Selective Oxidation of Organoboranes with Anhydrous Trimethylamine *N*-Oxide

John A. Soderquist* and M. Ramin Najafi[1]

Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

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The oxidation of several representative organoboranes with anhydrous trimethylamine *N*-oxide (TMANO) is described. Acyclic trialkylboranes are oxidized sequentially with stoichiometric quantities of the reagent to give first borinate, then boronate, and finally borate esters. Unsymmetrical trialkylboranes are oxidized with 1 equiv of TMANO to give mixtures of borinate esters with the oxidative reactivity of the alkyl groups following the order: 3° > 2° > 1°. By contrast, the monooxidation of B-substituted derivatives of 9-borabicyclo[3.3.1]nonane give the 9-oxa-10-borabicyclo[3.3.2]decane product, exclusively. The alcoholysis of 9-BBN followed by oxidation with TMANO gives the corresponding *B*-alkoxyoxaborabicyclic boronates in good yield. Unlike the acyclic boron esters, the further oxidation of these bicyclic compounds with TMANO is slow and gives product mixtures. Moreover, no volatile products containing the 1,3,2-dioxaborocane ring system could be isolated from these mixtures. The reaction of *B*-*tert*-butylborinanes with 1 equiv of TMANO also results in the oxidation of the ring B–C bond exclusively. The mechanism of the oxidation process is discussed in terms of an antiperiplanar conformation of the leaving trimethylamine to the specific B–C bond which is undergoing oxidation. This model is consistent with the observed experimental results. Spectroscopic data for the new organoboranes are presented.

Organoboranes are versatile intermediates for organic synthesis.[2-4] In addition to the wide variety of reactions known for trialkylboranes, partially alkylated boranes such as borinate esters (R_2BOR') have also been found to have several synthetic applications, including their conversion to ketones.[5] While there exist a number of methods to prepare such intermediates, their availability from the controlled oxidation of trialkylboranes has not been reported. Unfortunately, the usual alkaline hydrogen peroxide process is not suitable for this purpose owing to the hydrolysis of the intermediate alkoxyboranes.[2-4]

$$R_3B \xrightarrow{[O]} R_2BOR \xrightarrow{H_2O} R_2BOH + ROH \qquad (1)$$

Anhydrous trimethylamine *N*-oxide (TMANO) has been established, largely through the pioneering work of Köster, as a useful reagent for the oxidation of organoboranes,[6-9] but the boron products have neither been isolated nor fully characterized. More recently, Kabalka has demonstrated that the oxidation of organoboranes with the commercially available dihydrate form of the reagent has several advantages over the usual alkaline hydrogen peroxide method in certain cases where the organoboranes contain carbofunctionality.[10] The mild nature of the reagent in either the dihydrate or anhydrous form, has also been demonstrated in the preparation of acylsilanes from organoborane intermediates.[14-17]

In the present study, we describe the selective oxidation of organoboranes with anhydrous TMANO to give isolable borinate and borate esters.

Table I. Oxidation of Representative Unsymmetrical Organoboranes 5 with 1 Equiv of Trimethylamine *N*-Oxide at 0 °C in $CHCl_3$ Solution[a]

entry	borane[b]	alcohol products (relative yield)[c]		
1	$(Hx)_3B$[d]	*n*-HxOH (86)		2-HxOH (14)
2	(t-Hx)B-(*n*-Hx)$_2$	*n*-HxOH (37)		t-HxOH (63)
3	(c-Hx)$_2$B(*n*-Hx)	*n*-HxOH (8)		c-HxOH (92)
4	(c-Hx)(t-Hx)B(*n*-Hx)	*n*-HxOH (2)	c-HxOH (20)	t-HxOH (78)

[a] Reaction mixtures were treated with *n*-decanol and distilled, and the distillate was analyzed on a 10% Carbowax column (6 ft × 1/4 in.). [b] *n*-Hx = *n*-hexyl; t-Hx = $C(CH_3)_2CH(CH_3)_2$ (thexyl); c-Hx = cyclohexyl. [c] The total yield of alcohol products was 100 ± 5% in all cases as determined by the corrected response areas to that of hexadecane. [d] Obtained from the hydroboration of 1-hexene with BH_3·THF.

Results and Discussion

To avoid the difficulties encountered in the handling of the hygroscopic anhydrous solid reagent, we chose to determine the solubility of TMANO in several solvents to find a suitable medium which would facilitate the preparation of standard solutions of the reagent for use in the oxidation process. Despite their being common reaction media for the oxidation of organoboranes with TMANO, the reagent is virtually insoluble in toluene[6] or THF[17] at room temperature. TMANO is soluble in methylene chloride (1.2 M at 25 °C). However, its higher solubility in chloroform (>2 M at 25 °C) led us to prefer this solvent for the present study.

As a representative acyclic organoborane, we chose to

$$\underset{1}{Bu_3B} \xrightarrow{TMANO} \underset{2}{Bu_2BOBu} \xrightarrow{TMANO} \underset{3}{BuB(OBu)_2} \xrightarrow{TMANO} \underset{4}{B(OBu)_3} \qquad (2)$$

(1) Taken in part from the M.Sc. thesis of M.R.N., University of San Francisco (1984). Present address: Chemistry Department, University of California, Davis CA 95616.
(2) (a) Brown, H. C.; Midland, M. M.; Levy, A. B.; Kramer, G. W. "Organic Synthesis via Boranes"; Wiley-Interscience: New York, 1975. (b) Kabalka, G. W. *Aldrichimica Acta* **1975**, *8*, 14.
(3) Pelter, A.; Smith, K. "Comprehensive Organic Chemistry";, Barton, D., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 791.
(4) Brown, H.C "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.
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(6) (a) Köster, R.; Morita, Y. *Justus Liebigs Ann. Chem.* **1967**, *704*, 70. (b) Köster, R.; Arora, S.; Binger, P. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 205.
(7) Davis, A. G.; Roberts, B. P. *J. Chem. Soc. (C)* **1968**, 1474.
(8) Zweifel, G.; Polston, N. L.; Whitney, C. C. *J. Am. Chem. Soc.* **1968**, *90*, 6243. This work reported that thexyl groups were oxidized in preference to vinyl groups with TMANO. additionally, cyclohexyl groups are preferentially oxidized over vinyl groups with TMANO (cf. Zweifel, G., personal communication in Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370).
(9) Pelter, A.; Gould, K. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1029.
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(11) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 1512.
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(14) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1.
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(16) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184.
(17) (a) Miller, J. A.; Zweifel, G. *Synthesis* **1981**, 288. (b) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6217.

