greenish-white solid precipitated in the course of the reaction. After similar treatment, the organic part was distilled under reduced pressure to give the following fractions: (1) bp 78–85° (1.0 mm), 0.93 g of *p*-methylbenzyl alcohol; (2) bp 135–160° (1.0 mm), 2.70 g of colorless needles. Fraction 2 was recrystallized from ethanol to give colorless crystals, mp 54–55°, which were identified as *p,p'*-dimethyldibenzyl ketone: ir (KBr) 1703 cm^{-1} (C=O); nmr (CCl$_4$) τ 7.70 (s, 6, CH$_3$), 6.55 (s, 4, CH$_2$), and 3.10 (s, 8, C$_6$H$_4$).

Anal. Calcd for C$_{17}$H$_{18}$O: C, 85.67; H, 7.61. Found: C, 85.55; H, 7.39.

Glpc analysis (column, 20% SE-30; 200–280°, 4°/min program; carrier gas, He, 10 ml/min) of fraction 2 showed the presence of a trace amount of *p,p'*-dimethylbibenzyl as a sole impurity.

B. With *trans-β*-Bromostyrene in Water–Methanol.—Carbon monoxide was bubbled into a solution containing 0.035 ml of 1 in 120 ml of water and 100 ml of methanol. *trans-β*-Bromostyrene (9.2 g, 0.050 mol) in 20 ml of methanol was added, and stirring and gentle bubbling of CO were continued for 17 hr at 10–35°. After similar treatment, the organic part was distilled under reduced pressure. A fraction of bp 80–87° (2 mm) was collected to give 4.50 g of pale yellow liquid. The ir spectrum and quantitative glpc analysis (column 20% PEG-20M; 120–280°, 4°/min program; carrier gas, He, 10 ml/min) of the fraction showed the presence of the following compounds: 3.23 g (57.0%) of methyl *trans*-cinnamate, 0.47 g (10.2%) of cinnamaldehyde, 0.10 g (2.2%) of *trans-β*-cyanostyrene, and 0.59 g of recovered *trans-β*-bromostyrene.

Reaction of Potassium Hexacyanodinickelate(I) (1) with Benzyl Bromide in the Presence of Acrylonitrile or Ethyl Acrylate.—To a solution containing 0.035 mol of 1 in 120 ml of water and 40 ml of acetone was added 5.3 g (0.10 mol) of acrylonitrile with stirring. The color of the solution changed immediately to transparent yellow. Benzyl bromide (6.0 g, 0.035 mol) in 20 ml of acetone was added dropwise with stirring at −7° in a

period of 1 hr. The reaction mixture was gradually warmed to room temperature during 12 hr with efficient stirring. After similar treatment described above, the organic layer was distilled to give 3.00 g of distillate, bp 89–91° (0.7 mm), which was subjected to quantitative glpc analysis (column, 20% PEG-20M; 130–240°, 4°/min program; carrier gas, He, 12 ml/min) and was found to consist of the following two compounds: 1.17 g (23.0%) of 4-phenylbutyronitrile and 1.83 g (57.4%) of bibenzyl.

When a reaction similar to the preceding example was carried out using ethyl acrylate instead of acrylonitrile, ethyl 4-phenylbutyrate and bibenzyl were obtained in 8.0 and 20.0% yield, respectively (analyzed by ir spectra and glpc). Authentic samples of 4-phenylbutyronitrile and ethyl 4-phenylbutyrate were prepared by the reported methods.[15a]

Isolation of Benzylmercuric Chloride.—To a solution containing 0.035 mol of 1 in 140 ml of water and 40 ml of acetone was added 6.0 g (0.035 mol) of benzyl bromide in 30 ml of acetone at 0° with stirring. The red color of the solution turned pale yellow within 30 min. Mercuric chloride (9.50 g, 0.035 mol) in 30 ml of acetone was added dropwise at 0° over a period of 1 hr. After usual treatment, 1.88 g (17.0%) of benzylmercuric chloride, mp 104–106° (recrystallized from ethanol) (lit.[29] 104°), and 1.91 g (60.0%) of bibenzyl were isolated.

(29) K. C. Bass, *J. Organometal. Chem.*, **4**, 92 (1965).

