lized from 95% ethanol, affording 0.62 g (98%), mp 91–93°. See Table I for analytical and spectral data.

Reaction of α-Benzoyl-α-chlorobenzyl Benzyl Sulfide (1b) (Prepared *in Situ*) with Trichlorosilane and Tri-*n*-butylamine.—The 1:1 benzil–trimethylphosphite adduct **3** was generated as previously described[7] from benzil (2.10 g, 0.01 mol) and trimethyl phosphite (1.25 g, 0.01 mol). Dry 1,2-dimethoxyethane (10 ml) was added, followed by sulfenyl chloride (0.01 mol) in the same solvent (10 ml). The pale yellow solution was stirred for 15 min. Tri-*n*-butylamine (1.85 g, 0.01 mol) and trichlorosilane (1.80 g, 0.013 mol) were added. The reaction mixture was worked up as in the previous experiment. The product crystallized from 95% ethanol (60%). In a similar manner sulfide **2c** was prepared in 62% yield.

Reaction of α-Acetyl-α-chloroethyl Phenyl Sulfide (1d) with Trichlorosilane and Tri-*n*-butylamine.—As described above, α-acetyl-α-chloroethyl phenyl sulfide (**1d**) (1.20 g, 0.0056 mol) was dissolved in 1,2-dimethoxyethane (10 ml). Tri-*n*-butylamine (1.10 g, 0.006 mol) and trichlorosilane (1.40 g, 0.01 mol) were added and the reaction mixture was refluxed overnight with stirring. Work-up as in the preparation of **2a** from **1a** gave sulfide **2d**: bp 78–80° (0.003 mm); yield 0.80 g (80%); ir 1720 cm^{-1} (CO). Exact mass data: calculated for $C_{16}H_{12}OS$, 180.0609; found, 180.0608.

Attempted Reaction of α-Acetyl-α-chloroethyl Ethyl Sulfide (1e) with Trichlorosilane and Tri-*n*-butylamine.—The procedure described in the previous experiment was repeated with α-acetyl-α-chloroethyl ethyl sulfide (**1e**) (1.66 g, 0.01 mol), trichlorosilane (1.80 g, 0.013 mol), and tri-*n*-butylamine (1.85 g, 0.01 mol). A black tarry mass was obtained and yielded no identifiable products.

Reaction of α-Acetyl-α-chloroethyl Phenyl Sulfide (1d) (Prepared *in Situ*) with Trichlorosilane and Tri-*n*-butylamine.—Benzenesulfenyl chloride (1.45 g, 0.01 mol) was added to a solution of 1:1 biacetyl–trimethyl phosphite adduct **3** (2.10 g, 0.01 mol) in 1,2-dimethoxyethane (10 ml) under nitrogen. Once the exothermic reaction had subsided, trichlorosilane (1.80 g, 0.013 mol) and tri-*n*-butylamine (1.85 g, 0.01 mol) were added and the reaction mixture was refluxed overnight. Usual work-up provided an oil which was chromatographed on Florisil using methylene chloride. Pure α-acetylethyl phenyl sulfide was obtained, yield 1.10 g (61%). Spectroscopic data were identical with the data of the previous sample. When ethanesulfenyl chloride was used instead of benzenesulfenyl chloride in the above procedure, only an intractable tarry oil was obtained.

Registry No.—**2a**, 17527-58-1; **2b**, 23343-23-9; **2c**, 16222-12-1; **2d**, 13023-53-5; **2e**, 19170-22-0.

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(7) P. Mathiaparanam, Ph.D. Thesis, McGill University, Dec 1970; F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **85**, 3252 (1963), and references cited therein.

Alkylation of Pyridine with *tert*-Butyllithium. Convenient Syntheses of 2,6-Di-*tert*-butylpyridine and 2,4,6-Tri-*tert*-butylpyridine

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A large number of sterically hindered organic bases have been reported.[1] Perhaps most notable among these is 2,6-di-*tert*-butylpyridine (**1**), since it is the only base demonstrated as having the ability to distinguish between Brønsted (protonic) and Lewis acids.[2] We required pure **1** in decigram quantities for the purpose of utilizing this unique property in another investigation. An earlier report[2] of its synthesis described a multistep procedure beginning with 2-ethylpyridine and requiring purification after each step. However, it was suggested in that article that a more direct route from pyridine was feasible. A two-stage method was later employed in the synthesis of 2,6-di-*tert*-butyl-4-alkoxypyridines from 4-alkoxypyridines.[3]

Accordingly, we attempted the most straightforward route, namely, the direct alkylation of pyridine with excess *tert*-butyllithium. This approach met with success, for in one step we could obtain not only **1** in yields up to 30% but also 2,4,6-tri-*tert*-butylpyridine (**2**),[4] both compounds being isolated in the quantities we required. Under proper conditions, **2** was the predominant product (up to 55% yield). Also produced were smaller quantities of the new compound, 2,4-di-*tert*-butylpyridine (**3**), 6,6′-*tert*-butyl-2,2′-bipyridine (**4**),[2] and tarry material formed in some cases. Control over product distribution was accomplished by varying the molar ratio of *tert*-butyllithium to pyridine and the mode of addition. The use of excess *tert*-butyllithium also minimized the yields (max 8%) of monosubstitution product, 2-*tert*-butylpyridine (**5**). The results are summarized in Table I.

