Thiophen Photochemistry

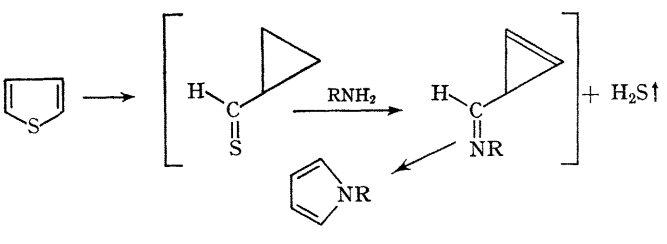
By A. COUTURE and A. LABLACHE-COMBIER

(*Laboratoire de Chimie Organique Physique. Faculte des Sciences, P.B.* 36—59 *Lille -Gare, France*)

Summary Irradiation of thiophens in primary amines leads to pyrroles.

IRRADIATION (Hanau NN 1544, 15 w, low-pressure mercury lamp, quartz vessel, 3 hr.) of solutions of thiophens in amines (1%) gave pyrroles. During the photoreactions H_2S was formed: it was removed in a stream of N_2 and characterised by reaction with lead(II) acetate. The pyrroles (5%) were isolated from tars by chromatography (silica gel) and/or by v.p.c. (Autoprep A 700 SE 30, 10 ft. column), and characterised by their n.m.r., i.r. and u.v. spectra and by analysis.

Thiophen in cyclohexylamine gave *N*-cyclohexylpyrrole,[1] 3-methylthiophen in cyclohexylamine gave *N*-cyclohexyl-3-methylpyrrole and in propylamine gave *N*-propyl-3-methylpyrrole.[2] 2-Methylthiophen in propylamine gave both *N*-propyl-2-methylpyrrole and *N*-propyl-3-methylpyrrole (5 : 1). In cyclohexylamine only *N*-cyclohexyl-2-methylpyrrole is formed.

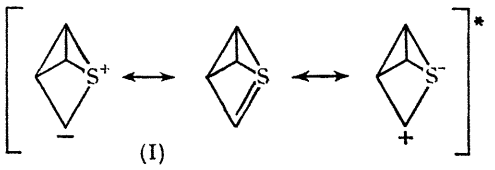


No pyrrole is formed by irradiation in piperidine. The pyrrole formation is not a thermal reaction.

A mechanism (Scheme) is suggested by analogy (a) with

the photo-rearrangement of 2,5-di-t-butylfuran to give 2,4-di-t-butylfuran,[3] (a cyclopropene ketone has been shown to be the intermediate), and (b) with the photo-rearrangement of 3,5-diarylisoxazoles to 2,5-diaryloxazoles (3-aroyl-2-aryl-1-azirine intermediates have been isolated).[4] The postulated intermediates (Scheme) have not been isolated, and a mechanism involving Wynberg's intermediate (I)[5] cannot be ruled out.

The formation of two pyrroles from 2-methylthiophen can be explained by the thioaldehyde route or by Wynberg's mechanism, but the fact that 3-methylthiophen leads only to the 3-methylpyrrole cannot. A possible explanation of this difference is prior rearrangement of 2-methyl- to 3-methyl-thiophen. However we found no trace of 3-methylthiophen in the recovered 2-methylthiophen, and irradiation of 2-methylthiophen in cyclohexane gave no observable 3-methylthiophen.



(I)

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[1] M. P. Fegley, N. M. Bortnick, and C. H. McKeever, *J. Amer. Chem. Soc.*, 1957, **79**, 4144.
[2] F. Ya. Perveev, V. Ya. Statsevich, and L. P. Gavryuchenkova, *Zhur. org. Khim.*, 1966, **2**, 397.
[3] E. E. van Tamelen and Th. H. Whitesides, *J. Amer. Chem. Soc.*, 1968, **90**, 3894.
[4] E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, 1967, **89**, 6911.
[5] H. Wynberg, R. M. Kellog, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, 1967, **89**, 3501.