Pyrolysis of Ketone N,N,N-Trimethylhydrazonium Fluoborates. Evidence for the Genesis of Pyridines[1a,b]

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The preparation of α-methyl ketone N,N,N-trimethylhydrazonium iodides (**3**) and fluoborates (**4**) is described. The pyrolysis of **4** affords predominately 2,6-diarylpyridines (**5**). The mechanism, which resembles the Hantzch synthesis, is proposed for the construction of the pyridine ring with the γ carbon arising from the trimethylamine moiety; this proposed pathway is substantiated by the pyrolytic mass spectral, radiolabeling, and product analysis data.

2,6-Diphenylpyridines[1b,2] and fused-ring pyridines[3] have been prepared by pyrolysis of α-methylenic ketone N,N,N-trimethylhydrazonium fluoborates. The details for syntheses of these quaternary salts and the mechanism for this unusual reaction are the subject of the present paper.

Although there are many synthetic schemes describing the preparation of 2,6-diarylpyridines[4] (**5**), most studies of related reactions have been limited by technical difficulties associated with isolation of the desired isomer or in preparation of the starting materials. The best preparative method of **5** is arylation of the pyridine nucleus with organometallic reagents.[5] An alternative less advantageous route to 2,6-disubstituted pyridines is the *in situ* generation of the pyridine nucleus from aldehydes and/or ketones with a source of ammonia.[4a] Cyclizations of this type are well known, but they often produce complex mixtures with low yields of any single isomer. The present work involves a similar ring construction reaction, except that a single 2,6-disubstituted pyridine nucleus is generated from the pyrolysis of α-methylenic ketone N,N,N-trimethylhydrazonium fluoborates.

The chemistry of these and related quaternary hydrazonium derivatives have been neglected except for some sporadic work which demonstrates the unusual sensitivity of this class of compound toward various reaction conditions. For example, acetophenone $N,N,$-N-trimethylhydrazonium iodide (**3a**) underwent a Neber-type reaction when subjected to protic base,[6] gave 2,4-diphenylpyrrole when treated with methylsulfinyl carbanion or sodium isopropoxide[7] and gave phenyl n-hexyl ketone when subjected to n-butyllithium in hexane.[8] Pyrolysis of neat **3a** was reported by Smith and Most[6a] to show no change until a deep-seated decomposition took place; no organic compounds were isolated from the tarry residue. Repetition of this pyrolysis (**3a**), in our hands, initially corroborated these gross observations.[2] Substitution of fluoborate for iodide as counterion changed the reaction course drastically; then, 2,6-diarylpyridines were isolated as the principal products.

In the present investigation, the influence of counterions and changes in reaction conditions were studied toward understanding the reaction mechanism.

Results

N,N-Dimethylhydrazones.—Most ketones react directly with anhydrous N,N-dimethylhydrazine to give excellent yields of the corresponding N,N-dimethylhydrazones[9] (Table I). Catalysts other than excess N,N-dimethylhydrazine are unnecessary, although several drops of glacial acetic acid[10] have been shown to facilitate this conversion. In general, minimal difficulties were encountered except for 7-nitro-1-tetralone[3] and 4′-nitroacetophenone,[9a] for which other reaction products were obtained without mineral acid catalysis.

N,N,N-Trimethylhydrazonium Iodides.—The quaternization of ketone N,N-dimethylhydrazones with alcoholic methyl iodide afforded the corresponding N,N,N-trimethylhydrazonium iodides (Table I). The facile preparation of these methiodides has been previously described in detail for aldehydes[11] and ketones.[3,6a,12a] Preparative difficulties experienced herein on attempted quaternization with methyl iodide were encountered when other nitrogen functions were present on or in the aromatic nucleus. 3′- or 4′-Nitroacetophenone N,N-dimethylhydrazone gave only a complex mixture of resinous tars from which the desired quaternary product was not obained. Preparation of 2- and 4-acetylpyridine N,N,N-trimethylhydrazonium iodide gave a mixture of the pyridinium

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[1] (a) Some of the preliminary results have been presented earlier: D. L. Fishel and G. R. Newkome, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1966, ORGN-204, and G. R. Newkome, Abstracts, Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970, ORGN-358. (b) Preliminary communication: G. R. Newkome and D. L. Fishel, *Chem. Commun.*, 916 (1970). (c) Louisiana State University. Submitted to Kent State University by G. R. N. in partial fulfillment for the Ph.D. degree, 1966. (d) Kent State University.

[2] D. L. Fishel and G. R. Newkome, *J. Amer. Chem. Soc.*, **88**, 3654 (1966).

[3] G. R. Newkome and D. L. Fishel, *J. Heterocycl. Chem.*, **4**, 427 (1967).

[4] (a) F. Brody and P. R. Ruby, "Pyridine and Its Derivatives," Part I, pp 99–589; (b) L. E. Tenenbaum, "Pyridine and Its Derivatives," Part II, E. Klingsberg, Ed., Interscience, New York, N. Y., 1961, pp 155–298.

[5] See (a) H. Gilman and J. T. Edward, *Can J. Chem.*, **31**, 457 (1953); (b) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Amer. Chem. Soc.*, **79**, 6430 (1957); (c) D. Bryce-Smith and A. C. Skinner, *J. Chem. Soc.*, 577 (1963).

[6] (a) P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957). (b) Other examples of this transformation have been documented: R. F. Parcell, *Chem. Ind. (London)*, 1396 (1963); D. F. Morrow and M. E. Butler, *J. Heterocycl. Chem.*, **1**, 53 (1964); D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 579 (1965).

[7] S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jap.*, **40**, 2936 (1967); S. Sato, *ibid.*, **41**, 1440 (1968).

[8] G. R. Newkome, *Chem. Commun.*, 1227 (1969).

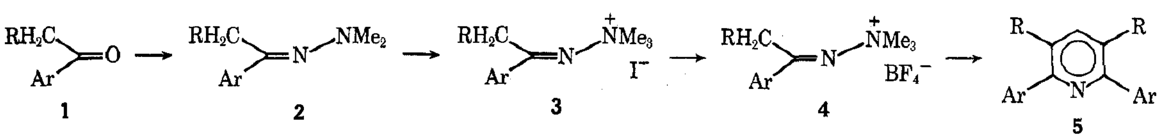
[9] (a) G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, **31**, 677 (1966); (b) *Org. Syn.*, **50**, 102 (1970).

[10] R. H. Wiley and S. H. Chang, *J. Med. Chem.*, **6**, 610 (1963).

[11] R. F. Smith and L. E. Walker, *J. Org. Chem.*, **27**, 4372 (1962).

[12] (a) W. Theilacker and O. R. Leichtle, *Justus Liebigs Ann. Chem.*, **572**, 121 (1951); (b) A. Roe, *Org. React.*, **5**, 193 (1949).

