

1,3-Dipolar Character of Six-membered Aromatic Rings. Part XXVII.¹ Photochemically Induced Valence Bond Tautomerism and Dimerisation of 3-Oxido-1-phenylpyridinium

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Irradiation of the title compound (1) yields one of the photochemically allowed symmetrical dimers (16) together with a bicyclic valence bond isomer (7) and two stereoisomers (18) and (20) of thermal addition products of (7) to a second molecule of the starting phenyl betaine. Analogues (19) and (21) of the dimers (18) and (20) were prepared by reaction of isolated (7) with the pyrimidine betaine (2). Irradiation of (1) in allyl alcohol affords an addition product (24) of (7).

1-SUBSTITUTED 3-oxidopyridiniums, *e.g.* (1) and (2), undergo thermal cycloadditions at the 2- and 6-positions with 2π - and 6π -electron addends, and at the 2- and 4-

¹ Part XXVI, J. Banerji, N. Dennis, J. Frank, A. R. Katritzky, and T. Matsuo, preceding paper.

² Part XX, N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Perkin I*, 1976, 2296.

positions with 4π -electron addends.^{2,3} The electro-, site, regio-, and stereo-selectivity of these cycloadditions is rationalised by FMO theory.³ We are now investigating photochemically induced cycloadditions. Photodimer-

³ Part XXI, N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Perkin I*, 1976, 2307.

isation should give products of 2,4-2',4' or 2,6-2',6' addition; there are four regio-possibilities (3)—(6), each of which can take place in two stereo-senses. Preliminary FMO calculations³ indicate that compounds of the type (3) or (4) should be formed preferentially.

four (A—D) were identified. Separation was achieved by preparative thick-layer chromatography (C₆H₆-EtOAc, 9 : 1) on silica gel.

Compound A was shown to be an isomer of (1) by mass spectrometry (*m/e* 171) and elemental analysis

¹H N.m.r. spectra (δ values) of cycloadducts^a

Proton(s)	(7) ^b	(16) ^b	(18) ^b	(19) ^b	(20) ^b	(24) ^b
1	3.23 ^e	3.19 ^d	4.47 ^e	5.08 ^e	4.65 ^f	2.90 ^f
2		4.35 ^e	2.40 ^f		3.21 ^h	
3	5.93 ⁱ		3.50 ^f	3.50 ^f	3.27 ^f	{ 2.09 ^f (3 α) 2.37 ^e (3 β)
4	7.65 ^e	6.59 ^f				4.34 ^f
5	3.65 ^j	4.63 ^h	3.26 ^f	3.18 ^f	3.11	3.40 ^f
6		3.19 ^d				
7		4.35 ^e	3.16 ^f	3.10 ^f	3.67 ^h	
8			4.84 ^f	5.34 ^f	4.85 ^h	
9		6.59 ^f	6.7—7.3 ^k	6.6—7.4 ^k	6.7—7.3 ^k	
10		4.63 ^h	5.90 ^e	5.81 ^e	5.93 ^e	
1'						4.03 ^l
2'						5.00—6.10 ^l
3'						5.00—6.10 ^l
5'				6.37 ^e		
NPh	6.88—7.26	6.70—7.30 ^l	6.7—7.3	6.6—7.4 ^l	6.7—7.3 ^l	6.60—7.30 ^l
CH ₃				2.23 ^e		
Coupling constants (Hz)	(7)	(16)	(18)	(19)	(20)	(24) ^m
1,2		3.3	0.0	0.0	9.1	
1,3	1.5					
1,5	3.8					4.0
1,7		1.5				
1,8						
1,10		6.0	1.5	1.5	1.5	
2,3			0.0	0.0	0.0	
2,6		1.0				
2,7			7.1	8.0	7.9	
3 α , 3 β						18.0
3 α , 4						0.0
3 β , 4						5.0
3,4	6.0					
3,5	1.4		3.7	3.7	3.7	
4,5	1.8	7.6				0.0
5,6		6.0				
6,7		3.3				
9,10		7.6	9.7	10.0	9.9	
8,9			4.8	4.5	4.3	
7,8			0.0	0.0	6.2	

^a In p.p.m. relative to internal Me₄Si. ^b In CDCl₃. ^c Doublet of doublets. ^d Quintet. ^e Singlet. ^f Doublet. ^g Triplet. ^h Quartet. ⁱ Doublet of triplets. ^j Octet. ^k Signal hidden in this region. ^l Complex. ^m *J*_{1,2} 6.0, *J*_{1,3} 1.0 Hz.

