referred to as the B (bathochromic) effect, the Fs (fine structure), C (conjugation) and S (steric) effects.

Alkyl and most alicyclic substituents produce only B-effects, *i. e.*, a shift of the whole absorption curve to longer wave lengths occurs, with little change of shape. A few alicyclic derivatives exhibit an increase in the fine structure resolution (Fs-effect). In many derivatives in which there is an unsaturated substituent with the double bond in a position to conjugate with the main aromatic ring system, a more profound change in the spectrum occurs (C-effect); such groups as $-NH_2$, $-OH$ and $-O^-$, in which there are donatable pairs of electrons on the atom attached directly to the aromatic ring system also show C-effects. In the fourth class (S-effect) are included the spectra of compounds containing formally conjugated systems which fail to exhibit such changes, and in which it is presumed that the failure is caused by steric interference with resonance.

It is noted that in the spectra of certain compounds which exhibit C-effects, the modification of the hydrocarbon spectrum is mainly associated with specific groups of maxima, other groups of maxima being relatively unchanged. An attempt is made to explain such localized influences by the assumption that the several absorption bands in the complex spectra of these aromatic compounds are associated with processes of electronic excitation vectorized in the plane of the aromatic ring system.

In cases where C- or S-effects are observed, calculations have been made of the minimum angle of approach between the plane of the aromatic ring system, and the main plane of the substituent group, in an attempt to determine whether steric interference with resonance can be predicted from purely geometrical considerations of molecular structure. In many cases such predictions do not agree with the spectrographic observations.

Certain compounds, notably those containing conjugated cyano and isocyanate groups, fail to exhibit normal C-effects, although the linear shape of these substituents eliminates the possibility of steric inhibition of resonance being responsible. Compounds containing these substituents tend to show quite large bathochromic shifts of the hydrocarbon spectrum, but do not show the accompanying loss of fine structure resolution usually seen in the spectra of amino, carbonyl and conjugated alkene substituents.

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[CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION LABORATORY AND FROM THE DEPARTMENT OF CHEMISTRY, No. 306 IN ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

New Aliphatic Borates[1]

BY ALLEN SCATTERGOOD, WARREN H. MILLER[2] AND JULIAN GAMMON, JR.[2]

Over a dozen aliphatic borates have been mentioned in the literature, but the constants and analyses of several of these are missing, including two which are sold commercially. Several of the known borates have therefore been prepared under more carefully controlled conditions and the missing data collected. In addition, ten new borates have been prepared in order to study their properties and possible applications, especially in sugar chemistry. Three of the new borates are crystalline.

Experimental

Most of the alcohols from which the borates were prepared are commercial products. They were fractionated through a 115-cm. electrically heated, helix-packed column with total condensation and a variable take-off. The H.E.T.P. of the column was 2.5 cm. Interchangeable ground glass joint equipment and Glas-col heating mantles were used throughout this research.

The new borates were prepared by the method of Bannister.[3] Quantities proportional to one mole of boric acid and three moles of the purified alcohol were employed. An excess of alcohol sufficient to remove three moles of water as the azeotrope was used. To ensure complete reaction, a 10% over-all excess of alcohol was generally taken. The mixture was distilled through the column described. During the distillation of the water–alcohol azeotrope, it was found that proper adjustment of the take-off returned the alcohol layer to the column so that an excess of alcohol may not be necessary. After the unreacted alcohol had been distilled off, the borate was fractionated through the column at atmospheric pressure unless it decomposed or boiled above 275°, in which case the column was operated at reduced pressure. Several borates which had been reported unstable in the literature were distilled successfully at atmospheric pressure.

A high boiling residue often was left after the distillation of the trialkyl borates. In the case of tri-*s*-butyl borate, an attempt to distil this residue at atmospheric pressure resulted in decomposition to a vapor which spontaneously ignited and burned with a green flame.