TABLE I[a]



	Ar	R	Bp, °C (mm)	n_D (°C)	Yield, %	Mp, °C[b]	Yield, %	Mp, °C[b,c]	Yield, %	Mp, °C	Yield, %
a	C_6H_5	H	55–56 (0.15)	1.5443 (26)	92	146–147[d]	87	153–154	96	82–83[e]	55
b	3′-CH_3-C_6H_4	H	*f*			151–152	72	128–130	79	64–65	30
c	4′-$CH_3C_6H_4$	H	*f*			159–160	83	159–160	78	165–166[g]	42
d	4′-FC_6H_4	H	*f*			155–156	90	120–121	87	94–95	*h*
e	4′-ClC_6H_4	H	*f*			145–146	81	146–147	83	155–156	42
f	4′-BrC_6H_4	H	*f*			153–154	72	151–153	75	185–186	39
g	4′-$CH_3OC_6H_4$	H	*f*			152–153	78	146–147	92	197–198	42
h	3′-$NO_2C_6H_4$	H	*f*				0				
i	4′-$NO_2C_6H_4$	H	*f*				0				
j	5-Indanyl	H	*f*			179–180	93	151–152	97	162–163	42
k	2-Naphthyl	H	115–119 (0.10)	1.6324 (20)	90	185–186	67	178–179	92	169–170	21
l	C_6H_5	CH_3	45–46 (0.10)	1.5311 (22)	91	153–156	84	110–111[i]	82	136–137[j]	56
m	C_6H_5	CH_3CH_2	55–56 (0.25)	1.5236 (20)	96	128–130	92	~80[k]	48	146–147	47
n	2-Pyridyl	H	44–45 (0.20)	1.5460 (26)	88	155–156	61	164–165	84		
o	2-(6-Picolyl)	H	53–54 (0.10)	1.5370 (26)	95	168–169	39	172–174	87	164–165	47
p	C_6H_5	C_6H_5	117–118 (0.25)	1.5864 (20)	95	123–124	84	*l*	0		

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds in this table: Ed. [b] Decomposition points were taken in sealed capillaries. [c] The decomposition points (separated into two layers) were normally 20–30° above the melting points, except where noted. [d] Lit.[6a] mp 145–146° dec. [e] Lit.[28] mp 82°; picrate mp 171° (lit.[29] mp 169°). [f] See ref 9a for the physical data. [g] Picrate mp 176°; M. Scholtz and A. Wiedemann [*Ber.*, **36**, 845 (1903)] reported mp 162° and picrate mp 174°. [h] Yield was not calculated. [i] Decomposition above 150°. [j] Lit.[32] mp 134–135°. [k] Decomposition above 170°. [l] Hydrolysis occurred during preparation.

salt and the diquaternary methiodide; separation was attempted on **3n** only. This difficulty could be easily circumvented by blocking the pyridine nitrogen with a bulky 6-methyl group, thus hindering pyridinium salt formation. Ortho substituted (*e.g.*, 2′,4′-dimethyl-) acetophenones, as well as partially hindered *N*,*N*-dimethylhydrazones, underwent slow quaternization with refluxing anhydrous methanolic methyl iodide with extended reaction times and usually resulting in lower yields. The use of methyl *p*-toluenesulfonate[11] to quaternize acetophenone *N*,*N*-dimethylhydrazone gave the desired product.

***N*,*N*,*N*-Trimethylhydrazonium Fluoborates.**—Most ketone *N*,*N*,*N*-trimethylhydrazonium iodides were easily converted to the corresponding fluoborates (Table I). Preparation of the *N*,*N*,*N*-trimethylhydrazonium fluoborates is quite analogous to formation of aromatic diazonium fluoborates as in the Schiemann reaction.[12b] The stable ketone *N*,*N*,*N*-trimethylhydrazonium fluoborates (**4**) immediately start to precipitate from a hot (*ca.* 100°) aqueous solution of the corresponding methiodide upon addition of an aqueous sodium fluoborate solution. Most of these fluoborates, **4**, melt sharply *in vacuo* without spontaneous decomposition (unlike the corresponding methiodides) but they do decompose slowly on prolonged heating at temperatures just above their melting points.

The main difficulty associated with the conversion of the methiodides into the corresponding fluoborates was concurrent hydrolysis. Acetophenone *N*,*N*,*N*-trimethylhydrazonium iodide (**3a**) rapidly underwent base-catalyzed hydrolysis[6a,13] to regenerate the original ketone and the water soluble *N*,*N*,*N*-trimethylhydrazinium iodide. The hydrolysis during conversion of **3** to **4** in the present study could in some instances be minimized by rigorously controlling the pH of the aqueous sodium fluoborate solution. Aqueous solutions of technical sodium fluoborate had a pH of *ca.* 4, which explains the accelerated rate of hydrolysis of certain quaternary hydrazonium iodides. The addition of dilute sodium hydroxide to this sodium fluoborate solution (to a pH of 7.0) resulted in excellent yields for most conversions.

The ketone *N*,*N*,*N*-trimethylhydrazonium iodides, with a benzyl group attached to the >C=N group (*e.g.*, **3p**), were rapidly hydrolyzed to the ketones even when treated with the neutral fluoborate solution. The increased rate of hydrolysis for these compounds is probably due to the facile tautomerization to the enamine, which is known to hydrolyze easily.[14]

Pyrolysis of Quaternary Hydrazonium Derivatives.—In this study all ketone *N*,*N*,*N*-trimethylhydrazonium fluoborates (**4**) contained an α-methylene to >C=N, and were pyrolytically decomposed at temperatures above their melting points either *in vacuo*, suspended in inert solvents, or in a dry nitrogen stream. The tarry residues gave 30–60% of the symmetrically disubstituted pyridine.

The pyrolysis conditions for most fluoborates **4** can be varied considerably with little effect on the overall yield of the pyridine products. When acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (**4a**) was pyrolyzed in a high vacuum system, 2,6-diphenylpyridine can be isolated, but, in light of the violently exothermic character of this reaction and rapid evolution of gases, this method was quite limited to sample size. Pyrolytic decomposition of **4a** by suspension in an "inert" refluxing solvent (*i.e.*, cumene, bp 150–155°) offered

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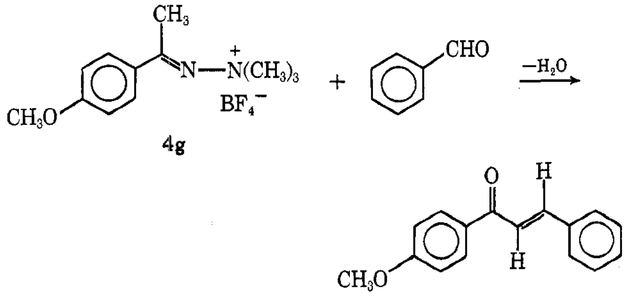
(13) M. Avaro, J. Levisalles, and H. Rudler [*Chem. Commun.*, 445 (1969)] have taken advantage of this facile hydrolysis after use of *N*,*N*-dimethylhydrazones as protection for aldehydes and ketones.

(14) C. R. Hauser, H. M. Taylor, and T. G. Ladford [*J. Amer. Chem. Soc.*, **82**, 1786 (1960)] reported the facile hydrolysis of α-dimethylaminostilbene to generate deoxybenzoin.

no apparent advantage, since the hydrazonium fluoborates were not appreciably soluble in nonpolar solvents even at elevated temperatures. The prolonged refluxing of these fluoborates (**4**) in lower boiling solvents (*e.g.*, ethanol) has been shown to give negligible yields of the pyridine derivatives.[15] Other solvents were not investigated due to the possible occurrence of undesirable side reactions as was observed with benzaldehyde. The pyrolysis of 4′-methoxyacetophenone *N*,*N*,-*N*-trimethylhydrazonium fluoborate (**4g**) in refluxing



benzaldehyde (bp 180°) afforded 2-benzal-4′-methoxyacetophenone, which was formed by simple condensation.

