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INVESTIGATION OF THE MECHANISMS OF THE AMIDE FORMING REACTIONS OF TRISDIALKYLAMINOBORANES

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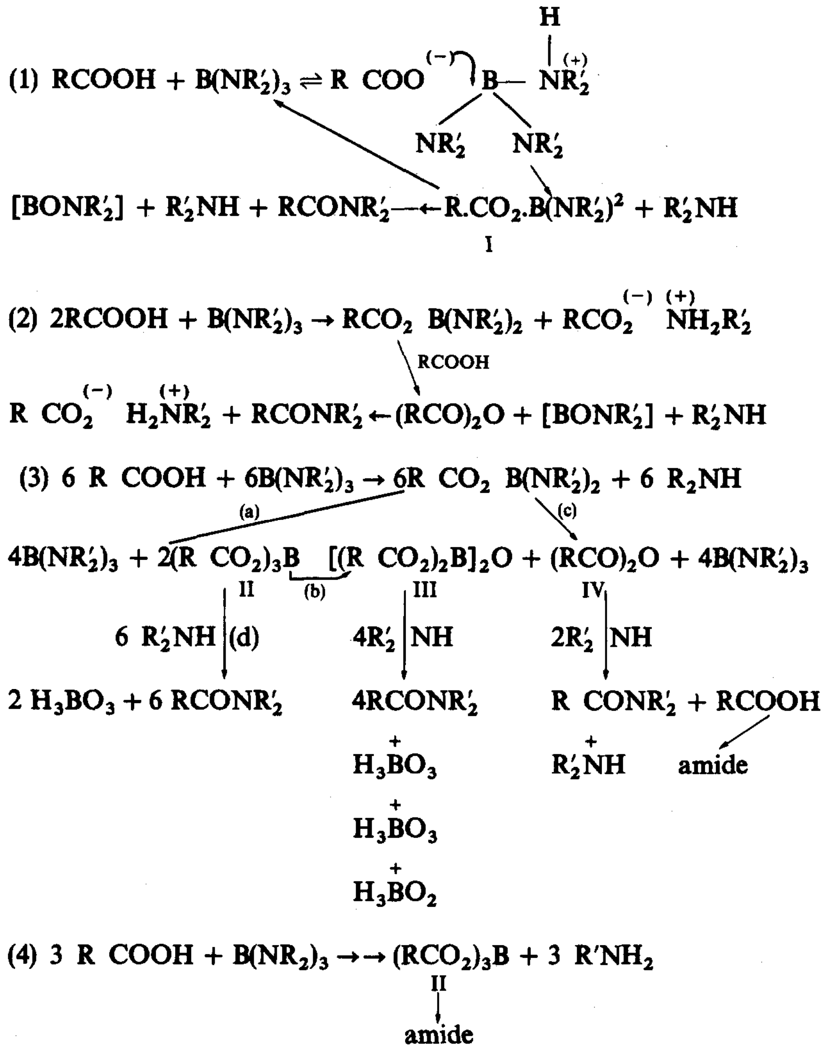
Abstract—The mechanisms of the high yield amide forming reactions between trisdialkylaminoboranes and carboxylic acids have been investigated. The reaction proceeds *via* a triacylocyborane amine adduct which may be attacked directly or dismute to an oxybisdiacyloxyborane and carboxylic anhydride, which react separately to give amide. Attempts to prepare acyloxydiaminoboranes led only to aminodiacyloxyboranes. A reaction between carboxylic anhydrides and aminoboranes has been defined. Adducts of oxybisacyloxyboranes and amines have been isolated but only gave amide in poor yield.

THE reactions of trisdialkyl- and trismonoalkylaminoboranes with carboxylic acids give amides in high yields.[1] The reaction is general and may be of some synthetic utility. In addition unlike the powerful titanium amides[2] the aminoboranes are rather selective for the formation of carboxylic amides. It was therefore decided that a mechanistic investigation was in order.

A priori various schemes for amide production based on plausible intermediates could be proposed.[3]

The main possibilities revolve around the production of the mixed anhydride (I). In route 1, this is attacked directly by amine either at the boron atom or at the carboxyl group to regenerate starting materials or amide. The latter is produced irreversibly and all the material would finally be converted to amide. Or, as in Eq. (2) the mixed anhydride could be attacked at the CO group by carboxylic acid to give carboxylic anhydride from which amide could be produced. Alternatively, as in Eq. (4), reaction of carboxylic acid at the boron atom of I would eventually lead to triacyloxyborane (II) which could yield amide as in scheme 3b or 3d. Route 3a envisages the rearrangement of I to yield II and aminoborane. The pathways 3a and 4 are of particular interest in view of the current lack of agreement on the stability of triacyloxyboranes[4] (II), and in that we have shown that when II is formed from diborane in neutral conditions, rearrangement 3b can occur.[4a] It should be noted that in the basic conditions of the reaction the triacyloxyboranes might be stabilized as amine adducts. The compound I could also yield III and carboxylic anhydride directly by 3c. We have provided a direct analogy to this in the rearrangement of $(R'O)_2B{\cdot}O{\cdot}COR$ (produced from $(R'O)_2BH$ and RCOOH) by this route[4a] as well as in the production of thioesters from trialkylthioboranes and carboxylic acids.[5] The rate of attack on the thioborane is so fast that intermediates III and IV could be isolated, though it is not certain that they do arise from II.