The Bannister method was applied successfully to all primary and secondary alcohols studied, but was unsuccessful in the case of the three tertiary alcohols tried. This suggests that primary and secondary alcohols contaminated with tertiary alcohols may be purified through their borates.

The data as to the preparation and properties of these borates are contained in Table I.

Hydrolysis of Borates

There is little information in the chemical literature concerning the rate of hydrolysis of alkyl borates, but the rates which are mentioned are stated to be very rapid. The

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[1] The material in this paper is taken in part from theses submitted to the Massachusetts Institute of Technology by Warren H. Miller and Julian Gammon, Jr., in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

[2] U. S. Navy, V-12 program.

[3] W. J. Bannister, U. S. Patent 1,668,797 [*C. A.*, **22**, 2172 (1928)]; J. R. Johnson and S. W. Tompkins, "Organic Syntheses," **13**, 16 (1933).

TABLE I

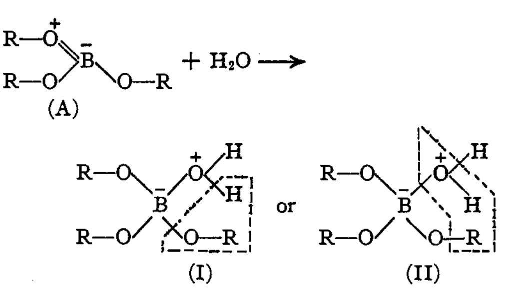
ALIPHATIC BORATES

R in $(RO)_3B$	Alcohol used: Name	Alcohol used: B. p.,[a] °C.	Yield,[b] %	Constants of borates: B. p., °C.	Constants of borates: D^t_4	Constants of borates: t	Constants of borates: $n^{20}D$	Analytical data: Formula	Analytical data: % Boron Calcd.	Analytical data: % Boron Found[c]
n-Propyl	Propanol-1[d,q]	97.0– 98.0	34	....	.....	..	....	....	..	..
n-Butyl[f]	Butanol-1[g]	117.0–118.0	64	230.0–231.0[h]	0.84703	28	1.4089	$C_{12}H_{27}O_3B$	4.70	4.70
s-Butyl[f]	Butanol-2[i]	99.0– 99.5	59	195.4–195.8[j]	.82643	25	1.3960	$C_{12}H_{27}O_3B$	4.70	4.69
i-Butyl[k]	2-Methylpropanol-1[d]	106.0–107.0	63	211.5–213.0[l]	.83909	25	1.4029	$C_{12}H_{27}O_3B$	4.70	4.69
	2-Methylpropanol-2[i]	82.0– 83.0	0		.....	..				
n-Amyl	Pentanol-1[m]	137.0–138.5	67	274.5–276.1[n]	.85224	27	1.4197	$C_{15}H_{33}O_3B$	3.97	3.95
Methyl-*n*-propyl-carbinyl	Pentanol-2[m]	118.7–119.0[o]	72	236.5–238.0[p]	.82976	27	1.4075	$C_{15}H_{33}O_3B$	3.97	4.00
Diethylcarbinyl	Pentanol-3[m]	114.0–115.6[q]	53	235.6–236.6	.83372	28	1.4097	$C_{15}H_{33}O_3B$	3.97	3.98
s-Butylcarbinyl	2-Methylbutanol-1[m]	128.5–130.0	67	260.0–261.2	.84699	28	1.4170	$C_{15}H_{33}O_3B$	3.97	4.00
	2-Methylbutanol-2[m]	101.0–102.0	0		.....	..				
Methylisopropyl-carbinyl	2-Methylbutanol-3[r]	111 –113[s]	62	226.0–230.0	.83395	28	1.4079	$C_{15}H_{33}O_3B$	3.97	4.16
Neopentyl[t]	2,2-Dimethylpropanol-1[u]	110 –111	77	229.0–230.0[v]	.....	..		$C_{13}H_{33}O_3B$	3.97	4.01
n-Hexyl	Hexanol-1[g]	157.2–158.6	68	182.2–183.0[w]	.84712	28	1.4250	$C_{18}H_{39}O_3B$	3.44	3.44
Methyl-*n*-butyl-carbinyl	Hexanol-2[r]	139.0–139.8	32	127.0–128.0[x]	.76935	25	1.4160	$C_{18}H_{39}O_3B$	3.44	3.47
2-Methyl-*n*-amyl	2-Methylpentanol-1[r]	147.0–149.0	68	139.0–140.0[x]	.85197	27	1.4261	$C_{18}H_{39}O_3B$	3.44	3.43
Methylisobutyl-carbinyl	2-Methylpentanol-4[g]	131.5–132.0	51	108.5–109.5[x]	.75750	25	1.4109	$C_{18}H_{39}O_3B$	3.44	3.46
2-Ethyl-*n*-butyl	2-Ethylbutanol-1[g]	148.0–149.0	50	169.0–169.2[w,y]	.85724	28	1.4283	$C_{18}H_{39}O_3B$	3.44	3.45
	3-Methylpentanol-3[r]	120 –122	0							
Diisopropyl-carbinyl[t]	2,4-Dimethylpentanol-3[d]	136.0–137.0	50	285.0–290.0[v-1]	.....	..	....	$C_{21}H_{45}O_3B$	3.02	3.04
2-Methoxyethyl	2-Methoxyethanol[z]	121.0–123.0	35	134.0–135.0[w,zz]	1.00961	28	1.4059	$C_9H_{21}O_6B$	4.58	4.59
Methallyl	2-Methylpropen-2-ol-1[z]	114.0–114.5	79	225.0–225.2[v-2]	.....	..	....	$C_{12}H_{21}O_3B$	4.83	4.84