The general method for these exothermic pyrolysis reactions, adopted in order to isolate the gases liberated, was decomposition of a "train"[16] of the fluoborate, **4**. The fluoborate closest to the nitrogen inlet was carefully heated, until decomposition commenced; the nitrogen swept the amine gases and inorganic sublimates into the series of cold traps. After the initial reaction, the residual tar in the pyrolysis tube was heated to 200–250° for several additional minutes.

Pyrolysis of **4a** in this manner[16] gave a white sublimate which was identical with an authentic sample of ammonium fluoborate. The trapped gases were bubbled through an ethereal methyl iodide solution from which tetramethylammonium iodide precipitated. To distinguish between alkylation of ammonia and/or any of the methyl amines, the carrier gas was passed through a saturated hydrogen chloride ether solution; a mixture of hygroscopic amine hydrochlorides precipitated. The nmr spectrum of this amine hydrochloride mixture showed the presence of three major singlets corresponding to the proton resonances for ammonium chloride, dimethylamine hydrochloride (δ 2.84, NCH_3) and trimethylamine hydrochloride (δ 2.96, NCH_3); there was no ($<0.5\%$) evidence for methylamine hydrochloride (δ 2.70, NCH_3).

The residual tar from the pyrolysis of **4a** was analyzed by glc and tlc, both of which indicate one major product, 2,6-diphenylpyridine, along with traces of acetophenone and 2,6-diphenyl-3-methylpyridine; these are the only identifiable organic products.

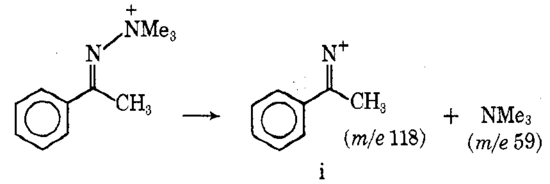
The major product from pyrolysis of **4l** was 2,6-diphenyl-3,5-dimethylpyridine, thus indicating that no rearrangement of the 3-carbon side chain had occurred during pyrolysis. This result suggested that the γ carbon (C_4) of the newly formed pyridine ring is derived from the trimethylamine moiety. The mass spectrometric studies suggest that there is a substantial amount of N-N cleavage as a primary process for the cation during pyrolysis of the fluoborates. This is indicated by a strong 59 *m/e* ion peak, presumed due to trimethylamine, in the low voltage spectrum of **4a** (Table II). This route could represent a reaction competitive with those leading to pyridine ring formation or might be a necessary preliminary step before transfer of carbon (destined to be the pyridine γ carbon) from the trimethylamine moiety to the acetophenoniminium residue, i. Intermolecular alkyl exchange between a quaternary salt and a tertiary amine[17] is a reasonably facile reaction at these temperatures.

TABLE II

PARTIAL LOW VOLTAGE[a] MASS SPECTRUM OF **4a**

m/e	Rel intensity		*m/e*	Rel intensity	
45	112	C_2H_7N	142	5	
58	6		143	3	
59	68	C_3H_9N	147	1	
60	3		148	1	
104	2		149	2	
106	2		162	10	$C_{10}H_{14}N_2$
119	19	C_6H_9N	231	120	M^+, $C_{17}H_{13}N$
120	2		232	19	
128	3		233	3	
130	1		244	3	
131	7	C_9H_9N	245	7	$C_{18}H_{15}N$
132	1		246	2	

[a] 12 eV operating voltage.



Radiolabeling experiments were then conducted to test the hypothesis that the pyridine γ carbon is constructed from the trimethylamine moiety. Pyrolysis of **4a**-*N*-^{14}C afforded the labeled 2,6-diphenylpyridine, in which the theoretical one-third incorporation was experienced. Other ^{14}C sources (*N*,*N*,*N*-trimethylhydrazinium-^{14}C fluoborate and tetramethylammonium fluoborate) were used; negligible incorporation of the radiolabel was experienced. The overall conclusion is that intermolecular radiolabeling did not occur to any appreciable extent in these experiments, suggesting either that the incipient γ carbon is transferred intramolecularly within the ketone *N*,*N*,*N*-trimethylhydrazonium fluoborate or that separation of the trimethylamine moiety before transfer of carbon is insufficiently complete to allow significant exchange with other quaternary nitrogen derivatives. The latter result would also be observed if one carbon on the leaving trimethylamine moiety was chemically different, incapable of simple exchange and was in fact the incipient γ carbon of the pyridine ring.

Several experiments were conducted in which mixtures of two different ketone *N*,*N*,*N*-trimethylhydrazonium fluoborates were pyrolyzed to determine the extent of formation of unsymmetric 2,6-diarylpyridines. For equimolar mixtures of **4a** and **4g**, the molar product distribution was 1:2:1 of 2,6-diphenylpyridine, 2-

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[15] R. Widmer, K. S. U., private communication.

[16] The "train" was composed of a horizontal Pyrex tube fitted with an inlet for an inert gas, followed by a series of traps cooled in liquid nitrogen.

[17] S. Hunig and W. Baron, *Chem. Ber.*, **90**, 395 (1957).

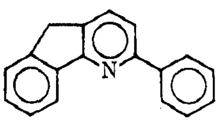
TABLE III

MASS SPECTRAL DATA FOR THE ACETOPHENONE DERIVED SEQUENCE[a]

m/e	**5a**	**4a**	**3a**[b]	**2a**	*m/e*	**5a**	**4a**	**3a**	**2a**	*m/e*	**5a**	**4a**	**3a**	**2a**
247			4		153	2	1			101	5	3		
246			5		152	2	1			100	1			
245		1.6[c]	6		148				2.3	91	1.3			4.3
244		4.0	5		147				21.7	90			5	
233	2.4	3.0	8		146			8	1.2	89	2.3		8	
232	27.5	16	10		142			100		88	2	2		
231	100[d]	100[d]	61		140			5		81				1.7
230	70	50	30		133			5	2	80				2.5
229	5	4			132		2	11	18.7	79		5		5.5
228	7	4			131		3[f]	10	3.0	78	1.5	4	10	10
227	1	1			130		2	10	2.0	77	6.4	14	41	40
219		2			129			5		76	3.2	7	10	5
218			3		128	3.2		61		75	2	3	5	2
217			5		127	6.2		45		74	1.2			
215		1			126	2.7				71				
208		2			121	1.5				63	1.5		6	2
207		7	10		120		1	5	2.5	59		10		
206		1			119		8[g]	19	6.0	58		20	52	
204	2.7	2			118		2	14	18	57		2	5	
203	3.0	3.0			117			7	2	54		1.5		
202	7.1	6	6		116	2.9	2	7		52	1.2	1	5	2
201		1			115.5	13	11	6		51	4.0	7	17	14.7
178		1			115	5	6	11		50	1.8	2	8	5
177		1			114.5	5	3			49		21		
176		1[e]			114	7.6	6	5		48		2		
163			9	10.3	107			7		45		18		20
162			23	100	106	2.3	1	6	8	44	1.5	30	15	35
161			6	7.6	105		2	13	1.5	43		6	33	7
160			33		104		20[h]	52	13	42		10	8	16
159			35		103	2.3	3[i]	26	11	41	1.1	2	31	3
158			10		102.5	2				40		4		2
154	4	5	6		102	12	6	23	1.3	39	1.6	3		

[a] Direct insertion method at 200° inlet temperature, 70 eV, 100 μA. [b] Other fragments: *m/e* (rel intensity) 399 (2), 397 (2), 396 (4), 385 (5), 384 (2), 383 (2), 382 (2), 373 (4), 372 (5), 371 (4), 370 (3), 359 (3), 358 (4), 357 (5), 356 (6), 346 (8), 322 (5), 321 (8), 308 (5), 307 (5), 306 (2), 263 (5), 261 (5), 260 (5), 259 (4); ions of relative intensity $\geq 2\%$. [c] High resolution data: $C_{18}H_{15}N$ (calcd 245.12044, found 245.12057). [d] High resolution data: $C_{17}H_{13}N$ (calcd 231.10479, found 231.10472). [e] High resolution data: $C_{11}H_{16}N_2$ (calcd 176.13134, found 176.13153). [f] High resolution data: C_9H_9N (calcd 131.07350, found 131.07374). [g] High resolution data: C_8H_9N (calcd 119.07349, found 119.07339). [h] High resolution data: C_7H_6N (calcd 104.05002, found 104.04945). [i] High resolution data: C_8H_7 (calcd 103.05477, found 103.05311) and C_7H_5N (calcd 103.04220, found 103.04242).