In view of the plethora of possible pathways and intermediates, kinetic studies could be of little help. Instead attempts were made to isolate the labile intermediates and also to synthesize possible intermediates and study their reactions.

Benzoic acid and pivalic acid were chosen as substrates, as amide production from trisdimethylaminoborane (V) proceeds relatively slowly with these acids.

When benzoic acid (3 equiv) in methylene dichloride is added, at room temperature to V (1 equiv) in the same solvent a solid is isolated (86% yield). The same solid is isolated when the order of addition is reversed and also when the stoichiometry is varied (i.e. 1:1; 2:1; 6:1 of acid to boron amine). Obviously the product, which is produced rapidly and may be recrystallized without decomposition is a highly stabilized intermediate. Its analysis is in accord with structures VI–VIII.

$(PhCO_2)_3\overset{(-)}{B}\text{—}\overset{(+)}{N}HMe_2$

VI

$(PhCO_2)_4\overset{(-)}{B}[(PhCO_2)_2B(NHMe_2)_2]^{(+)}$

VII

$PhCO_2^{(-)}[Me_2NH\cdot B\cdot(O_2C\cdot Ph)_2]^{(+)}$

VIII

The reactions of boron trichloride with secondary amines provide analogies for the formation of VI, VII and VIII; diethylamine for example, producing both compounds $[Et_2NH\ B\ Cl_2]^{(+)}Cl^{(-)}$ and $[(Et_2NH)_2B\ Cl_2]^{(+)}\ B\ Cl_4^{(-)}$ whilst from toluene the 1:1 complex $Et_2NH\cdot BCl_3$ was obtained.[6] Moreover boron trichloride in ether exists partly as $[BCl_2(OEt_2)]^{(+)}\ BCl_4^{(-)}$ and this behaviour, though little commented on is paralelled by solutions of diborane in tetrahydrofuran.[7]

Despite the very slow amide production from pivalic acid, it reacts rapidly at 0° with V to yield a compound analysing for $(Me_3C\cdot CO_2)_3B^{(-)}\text{—}^{(+)}NHMe_2$ (IX) with structural possibilities also corresponding to VII and VIII. The ir and relevant pmr spectra of the two products are so similar that there can be little doubt that they belong to the same class of compound. The rapid production of such intermediates was not anticipated and the structures were further investigated.

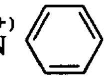
The ir spectra are incompatible with salts of type VIII as they lack a carboxylate stretching band at ca 1580 cm^{-1}. Both products have sharp N—H stretching frequencies in the 3200 cm^{-1} region, with little to be seen of the multiple bands between 2800–2400 cm^{-1} generally associated with ammonium salts. This criterion has been used to assign structures to adducts,[6, 8] but is fallible inasmuch as the positions of the "ammonium" stretching bands are dependent not only on the positively charged nitrogen but also upon the extensive H-bonding that may occur.[9] Thus $[Cl_2BHNMe_2]^{(+)}\ Cl^{(-)}$ has no bands above 3100 cm^{-1} but a series of intense bands between 2762 and 2650 cm^{-1}. However $[Cl_2BHNMe_2]^{(+)}FeCL_4^{(-)}$ obtained directly from the chloride has a strong band at 3120 cm^{-1}, other bands being of low intensity. Similar effects have been noted with tetraphenylborates and tetrafluoroborates.[10] The spectra of compounds $[(R_2NH)_2\ BCl_2]^{(+)}BCl_4^{(-)}$ contains bands characteristic of both adducts and salts so that although the spectra of the two compounds under consideration are very similar the those of known adducts[11] it is conceivable that the large tetracyloxyborate anion of VII could be non H-bonding. Moreover the salt $(Me_2NH_2)^{(+)}[(PhCO_2)_3BOMe]^{(-)}$ (see p. 1903) does contain a sharp band at 3160 cm^{-1} and therefore both VI and VII remain as possibilities.

It has been shown[12] that the molar conductivity of $Et_2\overset{(+)}{N}H\text{—}\overset{(-)}{B}Cl_3$ is very similar to that of $Et_3N\text{—}BCl_3$ being low for ionic compounds with values of ca. 0·2–0·3 Ω^{-1} in 0·4% solution in nitrobenzene.