Synthesis, Spectra, and Reactions of N-Triphenylmethylpyridinium Salts. Reaction of Triphenylmethyl Chloride with Pyridine under High Pressure

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N-Triphenylmethyl- (trityl-) pyridinium chloride (I) was synthesized from trityl chloride and pyridine by means of high pressure (4000–5000 atm) in dioxane or pyridine solution at 60–70°. Compound I was found to react rapidly with methanol and water to produce trityl methyl ether and triphenylcarbinol, respectively. With moisture, it was converted into the molecular complex (II) of triphenylcarbinol and pyridinium chloride in the solid state. The ir, uv, visible, and nmr spectra of I were compared to those of N-tritylpyridinium perchlorate and fluoroborate. The deshielding of pyridine ring protons of these N-tritylpyridinium compounds is much smaller than that of other N-alkylpyridinium compounds. Explanation of this phenomenon is suggested. N-tritylpyridinium bromide (III) was synthesized from trityl bromide and pyridine without applying high pressure. The differences between trityl chloride and bromide in the formation of N-tritylpyridinium compounds are also discussed.

It has long been known that the yellow color of the trityl ion in nitromethane solutions of trityl chloride discharged immediately upon addition of pyridine. This phenomenon was attributed to the formation of tritylpyridinium chloride (I).[1] The solids "tritylpyridinium chloride" reported in the literature[2] were

shown to be a complex (II) of triphenylcarbinol and pyridinium chloride associated through a weak hydrogen bond in the solid state.[3]

Generally, in nucleophilic reactions the stronger nucleophilic reagent, pyridine, would be expected to react faster with alkyl halides than methanol.[4] However, the synthesis of N-tritylpyridinium chloride from trityl chloride and pyridine by conventional procedures was unsuccessful, although under similar conditions methanol reacted readily with trityl chloride to form trityl methyl ether.[3] Failure to synthesize N-tritylpyridinium chloride may be attributed to its unfavorable

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(1) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 82.

(2) Prepared from trityl chloride and pyridine by J. F. Norris and L. R. Culver, *Amer. Chem. J.*, **29**, 134 (1903), by E. V. Meyer and P. Fischer, *J. Prakt. Chem.*, [2], **82**, 523 (1910); by C. A. Kraus and R. Rosen, *J. Amer. Chem. Soc.*, **47**, 2744 (1925). It was also obtained from a pyridine solution of triphenylcarbinol and hydrogen chloride by B. Helferich and H. Dehe, *Ber.*, **58**, 1605 (1925); this product was shown to contain the elements of one molecule of water by B. Helferich and H. Sieber, *ibid.*, **59**, 600 (1926), and Helferich's conclusions were later confirmed by E. D. Hughes, *J. Chem. Soc.*, 75 (1933).

(3) C. G. Swain and Y. Okamoto, *J. Amer. Chem. Soc.*, **92**, 3409 (1970).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 356.

equilibrium or slow rate relative to methanol captive, shown in eq 1.

(1)
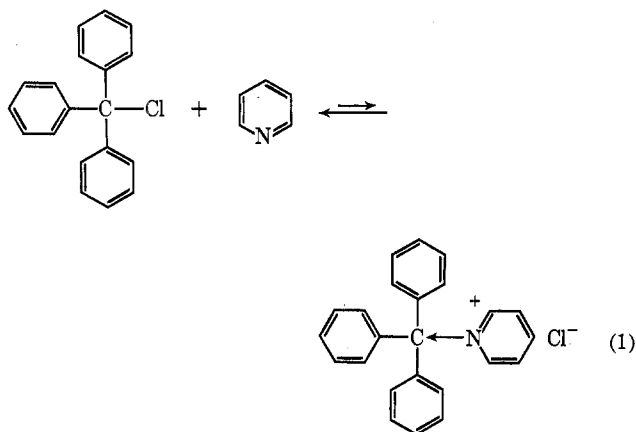
Reactions of alkyl halides with amines to give a quaternary ammonium salt have been extensively studied with respect to steric effect between reactants and the effects of pressure on rate and equilibrium. The rate generally increases with increasing applied pressure. The equilibrium of eq 1 would be expected to shift from left to right with increasing applied pressure on the system, due to decrease in volume on the reaction.[5]

The present investigation was initially undertaken to attempt the synthesis of I from trityl chloride and pyridine by means of high pressure. The properties of I successfully obtained are described.

