either ribose- or TMS-derived fragments and have been discussed previously.[21,24,25]

Conclusion

In Table IV are listed for comparison the relative intensities of those ions expected to distinguish between 2′- and 3′-linked isomers. The general trends can be used to differentiate between the isomers, but, because of exceptions in the relative intensities in a few cases, caution must be exercised and all the ions listed in Table IV should be considered. The data can be used to identify isomers if a gas chromatographic separation can be achieved and to enable predictions to be made on the general form of the mass spectra of isomers not yet prepared. However, the positive identification of a single unknown isomer from the mass spectral data alone would remain uncertain.

Experimental Section

The mass spectra were recorded on a Hitachi RMU-6D single-focusing mass spectrometer using published procedures,[24] at an electron energy of 50 V and a nominal 900-V ion-accelerating energy. Trimethylsilyl derivatives were prepared[24] by treating 0.5 mg of a sample with 100 μl of BSTFA and 15 μl of TMCS (Pierce Chemical Co.). Complete trimethylsilylation (*i.e.*, one hydrogen of each OH, NH, or NH_2 group of sugar and base moieties was replaced by a TMS group[34]) was achieved overnight at room temperature in all cases except for 8,2′-NHAnI. Three TMS groups were incorporated at room temperature but four were incorporated by heating to 60° for 30 min. For the preparation of the TMS-d_9 derivatives BSA-d_{18} and TMCS-d_9 (Merck Sharpe and Dohme, Montreal) were used.

Syntheses of the compounds have been previously described: 8,2′-OAnA,[35,36] 8,2′-SAnA,[36-39] 8,2′-NHAnA,[17,39] 8,2′-OAnI,[40] 8,2′-SAnI,[19,20,38,39] 8,2′-NHAnI,[39] 8,2′-SAnG,[20,38,39,41] 8,2′-NHAnG,[39] 8,2′-SAnX,[20,40] 8,3′-OAnA,[35] 8,3′-OAnI,[40] 8,3′-SAnA,[37] 8,3′-SAnI,[19,40] 8,3′-SAnG.[42]

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Noncoordinating Buffers. I. Synthesis and Characterization of Water-Soluble Derivatives of 2,6-Di-*tert*-butylpyridine

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Several derivatives of 2,6-di-*tert*-butylpyridine, containing alkyl, trimethylammonium [$-N(CH_3)_3^+$], or dimethylammonium [$-NH(CH_3)_2^+$] substituents, have been prepared and characterized. The mechanism of their synthesis, their water solubilities, pK_a's, and possible utilization as noncoordinating buffers and nonnucleophilic bases are briefly discussed.

Studies of reactions of metal ions in aqueous solution are limited by the fact that all common Lewis bases that may be used for buffering action will also coordinate to metals, making it impossible to investigate the behavior of uncomplexed metal ions in buffered media. In a search for water-soluble noncoordinating buffers, *i.e.*, weak bases that may donate their electron pair to a proton but not to a metal ion, several dimethylaminopyridines and quaternary ammonium pyridines with 2- and 6-*tert*-butyl substituents were prepared. The pyridine nitrogen of these compounds can coordinate to a proton, but is too sterically shielded to coordinate to Lewis acids even as small as CH_3^+ or BF_3.[1] This ensures that the title compounds will not coordinate to metal ions and that they will also have very low nucleophilic activity. It is now well known that the commonly used buffer 2,6-lutidine is not sufficiently shielded to prevent its coordination to metal ions.[2]

Results and Discussion

Synthesis.—The reaction of an alkyllithium compound with pyridine provides a direct method for the introduction of alkyl substituents ortho to the pyridine nitrogen. Since the original work of Ziegler and Zeiser[3] this reaction has been extensively utilized and studied, the intermediacy of a *N*-lithio 1,2-dihydropyridine derivative having been established.[4-6] In the presence of excess *tert*-butyllithium, pyridine is converted to 2,4,6-tri-*tert*-butylpyridine in one synthetic step.[7] Employing this one-step procedure, we have synthesized several *tert*-butylated pyridines (see Table I). Presumably these reactions proceed in a stepwise matter, there being enough *tert*-butyllithium present at the decomposition of the first dihydro derivative(s) so that subsequent reaction can occur.