A 0·12M solution of the benzoic acid product in chloroform had the very low conductivity of $1\cdot 1 \times 10^{-3}\ \Omega^{-1}$, but this was not conclusive as dimethylamine hydrochloride also had a very low conductivity in this solvent, presumably due to extensive ion-pairing.

In nitrobenzene it seemed that the conductivities of the products from the reactions of carboxylic acids and aminoboranes corresponded to adducts rather than salts, some representative figures being given in the Table. The distinction between salts and adducts seems reasonably clear and structures VI and IX are assigned to the intermediates isolated from the acid reactions with V.

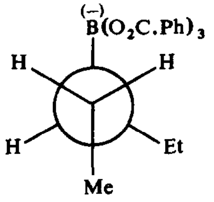
TABLE

	Compound	$\Lambda m\,(\Omega^{-1}\,cm^{-1})$
X	$(PhCO_2)_3\overset{(-)}{B}—\overset{(+)}{N}$ 	$1\cdot2 \times 10^{-1}$
	$(PhCO_2)_3\overset{(-)}{B}—\overset{(+)}{N}HMe_2$	$1\cdot2 \times 10^{-1}$
XI	$(PhCO_2)_3\overset{(-)}{B}—\overset{(+)}{N}HEt_2$	6×10^{-2}
	$(Me_3C.CO_2)_3\overset{(-)}{B}—NHMe_2$	3×10^{-2}
	$[MeO\overset{(-)}{B}(CO_2Ph)_3]_{(-)}\ H_2\overset{(+)}{N}Me_2$	$5\cdot6^{a}$
	$\overset{(-)}{B}(O_2C.C_3H_7)_2\ H_2\overset{(+)}{N}Et_2$	$3\cdot3$
	$\overset{(-)}{B}(O_2C.Ph)_2\ H_2\overset{(+)}{N}Et_2$	$2\cdot2$

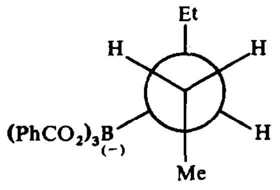
[a] Slight hydrolysis may have occurred here.

The ability of amines to stabilize triacyloxyboranes is shown by the isolation of XI from the reaction between diethylammonium benzoate and triethylthioborane, whereas in the absence of diethylamine there is a very rapid formation of oxybisdibenzoyloxyborane. Similarly, reaction in the presence of pyridine led to X. Compound XI is of some interest as it possesses intrinsic asymmetry of a type recently demonstrated for phosphonium and arsonium salts[13a] as well as for adducts of diborane.[13b] Compound XI had peaks which integrated as required at τ 1·8 and 2·6 (aromatic protons), 3·54(NH), 6·53(2H), 6·94(2H) (methylene protons) and 8·64 (methyl protons). Irradiation at either τ 6·53 or 6·94 caused the the Me "triplet" to collapse to a doublet, showing that it is an overlapping doublet of doublets and hence is coupling with two non-identical methylene protons. Strong irradiation at τ 6·73 caused the signal due to the Me group to collapse to a singlet. Irradiation of the Me triplet in turn transformed the multiplet at τ 6·53 to a broad doublet ($J = 14$ c/s) whilst that at τ 6·94 became a quartet, ($J_1 = 14$ c/s, $J_2 = 6$ c/s). High power irradiation of the N—H signal caused the methylene signals to give envelopes of very similar shape, as expected.

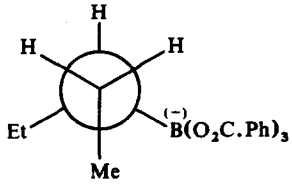
There may be three favoured conformations (XI a–c) for this compound and either XIa or XIb would explain the results.



XIa



XIb



When compared with the reactions between boron trichloride and secondary amines which interact to yield at least five types of compound[6, 14] depending upon the stoichiometry and conditions, the production of triacyloxyborane–amine adducts in such a variety of conditions is both straightforward and surprising. Their ready formation makes them likely intermediates in the amide production and, as they are produced in the presence of excess acetic acid route 2 is excluded as well as routes 1 and 3c.

A further and very interesting new class of salt was found in the investigation of the interaction of $Me_2N—B(OMe)_2$ and carboxylic acids. The aminodialkoxyborane reacted with acids in the same way as a mixture of trialkoxyborane and trisdialkylaminoborane. Attempts to isolate an intermediate in the case of benzoic acid, led to characterization of dimethylammonium tribenzoyloxymethoxyborate, (XII) Me_2NH_2 $[(PhCO_2)_3b\cdot OMe]^{(-)}$. It was then discovered that adduct VI reacted rapidly with trimethoxyborane to yield the same salt in good yield. The ir spectrum has three bands in the 1550–1600 cm^{-1}, one of which (1565 cm^{-1}) is broad relative to the aromatic ring frequencies and is assigned to NH_2 deformation. The NH stretching regions of the solid has the character partly of ammonium salt and partly of adduct (3150 cm^{-1}). As previously reported this compound shows asymmetry, most probably due to stereospecific ion-pair formation.[15] The route to XII from the adduct remains undefined.