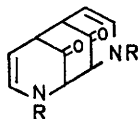
Irradiation of 3-oxido-1-phenylpyridinium (1) in ethyl acetate with a 3 500 Å lamp in a Rayonet reactor (RPQ-100) gave a mixture of five components of which

(C₁₁H₉NO). The i.r. spectrum shows a ν (C=O) at 1 725 cm⁻¹ characteristic of an $\alpha\beta$ -unsaturated ketone in a five-membered ring (*cf.* cyclopent-2-enone⁴ 1 710 cm⁻¹).

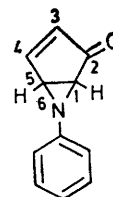


(1) R = Ph

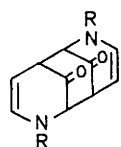
(2) R = 4,6-dimethylpyrimidin-2-yl



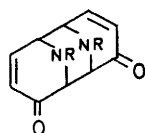
(3)



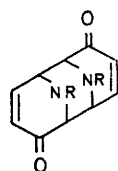
(7)



(4)



(5)



(6)

The n.m.r. spectrum (Table) clearly demonstrates the structure as that of 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7): the bridgehead proton, H-1, gives a double doublet by *cis*-coupling with the other bridgehead proton, H-5, and long-range four-bond coupling with

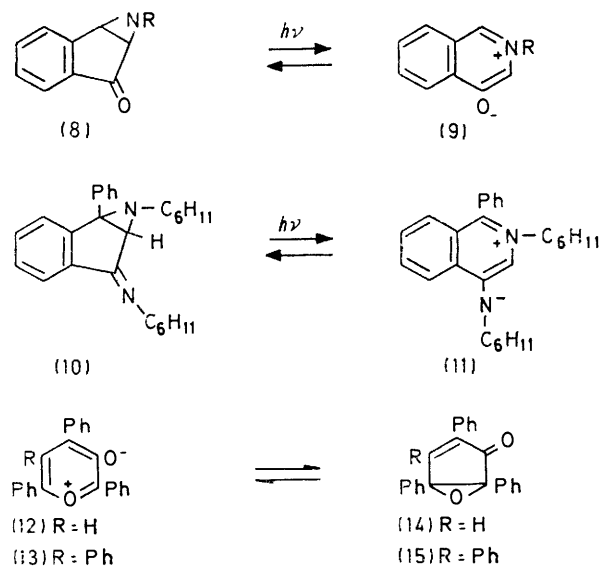
⁴ C. J. Pouchert, 'The Aldrich Library of Infrared Spectra,' Aldrich Chemical Co., Pitman, Bath, 1970, p. 203.

H-3 (*cf.* long-range coupling of 2.1 Hz in the case of 4,5-epoxy-3,4-diphenylcyclopent-2-enone⁵); the vinylic H-3 signal is a double triplet (*cis*-vicinal coupling with H-4 and long-range four-bond coupling with H-1 and -5); the vinylic H-4 signal appears as a double doublet (*cis*-vicinal coupling with H-3 and small vicinal coupling with H-5). All these assignments were confirmed by double resonance experiments; irradiation at the frequency of H-5 (an octet) caused the signals of H-1, -3, and -4 to collapse to doublets. Irradiation at the frequency of H-3 caused the signals of H-4 and -1 to collapse to a singlet and a doublet, respectively. Finally irradiation at the frequency of H-4 converted the double triplet of H-3 into a finely split doublet.

The photoisomer 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7) is presumably formed from 3-oxido-1-phenylpyridinium (1) by a photochemically allowed disrotatory ring closure. Thermal conrotatory ring opening⁶ of the aziridine, 2,3-fused to a five-membered ring, to give the pyridine valence isomer (1), is not formally allowed. Hence, despite the strained structure, the photoisomer (7) is stable in the crystalline form. Isomerism between 3-oxidopyridinium and 6-azabicyclo[3.1.0]hex-3-en-2-one has been postulated to explain the relatively high volatility of the 3-oxidopyridinium in the mass spectrometer.⁷ In the isoquinolinium series, Hansen and Undheim reported⁸ the reversible photochemically allowed valence isomerism between 1-aryl-1a,6a-dihydroindeno[1,2-*b*]azirin-6(1*H*)-ones (8) and 2-aryl-4-oxidoisoquinolinium (9). Again, Lown and Matsumoto⁹ have shown that 1-cyclohexyl-6-(cyclohexylimino)-1a,6a-dihydro-1a-phenylindeno[1,2-*b*]aziridine (10) undergoes photochemical valence tautomerisation to the isoquinolinium imide (11). In the related isoelectronic 3-oxidopyrylium series, the triphenyl derivative (12) is converted into the photoisomer, not isolated but suggested to have structure (14).¹⁰ In the analogous tetraphenyl series, (15) is the stable form and is converted into (13) on irradiation; (13) was isolated as the perchlorate.¹¹

