Isomers of Icosaborane(26): Some Synthetic Routes and Preliminary Characterisations in the Bis(*nido*-decaboranyl) System

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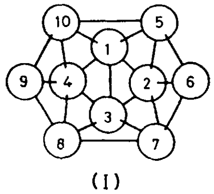
Bis(*nido*-decaboranyl), $(B_{10}H_{13})_2$, is the largest neutral borane yet reported; it has 11 possible geometric isomers and four of these should exist as enantiomeric pairs, making a total of 15 distinct structures. Photolytic, thermolytic, and metathetical routes to these compounds have been developed. Five of the geometric isomers have been isolated by chromatography and examined by u.v., n.m.r., and mass spectroscopy; another three isomers have been tentatively identified. The spectroscopic data do not permit unambiguous structural assignments at present, but the two major products from the reaction of $Mg(B_{10}H_{13})I$ with $B_{10}H_{13}(Cl\text{-}6)$ may be the (5,6′) and (6,6′) isomers.

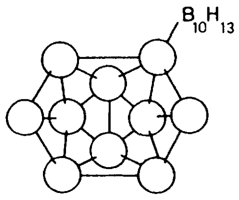
We have recently identified icosaborane(26), $B_{20}H_{26}$, as an impurity of low abundance in technical grade decaborane(14).[1] The compound may also be a product of the deuteron irradiation of $B_{10}H_{14}$,[2] although there has been some uncertainty [3] about this. These observations suggest that $B_{20}H_{26}$ is a bis(*nido*-decaboranyl), $(B_{10}H_{13})_2$, rather than an *arachno*-borane of formula B_nH_{n+6} ($n = 20$) and we here present the results of synthetic experiments based on this premise. Decaborane(14) itself is manufactured by the thermolysis of lower boranes,[4] and its contamination with, among other things, $B_{20}H_{26}$ suggested that continued thermolysis of decaborane should result in the increased production of the higher borane. We also surmised that photolysis of decaborane might result in the homolytic fission of a terminal B–H bond and that fusion of the resulting $B_{10}H_{13}^{\bullet}$ radicals would then yield $B_{20}H_{26}$. Finally, the metathetical reaction of a decaboranyl Grignard compound $Mg(B_{10}H_{13})X$ with a halogenodecaborane $B_{10}H_{13}X$ might also yield bis(decaboranyl) products.

Neutral B–B σ-bonded *conjuncto*-boranes previously characterised are bis(*nido*-pentaboranyl), $(B_5H_8)_2$, of which all three possible isomers have been identified,[5-7] and bis(*arachno*-tetraboranyl), $(B_4H_9)_2$, of which only the 2,2′ isomer has been reported.[6,8] In addition to these, all three possible isomers of the bis(*closo*-decaboranyl) anion, $[B_{20}H_{18}]^{4-}$, have been reported,[9,10] as have species related to a possible bis(*closo*-dodecaboranyl) species, $[B_{24}H_{22}]^{4-}$.[11]

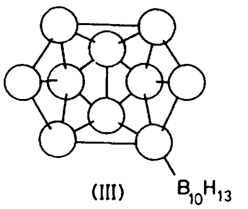
Before presenting the results of our synthetic studies on the $B_{20}H_{26}$ system, it is helpful to consider the structural implications of the formulation $(B_{10}H_{13})_2$ since 11 distinct geometric isomers are predicted, of which four should exist as enantiomeric pairs. For $B_{10}H_{14}$ itself, a projection of the skeletal structure convenient for this discussion is shown in (I); each boron atom has a terminal hydrogen atom and there are bridging atoms between the (5,6), (6,7), (8,9), and (9,10) positions. Of the possible $B_{20}H_{26}$ isomers, the (1,1′), (1,2′), (1,6′), (2,2′), (2,6′), and (6,6′) structures require no further comment. The 5, 7, 8, and 10 positions on decaborane, however, are chiral, and monosubstitution at these sites leads to enantiomeric pairs represented by (II) and (III). These have substituents at the 5 and 7 positions respectively, and in this regard 8- and 10-substitution are equivalent to 5- and 7-substitution respectively. Thus the geometrically distinct isomers (5,1′), (5,2′), and (5,6′) are paired enantiomerically with the isomers (7,1′), (7,2′), and (7,6′) respectively; the (5,5′) and (7,7′) isomers also constitute a geometrically distinct enantiomeric pair. In addition to these, the (5,7′) isomer (which is identical to the 7,5′ isomer) is also geometrically distinct, being the unique *meso*-diastereoisomer of the (5,5′) and (7,7′) enantiomeric pair.



