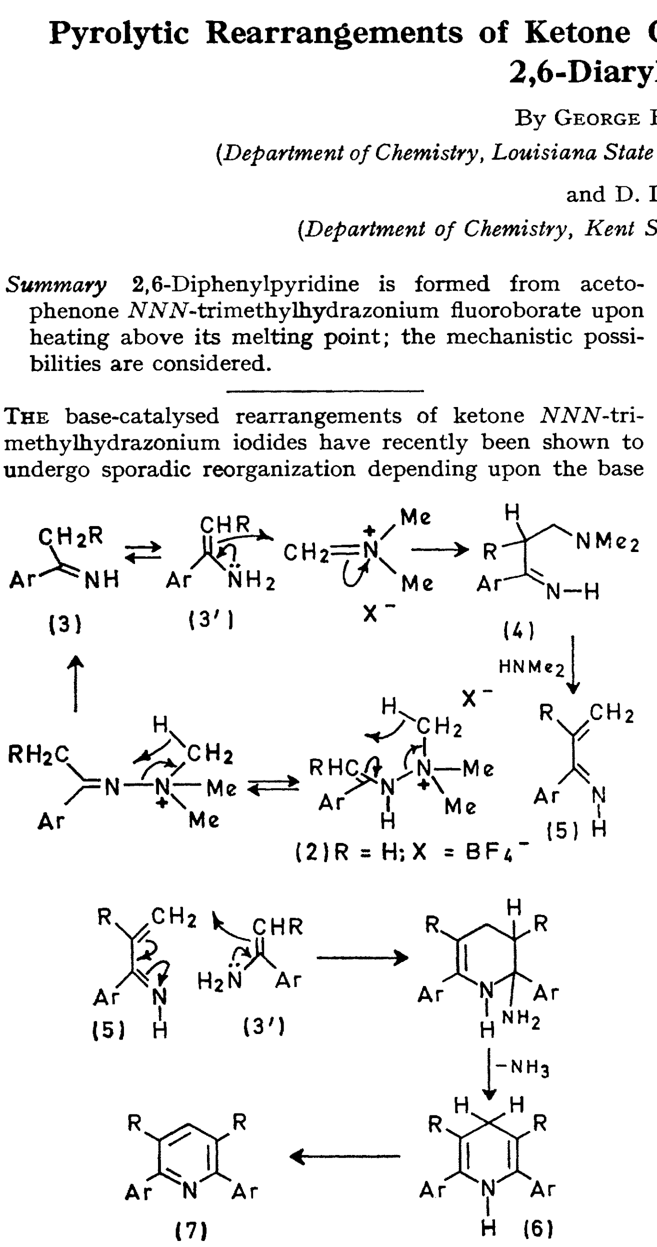
Pyrolytic Rearrangements of Ketone Quaternary Hydrazones. Formation of 2,6-Diarylpyridines

By GEORGE R. NEWKOME*
(*Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana* 70803)
and D. L. FISHEL
(*Department of Chemistry, Kent State University, Kent, Ohio* 44240)

Summary 2,6-Diphenylpyridine is formed from acetophenone *NNN*-trimethylhydrazonium fluoroborate upon heating above its melting point; the mechanistic possibilities are considered.

THE base-catalysed rearrangements of ketone *NNN*-trimethylhydrazonium iodides have recently been shown to undergo sporadic reorganization depending upon the base conditions.[1] Pyrolysis of pure acetophenone *NNN*-trimethylhydrazonium iodide (**1**) was described by Smith and Most.[2] (**1**) remained unchanged until a deep-seated decomposition took place. No organic compounds were isolated from the tarry residue. The iodide counterion is, of course, a good nucleophile and strong reducing agent; thus, the isolation of a high percentage of tar by these workers[2] does not seem unreasonable in retrospect. Recently, we have shown[3,4] that quaternary hydrazonium iodides can be easily converted into the corresponding fluoroborate (**2**), which greatly decreases the nucleophilic and reducing properties of the counterion. Alteration of counterion changes the reaction course drastically allowing, upon pyrolysis, the isolation of 2,6-diarylpyridines.[3,4] We report here our mechanistic results on the thermal rearrangement of (**2**) to 2,6-diphenylpyridine.