Compound B, m.p. 175–176 °C, was shown to be a dimer of the betaine (1) by mass spectrometry (*m/e* 342) and elemental analysis (C₂₂H₁₈N₂O₂). The i.r. spectrum had a $\nu(\text{C}=\text{O})$ band at 1744 cm⁻¹ characteristic of a saturated ketone. The n.m.r. spectrum (Table) clearly established the structure as that of (1*SR*,2*RS*,6*RS*,7*SR*)-3,8-diphenyl-3,8-diazatricyclo[5.3.1.1^{2,6}]dodeca-4,9-diene-11,12-dione (16). The pair of bridgehead protons H-1 and -6 give rise to a quintet (coupling with H-2 and -7, and H-10 and -5, and long-range *W*-type coupling with H-7 and -2). The second pair of bridgehead protons, H-2 and -7, give a triplet (coupling with

H-1 and -6 and long-range *W*-type coupling with H-6 and -1). The vinylic pair H-5 and -10 give a quartet (*cis*-vicinal coupling with H-4 and -9 and vicinal coupling with bridgehead protons H-6 and -1). The olefinic pair H-4 and -9 give a doublet by *cis*-coupling with H-5 and -10. These assignments were supported by spin-spin decoupling experiments. Irradiation at the H-1 and -6 frequency caused the signal of H-2 and -7 to collapse to a singlet and that of H-10 and -5 to collapse to a doublet. Irradiation at the frequency of the H-2 and -7 signal caused the signals of H-1 and -6 to collapse to a doublet. Again irradiation at the frequency of the olefinic protons H-5 and -10 produced a doublet from H-6 and -1 and a singlet from H-4 and -9. Finally, irradiation at the frequency of the olefinic protons H-4 and -9 caused the signals of H-5 and -10 to collapse to a doublet. The *exo*-stereochemistry is clearly defined by



the small coupling constant (J 3.3 Hz) between H-1 and -2 and H-6 and -7 (the dihedral angle of *ca.* 50° corresponds¹² to a calculated J of *ca.* 3 Hz). The dimer (16) can be crystallised from chloroform, but in solution it decomposes within a few hours at 20 °C. It is presumably formed by a photochemically allowed $[6 + 6]\pi$ 1,3-dipolar cycloaddition between two molecules of the betaine (1). Tropone also gives a $[6 + 6]$ dimer (17) on irradiation by a photochemically allowed $[\pi 6_s + \pi 6_s]$ cycloaddition.¹³

Compound (C), m.p. 221–222 °C, was shown by mass spectrometry (*m/e* 342) and elemental analysis (C₂₂H₁₈N₂O₂) to be another dimer of (1). The i.r. spectrum shows $\nu(\text{C}=\text{O})$ at 1740 cm⁻¹, characteristic¹⁴ of a satur-

⁵ J. W. Lown and K. Matsumoto, *Chem. Comm.*, 1970, 692; *Canad. J. Chem.*, 1971, **49**, 3443.

⁶ E. F. Ullman, *J. Amer. Chem. Soc.*, 1963, **85**, 3529.

⁷ J. M. Dunston and P. Yates, *Tetrahedron Letters*, 1964, 505.

⁸ S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

⁹ T. Mukai, T. Tezuka, and Y. Akasaki, *J. Amer. Chem. Soc.*, 1966, **88**, 5025.

¹⁰ J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, Englewood Cliffs, New Jersey, 1965, p. 34.

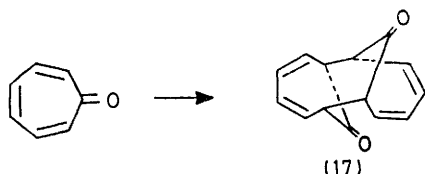
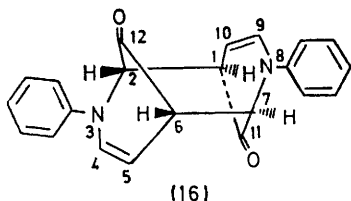
⁵ A. Padwa, *Tetrahedron Letters*, 1964, 813.

