214. *The Proton Magnetic Resonance Spectra of t-Butyl and Isobutyl Groups in Boron Compounds.*

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The proton magnetic resonance spectra of the t-butyl and isobutyl groups in a number of boranes, boronous and boronic anhydrides and esters, and boric esters have been recorded. The structure of the butyl groups and their location in the molecules can readily be determined.

This technique has been used to confirm the structure of the autoxidation product of tri-isobutylboron, and to follow the redox rearrangement of this product.

THE recent demonstration of the ready rearrangement of the t-butylboron to the isobutylboron structure,[1] and its generalisation to other systems,[2] is of theoretical and practical interest and renders open to question the structure of some compounds involving these two groups.

We have been investigating the relative reactivities of the t-butyl and the isobutyl group in some reactions involving partial dealkylation of di-isobutyl-t-butylboron and needed a method for determining the nature of the products unambiguously, on the scale of a few tenths of a gram. To this end we have studied the proton magnetic resonance spectra of some boranes, boronous and boronic anhydrides and esters, and boric esters containing t-butyl and isobutyl groups. We find that the structure of the butyl groups and their location in the molecule can readily be determined.

The spectra obtained are recorded in Table 1. Water was used as an external reference. The chemical shift, δ, of a peak is given in parts per million by the dimensionless function $\delta = \Delta\nu/40$, where $\Delta\nu$ is the separation in cycles/sec. between the water resonance and the peak; δ is taken as positive when the resonance occurs at high field with respect to water.

The t-butyl group, containing only one type of proton, gives a single-line spectrum (*e.g.*, t-butylboronic anhydride, Fig. 1).

The isobutyl group, if spin–spin interaction were neglected, would give three peaks of

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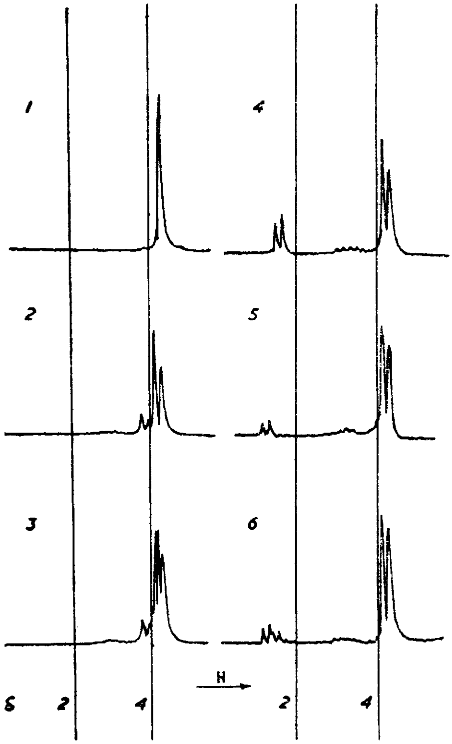
[1] Hennion, McCusker, Ashby, and Rutkowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5190; Hennion, McCusker, and Rutkowski, *ibid.*, 1958, **80**, 617.

[2] Brown and Subba Rao, *J. Org. Chem.*, 1957, **22**, 120.

relative areas 6 : 2 : 1. The CH_3 and CH_2 peaks are split into doublets by interaction with the CH proton, which itself appears as a large number of insignificant peaks. The isobutyl group can thus be identified as two doublets, ideally of relative areas 6 (methyl) : 2 (methylene), the separation within each doublet being 6 cycles/sec. (*e.g.*, tri-isobutylboron and tri-isobutyl borate, Figs. 2 and 4). The t-butyl and isobutyl groups can therefore readily be distinguished.



Proton magnetic resonance spectra.

Fig. 1, $(Bu^tBO)_3$.
,, 2, Bu^i_3B.
,, 3, $Bu^tBBu^i_2$.
,, 4, $B(OBu^i)_3$.
,, 5, $Bu^iB(O{\cdot}OBu^i)_2$ (I).
,, 6, (I) + $(Bu^iO)_2BO{\cdot}OBu^i$ (II).

The relative positions of these characteristic peaks can give evidence of the location of the groups in the molecule.

The singlet of the t-butyl group when joined to boron appears at δ 4·08—4·18 (Table 1, compounds 1, 4, and 7), but when joined to oxygen (compound 10) at 3·80.

