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INVESTIGATIONS OF THE MECHANISMS OF INTERACTION OF ACYLOXYALKOXYBORANES WITH AMINES

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Abstract—The reasons for the low conversions of acyloxydialkoxyboranes (I) to amides have been investigated systematically. Reaction of the liberated alcohol at the boron atom of I has been demonstrated. Triacyloxyboranes, formed by interaction of diborane and carboxylic acid (1:6) have been shown to rearrange to oxybisdiacyloxyboranes and carboxylic anhydrides in mild neutral conditions. Aminodialkoxyboranes rapidly undergo a hitherto unknown reaction with carboxylic acids to yield highly sensitive borate salts, which may only slowly be converted to amides. This reaction is not observed in the amide forming reaction and is probably not the reason for the low conversions. Carboxylate salts react with chloroborolanes to yield examples of a further series of mixed borate salts.

ALTHOUGH room temperature reactions of amines with *in situ* preparations of acyloxyldialkoxyboranes, $(R'O)_2BO.COR$ (I), gave good yields of amides the conversions were invariably low (of the order of 30–50%), with concomitant recovery of acid.[1] The reaction is attractive in that, with peptides racemization is low, utilization of amine is high and the reaction conditions are mild and neutral. It was therefore necessary to try to define the reasons for the low conversions as a guide to their improvement.

One attempt to produce compounds of type I is described by Eq. (1a). As standard

$$\text{(1)}\quad RCOOH + HB(OR')_2 \xrightarrow{a} \underset{(I)}{RCO_2B(OR')_2} + H_2 \xrightarrow{R''NH_2} R'OH + [OBOR'] + RCONHR''$$

reagents di-isopropoxyborane ($R' = Me_2CH$—), caproic acid and n-butyl amine were used. There was little variation in yield of amide with solvent: (solvent, % amide, % acid recovered) (i) n-hexane 44, 51; (ii) methylene dichloride, 42, 50; (iii) tetrahydrofuran (THF), 39, 49; (iv) diethyl ether, 37, 47. In all cases reaction was rapid and the IR spectra showed extensive carboxylic salt formation.

There were three broad possibilities to explain the low conversions. (a) The dialkoxyborane was not being produced efficiently or when formed underwent further reaction prior to addition of the acid. (b) The mixed anhydride I was decomposed either by various dismutations or by reduction. (c) The reaction of I with amine either took place at the boron atom or gave rise to products that could participate further in the reaction. These three propositions were each tested.

(a) Control experiments showed that in the case of di-isopropoxyborane the required compound was formed to the extent of 97% in hexane and 95% in THF.

It is known that alkoxyboranes derived from primary alcohols are prone to rearrange[2] as in Eq. (2) although di-isopropoxyborane, as far as could be observed, did not rearrange.[3] The diborane produced in such a rearrangement could reduce any acyloxyboranes present after addition of the acid or possibly produce triacyloxy-

boranes, either of which could reduce the yield of amide. However when di-isopropoxyborane was produced in the presence of excess acetone there were little loss of active hydrogen, this amounting to less than 10% in 21 hr at room temperature in THF. The presence of an acid (~5% HCl) did not catalyse the reaction and as the amide forming reactions were carried out speedily it would seem that this mode of rearrangement (Eq. 2) is not the cause of the low conversions.

(2) $$6(RO)_2BH \rightarrow 4(RO)_3B + B_2H_6$$

(b) It seemed possible that immediately following the formation of I, reduction of it by the dialkoxyborane could occur. Reduction was shown to depend upon the speed of the addition of the acid, as addition times of 60, 35, 15 and 2 min. gave rise respectively to 67, 71, 86 and 92% of the theoretical amount of hydrogen. If three equivalents of dialkoxyborane were present then the acid was reduced slowly to hexyl alcohol in 93% yield.[4] Even under these conditions however, if addition of the acid is rapidly followed by addition of the amine, then 40% of the amide is produced together with recovered acid (36%) and alcohol (13%). Under our standard conditions the loss of caproic acid by reduction amounts to ca. 5% only. Thus when hydrogen was displaced to the extent of 86% the amide yield was only 37% representing a 43% conversion of I to the amide.

