[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Studies in Stereochemistry. XVI. The Relative Stability of Addition Compounds of Boron Trifluoride with Aromatic Nitriles

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In aqueous solution 2-picoline and 2,6-lutidine are stronger bases than pyridine.[1] It would therefore be anticipated that 2-picoline and 2,6-lutidine would form more stable addition compounds than pyridine with such reference acids as boron trifluoride and trimethylboron. However, this is not the case.[2]

This discrepancy has been attributed to steric effects.[2] It was suggested that in aqueous solution, with the proton as the reference acid, the increased base strengths of 2-picoline and 2,6-lutidine reflect the increased electron density at the nitrogen atom resulting from the operation of the (+I) inductive effect of the methyl groups. However, the increased steric requirements of boron trifluoride and trimethylboron lead to steric strains in the addition compounds which are absent in the pyridine derivatives (compare Figs. 1 and 2). These strains bring about an apparent reversal in base strengths of the pyridine bases.

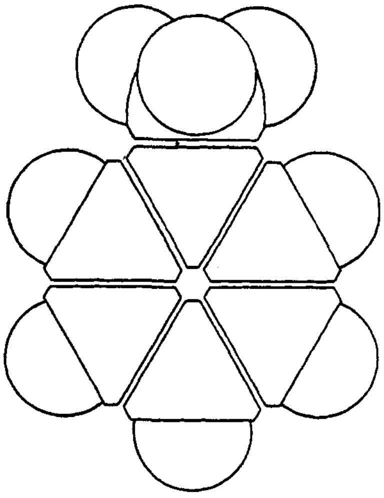


Fig. 1.—Molecular model of pyridine-boron trifluoride.

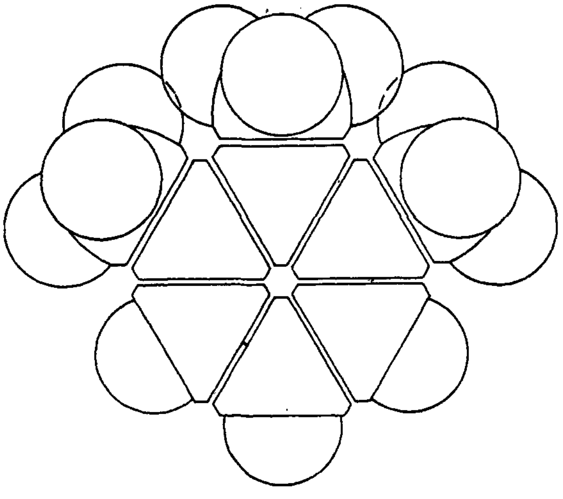
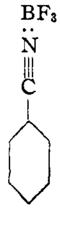


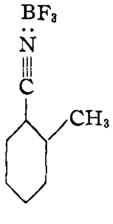
Fig. 2.—Molecular model of 2,6-lutidine-boron trifluoride.

Although interpretation of these phenomena in this way appears reasonable, it seemed desirable to test the hypothesis by an independent method. A study of the coördinating ability of benzonitrile and certain of its methyl homologs suggested itself. The polar effects of the methyl groups should be transmitted through the triple bond to the nitrogen atom of the nitrile group without appreciable diminution. However, the nitrile group is linear[3] and steric effects should be negligible. (Figures 3 and 4 show molecular models of representative addition compounds of aromatic nitriles and illustrate the absence of steric strains in these derivatives.)

Since nitriles are relatively weak bases, it was necessary to select a relatively strong acid to prepare addition compounds of sufficient stability. Boron trifluoride was selected and addition compounds of boron trifluoride with benzonitrile (I), *o*- (II), *m*- and *p*-tolunitrile, and *β*-isodurylonitrile or mesitonitrile (III) were prepared and studied.



I



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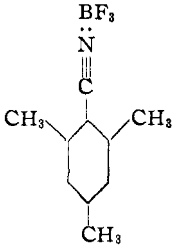

III

Results

The addition compound of boron trifluoride and acetonitrile has long been known[4] and has recently been the subject of a careful study.[5] However, addition compounds of boron trifluoride with aromatic nitriles have not been previously subjected to characterization and study.

