(100), 84 (73). Anal. $C_{17}H_{19}N$: C, H. When the crude oil remaining after evaporation of excess alkene was chromatographed on silica gel, elution with mixtures of benzene and ethyl acetate gave fractions containing first 0.3 g of **42**, followed by fractions which on evaporation gave 0.16 g of an oil which appears to be azetine **43**: IR 1660 cm^{-1}; NMR τ 2.2–2.7 (7 H, m), 8.62 (6 H, s), 8.69 (6 H, s); *m/e* 237 (Parent).

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Registry No.—**1**, 100-47-0; **15**, 37771-71-4; **16**, 61838-76-4; **17**, 18495-18-6; **18**, 62816-34-6; **20**, 37771-72-5; **21**, 63704-25-6; **22**, 63704-26-7; **23**, 63704-27-8; **24**, 63704-28-9; **25**, 63704-29-0; **26**, 63704-30-3; **27a**, 63704-31-4; **27b**, 63704-32-5; **28**, 36597-09-8; **29**, 37771-73-6; **29** NPM adduct, 63704-33-6; **31**, 63704-34-7; **33**, 37771-74-7; **33** NPM adduct, 63704-35-8; **34**, 37771-77-0; **34** NPM adduct, 63704-36-9; **35**, 37771-76-9; **35** NPM adduct, 63704-37-0; **36**, 37771-75-8; **36** NPM adduct, 63704-38-1; **37**, 63704-39-2; **38**, 63704-40-5; **40**, 613-46-7; **41**, 1003-31-2; **42**, 37771-79-2; **43**, 63765-57-1; **44**, 63704-41-6; NPM, 941-69-5; dimethyl tetramethylsuccinate, 17072-58-1; 2-methyl-1-phenyloctane-1,7-dione, 63704-42-7; acetone 2,4-DNPH, 1567-89-1.

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α- and β-Rearrangement Products, Benzoylpyridyltriphenylphosphonium Methylides and Phenylethynylpyridines, from Pyridine *N*-Oxides and Phenylethynyltriphenylphosphonium Bromide

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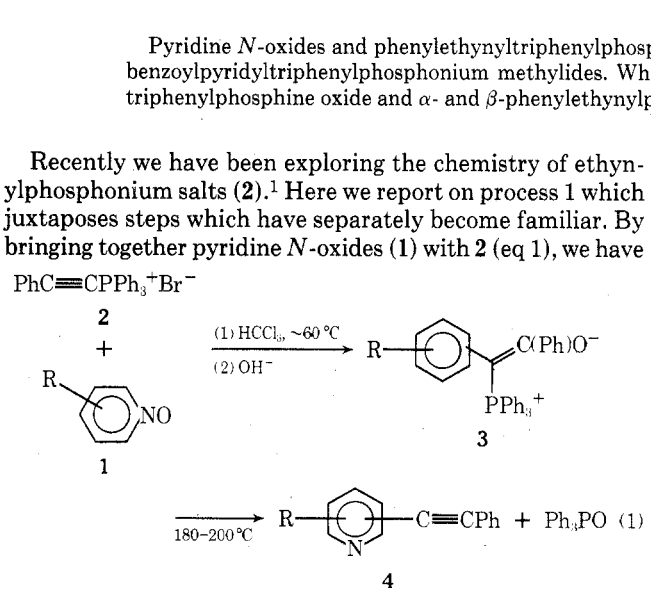
Pyridine *N*-oxides and phenylethynyltriphenylphosphonium bromide react in chloroform to produce α- and β-benzoylpyridyltriphenylphosphonium methylides. When sublimed at ca. 200 °C, these enol phosphoranes yield triphenylphosphine oxide and α- and β-phenylethynylpyridines.

Recently we have been exploring the chemistry of ethynylphosphonium salts (**2**).[1] Here we report on process 1 which juxtaposes steps which have separately become familiar. By bringing together pyridine *N*-oxides (**1**) with **2** (eq 1), we have



obtained some new enol phosphoranes (**3**) and pyridylacetylenes (**4**) which are collected in Table I.