2-phenyl-6-(4-methoxyphenyl)pyridine, and 2,6-di-(4-methoxyphenyl)pyridine, respectively. This statistically expected product distribution was not observed from pyrolysis of intimate mixtures of **4a** with 1-indanone *N,N,N*-trimethylhydrazonium fluoborate;[3] rather, a ratio of 0.16:0.8:1 was obtained for **5a**, 2-phenyl-5*H*-indeno[1,2-*b*]pyridine (**6**), and 1,12-dihydrodiindeno[1,2-*b*:2′,1′-*e*]pyridine (**7**), respectively. These results demonstrate that the reaction medium is essentially homogeneous (*i.e.*, there is no restriction of free movement of what must be two separate intermediates contributing to the final 2,6-diarylpyridine product) and, furthermore, that these intermediates have a significant lifetime even in condensed phases.



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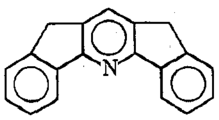

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Pyrolysis of either acetophenone *N,N,N*-trimethylhydrazonium iodide (**3a**) or the corresponding tosylate gave 2,6-diphenylpyridine (**5a**) in less than 2% yield as well as resinous oils which were not further investigated. Analysis of sublimates from the iodide pyrolysis indicated significant amounts of quaternary ammonium iodide salts; the quantitative composition was not determined.

Pyrolytic Mass Spectrometric Study. Formation of and Evidence for the Reactive Intermediates.—Small samples of the quaternary salts were pyrolyzed in the high vacuum of a mass spectrometer ion source by direct introduction to the heated source block. The pyrolysis mass spectra were in general reproducible for comparable source pressures, temperatures, and sample size and if scan times following sample introduction were the same. A rigorous investigation of the lifetimes of intermediates by time-resolved techniques has been made, from which several qualitative observations for specific intermediates are outlined. At source pressures ($p < 10^{-5}$ Torr) intermediates with lifetimes comparable to analysis scan times (1–15 sec) should be preserved in sufficient amounts for their mass spectra to be displayed along with those of stable products. Ion intensities of spectra thus produced may be corrected by selective subtraction of the contributions to the same ions from stable products.

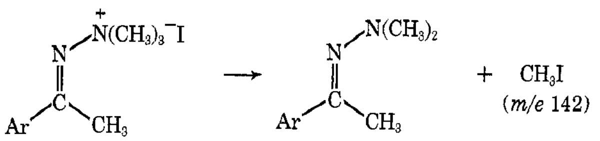
The spectra of analytical samples of known pyrolysis products were obtained under closely similar conditions in the same spectrometer used in the pyrolysis studies. The spectra of the *N,N*-dimethylhydrazones (**4a**, Table III) exhibit features at low mass numbers analogous to those reported by Goldsmith and Djerassi[18] in their study of hydrogen rearrangement and fragmentations of aliphatic ketone *N,N*-dimethylhydrazones. The principal fragmentation processes appear to be either loss of one or more methyl groups from the molecular ion or N–N cleavage. The latter process may also involve 1,3-hydrogen transfer between the two fragments.

The 2,6-diarylpyridines are extremely stable compounds. This is demonstrated by high intensities for molecular ions, doubly and triply charged ions, and by relatively low intensities for all fragment ions (**5a**, see Table III).

Acetophenone *N,N,N*-Trimethylhydrazonium Iodide (3a).—Strong ion intensities are observed in the pyrolysis mass spectrum of acetophenone *N,N,N*-trimethylhydrazonium iodide (**3a,** Table III) at *m/e* values of 231, 160–162, 142, 128, 127, 104, 77, and 58. Ions at *m/e* values of 231, 162, 142, and 128 represent **5a, 2a,** methyl iodide, and hydrogen iodide, respectively; this may be inferred by their persistence in low-voltage spectra, by exact mass measurement, and by isolation from pyrolysis residues.

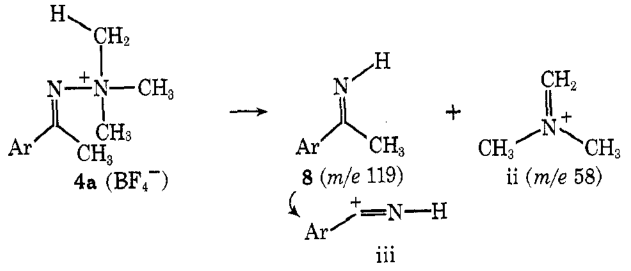
2,6-Diphenylpyridine (**5a**) is readily identified as a minor component by the molecular ion pattern; it is confirmed by a strong metastable at 229 (231 → 230) and characteristic doubly charged ion peaks at 114.5 115.5. Acetophenone *N,N*-dimethylhydrazone (**2a**) is also supported by well characterized metastable ion peaks at 160 (162 → 161), 133.4 (162 → 147, loss of CH_3), and 118.6 (147 → 132, loss of second CH_3) and the occurrence of all expected fragment ions for this compound.

The presumption that acetophenone *N,N*-dimethylhydrazone and methyl iodide must arise by simple nucleophilic displacement is supported by a metastable ion peak at ~ 86.4 (304 → 162). This process for the quaternary iodides (*e.g.*, **4a**) accounts for the major fragmentation pathway.



