of (10) appear at δ 4.87 and 5.97 (*J* 8 Hz) and H-5 (or H-5′) is further coupled with the cyclobutane protons. The olefinic H-3 and H-4 (or H-3′ and H-4′) signals of (11) appear at δ 5.90 and 6.27 (*J* 10 Hz) and H-4 (or H-4′) is further coupled with the cyclobutane protons.

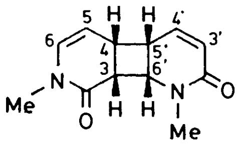
TABLE 2

N.m.r. spectral data for [2 + 2] dimers (9)—(13)

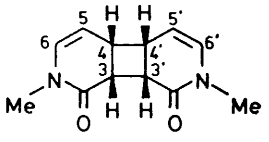
Compd.	3,4-H [a]	5-H [b]	6-H [c]	3′-H [d]	4′-H [e]	5′-H [a]	6′-H [f]	N-CH_3
(9)	3.2—3.8	4.77	6.02	5.83	6.40	3.2—3.8	4.2—4.7	2.98 2.95
(10)	3.2—3.8	4.87	5.97					2.97
(11)				5.90	6.27	3.4—3.7	4.2—4.4	2.90
(12) [g]	3.6—4.0	4.3—4.6	6.07					
(13) [g]				5.92	6.14	3.7—3.9	4.2—4.4	

[a] Multiplet. [b] Multiplet; changes to doublet on irradiation of 3,4-H and/or 5′-H. [c] Doublet, *J* 8 Hz; changes to singlet on irradiation of 5-H. [d] Doublet, *J* 10 Hz. [e] Doublet of triplets, *J* 10 and 2 Hz; changes to broad doublet on irradiation of 3,4-H and/or 5′-H. [f] Multiplet; changes to broad singlet on irradiation of 3,4-H and/or 5′-H. [g] Ref. 7.

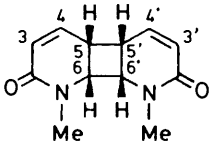
Since (9) was obtained from (7a), and (10) and (11) from (8a), compounds (7a) and (8a) must have Cope systems, and the double-bond and amide geometries of (7a) and (8a) are therefore assigned as *cis,anti* and *cis,syn*, respectively; the corresponding configurations of (9)—(10) and (11) are thus *cis,syn*.* The structural assignments are supported by n.m.r. decoupling experiments. Irradiation at the frequency of H-4, H-4′, H-5, and H-5′ in (7a) (at δ 6.17) shows that H-3 and H-6 are further coupled with H-6′ and H-3′ (*J* 10 Hz), whereas H-3 and H-6 of (8a) are coupled only with the H-4 and H-4′, and H-5 and H-5′, respectively.



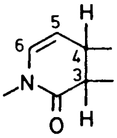
(AB)
(9)



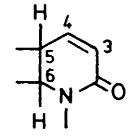
(AA)
(10)



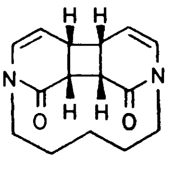
(BB)
(11)



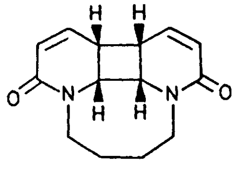
(A)



(B)



(12)



(13)

The thermally stable (5a) and (6a) are similarly assigned *trans,anti* and *trans,syn* structures, since the H-3 and H-6 of (5a) (at δ 3.58 and 3.96) are coupled with the

H-6′ and H-3′ (J 10 Hz), whereas the H-3 and H-6 of (6a) give singlets at δ 3.43 and 4.08, respectively, on irradiation at the olefinic proton frequency. The spectral data for (5a) agree well with reported data[2] for the *trans,anti* structure.

The above results indicate that photodimerization of the pyridone (1a) gives three new [4 + 4] cycloaddition products and a known [4 + 4] product; thus the four possible [4 + 4] dimers are formed. In the reaction in aqueous solution, no [2 + 2] or [4 + 2] dimers were detected.

Hammond[6] reported that the photoreaction of neat (1a) gave the known products (5) and (3) (R = Me) and two new dimers (4) and (14), isolated after preparative t.l.c. on silica gel. Compound (4) was identified as the *anti* [2 + 2] dimer without steric assignment, on the basis of spectroscopic data. The other new dimer (14), for which only an n.m.r. spectrum was obtained, was not identified because of the poor quality of the spectrum. However the spectral data for (4) obtained by Hammond agree well with our data for (9), and the spectrum of other dimer (14) agrees with that obtained by us for (11); thus it appears that these structures should be reassigned.