Michael additions of ylides, e.g., $\equiv N^+-N^-$—, $=S^+-N^-$—, $\equiv N^+-O^-$, to alkynes are known and have been reviewed both generally[2a] and in the context of specialized topics, e.g., nitrone,[2b] azomethine ylide[2c] and other dipolar cycloadditions,[2d] indolizine synthesis,[2e] and nuclear substitution in heteroaromatic *N*-oxides.[3,4] Pertinent here is the specific area of *N*-oxide attacks on activated alkynes. Although apparent rearrangements in pyridine *N*-oxide chemistry yield numerous α-substituted pyridines, those which give β-pyridines have few precedents but are not unknown.[3-5] Indeed, the recent elucidation of possible mechanisms and products of the reaction of pyridine (or quinoline) with phenylpropionitrile, described by Abramovitch's group, stimulated our interest in this area (eq 2):[3]

Now there are other syntheses which appear to be related to those of eq 1, at least in overall effect. Pyridine *N*-oxides and pyridines, usually as salts, and metal acetylides give 2- and occasionally 4-ethynylpyridines;[6a-d] pyridine, benzoyl chloride, and silver phenylacetylide yield *N*-benzoyl-2-phenylethynyl-1,2-dihydropyridine.[6e] The thermal conversion of the phosphorane enolate, **3** to **4**, has ample precedent in other alkyne syntheses.[7]

Table I. Products of the Reaction of RC_5H_4NO (1) and $PhC{\equiv}CPPH_3^+Br^-$ (2)

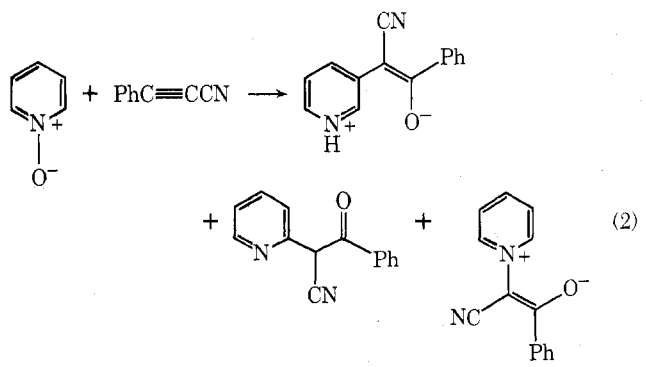
(RC_5H_3N)-*n*-$Ph_3P^+C{=}C(Ph)O^-$ (3)

3	R	n	Registry no.	Yield %	Mp, °C	Formula	C Calcd	C Found	H Calcd	H Found	NMR ($CDCl_3$), δ H2	H3	H4	H5	H6	IR (KBr), cm^{-1} ν_{CO}	ν_{PC}
a	H	2	63731-21-5	55.7[a]													
b		3	63731-22-6		203–204	$C_{31}H_{24}NOP$	81.38	81.15	5.28	5.33						1500	1101
c	2-Me	5	63731-23-7	45.5	222–223	$C_{32}H_{26}NOP$	81.51	81.88	5.56	5.54		6.61	6.97		7.93	1480	1100
d	3-Me	2	63731-24-8	61.7	189–190	$C_{32}H_{26}NOP$	81.51	81.89	5.56	5.55				6.51		1500	1100
e		5	63731-25-9	1.1	209.5–210.5			81.03		5.29	7.88		6.83		7.88	1502	1100
f	4-Me	2	63731-26-0	~13	178.5–179.5	$C_{32}H_{26}NOP$	81.51	81.98	5.56	5.46	6.75			6.53		1495	1100
g		3	63731-27-1	~27	230–231			81.94		5.56	8.05			6.80	8.05	1495	1097
h	4-Cl	2	63731-28-2	29	206–207	$C_{31}H_{23}NOP$-Cl	75.68	76.02	4.71	4.74		6.91		6.63		1507	1105
i	4-MeO	2	63731-29-3	~13	169.5–171	$C_{32}H_{26}NO_2P$	78.83	79.03	5.38	5.35		6.45		6.25		1510	1100
j		3	63731-30-6	~13	221.5–222			78.86		5.32	8.1			6.30	8.1	1480	1100

