chemical shifts of H_{7a} and H_{7s} may also be expressed as linear functions of the group electronegativities of the substituents, calculated by the method of Wilmshurst.[13] Correlations with group electronegativity appear equally as good as those with σ_I, except that in neither case does the equation fit the chemical shift of the appropriate proton of norbornene itself. Therefore, it appears that σ_I is a better measure of the effect of substituents at C_5 and C_6 than is group electronegativity.

Although the same trends are observed if the chemical shifts of H_{7a} and H_{7s} are treated as functions of $\mathcal{F}$, the field substituent constant of Swain and Lupton,[11] the correlations are not so good as those with σ_I.

Registry No.—**2**, 20224-38-8; **3**, 20224-39-9; **4**, 20224-40-2; **5**, 20224-41-3.

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[13] J. K. Wilmshurst, *J. Chem. Phys.*, **27**, 1129 (1957).

1,3-Diaza-2,4-diborolidines. Isocyanide–Borane Adducts. III[1]

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Evidence is presented supporting a 1,3-diaza-2,4-diborolidine structure for the thermodynamically most stable member of a series of isomers obtained from the reaction of isocyanides with organoboranes. Several compounds possessing that ring system have been prepared, and factors which influence the formation of these compounds are discussed.

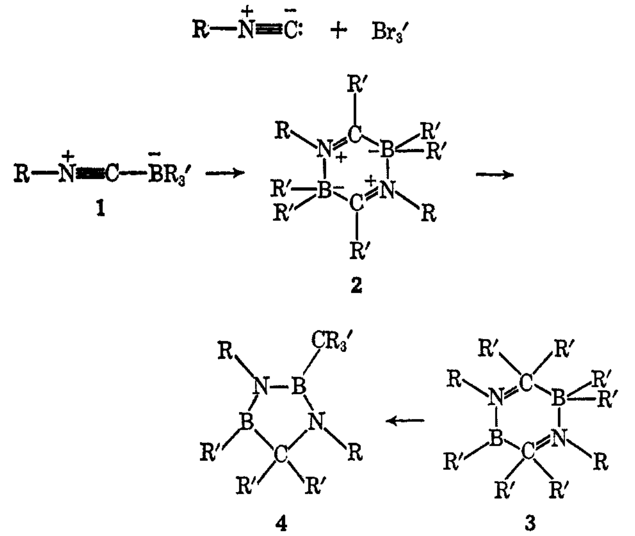
Interest in the chemistry of compounds which contain the >B—N< bond is reflected in the appearance of recent reviews[2] and reference books.[3] Substituted 2,5-dibora-3,6-dihydropyrazines represent an interesting case of this type. From them, 1,3-diaza-2,4-diborolidines may be prepared. The unusual stability of the latter compounds and factors which influence their preparation are the subjects of this paper.

Results and Discussion

The reaction between isonitriles and organoboranes to form 1:1 adducts had been reported.[4,5] Compounds of the general structure **1** (Chart I) are thermodynamically unstable with respect to the dimer **2**, first observed by Hesse and Witte.[6] Other examples of **2** have been reported by the same[7a] and other[7b-d] workers. Upon being heated, compounds of structure **2** rearrange to isomer **3**.

When certain compounds of structure **3** are heated briefly at 300–310°, ring contraction occurs to produce compounds which display the 1,3-diaza-2,4-diborolidine ring system **4**. Synthesis of this ring system from a compound of structure **3** using aluminum chloride has been reported previously for one case.[7e] An earlier report from this laboratory[1] suggested, incorrectly, the 1,3-diaza-2,4-diboretidine structure for compounds of structure **4**. Conclusive differentiation has now become possible through 32.1-Mc ^{11}B nmr and X-ray crystallographic analysis.[8] Efforts to carry out ring contraction to the 1,3-diaza-2,4-diboretidine nucleus have thus far been without success.

CHART I



a, R = C_6H_5; R′ = C_2H_5
b, R = p-ClC_6H_4; R′ = C_2H_5
c, R = p-$O_2NC_6H_4$; R′ = C_2H_5
d, R = p-$H_2NC_6H_4$; R′ = C_2H_5
e, R = C_6H_5; R′ = CH_3
f, R = C_6H_5; R′ = n-C_4H_9
g, R = p-$CH_3CONHC_6H_5$; R′ = C_2H_5
h, R = p-$Cl^-H_3N^+C_6H_4$; R′ = C_2H_5
i, R = c-C_6H_{11}; R′ = n-C_4H_9

Preparation and Reactions of 4a.—Compound **4a** can be obtained in nearly quantitative yield upon heating **3a** at 305°. A summary of the reactions of **4a** is shown in Chart II. The chemical and thermal stability of **4a** is unusual. The failure of **4a** to react with hydroxide is distinctly apart from observations for

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(1) Paper II: J. Casanova, Jr., H. R. Kiefer, D. Kuwada, and A. H. Boulton, *Tetrahedron Lett.*, 703 (1965).

