270 (5), 163 (55), 162 (100), 105 (50), 91 (30), 84 (20). Anal. Calcd for $C_{19}H_{29}N$: C, 84.07; H, 10.77; N, 5.16. Found: C, 84.03; H, 10.79; N, 5.15.

1-[1-(1,1'-Biphenyl-4-yl)cyclohexyl]piperidine (6). A solution of 7.3 g (0.031 mol) of 4-bromobiphenyl in 35 mL of Et_2O was added slowly to a refluxing mixture of 1.5 g (0.063 mol) of Mg in 20 mL of Et_2O. THF (30 mL) was added and the Et_2O distilled off. The mixture was maintained at reflux for 2 h and then 6.0 g (0.031 mol) of 1 in 30 mL of Et_2O was added dropwise over 30 min. Heating was continued for an additional 1 h, the mixture was cooled, and the reaction was quenched with 10% aqueous NH_4Cl. After filtration through glass wool to remove excess Mg, the THF was removed (60 °C, vacuum) and the basic aqueous solution extracted as before to yield the basic organics as a heavy oil, which was diluted with 30 mL of MeOH and refrigerated. The slightly yellow crystals which deposited were filtered and recrystallized from hot EtOH to yield 2.6 g (8.2 mmol, 26%) of white crystalline 6, mp 110–111 °C. HPLC analysis of synthetic 6, isolated 6, and combined synthetic and isolated 6 showed one peak at k' 1.38. Attempted GC showed evidence of decomposition under conditions of analysis: NMR δ 7.60 (m, 4 H) and 7.45 (m, 5 H) (aromatic protons), 2.35 (distorted t, 4 H, α piperidine protons),[13] 2.18 and 1.60 (br m, 4 H and 12 H, ring methylene protons); mass spectrum, m/e (% of base) 319 (55, M+), 318 (35), 277 (58), 276 (100), 262 (40), 223 (50), 222 (45), 167 (100), 166 (45), 138 (25), 84 (25). Anal. Calcd for $C_{23}H_{29}N$: C, 86.47; H, 9.15; N, 4.38. Found: C, 86.44; H, 9.16; N, 4.34.

1,1'-(1,4-Phenylenedicyclohexylidene)bis[piperidine] (9).[14] To 11.8 g (0.05 mol) of p-dibromobenzene in 150 mL of Et_2O was added 2.4 g (0.10 mol) of Mg turnings in 0.5-g portions. The mixture was refluxed throughout the Mg addition. Portions of Mg were added only after the preceding portion had completely reacted. Portions of Mg were added only after the preceding portion had completely reacted. After all Mg was added (ca. 7 h), 50 mL of THF was added, the Et_2O allowed to boil off, and the mixture allowed to reflux an additional 5 h. At this point, 19.2 g (0.10 mol) of PCC (1) dissolved in 100 mL of Et_2O was added dropwise with continued external heating. As the Et_2O was distilled a light tan precipitate formed in the remaining THF. Following a 1-h reflux after addition of the PCC was completed, the reaction was quenched with 100 mL of aqueous NH_4Cl. Extraction of the reaction mixture (as described above) yielded 50 mL of a heavy oil. The oil was diluted with 150 mL of MeOH, and, upon refrigeration, off-white crystals formed. Filtration of the crystals and recrystallization from hot toluene gave 2.2 g (5.4 mmol, 11% yield) of white crystalline 9, mp 171–172 °C. HPLC analysis of synthetic, isolated, and mixed synthetic and isolated 9 showed only single peaks at k' 0.08: NMR δ 7.26 (s with small shoulder on downfield side, 4 H, aromatic protons), 2.27 (br distorted t, 8 H, α piperidine protons),[13] 2.08 and 1.50 (br m, 8 H and 24 H, ring methylene protons); mass spectrum, m/e (% of base) 408 (100, M+), 407 (15), 365 (80), 324 (75), 281 (20), 240 (20), 165 (40), 84 (30). Anal. Calcd for $C_{28}H_{44}N$: C, 82.29; H, 10.85; N, 6.85. Found: C, 82.24; H, 10.87; N, 6.82.

Registry No. 1, 3867-15-0; 2, 77-10-1; 3, 77745-00-7; 6, 77415-81-7; 9, 76916-13-7; 1-bromoethylbenzene, 585-71-7; 4-bromobiphenyl, 92-66-0; p-dibromobenzene, 106-37-6.