Inverse addition of the reagents (borane to acid) gave quantitative yields of hydrogen, but small quantities of caproic anhydride (8–10%) were formed. A solution (THF) of I may be left overnight and therefore it is the free acid that promotes anhydride formation either by route (3) or by catalysing route (4).

(3) $$RCO_2B(OR')_2 + RCOOH \rightarrow (RCO)_2O + R'OH + (OBOR')$$

(4) $$6RCO_2B(OR')_2 \rightarrow (RCO)_2O + (RCO_2)_4B_2O + 4(R'O)_3B$$

II

Di-t-butoxyborane (R' = tBu) could be isolated and was thermally stable at room temperatures. The slow addition of acetic acid to this borane led to the rapid precipitation of oxybisdiacetoxyborane (II, R = Me) and tri-t-butoxyborane was also isolated. A similar result consistent with Eq. (4) was found with benzoic acid, the reaction being clearly similar to that previously found between acetic acid and di-n-butoxychloroborane.[5,6] As little carboxylic anhydride formation is noted under the standard conditions for amide production, rearrangement as in Eq. (4) is not the cause of the low conversions.

A possibility of some interest was that I could rearrange to III as in Eq. (5).

(5) $$3RCO_2B(OR')_2 \rightarrow (RCO_2)_3B + 2(R'O)_3B$$

III

(6) $$6RCOOH + B_2H_6 \xrightarrow{(a)} 2(RCO_2)_3B \xrightarrow{(b)} (RCO_2)_4B_2O + (RCO)_2O$$

Whether triacyloxyboranes (III) are stable as such, or very readily dismute as in 6b is not clear as most preparations have involved either acidic conditions or heating.[6] The preparation of tripropionyloxy-, tribenzoyloxy- and tricinnamoyloxyborane has been claimed, using the reaction of polymeric boron sulphide with the corresponding acid.[8]

Brown has shown that when carboxylic acids (6 parts) and diborane (1 part) are mixed, the acid may be quantitatively recovered, and in a footnote considered the possibility of reaction (6b) being involved. We have confirmed the lack of reduction in the case of caproic acid and diborane (6:1) at $-25°$, there being present bands at 1740 cm^{-1} and 1600 cm^{-1} (B-OCOR) but no carboxylic anhydride. The latter could be detected after 30 min at room temperature. In the case of acetic acid and diborane (6:1) at 0° in THF, acetic anhydride was formed and II (R = Me) was isolated. When benzoic acid and diborane were reacted in a similar fashion; both oxybis-dibenzoyloxyborane (II; R = Ph) and benzoic anhydride were isolated. It is difficult to reconcile these findings with the reported recrystallisation of tribenzoyloxyborane from hot benzene.[8] Thus reaction (6b) may proceed at room temperature with derivatives of both aromatic and aliphatic carboxylic acids. Whether it intervenes in any particular reduction of a carboxylic acid will depend upon the exact conditions used, in particular the temperature and presence of excess diborane. As the reaction is fast and produces carboxylic anhydride, it means that route (6b) is not followed to any large extent in the amide forming reactions.

Thus though compounds of type I may be reduced and also may rearrange, neither reaction occurs to a large extent under the conditions of the amide forming reaction. Therefore possibilities inherent in proposition (b) may be discounted as the major causes for the low conversions.

(c) From Eq. (1) it follows that a mole. of alcohol may be liberated in the attack of amine on I, and this could then compete with amine for I by routes (7) or (8). Salt formation will render route 8 virtually irreversible at room temperature.[1]

(7) $$R'OH + RCO_2B(OR')_2 \rightarrow RCO_2R' + R'OH + [OBOR']$$

(8) $$R'OH + RCO_2B(OR')_2 \xrightarrow{a} RCOOH + B(OR')_3$$
$$\downarrow R''NH_2$$
$$RCOO^{(-)} \quad \overset{(+)}{N}H_3R''$$