(2) K. Niedenzu, *Angew. Chem. Intern. Ed. Engl.*, **3**, 86 (1964).

(3) (a) Advances in Chemistry Series, No. 42, K. Niedenzu, Ed., American Chemical Society, Washington, D. C., 1964; (b) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer Verlag, New York, N. Y., 1965; (c) M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956); (d) K. Ziegler, *Advan. Organometal. Chem.*, **6**, 1 (1968); (e) D. Seyferth, "Survey of Organometallic Chem," Vol. 3, Elsevier Publishing Co., New York, N. Y., 1967.

(4) J. Casanova, Jr., and R. E. Schuster, *Tetrahedron Lett.*, 405 (1964).

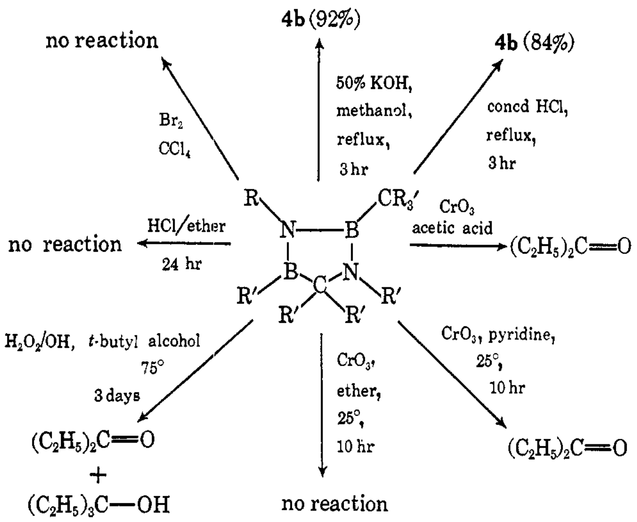
(5) G. Hesse, H. Witte, and G. Bittner, *Ann.*, **667**, 9 (1963).

(6) G. Hesse and H. Witte, *Angew. Chem.*, **75**, 791 (1963).

(7) (a) G. Hesse and H. Witte, *Ann.*, **687**, 1 (1965); (b) S. Bresadola, G. Carraro, C. Pecile, and A. Turro, *Tetrahedron Lett.*, 3185 (1964); (c) J. Tanaka and J. C. Carter, *ibid.*, 329 (1965); (d) S. Bresadola, F. Rosetto, and G. Puosi, *ibid.*, 4775 (1965); (e) H. Witte, *ibid.*, 1127 (1965).

(8) C. Tsai and W. E. Streib, *Tetrahedron Lett.*, 669 (1968).

CHART II



borazenes and aminoboranes.[9] Compound **4a** was unreactive toward potassium metal in tetrahydrofuran at room temperature, and did not produce an electron spin resonance spectrum either in the presence or absence of potassium. Although irradiation of **2a** in pentane produced a 75% yield of **3a**, no **4a** was formed upon irradiation of **3a**.

Because of variability in the success of converting compounds of structure **3** into the corresponding compound **4**, a number of N-aryl derivatives were prepared to study the effect of variation in *p*-aryl substituents. The nitrogen substituent, R, was held constant (R = C_2H_5). As with the N-phenyl series (**a**), the N-*p*-chlorophenyl series (**b**) could be prepared in very high yields throughout, starting with *p*-chlorophenylisonitrile. The *p*-nitrophenyl series (**c**) was very different in behavior. Even the mildest conditions for reaction sufficed to carry the reaction to compound **3c**. Although material which corresponded to the properties anticipated for **2c** could be isolated from the mother liquors of this reaction, **2c** could not be isolated in a pure state. Compound **3c** could not be converted into **4c**, but decomposed at 330°. However, **4c** could be prepared directly by nitration of **4a**, using fuming red nitric acid in trifluoroacetic acid at −5°. This latter reaction illustrates the great resistance of the 1,3-diaza-2,4-diborolidine ring in these compounds to chemical degradation, and the orientation effect of the -N(B)B and -N(B)B groupings in aromatic electrophilic substitution. Compound **3c** could be prepared in good yield by direct nitration of **3a**. The nitro groups of **3c** were smoothly reduced by hydrogen over platinum oxide to give the *p*-aminophenyl derivative, **3d**. Compound **3d** could be converted into **4d**, which could be converted into **4b** by a Sandmeyer reaction. Since compounds in series **a**, **b**, and **c** have been prepared separately from the corresponding *para*-substituted isonitriles, and are related to each other by interconversion, the aromatic ring substitution patterns are established.