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Table II. Oxidation of B-Substituted 9-BBN Derivatives (6) with 1 Equiv of TMANO[a]

B-R-9-BBN	R	yield of 10[b]	reaction temp (time, h)	bp of 10 torr
6a	Me	81	0 (1)	35 (0.6)
6b	*n*-Hx	84	0 (1)	80–82 (0.35)
6c	c-Hx	84	0 (1)	110–111 (0.65)
6d	*t*-Bu	80	25 (20)	58 (1.0)
6e	CH_2SiMe_3	93	0 (1)	72 (0.35)
6f	$C(SiMe_3)$=CHMe (*Z*)	87	0 (1)	92 (0.3)
6g	OMe	85	0 (1)	55 (0.5)
6h	*O*-(*n*-Hx)	86	0 (1)	120–124 (0.8)

[a] Reactions were barried out by the dropwise addition of a solution of TMANO in $CHCl_3$ to the organoborane. [b] Isolated yield of a 25-mmol reaction scale.

investigate the sequential oxidation of tri-*n*-butylborane with TMANO.[18]

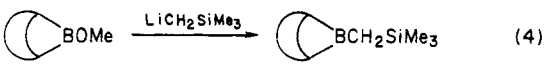
The oxidation of **1** with 1 equiv of TMANO is rapid and exothermic at 0 °C. ^{11}B NMR analysis of the degassed reaction mixture in $CDCl_3$ solvent revealed that **1** (87.1 ppm) is cleanly converted to the borinate **2** (53.6 ppm).[19] Similarly, the conversion of **1** to the boronate **3** (31.4 ppm) is achieved at 25 °C with the addition of 2 equiv of TMANO. However, even with 3 equiv of the reagent, the reaction stops cleanly at the boronate stage to give **3** at room temperature. The final oxidation to **4** (18.2 ppm) is complete only after 24 h at reflux temperature. Corroborative ^{13}C NMR data for the stepwise nature of this oxidation process were also obtained (see Experimental Section). Thus, depending on the stoichiometry and reaction conditions, the oxidation process can be controlled to give the desired boron ester in this system.

To determine the chemoselectivity of TMANO, the partial oxidation at 0 °C of several unsymmetrical organoboranes was carried out with 1 equiv of the reagent. These results, summarized in Table I, are consistent with the generality that bulkier groups are preferentially oxidized in the presence of smaller groups in the case of unsymmetrical organoboranes (i.e., 3° > 2° > 1°).[20]

$$\underset{\mathbf{5}}{R^1R^2R^3B} \xrightarrow[0\,^\circ C]{\text{TMANO}} \xrightarrow{n\text{-}C_{10}H_{21}OH} R^1OH, R^2OH, R^3OH \qquad (3)$$

Entry 1 reveals that most (i.e. ca. two-thirds) of the 2-hexyl groups formed in the hydroboration of 1-hexene with BH_3·THF[2] are oxidized by this process. Thus, most of the undesirable 2-hexyl impurities are no longer contained in the alkylborane portion of the molecule so that the many synthetic conversions which involve the transfer of R groups from boron to other atoms[2-4] would be expected to give products of high isomeric purity. The preference of secondary or tertiary groups to be oxidized in the presence of primary groups is also seen in the subsequent entries in Table I.[21] The last entry illustrates that secondary groups are oxidized more readily than 3° groups by a factor of 4 in this example.

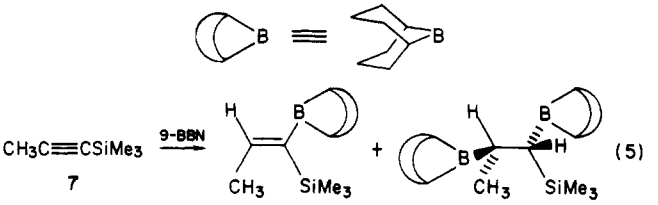
It was also of interest to examine the behavior of cyclic organoboranes toward oxidation. Owing to the ready availability of 9-BBN[22] and its subsequent conversion to B-substituted derivatives (**6**), this system was chosen for this study. In addition to the known compounds, we prepared the new *B*-[(trimethylsilyl)methyl]-9-BBN (**6e**) using the Brown–Kramer alkyllithium procedure.[23]



(4)

6e

Interested in a *B*-(1-silylvinyl)-9-BBN example, we carried out the hydroboration of propynyltrimethylsilane (**7**) with 1 equiv of 9-BBN, which gave the desired silylvinylborane (**6f**) as well as the diadduct, **8**.

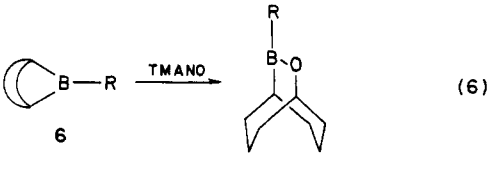


(5)

7 **6f** **8**

Protonolysis of the mixture with acetic acid after the complete consumption of the 9-BBN had occurred gives a GC yield of 53% for *cis*-1-propenyltrimethylsilane (**9**) as well as 16% of unreacted **7**. Therefore, it was clear that hydroboration of **6f** was also taking place. To determine the structure of this diadduct, the hydroboration of **7** was carried out using 2 equiv of 9-BBN. After 96 h at reflux temperature in THF solvent, the hydroboration was complete as ascertained by ^{11}B NMR. The product, **8**, exhibited a single resonance at 85 ppm. The ^1H NMR showed a doublet at 1.30 ppm for the methyl protons in **8** ruling out the possibility of the 1,1-diboryl configuration. ^{13}C NMR data for this compound also supports the *threo*-1,2-diboryl structure illustrated for **8** (see Experimental Section).

The oxidation of *B*-substituted-9-BBN derivatives (**6**) was examined with 1 equiv of TMANO in $CHCl_3$ at 0 °C. Unlike the acyclic compounds (**5**) which gave product mixtures, the monooxidation of **6** gave the oxaborabicyclo[3.3.2]decane product (**10**), exclusively (cf. Tables II and III). The reaction is quantitative in all of the representative cases examined and gives high isolated yields of **10** even on a small preparative scale. Further, the reaction is operationally simple in that a solution of TMANO is added to the organoborane (**6**), the solvents are removed in vacuo, and the product, **10**, is isolated by a short-path distillation.