Addition of isopropanol to caproyloxydi-isopropoxyborane rapidly gave free acid, no ester being produced. A high yield (70%) of tri-isopropoxyborane as well as caproic acid (92%) could be isolated, as expected from (8a). Other alcohols behave similarly and route 7 is excluded at room temperature. The alcohols therefore attack exclusively on boron, in line with previous observations on the rapid solvolysis of II (R = Me) under Fischer conditions[10] or on titration with sodium methoxide in methanol.[11]

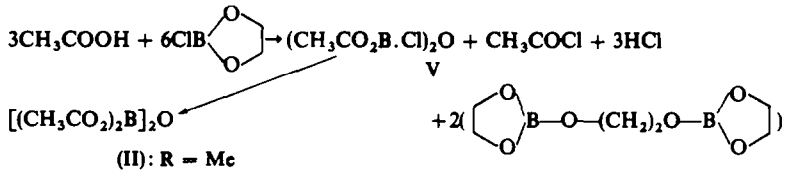
An amide forming reaction of the type (9a) could lead to salt formation and subsequent slow amide production. Such reactions might be less likely with a 2-acyloxy-

(9) $$RCO_2B(OR')_2 + R''NH_2 \xrightarrow[(a)]{\pm H^{(+)}} RCONHR'' + (R'O)_2BOH$$
$$RCO_2B(OR')_2$$
$$R''\overset{(+)}{N}H_3 \ \overset{(-)}{O}_2C.R \xleftarrow{R''NH_2} RCOOH + (R'O)_2B.O.B(OR')_2$$

1,3,2-dioxaborolane, $RCO_2B\begin{smallmatrix}O-CH_2\\ \\ O-CH_2\end{smallmatrix}$ (IV). The preparation of compounds of type IV in high yield has been claimed by reaction of the chloroborolane and carboxylic

acid.[12] We were unable to repeat this, all our preparations yielding complex mixtures from which V, II (R = Me) and acid chloride were obtained (Eq. 10). Various mechanisms, which will not be discussed here, may be involved in this complex reaction.

(10)

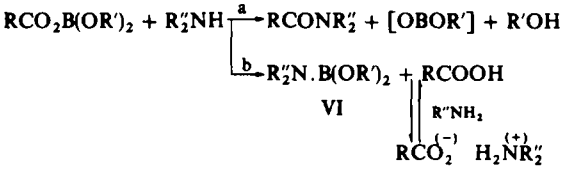


When acetic acid was added to chloroborolane (1 : 2), the product (V) could be isolated in 52% yield based on (10), and hence the result could not be due to small amounts of impurity in the chloroborolane. Even when V was isolated there were substantial amounts of other acetoxyboron compounds present.

It is not clear whether the discrepancy between the recorded results and our own is due to monomer-dimer interaction. 2-Chloro-1,3,2-borolane is dimeric[13] and may exist as  $BO.(CH_2)_2O.BCl_2$. There is evidence that 2-alkoxy-1,3,2-borolanes readily form ring opened compounds.[14] Therefore any evidence based on the stability of the ring closed forms is suspect and route (9) could not be tested in this way.

As alcohols attack acyloxydialkoxyboranes (I) at boron only, powerful nucleophiles such as amines might also attack at boron, (Eq. 11b) though less selectively to yield the aminodialkoxyborane (VI). If this reacted slowly or not at all to yield amide, the low conversion to amide at room temperature might be clarified.

(11)

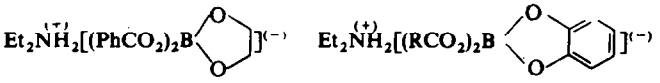


To test this hypothesis benzoic acid was added to di-n-butoxyethylaminoborane[15] (1 : 1) in benzene. Some heat was evolved but no amide was produced. After 5 hr reflux some amide was apparent and work-up after 72 hr reflux gave amide (51%) and acid (41%). Evidently amide production is very slow and if compounds of type VI were produced, the low conversions would be expected.

When 2-diethylamino-1,3,2-dioxaborolane (VII)[12] was mixed with caproic acid (1 : 1) no amide was produced but if the reaction was left at room temperature for 14 days the amide (44%) could be isolated. A similar result was obtained with benzoic acid under more vigorous conditions (46%, 72 hr reflux).