The methyls of the isobutyl group are too distant from the rest of the molecule to vary much in position, and the doublet is always centred at δ 4·12—4·23 (compounds 1—3, 5—9, 11). Thus only one doublet appears for the methyl groups in isobutyl isobutylboronate (compound 6).

On the other hand, the methylene of the isobutyl group, because of its proximity to the rest of the molecule, is very susceptible to the molecular environment. When joined to boron in boranes (compounds 1 and 2) it is centred at δ 3·87—3·89; in isobutylboronous and isobutylboronic anhydrides (compounds 3 and 5) it moves to slightly higher field and brackets one of the methyl peaks, and in isobutyl isobutylboronate (compound 6) it is not completely resolved from the methyl peaks. If the isobutyl group is joined to an oxygen atom (compounds 6, 7, and 11) the methylene resonance frequency drops drastically, to a δ value of 1·38—1·53.

On the basis of these data the spectrum of di-isobutyl-t-butylboron [1] (compound 1; Fig. 3) appears to be a special case, consisting of a superposition of the spectra of the isobutyl and t-butyl groups shown in Figs. 1 and 2, together with an unexpected small peak

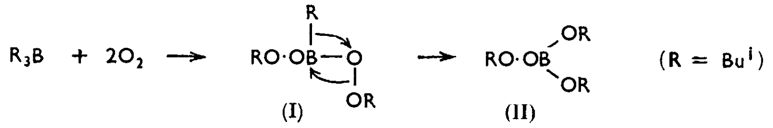
TABLE 1. *Proton chemical shifts.*

	Compound	t-Butyl CH$_3$	Isobutyl CH$_3$		Isobutyl CH$_2$		
1	Bu^{t}BBu$_2^i$	4·18	4·10	4·25	3·78	3·95	(4·04)
2	Bu$_3^i$B		4·15	4·30	3·80	3·98	
3	(Bu$_2^i$B)$_2$O		4·05	4·23	4·10	4·25	
4	(Bu^{t}BO)$_3$	4·13					
5	(Bu^{i}BO)$_3$		4·05	4·20	4·10	4·28	
6	Bu^{i}B(OBu^i)$_2$		4·10	4·28	1·43 [a]	1·58 [a]	
7	Bu^{t}B(OBu^i)$_2$	4·08	4·08	4·25	1·30	1·45	
8	Bu^{i}B(O·OBu^i)$_2$		4·05	4·20	1·18 [b]	1·35 [b]	
9	(Bu^{i}O)$_2$BO·OBu^i		4·05	4·20	1·18 [b] 1·43 [a]	1·35 [b] 1·55 [a]	
10	B(OBu^t)$_3$	3·80					
11	B(OBu^i)$_3$		4·15	4·30	1·45	1·60	
12	Bu^{t}OH	3·95					
13	Bu^{t}O·OH	3·98					
14	Bu^{i}OH		4·08	4·23	1·58	1·72, 1·88	
15	Bu^{i}OH(+HCl)		4·08	4·23	1·65	1·80	
16	Bu^{i}O·OH [c]		4·03	4·18	1·18	1·35	

[a] Refers to CH$_2$–O–B; CH$_2$–B is not resolved from CH$_3$ in 6 and 8. [b] Refers to CH$_2$–O–O–B. [c] In Pr^{n}O·OH, Bu^{n}O·OH, n-C$_5$H$_{11}$·O·OH, and n-C$_8$H$_{17}$·O·OH the separation between the CH$_3$ and CH$_2$ protons is approx. constant at δ 2·92.[3] Our corresponding value for Bu^{i}O·OH is 2·82.

at δ 4·04. We have shown that this peak does not arise through partial autoxidation; it was present in three samples prepared by two different routes, and it seems unlikely that it could be due to an impurity. The inspection of molecular models suggests that it may perhaps arise through steric restriction of rotation within the molecule. We hope to check this by determining the spectrum over a range of temperature.