(RC_5H_3N)-*n*-C≡CPh (4)

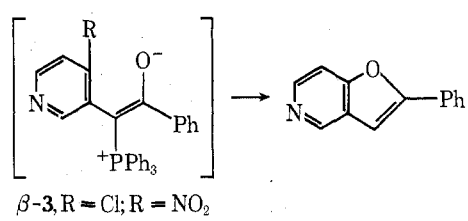
4	R	n	Registry no.	Yield, %	Mp or bp (mm), °C	Formula	C Calcd	C Found	H Calcd	H Found	NMR (CCl_4) δ H2	H3	H4	H5	H6	IR, cm^{-1}, $\nu_{C\equiv C}$
a	H	2	13141-42-9			$C_{13}H_9N$										2215 (m)
b	H	3	13238-38-5	95	50–51	$C_{13}H_9N$					8.77				8.51	2210 (w)
c	2-Me	5	63731-31-7	85	60.5–61	$C_{14}H_{11}N$	87.01	87.13	5.74	5.76		7.03	7.59		8.67	2200 (w)
d	3-Me	2	63731-32-8	94	105 (0.1)	$C_{14}H_{11}N$	87.01	86.88	5.74	5.60				7.00	8.35	2210 (s)
f	4-Me	2	63731-33-9	~100	105 (0.1)	$C_{14}H_{11}N$	87.01	86.65	5.74	5.67				6.9	8.35	2200 (w)
g	4-Me	3	63731-34-0	~100	105 (0.1)	$C_{14}H_{11}N$	87.01	86.82	5.74	5.70	8.45			7.03	8.45	2205 (w)
h	4Cl	2	63731-35-1	84	105 (0.1)	$C_{13}H_8N$-Cl[b]									8.45	2220 (s)

[a] Isomer mixture. [b] Analyzed as picrate.



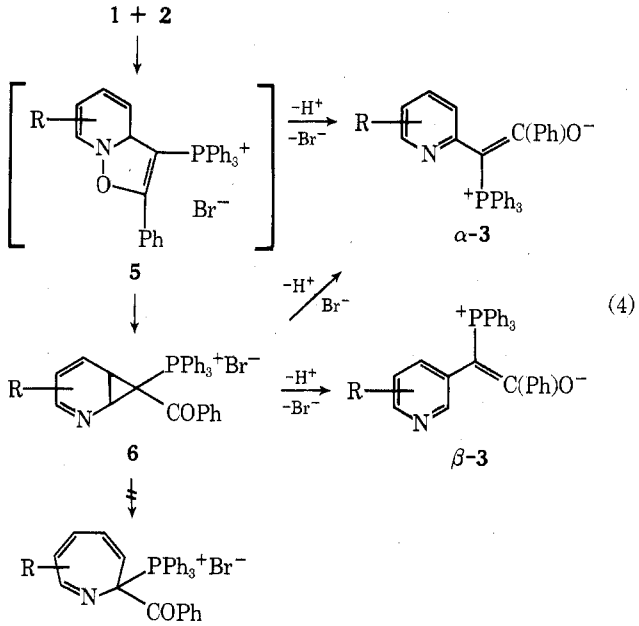
(2)

With respect to process 1, we found that 4-methoxy and 4-nitropyridine *N*-oxides produced at least some **3**; the subsequent conversion of **3** to **4** led to complex mixtures. Guided by the work on process 2 in which γ-Cl, NO_2 and MeO of **1** could be replaced,[3a,c] we also found another route whereby β-**3** could be consumed (eq 3). This constitutes a possible obstacle to β-**4** products. Although we did not isolate other plausible products of reaction of **3** with **2**, e.g., divinyl ethers,[3] the involvement of **2** in such reactions has precedent and would not be unexpected.[1] At this stage, therefore, we believe that speculations on extensions of process 1 or rationalizations of the orientation, α-**3** vs. β-**3**, are unwarranted. What does emerge is that we do have a practical route to some α- and β-ethynylpyridines.