All these reactions of aminodialkoxyboranes very rapidly gave bands at 1670–1700 cm^{-1} which diminished as amide was formed. From the 1 : 1 reaction of benzoic acid and VII a substance assigned the structure VIII was obtained, and when a 2 : 1 reaction was carried out the salt was obtained in 88% overall yield. The IR spectrum had the broad stretching frequencies of an ammonium salt (3200–2200 cm^{-1}) and no carboxylate frequencies (ca. 1580 cm^{-1}). There is a broad band at 1680 cm^{-1}, splitting

to two bands at 1700 and 1670 cm^{-1} on sufficient dilution. The PMR spectrum is completely consistent with VIII.

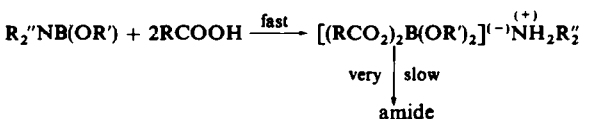


VIII IX

There do not seem to be any close analogies with this type of borate formation, although the addition of methanol to a mixture of trimethoxyborane and t-butyl amine gave the salt $^tBuNH_3^{(+)}B(OMe)_4^{(-)}$.[16] Like sodium tetramethoxyborate and similar compounds, VIII is very sensitive to moisture and is also completely cleaved by methanol. It was of interest that both benzoic acid and butyric acid react rapidly and exothermically with 2-diethylamino-1,3,2-benzodioxaborole (2:1) to give the salts IX (R = Pr, Ph) in yields of 80% and 70% respectively.

Production of amide directly by refluxing the salt VIII in benzene was slow, giving only 17% in 118 hr. Thus the sequence (12) is clear and could explain the results. However in the original preparation of amides from simple acids and dialkoxyboranes, addition of amines does *not* give rise to broad bands at 1670–1700 cm^{-1}, characteristic

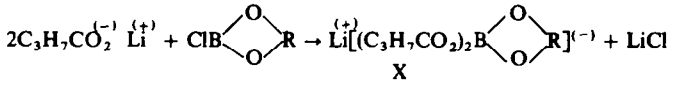
(12)



of the borate salt and thus, unexpectedly route (11b) does not appear to be followed.

An interesting side-light on the reactions of chlorodialkoxyboranes with metal salts, analogous to the previous borate preparations is the reaction of an excess of a lithium carboxylate with either 2-chloro-1,3,2-dioxaborolane or 2-chloro-1,3,2-benzodioxaborole by route (13).

(13)



X

(a) R =  ; (b) R = 

The salts Xa and Xb are highly moisture sensitive and readily soluble in organic solvents, in which however, like a number of tetra-alkoxyborates they cause a considerable increase in viscosity.[17]

It would seem that when amides are produced from dialkoxyboranes at room temperatures, the low conversions are an intrinsic part of the reaction. Route (8) has been demonstrated as a side reaction that could explain the results. but it has not been possible to test route (9). Route (11b) which could provide an explanation does not seem to be followed.

EXPERIMENTAL

General procedures. Hydrocarbon solvents were Na dried and distilled from P_2O_5. Chlorinated hydro-

carbons were shaken with conc H_2SO_4, washed and distilled from P_2O_5. Ether solvents were first dried over Na (or CaH_2), left over LAH and freshly distilled from LAH immediately before use. AcOH was dried by distillation from tetra-acetoxydiborate and the other organic reagents were dried by appropriate standard methods.[18] All glassware was assembled under vacuum and flame dried before use.

Analysis of boron compounds was carried out by addition of the compound to excess standard NaOH, and any amines distilled into standard H_2SO_4. Titration of the basic soln to pH 7·1–3 gave the carboxylic acid content and addition of mannitol followed by titration to pH 8·5–9 gave the boric acid present.

Estimation of di-isopropoxyborane

(a) To a soln of diborane in THF (6·23 ml of 0·69M soln, 1 molar equiv) at 0° was added acetone (1·00 g, 4 molar equiv). After 30 min, hydrolysis gave a gas (185 ml/759 mm/24°, 95%).