Because of the lack of chemical reactivity of **4a**, most of the evidence which bears on its structure is physical rather than chemical in nature. The structure assigned is supported by elemental analysis, molecular weight determinations, infrared, ^1H and ^{11}B resonance spectra, mass spectra and X-ray crystallographic analysis. The ^1H and ^{11}B data are summarized in Table I.

TABLE I

^{11}B AND ^1H NMR SPECTRA OF SOME COMPOUNDS OF STRUCTURES **3** AND **4**

Compd	$^{11}B\ \delta^a$	$^1H\ \delta$,[b] ppm (relative no. of H)		
		$H_{aromatic}$	$H_{C\text{-alkyl}}$	$H_{B\text{-alkyl}}$
3e		7.23 (5)	1.14 (6)[c]	0.10 (3)[c]
3a	−48.6	7.18 (5)	1.1 (10)[d]	0.53 (5)[c]
3b	−42.0	7.1 (4)[d]	1.1 (10)[d]	0.55 (5)[c]
3c		7.75 (4)[c]	1.0 (10)[d]	0.59 (5)[c]
3d		6.75 (4)[d]	1.2 (10)[d]	0.60 (5)[c]
4a	−43.2[e]	7.2 (5)[d]	1.3–0.8 (15)[d]	
4b	−45.0	7.1 (4)[f]	0.75 (15)[d]	
4c		7.65 (4)[f]	0.73 (15)[d]	
4d		6.6 (4)[d]	0.85 (15)[d]	
4f[g]	−45.0	6.9 (5)[d]	0.9 (∼27)[d]	

[a] Relative to external boron trifluoride etherate. [b] Positive value is downfield from tetramethylsilane. [c] Sharp singlet. [d] Complex multiplet centered at the value shown. [e] The ^{11}B chemical shift of this compound was previously reported as −36 ± 5 ppm (ref 1, this paper) and has been refined. [f] A_2B_2 spectrum. [g] We are grateful to Professor G. Hesse for this sample.

Possible Sources of Stability of 4a.—The chemical stability of the 1,3-diaza-2,4-diborolidine ring probably arises from steric shielding of the heteroring atoms, blocking the approach of polar reagent along an axis perpendicular to the ring plane. A dramatic decrease in reactivity toward polar reagents due to steric effects is not without precedent in BN ring compounds. Nagasawa[10] has recently shown B-trixylyl- and B-trimesityl-N-trimethylborazines are recovered quantitatively after standing for 150 hr at room temperature in either dilute sodium hydroxide or dilute hydrochloric acid in aqueous dioxane.

Anomalies in the Pattern of Conversion of 3 into 4.—Table II shows the result of heating compounds of structure **3** at 300–310° in a sealed tube for 5–10 min.

TABLE II

BEHAVIOR OF **3** AT 300–310°.

Compd	$\sigma_I{}^a$	Mp of **3**,[b] °C	Observation[c]
3a	0.00	203–205	**4a** (96%)
3d	+0.13	226–228	**4d** (75%)
3g	+0.27	350	Dec <350°
3b	+0.47	201–202	**4b** (84%)
3c	+0.63	256–260 dec	Dec <330°
3h	+0.90	350	Dec <330°
3e	0.00	170.5–171	Dec <330°
3f[d]	0.00	168–169	**4f** (92%)
3i		142–144	Dec <300°

[a] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963). [b] Corrected. [c] Compound identification (yield, per cent recrystallized). [d] We are grateful to Professor G. Hesse for this sample.

The results were strikingly different. Four compounds of structure **3** (**a**, **b**, **d**, **f**) gave compound **4** in high yield. The remaining five studied (**c**, **e**, **g**, **h**, **i**) gave a complex decomposition, yielding 5 to 15 spots on thin layer chromatography. No single product appeared to predominate, and no crystalline product could be isolated in these cases, in spite of the fact that com-

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(9) *Cf.* ref 3b, pp 131–138.