This technique of proton magnetic resonance has now been used to investigate the autoxidation product of tri-isobutylboron. In dilute solution in, for example, ether, the borane absorbed 2 mol. of oxygen, giving 2 mol. of peroxide (iodometrically). The product was treated with peroxyoctanoic acid, and isobutyl alcohol and isobutyl hydroperoxide were then detected on the vapour-phase chromatogram in the approximate ratio of 1 : 2. If the solvent was removed after the autoxidation a compound with the composition (I) could be isolated, with some loss of peroxide content which continued on storage. This peroxide loss probably occurs by a nucleophilic redox rearrangement of an alkyl group from boron to oxygen, as illustrated.[4]



From our previous results, the spectrum of (I) would be expected to show the usual large doublet for the methyl groups, centred at δ 4·12—4·23, and probably obscuring the small doublet for the methylene group on boron; the doublet representing the methyleneperoxy-groups might be expected to be located at a much lower δ-value, somewhere near the usual methyleneoxy-position of 1·38—1·53. Any rearrangement to structure (II) would show up by the appearance of this methyleneoxy-doublet at the expense of the methyleneperoxy- (and methyleneboron) doublets.

The predictions are fully borne out in the observed spectrum of freshly prepared material (I) (Fig. 5): the methyleneperoxy-doublet is centred at δ 1·27. Fig. 6 shows the spectrum of the same specimen after 2·5 hr. at room temperature, and it is clear that a considerable amount of rearrangement to the ester (II) has already occurred.

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[3] Fujiwara, Katayama, and Kamio, *Bull. Chem. Soc. Japan*, 1959, **32**, 656.
[4] Abraham and Davies, *J.*, 1959, 429; Davies and Hare, *ibid.*, p. 438.

EXPERIMENTAL

General Procedures.—Organoboron compounds were prepared and handled in an atmosphere of dry oxygen-free nitrogen. It was often convenient to transfer small amounts of the compounds through self-sealing rubber serum caps with a hypodermic syringe (filled with nitrogen). For example, a sample for boron analysis was taken up into the syringe from the capped container, and injected into a weighed capped conical flask filled with nitrogen, which was then reweighed. Similarly, refractive indices were determined with a Pulfrich refractometer by injecting the sample on to the prism which was fitted with a rubber cap carrying a nitrogen supply.

Preparative procedures (particularly esters ⟶ acids ⟶ anhydrides) were chosen which could be conducted almost quantitatively on the scale of a few tenths of a gram, so that in subsequent work proton magnetic resonance could be used for the determination of the structure of very small specimens.

Di-isobutyl-t-butylboron.—Boron trifluoride–ether complex (1 mol.) and t-butylmagnesium chloride (3 mol.) were caused to react in ether under nitrogen. Di-isobutyl-t-butylboron, isolated in 50% yield, had b. p. 49°/2·7 mm. (pot $\not>$60°), n_D^{25} 1·4240 (lit.,[1] b. p. 50—51°/3·3 mm., 48—49°/2·7 mm., n_D^{25} 1·4244) (Found: B, 5·9. Calc. for $C_{12}H_{27}B$: B, 5·9%). It was sealed in capsules under nitrogen as previously described.[4] It showed infrared absorption peaks at 7·93 and 8·93 μ (calibrated against the spectrum of ammonia); Hennion, McCusker, and Rutkowski [1] report 8·0 and 8·95 μ. A second preparation by the same method gave a product with similar physical properties.

The same compound was obtained in an attempt to prepare isobutyl-t-butylboronous acid by treating boron trifluoride (1 mol.) successively with t-butylmagnesium bromide (1 mol.), and isobutylmagnesium bromide (1 mol.). The di-isobutyl-t-butylboron produced had b. p. 56°/4 mm. (pot $\not>$60°), n_D^{25} 1·4235. The infrared and nuclear magnetic resonance spectra were similar to those of the two previous products.

Tri-isobutylboron.—Di-isobutyl-t-butylboron was heated under reflux at atmospheric pressure for 0·5 hr. to isomerise it to tri-isobutylboron. The product was then fractionally distilled and sealed under nitrogen: it had b. p. 189—190°/751 mm., n_D^{25} 1·4200 (lit.,[1] b. p. 188°, n_D^{25} 1·4203) (Found: B, 5·9%), $\nu_{max.}$ 7·87 and 8·81 μ (lit.,[1] 7·83 and 8·8 μ).