(13) In PCP and in each of the analogues described herein, the well-separated aliphatic resonance between δ 2.25 and 2.68 (4 H) (or 8 H in the case of 9) is assigned to the protons α to the nitrogen of the piperidine ring. These chemical shift values are in agreement with the values reported for the α-hydrogens of N-alkyl-substituted piperidines (axial δ ~2.3; equatorial δ ~3.3). See L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, New York, 1969, p 240.

(14) The synthesis of 9 was reported simultaneously to our report by P. Y. Johnson, R. Pan, and Q. Wen at The Combined Regional Southeast-Southwest Meeting of The American Chemical Society, December 10–13, 1980, New Orleans, LA (*J. Org. Chem.*, 46, 2049 (1981)).

The Question of N-Alkyl Nitrilium Ions from Nitriles, Alcohols, and Boron Trifluoride

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Nitrilium ions are becoming recognized as being important not only because of the role they play as intermediates in a rather large number of chemical reactions[1,2] but also because of the stereospecific manner in which they react.[3,4]

We recently formed N-alkyl nitrilium ions by the direct alkylation of nitriles with either triethyloxonium tetrafluoroborate or isopropyl chloride–iron(III) chloride[5] and demonstrated their reduction by trialkylorganosilicon hydrides to N-alkyl aldimines which yielded aldehydes upon hydrolysis (eq 1).[6]

$$RC\equiv N + R'X \longrightarrow RC\overset{+}{\equiv}NR' \ \bar{X} \xrightarrow{R''_3SiH} RCH=NR'$$
$$\downarrow H_2O \qquad (1)$$
$$RCHO$$
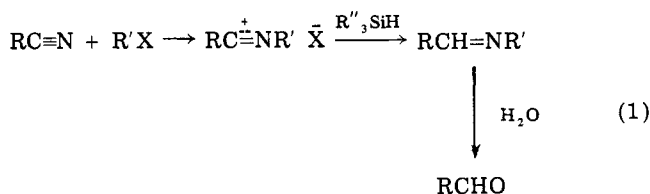
During the course of that study, it was found that, although N-alkyl nitrilium ions are reductively captured essentially quantitatively by organosilicon hydrides such as triethylsilane, incomplete alkylation of the starting nitriles by reasonable amounts of triethyloxonium tetrafluoroborate or, to a lesser extent, isopropyl chloride–iron(III) chloride reagents led to varying amounts of unreacted nitrile in the final product. In an attempt to effect a more quantitative, rapid alkylation of nitriles, we explored the system consisting of nitrile, an alcohol, and boron trifluoride. It was our expectation that this system using a Lewis acid would parallel the behavior of the usual Brønsted acid-catalyzed Ritter conditions[7] and would lead to similar formation of nitrilium ions (eq 2). This ex-

$$RC\equiv N + R'OH + BF_3 \longrightarrow RC\overset{+}{\equiv}NR' \ BF_3OH^- \qquad (2)$$
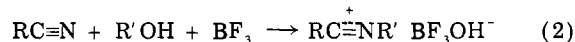
pectation was bolstered by a report that N-alkyl amides, the expected hydrolysis products from N-alkyl nitrilium ions, are formed from the reactions of nitriles and boron trifluoride with excess amounts of alcohols (eq 3).[8]

$$CH_3CN + CH_3CHOHCH_2CH_3 \xrightarrow{BF_3} \xrightarrow{H_2O}$$
$$CH_3CONHCH(CH_3)CH_2CH_3 \quad (3)$$
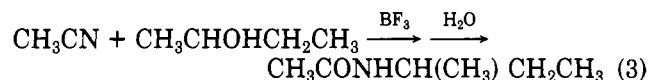
Results and Discussion

In an initial experiment, boron trifluoride gas was passed into a dichloromethane solution containing equimolar

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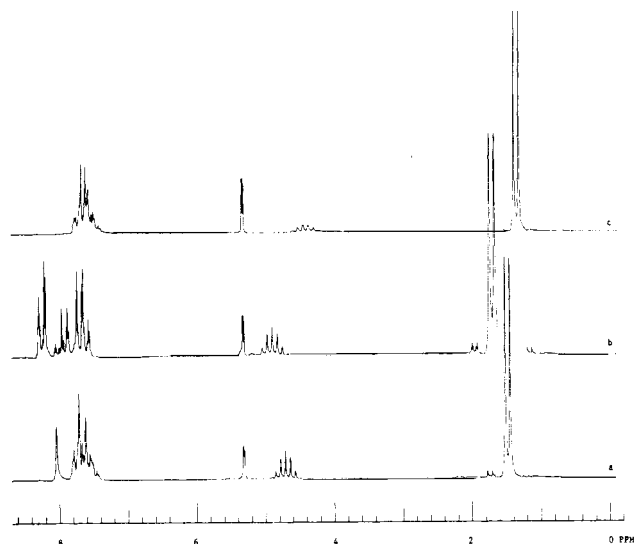(8) Sjöberg, K. *Acta Chem. Scand.* 1968, *22*, 1787.