[a] All boiling points given in this paper were taken by Anschütz thermometers completely immersed in the vapors. [b] High yields were sacrificed in order to get pure products. A zero per cent. yield indicates that the Bannister method did not work. [c] Carbon and hydrogen analyses were carried out by Mrs. Carolyn Klein Fitz. The boron analyses are the average of three closely agreeing determinations made by titration of the boric acid liberated upon hydrolysis with standard sodium hydroxide solution in the presence of mannitol. [d] E. I. du Pont, Ammonia Department. [e] We wish to thank those companies whose names are abbreviated in this table for generous samples of the indicated alcohols. [f] Although this is a known borate, no record of its analysis was found in the literature. [g] Carbide and Carbon Chem. Corp. [h] Johnson and Tompkins, "Org. Syn.," **13,** 16 (1933), report 230–235°. Otto, THIS JOURNAL, **57,** 1476 (1935), gives *d* 0.85349; n_D 1.40731. [i] Standard Alcohol Company. [j] Lewis and Smyth, THIS JOURNAL, **62,** 1529 (1940), report 193–194° uncor., d_{25} 0.82902, $n^{25}D$ 1.39444. [k] This analysis of a known and previously analyzed borate was carried out as a check on the titration method. [l] Concler, *J. prakt. Chem.*, (2) **18,** 383 (1878) gives 212°. Lewis and Smyth (note *j*) report d_{25} 0.84033; $n^{25}D$ 1.40101. [m] Sharples Chemicals, Inc. [n] Johnson and Tompkins, note *h*, report 146–148° at 16 mm. [o] $n^{20}D$ 1.4075; Huntress and Mulliken tables give 1.4060. [p] Wuyts and Duquesne, *Bull. soc. chim. Belge*, **48,** 85 (1939) give 109.8–114° at 12 mm.; *d* 0.8375. [q] $n^{20}D$ 1.4112; Huntress and Mulliken tables give 1.4103. [r] Eastman Kodak Company. [s] This boiling range is from the Eastman Kodak Company catalog. Because of the cost of the alcohol, it was used without further purification. [t] Anal. for carbon: calcd. 66.1; found, 66.0. Anal. for hydrogen: calcd. 12.2; found, 12.3. After the titration of the boric acid liberated upon hydrolysis had been completed, and neopentyl alcohol was salted out and recovered by crystallization in the refrigerator, m. p. about 40°. The recovered alcohol had the characteristic odor of neopentyl alcohol. [u] Student preparation. Prepared by O. A. Bredeson, m. p. 55–56°. [v] Melting point, 57–59° (cor.). [v-1] Melting point 54–55° (cor.). [v-2] Melting point 29–30° (cor.). [w] At 15 mm. [x] At 5 mm. [y] Previously made in this Laboratory by Curtis H. Elliot, Jr., b. p. 289–291° (uncor.). [z] Shell. [zz] Rippere and La Mer, *J. Phys. Chem.*, **47,** 204–234 (1943), give b. p. 130–131° at 13 mm.