TABLE 3

Photoreactions of N-alkyl-2-pyridones (1a—1c)

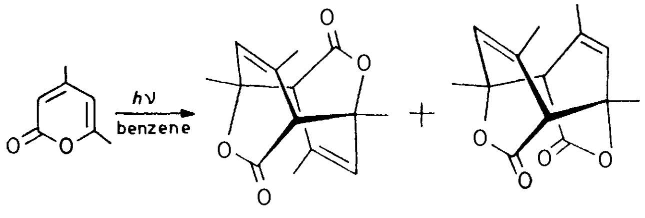
Compd.	Solvent	Concn. (mM)	Conversion[a] (%)	Yields (%)[b] Isomer	Yields (%)[b] Dimers	Ratio D : I[c]	Distribution of dimers[d] (%) *t,a*	*t,s*	*c,a*	*c,s*
(1a)	H_2O	170	94	12	79	6.6 : 1	67	1	22	10
		100	97	17	60	3.5 : 1	65	2	22	11
		32	95	30	49	1.6 : 1	62	3	22	13
	EtOH	170	62	9	52	5.8 : 1	56	0	44	0
		32	66	25	41	1.6 : 1	64	0	36	0
	Benzene	1 000	70	0	70	(100% D)	52	0	48	0
		170	82	10	72	7.2 : 1	60	0	40	0
		100	85	11	50	4.5 : 1	61	0	39	0
		10	88	50	25	0.5 : 1	67	0	33	0
(1b)	H_2O	170	93	17	71	4.2 : 1	61	4	19	16
		100	100	19	74	3.9 : 1	60	4	19	17
		30	100	43	51	1.2 : 1	62	3	18	17
		10	100	59	28	0.5 : 1	61	4	18	17
(1c)	EtOH	100	87	28	21	0.8 : 1	72	0	28	0
		34	92	57	21	0.4 : 1	72	0	28	0
	Benzene	100	96	25	23	0.9 : 1	73	0	27	0
		34	100	52	16	0.3 : 1	75	0	25	0

[a] Based on the recovered starting material. [b] Of isolated material. [c] D = dimer, I = isomer. [d] *t,a* = *trans,anti*; *t,s* = *trans,syn*; *c,a* = *cis,anti*; *c,s* = *cis,syn*.

To confirm these conclusions, we carefully examined the photoreaction of neat (1a). The only products obtained were the [4 + 4] dimers (5a), (6a), (7a), and (8a) in the ratios 80 : 1 : 16 : 3. We also examined the thermal stability of the products. Compound (7a) in $CHCl_3$ was stirred with silica gel at room temperature slowly to give (9). Compound (8a) in refluxing $CHCl_3$ gave two dimers (10) and (11) in the ratio 1 : 1, whereas in $CHCl_3$ with silica gel at room temperature (11) was the almost exclusive product [with a trace of (10)].

The results of our experiments indicate that the two new dimers (4) and (14) reported by Hammond should be reassigned as (9) and (11), respectively, probably formed by rearrangement from (7a) and (8a), respectively, during the preparation.

Effects of Solvent and of N-*Alkyl Group on the Relative Yields of Photoproducts*.—The photoreactions of the pyridones (1a—c) were studied under various conditions of solvent and concentration. The product distributions are shown in Table 3. Compounds (1a) and (1b) in aqueous solution gave all four [4 + 4] dimers. In contrast, in non-aqueous solution (EtOH or benzene), only the *anti* dimers were obtained. The distributions of the dimers were independent of substrate concentrations under the conditions examined. The observation that the use of non-aqueous solvent gives only *anti* dimers while the use of water gives the additional *syn* dimers is noteworthy in connection with a report by de Mayo[9] that 4,6-dimethyl-2-pyrone (15) in benzene gave only *anti* [4 + 4] photodimers (16) and (17) (the reaction was not studied in aqueous media).



(15) (16) (17)

EXPERIMENTAL

I.r. spectra were recorded with a Hitachi 215 grating spectrometer for solutions in $CHCl_3$, u.v. spectra with a Hitachi 100-50 spectrophotometer for solutions in EtOH, and ^1H n.m.r. spectra with a JEOL-PMX 60 instrument ($CDCl_3$ as solvent and $SiMe_4$ as internal standard). Mass spectra were recorded with a Shimazu LKB 900 spectrometer. M.p.s were determined with a Yanagimoto MP-S3

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* For structures (5)—(8), *cis* and *trans* define the relative positions of the double bonds, and *syn* and *anti* the relative orientations of the amide groups; however in (9)—(13), *cis* and *trans* describe the configuration of the cyclobutane ring and *syn* and *anti* the relative positions of the double bonds.

apparatus. Kieselgel 60 and 60 HF_{254} (Merck) were used for column chromatography and for analytical and preparative t.l.c., respectively.

N-Butyl-2-pyridone (1b) [10] and *N*-dodecyl-2-pyridone (1c) [11] were prepared by the reported procedures.