Figure 1. 90-MHz ^{1}H NMR spectra of complex 1 (a), nitrilium ion 2 (b), and complex 3 (c).

amounts of benzonitrile and 2-propanol. This was followed by addition of 1 equiv of triethylsilane and aqueous work-up. Surprisingly, neither benzaldehyde, the expected reduction–hydrolysis product of the N-isopropylbenzonitrilium ion, nor N-isopropylbenzamide, its direct hydrolysis product, was obtained. Rather, benzonitrile and 2-propanol were recovered quantitatively.

Puzzled by these results, we subjected the system to an ^{1}H NMR spectroscopy study. The spectrum of the product (1) formed by the interaction of benzonitrile, 2-propanol, and boron trifluoride in CD_2Cl_2 solution was found to be the same regardless of whether boron trifluoride was passed into a solution containing equimolar amounts of alcohol and nitrile or an equivalent amount of alcohol was added to a solution of preformed benzonitrile–boron trifluoride complex.[9] The spectrum of 1 (Figure 1a) was unique from that of any of the starting materials and remained unchanged for several days at room temperature. However, the composite spectrum of recovered benzonitrile and 2-propanol was instantly obtained upon addition of water to the sample solution.

A known sample of N-isopropylbenzonitrilium tetrafluoroborate (2) not only displayed different spectral properties from those of 1 (Figure 1b), but, significantly, yielded exclusively N-isopropylbenzamide upon aqueous quenching (eq 4).

$$\overset{+}{C_6H_5C\equiv NCH(CH_3)_2} \ BF_4^- \xrightarrow{H_2O} C_6H_5CONHCH(CH_3)_2 \qquad (4)$$

$$\mathbf{2}$$
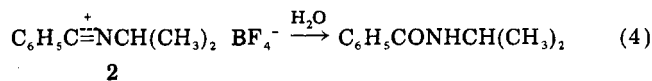
The spectral properties of a solution of 1 stored at room temperature underwent significant changes only very slowly. After 65 days, the spectrum obtained was identical with that of a known sample of the boron trifluoride adduct of N-isopropylbenzamide (3; Figure 1c).

$$\mathbf{3}$$
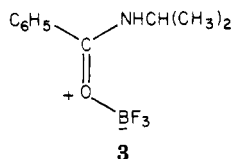
We conclude from these observations that the interaction of benzonitrile, 2-propanol, and boron trifluoride does

Scheme I
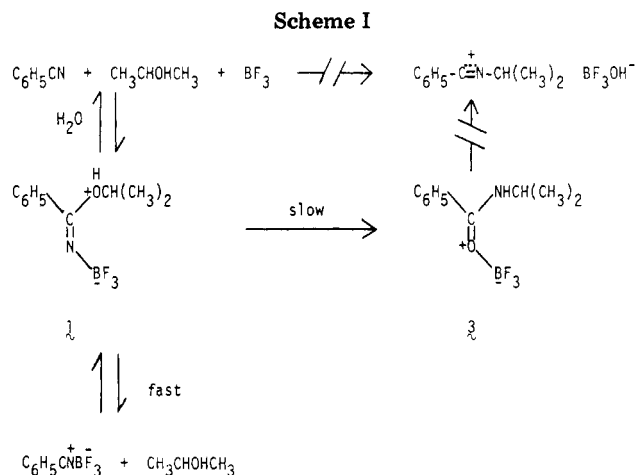
not lead to the formation of a nitrilium ion by a Ritter-like route. It instead follows a route which closely resembles the Brønsted acid-catalyzed Pinner synthesis[10] and leads to the formation of a kinetically labile product with a structure similar to that of an alkyl imidate (Scheme I).