(b) Diborane (9 mmole) was bubbled over 5 hr into a soln of acetone (24 mmole) in n-hexane (8 ml) at − 75°, the exit gases being passed through acetone traps. Addition of water (0·5 ml) in THF (5 ml) produced a gas (11·7 mmole, 285 ml, 754 mm/25°). The soln contained 11·6 mmole equiv of boron and the acetone traps a further 4·73 mmole equiv.

(c) Acetone (0·797 g, 4·4 mole equiv) was added to a 0·69M THF soln of diborane (4·49 ml, 1 mole equiv) at − 75°. The soln was brought to room temp and left for 21 hr, when acetone (0·79 g, 4·0 mole equiv) was added. Hydrolysis after a further 52 hr gave a gas (71 ml/759 mm/24°, 40%).

Caproic acid and di-isopropoxyborane

(a) Acetone (0·88 g, 4·2 mole equiv) was added to a 0·67M THF soln of diborane (5·7 ml, 1 mole equiv) at 0°. After 20 min at 24°, caproic acid (0·839 g, 2 mole equiv) was added over 2 min, when gas (150 ml; 766 mm/23°, 92%) was evolved. The IR spectrum showed a very small anhydride peak at 1820 cm^{-1}.

(b), (c), (d). Exactly similar experiments[19] in which the time of addition of the acid was varied from 60 min to 35 min to 15 min gave yields of hydrogen of 67, 71 and 86% respectively.

Reduction of caproyloxy di-isopropoxyborane

Acetone (1·43 g, 4 mole equiv) was added to a 0·21M soln of diborane in THF (26·8 ml, 1·1 mole equiv) at 0°. Caproic acid (0·229 g, 0·66 mole equiv) was added at room temp when a gas (45 ml/760 mm/23°, 100%) was rapidly evolved.

After 1 hr there were still bands at 2510, 1740 and 1610 cm^{-1}, no anhydride bands being in evidence. Weighed samples of the reaction mixture were hydrolysed by a slight excess of water. After removal of the water soluble boric acid and addition of n-pentanol as a standard, the mixture was analysed on a 1m, 10% butane diol succinate column at 110°. After 14 hr at room temp there was a 93% yield of hexyl alcohol. No hexaldehyde could be detected.

Rearrangement of caproyloxdi-isopropoxyborane

A soln of di-isopropoxyborane in THF, prepared from acetone (0·881 g, 4 mole equiv) and diborane (6·68 ml of 0·633 M. THF soln, 1 mole equiv), was slowly added to caproic acid (0·831 g, 1·90 mole equiv) in THF (2 ml) at room temp. There was a steady evolution of gas and the soln showed a band at 1820 cm^{-1} due to caproic anhydride.

By comparison of the spectra of both hydrolysed and non-hydrolysed reaction mixture with standard soln of caproic anhydride and mixtures of caproic acid and anhydride, the anhydride content of the reaction mixture was shown to be 8–10% theoretical for complete rearrangement. This did not significantly increase in 15 hr at room temp.

N-*Butyl caproamide*

Caproic acid (0·932 g, 1 mole equiv) was added over 15 min at room temp to di-isopropoxyborane (1 mole equiv) in THF. Gas evolution (165 ml, 763 mm/23°, 86%) was complete in 30 min. n-Butylamine (0·551 g, 0·95 mole equiv) was rapidly added and the mixture left overnight. Work up in the usual way[1] yielded n-butycaproamide (0·504 g, 37%) and caproic acid (0·511 g, 55%).

Di-t-butoxyborane

t-Butanol (12·3 g, 4 mole equiv) was slowly added at room temp to 0·59M THF soln of diborane (14·0

ml). The volatile liquids were removed (23°/0·5mm) leaving a viscous residual oil, b.p. 22–25°/0·05 mm. (Found active hydrogen: 0·68; B, 7·1. $(C_4H_9O)_2BH$ requires active hydrogen: 0·69; B, 7·0%).

Disproportionation of benzoyloxydi-t-butoxyborane

Di-t-butoxyborane (3·28 g, 1 mole equiv) in diethyl ether (5 ml) was added over 70 min to an ethereal soln of benzoic acid (2·53 g, 1 mole equiv). Gas was evolved and oxybisdibenzoyloxyborane (1·36 g, 75%) precipitated. (Found: $PhCO_2$, 92·0; B, 4·2. Required for $C_{28}H_{20}B_2O_9$: $PhCO_2$, 92·7; B, 4·2%).