In addition to alkylating pyridine bases in the above manner, an alkyllithium may also metalate either the

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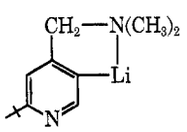
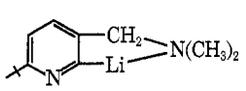
TABLE I
COMPOUNDS SYNTHESIZED

Compd[c]	Yield, %	Mp or bp, °C (mm)
(1) 2,4,6-Tri-*tert*-butylpyridine	33	70.1-70.3
(2) 2,6-Di-*tert*-butyl-4-methylpyridine	44	33.5-33.8
(3) 2,6-Di-*tert*-butyl-3-methylpyridine	40	48 (0.1)
(4) 4-Dimethylaminomethylpyridine	37	87 (10)
(5) 3-Dimethylaminomethylpyridine	80	90 (15)
(6) 2-*tert*-Butyl-4-dimethylaminomethylpyridine	20	60 (3)
(7) 2,6-Di-*tert*-butyl-4-dimethylaminomethylpyridine	<5	80 (2)
(8) 2-*tert*-Butyl-5-dimethylaminomethylpyridine	<10	97 (1)
(9) Trimethyl(2,6-di-*tert*-butyl-4-picolyl)ammonium perchlorate	50	246-247
(10) 2,6-Di-*tert*-butyl-4-dimethylaminopyridine	77	65-66
(11) Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)ammonium salts		
(a) Perchlorate	>95	202.5-204.5
(b) Nitrate[a]	>95	151.2-152.0 dec
(c) Chloride[a]	>95	Sublimes *ca.* 240
(d) Bromide[a]	>95	Sublimes *ca.* 255[b]
(12) Trimethyl(2,6-di-*tert*-butyl-4-pyridyl)ammonium salts		
(a) Iodide	>95	171.2-171.8 dec
(b) Perchlorate	>95	290-291
(c) Nitrate	>95	226.5-227.0
(13) 2-*tert*-Butyl-6-dimethylaminopyridine	52	46-48 (0.07)
(14) Trimethyl(2-*tert*-butyl-6-pyridyl)ammonium salts		
(a) Iodide	92	192.2-192.9
(b) Perchlorate	>95	226.0-226.8
(c) Trifluoromethanesulfonate	>95	142.0-143.5
(15) 2,4-Di-*tert*-butyl-6-dimethylaminopyridine	50	97 (0.7)
(16) Trimethyl(2,4-di-*tert*-butyl-6-pyridyl)ammonium salts		
(a) Iodide	>95	197.9-198.4
(b) Perchlorate	>95	233.0-234.5

[a] Isolated both as pure salt and as chloroform adduct; melting point is that of pure salt. [b] With decomposition. [c] 1-16 (a-d).



II



III

pyridine ring or an activated substituent.[8,9] Brown and Kanner[1] pointed out that ring metalation could account for the yields of bipyridyl derivatives obtained in these reactions. Ring metalation proves to be a serious obstacle to the di-*tert*-butylation of 3- and 4-dimethylaminomethylpyridine, since in these compounds the side chain is capable of chelating the lithium and thus stabilizing the metalated product, a phenomenon previously observed with benzyldimethylamine[10] and related compounds.[11] The 3 compound does not add a second *tert*-butyl at all, presumably because the ring-metalated product III (i) has the 6 position blocked and (ii) is more stable than the analogous 5-metalated II because of the ortho-directing influence of the ring nitrogen.[9]

Quaternization of the several tertiary amines prepared in this work is easily accomplished with methyl iodide. Reaction at the hindered pyridine nitrogen is not observed to be a complication, even with 2-*tert*-butyl-6-dimethylaminopyridine. The iodide salts are easily converted to perchlorates, trifluoromethanesulfonates, nitrates, and chlorides by treatment with the appropriate silver salt. Because of the singular importance of perchlorate as a noncoordinating anion, a cheaper, more direct route to the preparation of perchlorate salts was sought. It was found that the methylating agent[12] trimethylsulfoxonium perchlorate (*vide infra*) readily quaternizes tertiary amines to their perchlorate salts in one step.