(I)



(II)



(III)

The known variation in electron-charge density at various sites on the *nido*-decaborane cluster [12] and the varying chemical reactivity of these sites towards reagents of different types [13] suggested that several of these isomers might be preparable under appropriate conditions.

RESULTS

(*i*) *Photolytic Preparations.*—Ultraviolet irradiation of $B_{10}H_{14}$ (0.05 mol dm^{-3} in cyclohexane) for 8 h followed by removal of the solvent and remaining $B_{10}H_{14}$ under reduced pressure yielded a waxy off-white solid which was shown by analytical and preparative thin-layer chromatography (t.l.c.) to consist of three major components, identified by high-resolution mass spectrometry as isomers of icosaborane (26) (Table). The isomer numbering (1, 2, and 4) used in the Table and throughout the text corresponds to the order of chromatographic elution, isomers 3 and 5 being obtained as described below. The relative amounts of 1, 2, and 4 obtained by photolysis were *ca.* 8 : 8 : 1 and, typically, their combined yield was *ca.* 10% of the amount of $B_{10}H_{14}$

Melting points, chromatographic properties, and relative yields of isomers 1—5 of $B_{20}H_{26}$ prepared by various routes

Isomer	1	2	3	4	5	($B_{10}H_{14}$)
M.p. (θ_c/°C)	177—178 [a]	*b*	99—102 [c]	147—148 [d]	192—193 [e]	99.5 [c]
T.l.c., R_F [f]	0.30	0.22	0.15	0.14	0.10	0.40
G.l.c., t_R/min [g]	28.0	30.7	33.6	34.4	*b*	
Relative yields: [h]						
photolytic	8	8		1		
thermolytic	1	4		4		
catalytic [i]	1	2		7		
Grignard			4		1	

[a] Sample obtained from photolytic route. [b] Not measured. [c] Sample obtained from Grignard route. [d] Sample obtained from catalytic route. [e] Ref. 13. [f] Typical values; Kieselgel type G, hexane–benzene–acetic acid (74 : 25 : 1) as eluant; absolute values sensitive to eluant composition. Relative values given are to ±0.01. [g] Typical values ±0.05 min; for conditions see Experimental section. [h] In each case the combined yield was in the range 8—16%; relative yields estimated from spot intensities on t.l.c. plates. [i] Results using tetrahydrothiophen (*ca.* 2 mol%) as catalyst.

initially present; since >85% of the $B_{10}H_{14}$ was recovered, conversion of the reacting $B_{10}H_{14}$ was *ca.* 70%. The yield was not significantly improved by increasing either the irradiation time or the concentration; the limiting factor seemed to be the formation of an opaque deposit around the quartz vessel used for cooling the u.v. source (see Experimental section).

There were also three other components present in trace amounts; one was identified as hexyldecaborane, $B_{10}H_{13}(C_6H_{13})$, and presumably resulted from reaction involving the solvent. The second component had a t.l.c. R_F value close to that of $B_{10}H_{14}$ but mass spectrometry indicated that it may be a sixth isomer of $B_{20}H_{26}$. The third component remained uneluted under the conditons used and gave no mass spectrum with source temperatures up to 120 °C; it has therefore been tentatively ascribed to higher involatile polymeric boranes. In addition to these, the mass spectra of the products from prolonged irradiation (>36 h) showed very low-intensity peak envelopes typical of polyboranes with maxima at *m/e ca.* 356 and *ca.* 343 and with a high-mass cut-off at *m/e ca.* 360, possibly due to larger boranes such as $B_{30}H_{38}$. Photolyses conducted in benzene or in diethyl ether solutions gave no significant yield of any borane higher than $B_{10}H_{14}$.