Results and Discussion

Synthesis of N-Tritylpyridinium Chloride (I). —A dioxane solution of trityl chloride and pyridine or a mixture of both components (the latter in large excess ratio) was heated at 60–70°, for 10–15 hr under 4000–5000 atm pressure. The white solid I obtained was separated by filtration and washed three times with dried benzene. The crystals were dried in a desiccator under vacuum. The microanalysis of the compound fitted the molecular formula $C_{24}H_{20}NCl$. The melting point was 90–95° with some decomposition. However, when the solid was exposed to the atmosphere, the melting point gradually rose and finally reached 176°. The mixture melting point of the 176° compound with the complex II of triphenylcarbinol and pyridinium chloride did not show any depression. Furthermore, the 176° compound was identified by ir spectrum as II.

The ir spectrum of alkyl chloride shows a C–Cl bending absorption band at 280–360 cm^{-1} as well as its symmetrical stretching absorption in the region 500–600 cm^{-1} and an asymmetric absorption peak in the region 600–700 cm^{-1}.[6] The stretching absorption bands are usually difficult to distinguish from phenyl ring absorptions, whereas the bending absorption band is more reliable for identification. The C–Cl bending absorption band at 345 cm^{-1} of trityl chloride was not in the spectrum of I in the solid state (Nujol mull). However, the spectrum of an equimolar mixture of trityl chloride and

pyridine in Nujol mull shows the C–Cl bending absorption band. When I was treated with an excess of methanol at room temperature, trityl methyl ether and pyridinium chloride were obtained. With water, I was readily converted into triphenylcarbinol and pyridinium chloride.

Properties of I in Solution.—Compound I was insoluble in benzene or carbon tetrachloride, but soluble in chloroform, acetonitrile, and dimethyl sulfoxide. The ultraviolet absorption peaks of I in dichloromethane appeared at 234 mμ (ε 5400) and 257 (2500). The latter peak is due to pyridinium ion. N-Tritylpyridinium perchlorate and fluoroborate were prepared from the reactions of trityl perchlorate and fluoroborate with pyridine without applying pressure. The visible absorption spectrum of I as well as of tritylpyridinium perchlorate and fluoroborate in dichloromethane was recorded. However, adsorption in the region 400–450 mμ for the trityl ion was not observed.

The nmr spectrum of I was almost identical with those of N-tritylpyridinium perchloride and fluoroborate. The phenyl proton spectrum appeared at τ 2.70 as a singlet.[7]

For comparison, the chemical shifts of the α-, β-, and γ-pyridine ring protons for other pyridinium compounds are summarized in Table I.[9] The substantial deshielding of the pyridine ring protons in the pyridinium compounds are due to the decrease in electron charge density at the individual carbon nuclei as a result of the formation of the positively charged nitrogen.[10] The

(7) Recently, the recharacterization of "hexaphenylethane" produced by the dimerization of triphenylmethyl radical was reported by Lankamp, Nauta, and MacLean.[8] The 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene structure was proposed for the dimerization product. Accordingly, the question might arise for the structure of I; instead of I, the pyridine may attack at the para position of phenyl and form 1-diphenylmethylene-2,5-

IV
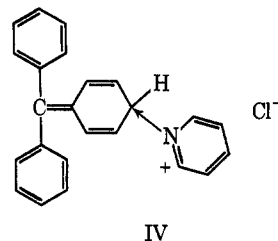
cyclohexadiene 4-pyridinium chloride (IV). However, the nmr spectra of I shows that the phenyl protons were a singlet (τ 2.70). The absorptions corresponding to the olefinic protons (τ 3.6–4.2) and aliphatic proton (τ ~5) were not observed. Moreover, the proton ratio of phenyls and pyridine were approximately 3:1.

(8) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(9) The chemical shifts of the pyridine ring protons in pyridinium salts were examined in various concentrations of CDCl₃. The concentrations

	Concentration (w/v%) value					
	5%			10%		
	α	β	γ	α	β	γ
Pyridinium chloride	0.96	1.88	1.42	0.93	1.83	1.39
Pyridinium bromide	0.87	1.75	1.37	0.81	1.71	1.27
	15%			20%		
	α	β	γ	α	β	γ
Pyridinium chloride	0.89	1.75	1.30	0.89	1.74	1.29
Pyridinium bromide	0.79	1.69	1.21	0.80	1.69	1.22

dependent on the shifts are about within τ ±0.1 over these concentration ranges. The nmr in Table I, II, and III were measured in 0.1~0.5 M solution.