Benzonitrile at 0° readily absorbs an equimolar quantity of boron trifluoride. The results of a

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(1) The values for the base dissociation constants are: pyridine-$k_B = 2.24 \times 10^{-9}$ [Barron, *J. Biol. Chem.*, **121**, 313 (1937)]; 2, picoline, $k_B = 1.05 \times 10^{-8}$ (*idem.*); 2,6-lutidine, $k_B = 1 \times 10^{-7}$ (Mündler, Diss. Heidelberg, 1901).

(2) Brown, Schlesinger and Cardon, THIS JOURNAL, **64**, 325 (1942).

(3) Brockway, *ibid.*, **58**, 2516 (1936).

(4) Patein, *Compt. rend.*, **113**, 85 (1891); Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

(5) Laubengayer and Sears, THIS JOURNAL, **67**, 164 (1945).

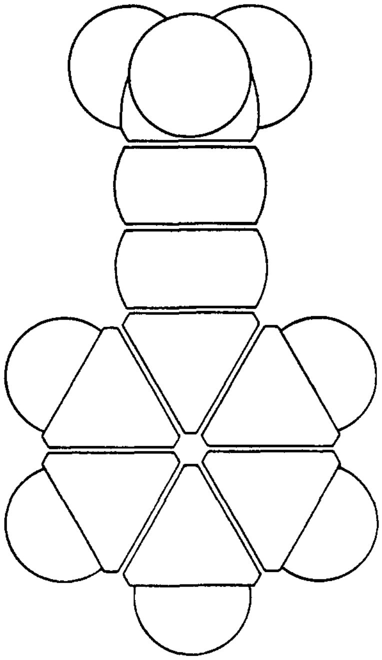

Fig. 3.—Molecular model of benzonitrile-boron trifluoride.

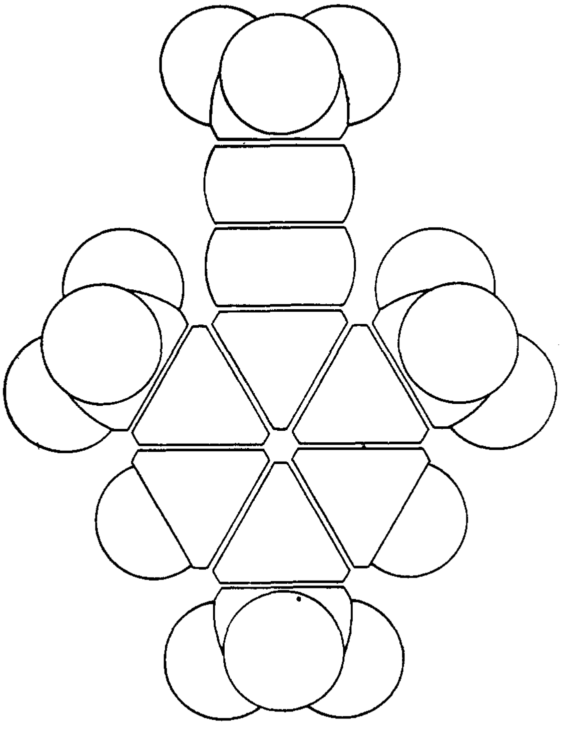

Fig. 4.—Molecular model of mesitonitrile-boron trifluoride.

typical pressure–composition study of the benzonitrile–boron trifluoride system at 40° are reported in Table I and illustrated in Fig. 5.

TABLE I

BENZONITRILE–BORON TRIFLUORIDE SYSTEM AT 40°

Mole % BF_3[a]	0	1.9	3.3	4.8	5.7
Press., mm.	1.9	3.2	3.8	4.6	5.1
Mole % BF_3	14.5	35.3	72.0	85.0	88.1
Press., mm.	6.7	6.9	7.0	7.2	7.0
Mole % BF_3	93.6	96.8	101.1	103.4	105.1
Press., mm.	7.2	7.7	58.2	87.8	120.8

[a] One hundred moles of boron trifluoride per 100 moles of benzonitrile.