(6)

6 **10**

Since it had been possible to sequentially oxidize acyclic organoboranes such as tri-*n*-butylborane to borinate, boronate, or borate esters, it was of interest to attempt the further oxidation of the bicyclic borinate esters, **10**, to give boronate esters of the type illustrated below.

(18) Köster[6a] reported that ^{11}B NMR data supproted the selective nature of the oxidation of tri-*n*-propylborane with stoichiometric quantities of TMANO.

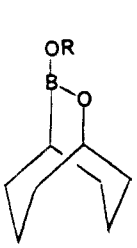
(19) The oxidation of **1** to **2** appears to be complete upon the addition of the TMANO to **1** at 0 °C. However, most of the trimethylamine was routinely removed from the samples prior to NMR analysis to prevent its influence on the chemical shifts of the organoboranes (cf. ref 23) and the analysis were performed approximately 1 h after the reagents were mixed. In the **2** to **3** conversion, reactions times of 3 h were employed.

(20) These results are in qualitative agreement with the results reported by Kabalka[10] for the dihydrate form of TMANO.

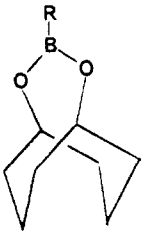
(21) Interestingly, despite the fact that thexylborane, like BH_3–THF, hydroborates 1-hexene to give a significant amount (i.e. 5%) of 2-hexyl adducts, no 2-hexanol was detected by GC analysis of the monooxidation/transesterification process for dihexylthexylborane. An attempt to increase the chemoselectivity of the oxidation reaction in this case by lowering the reaction temperature to −42 °C resulted in a slight improvement to a 25:75 mixture of 1-hexanol vs. 2,3-dimethyl-2-butanol. Further attempts to increase the selectivity by carrying out the oxidation at still lower temperatures were unsuccessful owing to problems with both the reagent's solubility and the solvent's freezing point.

(22) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1981**, *46*, 4599.

(23) Brown, H. C.; Kramer, G. W. *J. Organomet. Chem.* **1974**, *73*, 1.



A



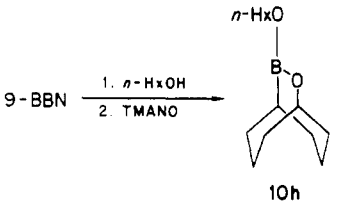
B

That these bicyclic borinate esters (**10**) were very unreactive toward further oxidation was apparent from the fact that, whereas the *B*-methyl compound **10a**, when exposed to the air for short periods of time (5–10 min) remains unoxidized, the isomeric *B*-methoxy-9-BBN (**6g**) reacts vigorously with air immediately. As is seen in Table II, **6g** also reacts rapidly with TMANO at 0 °C to give **10g**, a boronate ester which corresponds to one of the two possible isomeric structures illustrated above (i.e., A; R = Me). However, in contrast to the rapid oxidation of **6g** with TMANO, the oxidation of **10a** with this reagent was incomplete even after 5 days at reflux temperature in chloroform solution, as evidenced by the results of both GC and ^{11}B NMR analyses of the reaction mixture. While a broad signal at 30.3 ppm in the ^{11}B NMR spectrum of this mixture indicated that the oxidation of **10a** was occurring, no evidence for the formation of **10g** could be found. Clearly, **10a** is far less reactive toward TMANO oxidation than the isomeric **6g**. To rule out the possibility that the trimethylamine when formed in the oxidation process would complex **10a** so as to prevent its complete oxidation, these two borinate esters were treated with ca. 1 equiv of this base in $CDCl_3$ solvent. The dynamic nature of the equilibrium complexation of *B*-methoxy-9-BBN (**6g**) with pyridine base has been examined by both ^{11}B and ^{13}C NMR.[24] For the trimethylamine case, ^{11}B NMR analysis of the above mixtures indicates that this equilibrium process is occurring for both **6g** and **10a** to essentially the same extent. The chemical shift of **6g** is moved from 53.2 ppm in $CDCl_3$ to 27.7 ppm with an equimolar quantity of trimethylamine, while for **10a** the signal is shifted from 54.7 ppm to 25.3 ppm under identical conditions. Therefore, this similar complexation behavior of both **6g** and **10a**, with trimethylamine indicates that such processes are not retarding the oxidation of **10a** with TMANO.

The behavior of other bicyclic borinate esters (**10**) toward further oxidation with TMANO was also examined. The *tert*-butyl deriative, **10d**, underwent essentially no reaction with TMANO in refluxing chloroform solution even after 5 days. Less hindered derivatives such as **10b** (R = *n*-Hx) do undergo partial oxidation with TMANO. After 48 h at reflux temperature, the ^{11}B NMR spectrum of the reaciton mixture reveals new absorbances at 29.6 and 16.1 ppm indicating that both boronate and borate esters are formed in this oxidation process. Consistent with the formation of a borate ester ($B(OR)_3$), which requires the consumption of 2 mol of the oxidant, unreacted **10b** is also observed in the reaction mixture. Heating the mixture for an additional 50 h did not significantly change the ^{11}B NMR spectrum of the mixture. The increasing formation of an insoluble, gummy product was also observed during this oxidation. Distillative isolation of the volatiles gave a mixture of **10b** and boronate products, but no volatile borate products. The borate residue, therefore, probably has a polymeric, rather than bicyclic structure.[25]

(24) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846.

The presence of **10b** in the distillate was confirmed by ^{13}C NMR. Clearly, **10h** is a possible structure for one of the boronate oxidation products from **10b**. To determine if it is formed in this reaction, this compound was independently prepared in high yield from the hexanolysis of 9-BBN followed by TMANO oxidation.

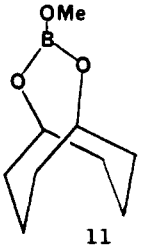


(7)

10h

Reexamination of the ^{13}C NMR spectrum of the volatile material obtained in the oxidation of **10b** revealed the presence of **10h** in the mixture as one of the components of the boronate products that were produced in this process. However, at least one other boronate species was suggested by an absorbance at 63.2 ppm. Thus, since this oxidative approach to **10h** from **10b** exhibited little synthetic promise, it was abandoned in favor of the superior alcoholysis/oxidation method described above for the preparation of this boronate ester.