β-**3**, R = Cl; R = NO_2 (3)

We apply the mechanism which Abramovitch used to account for the products of eq 2 to the formation of **3** in eq 4.[3] It is not clear whether **5** is formed in one or two steps but "dipolar" adducts of the type **5** have actually been isolated by others.[2,3] Elimination at the 1,2 positions of **5** yields α-**2** or α-**3**; the corresponding step in eq 2 is favored by added triethylamine.[3b]



Although the azanorcaradiene (**6**) appears to be the most plausible precursor of β-**3**, it is not obvious why this route competes so well. (Another postulated addition–rearrangement is on record: with mercaptans in acetic anhydride pyridine, *N*-oxides yield both 2- and 3-pyridyl sulfides, the latter presumably forming via a 2,3-episulfonium species analogous to **6**.[5]) An interesting option for **6** is that it may isomerize to the azepine. The literature does in fact indicate that *some* azepines are thermodynamically favored over isomeric azanorcaradienes and that the barrier is low, e.g., $\Delta G^{\ddagger} \leq 11$ kcal/mol at ≤ -40 °C.[8] On the other hand, pyrolysis of several 3-acyl-3*H*-azepines at 150 °C effected ring contraction to 3-acylmethylpyridines, presumably by way of an intermediate like **6**.[9] It would appear that the energetics favor the pyridine structure. Moreover, the presence of base, i.e., excess **1**, bromide ion, or pyridine products, may facilitate the formation of β-**3**. Clearly, the diversion of **6** in some way, e.g., to azepine, Diels–Alder adduct, etc., would provide additional support for the proposed route to β-**3**.

Several prominent spectral characteristics of **3** and **4** have been included in Table I. These correspond to literature correlations of IR and ^{1}H NMR data for pyridines[4a,10] and were invaluable aids in assigning isomeric structures.

Experimental Section

Melting points are uncorrected. Infrared spectra were measured on Perkin-Elmer 237 and Beckman IR8 spectrophotometers: solids were taken in KBr pellets while liquids were taken as films. NMR spectra were measured on a Varian T-60 instrument: compounds **3** were taken in $CDCl_3$ and **4** in CCl_4 solution, except as noted below. Mass spectra were measured on a Varian MAT CH-7 spectrograph.

The unsubstituted **1** was distilled before use; the other *N*-oxides were used directly. Compound **2** was prepared in the standard way.[11] Many of the properties of **3** and **4** are given in Table I. After a description of our standard methods of synthesis and purification, additional data for **3** and **4** will be listed in abbreviated form. IR absorptions are strong(s), unless otherwise indicated.

Reactions of Pyridine *N*-Oxides (1) with Phenylethynyltriphenylphosphonium Bromide (2). The *standard* procedure was to add **1** (7–10 mmol) to a solution of **2** (5 mmol) in chloroform (ca. 30 mL) under nitrogen and heat at reflux temperature for ca. 24 h. After the solvent was evaporated, the residue was taken up in methanol (30–40 mL) and heated with 10% aqueous potassium hydroxide (15–20 mL) at ca. 75 °C for 2–3 h. The methanol was evaporated and the aqueous mixture was extracted, usually with chloroform–ether, and occasionally with ether, then dried over magnesium sulfate and filtered. A few milliliters of ether was added to this filtrate, whereupon the bulk of the product(s), mainly β-**3** compound(s), precipitated. The solid was filtered off. At this point a purification *cycle* was started. The filtrate was treated with hydrochloric acid (3 M) and ether. The ether layer which was washed with aqueous base and dried usually yielded some triphenylphosphine oxide. The hydrochloric acid layer was treated with chloroform several times; this chloroform extract, which was washed with aqueous base and dried, yielded mainly α-**3**. The hydrochloric acid layer was treated with a slight excess of potassium hydroxide and extracted with chloroform. On workup the chloroform solution yielded mainly β-**3**.