The solvent was removed from the filtrate at 0°/0·2 mm. and tri-t-butoxyborane (2·34 g, 74%) was distilled (15–20° bath temp, 0·05 mm) from the residue of benzoic anhydride which was purified by washing with pentane and cold $NaHCO_3$ aq., (0·523 g, 67%). The anhydride had m.p. 43° and the same IR as an authentic sample.

Tri-t-butoxyborane has n_D^{20} 1·3879; B, 4·9%, required: B, 4·9%.

Interaction of acetic acid and diborane

A 0·41M THF soln of diborane (15 ml, 1 mole equiv) was added slowly to AcOH (2·43 g, 6 mole equiv) in diethyl ether (5 ml) at 0°. After evolution of gas had ceased the solvents were removed *in vacuo* and the residue crystallized from benzene to yield oxybisdiacetoxyborane (1·31 g, 72%). (Found: B, 7·8, CH_3CO_2, 85·9. required for $C_8H_{12}B_2O_9$: B, 7·9; CH_3CO_2, 86·3%). The PMR spectrum was simply a singlet at τ 7·73, and the IR was identical with an authentic sample.

Acetic anhydride was detected by the IR and GLC (2 m, 10% apiezon column at 150°) but not isolated.

Interaction of benzoic acid and diborane

Diborane in THF (5·0 ml, 0·59M soln, 1 mole equiv) was added over 35 min to benzoic acid (2·16 g, 6 mole) in benzene at room temp, gas (406 ml/761 mm/24°, 94%) being evolved.

After 1 hr the solvent was reduced in volume to 10 ml, when the oxybisdibenzoyloxyborane (0·759 g, 52%) separated out. (Found: $Ph.CO_2$, 91·8, B, 42. required: $PhCO_2$, 92·7; B, 4·2%). The IR was identical with an authentic sample.

Addition of diethyl ether to the filtrate precipitated more oxybisdibenzoyloxyborane (0·249 g, 17%) and the subsequent filtrate was extracted twice with $NaHCO_3$ aq and the organic phase, dried over $MgSO_4$, filtered and the solvent removed. Recrystallization from benzene/light petroleum gave benzoic anhydride m.p. 40–41° (0·120 g, 39%) identical in all respects with an authentic sample.

Reaction of caproyloxydi-isopropoxyborane with isopropanol

Caproic acid (2·41 g, 1 mole equiv) was added over 20 min to di-isopropoxyborane (1 mole equiv) and when gas evolution had finished isopropanol (1·25 g, 1 mole equiv) was added at room temp.

All liquids volatile at 23°/0·1 mm were removed, the residual oil taken into methylene dichloride and shaken with 3N HCl and Na_2CO aq. Caproic acid (2·22 g, 92%) was recovered from the carbonate extract. The volatile liquids gave tri-isopropoxyborane (2·65 g, 70%) b.p. 138–139°, n_D^{23} 1·3754 (lit 139–140°, n_D^{25} 1·3750).

Reaction of acetic acid with 2-chloro-1,3,2-dioxaborolane

(a) Acetic acid (1·92 g, 1 mole equiv) in methylene dichloride (15 ml) was added over 2 hr at room temp to the chloroborolane (6·82 g, 2 mole). The chloroborolane was prepared according to the lit method.[12] (Found: Cl, 33·5; B, 10·2%; n_D^{23} 1·4634. required: Cl, 33·3; B, 10·3%, lit. n_D^{23} 1·4640).

After the mixture had stood for 15 min,(V)was filtered off and washed with methylene dichloride (3 × 3 ml) yielding the product (1·26 g, 52%). (Found: CH_3CO_2, 50·7; B, 9·5; Cl 30·3. $C_4H_6B_2Cl_2O_5$ (V) requires: CH_3CO_2, 52·0; B, 9·6; Cl, 31·3%); IR spectrum (nujol), ν_{max} 1720 (v weak), 1605(s), 1100(s), 1020(s), 890(s) cm^{-1}.

