

## The Pyrolysis and Photolysis of Trimethylamine Benzimide

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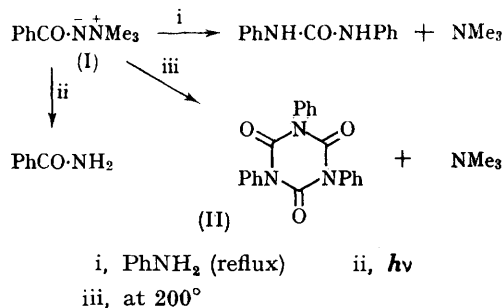
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THE synthesis of amine imides ( $\text{RCONNR}'_3$ ) derived from carboxylic acids was first reported by Hinman<sup>1</sup> in 1959. Since the amine imides possess an obvious structural similarity to the isocyanate precursors in the well-known Hofmann, Curtius, Schmidt, and Lossen rearrangements, we have initiated a study of the pyrolytic<sup>2</sup> and photolytic decomposition of these compounds with the objective of seeking analogous rearrangements which could conceivably be initiated by loss of the tertiary amine. We now report that trimethylamine benzimide (I) can be rearranged under rather drastic pyrolytic conditions.

Although the amine imide (I) was recovered unchanged after being boiled for 24 hours in 6*N* sodium hydroxide, it was smoothly rearranged in boiling aniline to give 73% of *sym*-diphenylurea (presumably *via* phenyl isocyanate). The reaction was conducted for 1.5 hours and was accompanied by evolution of trimethylamine (identified as the picrate).

Pyrolysis of (I) at 200° resulted in brisk evolution of trimethylamine\*. The characteristic odour of phenyl isocyanate was noted and the trimer (II) was isolated in 32% yield from the upper walls

of the pyrolysis tube. A trace of (II) was also isolated from the tarry residue.



Irradiation (10 hours) of an undegassed 20% methanolic solution of (I) in a quartz tube with a General Electric 400 w Mercury Lamp gave 22% benzamide, recovered (I), and dark unidentified oils.

Special attention is now being given to the possibility that acyl nitrenes<sup>3</sup> may be involved in the decomposition of amine imides.

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<sup>1</sup> R. L. Hinman, *J. Org. Chem.*, 1959, **24**, 660.

<sup>2</sup> S. Wawzonek and E. Yeakey (*J. Amer. Chem. Soc.*, 1960, **82**, 5718) have reported that dimethylbenzylamine acetimide and its *p*-nitro-analogue undergo *N*→*N* benzyl migrations on pyrolytic decomposition to give 1-acetyl-1-benzyl-2,2-dimethylhydrazine and 1-acetyl-1-(4-nitrobenzyl)hydrazine, respectively.

<sup>3</sup> For a recent review of nitrene chemistry see, L. Horner and A. Christmann, *Angew. Chem. Internat. Edn.*, 1963, **2**, 599.

\* Since this communication was submitted, our attention has been drawn to a paper by M. S. Gibson and A. W. Murray (*J. Chem. Soc.*, 1965, 880) who report similar pyrolysis studies on trimethylamine benzimide.