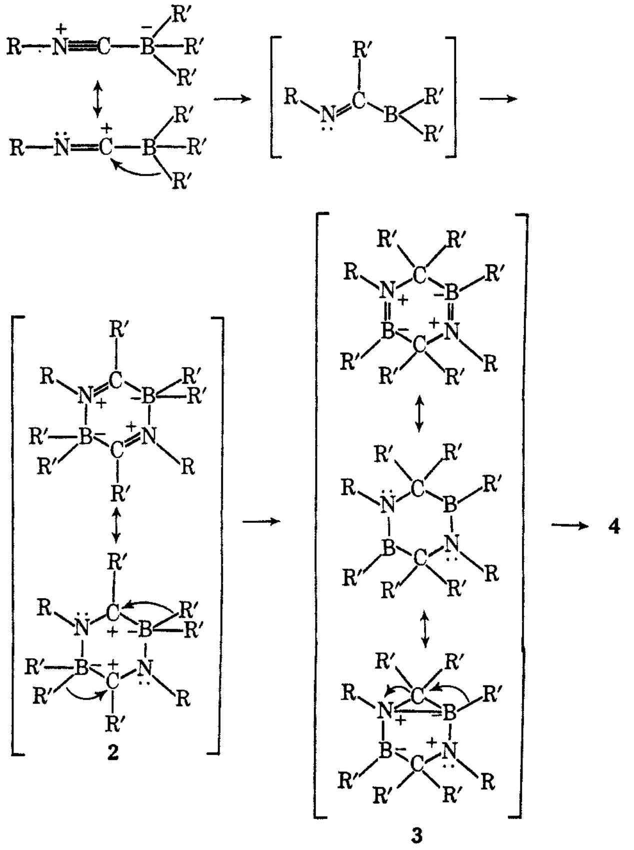
(10) K. Nagasawa, *Inorg. Chem.*, **5**, 442 (1966).

pounds of structure **4**, when they were present, could be isolated from the reaction mixture with no particular difficulty. The abrupt change in behavior which accompanies the change of ethyl to methyl as the boron substituents (**4a**–**4e**) is noteworthy.

Several common structural features which are present in those compounds of structure **3**, which can be isomerized to **4**. Those which do undergo rearrangement bear an aromatic substituent at the nitrogen atom. Of the B-ethyl, N-aryl compounds of structure **3** which fail to rearrange, all are crystalline solids at 300°. Those which do undergo rearrangement are molten at that temperature. It is possible that the reaction **3** → **4** may depend on the physical state of **3**. Still the behavior of **3e** (B-methyl) remains an anomaly.

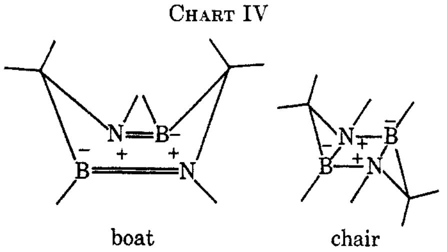
Possible Mechanisms for the Conversion of 3 into 4.—In each step in the interconversion of isomers in this series one or two boron-to-carbon alkyl group migrations occur, leading to products which are thermodynamically more stable than the starting materials. Each rearrangement may be viewed as the migration of an alkyl group from B^- to C^+, thus classifying these reactions as electron-deficient rearrangements of the Wagner–Meerwein type. For each compound which undergoes rearrangement it is possible to write a resonance structure in which an electron-deficient carbon atoms is located adjacent to (or transannular to) a tetracoordinated boron atom. This is shown in Chart III. Such a rearrangement is not unlike the Baeyer–Villager oxidation or the Kuivila mechanism for the oxidation of organoboranes by alkaline hydrogen peroxide.[11]

CHART III



The factors which determine whether or not conversion of **3** → **4** will occur are yet unknown. Although N-aryl substitution is necessary for the conversion of **3** to **4**, an additional requirement is that the alkyl group be larger than methyl. This invites speculation that diaxial nonbonded interaction between large alkyl groups in the normally more stable "boat" conformer is sufficiently large to overcome electronic favorability of the "boat" and force the ring into the "chair" conformer. Thus denied electron delocalization to an adjacent boron atom, because of unfavorable p-orbital overlap, the nitrogen atom is electronically better disposed to participate in transannular attack on a boron atom (see Chart IV). However the B—N stretching frequency provides a reliable measure of bond order in the B—N bond, lower frequency reflecting a lower bond order.[12] Table III shows the B—N infrared frequencies of compounds of structures **3** and **4**. These frequencies are remarkably constant from one compound to another, and provide no support for the "boat–chair" argument.