To purify α-**3**, it was dissolved in chloroform and extracted with 3 M hydrochloric acid. This tended to remove β-**3**.

To purify the β-**3**, it was dissolved in 3 M hydrochloric acid and extracted with chloroform. This tended to remove the α-**3**.

Occasionally, samples of impure **3** were purified by recrystallization from ethyl acetate or by column chromatography on alumina with chloroform as a solvent. The β-substituted compounds usually have the higher melting point and are easier to crystallize.

Conversion of Benzoylpyridyltriphenylphosphonium Methylides (3) to Phenylethynylpyridines (4). In the standard procedure, **3** was heated under nitrogen in a sublimation apparatus at 180–200 °C for 4–5 h. The product was then collected by sublimation at ca. 1 mm. The sublimate was further separated by column chromatography on alumina. Triphenylphosphine was eluted in high yields (88–100%) by chloroform.

Some picrates of **4**, e.g., **4a** and **4b**, are readily prepared in ethanol. Since these compounds may dissociate readily when heated in solution or treated with base, a picrate may be a useful form in which to store **4**.

Reaction of Pyridine *N*-Oxide (1a) and 2. Compound **3b** was (**3a** was not) separated from the mixture of **3a** and **3b**. For **3b**: NMR δ 7.0–8.27 (m); IR 3050 (w), 1449, 1357, 1213, 970 (m), 763, 752, 739, 732 cm^{-1}. Compound **4b**: lit.[12] mp 47–48.5 °C; NMR δ 7.0–7.8 (m), 8.51 (d, 1 H, J = 4 Hz); IR (KBr) 3030 ± 35 (b, w), 1488, 1411, 1018, 811, 755, 685 cm^{-1}; MS (*m/e*) 179 (parent).

The picrate of **4b** had mp 157–159 °C dec from ethanol.

Compound **4a**, prepared by another route,[6c] was shown to be essentially pure by GC. It is a low-melting solid (lit.[13] mp 29–32 °C; lit.[6e] bp 116 °C (0.1 mm)) whose picrate had mp 147–150 °C dec (lit.[13] mp 152–153 °C dec).

Since **3a** and **4a** were not separated free from their isomers **3b** and **4b** respectively, in eq 1, their presence was established in two ways. The mixture of **3a** and **3b** was pyrolyzed to give **4a** and **4b** which was oxidized with potassium permanganate according to a literature procedure.[14] Benzoic acid (66% yield) and pyridine carboxylic acids (39% yield) were formed. The latter were esterified with 1-butanol and analyzed by GC on an SE column kept at 145 °C. The retention times of the two esters were identical with those of authentic samples made from α-picolinic and nicotinic acids.

Another experiment was designed to estimate the product ratios **3a/3b** and **4a/4b**. Accordingly, **1a** (286 mg, 3 mmol) and **2** (887 mg) were combined in the standard way. Compounds **3** (510 mg, 55.7% yield) were carefully separated from triphenylphosphine oxide (108 mg) by the standard workup and sublimed under nitrogen at 180–200 °C for 5 h. The components of the sublimate were obtained by chromatography on alumina, **4a** and **4b** (142 mg, 71% yield) being eluted by benzene and triphenylphosphine oxide (185 mg, 60% yield) by chloroform. The ratio **4a/4b** = 1/3 was established by GC using an SE column at 180 °C. The retention times of **4a** and **4b** in the mixture were identical with those of the individual compounds.

Reaction of α-Picoline *N*-Oxide (1c) and 2. For **3c**: NMR δ 2.33 (d, 3 H, J = 2 Hz), 6.61 (d, 1 H, J = 8 Hz), 7.0–7.9 (m); IR 3010 ± 40 (b, w) 1480, 1370, 1260, 1170 (w), 1024 (m), 959 (m), 745, 690 cm^{-1}. For **4c**: NMR δ (CCl_4/$CDCl_3$) 2.53 (s, 3 H), 7.03 (d, 1 H, J = 8 Hz), 7.2–7.5 (m), 7.59 (dd, 1 H, J = 8 and 2 Hz); IR (KBr) 3025 (w), 2920 (w), 1593, 1493, 1020 (m), 823 (m), 745, 680 (m) cm^{-1}; MS (*m/e*) 193 (parent).