Properties.—Most of the sterically hindered pyridines prepared in this work have a measurable affinity for protons (see Table II) and are thus suitable for use in buffer systems. Brown and Kanner[1] first observed that the nitrogen of 2,6-di-*tert*-butylpyridine is so sterically shielded that it cannot comfortably coordinate to a fully solvated proton and thus the pK_a of this compound is 1.4 units lower than would be expected. Addition of an alkylammonium function to the pyridine nucleus further lowers the pK_a, since a formal positive charge repels the coordinated proton. The data in Table I show that this effect becomes larger as the positive charge is placed closer to the pyridine nitrogen, there being almost no effect in the trimethyl(2,6-di-*tert*-butyl-4-picolyl)ammonium ion while the trimethyl(2-*tert*-butyl-6-pyridyl)ammonium ion is so acidic that it is only half protonated in 7 *F* HCl.

The water solubilities of some of the salts synthesized in this work are listed in Table III. For all cations tested, a perchlorate or trifluoromethanesulfonate counterion leads to a relatively insoluble salt. Likewise, for all anions tested, trimethylammonium salts have only limited solubility in water. However, the dimethylammonium derivatives are much more soluble

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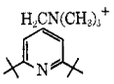
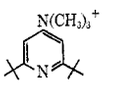
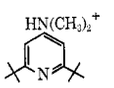
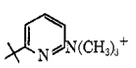
TABLE II
pK_a VALUES OF STERICALLY HINDERED PYRIDINES

Compd		pK_a[a]	Solvent
	2,6-Di-*tert*-butylpyridine	3.56[b]	50% EtOH
	2,4,6-Tri-*tert*-butylpyridine	4.02	50% EtOH
	2,6-Di-*tert*-butyl-4-methylpyridine	4.41	50% EtOH
	2,6-Di-*tert*-butyl-3-methylpyridine	4.25	50% EtOH
	Trimethyl(2,6-di-*tert*-butyl-4-picolyl)ammonium ion	3.51	Water
	Trimethyl(2,6-di-*tert*-butyl-4-pyridyl)ammonium ion	1.65	Water
	Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)ammonium ion	1.6[c] 1.85 8.80	Water (pK_1) 50% EtOH (pK_1) 50% EtOH (pK_2)
	Trimethyl(2-*tert*-butyl-6-pyridyl)ammonium ion	<-1[d]	Water

[a] pK_a's determined at 27 ± 2°, μ = 0.1 *F*. [b] Lit.[1] 3.58. [c] ±0.1 pK_a units. [d] Approximately half protonated in 7 *F* HCl.

than the trimethylammonium analogs, presumably because of increased hydrogen bonding to the solvent. Thus, the nitrate, chloride, and bromide salts of the dimethyl(2,6-di-*tert*-butyl-4-pyridyl)ammonium cation can be used in aqueous systems as noncoordinating buffers,[13] or as bases of low nucleophilic activity, when the presence of these anions is not obnoxious.

Experimental Section

Melting points (Thomas-Hoover apparatus) were determined in open-end capillaries and are uncorrected. Pmr spectra were recorded on a Varian A-60A instrument using tetramethylsilane as a reference; all integrations gave relative peak areas within ±10% of those calculated for the proposed structure and are therefore not reported individually. Analyses were performed by the Schwarzkopf Microanalytical Laboratory and PCR Inc. Chloroaurate derivatives were prepared by a reported method.[1]

The detailed syntheses and characterization (derivatives, elemental analyses, pmr spectra, etc.) of all the compounds in Table I, except of 9 which is given below, are reported in the microfilm edition of this journal;[14] also included in this report are 4,4′,6,6′-tetra-*tert*-butyl-2,2′-bipyridyl and 4-(2-dimethylaminoethyl)pyridine. The multiple *tert*-butylation procedure used in these syntheses is similar to previously published procedures.[1,7,15]

Trimethylsulfoxonium Perchlorate.—Trimethylsulfoxonium iodide was prepared by the method of Kuhn and Trischmann[16] and converted to the perchlorate by three crystallizations from aqueous perchloric acid. The final product was washed with 95% ethanol and dried under vacuum (over P_2O_5). *Anal.* Calcd for $C_3H_9ClO_5S$: C, 18.71; H, 4.71; S, 16.65. Found: C, 18.60; H, 4.87; S, 16.81.