(10) I. C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).

(5) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. 2, R. S. Bradly, Ed., Academic Press, New York, N. Y., 1963.

(6) N. B. Colthup, N. H. Daly, and F. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

TABLE I

CHEMICAL SHIFTS OF PYRIDINE RING PROTONS OF THE PYRIDINIUM DERIVATIVES (τ VALUES)[a]

Compd	CDCl₃ solution						CH₃CN solution						DMSO-d₆ solution					
	α	Δα[b]	β	Δβ	γ	Δγ	α	Δα	β	Δβ	γ	Δγ	α	Δα	β	Δβ	γ	Δγ
Pyridine	1.56 (0)		2.90 (0)		2.50 (0)		1.44 (0)		2.66 (0)		2.34 (0)		1.34 (0)		2.65 (0)		2.28 (0)	
Pyridinium chloride	0.98 (0.58)		1.88 (1.02)		1.44 (1.06)		1.16 (0.28)		1.94 (0.72)		1.44 (0.90)		0.90 (0.44)		1.75 (0.90)		1.25 (1.03)	
N-Methylpyridinium iodide	1.08 (0.48)		1.80 (1.10)		1.40 (1.10)													
N-Benzylpyridinium chloride	0 (1.56)		1.80 (1.10)		1.50 (1.00)		0.24 (1.20)		1.88 (0.78)		1.54 (0.80)							
N-Benzhydrylpyridinium chloride	0.56 (1.00)		1.84 (1.06)		1.40 (1.10)									0.88 (0.46)		1.72 (0.93)		1.25 (1.03)	
N-Tritylpyridinium chloride (I)	1.36 (0.20)		2.44 (0.46)		2.04 (0.46)		1.40 (0.04)		2.50 (0.11)[c]		2.18 (0.16)		1.30 (0.04)		2.42 (0.23)		2.08 (0.20)	
N-Tritylpyridinium bromide (III)	1.32 (0.24)		2.46 (0.44)[c]		2.24 (0.26)													
N-Tritylpyridinium perchlorate							1.30 (0.14)		2.44 (0.22)[c]		2.06 (0.28)		1.30 (0.04)		2.38 (0.27)		2.00 (0.28)	
N-Tritylpyridinium fluoroborate													1.25 (0.09)		2.35 (0.30)		1.92 (0.36)	

[a] All chemical shifts referred to tetramethylsilane as internal standard. [b] These values indicate applied shifts from the corresponding pyridine ring protons. [c] Peaks are partially overlapped with the phenyl proton absorption.

deshielding of the β- and γ-pyridine ring protons in benzyl and benzhydryl pyridinium chlorides is similar to that of N-methylpyridinium iodide and pyridinium chloride. On the other hand, the deshielding of the α-pyridine ring protons is quite varied. This may be due to the effect of counterions[11] (ion pair formation) or to the shielding by the adjacent phenyl group.[12] From Table I, it is clear that the deshielding of the β- and γ-pyridine ring protons of N-tritylpyridinium compounds is much smaller as compared to that in other pyridinium compounds. A similar trend is also observed in the chemical shifts of the methyl protons of the γ-picolinium compounds; i.e., the chemical shift of the methyl group of N-trityl-γ-picolinium perchlorate appears in between those of γ-picoline and γ-picolinium chloride (Table II). The exact explanation of this

TABLE II

CHEMICAL SHIFTS OF γ-PICOLINE RING PROTONS AND γ-METHYL PROTONS OF THE N-γ-PICOLINIUM (τ VALUES)

	DMSO-D₆ solution					
Compd	α	Δα[a]	β	Δβ	γ-CH₃	Δ[b]
γ-Picoline	1.50	(0)	2.80	(0)	7.70	(0)
N-γ-Picolinium chloride	1.00	(0.50)	1.90	(0.90)	7.28	(0.42)
N-Trityl-γ-picolinium perchlorate	1.40	(0.10)	2.55	(0.25)	7.56	(0.14)

[a] These values indicate applied shifts from the corresponding pyridine ring protons. [b] These values indicate shifts from the methyl protons of γ-picoline.

phenomenon is not clear. However, this may be attributed to the following: The coordination bond between the carbon and nitrogen in N-tritylpyridinium compounds is stretched in order to minimize the steric strain between phenyl groups and pyridine. This may also be enhanced by a gain in resonance energy of three phenyls in the partially developed trityl ion. Thus, the resulting electron charge density on the nitrogen atom is not as low as those of N-benzyl and N-benzylhydryl pyridinium chlorides. Consequently, the deshielding effect of the pyridine ring protons in I is not as pronounced as those in the other pyridinium compounds.