⁶ T. L. Gilchrist and R. C. Storr, 'Organic Reactions and Orbital Symmetry,' Cambridge University Press, 1972, p. 58; R. Huisgen and H. Mäder, *Angew. Chem. Internat. Edn.*, 1969, **8**, 604.

⁷ T. Grønneberg and K. Undheim, *Acta Chem. Scand.*, 1971, **25**, 2807; K. Undheim and T. Hurum, *ibid.*, 1972, **26**, 2385.

⁸ P. E. Hansen and K. Undheim, *J.C.S. Perkin I*, 1975, 305.

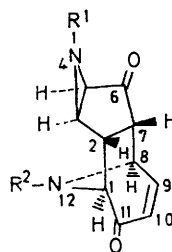
ated ketone in a five-membered ring, and at $1\ 685\ \text{cm}^{-1}$, characteristic¹⁵ of an $\alpha\beta$ -unsaturated ketone in a bicyclo-[3.2.1]octenone system. The n.m.r. spectrum (Table)



demonstrates the substance to be (1*RS*,2*RS*,3*RS*,5*SR*,7*SR*,8*RS*)-4,12-diphenyl-4,12-diazatetracyclo-[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (18). The signals for the vinylic protons H-9 and -10 form a characteristic pattern observed in *N*-phenyl¹⁵ cycloadducts: H-9 gives a quartet (*cis*-vicinal coupling with H-10 and coupling with the bridgehead proton H-8), and the H-10 signal is a doublet (coupling with H-9) further split by *W*-type long-range coupling with the bridgehead H-1. The signals for the bridgehead protons H-1 and -8 appear as a singlet (with fine structure due to long-range coupling with H-10) and a doublet (coupling with H-9), respectively. The signals for H-2 and -7 form a typical AB quartet due to *cis*-vicinal coupling. The lack of appreciable coupling between H-7 and -8 and between H-1 and -2 establishes the *exo*-configuration about the 2,7-bridge. The signals for the bridgehead protons H-3 and -5 also form a typical AB quartet due to *cis*-vicinal coupling. Again the lack of appreciable coupling between H-2 and -3 establishes the *endo*-configuration (relative to the 1,8-bridge) for the aziridine ring. These assignments were confirmed by double resonance: irradiation at the frequency of H-9 simplified the signals of H-8 and -10 to singlets. Irradiation at that of H-3 caused the signal of H-5 to collapse to a singlet, and irradiation at that of H-2 caused the signal of H-7 to collapse to a singlet. The dimer (18) is stable in crystal-line form but not in solution.

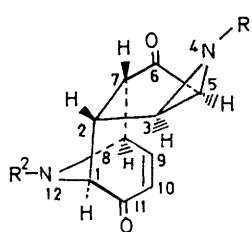
Compound (D), m.p. 218–219 °C, had a mass spectrum (*m/e* 342) identical with that of compound (C) and an elemental analysis consistent with the formula $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$. The i.r. spectrum had $\nu(\text{C}=\text{O})$ bands at $1\ 735\ \text{cm}^{-1}$, characteristic of a saturated ketone in a five-membered ring, and $1\ 680\ \text{cm}^{-1}$, characteristic of an $\alpha\beta$ -unsaturated ketone. The n.m.r. spectrum (Table) demonstrates the compound to be (1*RS*,2*SR*,3*SR*,5*RS*,7*RS*,8*RS*)-4,12-diphenyl-4,12-diazatetracyclo-[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (20). Again the signals of the vinylic protons H-9 and -10 form the characteristic pattern observed in *N*-phenyl cyclo-