The product is a white crystalline solid, sufficiently volatile at room temperature to permit sublimation in the high vacuum apparatus. The other aromatic nitriles form similar molecular compounds by addition of one mole of boron trifluoride at 0°, or at temperatures just above the melting point in the case of the solid nitriles.

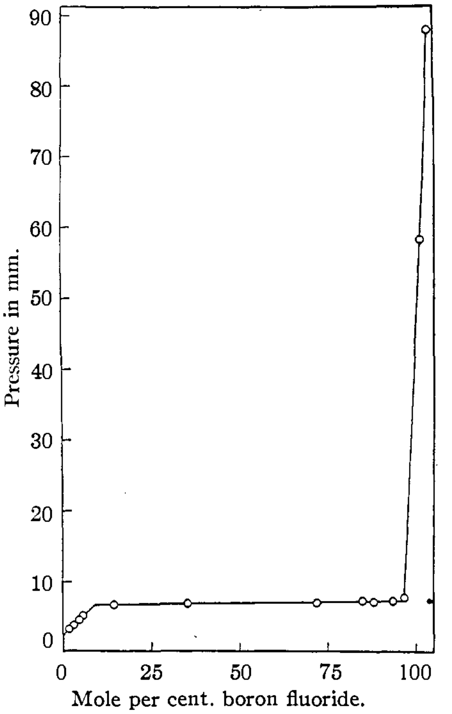

Fig. 5.—Benzonitrile-boron trifluoride system at 40°.

The addition compounds are only moderately soluble in the parent nitriles. At 40° the addition of boron trifluoride to benzonitrile does not produce a solid phase until 9.0 ± 0.5 mole per cent. has been added (Fig. 1). The solubilities of the remaining addition compounds appear to be similar.

The products all appeared to have high melting points. An attempt was made to measure these melting points by placing the addition compounds in small sealed tubes, completely immersed in an oil-bath. However, the observed melting point ranges were rather large (20°). Calculation indicated that the dissociation pressures in these tubes must be quite high, in the neighborhood of several atmospheres. Thus, the melting point is not a good criterion of purity and has no significance at ordinary pressures.

As has been indicated, the dissociation pressure of boron trifluoride over the benzonitrile addition compound is sufficiently low at room temperatures to permit purification of the product by sublimation, whereas at elevated temperatures the dissociation pressure is quite high. These properties suggested the application of benzonitrile–boron trifluoride as a means of purifying, storing, and generating pure boron trifluoride. The procedure proved highly satisfactory and was adopted for the preparation of the pure boron trifluoride required in this work. The method offers a convenient procedure of obtaining pure boron trifluoride from the commercial product. The pressure of boron trifluoride over each of the addition compounds was measured at several temperatures and the data fitted to equations of the type $\log p = -A/T + B$ (Fig. 6). From the slope of the line, the value of ΔH for the reaction

$$\mathrm{ArCN:BF_3(s)} \rightleftarrows \mathrm{ArCN\ (l,\ satd.\ with\ ArCN:BF_3)} + \mathrm{BF_3(g)}$$

was calculated. Table II lists the nitriles used, their melting points, the value of ΔH for the dissociation of the addition compounds, the dissociation pressure at 50.1°, and the constants A and B for dissociation pressure equation.