Although the mixed anhydrides (I) would seem to be involved in amide production from simple acids only insofar as they yield amine adducts of II, a direct synthesis of this class of compound was undertaken with the intention of studying their properties.

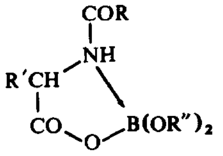
Lead pivalate was reacted with chlorobisdimethylaminoborane and also with dimethylaminoethylthioborane. A rapid precipitate of either lead chloride or diethylthiolead resulted, with no formation of either amide or anhydride (no route 3c). However examination of the PMR spectrum of the reaction mixture showed that even in these neutral conditions at −15° there were several types of pivaloyloxyborane present. Thus it would seem that I is a highly unstable class of compound. The mixture could be partially resolved and yielded a solid of composition $(Me_3C\cdot CO_2)_2B\cdot NMe_2$, (XIII). The substance is stable enough to be sublimed (though small changes occur in the PMR spectrum) and it requires heating with aqueous base to effect complete hydrolysis. In the mass spectrometer (80°) a peak corresponding to the dimer $C_{24}H_{28}B_2N_2O_8$ is seen, the base peak being at *m/e* 258 arising from the molecular ion.

The nature of the product was confirmed by reacting dimethylaminodichloroborane with lead pivalate, and the solid that precipitated from hexane at −75° was collected. The solid had an ir spectrum virtually identical with the previous product XIII, and the pmr was almost exactly the same as XIII prior to sublimation. The mol wt was ascertained by osmometry as 502 (theor 514). Although sublimation produced some minor changes, no amide was formed from XIII. The stablilty of the dimer of XIII is reminiscent of the situation with dimethylaminodichloroborane itself which slowly dimerises (monomer half life at 25° is 37 hr) to yield $(Me_2N\cdot BCl_2)_2$, very much more stable than the monomer and possibly even more resistant to hydrolysis than the dimer of XIII.[16]

The reaction sequence (5) seems to be proceeding, though not necessarily exclusively. From the volatile fraction of the reaction product, the isolation of V helped to confirm the sequence. It is worth remarking that in the case of the peptide synthesis,[17]

$$\begin{array}{l} (5)\quad 4(NMe_2)_2BX + 2Pb(O_2C\cdot CMe_3)_2 \xrightarrow{(a)} 2Me_3C\cdot CO_2B(NMe_2) + PbX_2 \\ \qquad\qquad\qquad\qquad \swarrow (b) \\ \text{dimer} \leftarrow \underset{\text{VIII}}{(Me_3C\cdot CO_2)_2B\cdot NMe_2} + \underset{\text{V}}{B(NMe_2)_3} \end{array}$$

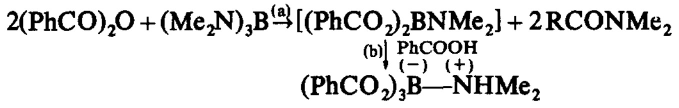
intermediates of the same type as I could be stabilized by forms such as XIV, even though in the case of simple acids dismutations may readily occur.



XIV

We have previously shown[5] that various anhydrides react with $B(SEt)_3$ directly as well as with EtSH, and it was of interest to see whether boron amines also could react with carboxylic anhydrides.

When acetic anhydride or benzoic anhydrides are added to V the first equivalent reacts very rapidly, the second less rapidly and the third hardly at all. If, after two equivalents of benzoic anhydride were added, two equivalents of benzoic acid were introduced the amine adduct VI was produced and one equivalent of benzoic acid was recovered. Amide was produced in the direct interactions in ca. 70% yield, and in the reaction with acid added in 55% yield (allowing for recovered acid). The sequence shown in eq. 6 is suggested.

(6) 

$$2(PhCO)_2O + (Me_2N)_3B \xrightarrow{(a)} [(PhCO_2)_2BNMe_2] + 2RCONMe_2$$

$$\Big\downarrow{\scriptstyle (b)\ PhCOOH}$$

$$(PhCO_2)_3\overset{(-)}{B}—\overset{(+)}{N}HMe_2$$

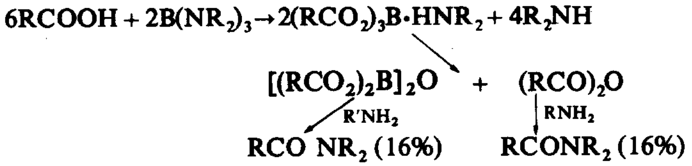
VI

If anhydrides were produced in the reaction by 3b they could therefore interact with any aminoborane present.