adducts,¹⁵ *i.e.* a quartet (coupling with H-8 and -10) and a double doublet (coupling with H-9 and -1), respectively. The signals of the bridgehead protons H-8 and -1 appear as a quartet (coupling with both H-7 and -9) and a doublet (coupling with H-2, with fine structure due to long-range *W*-type coupling with H-10), respectively. The signals for H-7 and -2 can be analysed as a pair of quartets on a first-order basis. The appreciable coupling between H-1 and -2 and between H-8 and -7 establishes the *endo*-configuration about the 2,7-bridge. Again the signals for the bridgehead protons H-3 and -5 form a typical AB quartet due to *cis*-vicinal coupling. The lack of appreciable coupling between H-2 and -3 establishes the *exo*-configuration (relative to the 1,8-bridge) for the aziridine ring. These assignments were confirmed by double resonance. Irradiation at the frequency of H-1 caused the broad doublet of H-10 to sharpen, and irradiation at that of H-10 caused the broad doublet of H-1 to sharpen. Irradiation at the frequency of H-9 caused the H-10 and -8 signals to collapse to a broad singlet and a doublet, respectively. Irradiation at that of the bridgehead H-8 caused the H-7 signal to collapse to a doublet, and irradiation at that of the bridgehead H-7 caused the quartet of H-8 to



(18) $\text{R}^1 = \text{R}^2 = \text{Ph}$

(19) $\text{R}^1 = \text{Ph}, \text{R}^2 = 4,6\text{-dimethylpyrimidin-2-yl}$



(20) $\text{R}^1 = \text{R}^2 = \text{Ph}$

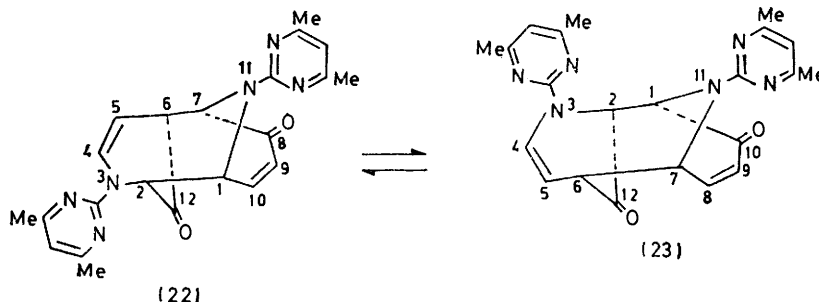
(21) $\text{R}^1 = \text{Ph}, \text{R}^2 = 4,6\text{-dimethylpyrimidin-2-yl}$

collapse to a doublet. Finally irradiation at the frequency of H-2 caused the H-1 signal to collapse to a broad singlet.

6-Phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7), acting as a 2π -electron component, reacted with 1-(4,6-dimethylpyrimidin-2-yl)-3-oxidopyridinium (2), generated from the dimeric mixture (22) \rightleftharpoons (23), to give a mixture of

¹⁵ N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 746.

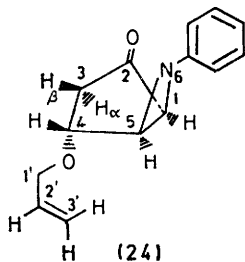
two stereoisomeric cycloadducts. The cycloadduct of m.p. 268–269 °C had an elemental analysis consistent with the formula $C_{22}H_{20}N_4O_2$ and its mass spectrum showed m/e 372. The i.r. spectrum showed $\nu(C=O)$ bands at 1 742 cm^{-1} , characteristic of a saturated ketone in a five-membered ring, and 1 695 cm^{-1} , characteristic of an $\alpha\beta$ -unsaturated ketone. The u.v. spectrum has λ_{max} 235 nm, characteristic of an $\alpha\beta$ -unsaturated ketone



in an azabicyclo[3.2.1]octenone system.¹⁵ The n.m.r. spectrum (Table) confirmed the identification as (1*RS*, 2*RS*, 3*RS*, 5*SR*, 7*SR*, 8*RS*)-12-(4,6-dimethylpyrimidin-2-yl)-4-phenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (19).

A second cycloadduct, m.p. 260–261 °C, $C_{22}H_{20}N_4O_2$ (elemental analysis and m/e 372), $\nu(C=O)$ 1 740 and 1 695 cm^{-1} , λ_{max} 235 nm, proved to be (1*RS*, 2*SR*, 3*SR*, 5*RS*, 7*RS*, 8*RS*)-12-(4,6-dimethylpyrimidin-2-yl)-4-phenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (21).

The stereoisomeric pairs (18) and (20), and (19) and (21) are formed by thermally allowed $[4 + 2]\pi$ 1,3-dipolar cycloadditions of the valence bond tautomer (7), acting as a 2π -electron component, with the betaines (1) and (2), respectively.