3a (*m/e* 304) **2a** (*m/e* 162)

Acetophenone *N,N,N*-Trimethylhydrazonium Fluoborate (4a).—Although the construction of the pyridine ring is a minor route in the pyrolytic mass spectrum of **3a**, the formation of substituted pyridines from the corresponding fluoborates (**4a**) constitutes the major pathway. Construction of the pyridine γ carbon by internal transfer of an *N*-methyl group may be envisioned in several ways on the basis of ions which are present in the pyrolysis mass spectra of all the quaternary salts, but especially the fluoborates. The acetophenone *N,N,N*-trimethylhydrazonium cation is expected to undergo simple N–N cleavage as the most likely thermal process independent of interactions with the anion. This would give a stable product trimethylamine, *m/e* 59, as well as the hypothetical reactive intermediate, acetophenoniminium cation, i, *m/e* 118. Alternately, 1,3-hydrogen migration may occur with N–N cleavage to give dimethylmethyleneammonium cation, ii, *m/e* 58, and the imine, **8**, *m/e* 119. Low-voltage mass spectra of acetophenone *N,N,N*-trimethylhydrazonium fluoborate (as well as iodide and tosylate) all have prominent ion peaks at *m/e* values of 119 and 58. Subsequent methyl loss by electron-impact fragmentation of imine **8** would give an *m/e* 104 species, iii, which is supported by a metastable ion at 90.0 (119 → 104). Exact mass measurement of both the 119 and 104 ions is consistent with the proposed composition for these ions (footnotes, Table III). There is inherent in this datum the implication that the imine **8** has a lifetime sufficient to undergo subsequent rearrangement and reaction. Tautomerization of **8** to α-aminostyrene (**8′**) followed by electrophilic alkylation of the resulting enamine with Mannich reagent, dimethylmethyleneammonium cation,[19] ii, is proposed as a convenient mechanistic route to the incipient pyridine γ carbon. This condensation product readily eliminates dimethylamine and a proton to give the diene **9** as a potential reactive intermediate (Scheme I). Evidence for **9** exists as the ion at *m/e* 131 in the spectra of all the quaternary salts. This ion is absent in the spectrum of 2,6-diphenylpyridine; therefore, it does not arise by electron-impact fragmentation of this product.

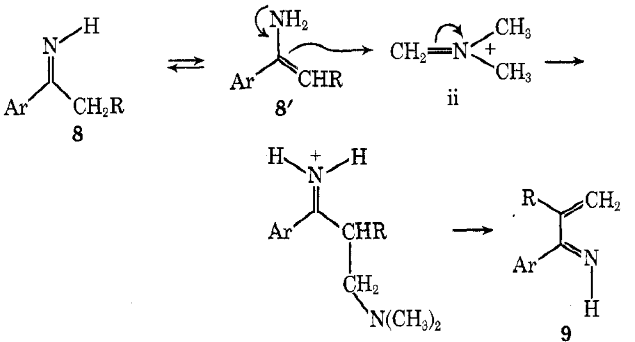


4a (BF_4^-) **8** (*m/e* 119) ii (*m/e* 58) iii

Although acetophenone *N,N*-dimethylhydrazone has an ion peak at *m/e* 131 in its spectrum, this is an insufficient source of this ion in spectra of quaternary salts. Even though the iodide and tosylate spectra have as a significant feature the molecular ion (*m/e* 162) for acetophenone *N,N*-dimethylhydrazone, the *m/e* 131 peak exceeds the expected intensity if it were to be derived as a fragment ion from this hydrazone.

In a series of mass spectra obtained by rapid scanning immediately following pyrolysis of quaternary salts in the ion source, the intensity of the *m/e* 131

Scheme I



8 **8′** ii *m/e* 176 **9**

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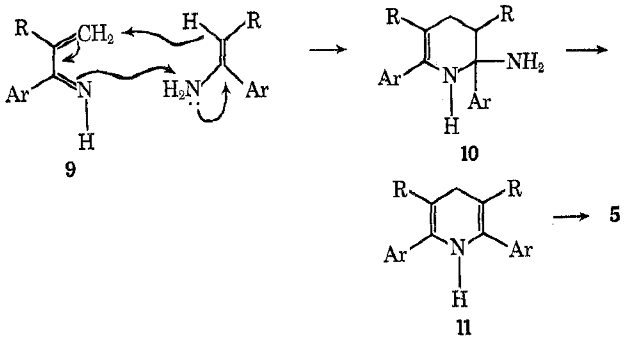
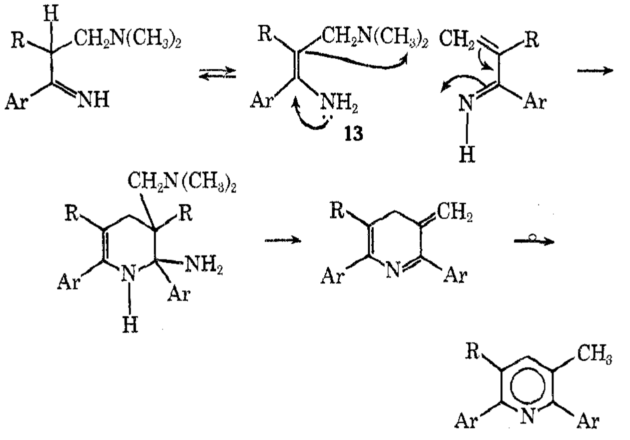
[18] D. Goldsmith and C. Djerassi, *J. Org. Chem.*, **31**, 3661 (1966).

[19] Recently, Eschenmoser, *et al.* [*Angew. Chem., Int. Ed. Engl.*, **10**, 330 (1971)], have isolated (80%) this methyleneammonium salt, ii (I^-). This Mannich reagent can be recrystallized and sublimed at reduced pressure without decomposition.

SCHEME II



SCHEME III



peak may be seen to rise and then fall off to a much greater extent than other ions identifiable as stable molecular species (m/e 231, 162, 142, 128, and 59). Furthermore, there is a rough inverse correlation between the intensity of 131 and 231 ion peaks, the latter rising and persisting after the 131 ion peak has nearly vanished during repetitive scanning.

It is our belief, therefore, that **9** (m/e 131) represents one of the reactive intermediates, which will supply the γ carbon of the pyridine nucleus during the pyrolysis of the ketone N,N,N-trimethylhydrazonium salts.

Mechanistic Construction of the Pyridine Nucleus.—The mechanism envisaged to account for the final construction of the pyridine nucleus can be considered a ramification of the Hantzch synthesis[4a] by the recombination of the evidenced fragments (Scheme II). The reunion of the electron-rich β carbon of the enamine **8′** and **9** by a Michael-type addition gives a dihydropyridine (**11**) after the elimination of ammonia. There is no mass spectral evidence for this cycloaddition intermediate (**10**) due to the facile loss of ammonia under the reaction temperatures. Aromatization of the pyridine nucleus can occur by "transfer" of hydrogen to molecules with isolated double bonds,[20] e.g., with the Mannich reagent ii, or by loss of molecular hydrogen.[21] Isolation of trimethylamine has been accomplished, although there is no direct evidence to support this proposed reductive sequence.

The 2,6-diphenyl-3-methylpyridine (**12**) can arise from a similar Michael-type addition of the enamine (**9**) and the tautomer of its precursor (**13**), followed by loss of ammonia and dimethylamine, then aromatization (Scheme III).

The mass spectrum data and the detailed analyses of the products from this pyrolysis reaction have substantiated the Hantzch-type mechanistic scheme for the production of the pyridine nucleus. In our studies, as well as in many historical examples, the actual isolation of these proposed intermediates has been difficult to realize. Additional studies on the trapping of these elusive intermediates are currently underway on other closely related systems.

Experimental Section[22]

Reagents.—Anhydrous N,N-dimethylhydrazine (99%), iodomethane (reagent, 99+%), and sodium fluoborate (technical grade) were obtained from Matheson Coleman and Bell. Radioactive methyl-^{14}C iodide was purchased from New England Nuclear Corp., Boston, Mass. Samples of the starting carbonyl compounds were available from ordinary commercial sources and were purified by redistillation or recrystallization prior to use.

Methyl iodide had mass spectrum (70 eV) m/e (rel intensity) 143 (0.69), 142 (100), 141 (7.2), 140 (2.1), 139 (2.3), 128 (1.7), 127 (13.5), and 15 (17.9).

General procedure for the preparation of dimethylhydrazones has been previously described in detail.[9] Properties of various N,N-dimethylhydrazones which have not been previously reported[9] are cited in Table I.