(*ii*) *Sealed-tube Thermolytic Preparations.*—When $B_{10}H_{14}$ was heated at 180—185 °C in a sealed tube for 5 d hydrogen was evolved and an orange gummy substance produced which contained unchanged $B_{10}H_{14}$ and three other major components comprising isomers of $B_{20}H_{26}$. Within experimental error, these had identical t.l.c. and g.l.c. properties to those of isomers 1, 2, and 4 prepared by photolysis and were given the same numbering. The relative amounts of isomers 1, 2, and 4 produced were *ca.* 1 : 4 : 4, and their combined yield was *ca.* 10%. The yield decreased significantly when other reaction temperatures and times were used. In addition to 1, 2, and 4 there were also yellow products which, in t.l.c. experiments, caused a ' tail ' extending to the point of application. These were not identified, but solubility and ease of chromatographic elution suggested polymeric boranes of relatively low molecular weight; mass spectrometry at high sensitivity showed peaks in the *m/e* 360 region possibly due to $B_{30}H_{38}$.

(*iii*) *Catalytic Preparations.*—(*a*) *Sealed-tube experiments.* The sealed-tube thermolytic preparation of isomers 1, 2, and 4 of $B_{20}H_{26}$ occurred more readily in the presence of catalytic amounts of appropriate substances. Dimethyl sulphide, tetrahydrothiophen, methyl cyanide, and diethylamine, together with their corresponding decaborane adducts $B_{10}H_{12}L_2$,[14] were examined as possible catalysts; diethyl ether, tetrahydrofuran, triethylamine, pyridine, and $B_{10}H_{13}(PPh_2)$ were also tried. Of these, the amines and their derivatives were ineffective although they produced substantial yields of $B_{18}H_{22}$. Of the others, the thioethers, particularly tetrahydrothiophen, were preferred. The best yields (10—15%) of $B_{20}H_{26}$ were obtained after heating for *ca.* 0.5 h at 100 °C in the presence of 1—2.5 mol % of either a thioether or its 2 : 1 adduct with decaborane, $B_{10}H_{12}L_2$. In these catalysed experiments the relative yields of isomers 1, 2, and 4 were *ca.* 1 : 2 : 7.

(*b*) *Catalytic solution experiments.* The results of the lower-temperature sealed-tube thermolyses suggested that the reactions might more conveniently be carried out in solution. When a 0.6 mol dm^{-3} solution of $B_{10}H_{14}$ in toluene was heated for 1 d under reflux in an inert atmosphere (N_2) in the presence of *ca.* 2.5 mol % of thioether a slightly higher yield of $B_{20}H_{26}$ isomers was obtained than in the sealed-tube experiments, with a somewhat greater proportion of isomer 4. Smaller amounts of catalysts yielded additional products and initial experiments indicate that one of these may be a seventh $B_{20}H_{26}$ isomer [R_F *ca.* 0.09 under the standard conditions used; for a possible sixth isomer see section (*i*) above] although insufficient material is at present available for a thorough characterisation.

When pure $B_{10}H_{12}(SMe_2)_2$ or $B_{10}H_{12}(SMe_2)$ [15] were heated under reflux in toluene or mesitylene solution under N_2, $B_{18}H_{22}$ was the only identified higher borane product; under aerobic conditions $B_{20}H_{26}O$ [16] was the only product in the appropriate mass and volatility range. When a solution of $B_{10}H_{14}$ in toluene was heated under reflux with an equimolar amount or an excess of the free-radical initiator dibenzoyl peroxide no higher boranes were obtained; in both cases the $B_{10}H_{14}$ was recovered almost quantitatively.

(*iv*) *Preparations involving the Decaboranyl Grignard-type Reagent.*—Decaboranylmagnesium iodide [17] was allowed to react directly with $B_{10}H_{13}(Cl\text{-}6)$ in diethyl ether solution for 4 h at 0 °C:

$$\mathrm{MeI + Mg \xrightarrow{OEt_2} MgMe(I) \xrightarrow[0\,^{\circ}C]{B_{10}H_{14}} Mg(B_{10}H_{13})I + CH_4}$$

$$\mathrm{Mg(B_{10}H_{13})I + B_{10}H_{13}(Cl\text{-}6) \xrightarrow[0\,^{\circ}C,4h]{OEt_2} B_{20}H_{26} + MgCl(I)}$$