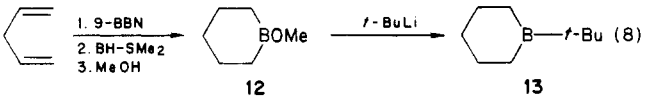
It was also of interest to determine whether or not this stepwise oxidation process could be extended to prepare bicyclic borate esters (**11**). To this end, the further oxi-



11

dation of **10g** was attempted using Köster's conditions.[6] However, no 2,4-dioxa-3-borabicyclo[3.3.3]undecane product such as **11** could be observed and only an insoluble, gummy product was formed. After the theoretical quantity of trimethylamine had been evolved, the alkaline hydrolysis of this solid produced *cis*-1,5-cycloöctanediol cleanly, confirming that the oxidation of the remaining ring B-C bond had occurred under these conditions. Evidently, the instability of the 1,3,2-dioxaborocane ring system toward ring-opening polymerization[25] accounts for the lack of formation of products such as **11** which also contain this heterocyclic component.

From the results discussed above it was apparent that the oxidation of the bicyclic 9-BBN ring system was quite different from the oxidation of acyclic derivatives, both in the selectivity and in the extent of reaction with TMANO. To examine further the oxidation process, the borinane system (**13**) was prepared as an example of a monocyclic organoborane.



(8)

12 13

(25) A variety of heterocyclic systems which contain atoms that react with nucleophiles undergo a ring-opening polymerization, particularly under anhydrous conditions (cf. Allcock, H. R.; Lampe, F. W. "Contemporary Polymer Chemistry"; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1981; Chapters 6 and 7). For example, the eight-membered ring tetramer of dimethylsiloxane readily polymerizes with heat under basic conditions. Moreover, attempts to prepare the 1,3,2-dioxaborocane system by a condensation route gave oligimeric rather than cyclic products (cf. Gerwarth, U. W. *Z. Naturforsch. B* **1977**, *32B*, 1408).

Table III. Spectroscopic Data for 10[a]

compd	^{11}B	^{13}C(ring)[b] C-1	C-2,8	C-3,7	C-4,6	^{13}C(R)[b]
10a	54.7	73.6	32.2	22.7	26.1	
10b	58.4	73.6	32.3	22.7	26.4	24.3; 32.9; 32.3; 23.0; 14.5
10c	51.0	72.8	32.0	22.6	26.5	28.0; 28.0; 27.6
10d	57.3	73.3	32.2	22.6	26.9	26.9
10e	57.5	73.4	32.3	22.6	26.2	1.3
10f	48.3	72.8	32.1	22.6	26.8	1.9; 20.8; 152
10g	30.0	71.3	32.6	22.4	26.8	50.3
10h	29.4	71.2	32.7	22.5	27.0	62.9; 32.1; 26.0; 32.1; 23.1; 14.5

[a] Recorded in $CDCl_3$ solution except for **10c** (C_6D_6) [Me_4Si (δ = 0.00 ppm), $BF_3{\cdot}OEt_2$ (δ = 0.0 ppm)]. [b] See Table II for the identification of the R groups on the boron atom. R group signals are presented in order from the boron atom. The ring is numbered as given below.

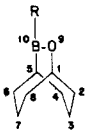
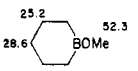
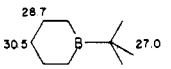
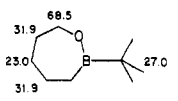
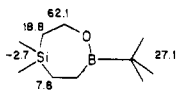
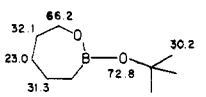
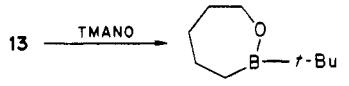


Table IV. NMR Data for Monocyclic Boranes[a]

compd	^{11}B	^{13}C
16	52.2	
17	85.5	
18	51.4	
20	50.8	
21	29.7	

[a] Recorded in $CDCl_3$ solution (cf. Table III).

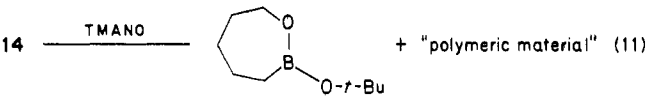
Borinane[26] was methanolyzed to give **12**, which was converted to the corresponding *B-tert*-butyl derivative (**13**) by the Brown–Kramer method.[23] Whereas *B-t*-Bu-9-BBN (**6d**) undergoes a slow oxidation with TMANO (20 h at 25 °C), the related monocyclic compound, **13**, reacts with TMANO instantaneously at 0 °C to give the ring boron–carbon bond oxidized product (**14**) (cf. Table IV). Thus, while the rates of oxidation of **6d** and **13** are quite different, the oxidation process is similar. Similarly, the related silaborinane (**15**)[27] undergoes oxidation to give the novel oxasilaborepane ring system (**16**).



(9)

(10)

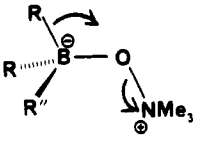
Further, whereas the bicyclic borinate esters (**10**) were very unreactive toward further oxidation, **14** reacts rapidly with TMANO at 0 °C to give a low yield of the corresponding boronate ester (**17**), together with a nonvolatile material.



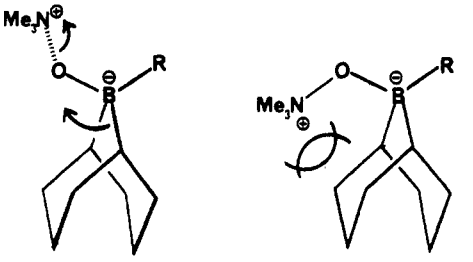
(11)

17

To aid in the understanding of the oxidation process of organoboranes with TMANO, the following model, consistent with the observed experimental results, is proposed. *The trimethylamine prefers to leave antiperiplanar to the migrating group in the oxidation process.*[30]



This model explains the preference for bulkier groups to be oxidized in the unsymmetrical acyclic organoboranes. Further, for **6**, the trimethylamine can leave easily from the side of the bicyclic system to result in the oxidation of a ring boron–carbon bond (case 1). However, oxidation of the alkyl group would result in the ring interfering with the leaving trimethylamine (case 2), and thus *this process does not occur.*



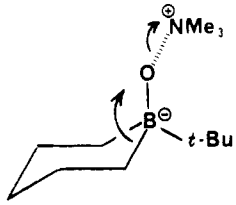
Case 1 **Case 2**

It is interesting to note the conformational effects possible in the oxidation of these bicyclic systems (**6**). When "ate" complexes of the type illustrated above form, both the R group and the TMANO must occupy *both* an axial and equatorial position since both cyclohexyl rings contain

