

## Extrusion of Nitrogen in Sulphoximine Pyrolyses

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**Summary** Vapour phase pyrolysis of phthalimidodiphenylsulphoximide (**1a**) gives benzocyclobutenedione (70%), diphenyl sulphoxide (80%), and nitrogen; other sulphoximides fragment analogously.

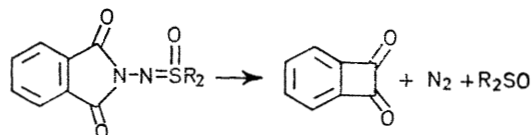
THE oxidation of several *N*-amino-lactams by lead tetraacetate in the presence of sulphoxides leads to the formation of sulphoximides [e.g. (**1**)], usually in high yields.<sup>1</sup> The sulphoximides can be cleaved thermally<sup>2</sup> or photochemically<sup>1</sup> to give products derived from the amino-nitrene intermediates. For example, these intermediates add to olefins to give aziridines.<sup>1</sup>

Pyrolysis of sulphoximides by sublimation of the vapour through a heated tube at low pressure has now been investigated, and found to provide a very efficient way of cleaving the sulphoximides. Moreover, the products are mainly those derived by extrusion of nitrogen from the heterocyclic system. Thus, pyrolysis of the diphenylsulphoximide (**1a**)† at 420°/0.01 Torr gave benzocyclobutenedione (70%) and diphenyl sulphoxide (80%). The dimethylsulphoximide (**1b**) also gave benzocyclobutenedione (35%), but in this case there was a competitive reaction (see below) which gave phthalimide (48%). Benzocyclobutenedione has not previously been observed in reactions which formally involve phthalimidonitrene; nitrogen has been retained in all the products reported so far.<sup>1,3</sup>

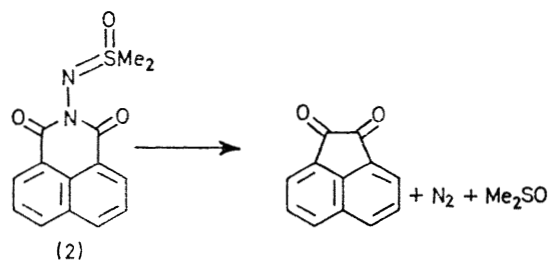
The naphthalimidodisulphoximide (**2**) was pyrolysed at 450°/0.005 Torr and gave acenaphthaquinone (55%) and naphthalimide (41%). Similarly, the dimethylsulphoximide derived from *N*-aminophenanthridone gave fluorenone (10%) and phenanthridone (80%) at 400°/0.01 Torr; neither biphenylene nor benzocinnoline was formed in this reaction.

These results suggest that the apparent distinction between "fragmenting" and "non-fragmenting" amino-nitrenes<sup>3a,4</sup> is simply due to differences in activation energy

for the fragmentations, and that even the relatively stable nitrenes, such as those involved here, can be induced to fragment in the vapour phase at high temperatures.



(1) a; R = Ph  
b; R = Me



The competitive formation of phthalimide, naphthalimide and phenanthridone in the dimethylsulphoximide pyrolyses probably involves transfer of a hydrogen atom from the *S*-methyl group, since it does not occur with the diphenylsulphoximides. This suggestion is supported by pyrolysis of phthalimidodibenzylsulphoximide, (**1**; R = CH<sub>2</sub>Ph), which has more active  $\alpha$ -hydrogens and gives an increased yield of phthalimide (80%) and virtually no benzocyclobutenedione.

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† Satisfactory analytical and spectral data have been obtained for new compounds.

<sup>1</sup> D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Comm.*, 1969, 146.

<sup>2</sup> C. W. Rees and M. Yelland, *Chem. Comm.*, 1969, 377.

<sup>3</sup> (a) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576; (b) T. L. Gilchrist, C. W. Rees, and E. Stanton, *ibid.*, 1971, 988; (c) L. Hoesch and A. S. Dreiding, *Chimia(Switz.)*, 1969, **23**, 405; (d) D. W. Jones, *Chem. Comm.*, 1970, 1084

<sup>4</sup> D. M. Lernal in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 345; K. Sakai and J.-P. Anselme, *Tetrahedron Letters*, 1970, 3851.