An Aryl Stevens Migration

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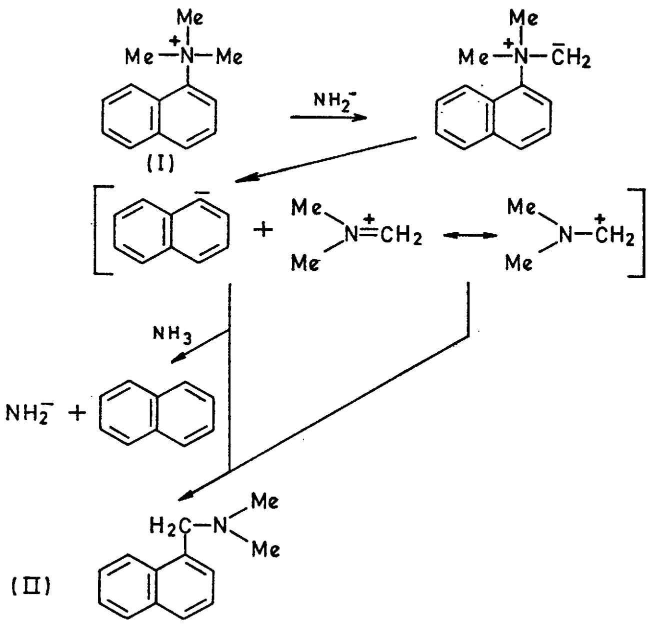
Summary A Stevens rearrangement in which the migrating group is α-naphthyl has been observed in high yield.

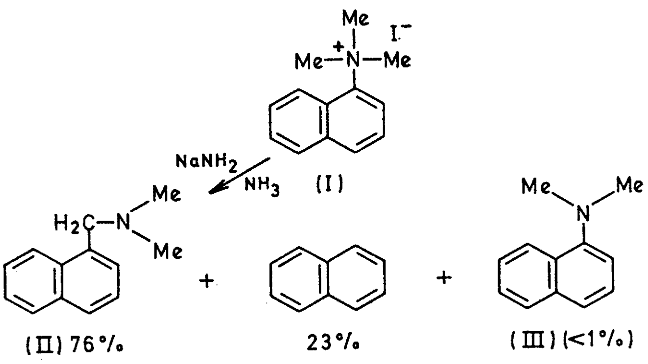
THE recent communication[1] of a Stevens rearrangement with aryl migration prompts us to report our findings in this area. Aryl migration occurs in high yield when the migrating aryl grouping is α-naphthyl, *i.e.*, treatment of α-naphthyltrimethylammonium iodide (I) with two equivalents of sodium amide in liquid ammonia under reflux, yields quantitatively a mixture of 76% α-naphthylmethyldimethylamine (II), 23% naphthalene, and 1% or less of the dealkylation product, *NN*-dimethyl-α-naphthylamine (III).

The fact that naphthalene is observed in conjunction with rearrangement product is consistent with the following ion-pair mechanism:[2]



However, a radical-pair mechanism[3] would also account for these products.

When β-naphthyltrimethylammonium iodide was subjected to the rearrangement conditions, the major product was β-naphthylamine, apparently resulting from NH_3 addition to naphthyne. No rearranged product could be detected by n.m.r. as shown by the total absence of signals in the vicinity of δ 2·1. A trace of the dealkylation product *NN*-dimethyl-β-naphthylamine could be detected by n.m.r. The α-hydrogen of naphthalene is more acidic than the β-hydrogen,[4] possibly accounting in part for naphthyne formation being dominant with the β-quaternary salt.



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