CHART IV



4

TABLE III

INFRARED B—N STRETCHING FREQUENCIES OF SOME COMPOUNDS OF STRUCTURES 3 AND 4

Designation	Infrared maxima, $\bar{\nu}$ (cm^{-1})			
			B—N[a]	NO$_2$
3a		1453	1397	
3b		1453	1397	
3c	1504	1453	1397[b]	1333[a]
3d	1504	1453	1397	
3g	1504		1397	
3e			1399	
3i			1471[c]	
4a	1481	1449	1385	
4b	1481	1449	1387	
4c	1490	1449	1389[b]	1337[a]
4f	1481	1449	1387	

[a] Most intense band in the spectrum. [b] Second most intense band in the spectrum. [c] *Cf.* ref 7a.

Experimental Section

Starting Materials.—Cyclohexylisonitrile (Aldrich Chemical Co.) was distilled before use. Phenyl-, *p*-chlorophenyl-, and *p*-nitrophenylisonitrile were prepared according to the method of Ugi.[13] Trimethylborane and triethylborane were prepared by a modification[14a] of the the method of Koster:[14b] bp −78° (25 mm) and −20° (755 mm)[14c] and bp 93–94° (755 mm),[14c] respectively.

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[11] H. G. Kuivila, *J. Amer. Chem. Soc.*, **76**, 870 (1954).

[12] (a) H. J. Becher, *Spectrochim. Acta*, **19**, 575 (1965); (b) *cf.* ref 3b, p 50.

[13] I. Ugi, U. Fetzer, H. Knupfer, and K. Offermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 472 (1965).

[14] (a) J. Casanova, Jr., H. R. Kiefer, and R. E. Williams, *Org. Prep. Proc.*, **1**, 57 (1969); (b) R. Koster, *Ann.*, **618**, 31 (1958); (c) G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1960, p 94.

Compound 4a.—A 1.50-g sample of **3a**,[7a,e] mp 204°, was heated in an evacuated sealed tube at 300–305° for 5–6 min, 1.15 g, mp 138–140° (methanol). Recrystallization gave 1.02 g of white solid, mp 140–141°. Mother liquors gave 0.46 g, mp 138–140°, combined yield 1.46 g (97%).

Anal. Calcd for $C_{25}H_{40}B_2N_2$: C, 77.63; H, 10.02; N, 6.96. Found: C, 77.48; H, 10.04; N, 6.82.

The molecular weight, osmometric in benzene, was 390 ± 8; isopiestic in benzene,[15] 395 (required for $C_{26}H_{40}B_2N_2$, 402.24). Spectral data for compound **4a** are found in Tables I, III, and IV.

TABLE IV

ULTRAVIOLET SPECTRA OF SOME COMPOUNDS OF STRUCTURE 4

Designation	Absorption maxima, λ, mμ (log ε)[a]			
a	272 (2.72)	265 (2.92)	233 (3.7)	216 (4.2)
b	280 (2.87)	272 (3.04)	266 (4.7)	
c	283 (4.34)			216 (4.2)

[a] All values reported are for solutions in 95% ethanol.

Attempted Saponification of 4a.—**4a** (50 mg) in 20 ml of 50% aqueous potassium hydroxide and 5 ml of methanol was refluxed for 3 hr. Water (10 ml) was added. Ether extraction gave **4a** (92%), identified by tlc, melting point, and ir.

Attempted Acid Hydrolysis of 4a.—**4a** (50 mg) was refluxed in 30 ml of concentrated hydrochloric acid for 3 hr. Ether extraction gave **4a** (42 mg, 84%) identified by tlc, melting point, and ir.

Chromic Anhydride Oxidation of 4a in Acetic Acid.—Chromic anhydride (95 mg, 0.82 mmol) in glacial acetic acid (7 ml) at 90° was treated with 216 mg (0.54 mmol) of **4a**. The cooled, diluted reaction mixture was extracted with ether. The ether was washed with aqueous sodium bicarbonate. The dried extract was concentrated to *ca.* 1 ml using a 4-ft Vigreaux column. The volatile portion of this residue was separated by a high vacuum transfer and analyzed by glpc, which showed 15% 3-pentanone. No 3-ethyl-3-pentanol was present. In a control experiment, 3-ethyl-3-pentanol was found to react with chromic anhydride in acetic acid at 90° to give 3-pentanone in low yield.