Isobutylboronous Acid and Anhydride.—A capsule of tri-isobutylboron (1·003 g., 1·0 mol.) was broken in dry ether (3 c.c.) under nitrogen by a technique similar to that described for experiments with the gas burette.[4] Anhydrous hydrogen peroxide (0·1875 g., 1·0 mol.) in ether (3·38 c.c.) was then added from a dropping funnel during 0·75 hr. to the stirred solution at 0°; stirring was then continued for 3 hr. at 0°. The clear solution was transferred to one limb of a molecular still of inverted Y design and degassed at <0·005 mm. Ether and isobutyl alcohol were removed into the second limb at −75°, leaving isobutylboronous acid as a white solid which was sublimed into a receiver at −180°. It melted at 93—95° with dehydration. The infrared spectrum showed the presence of a strong OH absorption. The acid was too insoluble in carbon disulphide and carbon tetrachloride to permit accurate nuclear magnetic resonance measurements. It was therefore dehydrated by storage overnight in one limb of the apparatus at 18 mm., the second limb containing phosphoric oxide. *Isobutylboronous anhydride* was obtained as a colourless oil (Found: B, 8·9. $C_{16}H_{36}B_2O$ requires B, 8·15%).

t-Butylboronic Acid.—We are very grateful to Dr. M. F. Lappert for a specimen of t-butylboronic anhydride; it was hydrolysed immediately in an excess of water, and the product was recrystallised from water, and dried, giving t-butylboronic acid, m. p. 106°.

Isobutylboronic Acid.—n-Butyl isobutylboronate was given us by Dr. Lappert. More was prepared by treating n-butyl borate with isobutylmagnesium bromide by a method similar to that described for the preparation of n-butyl s-butylboronate.[4] The product was isolated in 47% yield as a colourless oil, b. p. 105°/15 mm., n_D^{25} 1·4113.

Boronic esters appear to be more resistant to hydrolysis than are the corresponding boronous or boric esters. The acid was obtained as follows. The boronic ester (15 g.) and water (25 c.c.) were heated together at 100°, a butanol–water azeotrope distilling. When the residual liquid was homogeneous it was cooled to 0°; isobutylboronic acid crystallised as plates. After two recrystallisations from water, the pure acid (3·2 g.) had m. p. 113° (lit.,[5] 113°) (Found: B, 10·2. Calc. for $C_4H_{11}O_2B$: B, 10·6%).

[5] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1954, **76**, 4174.

t-Butylboronic Anhydride.—Boronic acids could not efficiently be dehydrated over phosphoric oxide by the method used for the boronous acids. Reaction with thionyl chloride, however, gave the anhydrides in almost quantitative yield.

Redistilled thionyl chloride (0·40 c.c., 3 mol.) was added to t-butylboronic acid (0·1890 g., 1 mol.) in the molecular still illustrated previously.[6] Hydrogen chloride and sulphur dioxide were evolved in a reaction which was vigorous but endothermic. The mixture was heated under reflux for 1 hr., and the excess of thionyl chloride removed at 10 mm. The cold-finger condenser at −80° was then turned into the position for distillation, and t-butylboronic anhydride (0·140 g.), b. p. 100° (bath)/10 mm., was collected in the side arm. The infrared and nuclear magnetic resonance spectra showed that no rearrangement to the isobutyl structure had occurred.

Isobutylboronic Anhydride.—Isobutylboronic acid was dehydrated with thionyl chloride as above, giving isobutylboronic anhydride (Found: B, 13·0. Calc. for C_4H_9BO: B, 12·9%).

Isobutyl Isobutylboronate.—A capsule of tri-isobutylboron (1·2423 g.) was broken in a flask filled with nitrogen, and transferred, loosely stoppered, to a glove-box full of dry air. Autoxidation to the boronate took place over a period of 42 days.

Isobutyl t-Butylboronate.—A capsule of t-butylboronic anhydride (0·3 g.) was broken in isobutan-1-ol in a distilling flask, and the solution slowly fractionated, giving first the water–isobutanol azeotrope, then isobutanol, and finally *isobutyl t-butylboronate*, b. p. 81—82°/7·4 mm. (Found: C, 66·5; H, 12·6. $C_{12}H_{27}BO_2$ requires C, 67·3; H, 12·6%).

Isobutyl Hydroperoxide.—This compound was prepared by the "inverse" autoxidation of isobutylmagnesium chloride at −80°.[7,8] The crude material (46% pure; equivalent to a 13% yield of hydroperoxide) was purified from alcohol and aldehyde in batches of 1·5—2·0 g. by gas–liquid chromatography on a column (½″ × 12′) of Silicone Elastomer 301 on kieselguhr at 82° in a Griffin and George Mark II apparatus fitted with a device for collection of fractions.[9] The product had an infrared band at 11·52 μ, characteristic of the O–O link, but also at 5·83 μ indicating the presence of a carbonyl-containing impurity with a retention time very slightly greater than that of the hydroperoxide; this did not complicate the interpretation of the nuclear magnetic resonance spectrum.