rate of hydrolysis of the esters reported in this paper was determined qualitatively by shaking 1 ml. of each ester with 3–5 drops of water at room temperature. The time taken for boric acid to crystallize was noted. Qualitative observations on the rate of hydrolysis were also made during the analyses for boron. The following generalizations seem to be justified by these experiments. The *n*-alkyl borates studied are rapidly hydrolyzed. The branched chain primary alkyl borates are hydrolyzed at rates varying from those of the *n*-alkyl borates to the unusually slow rate of tri-neopentyl borate. The secondary alkyl borates are more slowly hydrolyzed than the *n*-alkyl borates, branching of the chain having the same effect as with the primary alkyl borates. Thus, of the borates studied, the most resistant to hydrolysis is tris-(diisopropylcarbinyl) borate which defied all attempts at hydrolysis even in alkaline solution at 100°. It is hoped that quantitative data on hydrolysis may be presented later.

The dependence of the rate of hydrolysis of a borate upon the branching of the alkyl group can be explained in a general way if the rate-determining step of hydrolysis is assumed to be the addition of a molecule of water.



The boron atom in an alkyl borate molecule is considered[4] to lie at the center of an equilateral triangle with the oxygen atoms at the three apices. Large compact alkyl groups would be expected to hinder the approach of the water molecule to the boron atom, resulting in a slow rate of hydrolysis for such borates.

The *n*-alkyl borates appear to hydrolyze rapidly even

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[4] Lewis and Smyth, THIS JOURNAL, **62,** 1529–1533 (1940).

in normal hydrochloric acid. This observation makes it seem unlikely that the addition of hydroxyl ion is the first step in the hydrolysis by water, since the rate of such an addition would presumably be decreased by an increase in hydrogen ion concentration.

The loss of a molecule of alcohol from the borate-water adduct can proceed by two possible mechanisms, (I) and (II). In mechanism (II), the carbon-oxygen bond is depicted as breaking, while in formulation (I) the bond remains intact. Whitmore[5] has summarized the literature in which it is shown that in any reaction in which the bond between the neopentyl radical and the rest of the molecule is broken, the neopentyl radical undergoes rearrangement. Whitmore and Rothrock[6] used the melting point of recovered neopentyl alcohol as a criterion of rearrangement.

In order to choose between the two possible mechanisms of hydrolysis, neopentyl borate was prepared and a sample submitted to hydrolysis. Neopentyl alcohol was recovered unchanged, thus demonstrating that the hydrolysis of trineopentyl borate proceeds by mechanism (I). This conclusion is undoubtedly valid for the hydrolysis of other alkyl borates also. By contrast, the esters of another inorganic acid, sulfuric acid, are known[7] to hydrolyze by mechanism (II).

Acknowledgments.—The authors wish to thank Dr. Robert C. Hockett, Scientific Director of the Sugar Research Foundation, for helpful suggestions in the preparation of this manuscript. The valuable suggestions concerning nomenclature, made by Professor Ernest H. Huntress, are also appreciated.

Summary

1. Twenty-one alcohols were allowed to react with boric acid according to the general method of Bannister. Eighteen borates were secured, sixteen of which had never before been obtained by this method. Ten of these borates are new. Three are crystalline.