Trimethyl(2,6-di-*tert*-butyl-4-picolyl)ammonium Perchlorate.—2,6-Di-*tert*-butyl-4-dimethylaminomethylpyridine (1.2 g, 4.8 mmol) and trimethylsulfoxonium perchlorate (1.9 g, 10 mmol) were dissolved in 12 ml of sulfolane and heated under nitrogen at 140° for 5 hr to yield crystals (0.9 g, 50%): mp 246–247° (aqueous EtOH); pmr (DMSO-d_6) τ 8.60 [s, 2,6-C(CH_3)$_3$], 6.86 (s, NCH_3), 5.37 (s, CH_2), 2.53 (s, 3,5-H_{py}). *Anal.* Calcd for $C_{17}H_{31}N_2ClO_4$: C, 56.27; H, 8.61; N, 7.72. Found: C, 56.02; H, 8.99; N, 7.60.

pK_a and Solubility Measurements.—pK_a's were either determined spectrophotometrically *via* the method described by Brown and Kanner,[1] or were calculated directly from titration data. Spectra were recorded using a Cary 14 uv–visible spectrophotometer and pH readings were taken with a Beckman Research pH meter. Determinations were made at 27 ± 2°, ionic

TABLE III
SOLUBILITIES OF STERICALLY HINDERED PYRIDINES IN WATER AT 27 ± 2°

Compd	Solubility, *F*
Trimethyl(2,6-di-*tert*-butyl-4-picolyl)-ammonium perchlorate	0.00141
Trimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium perchlorate	0.00194
Trimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium nitrate	0.021
Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium perchlorate	0.016
Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium nitrate	1.5
Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium chloride	1.85
Dimethyl(2,6-di-*tert*-butyl-4-pyridyl)-ammonium bromide	1.0
Trimethyl(2-*tert*-butyl-6-pyridyl)-ammonium perchlorate	0.0205
Trimethyl(2-*tert*-butyl-6-pyridyl)-ammonium trifluoromethanesulfonate	0.0089

(13) The disparate pK_a's of the aniline and pyridine nitrogens (see Table II) ensure that in the pyridine buffer region the aniline nitrogen will be completely protonated and thus unable to coordinate to a metal ion.

(14) Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-1123. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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strength 0.1 F. The spectrophotometric pK_a values were obtained at two different wavelengths, agreement always being better than ±0.03 units. The error in reported pK_a values is estimated to be less than ±0.05 pK_a units. Solubilities were determined spectrophotometrically at 27 ± 2° and are estimated to be accurate to within ±5%.

