Analogy between Furan and Thiophen Photochemistry

By AXEL COUTURE and ALAIN LABLACHE-COMBIER*

(*Laboratoire de Chimie Organique Physique, Université des Sciences et Techniques de Lille, B.P. 36, 59, Villeneuve d'Ascq, France*)

Summary Irradiation in propylamine of furan and 2,4- and 2,5-dimethylfuran leads to the same *N*-propylpyrrole as is obtained from the corresponding thiophens.

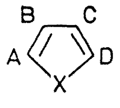
WE report that the irradiation of furans in propylamine (Hanau NN 1544; 15 W low-pressure mercury lamp; quartz vessel; N_2 bubbled through reactor) leads to the same pyrroles as does irradiation of the corresponding thiophens under the same condition (see Table).[1,2]

Srinivasan and Hiraoka, in a study of the gas-phase photochemistry of the furans we irradiated,[3–5] suggested that a primary product, depending upon the compound, is a cyclopropenyl-ketone or -aldehyde formed by ring contraction. Hiraoka has predicted which cyclopropenyl-ketones or -aldehydes would be intermediates in the photoreaction of furans.[6] (I)(O) has been already trapped,[3] and (VI)(O) is a minor product of the gas-phase photolysis of 2,5-dimethylfuran.[7] The formation of cyclopropenyl-ketones or -aldehydes from the other methyl- and dimethyl-furans has not yet been proved. Van Tamelen[8] isolated ketone (VIII) in the irradiation of 2,5-di-t-butylfuran in pentane, and (VIII) is an intermediate in the photoisomerisation of 2,5-di-t-butylfuran to 2,4-di-t-butylfuran.

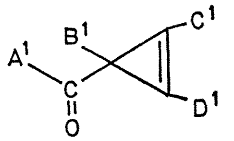
We suggest that the pyrroles are formed by the mechanism in the Scheme, which is analogous to that proposed for the reactions of thiophens.[2] Pyrroles are formed from an unstable imine obtained by the reaction with propylamine of the cyclopropenyl-ketone or -aldehyde from furans or the thioketone of thioaldehyde from thiophens.

The structure of the cyclopropenyl-ketone or -aldehyde which is a primary product of the irradiation can be deduced from the pyrroles formed. The Table shows that the ones trapped are those which were predicted.[6] (V)(O) is the major product of the photoreaction of 3-methylfuran, and (IV)(O), enantiomer of (II)(O), would lead, at least partially, to 2-methyl-*N*-propylpyrrole, as does (II)(O).

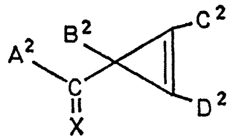
The formation of the same pyrroles from furans as from the corresponding thiophens indicates that pyrroles are formed from thiophens by reaction of a cyclopropenyl-thioketone or -thioaldehyde with the primary amine, and not by a mechanism in which the intermediate involves sulphur 3*d* orbitals as proposed by Wynberg *et al.* for photoisomerisation of thiophen.[9] Irradiation of the thiophens we studied leads to the cyclopropenyl-thioketones or -thioaldehydes analogous to the cyclopropenyl-ketones or -aldehydes formed from the corresponding furans. The fact that the ratio of 2-methyl-*N*-propylpyrrole to 3-methyl-*N*-propylpyrrole obtained from 2-methylthiophen is the reverse of that obtained from 2-methyl-furan might be due to the formation of more (III)(S) than (II)(S). The greater amount of 3-methyl-*N*-propylpyrrole formed from



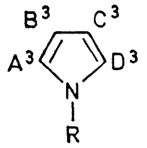
(A)



(B)



(C)

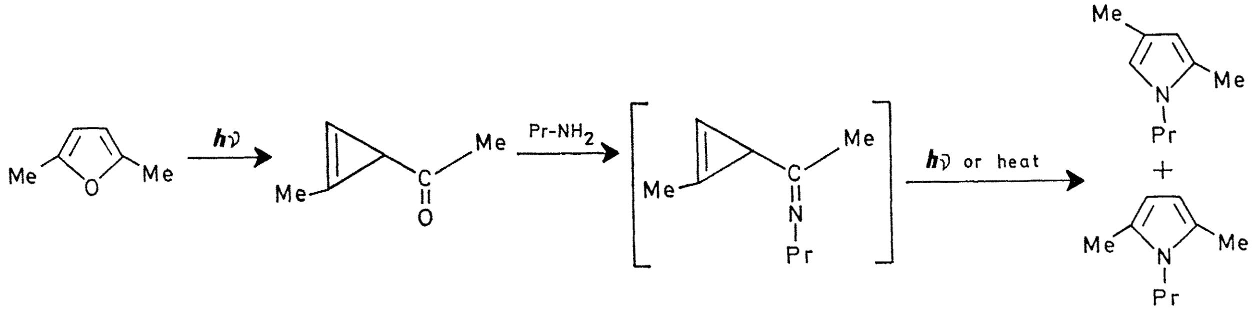


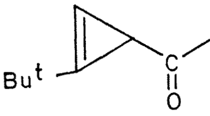
(D)