Irradiation of N-*Methyl-2-pyridone* (1a) *in Aqueous Solution.*—A 0.5M solution of (1a) [546 mg; purified by distillation (from Tokyo-kasei)] in distilled water (10 ml) was irradiated with a 400 W high-pressure mercury arc in a Pyrex cell through which a fine stream of nitrogen bubbles was passed at 20 °C for 15 h. The mixture was evaporated *in vacuo* below 40 °C. To the residue was added a little EtOH, and the precipitate (5a) (238 mg) formed was filtered off. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on silica gel (CH_2Cl_2–MeOH 99 : 1) to separate compounds (1a) (104 mg), (7a) (61 mg), (5a) (39 mg), (8a) (37.4 mg), and (6a) (3.5 mg) (in order of elution). Total yields of (5a), (6a), (7a), and (8a) were 277 mg (50.7%), 3.5 mg (0.6%), 61 mg (11.2%) and 37.4 mg (6.8%), respectively; that of recovered (1a) was 104 mg (19%). The *trans,anti*-photodimer (5a) formed colourless prisms, m.p. 222—222.5 °C (lit.,[3] 221.5—222 °C) (Found: C, 65.95; H, 6.45; N, 12.75. Calc. for $C_{12}H_{14}N_2O_2$: C, 66.05; H, 6.45; N, 12.85%); $\nu_{max.}$ 1 660 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption. The trans,syn-*photodimer* (6a) gave colourless prisms, m.p. 217 °C (from Et_2O) (Found: C, 65.95; H, 6.25; N, 12.7%); $\nu_{max.}$ 1 660 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption. The cis,anti-*photodimer* (7a) afforded colourless prisms, m.p. 122—124 °C (from CH_2Cl_2–Et_2O) (Found: C, 65.95; H, 6.45; N, 12.9%); $\nu_{max.}$ 1 660 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption. The cis,syn-*photodimer* (8a) gave colourless prisms, m.p. 115—117 °C (from CH_2Cl_2–hexane) (Found: C, 65.6; H, 6.35; N, 12.85%); $\nu_{max.}$ 1 660 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption.

Thermal Rearrangement of the Photodimer (7a).—A solution of (7a) (51 mg) in $CHCl_3$ (10 ml) was refluxed for 2 h and then evaporated *in vacuo*. The residue was distilled to give the *cyclobuta*[1,2-b;4,3-c′]*dipyridine derivative* (9) as a colourless oil (43 mg, 84%), b.p. 110—120 °C at 2.5 × 10^{-5} Torr (Kugelrohr) (Found: C, 66.35; H, 6.45; N, 12.95. $C_{12}H_{14}N_2O_2$ requires C, 66.05; H, 6.45; N, 12.85%); $\nu_{max.}$ 1 660 (C=O) and 1 610s cm^{-1} (C=C); $\lambda_{max.}$ 262 nm (ε 3 240).

Thermal Rearrangement of the Photodimer (8a).—A solution of (8a) (32 mg) in $CHCl_3$ (5 ml) was refluxed for 2 h and then evaporated *in vacuo*. The residue was separated by p.l.c. on silica gel (acetone) to give the *cyclobuta*[1,2-c;4,3-c′]-*dipyridine derivative* (10) as colourless prisms (9 mg, 28%), m.p. 141—142 °C (from EtOH–Et_2O) (Found: C, 66.1; H, 6.35; N, 12.8%; $\nu_{max.}$ 1 665 cm^{-1} (C=O); $\lambda_{max.}$ 263 nm (ε 7 240); and the *cyclobuta*[1,2-b;4,3-b′]*dipyridine derivative* (11) as colourless prisms (11 mg, 34%), m.p. 182 °C (from EtOH–Et_2O) (Found: C, 66.15; H, 6.25; N, 12.9%); $\nu_{max.}$ 1 670 (C=O) and 1 615s cm^{-1} (C=C); $\lambda_{max.}$ 257 nm (ε 2 820).

Irradiation of N-*Alkyl-2-pyridones under Other Conditions.*—The photoreactions shown in Table 3 were carried out as follows. Solutions of the pyridones were irradiated under the reaction conditions already described except for solvents and concentrations. The mixtures obtained from reactions in aqueous media were extracted with $CHCl_3$ and the extracts were dried ($MgSO_4$) and evaporated *in vacuo*; mixtures from reactions in organic media were directly evaporated *in vacuo*. To the residues a little ethanol was added. The precipitates (5) were filtered off and the filtrates were chromatographed on silica gel (p.l.c.) to separate compounds (3), (5), (7), and mixtures of (6) and (8). The ratios of (6) and (8) were determined on the basis of the olefinic proton n.m.r. signals.