General Preparation of Ketone N,N,N-Trimethylhydrazonium Iodides.[24] Method A.—A mixture of acetophenone N,N-dimethylhydrazone (5.0 g, 0.033 mol) and excess methyl iodide in anhydrous ether (20 ml) was allowed to stand for several days at room temperature. The crude product was filtered, washed with ether, dried in vacuo, and recrystallized from absolute ethanol–ethyl acetate to afford 6.3 g (67%) of acetophenone N,N,N-trimethylhydrazonium iodide: mp 146° dec; nmr (D_2O) δ 2.6 (CCH_3, s, 3 H), 3.5 [$N^+(CH_3)_3$, s, 9 H], and ca. 7–8 (m, Ar H, 5 H); uv (EtOH) λ_{max} 215 mμ (shoulder) and 249 (ϵ 13,300); mass spectrum, see Table III.

Method B.—The following preparation of **3a** will exemplify the general procedure. Acetophenone N,N-dimethylhydrazone (10 g, 0.066 mol) and excess methyl iodide in anhydrous methanol (50 ml) were refluxed under nitrogen for 6 hr. After cooling, cold anhydrous ether was added; the crude precipitated methiodide was collected and recrystallized. The yield was increased (87%); samples prepared by method B were identical in all respects with those from prepared by method A.

Acetophenone N,N,N-Trimethylhydrazonium Tosylate.—An ethanolic solution of acetophenone N,N-dimethylhydrazone (10 g, 0.066 mol) and methyl p-toluenesulfonate (15 g, 0.081 mol) was allowed to stand at room temperature for 2 days; the mixture was then poured into anhydrous ether. The crude tosylate was filtered and recrystallized from absolute ethanol, affording 18.2 g (79%) of acetophenone N,N,N-trimethylhy-

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[20] R. L. Frank and R. P. Seven, J. Amer. Chem. Soc., **71**, 2629 (1949).

[21] G. J. Janz, R. G. Ascah, and A. G. Keenan, Can. J. Res., **25B**, 272 (1947); G. J. Janz and A. G. Keenan, ibid., **25B**, 283 (1947).

[22] All melting points were taken in sealed capillaries with a Thomas-Hoover Unimelt and are uncorrected. The infrared spectra were determined with either a Perkin-Elmer 237-B or 337-B spectrophotometer and the ultraviolet data were recorded on a Cary 14 spectrometer. Refractive indices were obtained with a Bausch and Lomb Abbé-type refractometer. Nmr spectra were obtained on a Varian Associates Model A-60 spectrometer. The chemical shift values are expressed in δ (parts per million) relative to a tetramethylsilane internal standard. Radioactive samples were assayed on either a Packard Tri-Carb liquid scintillation spectrometer system Series 3000, or Model 3003 (for those compounds which were soluble, without decomposition or coloration, in Bray's Cocktail[23]) or a Nuclear-Chicago thin window gas flow detector Model D47, equipped with a Nuclear-Chicago automatic sample changer Model C110B. Mass spectra were measured by Mr. Nathan Ingber or Mr. Robert Wadsworth of the Standard Oil Co., Cleveland, Ohio, on their CEC 21-103C spectrometer equipped with an MS 7500 Universal heated inlet system and in these laboratories on an A. E. I. MS-12 medium resolution mass spectrometer; spectra were 70 eV, electron-impact fragmentation unless otherwise indicated. The microanalyses were performed by Spang Microanalytic Laboratories, Ann Arbor, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn.

[23] G. A. Bray, Anal. Biochem., **1**, 279 (1961).

[24] The yields and physical constants are quoted in Table I.

drazonium tosylate: mp 175–176° dec; nmr (D_2O) δ 3.44 [$N^+(CH_3)_3$, s, 9 H], 2.54 (CCH_3, s, 3 H), 2.13 ($ArCH_3$, s, 3 H), and *ca.* 7–8 (m, ArH, 9 H).

Anal. Calcd for $C_{18}H_{24}N_2SO_3$: C, 62.04; H, 6.94; N, 8.04. Found: C, 61.97; H, 6.87; N, 8.00.

General Preparation of Ketone *N*,*N*,*N*-Trimethylhydrazonium Fluoborates.—The following preparation of acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate will exemplify the procedure.[24]

A hot aqueous solution[25] of sodium fluoborate (30 g) was slowly added to a refluxing solution of acetophenone *N*,*N*,*N*-trimethylhydrazonium iodide (30 g, 0.098 mol) dissolved in minimum water to ensure complete dissolution. The mixture was then cooled to room temperature; the crude crystalline product was filtered, dried *in vacuo*, and recrystallized from acetone–absolute ethanol, giving 25.5 g (96%) of acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate: mp 153–154° dec; nmr (D_2O) δ 2.75 (CCH_3, s, 3 H), 3.60 [$N^+(CH_3)_3$, s, 9 H], and a complex aromatic proton region; uv (EtOH) λ_{max} 214 mμ (ε 16,900) and 248 (9850); mass spectrum (see Table III).

Attempted Synthesis of Deoxybenzoin *N*,*N*,*N*-Trimethylhydrazonium Fluoborate.—A hot aqueous solution of deoxybenzoin *N*,*N*,*N*-trimethylhydrazonium iodide (15.4 g, 0.0405 mol) was added to the aqueous sodium fluoborate solution;[25] after cooling to ice bath temperature, the pale yellow oil which separated was worked up and distilled, giving 4.1 g (52%) of deoxybenzoin, bp 136–138° (0.25 mm). The physical and spectral data were identical with those of the starting ketone.

Pyrolysis of Acetophenone *N*,*N*,*N*-Trimethylhydrazonium Fluoborate. Method A.—Acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (20 g, 0.0758 mol), which was dried *in vacuo* at 40° for several days, was heated to decomposition (*ca.* 200°) in 5-g quantities in a pyrolysis tube (1 × 12 in.) flushing continuously with a slow stream of dry nitrogen. During the pyrolysis, the liberated gases and a white sublimate were trapped in two liquid nitrogen gas traps. After cooling, extraction of the pyrolysis vessel with benzene afforded a viscous red oil (9.371 g), along with an inorganic residue which was insoluble in benzene.

Column chromatography of this crude oil (2.00 g) was performed on Brinkmann silica gel G ($^3/_4$ in. × 3 ft) eluting with a mixture of *n*-hexane, benzene, and ethyl acetate (85:5:10, respectively) under nitrogen collecting 15-ml fractions. Fractions 1 to 10 upon concentration yielded 100 mg of acetophenone: bp 201°; ir (neat) 1680 (C=O) and 1265 cm^{-1}; nmr (CCl_4) δ 2.0 (CCH_3, s); 2,4-dinitrophenylhydrazone mp 249° (lit.[26] mp 250°). Fractions 12–18 (R_f 74)[27] upon concentration afforded a white solid which was recrystallized from low-boiling petroleum ether, giving 867 mg (49.5%) of the crystalline 2,6-diphenylpyridine: mp 82–83° (lit.[28] mp 82°); picrate mp 171° (ethanol) (lit.[29] mp 169°); uv (EtOH) λ_{max} 243 mμ (ε 27,600), 286 (10,500), 302 (12,200); mass spectrum (see Table III). Fractions 18–22 (R_f 72)[27] upon concentration afford a viscous yellow oil, which was distilled in a molecular still affording 108 mg (5.5%) of 3-methyl-2,6-diphenylpyridine: bp 150–160° (0.5 mm) [lit.[30] bp 253–255° (25 mm)]; nmr ($CDCl_3$) δ 2.22 ($ArCH_3$, s, 3 H); mass spectrum *m*/*e* (rel intensity) 245.12057 (M^+, 53), 244 ($M - 1^+$, 100), 230 ($M^+ - CH_3$, 30), 77 (C_6H_5, 7).