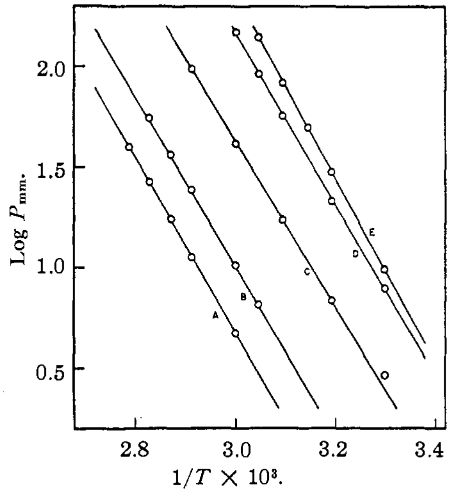

Fig. 6.—Saturation pressures for addition compounds of boron trifluoride with (A) mesitonitrile, (B) *p*-tolunitrile, (C) benzonitrile, (D) *o*-tolunitrile, and (E) *m*-tolunitrile.

TABLE II

PHYSICAL PROPERTIES OF NITRILES AND NITRILE–BORON TRIFLUORIDE ADDITION COMPOUNDS

ArCN		ArCN:BF$_3$			
Nitrile	M. p., °C.	ΔH, kcal.	Press., mm. at 50.1°	A	B
Benzo-	−13	18.7	17.1	4094	13.902
o-Tolu-	−13	19.4	56.5	4246	14.895
m-Tolu-	−23[a]	20.8	82.3	4554	16.011
p-Tolu-	27	19.4	4.1[b]	4252	13.763
Mesito-	51	20.0	1.8[b]	4380	13.810

[a] van Scherpenzeel, *Rec. trav. chim.*, **20**, 149 (1901). All other melting points are by direct observation. See Table III for comparison with literature values. [b] Calculated from equations.

The introduction of a methyl group into the *para* position of benzonitrile leads to a decrease in the dissociation pressure at 50.1° from 17.1 to 4.1 mm. This is the expected (+I) effect of a methyl group. However, in the *ortho* position the methyl group brings about an increase in the dissociation pressure to 56.5 mm. At first sight this would appear to indicate an effect similar to those which have been attributed to steric causes in the case of the pyridine bases. However, the *meta* derivative exhibits an even higher dissociation pressure, 82.3 mm. at 50.1°. Moreover, the presence of two *ortho* methyl groups in mesitonitrile does not lead to a further increase in the dissociation pressure. Instead, a marked drop in pressure to 1.8 mm. is observed. The addition compound of boron trifluoride with mesitonitrile is the stablest of the series, whereas in the pyridine series 2,6-lutidine invariably yields addition compounds which are far less stable than are similar derivatives which do not contain two methyl groups in the *alpha* positions.

It is further significant that ΔH of dissociation for the five addition compounds all fall within the limits 19.8 ± 1.1 kcal. In the pyridine series, the presence of methyl groups in the *alpha* positions brings about decreases in the heats of dissociation of 10 to 20 kcal.[2,6]

It is probable that the slight increases in pressure observed with *o*- and *m*-tolunitriles are the result of slight decreases in crystal lattice energy resulting from the unsymmetrical nature of the product. Certainly the lower melting points of *o*- and *m*-tolunitrile as compared to *p*-tolunitrile and mesitonitrile may be considered as evidence of a lower degree of symmetry in the parent nitriles and it is not unreasonable that this lower degree of symmetry should be carried over into the addition compounds.

Although interpretation of the data is complicated by neglect of the crystal lattice energies of the solid addition compounds, the results clearly indicate that one or two methyl groups in the *ortho* position have relatively little effect on the stability of the addition compounds formed by the resulting nitriles. In this respect the substituted nitriles differ markedly from the pyridine bases, where one or two methyl groups in the *alpha* position have a tremendous effect upon the stability of addition compounds. The results, therefore, lend strong support to the conclusion that the marked effects of such alpha methyl groups in the pyridine series must be *steric* rather than *polar* in nature.