The reactions of the mixed anhydrides III with amines was examined. Compound IIIa ($R = C_5H_{11}$) was prepared by the displacement of acetic acid from the acetoxy-derivative. When diethylamine and IIIa mixed (4 : 1) one of the caproyloxy-groups was converted to amide but there was little further change after 14 hr at room temperature. With IIIb (R = Ph) under similar conditions there was a rapid interaction to yield a mixture with bands at 1690 and 1670 cm^{-1} but amide formation occurred only to the extent of 17% in 110 hr. Repetition of this reaction with a 1 : 1 ratio of dibutyl amine and IIIb led to the isolation of an 'adduct' $[(PhCO_2)_4B_2O]\cdot NHBu_2\cdot$ (XV).

When dibutyl amine was added to IIIc (R = Me) one equivalent at a time (4 : 1 overall) the first equivalent produced no amide at all, the second equivalent considerably reduced the band at 1600 cm^{-1} and slowly produced a little amide. With the addition of the third and fourth equivalents amide product was rapid but only to the extent of 25°. The exact route to the amide from the mixed anhydrides (III) remains to be defined and indeed it is not certain that XV is an adduct rather than a salt. The mono-adduct of IIIc and pyridine has been isolated.

It is interesting to note that the above reactions can account for the previously reported yield of 33% of amide in the room temperature reaction of a trisdialkylaminoborane (1 part) and carboxylic acid (3 parts) if routes 3a and 3c are followed, as in eq. (7).

(7)


$$6RCOOH + 2B(NR_2)_3 \rightarrow 2(RCO_2)_3B\cdot HNR_2 + 4R_2NH$$
$$2(RCO_2)_3B\cdot HNR_2 \rightarrow [(RCO_2)_2B]_2O + (RCO)_2O$$
$$[(RCO_2)_2B]_2O \xrightarrow{R'NH_2} RCONR_2\ (16\%) \qquad (RCO)_2O \xrightarrow{RNH_2} RCONR_2\ (16\%)$$

Equally the reported yield[4a] of 44% of amide by the reaction of $RCO_2B(OR')_2$ with amine, shows that reaction does not only go *via* route 3b.

The reactions of amines with compounds of type III therefore do not produce amide efficiently at room temperature, although their reactions with aminoboranes remains to be tested. The main route to amides in the reactions between trisdialkylaminoboranes and carboxylic acids is *via* the triacyloxy-amine adducts of type VI which can yield amide either directly, or *via* III and IV. The exact route to adducts VI is not clear, reactions such as 5b and 6b possibly being involved, as well as 3a and 4.

EXPERIMENTAL

General procedures were as in the preceding paper. Trisdimethylaminoborane was kindly supplied in bulk by B.D.H. Ltd.

Interaction of benzoic acid and $B(NMe_2)_3$

(a) Benzoic acid (3·13 g, 2 mole equiv) in methylene dichloride (25 ml) was added during 15 min at room temp to V (1·84 g, 1 mole equiv) in methylene dichloride (10 ml). The mixture was left for 3 hr and then solvent removed *in vacuo* until solid just began to precipitate. The soln was cooled to −20° and VI (2·12 g, 59%) m.p. 143–5° was filtered off. (Found: $PhCO_2$, 85·5; B, 2·6; Me_2NH, 10·3. $C_{23}H_{22}BNO_6$ requires: $PhCO_2$, 86·6; B, 2·6; Me_2NH, 10·7%); ν_{max}(nujol) 3210, 1710, 1690, 1455, 1420, 1390, 1120, 985, 715 cm^{-1}; PMR spectrum ($CDCl_3$), τ 7·14 and 7·23 (6H) broad doublet, 2·3–2·9 (10H) m, 1·6–2·0 (6H) m, $\Lambda_m^{18°}(PhNO_2) = 1{\cdot}2 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$

(b) The aminoborane V (1·45 g, 1 mole equiv) was rapidly added to benzoic acid (3·71 g, 3 mole equiv) in methylene dichloride (total 25 ml) at room temp. After 1 hr the solvent was reduced in volume to 15 ml, the soln cooled to 0° and VI, (m.p. 143–145°, 3·66 g, 86%) isolated. (Found: $PhCO_2$, 85·8; B, 2·6; Me_2N, 10·5%); The ir and pmr spectra were as for (a).

(c) Benzoic acid (1·5 g, 1 mole equiv) in benzene (10 ml) was added over 10 min to the aminoborane (1·76 g, 1 mole equiv) in benzene (5 ml). The soln was left at room temp and VI filtered off (0·721 g, 42%). A further 0·6 g (35%) was isolated from the filtrate on addition of light petroleum (40–60°). The volatile liquids were removed (24%, 005 mm) and on distillation gave trisdimethylaminoborane (0·761 g, 65%) identical with an authentic sample.