Anal. Calcd for $C_{18}H_{15}N$: C, 88.12; H, 6.17; N, 5.71. Found: C, 88.05; H, 6.12; N, 5.71.

Fractions 24–44 (R_f 52)[27] upon concentration gave an unidentified red oil (52 mg). Fractions 45–180 yielded no identifiable compounds comprising of polymeric residues remaining on the column. Attempted elution of this material afforded no discernible organic compounds.

The white sublimate, produced during the pyrolysis, was identical with an authentic sample of ammonium fluoborate; on comparison ir and nmr spectrum properties were superimpossible.

The gas, after removal of the sublimed ammonium fluoborate, was warmed slowly and bubbled through a solution of anhydrous methyl iodide in ether. The white quaternary salt was collected, dried *in vacuo*, and recrystallized from deuterium oxide, giving tetramethylammonium iodide: mp <300° dec; nmr (D_2O) δ 3.26 [$N(CH_3)_4$, t, $J = 0.5$ Hz], which is identical with the nmr spectrum of an authentic sample.

Anal. Calcd for $C_4H_{12}NI$: C, 24.04; H, 6.18; N, 6.94. Found: C, 23.91; H, 6.25; N, 6.84.

A second sample of gas was bubbled into anhydrous hydrogen chloride (*ca.* 5%) dissolved in anhydrous ether. The white precipitate which formed was carefully filtered (with complete exclusion of moisture) and dried *in vacuo*, giving a hydroscopic mixture of amine hydrochlorides, nmr (D_2O) δ 4.70 (s, NH), 2.95 [s, $^+N(CH_3)_3$], and 2.80 [s, $^+N(CH_3)_2$]. These peaks corresponded to nmr spectra (D_2O) of authentic samples of ammonium chloride, trimethylamine hydrochloride, and dimethylamine hydrochloride.

The other substituted diarylpyridines are listed in Table I and were prepared in the same manner, except where noted.

Method B. Pyrolysis in Cumene as Solvent.—Acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (10 g, 0.038 mol) in cumene (20 g, bp 150–155°) as solvent was slowly heated to about 154–150°; the exothermicity of the reaction then causes the solution to reflux for *ca.* 1 min. The mixture was refluxed for an additional 1 hr. After cooling, the solution was decanted from an inorganic residue and concentrated *in vacuo*, leaving a crude residue which was chromatographed on Merck alumina ($^3/_4$ in. × 2 ft) eluting with 1% benzene in low-boiling petroleum ether. Upon concentration and recrystallization of the eluent, 2,6-diphenylpyridine (mp 81–82°) was obtained (55%); mixture melting point with authentic sample was undepressed.

Pyrolysis of Acetophenone *N*,*N*,*N*-Trimethylhydrazonium Iodide.—Acetophenone *N*,*N*,*N*-trimethylhydrazonium iodide (20 g, 0.067 mol) was pyrolyzed as described under method A. 2,6-Diphenylpyridine (mp 80°) was isolated (1.3%) from the dark polymeric tar. No other organic compounds were isolated from the polymeric residue.

Pyrolysis of acetophenone *N*,*N*,*N*-trimethylhydrazonium tosylate was conducted as previously described under method A. 2,6-Diphenylpyridine (mp 81°) was isolated in less than 2% yield from the black viscous residue; no other discernible organic products were detected.

2-Phenyl-6-(4-methoxyphenyl)pyridine.—Acetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (5.71 g, 18.6 mmol) and 4′-methoxyacetophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (6.4 g, 18.6 mmol) were mechanically mixed and pyrolyzed as described in method A. The concentrated benzene extract was chromatographed on Merck alumina ($^3/_4$ in. × 2.2 ft); the first fraction was eluted with 2% benzene in petroleum ether. After concentration and recrystallization, only 2,6-diphenylpyridine (mp 78–80°) identical with previously obtained sample was isolated. A second component was eluted with 20% benzene in petroleum ether, giving, upon concentration, 2-phenyl-6-(4-methoxyphenyl)pyridine, which upon recrystallization from petroleum ether (bp 60–70°) gave an analytical sample: 0.335 g; mp 125° (lit.[31] mp 119°); nmr ($DCCl_3$) δ 3.78 ($ArOCH_3$, s, 3 H); uv (EtOH) λ_{max} 525 mμ (ε 22,400), 274 (18,000), 289 (15,000), and 308 (11,500).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.37. Found: C, 82.77; H, 5.79; N, 5.29.

A third component was eluted with 50% benzene in petroleum ether, yielding 2,6-di(4-methoxyphenyl)pyridine (mp 189–190°; recrystallization from petroleum ether (bp 60–80°) raised the melting point to 197–198°): nmr ($DCCl_3$) δ 3.89 ($C_{aromatic}OCH_3$, 6 H, s); uv (EtOH) λ_{max} 273 mμ (ε 31,200) and 316 (14,350).

3,5-Dimethyl-2,6-diphenylpyridine.—Propiophenone *N*,*N*,*N*-trimethylhydrazonium fluoborate (17 g, 0.062 mol) was pyrolyzed and worked up as described above in method A. Recrystallization from petroleum ether of the crude eluent gave 4.5 g (50%) of the white crystalline 3,5-dimethyl-2,6-diphenylpyridine: mp 136–137° (lit.[32] mp 134–135°); nmr (CCl_4) δ 2.36 ($ArCH_3$, d, $J = 0.5$ Hz, 6 H); uv (EtOH) λ_{max} 233 mμ (ε 20,000), 250

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(25) The aqueous sodium fluoborate solution was prepared by assuring neutral pH (*i.e.*, addition of either dilute sodium hydroxide or fluoboric acid), then filtration to remove all insoluble salts. Rapid hydrolysis of the quaternary salt occurs, if neutrality is not rigorously maintained.

(26) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964, p 363.

(27) R_f values were determined by thin layer chromatograph using Brinkmann Silica Gel G eluting with column solvent system.

(28) D. Bryce-Smith and A. C. Skinner, *J. Chem. Soc.*, 577 (1963). We thank Professors Bryce-Smith and Skinner for a sample of authentic 2,6-diphenylpyridine.

(29) M. Scholtz, *Ber.*, **28**, 1726 (1895).

(30) M. Scholtz, *ibid.*, **32**, 1935 (1899).

(31) M. Scholtz and W. Meyer, *ibid.*, **43**, 1861 (1910).

(32) V. Galiah and A. Ekambaram, *J. Indian Chem. Soc.*, **32**, 274 (1955).

(shoulder), 288 (9880); mass spectrum (mol wt) calcd 259, found 259.