The slow rearrangement of 1 into 3 resembles the Lander rearrangement[11] of alkyl imidates to amides and very likely involves a similar bimolecular $O \rightarrow N$ transfer of the alkyl group.[12,13] In order to see if excess alcohol would enhance the rate of rearrangement of 1 to 3, 1 equiv of 2-propanol was added to a solution of 1. At ambient probe temperature (ca. 37 °C), the resulting ^{1}H NMR spectrum revealed somewhat broadened methine and methyl signals with chemical shifts the averages of those of the corresponding signals in 1 and pure 2-propanol. In spite of the apparent rapid chemical exchange of isopropyl groups, no spectral changes had occurred after 4 days, at which time aqueous quenching of the solution yielded only pure benzonitrile and 2-propanol in a 1:2 ratio.

In sharp contrast to the time-averaged spectra obtained at ambient probe temperature, solutions containing complex 1 and an excess of 2-propanol showed ^{1}H and ^{13}C NMR spectra at 0 °C which were composites of both 1 and 2-propanol. Solutions obtained from a 1:1 ratio of benzonitrile–boron trifluoride complex and 2-propanol gave the same spectra at 0 °C as at ambient temperature. These results, together with the observation that 2-propanol suffers rapid decomposition and polymerization upon contact with free boron trifluoride, even at low temperatures,[14] strongly suggest that complex 1 is in rapid equilibrium with very small amounts of benzonitrile–boron trifluoride complex and uncomplexed 2-propanol at ambient temperatures (Scheme I).

As an adjunct to the above studies, we monitored a solution of the BF_3–amide adduct 3 for changes. Meerwein reported that the BF_3 adduct of N-phenylbenzamide underwent slow rearrangement to N-phenylbenzonitrilium tetrafluoroborate (eq 5).[15] Under our conditions, there was no spectral evidence of any rearrangement of 3 to nitrilium ion 2 even after several weeks.

In conclusion, we find no evidence that N-alkyl nitrilium ions are formed under these reaction conditions.

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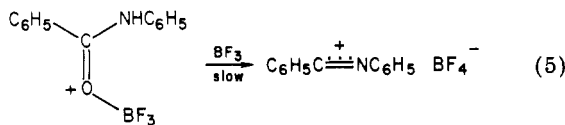(11) Schulenberg, J. W.; Archer, S. *Org. React.* **1965**, *14*, 1.

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$$C_6H_5C(NHC_6H_5)(\overset{+}{O}BF_3) \xrightarrow[\text{slow}]{BF_3} C_6H_5C\overset{+}{\equiv}NC_6H_5 \ BF_4^{-} \qquad (5)$$

Experimental Section

Nuclear magnetic resonance spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer, using CD_2Cl_2 as a solvent and lock in 5-mm tubes. ^1H chemical shifts are related to the center of the triplet of $CHCl_2$, taken to be 5.32 ppm from external Me_4Si. ^{13}C chemical shifts are related to the center of the quintet of CD_2Cl_2, taken to be 53.8 ppm from external Me_4Si. Infrared spectra were obtained on a Pye Unicam SP3-200 instrument with 0.1-mm NaCl cells.

Complex 1 was prepared by passing gaseous boron trifluoride into a solution of 0.25 mmol of benzonitrile in 0.4 mL of CD_2Cl_2 at 0 °C until the formation of the benzonitrile–BF_3 adduct[9] was complete. The protons of the adduct resonate at ca. 0.3 ppm farther downfield than do those of the free nitrile, and the C≡N vibration which occurs at 2215 cm^{-1} in the free nitrile appears at 2300 cm^{-1} in the adduct. Addition of 0.25 mmol of neat 2-propanol to the solution produced the complex 1: ^1H NMR δ 8.01 (1 H, br s), 7.8–7.2 (5 H, m), 4.71 (1 H, septet, J = 6.4 Hz), 1.48 (6 H, d, J = 6.4 Hz); ^{13}C NMR δ 134.2, 132.9, 129.7, 119.0, 111.4, 75.5, 22.4; IR (CH_2Cl_2) 3565, 3400, 3060, 2975, 2740, 2245, 1490, 1390, 1380, 1155, 867 cm^{-1}. The ^1H and ^{13}C NMR spectra were essentially identical at 0 and 37 °C. The same spectra were obtained when boron trifluoride was passed into a solution containing equimolar quantities of nitrile and alcohol. Addition of water to these solutions yielded only recovered nitrile and alcohol.

