Photochemically Induced Valence Bond Tautomerism and Dimerisation of 3-Oxido-1-phenylpyridinium[1]

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Summary Irradiation of the title compound (**1a**) yields one of the expected dimers (**4**) together with the valence bond isomer (**5**) and two isomeric products (**10**) and (**11**) of thermal cycloaddition of the valence bond tautomer (**5**) to the starting betaine (**1a**).

1-Substituted 3-oxidopyridiniums (**1**) undergo thermal cycloadditions at the 2,6-positions with 2π and 6π electron addends and at the 2,4-positions with 4π addends.[2] The electro-, site-, regio- and stereo-selectivity of these cycloadditions is rationalised by FMO theory.[3] We are now investigating photochemically induced cycloadditions. Photo-dimerisation should give products of 2,4–2′,4′ or 2,6–2′,6′ addition; there are four regio-possibilities including (**2**) and (**3**), each of which can take place in two stereosenses. Preliminary FMO calculations (*cf.* ref. 3) indicate that compounds of type (**2**) or (**3**) should be formed preferentially.

Irradiation of 3-oxido-1-phenylpyridinium (**1a**) in ethyl acetate with a 3500 Å lamp in a Rayonet reactor RPQ-100 gave a mixture shown by t.l.c. to contain five spots which we designate A—E in order of decreasing R_f. Separation was achieved by preparative layer chromatography (C_6H_6–EtOAc, 9 : 1) on silica gel.

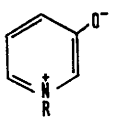
Compound A was shown to be a dimer of (**1a**) by mass spectrometry and analysis. The n.m.r. spectrum clearly established structure (**4**): the stereochemistry is defined as *exo* by the *J* values given in (**4**). The mass spectral frag-

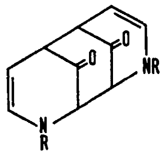
Table. ^1H n.m.r. chemical shifts (δ) and coupling constants at 100 MHz[a].

H	(**10**)		(**11**)	
	δ	*J*/Hz	δ	*J*/Hz
1	4·47s	1·5 (H-10)	4·65d	1·5 (H-10), 9·1 (H-2)
10	5·90dd	1·5 (H-1), 9·7 (H-9)	5·93dd	1·5 (H-1), 9·9 (H-9)
8	4·84d	4·8 (H-9)	4·85t	4·3 (H-9), 6·2 (H-7)
7	3·16d	7·1 (H-2)	3·67dd	6·2 (H-8), 7·9 (H-2)
5	3·26d	3·7 (H-3)	3·11d	3·7 (H-3)
3	3·50d	3·7 (H-5)	3·27d	3·7 (H-5)
2	2·40d	7·1 (H-7)	3·21d	9·1 (H-1), 7·9 (H-7)

[a] H-9 signal is hidden by aromatic proton peaks.

mentation pattern showed a prominent molecular ion, but then no further peaks (with the exception of loss of CO from the dimer) until the base peak at m/e 171 for the monomer: the fragmentation then proceeds as for the monomer.[4] Dimer (**4**) can be crystallised from $CHCl_3$,† but on standing in solution decomposes within a few hours at 20 °C; hence isolation must be carried out rapidly. The formation of (**4**) from (**1a**) is clearly in line with the preliminary FMO approach and further calculations are in progress.


(1)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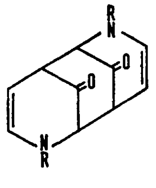
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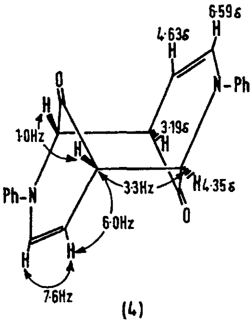

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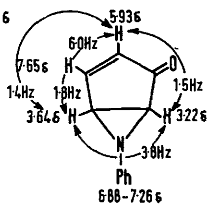
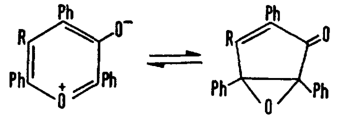


(5)

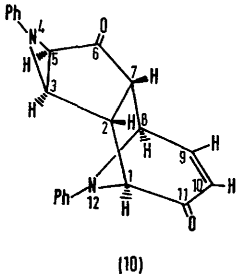
Compound D was shown to be an isomer of (**1a**) by mass spectrometry and analysis. The n.m.r. spectral parameters indicated in (**5**) clearly demonstrate the structure as 6-phenyl-6-azabicyclo[3,1,0]hex-3-en-2-one (**5**). There is no precedent to such valence bond tautomerism in pyridine chemistry; however, in the related 3-oxidopyrylium series, the triphenyl derivative (**6**) is converted into a photoisomer, not isolated but suggested to be (**7**).[5] In the analogous tetraphenyl series (**9**) is the stable form and is converted into (**8**) on irradiation; (**8**) was isolated as its perchlorate.[6]

The azabicyclohexenone (**5**) is stable in crystalline form, but rapidly decomposes in solution. The formation of (**5**) from (**1a**) is a photochemically allowed process.

Compound C was shown by mass spectrometry and analysis to be another dimer of (**1a**), and structure (**10**) is demonstrated by the n.m.r. spectral parameters indicated in the Table. Our belief that (**10**) is formed by a thermally allowed cycloaddition of 3-oxido-1-phenylpyridinium (**1a**) with the valence bond tautomer (**5**) acting as a 2π electron component, is supported by the isolation of the expected addition product from isolated (**5**) and 1-(4,6-dimethylpyrimidin-2-yl)-3-oxidopyridinium. The regioselectivity of formation of (**10**) is presently under investigation by the FMO method. Again dimer (**10**) is stable in crystalline form, but not in solution.


(6) R = H (7) R = H

(8) R = Ph (9) R = Ph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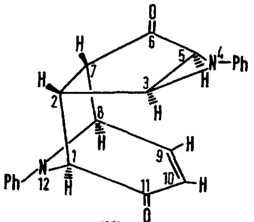
(11)

Compound E is the *endo*-analogue of the *exo*-dimer (**10**). Structure (**11**) was demonstrated for E by spectral data, particularly the n.m.r. (see Table) and the mass spectrum which was identical with that of (**10**). The structure of compound B is under investigation.

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† Satisfactory analytical data were obtained for all the compounds reported.

[1] *Cf.* the series '1,3-Dipolar Character of Six-Membered Aromatic Rings,' Part XVIII, N. Dennis, A. R. Katritzky, S. K. Parton, Y. Nomura, Y. Takahashi, and Y. Takeuchi, to be submitted to *J.C.S. Perkin I.*

[2] N. Dennis, B. Ibrahim, and A. R. Katritzky, to be submitted to *J.C.S. Perkin I.*

[3] N. Dennis, B. Ibrahim, and A. R. Katritzky, to be submitted to *J.C.S. Perkin I.*

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

[5] E. F. Ullman, *J. Amer. Chem. Soc.*, 1963, **85**, 3529.

[6] J. M. Dunston and P. Yates, *Tetrahedron Letters*, 1964, 505.