Interaction of triethylthioborane with diethylammonium benzoate

A mixture of benzoic acid (2·19 g, 1 mole equiv) and diethylamine (1·34 g, 1 mole equiv) in benzene (15 ml) was added during 15 min to the thioborane (3·56 g, 1 mole equiv) in benzene (20 ml) at room temp. After 4 hr at room temp, pentane (ca. 20 ml) was added and XI m.p. 136–7° (2·27 g, 85%) was filtered off. (Found: $PhCO_2$, 81·7; B, 2·4. $C_{25}H_{26}BNO_6$ requires: $PhCO_2$, 81·2; B, 2·45%); ν_{max}(nujol) 3150, 1700, 1600, 1580, 1305, 1130, 990, 720 cm^{-1}; pmr spectrum ($CDCl_3$), τ 8·64 (6H) t, 6·94 (2H) m, 6173 (2H) m, 5·54 (1H) s, 2·65 (9H) m, 1·89 (6H) m, $\Lambda_m^{18°}(PhNO_2) = 6 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Preparation of tribenzoyloxyborane-pyridine adduct (X)

Benzoic acid (3·99 g, 3 mole equiv) in benzene (25 ml) was added to a mixture of the thioborane (2·11 g, 1 mole equiv) and pyridine (0·861, 1 mole equiv) in benzene (10 ml) over 15 hr at room temp. Pentane (30 ml) was added and the reaction mixture set aside for 1 hr when X m.p. 167–9° (3·56 g, 72%) was isolated. (Found: $PhCO_2$, 80·3; B, 2·4. $C_{26}H_{20}BNO_6$ requires: $C_6H_5CO_2$, 80·1; B, 2·4%); ν_{max} 1710, 1635, 1600, 1580, 1300, 1115, 1030, 720 cm^{-1}.

The solvent was removed *in vacuo* from the filtrate leaving a residue of the amine adduct (1·33 g, 27%) with an IR spectrum identical to that of previously isolated X, $\Lambda_m^{18°}(PhNO_2) = 1{\cdot}2 \times 10^{-1}\ \Omega^{-1}$ cm—1.

Preparation of tripivaloyloxyborane-dimethylamine adduct (IX).

Trisdimethylaminoborane (1·50 g, 1 mole equiv) was added over 10 min to a soln of pivalic acid (3·22 g, 3 mole equiv) in light petroleum (40–60°, 30 ml) at 0°. The adduct IX m.p. 123–5°, immediately came out (2·36 g, 63%). (Found: $Me_3C{\cdot}CO_2$, 83·9; B, 3·08, Me_2NH, 12·3. The adduct $C_{17}H_{34}BNO_6$ requires: $Me_3C{\cdot}CO_2$, 84·4; B, 3·06; Me_2NH, 12·5%; ν_{max}(nujol) 3200, 1715, 1685, 1300, 1180, 1140, 1030, 1005 cm^{-1}.

Further concentration of the light petroleum filtrate gave more of the adduct (0·969 g, 25·7%), $\Lambda_m = 2{\cdot}8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Preparation of dimethylammonium tribenzoyloxymethoxyborate (XII)

(a) The aminoborane V (1·29 g, 1 mole equiv) was added to benzoic acid (3·23 g, 3 mole equiv) in benzene (25 ml) to precipitate the adduct $(PhCO_2)_3\overset{(-)}{B}—\overset{+}{N}HMe_2$ (Vi). Addition of trimethoxyborane (1·82 g, 2 mole equiv) in benzene (5 ml) produced a clear soln. After 4 hr the solvent was slowly removed *in vacuo* until a solid began to precipitate, when pentane (15 ml) was added, and XII filtered off. (2·65 g, 64%). (Found: $PhCO_2$, 81·2; B, 2·4; Me_2NH_2, 10·1. $C_{24}H_{26}BNO_6$ (XII) requires: $PhCO_2$, 80·5; B, 2·4; Me_2NH_2 10·2%); ν_{max} (nujol) 3150, 1685, 1670, 1600, 1580, 1565, 1320, 1125, 1095, 1070, 940, 830, 705 cm^{-1}; ν_{max} ($CHCl_3$). 3200–2100 (broad). 1695. 1600m 1580. 1660. $\Lambda_m = 5{\cdot}6\ \Omega^{-1}\ cm^{-1}$; PMR spectrum ($CDCl_3$, ~ 80 mg 1 ml), τ 7·23 (6H s, 6·44 (s), 6·49 (s) (3H), 2·4–2·8 (6H) m, 1·6–2·15 (9H) m, 0·07 (2H) broad.

(b) Benzoic acid (5·01 g, 3 mole equiv) was added to a mixture of V (1·99 g, 1 mole equiv) and trimethoxyborane (2·89 g, 2 mole equiv) in methylene dichloride (total 50 ml). After ca. 15 min at room temp all the volatile liquids were removed *in vacuo* and the residual oils were taken into benzene (10 ml). Addition of light petroleum (60–80°) brought out an oil which slowly crystallized. After recrystallization XII (3·34 g. 53%) was recovered. (Found: $PhCO_2$. 80·6. B. 2·5%). The IR and PMR spectra were identical with that of experiment (a).