Experimental Part

Apparatus and Techniques.—The apparatus and techniques used in this study are described in previous papers

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[6] Brown and Barbaras, THIS JOURNAL, **69**, 1137 (1947); also work in progress.

in this series and in a recent book on high vacuum methods.[7]

Materials.—Benzonitrile was obtained from the Socony-Vacuum Corp., and the tolunitriles from Eastman Kodak Co. Mesitonitrile was synthesized by the reaction of cuprous cyanide[8] on 2-bromomesitylene[9] in the presence of pyridine.[10]

The liquid nitriles were distilled through a fractionating column (15 theoretical plates), washed with aqueous acid to remove possible traces of amines in the same boiling range, dried over calcium chloride, and redistilled. *p*-Tolunitrile was purified by fractional freezing and melting. Mesitonitrile was crystallized from 30–60° petroleum ether, melted and heated under vacuum to remove traces of the solvent. Table III lists the observed physical properties together with previously reported values.

TABLE III

PHYSICAL PROPERTIES OF AROMATIC NITRILES

	Boiling range, °C.					
	Obsd.		Literature		Refractive index $n^{20}D$	
Nitrile	°C.	Mm.	°C.	Mm.	Obsd.	Literature
Benzo-	97	38	97.3	38[a]	1.5284	1.5257(25.5°)[b]
o-Tolu-	201–204	748	205.2	760[c]	1.5279	1.5272(23.1°)[b]
m-Tolu-	211–212	742	209.5–210	773[d]	1.5250	
p-Tolu-	M. p. 26–27		29.5[e]			
Mesito-	M. p. 50–51		50–52[f]			

[a] Kahlbaum, *Z. physik. Chem.*, **26**, 577 (1898). [b] Brühl, *ibid.*, **16**, 193 (1895). [c] Perkin, *J. Chem. Soc.*, **69**, 1025 (1896). [d] van Scherpenzeel, *Rec. trav. chim.*, **20**, 149 (1901). [e] Kröber, *Ber.*, **23**, 1026 (1890). [f] Fuson and Denton, THIS JOURNAL, **63**, 654 (1941).

Purification of Boron Trifluoride.—Boron trifluoride was obtained from a commercial cylinder of the gas (Matheson) and was purified through its addition compound with benzonitrile. Boron trifluoride was passed into a weighed sample of benzonitrile at 0° until the material was saturated with the gas. The gain in weight was theoretical. The flask and its contents were attached to the high vacuum apparatus at a point next to two U-tubes separated by a mercury float valve. The system and its contents were evacuated to a pressure of 10^{-5} mm. to remove all traces of silicon tetrafluoride and other gaseous impurities. The small quantity of addition compound which sublimed during this evacuation was collected in a suitably situated U-tube cooled to −80°. Dry air was then introduced until the pressure was approximately 20 mm. The U-tube immediately adjacent to the addition compound was cooled to −80°, the second U-tube was cooled in liquid air, and the intervening mercury float valve was partially closed so that it would require an excess pressure of 5–10 mm. on one side to permit gas to pass through.

The addition compound was warmed with hot water. Boron trifluoride was evolved. It passed through the −80° trap, where small amounts of benzonitrile which vaporized were removed as the addition compound, through the partially closed valve, and condensed in the liquid air trap. The boron trifluoride was readily separated from the dry air and placed in a storage bulb. All fractions of the boron trifluoride exhibited a vapor pressure of 300 mm. at −111.8° (melting carbon disulfide).

Preparation and Properties of Addition Compounds.—After a number of preliminary trials, the following apparatus (Fig. 7) and procedure was adopted for the preparation and study of the addition compounds. After thoroughly evacuating the system, dry air was introduced, and the mercury sealed transfer tube TT removed. Approximately 1 millimole of nitrile was introduced into the transfer tube with minimum exposure to the atmosphere and the amount exactly determined by weighing. A small crystal of calcium hydride was then introduced into the transfer tube and the tube was then attached to the apparatus. After hydrogen evolution ceased (such hydrogen evolution was always rather small), tube U was cooled in a Dry Ice bath and the system evacuated. The nitrile collected in tube U. When the pressure dropped below 10^{-4} mm., the float valve V2 was closed and the nitrile transferred to tensimeter bulb TB by moving the Dry Ice bath from tube U to TB. No visible residue remained in TT or U after thirty minutes, but two hours or more were allowed to insure complete transfer. Mercury was then raised in the tensimeter manometer TM by operating the control rod R, and V2 was opened to the pump. The calcium hydride was removed by sealing off the lower part of TT while it was open to the pump.