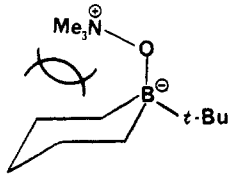
(26) (a) Brown, H. C.; Pai, G. G. *Heterocycles* **1982**, *17*, 77. (b) Brown, H. C.; Pai, G. G. *J. Organomet. Chem.* **1983**, *250*, 13.
(27) Soderquist, J. A.; Shiau, F-Y.; Lemesh, R. A. *J. Org. Chem.* **1984**, *49*, 2565.
(28) Hart, D. J.; Ford, W. T. *J. Org. Chem.* **1974**, *39*, 363.
(29) Sadtler Standard Carbon-13 NMR Spectra: S 6800.
(30) For another example of borate migrations involving conformational effects, see Slayden, S. W. *J. Org. Chem.* **1982**, *47*, 2753.
(31) The magnetic nonequivalence of the 2,6 and 4,8 positions in the ^{13}C NMR spectrum of 9-BBN derivatives which contain an R group which has a chiral center has been reported.[24] However, either this phenomenon or the nonequivalence of the boryl groups for the case of the diboryl compound, **8**, could account for the observed fact that the peak heights for the 23.4, 33.9 and 34.4 ppm absorbances are similar.

the boron atom. The energetically disfavored axial position for bulky groups such as *tert*-butyl (**6d**) is consistent with the slow oxidation of this derivative with TMANO.

For simple borinanes such as **13** or **15**, this situation is different in the sense that the R group in the related TMANO "ate" complexes can be *either* axial or equatorial. Clearly, the *tert*-butyl group would prefer to occupy the equatorial position and, thus, never need be forced into a highly disfavored axial position. This results in a much faster oxidation process for the *B*-*tert*-butylborinane than for its bicyclic counterpart, **6d**. However, like the oxidation of the 9-BBN derivatives (**6**), the trimethylamine still must avoid the interference with the ring and, consequently, leaves antiperiplanar to the ring B–C bond to give the observed oxidation products. The oxidation is, thus, a specific process which has a conformational dependence.



Case 1



Case 2

Conclusions

The oxidation of trialkylboranes with TMANO proceeds cleanly to give isolable borinate esters for the acyclic, cyclic, and bicyclic organoboranes examined. Acyclic compounds give product mixtures for unsymmetrical organoboranes with the general oxidative selectivity: 3° > 2° > 1°. *B*-Alkyl-9-BBN and *B*-*tert*-butylborinane derivatives undergo exclusive ring B–C bond oxidation. The selectivities observed in these oxidations are explained in terms of a required antiperiplanar relationship of the B–C bond which undergoes oxidation to the leaving trimethylamine. While acylcic organoboranes can be oxidized to give boronate products with 2 equiv of TMANO, the conversion of either mono- or bicyclic derivatives with 2 equiv of TMANO does not give high yields of volatile boronate products. In no case were volatile products observed which contain a 1,3,2-dioxaborocane component. If formed in the oxidaiton process, such products would be expected to undergo polymerization under the reaction conditions.[25] However, boronate esters which contain the 9-oxa-10-borabicyclic[3.3.2]decane ring system can be prepared from the single oxidation of *B*-alkoxy-9-BBN derivatives with TMANO. Thus, our data indicates that the further oxidation of systems which contain an oxaborepane ring system give mixtures of boronate products, and, in the case of **10**, even borate products with 1 equiv of TMANO.[32] Those boronate products which contain the *B*-alkoxy-oxaborepane ring system are isolable while those which result from the further oxidation of the ring to give, in principle, the 1,3,2-dioxaborocane system, in reality, produce polymeric products.

Experimental Section

General Methods. All experiments were carried out in predried (4 h at 110 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[2] THF was distilled from sodium/benzophenone prior to use. Chloroform was purified by filtration through alumina. Alkanes were purified using reported methods.[2] Other reagents were either prepared as reported[2-4] or obtained from commercial sources. NMR data were recorded using either a Varian XL-100 or FT-80A NMR spectrometer. Broadened signals for the carbon atoms directly bonded to boron atoms were observed in the ^{13}C NMR spectra of the organoboranes.[15] MS data was obtained using AEI-MS-12 and Krato-MS-50 mass spectrometers. Analyses of organoboranes were performed using a Perkin-Elmer model Sigma 1B gas chromatographic system equipped with either a 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS-treated Chrom W or a 30m × 0.23 mm i.d. 20% SE-30 vitreous silica open tubular column. Columns were silylated (MSTFA, Pierce) prior to analytical runs for organoboranes and used with a low injection port temperature (120 °C). Alcohols were analyzed using a 6 ft × $^1/_8$ in. 10% Carbowax column. IR data were obtained by using a Perkin-Elmer Model 337 spectrophotometer.

Preparation of Standard Solutions of Anhydrous TMANO. Trimethylamine *N*-oxide dihydrate was converted to the anhydrous form by a modification of the azeotropic removal of water with toluene used by Köster.[6a] In a well-ventilated hood, a flash evaporator was charged with the dihydrate and alumina-dried toluene. With vigorous rotation of the clamp-secured flask, the water was azeotropically removed at atmospheric pressure. After the completion of the removal of water, the remaining toluene was removed under high vacuum. The dry TMANO was sublimed at ca. 1 torr (oil bath temperature 80 °C). The solid material was transferred to a volumetric flask under a nitrogen atmosphere and a 1.5 M solution of TMANO in $CHCl_3$ was prepared. The molarity was checked by the GC analysis of its reaction with a known amount of **6a**.

Oxidation of 1 with TMANO. A standard solution of anhydrous TMANO in $CDCl_3$ was added to 1 at the temperature given in the text. At the cited times, no further oxidation was observed by ^{11}B NMR. For **1**, ^{13}C NMR analysis reveals signals at 26.8, 26.0, and 13.9 ppm for C-2, C-3, and C-4, respectively, in good agreement with reported values.[28] For **2**, these butyl signals are shifted to 25.7, 26.3, and 13.7 with the appearance of butoxy signals at 64.6, 33.9, 18.9, and 13.7 ppm for C-1, C-2, C-3, and C-4, respectively. The last signal is coincident with the methyl carbon of the butyl chain and its height reflects this feature. The remaining butyl group in **3** exhibits signals at 25.4, 26.3, and 13.6 ppm with the butoxy groups absorbing at 62.7, 33.8, 18.8, and 13.6 ppm. Four signals are observed for **4** at 62.6, 33.8, 18.9, and 13.6 ppm in reasonable agreement with literature values.[29] However, it must be pointed out that small amounts of trimethylamine (47.2 ppm) and TMANO (60.4 ppm) were present in all of these solutions and such compounds can effect the chemical shifts of organoboranes (cf. ref 24).