Interaction of lead pivalate with bisdimethylaminochloroborane

The aminochloroborane (2·09 g, 2 mole equiv) in methylene dichloride (15 ml) was slowly added to a soln of lead pivalate (3·18 g, 1 mole equiv) in methylene dichloride (20 ml). After 1 hr at room temp the lead chloride was removed and the volatile liquids (0·002 mm/24°) brought over into a trap. Sublimation of the residue at 90°/0·02 mm gave XIII m.p. 106–8° (0·701 g, 35%). (Found: $Me_3C{\cdot}CO_2$, 77·9; B, 4·3; Me_2N, 16·9%. $C_{12}H_{24}BNO_4$ (XIII) requires: $Me_3C{\cdot}CO_2$, 78·6; B, 4·3; Me_2N, 17·1%); ν_{max} (nujol) 1725, 1300, 1180, 1150, 1085 cm^{-1}; PMR spectrum (CCl_4), 8·77 (s) and 8·74 (s) (total 18H), 7·86 and 7·51 (6H total). The mass spectrum had M* 514·361775 corresponding to the dimer $C_{24}H_{48}B_2N_2O_8$ (514·359674).

From the volatile liquids a further 21% of XIII was obtained, as well as trisdimethylaminoborane (0·477 g. 35%) b.p. 34–40°/10 mm. n_D^{20} 1·4446.

Interaction of dichlorodimethylaminoborane with lead pivalate

The dichlorodimethylaminoborane (3·20 g, 1 mole equiv) in methylene dichloride (ca. 20 ml) was added over 30 min to the lead pivalate (10·5 g, 2 mole equiv) in methylene dichloride (ca. 30 ml). Some warming occurred and the reaction mixture was left for 1 hr at room temp and then overnight at −30°. The volatile constituents were removed (80°/0·1 mm) but the trap contained only methylene dichloride, no monomeric XIII being present. The residue was extracted with n-hexane (2 × 15 ml), filtered and the filtrate cooled to −75° when dimeric XIII (2·31 g, 36%) separated out. The IR and PMR spectra were almost identical with an unsublimed sample of XIII prepared as above; XIII had M. Wt. (60·8 mg, 3·82 g, $CHCl_3$) of 504 (514 required) PMR spectrum. 8·76 s (18H), 7·51 broad s (6H); IR (nujol) 1725, 1300, 1180, 1155, 1155, 1085, 975, 895, 855, 772, 737 cm^{-1}, $\Lambda_m^{18°}$ ($PhNO_2$), $0{\cdot}12 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

The volatiles were removed from the filtrate and the residue sublimed (90–100°/5 × 10^{-3} mm) to give a substance (1·91 g, 30%). Two determinations of M.Wt. gave values of 443 and 471. In the PMR two peaks at 8·76 and 8·78 appeared in the C-Me region, and the N-Me region had also split. The substance was very similar to the sublimed sample of XIII previously obtained. No carboxylic amide was present.

Interaction of lead pivalate with bisdimethylamino(ethylthio)borane

The borane (1·07 g, 2 mole equiv) in methylene dichloride (5 ml) was added over 25 min to a soln of lead pivalate (1·37 g, 1 mole equiv) in methylene dichloride (10 ml) at 0°. After stirring at 0° for 20 min the solvent was removed (0°/12 mm) and replaced by pentane. The solid was spun down at 5° and removed, and then the pentane slowly taken off from the soln at 0°. The NMR of the resulting mixture showed several pivaloyloxy species to be present. Prolonged evaporation (24°/0·005 mm) gave impure XIII (0·54 g, 53%). Found: $Me_3 \cdot C \cdot CO_2$, 77·5, B, 4·3, IR spectrum almost identical to that of XIII previously obtained.

Interaction of trisdimethylaminoborane (V) *and carboxylic anhydrides*

(a) Acetic anhydride (3·12 g, 1 mole equiv) was slowly added to V (4·37 g, 1 mole equiv) in methylene dichloride (25 ml) at 0°. There was an immediate reaction and bands appeared at 1715 and 1635 cm^{-1}. After 27 hr at 25° there was only the amide band (1635 cm^{-1}) in the CO region. Fractionation of the mixture gave N,N-dimethylacetamide (3·88 g, 73%) b.p. 34–38°/0·2 mm.

Attempts to fractionate the remaining oil led to decomposition with the production of Ac_2O and acetoxyboranes.