Starting material (A)	Hiroaka calculations for (B)	Intermediates trapped (C)		Products obtained (ratio) (D)		Pyrroles formed (%)	
		X=O	X=S	X=O	X=S	X=O	X=S
$A=B=C=D=H$	$A^1=B^1=C^1=D^1=H$ (I)(O)	$A^2=B^2=C^2=D^2=H$ (I)(O)	$A^2=B^2=C^2=D^2=H$ (I)(S)	$A^3=B^3=C^3=D^3=H$[a]	$A^3=B^3=C^3=D^3=H$	1	8
$A=Me,B=C=D=H$	$A^1=B^1=C^1=H,D^1=Me$ (II)(O)	$A^2=B^2=C^2=H,D^2=Me$ (II)(O)	$A^2=B^2=C^2=H,D^2=Me$ (II)(S) $A^2=Me,B^2=C^2=D^2=H$ (III)(S)	$A^3=Me,B^3=C^3=D^3=H$[b] + $A^3=C^3=D^3=H,B^3=Me$[c] (1:8)	$A^3=Me,B^3=C^3=D^3=H$ + $A^3=C^3=D^3=H,B^3=Me$ (8:1)	3	6
$A=C=D=H,B=Me$[d]	$A^1=B^1=D^1=H,C^1=Me$ (IV)(O) $A^1=C^1=D^1,B^1=Me$ (V)(O)	$A^2=C^2=D^2=H,B^2=Me$ (V)(O)	$A^2=C^2=D^2=H,B^2=Me$ (V)(S)	$A^3=C^3=D^3=H,B^3=Me$[e]	$A^3=C^3=D^3=H,B^3=Me$	1	7
$A=D=Me,B=C=H$	$A^1=D^1=Me,B^1=C^1=H$ (VI)(O)	$A^2=D^2=Me,B^2=C^2=H$ (VI)(O)	$A^2=D^2=Me,B^2=C^2=H$ (VI)(S)	$A^3=C^3=Me,B^3=D^3=H$[c] + $A^3=D^3=Me,B^3=C^3=H$[e] (1:8)	$A^3=C^3=Me,B^3=D^3=H$ + $A^3=D^3=Me,B^3=C^3=H$	3	5
$A=C=Me,B=D=H$[f]	$B^1=D^1=Me,A^1=C^1=H$ (VII)(O)	$B^2=D^2=Me,A^2=C^2=H$ (VII)(O)	$A^2=C^2=Me,B^2=D^2=H$ (VII)(S)	$A^3=C^3=Me,B^3=D^3=H$[e]	$A^3=C^3=Me,B^3=D^3=H$ + $A^3=D^3=Me,B^3=C^3=H$ (1:4)	1	6

[a] Characterised by mass spectroscopy.
[b] Mass spectral comparison.
[c] N.m.r. comparison.
[d] Prepared as in ref. 10.
[e] Prepared as in ref. 11.

2-methylfuran could arise from isomerization of 2-methylfuran to 3-methylfuran prior to reaction of the furan with the amine. Formation† of only a small amount of 3-methylfuran in the unchanged furan rules out this hypothesis.





(VIII)

SCHEME

(*Received, March* 22*nd*, 1971; *Com.* 378.)

---

† G.l.c. on the crude irradiation mixture of 2-methylfuran in propylamine indicated the presence of a product (3% of unchanged 2-methylfuran) having the same retention time as that of 3-methylfuran.

[1] A. Couture and A. Lablache-Combier, *Chem. Comm.*, 1969, 524.
[2] A. Couture and A. Lablache-Combier, *Tetrahedron*, 1971, **27**, 1059.
[3] R. Srinivasan, *Pure Appl. Chem.*, 1968, **16**, 65 and refs. cited therein.
[4] H. Hiraoka and R. Srinivasan, *J. Amer. Chem. Soc.*, 1968, **90**, 2720.
[5] A. Lablache-Combier and M. A. Rémy, *Bull. Soc. chim. France*, 1971, 679.
[6] H. Hiraoka, *J. Phys. Chem.*, 1970, **74**, 574.
[7] S. Boue and R. Srinivasan, *J. Amer. Chem. Soc.*, 1970, **92**, 1824.
[8] E. E. Van Tamelen and Th. H. Whitesides, *J. Amer. Chem. Soc.*, 1968, **90**, 3894.
[9] H. Wynberg, R. M. Kellog, H. Van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, 1967, **89**, 3501.
[10] D. M. Burns, *Organic Syntheses*, 1963, Col. Vol. IV, 628.
[11] Th. Morel and P. E. Verkade, *Rec. trav. Chim.* 1951, **70**, 35.