2. Physical constants of the new borates and missing constants and analyses of the previously known borates have been determined.

3. The mechanism of hydrolysis of alkyl borates has been studied.

CAMBRIDGE 39, MASS. RECEIVED JUNE 12, 1945

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[5] Whitmore, THIS JOURNAL, **54**, 3274 (1930).

[6] Whitmore and Rothrock, *ibid.*, **52**, 3431 (1930).

[7] Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

The Alkylation and Arylation of Aliphatic Nitriles in Liquid Ammonia

BY F. W. BERGSTROM AND ROBERT AGOSTINHO

Cornell[1] working in these Laboratories found that nitriles react with the alkali amides in liquid ammonia to give crystallizable compounds which were assumed to be formed in accordance with the equation

$$R{\cdot}CN + MNH_2 = RC({=}NH)NHM \qquad (1)$$

(M is an alkali metal)

Hydrolysis of the amidine salt, $RC({=}NH)NHM$, to the corresponding amidine was realized only where R was a phenyl group. Kirssanov and Poliakova[2] observed that sodium amide reacts vigorously with acetonitrile, but were unable to isolate any acetamidine; they are consequently of the opinion that Cornell's preparations are double compounds of the nitrile and the alkali metal amide. Secondary nitriles react with lithium diethylamide to form salts which are readily alkylated.[3] Primary nitriles such as acetonitrile may be alkylated by treating them with an alkyl halide and a fine suspension of sodium amide in benzene or in paraffin oil.[3]

Aliphatic nitriles may also be alkylated by the combined action on them of metallic sodium or sodium amide and an alkyl halide in a solvent.[4] Sodium ethylate or potassium ethylate is a good condensing agent for Claisen type condensations involving aliphatic nitriles; an alkali metal salt of the nitrile is a possible intermediate.[5]

There is accordingly ample evidence for believing that the alkali amides in liquid ammonia will react with nitriles that contain alpha hydrogen atoms to form salts of the type, $RCHNaCN$ or $(RCHCN)^- Na^+$. If this is the case, Cornell's preparations, in so far as the analyses are in agreement with the amidine salt formula, will have the structure, $RCHNaCN{\cdot}NH_3$.

In the present work, acetonitrile was found to react readily with a solution and suspension of sodium amide in liquid ammonia to form a soluble salt, which may be alkylated in accordance with the equation

$$NaCH_2CN + RX = NaX + RCH_2CN \qquad (2)$$

RX is an alkyl halide or alkyl *p*-toluenesulfonate; solvation of the sodium acetonitrile has been disregarded.

Secondary and tertiary nitriles are obtained by reactions which resemble the following

$$RCH_2CN + NaCH_2CN \rightleftarrows RCHNaCN + CH_3CN \qquad (3)$$

$$RCHNaCN + RX = R_2CHCN + NaX$$

The direct introduction of phenyl groups ($R = C_6H_5$) in the manner of equations (2) and (3) may

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[1] E. F. Cornell, THIS JOURNAL, **50**, 3311–3318 (1928).

[2] Kirssanov and Poliakova, *Bull. soc. chim.*, (5) **3**, 1601–1602 (1936).

[3] Ziegler and Ohlinger, *Ann.*, **495**, 84–112 (1932); Ziegler, German Patents 570,594, 581,728, 583,561, *C. A.*, **27**, 4251 (1933); **28**, 1057 (1934); see *Chem. Rev.*, **20**, 451–454 (1937), for references.

[4] Holtzwart, *J. prakt. Chem.*, (2) **39**, 233 (1889); Ramart, *Compt. rend.*, **182**, 1226 (1926).

[5] Wislicenus and Silberstein, *Ber.*, **43**, 1825 ff. (1910); Dorsch and McElvain, THIS JOURNAL, **54**, 2960–2964 (1932); Borsche and Manteuffel, *Ann.*, **512**, 97–111 (1934); *cf.* Bergstrom and Fernelius, *Chem. Rev.*, **20**, 451 ff. (1937).