# Aprotic Base-catalysed Rearrangements of Ketone Quaternary Hydrazones

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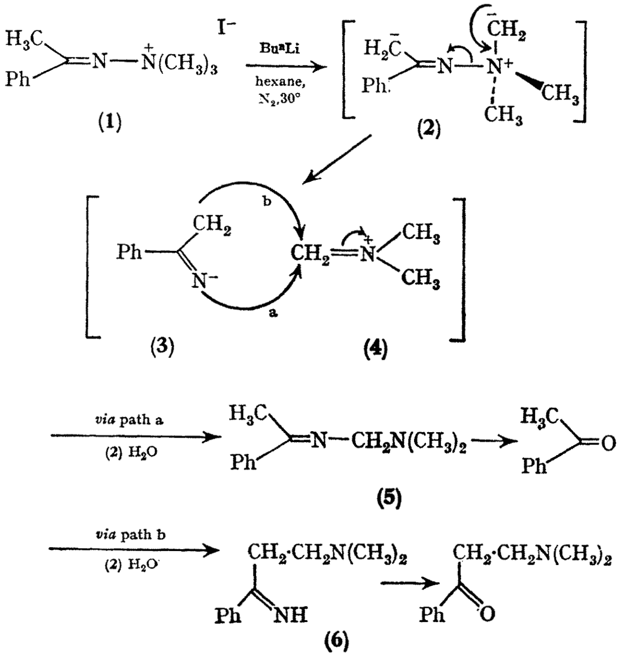
*Summary* n-Hexyl phenyl ketone is formed from acetophenone *NNN*-trimethylhydrazonium iodide and n-butyl-lithium at room temperature; the mechanistic possibilities are considered.

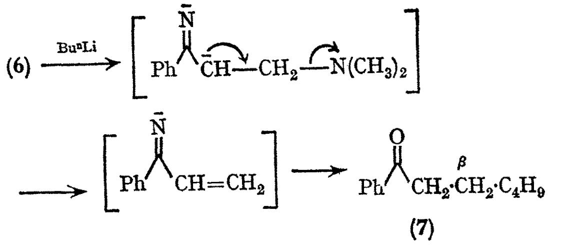
THE Neber-type rearrangement of ketone *NNN*-trimethylhydrazonium iodides with base to give amino-ketones has been well documented.[1] Under aprotic reaction conditions, however, acetophenone *NNN*-trimethylhydrazonium iodide (**1**) with sodium methylsulphinylmethide in dimethyl sulphoxide gave 2,4-diphenylpyrrole possibly *via* a reaction upon the intermediary 2-phenylazirine.[2] Recently Smith and Tan[3] treated benzophenone methylpentamethylenehydrazonium iodide with Grignard reagents in refluxing tetrahydrofuran. The major reaction path was reductive cleavage of the N–N bond, affording the corresponding imine and an equivalent amount of bialkyl or biaryl, along with trace products arising from carbon → nitrogen migration. I report here a preliminary investigation of the reaction between ketone *NNN*-trimethylhydrazonium iodides and butyl-lithium.

Acetophenone *NNN*-trimethylhydrazonium iodide (**1**) was prepared by the quaternization[4] of the corresponding *NN*-dimethylhydrazone[5] with methyl iodide. Upon treatment of (**1**) suspended in hexane with an excess of n-butyl-lithium in hexane at ambient temperature, the attempt was made initially to generate the anion-ylide (**2**), which could fragment into the dianion (**3**) and the Mannich reagent, dimethylmethyleneammonium iodide (**4**). Recombination of (**3**) and (**4**) can be envisaged as occurring by two possible pathways (Scheme 1): (a) formation of a C–N bond, affording the substituted imine (**5**), or (b) formation of the more stable C–C bond, thus giving β-dimethylaminopropiophenone imine (**6**). Hydrolysis of (**5**) and (**6**) will give acetophenone and β-dimethylaminopropiophenone, respectively. Acetophenone was isolated in 51% yield upon hydrolysis of the reaction mixture along with n-hexyl phenyl ketone (**7**, 39%, b.p. 100—102°/2 mm. Hg; 2,4-dinitrophenylhydrazone m.p. 135°, lit.[6] m.p. 135°) and two unidentified compounds. Although part of the acetophenone



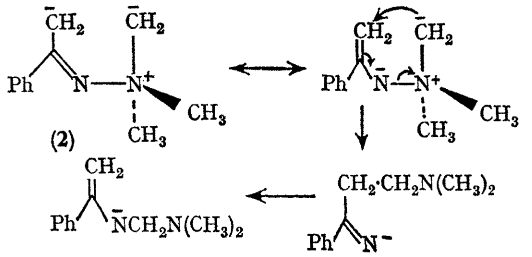
SCHEME 1.

could have arisen from hydrolysis of any unreacted (**1**), as well as from imine (**5**) *via* path a, the n-hexyl phenyl ketone must have incorporated its $\beta$-carbon from the *in situ* generated Mannich reagent as postulated in path b. Since an excess of n-butyl-lithium was used, (**6**) underwent hydrogen abstraction, followed by $\beta$-elimination of dimethylamide, and a Michael addition of the butyl anion to the phenyl vinyl ketimine intermediate to afford (**7**) after hydrolysis (Scheme 2).



SCHEME 2

The rearrangement of the anion-ylide (**2**) can be visualized as occurring through at least two thermally feasible reaction mechanisms. The non-concerted fragmentation–recombination mechanism illustrated in Scheme 1 has been utilized here to exemplify this reaction, since further studies will be necessary to establish the concerted process, with its more demanding requirements. An alternative mechanism can be rationalized in terms of a [3,2] sigmatropic rearrangement which can be classified formally as a $[_{\pi}2 + {}_{\sigma}2 + {}_{\omega}2]$ electrocyclic reaction,[7] that is thermally-allowed when the number of suprafacial additions is odd. The imine (**5**) can be described then as arising either in a second step by a thermal antarafacial [3,1] sigmatropic rearrangement[8] or directly from (**2**) by an [1,2] anionic shift, as demonstrated in the Stevens rearrangement. This may be a symmetry-allowed process if inversion occurs at both nitrogen and the migrating carbon and a $p$-orbital of the metal is involved.[7]



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