TABLE I

REACTION OF PYRIDINE WITH *tert*-BUTYLLITHIUM[a]

tert-BuLi/pyridine[g]	Overall yield, %	Yield, %[b] 1	2	3	4[c]	5
2.5[d]	69	30 (25)	20 (19)	10 (9)	1	8 (6)
5[d]	70	27 (17)	31 (31)	7	1	4 (3)
10[e]	72	6	54 (43)[f]	9	2	1
20[e]	90	5	55 (26)[f]	11	15	4

[a] Addition was carried out at −75° under dry nitrogen followed by 7-hr reflux at 100°. [b] Glpc yields, based on pyridine. Isolated yields are in parentheses. All compounds were isolated in >95% purity by fractional distillation, sublimation, and/or crystallization. [c] Approximately 0.5 g was isolated in pure form from the reaction residue. [d] See Experimental Section, procedure A; scale, 0.2 mol of pyridine. [e] See Experimental Section, procedure B; scale, 0.01 mol or 0.02 mol of pyridine. [f] Low isolated yield is due to small scale with unavoidable mechanical losses. [g] Molar ratio.

The crude product mixture was directly resolved into its components, each >95% pure, by one careful fractionation using a highly efficient distilling apparatus. In those trials in which >50% yield of **2** were realized, this solid could be crystallized out of the crude mixture upon cooling and subsequently purified by vacuum sublimation. This procedure thus constitutes the preferred method for obtaining **1** and **2**.

The identities of compounds **1** and **5** were established by comparison of boiling points, infrared and proton nmr spectra, and melting points of the chloroaurates

(1) See, for example, F. E. Condon, *J. Amer. Chem. Soc.*, **87**, 4494 (1965), and reference cited therein.

(2) H. C. Brown and B. Kanner, *ibid.*, **88**, 986 (1966); **75**, 3865 (1953).

(3) H. C. van der Plas and H. J. den Hertog, *Recl. Trav. Chim. Pays-Bas*, **81**, 841 (1962).

(4) A multistep synthesis (overall yield, 42%) of **2** *via* treatment of 2,4,6-tri-*tert*-butylpyrylium tetrafluoroborate with alcoholic ammonia has been reported: K. Dimroth and W. Mach, *Angew. Chem., Int. Ed. Engl.*, **7**, 460 (1968).

with those of authentic samples.[5] Compound **2** was identified by comparison of its melting point[4] and infrared[6] and proton nmr[4] spectra with literature data. Compound **3** was characterized by elemental analysis and by comparison of its infrared spectrum with literature data.[6] Characteristic bands for β CH and ring breathing vibrational modes were identified in the 1300–1000 cm^{-1} region, as well as diagnostic substitution pattern bands below 1000 cm^{-1} (Table II) and

TABLE II

PHYSICAL PROPERTIES OF PRODUCTS[a]

Compd	Bp, °C (mm)	Mp, °C	Mp of chloroaurate,[b] °C	Ir,[c] cm^{-1}
1	90–93 (20)		184–185[d]	993, 890, 817, 750
2	115–120 (20)	70.9–71.2[e]	277–278 dec	1022, 998, 875
3	100–102 (17)		197.5–199 dec	1150, 995, 887, 839
4		122.5–123[f]		1140, 1083, 990, 805, 757
5	63–67 (20)			

[a] Compounds **1** and **2** were obtained in >99% purity by a single distillation or by sublimation. Compound **3** required a second distillation of combined fractions of >90% purity to achieve >99% purity. No attempt was made to purify **5** beyond 95% purity. Satisfactory analytical values (±0.3% for C, H, N) were reported for compounds **1**, **2**, and **3**: Ed. [b] Prepared according to procedure of Brown.[2] Compounds **1**, **2**, and **3** did not give picrates. [c] Only those bands pertinent to characterization are given. [d] Lit.[2] 184.2–184.5°. [e] Lit.[4] 69°. [f] Crystallized out of the reaction residues. Lit.[2] 122.3–122.8°.

their characteristic overtone patterns in the 2100–1700-cm^{-1} region. In addition, the splitting patterns in the δ 6.5–8.5 region of the proton nmr spectra of **1**, **2**, and **3** are quite comparable to those of 2,6-lutidine, 2,4,6-trimethylpyridine, and 2,4-lutidine, respectively.

