

Further Evidence for Scrambling in the Photochemical Rearrangement of 2-Phenylthiophen

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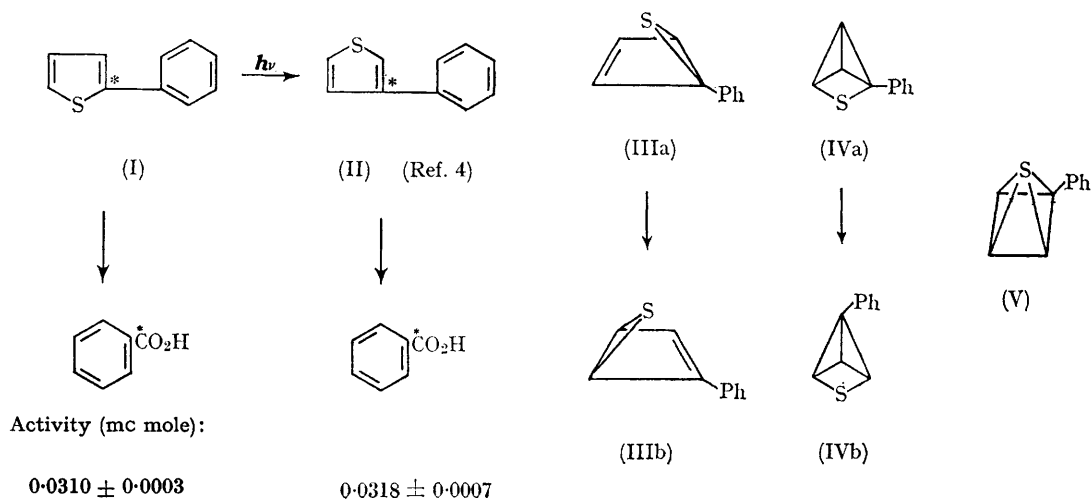
OUR recent discovery¹ that 2-phenylthiophen (I) rearranged smoothly to 3-phenylthiophen (II) upon irradiation in solution, prompted us to propose Dewar-type intermediates (IIIa, b) for this reaction.

We have now carried out a ¹⁴C tracer experiment²

which shows unequivocally that the phenyl group remains attached to the same carbon atom of the thiophen ring throughout the rearrangement. Thus when 2-phenyl-[2,5-¹⁴C]thiophen (I) in ether solution was irradiated¹ and the product (II) isolated by preparative gas-liquid chromatography,

the benzoic acid obtained by oxidation³ of (II) had the same activity as the benzoic acid obtained from (I).

This evidence supports Dewar structures (IIIa,



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¹ H. Wynberg and H. van Driel, *J. Amer. Chem. Soc.*, **1965**, **87**, 3998.

² For a similar experiment with alkylbenzenes see: K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Amer. Chem. Soc.*, **1965**, **87**, 675; E. M. Arnett and I. M. Bollinger, *Tetrahedron Letters*, **1964**, 3803. The synthesis of radioactive (I) from [1,4-¹⁴C]succinic acid according to A. Chrzaszczewska, *Roczniki Chem.*, **1925**, **5**, 33; [*Chem. Abs.*, **1926**, **20**, 1078], was worked out by Mr. H. J. M. Sinnige, using the facilities of Prof. Dr. N. Gruber, Department of Biochemistry of this University. The activity measurements were performed by Dr. J. U. Veenland using a Packard Tri-Carb liquid-scintillation spectrometer 314-ES, in the laboratory of Prof. Dr. Th. J. de Boer, University of Amsterdam. The co-operation of all is gratefully acknowledged.

³ The oxidation of the phenylthiophens to benzoic acid proceeded in 12–30% yield using essentially the conditions described previously, H. Wynberg and A. P. Wolf, *J. Amer. Chem. Soc.*, **1963**, **85**, 3308, except that the reaction time was shorter (2 hrs.). The benzoic acid was rigorously purified and identified.

⁴ Formulae (I) and (II) do not include the location nor extent of the activity of the carbon atoms other than the one identified in our degradative experiments. Although this is known for (I) (namely C-5), it is unknown for (II).

⁵ E. E. van Tamelen, *Angew. Chem.*, **1965**, **77**, 759, mentions a "valene" structure for furan. The number of distinguishable "valene" structures one can write for thiophen obviously depends on the substitution pattern. For identically doubly labelled monosubstituted thiophens, four "valene" structures are possible.

⁶ Using unsymmetrically disubstituted thiophens we have recently obtained support for (IV) (H. Wynberg, H. van Driel, and G. E. Beekhuis, paper in preparation).