Oxidation of Unsymmetrical Organoboranes (5). After the organoboranes (**5**) has been prepared in THF solution as described,[2] 1 equiv of TMANO solution was added to the stirred mixture at 0 °C. After 2 h, *n*-decanol (5 equiv) was added and the mixture was distilled at 760 torr under a nitrogen atmosphere into a receiver flask containing a known quantity of a hydrocarbon standard until a distillation temperature of ca. 230 °C was reached. The results are given in Table I.

***B*-[(Trimethylsilyl)methyl]-9-BBN (6e).** To a solution of **6g** (9.12 g, 60.2 mmol) in pentane (40 mL) at −78 °C, was added a solution of $LiCH_2SiMe_3$ in hexanes (83 mL 0.73 M, 60.6 mmol) under a nitrogen atmosphere. The stirred mixture was allowed to warm to room temperature and, after the LiOMe had settled, the clear supernatant was transferred to a second flask by use of a double-ended needle, and the solid was washed with pentane (2 × 20 mL) and similarly transferred. After removal of the solvents in vacuo, the residue was distilled at 0.45 torr to give 7.76g (62%) of **6e** (bp 68–70 °C): ^1H NMR ($CDCl_3$) 0.07 (s, 9 H), 1.14 (s, 2 H), 1.5–1.8 (m, 14 H) ppm; ^{11}B NMR ($CDCl_3$) 85.9 ppm; ^{13}C NMR ($CDCl_3$) 1.7, 23.7, 33.4 ppm; MS, *m/z* 208(68%), 125(100%).

***(Z)*-1-(Trimethylsilyl)-1-propenyl-9-BBN (6f).** To 9-BBN (21.78 g, 178.6 mmol) in THF (350 mL) was added **7** (20.0 g, 180 mmol) dropwise. The reaction mixture was allowed to stir for 48 h at room temperature. The solvent was removed using high vacuum, and the product was distilled at 0.6 torr to to give 23

(32) In reactions which appear to have mechanistic similarities to this oxidation process, such as the ring expansions of ketones with diazomethane, the selectivity as well as the rate of reaction is greater for cyclohexanone than for cycloheptanone (cf.: Gutsche, C. D. *Org. React.* **1954**, *8*, 364).

g, 55% of **6f** (bp 82 °C): ^{1}H NMR ($CDCl_3$) 0.21 (s, 9 H), 1.7–1.9 (m, 13 H), 1.99 (d, 3 H, J = 6.8 Hz), 6.9 (q, 1 H, J = 6.8 Hz) ppm; ^{11}B NMR(C_6D_6) 79.3 ppm; ^{13}C NMR (C_6D_6) 1.6, 21.2, 23.5, 34.2, 150.5 ppm; IR ($CHCl_3$) 3000 (m), 2900 (bs), 2840 (s), 2400 (m), 1575 (w), 1470 (m), 1250 (m), 1205 (s), 850 (w), 835 (w), 750 (bs), 665 (m); MS, m/z 234 (20%), 151 (14%), 99 (33%), 97 (39%), 73 (100%), 67 (19%), 59 (41%), 45 (19%), 43 (18%), 41 (24%). To a slurry of 9-BBN (1.13 g, 9.26 mmol) in THF (10 mL) was added **7** (1.04 g, 9.26 mmol) dropwise. The reaction mixture was stirred at room temperature for 72 h. To this was added absolute ethanol (3.5 mL), followed by the addition of acetic acid (0.85 g, 14.5 mmol) at 0 °C. Nonane (0.64 g, 5 mmol) was added and the mixture was analyzed by GC. No change could be detected in the product distribution with time indicating that the protonolysis of the vinylborane was complete upon the addition of the acetic acid.

Dihydroboration of 7. To a 9-BBN (6.60 g, 54.1 mmol) slurry in THF (100 mL) was added **7** (3.03 g, 27.1 mmol), and this mixture was heated at reflux temperature. At various intervals samples were removed, concentrated, and analyzed. For **8** after 96 h at reflux temperatures: ^{11}B NMR ($CDCl_3$) 85 ppm; ^{13}C NMR ($CDCl_3$) 2.8, 18.3, 23.6, 33.9, 34.4 ppm;[31] minor peaks at 2.3, 30.4, 31.5, and 36.3 ppm were also detected; ^{1}H NMR ($CDCl_3$) 0.11 (s, 9 H); 1.30 (d, 3 H, J = 7.0 Hz); 1.4–2.2 (m, 30 H) ppm.

10-Methyl-9-oxa-10-borabicyclo[3.3.2]decane (10a). To **6a** (7.88 g, 58 mmol) at 0 °C was added TMANO solution (64.4 mL, 0.9 M; 58 mmol). After 30 min, the solvent was removed under vacuum, and the residual oil was distilled at 0.6 torr to give 7.09 g, 81% of **10a** (bp 35 °C): ^{1}H NMR (C_6D_6) 0.55 (s, 3 H); 1.2–1.6 (m, 13 H), 4.47 (bs, 1 H) ppm; MS, m/z 152 (7%), 68 (100%).

The remaining compounds given in Table II were obtained following a similar procedure to that described for **10a** above. 10b: ^{1}H NMR ($CDCl_3$) 0.83–1.68 (m, 26 H), 4.48 (bs, 1 H) ppm; MS, m/z 222(0.4%), 67(100%). 10c: ^{1}H NMR ($CDCl_3$) 0.98–1.70 (m, 24 H), 4.5 (bs, 1 H) ppm; MS, m/z 220(30%), 67(100%). 10d: ^{1}H NMR ($CDCl_3$) 0.34 (s, 9 H), 1.45–1.71 (m, 13 H), 4.5 (bs 1 H) ppm; MS, m/z 194 (6%), 67 (100%). 10e: ^{1}H NMR ($CDCl_3$) 0.01 (s, 9 H), 0.28 (s, 2 H), 1.52–1.64 (m, 13 H), 4.46 (s, 1 H) ppm; MS, m/z 224 (0%), 209 (32%), 67 (100%). 10f: ^{1}H NMR ($CDCl_3$) 0.15 (s, 9 H), 1.49–1.75 (m, 13 H), 1.88 (d, 3 H, J = 6.7 Hz), 4.56 (s, 1 H), 6.84 (q, 1 H, J = 6.7 Hz) ppm; MS, m/z 250 (1%), 67 (100%). **10g**: ^{1}H NMR ($CDCl_3$) 1.32–1.61 (m, 13 H), 3.36 (s, 3 H), 4.26 (bs, 1 ppm H); MS, m/z 168 (1%), 67 (100%).