(b) Benzoic anhydride (1·86 g, 2 mole equiv) in benzene (15 ml) was added slowly, at 24° to the aminoborane (0·590 g, 1 mole equiv) in benzene (5 ml). The IR spectrum showed bands at 1700 and 1630 cm^{-1} but nothing in the N—H stretching region. After 16 hr benzoic acid (1·01 g, 2 mole equiv) was added, in benzene, when there was an immediate ppt of adduct. Pentane (15 ml) was added and the adduct (1·32 g, 77%) was removed and identified by IR and NMR spectra. The filtrate was washed with 3N NCl (×2) and $NaHCO_3$ aq. (×2). The neutral product was N,N-dimethylbenzamide (0·672 g, 54·5%) identical with an authentic sample. From the basic washings the excess benzoic acid (0·492 g) was recovered.

Preparation of oxybisdicaproyloxyborane (IIIa)

Caproic acid (7·72 g, 4 mole equiv) and oxybisdiacetoxyborane (4·5 g, 1 mole equiv) were thoroughly stirred at 150° and the AcOH slowly distilled out over several hr. Vacuum was applied to remove any traces of AcOH and the residue was stirred with pentane. The product IIIa (5·31 g, 64%) was isolated by several decantations with pentane at −20°. (Found: $C_5H_{11}CO_1$, 92·2; B, 4·37%, (IIIa) $C_{24}H_{44}B_2O_9$ requires: $C_5H_{11}CO_2$, 92·2, B, 4·4%).

Interaction of IIIa *and diethylamine*

Diethylamine (1·24 g, 4 mole equiv) in CCl_4 (10 ml) was rapidly added to IIIa (2·11 g, 1 mole equiv) in CCl_4 (10 ml). Hexadecane (0·110 g) was added as an internal standard and samples were withdrawn every hr for 14 hr. Each sample was washed dried and analysed for amide (1 m 10% PEGA column at 90°). The caproamide content remained constant throughout at 26 ± 2%. After 30 hr at 24° the reaction mixture was worked up as usual to give the amide (27% corrected for sampling).

Interaction of oxybisdiacetoxyborane (IIIc) *with di-n-butylamine*

Dibutylamine (2·16 g, 4 mole equiv) in methylene dichloride (20 ml) was added in four 5 ml portions to IIIc (1·145 g, 1 mole equiv) in methylene dichloride. Addition of the first portion gave IR bands at 1710, 1690 and 1600 cm^{-1}. Addition of the second equiv of amine caused the band at 1600 cm^{-1} to diminish strongly and a band at 1630 cm^{-1} (amide) to appear. After addition of the third equiv the band at 1630 cm^{-1} was the largest in this region. and after the fourth equiv there was a strong band at 1630 cm^{-1} and a weak band at 1690 cm^{-1}. Two hr after completion of the addition, analysis as above (but using a 2 m SE 30, 1¼% silicone column at 120°) showed an amide content of 23%, raised only to 26% after 10 hr.

Interaction of oxybisdibenzoyloxyborane (IIIb) *with di-*n*-butylamine*

Di-n-butylamine (0·312 g, 1 mole equiv) in methylene dichloride (25 ml) was added to IIIb (1·26 g, 1 mole equiv) at room temp over 30 min. After 1 hr the solvent was removed *in vacuo* and replaced by benzene (5 ml). Addition of light petroleum (40–60°) brought out an oil which gradually solidified. The product XV m.p. 70–76°, (0·931 g, 59%) was filtered and washed with cold pentane. (Found: $PhCO_2$, 75·1; B, 3·3. The adduct $C_{36}H_{39}B_2NO_9$ requires: $PhCO_2$, 74·3; B, 3·38%); ν_{max} (hexachlorobutadiene), 3060, 1695, 1670, 1600, 1580, 1570, 1130, 1020, 970, 720 cm^{-1}; PMR spectrum ($CDCl_3$) τ 9·50 t, 9·06 m, 8·41 m (total 14H), 7·08 (4H) t, 2·65 (12H) m, 1·94 (8H) m, 1·28 (1H) s.

Interaction of oxybisdiacetoxyborane (IIIc) *with pyridine*

Pyridine (1·55 g, 1 mole equiv) in methylene dichloride (10 ml) was rapidly added to IIIc (5·37 g, 1 mole equiv) in methylene dichloride (20 ml). The volume of the solvent was reduced *in vacuo* to ca. 20 ml and pentane (30 ml) added. After cooling at 0° for 1 hr the adduct oxybisdiacetoxyborane–pyridine (6·43 g, 93%) was filtered off. (Found: CH_3CO_2, 66·7; B, 6·1. The adduct $C_{13}H_{17}B_2NO_9$ requires: CH_3CO_2, 66·8; B, 6·2%); ν_{max} (nujol) 1710, 1600, 1500, 1290, 1100, 1030, 880 cm^{-1}; PMR spectrum ($CDCl_3$) τ 8·02 (6H)s, 7·86 (6H) s, 2·20 (2H) t, 1·70 (1H) t, 1·06 (2H) d.

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