The product contained $B_{10}H_{14}$ and two isomers of $B_{20}H_{26}$, which were numbered 3 and 5 corresponding to their order of elution by t.l.c., column chromatography, and g.l.c. (when compared with isomers 1, 2, and 4 described above). The overall yield of components 3 and 5 was *ca.* 15% and their relative proportion was *ca.* 4 : 1. In addition to these there were three minor components; two were identified (defintely) as methyldecaborane, $B_{10}H_{13}Me$, and (tentatively) as ethyl(methyl)decaborane $B_{10}H_{12}Me(Et)$. The third (R_F *ca.* 0.2 under the standard t.l.c. conditions of the Table) was present in trace amounts, and was tentatively identified as an eighth $B_{20}H_{26}$ isomer but insufficient material has been isolated for a thorough characterisation [for possible sixth and seventh isomers see sections (*i*) and (*iiib*) above].

At higher temperatures or with longer reaction times the yield of $B_{20}H_{26}$ isomers diminished and $B_{18}H_{22}$ was produced. For example, when the ether reaction mixture was heated under reflux for 12 h the principal identified higher borane (>90%) was $B_{18}H_{22}$. Use of $B_{10}H_{13}$(Cl-2) instead of $B_{10}H_{13}$(Cl-6) produced no $B_{20}H_{26}$ isomers; $B_{10}H_{13}Me$, $B_{10}H_{13}I$, and $B_{18}H_{21}Cl$ were the only products in the expected volatility and elution ranges.

(*v*) *Pure Isomers.*—Samples of isomers 1—5 in sufficient quantities (<*ca.* 25 mg) for spectroscopic and other characterisation were obtained as follows: isomer 1, column chromatography of the product of the photolysis reaction; 2, column chromatography and preparative t.l.c. of the product obtained by sealed-tube thermolysis at 180 °C for 5 d; 3, both column and preparative t.l.c. of the product of the Grignard-type reaction; 4, preparative t.l.c. (and also column chromatography) of the product of either the sealed-tube catalytic reaction or the solution catalytic reaction; and 5, as for isomer 3.

The isomers were all colourless solids readily soluble without change in benzene; they were less readily soluble in aliphatic hydrocarbons. We have not as yet unequivocally established that the components labelled as 1, 2, and 4 from the photolytic reaction are precisely identical with those numbered 1, 2, and 4 from the thermolytic reactions: within experimental error, the t.l.c. and g.l.c. retention times of components assigned the same number are identical as are their mass spectra, but at present insufficient material is available for sacrifice in determinations of mixed melting points. Also, although there are differences in R_F values and retention times for the five fractions identified, the possibilities remain that two structurally similar geometric isomers have almost identical chromatographic properties and that a single chromatographic fraction contains more than one isomer.

All five pure isomers were reasonably stable in air. Isomer 1 appears to be indefinitely stable (months) at room temperature but 3 and 5 show some decomposition over this period. The stabilities of isomers 2 and 4 appear to be between these two extremes. In this connection it should be noted that the occurrence[1] of at least one $B_{20}H_{26}$ isomer in technical grade $B_{10}H_{14}$ implies considerable long-term stability. It is also noteworthy that, although several compounds other than $B_{20}H_{26}$ were identified in this work, there has been no evidence for icosaborane(16), $B_{20}H_{16}$,[18] as a product of these reactions. The latter compound was identified as a trace impurity in the technical grade $B_{10}H_{14}$ used,[1] but this was removed before the experiments described above were performed.

(*vi*) *Spectroscopic Properties.*—(*a*) *Mass spectra.* The low-resolution spectra of isomers 1—5 were generally similar with three major ion envelopes at *m/e* 110—122, 220—233, and 233—246; a typical mass spectrum (for isomer 4) is shown in Figure 1. All spectra exhibited the termination of ions at *m/e* 246. High-resolution measurements confirmed the molecular formula $B_{20}H_{26}$ for 1, 3, and 4. The low-resolution spectra of 3 and 5 had very similar ion abundances throughout and were comparable to 4 (Figure 1). Isomers 1 and 2 showed higher abundances in the envelopes at *m/e* 220—233 and 233—246 compared to 3—5. However, as with hydrocarbons containing a similar number of atoms,[19] a change in ion-source temperature of 30—50 °C produced a considerable change in the appearance of the spectra. It is hoped to discuss such effects in the spectra of these and other boranes in a future publication.