Experimental Section

General.—Melting points (Mel-Temp apparatus) are corrected. Boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were determined in spectrograde carbon tetrachloride using tetramethylsilane as reference and measured with a Varian T60 spectrometer. Both infrared and proton nmr spectra have been subsequently published by the Sadtler Research Laboratories, Inc., for compounds **1**, **2**, and **3**.[7] All distillations were performed on a manually operated, 24-in. Teflon annular spinning-band column (Nester-Faust) at approximately 20-mm pressure, which resolved a persistant foaming problem encountered with other columns. Glpc analysis of reagents, crude reaction mixture, and purified products were performed on a Perkin-Elmer Model 800 instrument equipped with thermal conductivity and flame ionization detectors. One or both of the following columns were used throughout this work: column A (11 ft × 0.25 in., 20% Siponate Ds-10 on 45–60 mesh Chromosorb W, 5% NaOH, carrier gas flow 60 ml/min) and column B (6 ft × 0.25 in., 15% Carbowax 6000 on 40–60 mesh Chromosorb W, 5% NaOH, carrier gas flow 60 ml/min). Pyridine (Fisher or Baker reagent grade), *tert*-butyllithium, 2 *M* in pentane (Ventron ALFA), and heptane (Phillips pure grade) were all used without further purification. The microanalyses were performed by Crobaugh Laboratories, Cleveland, Ohio, or on a F & M CHN analyzer Model 185.

General Procedures for Alkylation. A. Addition of *tert*-Butyllithium to Pyridine.—Pyridine (15.8 g, 0.20 mol) in 200 ml of heptane was placed in a flask equipped with magnetic or mechanical stirrer, dewar condenser, alcohol thermometer, pressure-compensated addition funnel, CO_2–acetone cooling bath, and provision for introducing dry nitrogen below the surface of the reaction mixture. With thorough flushing with dry nitrogen, the solution was cooled to −75°. The volume of *tert*-butyllithium, 2 *M* in pentane, necessary to provide the desired molar ratio (Table I) of *tert*-butyllithium to pyridine was introduced to the addition funnel by expelling it with dry nitrogen pressure from a glass wash bottle previously filled in a glove bag under dry nitrogen.[8] Addition required 2 hr and stirring at −75° was continued for 1 hr. The mixture was then allowed to warm to room temperature. Under a dry nitrogen stream, the pentane was removed by distillation and the reaction mixture was refluxed for 7 hr. After being cooled to 10°, the reaction was carefully quenched by dropwise addition of water. The aqueous layer was thoroughly extracted with pentane and the combined organic layers were washed once with water and dried ($MgSO_4$). Removal of solvents left a red-brown oil (*ca.* 44 g) which was distilled and analyzed by glpc. Yields are given in Table I and physical properties in Table II.

B. Addition of Pyridine to *tert*-Butyllithium.—The volume of *tert*-butyllithium, 2 *M* in pentane, necessary to provide the desired molar ratio (Table I) of *tert*-butyllithium to pyridine was carefully introduced into the apparatus as described in procedure A. After the mixture was cooled to −75°, pyridine (1.58 g, 0.02 mol) in 50 ml of heptane was added dropwise (45 min) with dry nitrogen flush and the stirring was continued an additional hour. Procedure A was then followed. The resulting oil (*ca.* 5.8 g) was either distilled or allowed to crystallize at room temperature. Filtration and vacuum sublimation gave pure **2**.

Registry No.—**1**, 585-48-8; **2**, 20336-15-6; **2** chloroaurate, 29930-36-7; **3**, 29939-31-9; **3** chloroaurate, 29930-37-8; **5**, 5944-41-2; pyridine, 110-86-1; *tert*-butyllithium, 594-19-4.

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(5) We are indebted to Professor H. C. Brown for providing authentic samples of **1** and **5**.

(6) A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, Chapter 10, pp 276–279.

(7) "Sadtler Standard Spectra" references, compound (ir spectrum no, nmr spectrum no): **1** (702339, 9708M); **2** (702340, 9709M); **3** (708021, 10509M).

(8) For an alternative procedure, see S. Farber and R. T. Conley, *J. Chem. Educ.*, **45**, 704 (1968).

New General Methods for the Substitution of 5-Chloropyrazoles. The Synthesis of 1,3-Dialkyl-5-chloropyrazol-4-yl Aryl Ketones and New 1,3-Dialkyl-2-pyrazolin-5-ones

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In connection with other synthetic studies underway in this laboratory, we required a large variety of the previously unknown 1,3-dialkyl-5-chloropyrazol-4-yl aryl ketones. Based on the ready availability of