10-(Hexyloxy)-9-oxa-10-borabicyclo[3.3.2]decane (10h). In a 100-mL 2-necked flask equipped with a condenser was placed 9-BBN (5.40 g, 44.3 mmol). To this was added chloroform (13 mL), followed by the slow addition of 1-hexanol (4.51 g, 44.3 mmol). After the completion of H_2 evolution, the mixture was heated at reflux temperature for 30 min. After reaching room temperature, TMANO in $CHCl_3$ (29.50 mL, 1.5 M) was added dropwise. After 15 min, the solvent was removed *in vacuo*, and the product was distilled at 0.8 torr to give 9.12 g of **10h** 86% (bp 120–124 °C): ^{1}H NMR($CDCl_3$) 0.78–1.68 (m, 24 H), 3.70 (ct, 2 H), 4.4 (bs, 1 H) ppm; MS, m/z 238 (10%), 82 (100%).

Attempted Oxidation of 10b. To **10b** (3.0 g, 13.5 mmol) was added TMANO at room temperature (9.0 mL, 1.5 M), and the mixture was heated at reflux temperature for 48 h. Analysis of the reaction mixture by GC showed no change in the relative amounts of **10b** and **10h** with longer reaction times. The solvent was removed in vacuo and the mixture was distilled at 0.3 torr to give 1.37 g (bp 93–97 °C). ^{11}B NMR analysis revealed two absorptions at 57.8 and 34.9 ppm in proportions of ca. 55:45 for mono- and dioxidized species. The ^{13}C NMR spectrum of this mixture showed the presence of **10b** and **10h** and an unidentified component. Under these reaction conditions, **10a** was partially oxidized, while **10d** was unaffected as is described in the text.

Attempted Preparation of 11. To **10g** (1.24 g, 7.4 mmol) in toluene (30 mL) was added solid TMANO (0.55 g, 7.4 mmol). The mixture was heated at reflux temperature under a slow stream of N_2. The evolved trimethylamine was titrated to a methyl orange endpoint with 1.0 M HCl which revealed that the oxidation was essentially complete after 1 h. During this time, a solid material formed, but no volatile products could be observed by GC. Owing to its insolubility, a reproducible analysis of this material by ^{11}B NMR could not be achieved. Heating a second reaction mixture with 3.0 N NaOH (4 equiv) for 15 min resulted in the dissolution of the material with the formation of *cis*-1,5-cyclooctanediol as determined by GC comparison of the silylated mixture with authentic material.[27]

***B*-Methoxyborinane (12).** To 9-BBN (35.9 g, 294 mmol) in hexane (300 mL) in a flask surmounted by a dry-ice condenser, was added 1,4-pentadiene (10 g, 147 mmol). After 1 h, the mixture was refluxed for 2 h. After cooling to room temperature, BMS (14.7 mL, 147 mmol) was added. Upon completion of the addition, the mixture was refluxed for an additional 2 h and subsequently, methanol (ca. 20 mL) was added dropwise. The solvents were distilled using a NF-50 spinning band column, and the product was collected at 46 °C (26 torr) to give 15.3 g of **12**, 93%: ^{1}H NMR ($CDCl_3$) 0.86 (m, 4 H), 1.51 (M, 6 H), 3.64 (s, 3 H) ppm; MS, m/z 112 (34%), 84 (20%), 70 (29%), 69 (96%), 68 (29%), 57 (28%), 56 (100%), 55 (45%), 44 (42%), 43 (52%), 42 (26%), 41 (23%), 40 (52%); HRMS, calcd for $C_6H_{13}BO$, 112.1059; found, 112.1054.

***B*-*tert*-Butylborinane (13).** To **12** (9.82 g, 87.9 mmol) in hexanes (160 mL) at −78 °C was added *tert*-butyllithium solution (48.9 mL, 1.8 M). After being stirred for 15 min at −78 °C, the mixture was allowed to warm to room temperature. Lithium methoxide precipitated, and after standing for 12 h, the supernatant liquid was decanted using a double-ended needle, and the solid was washed twice with hexanes (30 mL). Distillation at atmospheric pressure under N_2 removed the solvents, and **13** was isolated by distillation at 13 mm to give 4.8 g, 40% (bp 53 °C): ^{1}H NMR ($CDCl_3$) 0.88 (s, 9 H), 1.24 (m, 4 H), 1.54 (m, 6 H) ppm; MS, m/z 138 (12%), 81 (43%), 69 (34%), 68 (18%), 59 (100%), 87 (31%), 56 (65%), 55 (22%), 53 (31%), 43 (42%), 42 (18%), 41 (73%); HRMS, calcd for $C_6H_{19}B$, 138.1578; found, 138.1583.

2-*tert*-Butyl-1-oxa-2-borepane (14). To **13** (0.85 g, 6.16 mmol) at 0 °C was added TMANO solution 3.69 mL, 1.5 M). The GC analysis of the the reaction mixture indicated that **13** was absent and that **14** was formed immediately after the completion of the addition of TMANO. The solvent was removed under aspirator pressure, and the product was distilled at 17 torr to give 0.6 g of **14**, 64% (bp 66 °C): ^{1}H NMR ($CDCl_3$) 1.07 (s, 9 H), 1.46 (bs, 8 H), 3.86 (m, 2 H) ppm; MS, m/z 154 (14%), 97 (93%), 96 (39%), 69 (100%), 68 (45%), 59 (21%), 57 (39%), 56 (19%); HRMS, calcd for $C_9H_{19}BO$, 154.1529; found, 154.1533.

2-*tert*-Butyl-4,4-dimethyl-1-oxa-4-sila-2-borepane (16). To **15** (1.68 g, 9.23 mmol) was added TMANO solution (5.53 mL, 1.67 M) at 0 °C. As for **14**, distillation at 14 torr gives 1.28 g of **16**, 70% (bp 88 °C): ^{1}H NMR ($CDCl_3$) 0.02 (s, 6 H), 0.69 (m, 6 H), 1.1 (m, 2 H), 1.14 (s, 9 H), 4.08 (complex t, 2 H) ppm; MS, m/z 198 (0.6%), 114 (19%), 113 (100%), 112 (36%), 100 (15%), 86 (19%), 85 (18%); HRMS, calcd for $C_{10}H_{23}BOSi$, 198.1619; found, 198.1615.