Chromic Anhydride Oxidation of 4a in Pyridine.—**4a** (40 mg) was dissolved in 2 ml of pyridine and 200 mg of chromic anhydride in 2 ml of pyridine was added and the solution was stirred at room temperature overnight. The cooled solution was acidified to Congo red with hydrochloric acid and extracted with ether. The dried ether extract afforded 12 mg of an oil. 2,4-Dinitrophenylhydrazine reagent[16a] gave red crystals (18 mg), mp 144–148°. Recrystallization from (ethanol–ethyl acetate) raised this to 157–159°. This material was identical (melting point and tlc) with authentic 3-pentanone 2,4-dinitrophenylhydrazone, mp 157–159° (lit.[16b] mp 156°).

Attempted Oxidation of 4a with Chromic Acid in Ether.[17]—To 40 mg of **4a** in 15 ml of ether, 0.5 ml of chromic acid (prepared from 5.5 g of sodium dichromate, 4.1 ml of 96% sulfuric acid and diluted to 22.5 ml with water) was added dropwise. The mixture was stirred overnight at room temperature. The ether was separated, washed with saturated salt water, and dried to give **4a** (32 mg, 80%), identified by tlc, melting point, and ir.

Oxidation of 4a with Alkaline Hydrogen Peroxide.—A 400-mg sample of **4a** in 15 ml of *t*-butyl alcohol was heated to 70°. To this solution was added 150 mg of sodium hydroxide in 0.5 ml of water, followed by 0.3 ml of 33% hydrogen peroxide. The mixture was stirred overnight. The *t*-butyl alcohol was removed by slow concentration through a spinning-band column up to 85°. The distilled *t*-butyl alcohol was 99.4% pure by glpc. The residue from the distillation was made strongly alkaline with 2 *N* sodium hydroxide and extracted with several small portions of ether. The extract was washed with dilute hydrochloric acid, then water, and dried. The residual oily solid was distilled at 50° (0.1 mm). The residue 210 mg (52%, methanol) was **4a**, identified by melting point and ir. The distillate (30 mg) gave three peaks on glpc, identified as *t*-butyl alcohol (10%), 3-pentanone (30%), and 3-ethyl-3-pentanol (60%). A 500-mg sample of authentic pure 3-ethyl-3-pentanol, when treated in the same way, gave 322 mg after distillation (25% 3-pentanone and 75% 3-ethyl-3-pentanol).

Tests of Basicity and Saturation of 4a.—Compound **4a** in ether saturated with dry hydrogen chloride gave no solid even on standing overnight. Compound **4a** was recovered unchanged by evaporation of the solvent. Compound **4a** failed to decolorize a solution of bromine in carbon tetrachloride.

Preparation of 2b.—*p*-Chlorophenylisonitrile[13] (12 g, 0.087 mol) in 50 ml of anhydrous ether was cooled and treated with 9 g (0.092 mol) of triethylborane in 80 ml of ether in an inert atmosphere. The isonitrile was added over 30 min. The mixture was stirred at room temperature for 2 hr. The white precipitate was washed with pentane. The filtrate was evaporated to 30 ml and cooled to give a second crop of solid. The combined solids were recrystallized to give 15 g (75%, acetone): mp 171–172°; ir (CCl_4) 1548 cm^{-1} ($>C{=}N^+<$); ^{1}H nmr 7.08 ppm (4 H), a quartet (J = 5.6 Hz) at 2.22 ppm (2 H), a complex region at 0.79 ppm (10 H), and a triplet (J = 5.6 Hz) at 0.35 ppm (3 H). The ^{11}B nmr of this compound was a very broad single line at +2.4 ppm [relative to $(C_2H_5)_2O \cdot BF_3$].

Anal. Calcd for $C_{26}H_{38}B_2Cl_2N_2$: C, 66.28; H, 8.14; N, 5.94. Found: C, 66.30; H, 8.12; N, 5.88.

Preparation of 3b.—Compound **2b** (3.80 g) was heated in a sealed tube at 185° (10 min). The product gave 3.51 g (92%, benzene–methanol) of **3b**: mp 201–202°; ir (CCl_4) 1389 cm^{-1} ($>B{-}N<$). The ^{11}B and ^{1}H resonance spectra are shown in Table I.

Anal. Calcd for $C_{26}H_{38}B_2Cl_2N_2$: C, 66.28; H, 8.14; N, 5.94. Found: C, 66.11; H, 8.03; N, 5.90.