Reaction of β-Picoline *N*-Oxide (1d) and 2. For **3d**: NMR δ 2.10 (s, 3 H), 6.51 (ddm, 1 H, J = 7.5 Hz), 7–8 (m); IR (KBr) 3023 (w), 1473, 1463, 1367, 743 (m), 716 (m), 688 cm^{-1}. For **3e**: NMR δ 1.78 (s, 3 H), 7.0–7.8 (m); IR (KBr) 3000 (w), 1433 (m), 1363 (m), 1277 (m), 760 (w), 745 (w), 715 (m), 691 cm^{-1}. For **4d**: NMR (CCl_4) 2.45 (s, 3 H), 7.00 (dd, 1 H, J = 8 Hz, J = 5 Hz), 7.2–7.6 (m), 8.35 (dm, 1 H, J = 5 Hz); IR (neat) 3050 (m), 1580 (m), 1490, 1441, 1105 (m), 785 (m), 755, 685 cm^{-1}; MS (*m/e*) 193 (parent).

Reaction of γ-Picoline *N*-Oxide (1f) with 2. For **3f**: NMR δ 1.97 (s, 3 H), 6.53 (dm, 1 H, J = 5 Hz), 7.0–7.9 (m), 7.97 (d, 1 H, J = 5 Hz); IR 3041 (w), 1594, 1495, 1436, 1358, 1270 (m) 1100, 1021 (m), 780 (m), 750, 719, 675 cm^{-1}. For **3g**: NMR δ 2.07 (s, 3 H), 6.80 (dm, 1 H, J = 5 Hz), 7.0–7.8 (m); IR 3040 ± 40 (w) 1495, 1437 (m), 1375 (m), 1124 (m), 1095, 957 (m), 760 (m), 721, 685 cm^{-1}. For **4f**: NMR δ 2.28 (s, 3 H), 6.9 (d, 1 H, J = 5 Hz), 7.1–7.7 (m) 8.35 (d, 1 H, J = 5 Hz); IR (neat) 3050

(w), 2915 (w), 1599, 1492 (m), 920 (w), 820 (m), 751, 684 cm^{-1}; MS (*m/e*) 193 (parent). For **4g**: NMR δ 2.47 (s, 3 H), 7.2–7.7 (m); IR (neat) 3050 (b, w), 2920 (b, w), 1588, 1492, 1440, 1400, 1216 (w), 1117 (w), 823 (m), 750, 685 cm^{-1}; MS (*m/e*) 193 (parent).

Reaction of 4-Chloropyridine *N*-Oxide (1h) with 2. For **3h**: NMR δ 6.63 (dm, 1 H, J = 5 Hz), 7–8 (m); IR 3050 (b, w), 1563 (m), 1540 (m), 1476 (m), 1430, 1392, 1340, 1127 (m), 1013 (m), 755 (m), 739 (m), 720, 686 cm^{-1}. For **4h**: NMR δ 7.1–7.7 (m), 8.45 (d, 1 H, J = 5 Hz); IR (neat) 3050 (m), 1597 (w), 1567, 1545, 1491 (m), 1453 (m), 1381 (m), 1095 (m), 890 (m), 823 (m), 755, 685 cm^{-1}; MS (*m/e*) 213 (parent).

A picrate of **4h** had mp 165–167 °C dec from ethanol: IR (KBr) 2205 (m) 1640 cm^{-1}. Anal. Calcd for $C_{19}H_{11}N_4O_7Cl$: C, 51.53; H, 2.50. Found: C, 51.54; H, 2.74.