(b) Acetic acid (3·12 g, 1 mole equiv) in methylene dichloride (5 ml) was added during 30 min to the chloroborolane (5·57 g, 1 mole equiv) in methylene dichloride (15 ml) at room temp. The volatile liquids were removed *in vacuo*, and the residue taken into methylene dichloride (8 ml). Addition of diethyl ether (30 ml) precipitated oxybisdiacetoxyborane (2.38 mg, 35%), identical in all respects with an authentic sample.

Interaction of caproic acid and 2-diethylamino-1,3,2-dioxaborolane

Caproic acid (1·33 g, 1 mole equiv) was rapidly added to the aminoborolane[12] (1·75 g, 1·1 mole equiv) in methylene dichloride. After 14 days at 24° there were no 1740 cm^{-1} or 1680 cm^{-1} bands in the IR, and the

usual work-up produced the amide (0·594 g, 44%) identical with an authentic sample and caproic acid (0·88 g, 45%).

Interaction of benzoic acid and 2-diethylamino-1,3,2-dioxaborolane

(a) Benzoic acid (0·868 g, 1 mole equiv) and the aminoborolane (1·12 g, 1·1 mole equiv) were reacted in refluxing benzene for 14 hr. The usual work-up produced benzoic acid (0·365 g, 42%) and N,N-diethylbenzamide (0·581 g, 46%) identical with an authentic sample.

(b) Benzoic acid (0·937 g, 1 mole equiv) in benzene (10 ml) was added slowly at room temp to the aminoborolane (1·10 g, 1 mole equiv) in benzene (5 ml). After 30 min all the volatile liquids were removed (23°/0·05 mm) leaving a residue of waxy diethylammonium ethylenedioxydibenzoyloxyborate (1·46 g, 97·6%).

(Found: $PhCO_2$, 59·9; B, 2·9, $C_{20}H_{26}BNO_6$ (VIII) requires: $PhCO_2$, 62·5; B, 2·8%). From the volatile liquid the aminoborolane (0·385 g) b.p. 33–36/0·4 mm was isolated.

(c) Addition of benzoic acid (1·75 g, 2 mole equiv) in benzene (20 ml), to the aminoborolane (1·03 g, 1 mole) produced heat and VIII slowly crystallized out over a period of 2 days (1·87 g, 67%). (Found: $PhCO_2$, 62·9; Et_2NH_2, 18·7; B, 2·8. required for (VIII) $C_{20}H_{26}BNO_6$: $PhCO_2$, 62·5; Et_2NH_2, 19·1; B, 2·8%); ν_{max} 3300–2250, 1685, 1600, 1580, 1350, 1070, 1015, 840, 720 cm^{-1}; PMR spectrum ($CDCl_3$) 8·76(6H)t, 7·00(4H)q, 5·94(4H)s, 2·6(6H)m, 1·9τ(4H)m.

Removal of the solvent from the filtrate gave more VIII (0·55 g, 21%) identical with the above product.

Production of N,N-*diethylbenzamide from* VIII.

The borate VIII (0·715 g) was heated under reflux in benzene (10 ml). After 118 hr the IR spectrum showed small amide (1635 cm^{-1}) and carboxylate (1560 cm^{-1}) bands as well as the broad borate band at 1690 cm^{-1}. The standard work-up produced N,N-diethylbenzamide (55·6 mg, 17%).

N,N-*Diethylbenzamide from di-*n*-butoxydiethylaminoborane and benzoic acid*

Addition of benzoic acid (0·824 g, 1 mole equiv) to the aminoborane (1·70 g, 1·1 mole equiv) in benzene (13 ml), gave rise to heat and an IR spectrum with bands at 1700 cm^{-1} and 1665 cm^{-1}, which did not change in 10 hr at 24°. After 5 hr under reflux the only bands in this region were at 1675 cm^{-1} and 1635 cm^{-1} (amide), the former slowly diminishing. After 72 hr reflux, amide (0·612 g, 51%) and acid (0·34 g, 41%) were produced. No ester could be detected in the neutral product.