It can also be attributed to ion-pair formation. The pyridinium ion pairs with counterions such as chloride or iodide in acetonitrile or nitrobenzene. The counter-

ion is most probably situated close to the positively charged nitrogen,[13] and thus reduces considerably the π-electron polarization calculated for an isolated pyridinium ion.[14] Thus, when the bulky group is bonded to the α position or on the nitrogen atom of pyridine, the counterion may not be as close to the positive nitrogen and may be situated near the electron deficient and less sterically hindered β and γ positions of the pyridine. As a result, the low field shifts of the β and γ protons in N-tritylpyridinium compounds are found to be smaller than those of other pyridinium compounds cited in Table I.[15]

A similar phenomenon was observed in the chemical shift of α-substituted pyridinium compounds (Table III). The magnitude of the low field chemical shift (∼1 ppm) of the β- and γ-pyridine ring protons of 2,6-lutidinium compounds is similar to those in pyridinium or N-methylpyridinium halides. However, the low field chemical shifts of the β- and γ-pyridine ring protons in 2,6-di-tert-butyl-N-pyridinium iodide are not as large as those of less sterically hindered pyridinium compounds. This may also be attributed to the counterion association close to the electron deficient β and γ positions of the pyridinium and to the reduced polarity of C-H bonds.

The nmr spectrum of I did not change after the chloroform solution was allowed to stand for 10 days at room temperature. However, when I was dissolved in chloroform at room temperature and then the solvent was removed under vacuum, trityl chloride was isolated instead of I. These results indicate that, as the solvent is removed, the chloride ion reacts with the trityl moiety to form trityl chloride and pyridine.

Recently, syntheses of N-tritylpyridinium bromide (III) from trityl bromide and pyridine in acetonitrile[17]

(11) G. Kotowycz, T. Shaffer, and E. Bock, *Can. J. Chem.*, **42**, 2541 (1964).

(12) D. G. Farnum, *J. Amer. Chem. Soc.*, **86**, 934 (1964).

(13) C. Rerat, *Acta Crystallogr.*, **15**, 427 (1962).

(14) G. Kotowycz, T. Shaefer, and E. Bock, *Can. J. Chem.*, **42**, 2541 (1964).

(15) The structure of tritylpyridinium may be similar to that of tetraphenylmethane of which phenyl groups are twisted to each other (55° angle between the ring and the vertical planes).[16] This unique configuration may be effected to shield (∼0.5 ppm) the β- and γ-pyridine ring protons by the adjacent phenyl ring current. However, the phenyl ring protons of tetraphenylmethane are absorbed at τ 2.76 (as a singlet) which is not different from the phenyl ring proton absorption (τ 2.70) of trityl chloride in CDCl₃.

(16) A. I. Kitaigorodskii "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961, p 404.

(17) R. Damico and C. D. Broadlus, *J. Org. Chem.*, **31**, 1607 (1966). Damico and Broadlus report the chemical shifts of the α-, β-, and γ-pyridine ring protons of III in chloroform, and 0.9–1.9 which are similar to those of pyridinium salt. However, we could not reproduce these data and obtained the values cited in Table I.