Preparation of 4b.—Compound **3b** (3.00 g), heated in a sealed tube at 305° (12 min), gave (2.50 g, 84%, acetone), mp 158–160°.

Anal. Calcd for $C_{26}H_{38}B_2Cl_2N_2$: C, 66.28; H, 8.14; N, 5.94; Cl, 15.05. Found: C, 66.08; H, 7.97; N, 6.02; Cl, 15.15.

Spectral data for **4b** are found in Tables I, III, and IV.

Preparation of 4f.—A 300-mg sample of **3f**[18] was heated at 305° (10 min) in a sealed tube and gave 275 mg (91%, acetone), mp 131°.

Anal. Calcd for $C_{38}H_{64}B_2N_2$: C, 79.99; H, 11.31; N, 4.91. Found: C, 79.58; H, 11.16; N, 5.04.

Spectral data for compound **4f** are found in Tables I and III.

Preparation of 3c from *p*-Nitrophenylisonitrile.—*p*-Nitrophenylisonitrile[13] (1.3 g) in 10 ml of tetrahydrofuran was added dropwise to a stirred solution of 900 mg of triethylborane in 20 ml of tetrahydrofuran at 0°. A dense precipitate was formed after 10 min. The reaction mixture was stirred at 50° for 1 hr, cooled in ice, and 1 ml of methanol was added. The solvent was evaporated under reduced pressure at 20°, and the residue was recrystallized to give 200 mg (10%, chloroform), mp 256° dec.

Anal. Calcd for $C_{26}H_{38}B_2N_4O_4$: C, 63.44; H, 7.78; N, 11.38. Found: C, 63.09; H, 7.67; N, 11.47.

Spectral data relevant to compound **3c** are found in Tables I, III, and IV.

Preparation of 3c by Nitration of 3a.—A finely powdered sample of **3a** (2.5 g) suspended in 100 ml of trifluoroacetic anhydride at −5° was stirred, treated with 10 ml of red fuming nitric acid (dropwise over a period of 15 min), and stirred at this temperature for 45 min. The reaction mixture was poured cautiously onto *ca.* 500 g of crushed ice, and the solid which separated was removed by filtration and washed with cold acetone. Recrystallization afforded 1.5 g (48%, chloroform), mp 256° dec. The ir of this material was identical with that of a sample prepared from *p*-nitrophenylisonitrile and triethylborane.

Reduction of 3c to 3d.—A solution of 2.0 g of **3c** in 150 ml of acetic acid was shaken in an atmosphere of hydrogen at 29 psi in a Parr apparatus for 14 hr, using 150 mg of platinum oxide as a catalyst. A tan solid which rapidly darkened in air was obtained. A sample was prepared for analysis by chromatography on alumina followed by rapid recrystallization, mp 226–228° (methanol). The analysis was unsatisfactory, owing to the instability of **3d**.

Anal. Calcd for $C_{26}H_{42}B_2N_4$: C, 72.23; H, 9.79; N, 12.96. Found: C, 71.20; H, 9.68; N, 14.16.

Spectral data for compound **3d** are found in Tables I, II, and III.

Compound **3d** was usually converted quickly into the acetamide or hydrochloride. The acetamido derivative (**3g**) was prepared by dissolving 300 mg of **3d** in 5 ml of anhydrous pyridine and adding 0.5 ml of acetyl chloride to the cooled solution. The mixture was poured into ice water, filtered, and the solid residue

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[15] D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); R. A. Robinson and D. A. Sinclair, *J. Amer. Chem. Soc.*, **56**, 1830 (1934).

[16] (a) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley & Sons, Inc., New York, N. Y., 1964, p 253; (b) p 362.

[17] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2951 (1961).

[18] The authors are indebted to Professor G. Hesse for a generous supply of this compound.

(350 mg) recrystallized from 95% ethanol (mp >350°): ir (KBr) 3247 (NH), 1665 (amide I), and 1600 cm^{-1} (amide II).

The hydrochloride (**3h**) was prepared by treating a solution of 100 mg of **3d** dissolved in 5 ml of anhydrous ether with dry hydrogen chloride gas. Recrystallized of the residue from evaporation gave 80 mg, mp 336–340° dec (methanol–ethanol).

Preparation of 4c by Nitration of 4a.—A finely powdered sample of **4a** (500 mg) in 50 ml of acetic anhydride at −5° was treated with 6 ml of fuming red nitric acid by dropwise addition. The mixture was stirred for 1 hr, then poured into ice water. The product was 240 mg (33%, ethanol), mp 225–228°. Two further recrystallizations raised the melting point to 230°.