SCHEME 1

Pyrolysis of (**2**) at *ca.* 200° under a slow stream of nitrogen afforded 2,6-diphenylpyridine† (**7**, m.p. 82°, 55%), 2,6-diphenyl-3-methylpyridine† (**8**, b.p. 150—160°/0·5 mm Hg, 5%), acetophenone (6%, from imine hydrolysis), Me_3N, Me_2NH, NH_3, and NH_4BF_4, but no $MeNH_2$. Propiophenone *NNN*-trimethylhydrazonium fluoroborate (**2**; R = Me) gave 2,6-diphenyl-3,5-dimethylpyridine† (**7**; R = Me, 56%), thus indicating the three-carbon side chain must have remained intact during pyrolysis. Labelling with ^{14}C of the N-CH_3 group of (**2**), followed by pyrolysis, gave (**7**), in which one-third of the original activity was retained; accordingly, the γ-carbon of the pyridine ring was derived from the trimethylamine moiety.

The mechanism envisaged (Scheme 1) to account for the construction of the pyridine nucleus can be considered a ramification of the Hantzsch synthesis.[5] The initial fragmentation of (**2**) will afford acetophenone imine (**3**) or the tautomeric α-aminostyrene (**3'**) and the Mannich reagent, dimethylmethyleneammonium fluoroborate. Recombination of these fragments will form β-dimethylaminopropiophenone imine (**4**), which, under pyrolysis conditions, loses dimethylamine to give the imine (**5**). After the formation of these

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† Satisfactory spectra and elemental analyses were obtained for all compounds.

fragments, the reunion of the electron-rich β-carbon of the enamine (**3′**) and (**5**) by a Michael-type addition gives the dihydropyridine (**6**), after elimination of ammonia. Aromatization of the pyridine nucleus can occur by "transfer" of hydrogen to molecules with isolated double bonds[6] (*e.g.*, with the Mannich reagent to give trimethylamine hydrofluoroborate), or loss of molecular hydrogen.[7]

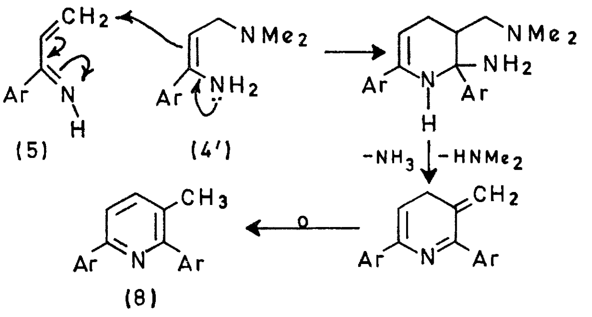
The 2,6-diphenyl-3-methylpyridine (**8**) can arise from a similar Michael-type addition of the enamine (**4′**) to (**5**), followed by loss of NH_3 and Me_2NH and subsequent aromatization (Scheme 2).

Although no intermediates were isolated from this pyrolysis reaction, evidence for these suggested intermediates was obtained by mass spectrometry (Table).

m/e	Found	Calc.[8]	Ion	
119	119·07339	119·07349	C_8H_9N	(**3**)
131	131·07374	131·07374	C_9H_9N	(**5**)
176	176·13153	176·13134	$C_{11}H_{16}N_2$	(**4**)
231	231·10472	231·10479	$C_{17}H_{13}N$	(**7**; R=H)
245	245·12057	245·12044	$C_{18}H_{15}N$	(**8**)

The low-energy (9 ev) spectrum of (**2**) verified the molecular weight for these individual components derived from both the initial fragmentation and the following thermal rearrangements.

Reinvestigation of the original methiodide pyrolysis[2] in the mass spectrometer inlet port indicated an ion of *m/e* 231 in very low abundance, along with strong evidence for thermal dequaternization to give acetophenone *NN*-dimethylhydrazone (*m/e* 162) and methyl iodide (*m/e* 142) as well as for complex polymerization. Isolation (1·3%) of (**7**) from this methiodide was subsequently accomplished by thick-layer chromatography only with great difficulty.



SCHEME 2

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