Rearrangement of 1 to 3. After a solution of 1 in CD_2Cl_2 was allowed to stand at room temperature for 65 days, the ^1H NMR spectrum had completely changed to that of complex 3, identical with that formed from a known sample of N-isopropylbenzamide: δ 7.8–7.4 (5 H, m), 4.45 and 4.36 (1 H total, pair of overlapping septets of almost equal intensity, both with J = 6.6 Hz), 1.34 (6 H, d, J = 6.6 Hz). Solutions of this complex were stable for several weeks at room temperature.

N-Isopropylbenzonitrilium tetrafluoroborate (2) was prepared by stirring 0.50 mmol of benzonitrile and 0.50 mmol of 2-bromopropane with 0.55 mmol of silver tetrafluoroborate (PCR) in 0.7 mL of CD_2Cl_2 for 3.5 h at room temperature; ^1H NMR δ 8.3–7.2 (5 H, m), 4.90 (1 H, septet, J = 6.6 Hz), 1.70 (6 H, d, J = 6.6 Hz). Addition of water to the solution of 2 gave a single product whose ^1H NMR and IR spectra were identical with those of a known sample of N-isopropylbenzamide.

Registry No. 1, 77745-19-8; 2, 77745-13-2; 3, 77773-71-8; BF_3, 7637-07-2; C_6H_5CN, 100-47-0; $CH_3CHOHCH_3$, 67-63-0.

Synthesis of 2,2,2-Trifluoroethanesulfonic Acid

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Introduction

A literature search indicated several probable methods for the preparation of fluoroalkanesulfonic acids. In one of these methods, Haszeldine and Kidd[1] oxidized (CF$_3$-

Scheme I. Preparation of 2,2,2-Trifluoroethanesulfonic Acid
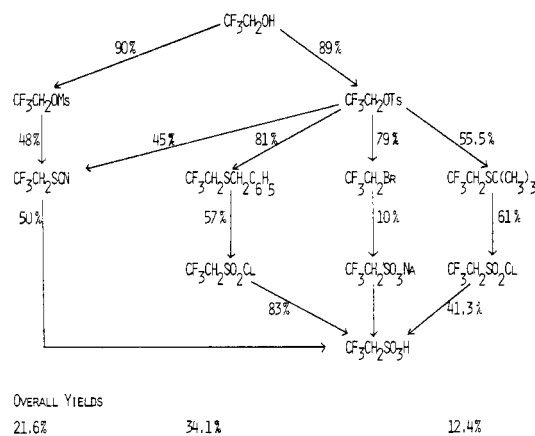
S)$_2$Hg with 35% hydrogen peroxide at 105 °C.

The end product of the oxidation of mercaptans, sulfides, disulfides, sulfones, etc. is a sulfonic acid. Oxidation by potassium permanganate,[2] chromic anhydride,[2] bromine–water,[3,4] hydrogen peroxide,[5] nitric acid,[6] and alkalis[7] is reported.

Many halogen compounds react with sodium, potassium, or ammonium sulfites to give high yields of sulfonic acid salts,[8-10] i.e., alkylation of alkali sulfites (Strecker).

Results and Discussion

The first method selected for evaluation was Strecker's method. It is commonly used for the synthesis of non-fluorinated alkanesulfonic acids. By use of this procedure, the reaction of CF_3CH_2Br and Na_2SO_3, conducted in a Parr pressure reactor because of its very low boiling point (25 °C), produced a complicated mixture. The yields varied from 5 to 10% and purification of the sulfonate salt was very difficult.

The second method involved the oxidation of CF_3CH_2SCN. The latter was obtained from CF_3CH_2OH by converting it into mesylate according to Crossland and Servis[11] or to the tosylate, a method described by Edgell and Parts.[12] These products were then reacted with NaSCN according to Crossland, Wells, and Shiner[13] to yield the corresponding thiocyanate. We found that the nitric acid oxidation of the crude thiocyanate compound gave $CF_3CH_2SO_3H$ of high purity, but the overall yield was only 20%.

2,2,2-Trifluoroethanesulfonic acid was also prepared by the introduction of sulfur into CF_3CH_2OH with subsequent oxidation to the respective sulfonic acid. This was accomplished by reacting the CF_3CH_2OTs with the sodium salt of benzyl or *tert*-butyl mercaptan to yield the corresponding $CF_3CH_2SCH_2C_6H_5$ or $CF_3CH_2SC(CH_3)_3$. These sulfides were then subjected to oxidative chlorination to

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