Registry No.—**1**, 20336-15-6; **2**, 38222-83-2; **3**, 38222-84-3; **4**, 38222-85-4; **5**, 2055-21-2; **6**, 38222-86-5; **7**, 38222-87-6; **8**, 38222-88-7; **9**, 38222-89-8; **10**, 38222-90-1; **11a**, 38222-91-2; **11b**, 38222-92-3; **11c**, 38222-93-4; **11d**, 38222-94-5; **12a**, 38222-95-6; **12b**, 38222-96-7; **12c**, 38222-97-8; **13**, 38222-98-9; **14a**, 38222-99-0; **14b**, 38222-00-6; **14c**, 38222-01-7; **15**, 38223-02-8; **16a**, 38222-03-9; **16b**, 38223-04-0; pyridine, 110-86-1; 2,4,6-tri-*tert*-butylpyridine $HAuCl_4$ salt, 29930-36-7; 4,4′,6,6′-tetra-*tert*-butyl-2,2′-bipyridyl, 38223-05-1; 4-picoline, 108-894; 2,6-di-*tert*-butyl-4-methylpyridine $HAuCl_4$ salt, 38218-84-7; 3-picoline, 108-99-6; 2,6-di-*tert*-butyl-3-methylpyridine $HAuCl_4$ salt, 38295-40-8; 4-picolylamine, 3731-53-1; 3-picolylamine, 3731-52-0; 4-(2-dimethylaminoethyl)pyridine, 38223-06-2; 4-vinylpyridine, 100-43-6; 4-dimethylaminopyridine, 1122-58-3; 2-dimethylaminopyridine, 5683-33-0; 2-*tert*-butyl-6-dimethylaminopyridine $HAuCl_4$ salt, 38218-85-8; methyl iodide, 74-88-4; 2,6-di-*tert*-butylpyridine, 585-48-8; trimethylsulfoxonium iodide, 1774-47-6; trimethylsulfoxonium perchlorate, 38223-07-3.

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Amine Copper(I) Perchlorates. A Novel Class of Copper Species for Promoting Diazonium Ion Reactions

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Copper(I) perchlorates, complexed by heterocyclic amines, are effective at promoting homolytic cleavage of aryl diazonium salts in neutral medium. For 2-diazobenzophenone tetrafluoroborate the major products are 2,2′-dibenzoylbiphenyl (~70%) and 9-fluorenone (~30%). In the presence of cupric ion a high yield of 2-hydroxybenzophenone is obtained; with hydrogen atom donors, *e.g.*, ethanol, the major product is benzophenone.

The homolytic decomposition of aryl diazonium salts has been shown to be more effectively promoted by cuprous copper than by the metal itself.[2,3] In fact, the replacement of metallic copper by cuprous oxide in the decomposition of 2-diazobenzophenone tetrafluoroborate (**1**) at 45° has demonstrated that by accelerating homolytic carbon–nitrogen bond scission, competition by the heterolytic pathway is essentially eliminated. Not all cuprous salts are, however, suitable as catalysts. Owing to the greater solvation energy of copper(II) ion, as compared to that of copper(I) ion, in water,[4] all aquated copper(I) salts disproportionate to Cu(II) and Cu(0).[5] Cuprous oxide, which had been the catalyst of choice,[2,3] has the disadvantage of being effective in highly acidic medium only, owing to its insolubility in neutral water. Thus, diazonium ion decomposition requiring a neutral medium cannot be promoted by cuprous copper.

We have developed a series of relatively stable, soluble copper(I) salts, complexed by heterocyclic amines, which are effective in catalyzing homolytic diazonium ion decomposition in the pH range 2–6.

Results and Discussion

In the course of our investigations of aryl diazonium ion decompositions we have become interested in carrying out homolytic reactions in neutral water. The 2-diazobenzophenone system was selected for study because of the considerable amount of reliable data already available concerning both the thermal[3,6] and the copper-promoted[3] reactions.

Cuprous oxide, reported to be an effective catalyst in acid solution,[2,3] was found to promote homolytic decomposition of 2-diazobenzophenone tetrafluoroborate only at pH 1.25 or less. Other commercially available copper(I) salts (bromide, chloride, iodide, thiocyanate, and acetate) also failed to promote the reaction in neutral water. Copper(I) hydride,[7] prepared by the procedure of Whitesides, *et al.*,[8] was ineffective in catalyzing the decomposition.

Several known acetonitrile complexes of copper(I),[9] as well as bis(2,9-dimethyl-1,10-phenanthroline)copper(I) sulfate[10] and two pyridinecopper(I) salts, were prepared and examined for suitability in promoting the homolytic decomposition of **1** in neutral water. The results, summarized in Table I, indicated that although two of the acetonitrile complexes were effective within the desired pH range (entries 1, 2) they formed copper (II), either by oxidation or by disproportionation, too rapidly to serve as useful catalysts. In the very stable phenanthroline complex (entry 5), on the other hand, copper(I) was stabilized to the point where it was in-

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