Anal. Calcd for $C_{26}H_{38}B_2N_2O_4$: C, 63.44; H, 7.78; N, 11.38. Found: C, 63.16; H, 7.78; N, 11.49.

Spectral data for compound **4c** are found in Tables I, III, and IV.

Conversion of 4h to 4b.—**4h** (100 mg) in 4.5 ml of concentrated hydrochloric acid in an ice bath was treated with sodium nitrite (1.4 g) in small portions. A cold solution of 3 g of freshly prepared cuprous chloride[19] in 10 ml of 8 *N* hydrochloric acid was added and the mixture allowed to warm to room temperature. It was heated for 30 min on a steam bath, then diluted with cold water. The brown residue which remained was chromatographed on Florisil using ether to give 20 mg of a pale yellow semisolid which was identical with authentic **4b** (ir).

Registry No.—**2b**, 20116-72-7; **3a**, 1756-53-2; **3b**, 20122-54-7; **3c**, 20122-55-8; **3d**, 20122-56-9; **3e**, 3657-04-3; **3f**, 4040-72-6; **3g**, 20122-59-2; **3h**, 20122-60-5; **3i**, 3657-05-4; **4a**, 20122-62-7; **4b**, 20122-63-8; **4c**, 20122-64-9; **4d**, 20122-65-0; **4f**, 2179-88-6.

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Heteronuclear Stabilized Carbonium Ions. I. Nuclear Magnetic Resonance Examination of Aryl Oxocarbonium Ions

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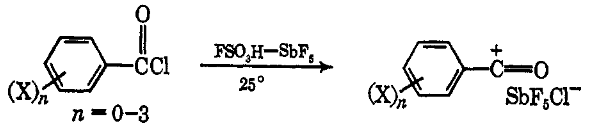
Aryl oxocarbonium ions were generated by the addition of benzoyl chlorides to FSO_3H–SbF_5 and were characterized by nmr spectroscopy at room temperature. In some instances ionizations were observed in neat FSO_3H. Chemical shift assignments were deduced from model compounds. For 28 cations the ranges of deshielding from the covalent precursors were as follows: $\Delta\delta_o$ 0.44–0.62 ppm, $\Delta\delta_m$ 0.44–0.57 ppm, and $\Delta\delta_p$ 0.93–1.09 ppm. Evidence is presented for alternating charge delocalization in the aromatic nucleus. Sulfonation products were observed when the cations possessed suitable electron-donating groups.

Oxocarbonium ions have been generated from acyl fluorides and SbF_5,[1-4] acyl chlorides and silver hexafluoroantimonate[1,2] or in some cases $SbCl_5$,[2,5] acyl sulfinylamines, or isocyanates and nitrosonium salts[6] as well as from the cleavage of esters[7] or carboxylic acids[8] in strong acid media. To date alkenyl,[8] alkylene,[9] cycloalkyl,[10] and alkyl[1-4] oxocarbonium ions have been directly observed and systematicly examined by nmr spectroscopy; however, such an examination of aryl oxocarbonium ions has not yet been reported.[11] As part of a related study of the behavior of methyl benzoates in strong acid media[12] it was necessary to characterize spectroscopically a number of aryl oxocarbonium ions. Characterization of these carbonium ions is reported herein.

Results and Discussion

Using a modified version of the procedures employed by Volz[5] and Olah[1-4] a number of *ortho*-, *meta*-, and *para*-substituted aryl oxocarbonium ions were prepared, by merely adding appropriate benzoyl chlorides to an excess of 1:1 *M* FSO_3H–SbF_5 solutions. The resulting homogeneous, although sometimes colored, solutions were for the most part stable enough to be examined by nmr spectroscopy at room temperature. Well-resolved spectra were generally obtained. In some cases, when steric and electronic effects were appropriate, the benzoyl chlorides could be ionized to their respective oxocarbonium ions in neat FSO_3H at room temperature.



The adequacy of the FSO_3H–SbF_5 method was demonstrated by converting acetyl chloride into its previously reported oxocarbonium. By this method a singlet was observed for this cation at −3.91 ppm and compares with a value of −3.93 ppm (20% oleum) reported by Deno and coworkers.[13] Additional efficacy was provided by observing chemical shift changes that occurred upon dissolving the benzoyl chlorides in neat

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