2-*tert*-Butoxy-1-oxa-2-borepane (17). To **14** (1.7 g, 11.04 mmol) was added TMANO solution (7.4 mL, 1.5 M) at 0 °C. At selected intermediate times during the addition, the reaction mixture was analyzed by GC which indicated that **14** was consumed immediately as the TMANO was added with the formation of a second peak at a slightly longer (rrt = 1.01) retention time. The solvent was removed in vacuo, and the product was distilled at 15 torr to give 0.09 g of **17**, 5% (bp 67 °C): ^{1}H NMR ($CDCl_3$) 0.8 (m, 2 H), 1.31 (s, 9 H), 1.62 (m, 4 H), 3.89 (m, 2 H) ppm; MS, m/z 155 (72%), 154 (18%), 84 (23%), 71 (26%), 70 (15%), 69 (21%), 68 (23%), 59 (100%), 57 (40%), 56 (37%), 42 (22%), 41 (21%). The ^{11}B and ^{13}C NMR data agreed well with that obtained for a sample of **17** prepared from the treatment of borinane with *tert*-butyl alcohol followed by oxidation with 1 equiv of TMANO as described for the preparation of **10h**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to a William and Flora Hewlett Grant of Research Corporation for their sponsorship of this work. We thank Fuu-Yau Shiau for providing us a sample of **15**. Further, we would like to express our thanks to the staff of the NMR laboratory at UCSF and the MS laboratory at UC Berkeley and to Professors H. C. Brown, O. Cox, and G. L. Larson for their assistance with this study.

Registry No. **1**, 122-56-5; **2**, 3027-56-3; **3**, 3027-58-5; **4**, 688-74-4; **5** (R^1 = R^2 = R^3 = Hx), 1188-92-7; **5** (R^1 = *t*-Hx, R^2 = R^3 = Hx), 30038-49-4; **5** (R^1 = R^2 = c-Hx, R^3 = Hx), 52251-52-2; **5** (R^1 = c-Hx,

R^2 = *t*-Hx, R^3 = Hx), 42437-34-3; **6a**, 23418-81-7; **6b**, 42371-64-2; **6c**, 53535-83-4; **6d**, 42928-43-8; **6e**, 100019-68-9; **6f**, 99966-24-2; **6g**, 38050-71-4; **6h**, 99966-25-3; **7**, 6224-91-5; **8**, 100019-67-8; **10a**, 99966-26-4; **10b**, 99966-27-5; **10c**, 99966-28-6; **10d**, 99966-29-7; **10e**, 99966-30-0; **10f**, 99966-31-1; **10g**, 99966-32-2; **10h**, 99966-33-3; **12**, 38050-70-3; **13**, 99966-34-4; **14**, 99966-35-5; **15**, 18162-76-0; **16**, 99966-36-6; **17**, 99966-37-7; TMANO, 1184-78-7; 9-BBN, 280-64-8; BMS, 13292-87-0; *n*-HxOH, 111-27-3; 2-HxOH, 626-93-7; *t*-HxOH, 594-60-5; *c*-HxOH, 108-93-0; $LiCH_2SiMe_3$, 1822-00-0; 1,4-pentadiene, 591-93-5.

Supplementary Material Available: Infrared and mass spectral data for the oxaborabicyclo[3.3.2]decanes (**10**) (1 page). Ordering information is given on any current masthead page.

Empirical Correlations in Ultraviolet Spectra of Substituted Benzenes. 1. Compounds with Electron-Withdrawing "Parent Groups"

Edward J. Cowles[1]

Department of Chemistry, University of Minnesota—Duluth, Duluth, Minnesota 55812

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The empirical method of Scott[2c] for estimating the position of the "primary band" in the ultraviolet absorption spectrum of substituted benzenes has been expanded to achieve satisfactory agreement between calculated and experimental λ_{max}'s (and ν_{max}'s) for 536 different compounds. These involve eight electron-withdrawing "parent groups" and twelve electron-releasing secondary substituents, plus six of the electron-withdrawing groups serving as secondary substituents. The procedures were able to accommodate compounds with strongly electron-releasing substituents para to strongly electron-withdrawing groups.

An empirical method[2a,b] of predicting the UV λ_{max} of polyenes and α,β-unsaturated carbonyl compounds has been valuable in confirming the structures of such organic molecules. Scott[2c] has extended the method to predict the λ_{max} of the "primary band" in the spectra of substituted benzenes (the 203-nm band of benzene itself). His work was limited to compounds having "parent groups" of the type C(O)Z and electron-releasing secondary substituents. The predicted λ_{max} of a given compound is given by eq 1,

$$\lambda_{max} = (\lambda_{max})_{parent} + \sum \Delta_i \quad (1)$$

where $(\lambda_{max})_{parent}$ is an empirically assigned value for $C_6H_5C(O)Z$ and the Δ_i are empirically determined increments for electron-releasing secondary substituents positioned ortho, meta, or para to the parent group.

The present study was a (successful) attempt (a) to broaden the range of Scott's method with respect to both (electron-withdrawing) parent groups and secondary substituents and (b) to obtain the required parent λ_{max}'s or base values, as well as the substituent increments, by a systematic linear-regression procedure applied to the whole set of data.

Methods

Data. The study was based almost entirely on data taken from the literature, chiefly the "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds"[3] and "Organic Electronic Spectral Data".[4]

Spectra obtained in this laboratory were run on a Bausch and Lomb Spectronic 2000 Spectrophotometer.

The "standard" solvent selected was MeOH or EtOH, but some data for solutions in water or hydrocarbon solvents were used, and solvent corrections were calculated for these solvents, the solvent parameters being handled in the statistical treatment in the same way as substituent increments.

Many of the λ_{max}'s used were averages of two or more measurements (rounded to the nearest even number where there was a choice).

At least two examples of each type of substitution (e.g., substituent Y meta to specific parent group Q) were used.

Mathematical Procedures. Computations were done with the CDC Cyber 171 computer at the University of Minnesota—Duluth.

FORTRAN programs were used to prepare the data (including modified Wiswesser line-notation formulas) for presentation to the multiple-regression-analysis program of the "Statistical Package for the Social Sciences" (SPSS).[5] With the base values and substituent increments thus obtained, FORTRAN programs were used again for obtaining calculated values of λ_{max}'s and comparing these with the measured values.

The same calculations were performed for wavelengths converted into frequencies (10^3 cm^{-1}).

Results and Discussion

This study has been entirely empirical and is based on no assumptions concerning the nature of the electron

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