2,6-Di[2-(6-methylpyridyl)]pyridine.—2-Acetyl-6-methylpyridine *N,N,N*-trimethylhydrazonium fluoborate (10 g, 0.036 mol) was pyrolyzed as described above in method A. The black viscous oil from the pyrolysis reactor was treated with aqueous sodium hydroxide (5 *N*, 2 ml), extracted with benzene, and concentrated. Purification by elution chromatography on Florosil with benzene afforded a pale yellow solid (mp 162–164°). Recrystallization from benzene–petroleum ether (bp 60–70°) gave 2.2 g (47%) of 2,6-di[2-(6-picolyl)]pyridine: mp 164–165°; nmr (CDCl$_3$) δ 2.62 (ArCH$_3$, s, 6 H), and a complex aromatic proton region including 8.4 (t, J = 4 Hz), 7.17 (t, J = 8 Hz), 7.24 (d, J = 4 Hz), and 7.17 (d, J = 8 Hz); uv (EtOH) λ_{max} 231 mμ (ϵ 11,700), 242 (11,900), and 289 (22,400).

An ethanolic solution of 2,6-di[2-(6-picolyl)]pyridine was slowly added to a solution of ethanolic ferric chloride, giving an ethanol insoluble, uncharacterized substituted 2,2′,2′′-tripyridyl complex, mp 278°.

Attempted Synthesis of 4-Phenyl-2,6-di(4-methoxyphenyl)-pyridine.—A mixture of 4′-methoxyacetophenone *N,N,N*-trimethylhydrazonium fluoborate (5.0 g, 17 mmol) and redistilled benzaldehyde (20 ml) was refluxed for 1 hr. At *ca.* 130–150°, the solution turned dark red with azeotropic distillation of water. The solvent (benzaldehyde) and last traces of water were removed by vacuum distillation, leaving a dark oil. Elution chromatography on Merck alumina with 20% benzene in petroleum ether gave a pale yellow solid, which when recrystallized from petroleum ether afforded 1.0 g (25%) of 2-benzal-4′-methoxyacetophenone: mp 104–105° (lit.[33] mp 106°); nmr (CDCl$_3$) δ 3.88 (ArOCH$_3$, s).

Anal. Calcd for C$_{16}$H$_{14}$O$_2$: C, 80.64; H, 5.92. Found: C, 80.67; H, 6.00.

2-Phenyl-5*H*-indeno[1,2-*b*]pyridine.—An intimate mixture of acetophenone *N,N,N*-trimethylhydrazonium fluoborate (6.5 g, 25 mmol) and 1-indanone *N,N,N*-trimethylhydrazonium fluoborate[3] (7.09 g, 25 mmol) was dried *in vacuo* at *ca.* 50° for several hours. The mixture was pyrolyzed as described under method A. The residual pyrolysate was extracted with benzene, concentrated, and chromatographed on alumina. Fraction 1 was eluted with 2% benzene in low-boiling petroleum ether (bp 30–60°, *ca.* 500–1000 ml) and gave 2,6-diphenylpyridine (150 mg, mp 79–80°) which was identical with an authentic sample.

The second fraction was eluted with 20% benzene in petroleum ether (bp 30–60°, 1000 ml) affording 2-phenyl-5*H*-indeno[1,2-*b*]-pyridine (760 mg), mp 120°. Recrystallization gave an analytical sample: mp 126–128°; nmr (DCCl$_3$) δ 3.67 (ArCH$_2$–, s, 2 H) and a complex aromatic region; uv (EtOH) λ_{max} 245 mμ (ϵ 30,200), 261 (10,800), and 318 (20,500).

Anal. Calcd for C$_{18}$H$_{13}$N: C, 88.85; H, 5.39; N, 5.76. Found: C, 88.88; H, 5.47; N, 5.72.

The third fraction was eluted with 50% benzene in petroleum ether (1000 ml) giving 10,12-dihydrodiindeno[1,2-*b*:2′,1′-*e*]-pyridine (1.05 g)[3], mp 203° (lit.[34] mp 206–207°).

2,6-Diphenylpyridine-^{14}C.—Acetophenone *N,N,N*-trimethylhydrazonium-^{14}C fluoborate (average activity 1320 cpm/μmol) was prepared in the same manner as unlabeled material, except for substitution of methyl-^{14}C iodide in the initial quaternization. The labeled fluoborate was pyrolyzed; the product was extracted and purified as previously described under method A. Five additional recrystallizations from petroleum ether gave an analytical sample of 2,6-diphenylpyridine-^{14}C: mp 82–83°, average activity 445 cpm/μmol. The ^{14}C ratio in the product, 2,6-diphenylpyridine, relative to the starting fluoborate was 1:2.96.

Pyrolysis of 4′-methoxyacetophenone *N,N,N*-trimethylhydrazonium fluoborate and *N,N,N*-trimethylhydrazonium-^{14}C fluoborate, prepared from the corresponding labeled iodide by precipitation of the less soluble fluoborate, was conducted as previously described under method A; recrystallization of the 2,6-di(4-methoxyphenyl)pyridine from benzene–petroleum ether afforded an analytical sample: mp 189–190°; the ratio of radioactive carbon was 34 cpm/μmol (product) to 635 cpm/μmol (*N,N,N*-trimethylhydrazonium fluoborate) or 5% incorporation of the original radiolabel.

Pyrolysis of 4′-methoxyacetophenone *N,N,N*-trimethylhydrazonium fluoborate and tetramethylammonium-^{14}C fluoborate, prepared from the corresponding labeled quaternary iodide by precipitation of the less soluble fluoborate, was executed as previously described under method A; recrystallization afforded 2,6-di(4-methoxyphenyl)pyridine, mp 190°. The ratio of radioactivity was 0.25 cpm/μmol (product) to 47 cpm/μmol (ammonium salt); the product therefore contains less than 0.5% ^{14}C of the original radiolabel.

Registry No.—**29,** 13466-32-5; **2k,** 33785-76-1; **2l,** 19679-59-5; **2m,** 33785-78-3; **2n,** 33785-79-4; **2o,** 33785-80-7; **2p,** 33785-81-8; **3a,** 33785-82-9; **3b,** 33785-83-0; **3c,** 33785-84-1; **3d,** 33777-72-9; **3e,** 33777-73-0; **3f,** 33777-74-1; **3g,** 33777-75-2; **3j,** 33777-76-3; **3k,** 33777-77-4; **3l,** 19679-61-9; **3m,** 33777-79-6; **3n,** 33777-80-9; **3o,** 33777-81-0; **3p,** 33777-82-1; **4a,** 10467-41-1; **4b,** 33775-44-9; **4c,** 10467-42-2; **4d,** 33775-46-1; **4e,** 33775-47-2; **4f,** 33775-48-3; **4g,** 33775-49-4; **4j,** 33775-50-7; **4k,** 33775-51-8; **4l,** 10467-43-3; **4m,** 33775-53-0; **4n,** 33775-54-1; **4o,** 33775-55-2; **5a,** 3558-69-8; **5b,** 33777-84-3; **5d,** 33777-85-4; **5e,** 33777-86-5; **5f,** 33777-87-6; **5g,** 21172-80-5; **5j,** 33777-89-8; **5k,** 33777-90-1; **5m,** 33777-91-2; **5o,** 33777-92-3; acetophenone *N,N,N*-trimethylhydrazonium tosylate, 33777-93-4; 3-methyl-2,6-diphenylpyridine, 28489-52-3; tetramethylammonium iodide, 75-58-1; 2-phenyl-6-(4-methoxyphenyl)pyridine, 33777-95-6; 2-benzyl-4′-methoxyacetophenone, 959-23-9; 2-phenyl-5*H*-indeno[1,2-*b*]pyridine, 33777-97-8.

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