Table III

Chemical Shifts of β- and γ-Ring Protons of α-Substituted Pyridine Derivatives (τ Values)

Compd	Registry no.	DMSO-d_6 solution			
		β	$(\Delta\beta)^a$	γ	$(\Delta\gamma)^a$
2,6-Dimethylpyridine	708-48-5	3.00	0)	2.44	(0)
2,6-Dimethyl-N-pyridinium iodide	24994-62-5	2.18	(0.82)	1.66	(0.78)
2,6-Dimethyl-N-methylpyridinium iodide	2525-19-1	2.06	(0.94)	1.60	(0.84)
2,6-Di-*tert*-butylpyridine	585-48-8	2.85	(0)	2.38	(0)
2,6-Di-*tert*-butyl-N-pyridinium iodide	26154-14-3	2.40	(0.45)	2.00	(0.38)

^{a} These values indicate shifts from the corresponding pyridine ring protons.

and in acetone–dimethyl sulfoxide[18,19] were reported. III was readily synthesized at room temperature, whereas under similar conditions or under more drastic conditions, the preparation of I was not successful without applying high pressure. The ir spectrum of III in Nujol mull was almost identical with that of I. Furthermore, the pyridine ring protons of III have similar deshielding effects to those observed in other tritylpyridinium salts (Table I). These results show that trityl bromide and pyridine react in the solvents such as acetonitrile to form III. When the solvent was removed, III was recovered, unlike the case of I, which dissociated into trityl chloride and pyridine. These remarkably different results may be due to the differences of reactivity of Br⁻ and Cl⁻. In general, Br⁻ is a stronger nucleophilic reagent than Cl⁻. However in aprotic solvents, Cl⁻ is more reactive than Br⁻.[20,21] Thus, the above result may be accounted for by the sequence of (i) nucleophilicity and (ii) the size of ions. The larger and less reactive ion, Br⁻, does not react with the trityl moiety of III, upon solvent removal. As a result, III was synthesized by evaporation of solvents from the mixture of trityl bromide and pyridine in polar solvents. This explanation is further supported by the following result: When III was mixed with pyridinium chloride in acetonitrile at room temperature and the solvent removed to dryness, the solid obtained was treated with petroleum ether. After the petroleum ether was evaporated, trityl chloride was obtained in good yield (80%). This result shows that, as solvent was evaporated, Cl⁻ readily reacts with the trityl moiety of III to form trityl chloride and pyridine.

The reactions of trityl chloride with 2,6-lutidine were attempted under high pressure (up to 6000 atm). However, no reaction was detected and trityl chloride was recovered quantitatively.

Experimental Section

Solvents and Reagents.—All solvents were dried over Drierite and distilled. Pyridine, γ-picoline, and 2,6-lutidine (Eastman Kodak Co.) were dried over calcium hydride and distilled. Trityl chloride (K and K Laboratories, Inc.) was twice recrystallized from benzene–petroleum ether with acetyl chloride, mp 111–112°.[22] Triphenylcarbinol (Eastman Kodak Co.) was recrystallized from ethanol, mp 161°.

Instrumental Analyses.—Nmr spectra were obtained on a Varian A60 instrument. A Perkin-Elmer Model 237 infrared spectrophotometer equipped with sodium chloride optics was used for ir measurements in the wavelength region 4000–700 cm⁻¹. For the far-infrared region, a Perkin-Elmer Model 621

grating spectrophotometer with cesium iodide cell was used. Ultraviolet and visible spectra were measured with a Perkin-Elmer Model 202 spectrophotometer.

Trityl Fluoroborate and Perchlorate.—These compounds were prepared by the method previously reported.[23] Trityl fluoroborate and perchlorate melted at 198° dec and 142°, respectively.

N-Benzyl- and N-Benzhydrylpyridinium Chloride.—These pyridinium compounds were prepared from benzyl chloride and benzhydryl chloride with excess pyridine by refluxing. The products were recrystallized from chloroform–benzene solution. Benzylpyridinium chloride (hygroscopic)[24] and benzhydrylpyridinium chloride[25] melted at 125 and 207°, respectively.

Reaction of Trityl Chloride with Pyridine by High Pressure.—The reactions of trityl chloride with pyridine under high pressure were carried out in either dioxane or pyridine as solvent. Trityl chloride (1.15 g) and pyridine (2.20 g) were dissolved in 5 ml of dioxane in a drybox. The high pressure technique described earlier was followed.[26]

N-Tritylpyridinium Chloride (I).—A dioxane solution of trityl chloride and pyridine was heated at 60–70° for 10–15 hr under 5500–6000 atm. After the die had cooled, the pressure was released to 1 atm. The capsule was opened in a drybox. The white crystals obtained (60–70% yield) were separated by filtration from the dark red solution and washed three times with dry benzene. The crystals were dried in a desiccator under vacuum, mp 90–95° dec.