Irradiation of 3-oxido-1-phenylpyridinium in allyl alcohol yielded a single major product (20%) [small quantities of compounds (7), (16), (18), and (20) could be detected by t.l.c.], $C_{14}H_{15}NO_2$ (analysis and m/e 229). The i.r. spectrum had a $\nu(C=O)$ band at 1 745 cm^{-1} , characteristic of a saturated ketone in a five-membered ring. The n.m.r. spectrum (Table) showed the compound to be (1*SR*, 4*RS*, 5*RS*)-6-phenyl-4-(prop-2-enyloxy)-6-azabicyclo[3.1.0]hexan-2-one (24). The signals for the bridgehead protons, H-1 and -5, form an AB quartet (J_{cis} 4 Hz). The methine proton H-4 gives a

¹⁶ R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, Suppl. 7, p. 383.

doublet [*cis*-coupling with H-3 β ; $J_{4,3\alpha}$ 0 Hz since the dihedral angle $H(4)CCH(3\alpha) = 90^\circ$]. The methylene proton H-3 α gives a doublet (geminal $J_{3\alpha,3\beta}$ 18 Hz, *cf.* cyclopentanone, $J_{gem}^{16} - 19.0$ to -19.5 Hz) and the methylene proton H-3 β gives a double doublet by further coupling to H-4 (5 Hz). The propenyloxy-group is *trans* to the aziridine ring since the signals of both H-4 and -5 are doublets. The olefinic proton signals form

a complex ABX multiplet. The double doublet at δ 4.03 is due to the methyleneoxy-group (H-1') coupled to the adjacent vinyl α -proton by 6 Hz (*cf.* 4–10 Hz for similar systems¹⁷) and to the *trans*- β -vinyl proton by 1 Hz (*cf.* 0.5–2 Hz for similar systems¹⁷). The aziridine (24) was presumably formed by Michael addition of the allyl alcohol to the initially formed photoisomer, 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7). Preferential addition of the alcohol to the least hindered face of the photoisomer (the face *trans* to the aziridine ring) accounts for the observed stereochemistry.

EXPERIMENTAL

M.p.s. were determined with a Reichert apparatus. Spectra were recorded with the following instruments: i.r. Perkin-Elmer 257; mass, Hitachi-Perkin-Elmer RMU-6E; u.v. Unicam SP 800A; n.m.r., Varian HA-100. Compounds were purified until they were observed as single spots on t.l.c. [silica gel (PF 254); benzene-EtOAc (9:1)] Irradiations with an external light source were performed with a Rayonet reactor (RPQ-100), with 3 500 Å lamps, in quartz flasks.

For irradiation with an internal light source a medium-pressure mercury arc, type Hanovia PCR 1L, and water-cooled Pyrex containers were used. All irradiations were performed at 25–35 °C.

Preparative layer chromatography was performed on silica gel (Merck PF 254). The plates were developed with benzene-EtOAc (9:1). The fractions were scraped off the plates and isolated by extraction with EtOAc.

Irradiation of 3-Oxido-1-phenylpyridinium (1).—(a) In EtOH-EtOAc. 3-Oxido-1-phenylpyridinium (3.4 g, 0.02 mol) in absolute EtOH (30 ml) and EtOAc (350 ml) was irradiated with an external light source for 20 h. The red solution was evaporated to dryness at 30 °C and 10 mmHg, and the residue separated by thick-layer chromatography. 6-Phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7) (180 mg, 6%; R_F 0.33) crystallised from EtOH-H₂O as yellow needles, m.p. 78–79 °C (Found: C, 76.7; H, 5.4; N, 8.3. $C_{11}H_9NO$

¹⁷ L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' eds. D. H. R. Barton and W. Doering, Pergamon, Oxford, 1959, p. 85.

requires C, 77.2; H, 5.3; N, 8.2%); ν_{\max} (Nujol) 1 725 ($\alpha\beta$ -unsat. ketone C=O) and 1 600 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 229 nm (log ϵ 4.00); m/e 171.