2-Phenylfuro[3,2-*c*]pyridine. This compound was obtained both from the aqueous and chloroform portions in the preparation of **3h**. Column chromatography yielded the furopyridine (27% yield), from the benzene eluate: mp 123.5–124 °C; NMR ($CDCl_3$) 7.0 (d, H_3, J = 1 Hz), 7.43 (m, 4 H), 7.83 (m, 2 H), 8.45 (d, H_6, J = 6 Hz), 8.90 (d, H_4, J = 1 Hz); IR (KBr) 1462 (m), 1456 (m), 1260 (m), 1011 (m), 883, 826, 752, 680 (m) cm^{-1}; MS (*m/e*) 195 (parent). Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65. Found: C, 80.52; H, 4.67.

Reaction of 4-Methoxypyridine *N*-Oxide (1i) with 2. For **3i**: NMR δ 3.4 (s, 3 H), 6.25 (dm, 1 H, J = 6 Hz), 7–8 (m); IR 3050 (w), 1580, 1475, 1437, 1365, 1207 (m), 742 (m), 718 (m), 687 (m) cm^{-1}. For **3j**: NMR δ 3.33 (s, 3 H), 6.30 (d, 1 H, J = 6 Hz), 7–7.8 (m), 8.1 (2 H); IR 3021 (b, w), 1573, 1430, 1368, 1272, 1020, 960 (m), 850 (m), 800 (m), 743, 705 ± 20 (b) cm^{-1}.

Reaction of 4-Nitropyridine *N*-Oxide (1k) with 2. In this system, the "standard" conditions were altered: The reaction was carried out in DMF as solvent at 110 °C for **3d**. The solvent was then evaporated under reduced pressure and the residue was treated with methanol and 10% aqueous potassium hydroxide at reflux temperature for 3 h. The solid was filtered and purified by chromatography; the filtrate was extracted with chloroform and subjected to the standard purification cycle yielding 2-phenylfuro[3,2-*c*]pyridine (4% yield), mp 118.5–119 °C, by column chromatography and sublimation.

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Registry No.—**1a,** 694-59-7; **1c,** 931-19-1; **1d,** 1003-73-2; **1f,** 1003-67-4; **1h,** 1121-76-2; **1i,** 1122-96-9; **1k,** 1124-33-0; **2,** 34387-64-9; **4b** picrate, 63731-36-2; **4h** picrate, 63731-37-3; 2-phenylfuro[3,2-*c*]-pyridine, 63731-38-4.

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The Vilsmeier–Haack Aroylation of Pyrroles Reexamined

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Vilsmeier–Haack formylation of pyrroles is well established, but its extension to aroylation, despite offering advantages over other methods, has not been properly exploited as no systematic study of the reaction has been reported. The latter reaction has been reexamined and a method for the aroylation of certian pyrroles on a 5–200-mmol scale in yields of 85–96% is given together with a brief discussion of the reactivity of pyrroles and carboxamides, the preparation of the amide–phosphoryl chloride complex, azafulvene formation, and general experimental conditions necessary for efficient reaction. The preparation of 2-benzoylpyrrole is described to illustrate the improvements, and several new aroylpyrroles are reported.

The Vilsmeier–Haack reaction[1] (Scheme I[2]) is well established[3] as a means of formylating pyrroles (Scheme I, R = H) and the experimental procedure widely used is that of Silverstein et al.[4] The reaction offers the advantages of monoformylation,[5] virtually exclusive attack[6] at the α position of unsubstituted pyrroles lacking bulky N substituents[7] and consistently high yields.

The reaction was later extended to include the acylation[8] (Scheme I, R = alkyl) and aroylation[9] (Scheme I, R = aryl) of pyrroles. While retaining the other advantages of the formylation reaction, the extended processes usually gave poorer yields. Consequently, aroylation by the Vilsmeier–Haack method, notwithstanding occasional reported yields of 80% or more,[10,11] appears to have fallen into disfavor and to have been supplanted by other procedures,[12] themselves often severely limited in their application to pyrrolic substrates.

Despite recognition[13] that "the conditions employed in the Vilsmeier–Haack condensation can be critical", no systematic investigation of the experimental conditions necessary for efficient aroylation by this procedure has yet been reported. Consequently, the conditions commonly employed are those reported for the formylation of pyrrole,[4] which are, in fact, unnecessarily harsh and unsuitable for the aroylation of pyrroles.