The *photodimer* (5b) gave colourless prisms, m.p. 214 °C (from EtOH) (Found: C, 71.45; H, 8.6; N, 9.35. $C_{18}H_{26}$-

TABLE 4

N.m.r. data for the products of the reactions of *N*-alkyl-2-pyridones (1b and c)

Compd.	3,3′-H	4,4′-H	5,5′-H	6,6′-H	N-CH_2 [a]	$[CH_2]_n$	CH_3
(3b)	4.03—4.17 m	6.57 br, s	6.57 br, s	4.23—4.37 m	3.00—3.32 m	1.10—1.73 m	0.93 t *J* 7
(5b)	3.57 ddd *J* 10, 5, 2	6.15 ddd *J* 8, 5, 2	6.60 ddd *J* 8, 5, 2	4.08 ddd *J* 10, 5, 2	1.83—2.83 3.37—4.27 [b] m	1.08—1.67 m	0.90 t *J* 7
(6b)	3.27—3.43 m	6.25—6.47 m	6.25—6.47 m	3.97—4.15 m	2.13—2.52 3.10—4.35 [b] m	1.10—1.76 m	0.90 t *J* 7
(7b)	3.31—3.78 m	6.10—6.28 m	6.10—6.28 m	4.01—4.48 m	2.50—3.13 3.20—4.37 [b] m	1.10—1.67 m	0.87 t *J* 7
(8b)	3.50—3.72 m	5.72—6.05 m	6.27—6.67 m	4.00—4.27 m	2.10—2.50 3.10—4.33 [b] m	1.10—1.77 m	0.88 t *J* 7
(3c)	4.00—4.17 m	6.53 br, s	6.53 br, s	4.23—4.37 m	3.00—3.33 m	1.03—1.67 m	0.90 t *J* 7
(5c)	3.58 ddd *J* 10, 5, 2	6.12 ddd *J* 8, 5, 2	6.57 ddd *J* 8, 5, 2	4.08 ddd *J* 10, 5, 2	2.13—2.70 3.33—4.27 [b] m	1.07—1.67 m	0.87 t *J* 7
(6c)	3.27—3.44 m	6.25—6.47 m	6.25—6.47 m	3.97—4.15 m	2.00—2.90 3.13—4.20 [b] m	1.03—1.66 m	0.90 t *J* 7
(7c)	3.30—3.78 m	6.08—6.25 m	6.08—6.25 m	4.00—4.48 m	2.67—4.27 [b] m	1.03—1.67 m	0.90 t *J* 7
(8c)	3.51—3.72 m	5.75—6.08 m	6.25—6.67 m	3.99—4.25 m	1.90—2.80 3.17—4.50 [b] m	1.03—1.63 m	0.88 t *J* 7

[a] The methylene protons of the dimers show different chemical shifts. [b] Overlapped with 3,3′- and 6,6′-H signals.

N_2O_2 requires C, 71.5; H, 8.65; N, 9.25%); $\nu_{max.}$ 1 655 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption. The *photodimer* (5c) gave colourless prisms, m.p. 127 °C (from EtOH) (Found: C, 77.3; H, 10.95; N, 5.25. $C_{34}H_{58}N_2O_2$ requires C, 77.5; H, 11.1; N, 5.35%); $\nu_{max.}$ 1 655 (C=O) and 1 640sh cm^{-1} (C=C); u.v. end absorption.

The other products were not purified for analysis, but their identities were confirmed by the n.m.r. spectra (Table 4) which showed very similar patterns for the pyridone moieties to those of the dimers from (1a).

Irradiation of Neat N-*Methyl-2-pyridone* (1a).—A Pyrex vessel containing (1a) (1 g, 0.009 mol) was irradiated at 25 °C for 15 h. The resulting mixture contained all four dimers (5a)—(8a), and starting material (1a) (t.l.c.); it was carefully chromatographed on silica gel (p.l.c.) ($CHCl_3$–MeOH 95 : 5) to give (5a) (182 mg, 18.2%), (6a) (3.3 mg, 0.3%), (7a) (37 mg, 3.7%), (8a) (6.6 mg, 0.7%), and (1a) (685 mg, 68.5%).

Rearrangement of the Photodimer (7a) *on Silica Gel.*—A mixture of (7a) (37 mg) in $CHCl_3$ with silica gel (300 mg) used for p.l.c. was stirred at room temperature overnight. T.l.c. of the product showed starting material (7a) and the rearrangement product (9).

Rearrangement of the Photodimer (8a) *on Silica Gel.*—A mixture of (8a) (6.6 mg) in $CHCl_3$ (2 ml) with silica gel (100 mg) was stirred at room temperature overnight. T.l.c. of the product mixture showed almost exclusively the rearrangement product (11) [with a trace of (10)].

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