Small quantities of boron trifluoride were measured out and introduced into the tensimeter. In each case a pressure–composition curve similar to that shown in Fig. 5 was obtained. The quantity of boron trifluoride added was adjusted to 99.5 ± 0.3% of the equivalent quantity of nitrile. If necessary, small quantities of the product were sublimed away until the observed pressure was in good agreement with that previously determined for the plateau portion of the pressure–composition curve. A bath which could be controlled to ±0.1° was then placed about the tensimeter and the pressures exhibited by the addition compound at several temperatures were determined.

The plots of $\log_{10} p$ *vs.* $1/T$ exhibited satisfactory linearity (Fig. 6) and the data could be reproduced with excellent precision. In Table IV are reported the observed pressures and the values calculated with the equation, $\log_{10} p = -4252/T + 13.7630$ (Table II).

TABLE IV

DISSOCIATION PRESSURE DATA FOR *p*-TOLUNITRILE–BORON TRIFLUORIDE

Temp., °C.	Press., mm. obsd.	Press., mm. calcd.
55.1	6.5	6.5
60.1	10.2	10.2
70.3	24.1	24.1
75.3	36.2	36.3
80.4	55.1	54.7

The pressures observed are the pressures for the system $ArCN:BF_3(s) \rightleftarrows ArCN(l, \text{satd. with } ArCN:BF_3) + BF_3(g)$. It is assumed that the vapor is completely dissociated, by analogy with acetonitrile-boron trifluoride.[5] The exact equilibrium constant is

$$K = a_{ArCN} \cdot a_{BF_3} / a_{ArCN:BF_3}$$

In accordance with usual convention, $a_{ArCN:BF_3}$ and a_{ArCN} are taken as unity. At the pressures and temperatures employed, a_{BF_3} is closely approximated by p_{BF_3}. The total pressure over the addition compound consists of the vapor pressure of the aromatic nitrile (saturated with addition compound) plus the pressure of boron trifluoride. The vapor pressure of the saturated solution of nitrile is unknown. However, at this temperature the vapor pressures of the pure nitriles are quite small. Accordingly, the total pressure is taken as the pressure of boron trifluoride. The equilibrium constant thus becomes

$$K_P = P_T$$

The constants A and B (Table II) for the equation $\log_{10} p = -A/T + B$ were calculated by the methods of least squares. The values of ΔH for the dissociation process were calculated from the slopes of these lines.

After the pressure measurements had been completed, the addition compound was transferred to tube SR with

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[7] Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.

[8] Supniewski and Salzberg, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, New York, N. Y., 1941, p. 46.

[9] Lee Irvin Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 95.

[10] The procedure employed is that described by Fuson and Denton, THIS JOURNAL, **63**, 654 (1941).