Anal. Calcd for $C_{24}H_{20}NC$: C, 80.55; H, 5.58; N, 3.92; Cl, 10.00. Found: C, 80.40; H, 5.80; N, 3.85; Cl, 9.71.

The melting point of I was determined in an open-ended Pyrex capillary tube. After 4 hr from the first measurement, the melting point of the compound had risen to 160–169° and it reached 175–176° a few days later. When I was exposed to the atmosphere, it was converted rapidly into the high melting compound.

Reactions of N-Tritylpyridinium Chloride with Water and Methanol.—I (0.1 g) was dissolved in chloroform and the solution was treated with water at room temperature for 10 min. The chloroform solution was separated and dried over Drierite. Upon evaporating the chloroform, white crystals (0.07 g) were obtained and recrystallized from ethanol, mp 160°, undepressed by admixture with triphenylcarbinol.

I (0.1 g) was treated with 2 ml of methanol for 5 min at room temperature. The solid material was isolated and washed with methanol, mp 82°, no depression on mixing with pure trityl methyl ether, mp 84°, prepared from a methanol solution of trityl chloride and pyridine. The triphenylcarbinol and trityl methyl ether isolated were also identified by infrared spectroscopic study.

N-Tritylpyridinium Perchlorate and Tetrafluoroborate. Trityl perchlorate (2.0 g) was dissolved in 10 ml of acetonitrile (yellow solution). Pyridine (1 ml) was added to the acetonitrile solution to give a colorless solution. After the solution was allowed to stand at room temperature for 10 min, the solvent was removed *in vacuo* to give the yellow solid. The solid was washed with benzene three times and dried under vacuum. There was obtained an 82% yield of N-tritylpyridinium perchlorate, mp 209–212° dec.

N-Tritylpyridinium tetrafluoroborate was prepared from a mixture of solution of trityl tetrafluoroborate and pyridine in acetonitrile in the same way as the perchlorate, mp 155–157°.

(18) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, **2**, 545 (1963).
(19) Personal communication with Professor G. Briegleb.
(20) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, **9**, 24 (1964).
(21) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, **86**, 261 (1964).
(22) C. G. Swain and E. E. Pegues, *ibid.*, **80**, 812 (1958).

(23) H. J. Dauben, Jr., L. R. Honner, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
(24) A. G. Anderson, Jr., and G. Berkelhammer, *ibid.*, **23**, 1109 (1958).
(25) G. D. Sichev, *J. Russ. Phys. Chem.*, **60**, 325 (1928); *Chem. Abstr.*, **23**, 1330 (1929).
(26) Y. Okamoto and H. Shimizu, *J. Amer. Chem. Soc.*, **90**, 6145 (1968).

Trityl Bromide.—Trityl bromide was prepared by the method previously reported.[27] The colorless solid melted at 145–147°.

N-Tritylpyridinium Bromide.—The solution of 5.2 g (0.016 mol) of trityl bromide and 7.1 g (0.09 mol) of pyridine in 50 ml of acetonitrile was stirred for 24 hr and then the solvent and excess pyridine were removed under vacuum. After washing with pentane, a slightly tan solid was recovered in 40% yield, mp 137–139° dec (lit.[27] mp 139° dec).

Reaction of N-Tritylpyridinium Bromide with Pyridinium Chloride.—The mixture of solution of 2.00 g (0.005 mol) of N-tritylpyridinium bromide and 1.50 g (0.013 mol) of pyridinium chloride in 50 ml of dry acetonitrile was stirred at room temperature for 10 min and the solvent was evaporated under reduced pressure. The residue was extracted with 50 ml of dry petroleum ether and then the solvent was removed under reduced pressure. The white solid, recovered in 80% yield, melted at 111–112° and proved to be trityl chloride by mixture melting point measurement and infrared spectroscopy.

α-Substituted Pyridinium Compounds.—2,6-Dimethyl-N-pyridinium iodide was obtained by passing dry hydrogen iodide into the benzene solution of 2,6-dimethylpyridine, mp 185°. 2,6-Dimethyl-N-methylpyridinium iodide was synthesized from 2,6-dimethylpyridine with methyl iodide by refluxing. The product was recrystallized from ethanol, mp 239–240°.

(27) W. E. Backmann, "Organic Syntheses," Coll. Vol. 3, Wiley, New York, N. Y., p 841.