Autoxidation of Tri-isobutylboron.—The autoxidations were carried out at the gas-burette as described earlier.[4] The peroxide contents of the products were determined iodometrically. We have since found that quantitative hydrogenation gives slightly higher, and, we believe, more accurate results. The values given here are therefore minimal. The results are recorded in Table 2.

TABLE 2. *Autoxidation of tri-isobutylboron.*

Solvent [a]	Bu^i_3B (g.)	Time (min.)	O_2 absorbed (mol.)	Peroxide formed (mol.)
Et_2O	0·2358	40 [b]	1·91	1·84
$MeNO_2$	0·3020	70	1·93	1·86
$Ph{\cdot}CH_2{\cdot}NH_2$	0·3654	180	0·0	0·0
C_6H_6	0·3042	50	1·82	1·69
PhOMe	0·3089	25	1·84	1·76
CCl_4 [c]	0·2654	180	1·54	1·42

[a] 50 c.c. [b] for 90% reaction. [c] We have established with other boron alkyls that autoxidation in carbon tetrachloride induces oxidation of the solvent; alkyl chloride and carbonyl chloride are major products.

Isolation of Isobutyldi-(isobutylperoxy)boron.—A capsule of tri-isobutylboron (1·2565 g.) was broken in dry ether (500 c.c.) through which nitrogen was passed, to give a dilute solution of the alkyl before autoxidation commenced. Oxygen was then dispersed through the solution for 7·5 hr., giving a product containing 1·96 mol. of peroxide. Stringent precautions were taken throughout to exclude moisture. The resulting solution was filtered from broken glass in the glove-box and from one half of the filtrate the ether was removed under reduced pressure, giving isobutyldi-(isobutylperoxy)boron as a colourless oil, n_D^{25} 1·4134 (Found: C, 58·9; H, 11·3; B, 4·4; peroxidic O, 20·2. Calc. for $C_{12}H_{27}BO_4$: C, 58·5; H, 11·1; B, 4·4; peroxidic O, 26·0%). The low value of the peroxide content shows that some redox rearrangement had

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[6] Davies and Moodie, *J.*, 1958, 2372.

[7] Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

[8] M. H. Abraham, Thesis, London, 1957.

[9] Napier and Rodda, *Chem. and Ind.*, 1958, 1319.

occurred during the working up, and this was confirmed by the presence of a small methyleneoxy-doublet in the proton magnetic resonance spectrum. The spectrum shown in Fig. 5 was obtained by carrying through the filtration, evaporation, and spectral measurement within 10 min. of the end of the autoxidation.

The other half of the filtrate was concentrated to 6 c.c. at room temperature, and peroxyoctanoic acid [10] (0·56 g., 1·0 mol.) in dry ether (20 c.c.) was added. After 1 hr. at room temperature, water (0·189 g., 3 mol.) was added to hydrolyse the boric ester, the mixture was stirred for 1 hr., and all the volatile material was removed at room temperature and 1 mm. into a trap at −75°. On the vapour-phase chromatogram [11] the distillate showed that isobutanol and isobutyl hydroperoxide, in the approx. molar ratio of 1 : 2, were the only products.

Proton Magnetic Resonance.—Spectra were obtained with a Varian V-4300 B high-resolution spectrometer operating at 40 mc/sec. Because of their sensitivity to air the compounds were sealed under dry nitrogen in tubes of 2—3 mm. external diameter. The sample tube was placed in a tube of 5 mm. external diameter, and the annular space could be filled with water for use as an external reference. When a number of specimens of the same compound were investigated, mean values of δ are given in Table 1; individual values did not differ by more than $\pm 0{\cdot}02$. The spectra were calibrated by the sideband technique.[12]

No correction has been made for magnetic-susceptibility differences. In a series of such closely related compounds it is reasonable to expect such differences to be small; the constancy in position of the methyl peak of the isobutyl groups supports this assumption.

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[10] Parker, Ricciuti, Ogg, and Swern, *J. Amer. Chem. Soc.*, 1955, **77**, 4037.
[11] Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, **17**, 499.
[12] Arnold and Packard, *J. Chem. Phys.*, 1951, **19**, 1608.