Interaction of 2-diethylamino-1,3,2-benzodioxaborale and butyric acid

Butyric acid (0·993 g, 2 mole equiv) was added rapidly to the aminoborane (1·08 g, 1 mole equiv) in benzene (15 ml). Heat was evolved and a band at 1675 cm^{-1} appeared, no further change being evidenced after 24 hr at room temp. Pentane was added until the mixture was just cloudy, the reaction left for 18 hr and diethylammonium O-phenylenedioxydibutyryloxyborate (IX) (1·68 g, 80·5%) filtered off.

(Found: $C_3H_7CO_2$, 46·9; Et_2NH_2, 20·0; B, 3·8. required for $C_{18}H_{30}BNO_6$ (IX, R = C_3H_7); $C_3H_7CO_2$, 47·3; Et_2NH_2, 20·2; B, 4·0%); ν_{max} (nujol), 3100, 3050, 1690, 1665, 1490, 1380, 1240, 1220, 1100, 1050, 730 cm^{-1}; NMR spectra ($CDCl_3$), τ 9·12 (6H)t, 8·75 (6H)t, 8·42m, 7·75(4H)t, 6·90(4H)q, 3·30(4H)s, 1·82(2H)s, λ_{max} 284 mμ (3900).

Diethylammonium o-*phenylenedioxydibenzoyloxyborate*

Addition of benzoic acid (2·83 g, 2 mole equiv) in benzene (15 ml) to 2-diethylamino-1,3,2-benzodioxaborole (2·21 g, 1 mole equiv) led to rapid precipitation of IX (R = Ph) (3·68 g, 73%).

(Found: B, 2·5; Et_2NH_2, 16·8. required for $C_{24}H_{25}BNO_6$ (IX): B, 2·5; Et_2NH_2, 17·0%); ν_{max} 3020, 1680, 1665, 1600, 1580, 1490, 1350, 1330, 1240, 1140, 1067, 1025, 950, 730 cm^{-1}, λ_{max} 283 mμ (1300).

Lithium ethylenedioxydibutyryloxyborate Xa

2-Chloro-1,3,2-dioxaborolane (1·24 g, 1 mole equiv) in benzene (10 ml) was added to lithium butyrate (2.41 g, 2·2 mole equiv) in benzene (40 ml) at room temp over 30–40 min. The reaction was stirred for 4 hr, the solid filtered off and extracted with benzene (4 × 15 ml). The solvent from the combined filtrates was removed *in vacuo* leaving a glassy solid, which was washed with pentane (2 × 20 ml) to yield Xa (1·41 g, 48%). (Found: $C_3H_7CO_2$, 68·5; B, 4·3. $C_{10}H_{18}BLiO_4$ requires: $C_3H_7CO_2$, 69·0; B, 4·3%); ν_{max} (benzene) 1700 (vs), 1430, 1370, 1340, 1320, 1250, 1220, 1110, 1010, 920, 800 cm^{-1}; PMR τ 9·10(6H)t, 8·33(4H)m, 7·74(4H)t, 6·05(4H).

Lithium o-phenylenedioxydibutyryloxyborate (Xb)

2-Chloro-1,3,2-benzodioxaborole (2·15 g, 1 mole equiv) in benzene (15 ml) was added during 90 min to lithium butyrate (2·95 g, 2 mole equiv). The reaction mixture was stirred for an hr at room temp and the lithium chloride spun down (1500 r.m. for 5 hr). The viscous supernatent liquid was removed and the solid extracted with benzene (50 ml) from which it was once more spun down. The benzene was removed from the combined extracts to give the crystalline Xb (4·21 g, 87%). (Found: Li, 2·2; B, 3·7; $C_3H_7CO_2$, 53·9. $C_{14}H_{18}BLiO_6$ (Xb) requires: Li, 2·33; B, 3·66; $C_3H_7CO_2$, 54·7%); ν_{max} 1670, 1625, 1490, 1360, 1240, 1215, 1100, 1060, 1030, 740 cm^{-1}: PMR (CCl_4), τ 9·10(6H)t, 8·45(4H)m, 7·70(4H)q, 3·30(4H)s.

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