Anal. Calcd for $C_8H_{12}NI$: C, 38.6; H, 4.82; N, 5.63; I, 51.0. Found: C, 38.4; H, 4.83; N, 5.77; I, 51.1.

2,6-Di-*tert*-butylpyridine was prepared by the method of Brown and Kanner,[28] bp 61–62° (1 mm), the chloroaurate, mp 188° (lit.[28] 184.5°).

Anal. Calcd for $C_{13}H_{22}NAuCl_4$: C, 29.4; H, 4.15; Cl, 26.7; N, 2.64. Found: C, 29.9; H, 4.29; Cl, 26.4; N, 3.08.

2,6-Di-*tert*-butyl-N-pyridinium iodide was synthesized by passing dry hydrogen iodide into the benzene solution of 2,6-di-*tert*-butylpyridine, mp 196–197°.

(28) H. C. Brown and B. Kanner, *J. Amer. Chem. Soc.*, **88**, 986 (1966).

Bromine–Lithium Exchange of p-Bromo-N,N-dimethylaniline with n-Butyllithium

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A product study of the reaction between p-bromo-N,N-dimethylaniline (1) and n-butyllithium (2) was made. Yields as high as 91% of p-(N,N-dimethylamino)phenyllithium (3) were obtained at 25° with a contact time of 30 hr. Several amines arising from nitrogen, ring, and chain alkylation were found at all temperatures. A dimeric amine, N,N,N',N'-tetramethyl-p-benzidine (9), was isolated from runs at high temperature. N-Methyl alkylation of 3 with 2 failed. Ring carbon alkylation with 1-iodobutane gave the expected product, p-(n-butyl)-N,N-dimethylaniline (8).

The halogen–lithium exchange reaction between organolithium compounds and organic halides, mainly bromides and iodides, first discovered by the schools of Gilman[1b] and Wittig[2] has received wide synthetic application. Mechanistic studies have also been carried out in order to unveil the details of the reaction.[3]

Our interest in halogen–lithium exchange reactions and in the chemistry of tertiary amines has led us to reinvestigate the reaction between p-bromo-N,N-dimethylaniline (1) and n-butyllithium (2) in the inert solvent n-hexane. The reaction is known to yield p-(N,N-dimethylamino)phenyllithium (3), which was derivatized with carbon dioxide and eventually identified as the methyl ether.[4] Since 1 is also used for a color test of aliphatic organolithium compounds,[5] it was of interest to know the spectrum of products arising from the exchange reaction as well as their dependence on reaction conditions.

Results and Discussion

Glc quantitative determination[6] showed that N,N-dimethylaniline was obtained in 91% yield by quenching with water the reaction mixture from the interaction of 1 with a 60% excess of 2 at 0°. Quenching with D_2O (Table II, run 6) gave p-deuterio-N,N-dimethylaniline (5),[7] whose mass spectrum (M^+ 122, Table I) was consistent with nuclear deuteration (m/e at 78), but was not distinct from that of o-deuterio-N,N-dimethylaniline, which was prepared by direct metalation of N,N-dimethylaniline with n-butyllithium,[8] followed by quenching with deuterium oxide. The pmr spectrum of 5, however, besides revealing no significant m-deuteration and an isotopic purity of ~80%, showed a distinct A_2B_2 quartet in the aromatic region and the ir spectrum confirmed the position of deuteration with the characteristic o-o-p bending absorption of aromatic hydrogen at 12.15 μ as well as the expected pattern[9] at 5–6 μ. Table II shows all the

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(2) G. Wittig, U. Pockels, and H. Dröge, *Chem. Ber.*, **71**, 1903 (1938).

(3) (a) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963). (b) H. J. S. Winkler and H. Winkler, *ibid.*, **88**, 964, 969 (1966). (c) A. R. Lepley, *Chem. Commun.*, 64 (1969).

(4) H. Gilman and I. Banner, *J. Amer. Chem. Soc.*, **62**, 344 (1940).

(5) H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

(6) Essential glc data are collected in Table I and conditions are reported in the Experimental Section.

(7) G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, **88**, 4203 (1966).

(8) A. R. Lepley, W. A. Khan, A. B. Giumanini, and A. G. Giumanini, *J. Org. Chem.*, **31**, 2047 (1966).

(9) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 118.