(1RS,2RS,6RS,7SR)-3,8-Diphenyl-3,8-diazatricyclo-[5.3.1.1^{2,6}]dodeca-4,9-diene-11,12-dione (16) (1 g, 29%; R_F 0.60) was isolated as pale yellow needles, m.p. 175–176 °C (decomp.) (from CHCl_3) (Found: C, 76.8; H, 5.3; N, 8.1. $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ requires C, 77.2; H, 5.3; N, 8.2%); ν_{\max} (Nujol) 1 744 (sat. ketone C=O), 1 632 (enamine C=C), 1 600 and 1 500 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 222 (log ϵ 4.35), 268 (4.35), and 341 nm (3.86); m/e 342. (1RS,-2RS,3RS,5SR,7SR,8RS)-4,12-Diphenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (18) (95 mg, 3%; R_F 0.44) was isolated as yellow needles, m.p. 221–222 °C (from EtOH) (Found: C, 77.0; H, 5.4; N, 7.9%); ν_{\max} (CDCl_3) 1 740 (sat. ketone C=O), 1 685 ($\alpha\beta$ -unsat. ketone C=O), 1 600, and 1 500 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 236 nm (log ϵ 4.35); m/e 342. (1RS,2SR,3SR,5RS,7RS,-8RS)-4,12-Diphenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]-dodec-9-ene-6,11-dione (20) (30 mg, 1%; R_F 0.22) crystallised as yellow needles, m.p. 218–219 °C (EtOH) (Found: C, 76.7; H, 5.3; N, 7.9%); ν_{\max} (CDCl_3) 1 735 (sat. ketone C=O), 1 680 ($\alpha\beta$ -unsat ketone, C=O), 1 600, and 1 500 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 236 nm (log ϵ 4.33); m/e 342.

(b) *In allyl alcohol.* 3-Oxido-1-phenylpyridinium (2.8 g, 0.016 mol) in allyl alcohol (80 ml) was irradiated with an internal light source for 30 h. The red solution was evaporated to dryness at 80 °C and 10 mmHg and the red oily residue purified by preparative thick-layer chromatography. (1SR,4RS,5RS)-6-Phenyl-4-(prop-2-enyloxy)-6-azabicyclo[3.1.0]hexan-2-one (24) (0.7 g, 20%; R_F 0.44) was isolated as a yellow unstable oil (Found: C, 73.6; H, 6.2; N, 6.8. $\text{C}_{14}\text{H}_{15}\text{NO}_2$ requires C, 73.3; H, 6.6; N, 6.1%);

ν_{\max} (CDCl_3) 1 745 (sat. ketone C=O), 1 600, and 1 500 cm^{-1} (benzene, C=C); m/e 229.

Reaction of 6-Phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one (7) with the Mixture of 3,11-Bis-(4,6-dimethylpyrimidin-2-yl)-3,11-diazatricyclo[5.3.1.1^{2,6}]dodeca-4,9-diene-8,12-dione (22) and 3,11-Bis-(4,6-dimethylpyrimidin-2-yl)-3,11-diazatricyclo[5.3.1.1^{2,6}]dodeca-4,8-diene-10,12-dione (23).—Compound (7) (100 mg, 0.6×10^{-3} mol) and the betaine dimer mixture (120 mg, 0.3×10^{-3} mol) in dry MeCN (30 ml) were stirred at room temp. for 100 h. The solvent was removed at 60 °C and 10 mmHg and the solid residue separated by thick-layer chromatography. (1RS,2RS,-3RS,5SR,7SR,8RS)-12-(4,6-Dimethylpyrimidin-2-yl)-4-phenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (19) (60 mg, 27%) was isolated as pale yellow needles, m.p. 268–269 °C (from EtOH) (Found: C, 71.1; H, 5.8; N, 14.5. $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2$ requires C, 71.0; H, 5.4; N, 15.0%); ν_{\max} (CDCl_3) 1 742 (sat. ketone C=O), 1 695 ($\alpha\beta$ -unsat. ketone C=O), 1 595, and 1 495 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 235 nm (log ϵ 4.41); m/e 372. (1RS,2SR,3SR,-5RS,7RS,8RS)-12-(4,6-Dimethylpyrimidin-2-yl)-4-phenyl-4,12-diazatetracyclo[6.3.1.0^{2,7}.0^{3,5}]dodec-9-ene-6,11-dione (21) (15 mg, 7%) crystallised as yellow needles, m.p. 260–261 °C (EtOH) (Found: C, 71.2; H, 5.3; N, 14.6%); ν_{\max} (CDCl_3) 1 740 (sat. ketone C=O), 1 695 ($\alpha\beta$ -unsat. ketone C=O), 1 595 and 1 500 cm^{-1} (benzene C=C); λ_{\max} (EtOH) 235 nm (log ϵ 4.44); m/e 372.

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