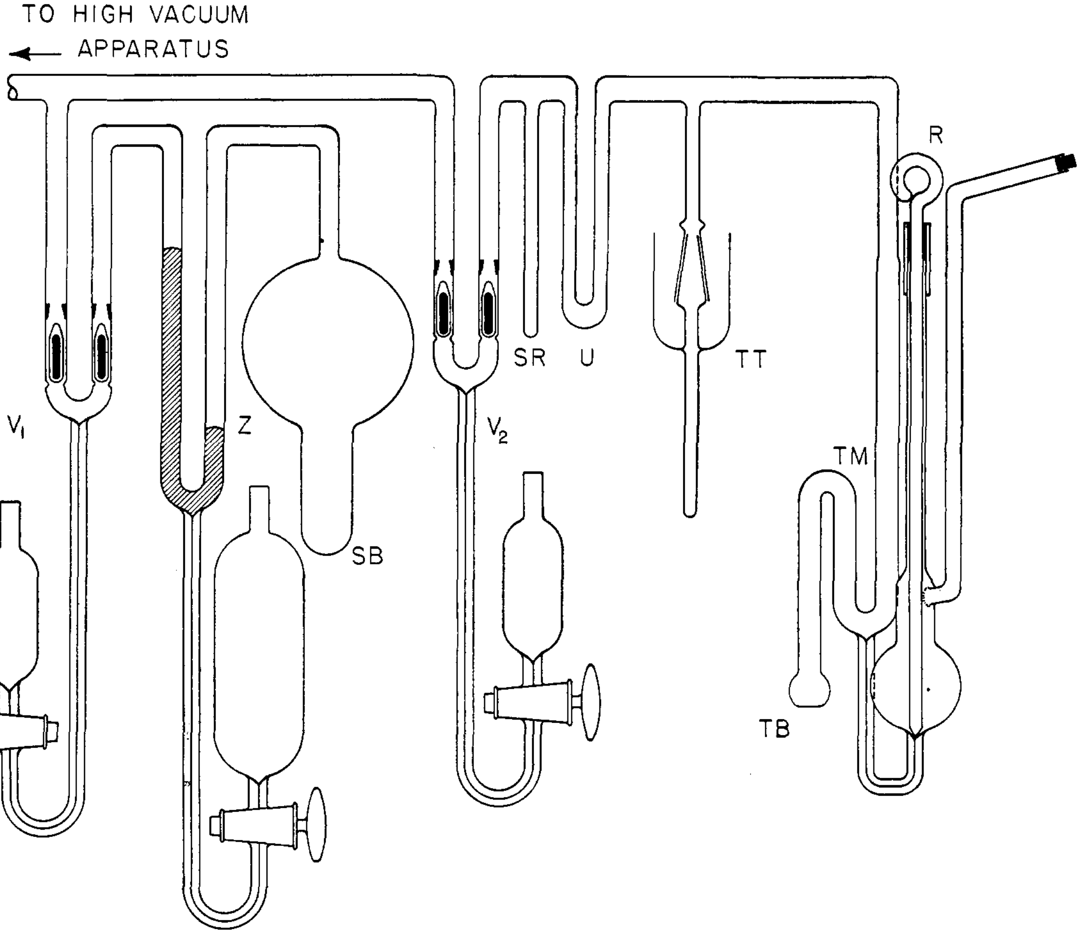

Fig. 7.—Apparatus for preparation of nitrile-boron trifluoride addition compounds and study of their relative stability.

liquid air, and SR was sealed off and removed from the line. The addition compound at this point was in the form of very small crystals and appeared gray due to the presence of mercury. However, after a few days the compound assumes the form of a single, large, well-defined, colorless crystal. After several months these crystals take on a yellow tinge. Whether this is a property of the substance itself or due to residual traces of impurities cannot be stated.

In an attempt to observe the melting points of the addition compounds the sealed tubes were totally immersed in an oil-bath and the melting ranges of the substances recorded: benzonitrile–boron trifluoride, 105–121°; *o*-tolunitrile–boron trifluoride, 77–86°; *m*-tolunitrile–boron trifluoride, 65–76°; *p*-tolunitrile–boron trifluoride, 111–133°. It may be calculated from the dissociation pressure equations that the pressures in these tubes were from one to five atmospheres so that these melting ranges have little significance.

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Summary

1. One-to-one addition compounds of boron trifluoride with the following aromatic nitriles have been prepared and characterized: benzonitrile, *o*-tolunitrile, *m*-tolunitrile, *p*-tolunitrile, and mesitonitrile.

2. A convenient procedure for utilizing the addition compound, benzonitrile-boron trifluoride, for the preparation of pure boron trifluoride is described.

3. The relative stabilities of the nitrile addition compounds indicate that methyl groups in the *ortho* position do not have a marked effect on the stabilities of the addition compounds. It is concluded that steric effects by *ortho* substituents are absent in this series and that the marked effects of *alpha* methyl groups in the pyridine series must be a true steric effect.

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