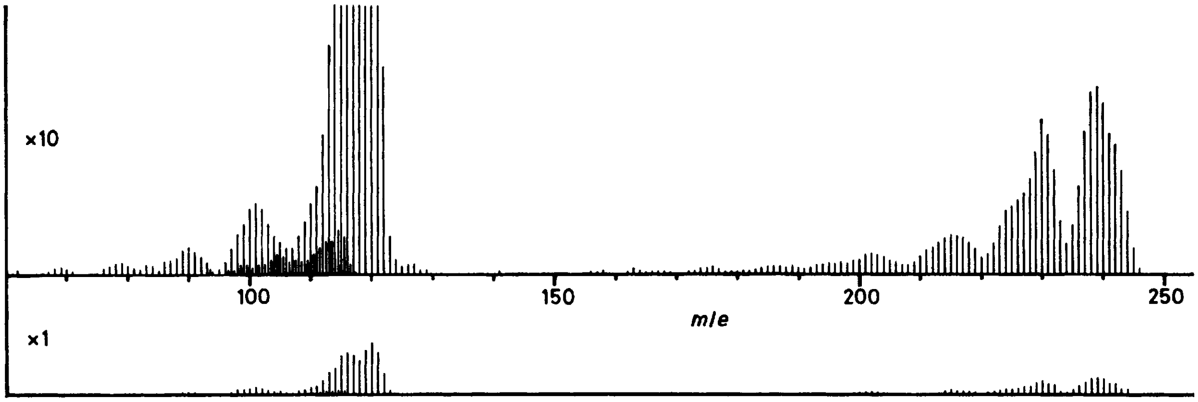


FIGURE 1 Low-resolution 70-eV mass spectrum of $B_{20}H_{26}$, isomer 4, *m/e* 60—250 (MS30 instrument). The spectra of isomers 1—3 and 5 were similar to that of 4. All showed marked variation in fragmentation behaviour with source temperature

High-resolution work on isomer 4 showed that the main fragmentation of $B_{20}H_{26}$ was either by successive hydrogen losses (probably as H_2), giving $[B_{20}H_{22}]^{+\cdot}$ and $[B_{20}H_{14}]^{+\cdot}$ in highest abundance, or by cleavage of the B–B bond. Whilst the loss of hydrogen is typical in borane mass spectra[20] and cleavage of the B–B bond in the molecular-beam mass spectrum of $2,2'-(B_4H_9)_2$ was observed as the predominant path,[21] such B–B cleavage was not very significant in the (conventional) spectrum of $1,1'-(B_5H_8)_2$.[7,22]

(*b*) *U.v. spectra.* The u.v. spectra of cyclohexane solutions of isomers 1—5 all had a maximum absorption in the 270—280 nm region (in common with decaborane), and 3—5 also showed significant absorption maxima in the 220—230 nm region. Molar (linear) absorption coefficients for the 270—280 nm maxima were of the order of 10^2 m^2 mol^{-1}.

(*c*) *Boron*-11 *n.m.r. spectra.* The ^{11}B n.m.r. spectra of isomers 1—5 at 28.9 MHz were all similar to that of $B_{10}H_{14}$, which consists of four resonances of intensity ratio 2 : 4 : 2 : 2 at δ −35.1, +0.8, +11.0, and +12.8 p.p.m. respectively. These are doublets due to coupling $^1J(^{11}B-^1H)$ of 156, 158, 145, and 162 Hz respectively,[23] and the resulting 28.9-MHz

^{11}B spectrum appears as three doublets at −35.1, +0.8, and *ca.* +12 (br) p.p.m., of intensity ratio 2 : 4 : 4 respectively. This was qualitatively similar to the 28.9-MHz spectra of isomers 1—5 in which no isolated singlet resonances were apparent. With complete broad-band proton decoupling the doublet structure was lost (Figure 2) and for 1 and 4 some fine structure became apparent. Line-narrowing techniques gave a trace for 1 which consisted of peaks at δ −34.5, −31.5, +1.1, +11.1, and +14.1 p.p.m., of apparent intensity ratio *ca.* 3 : 1 : 8 : 1 : 7 respectively. With 4 the fine structure was not sufficiently well resolved for satisfactory line-narrowing experiments with the equipment available.

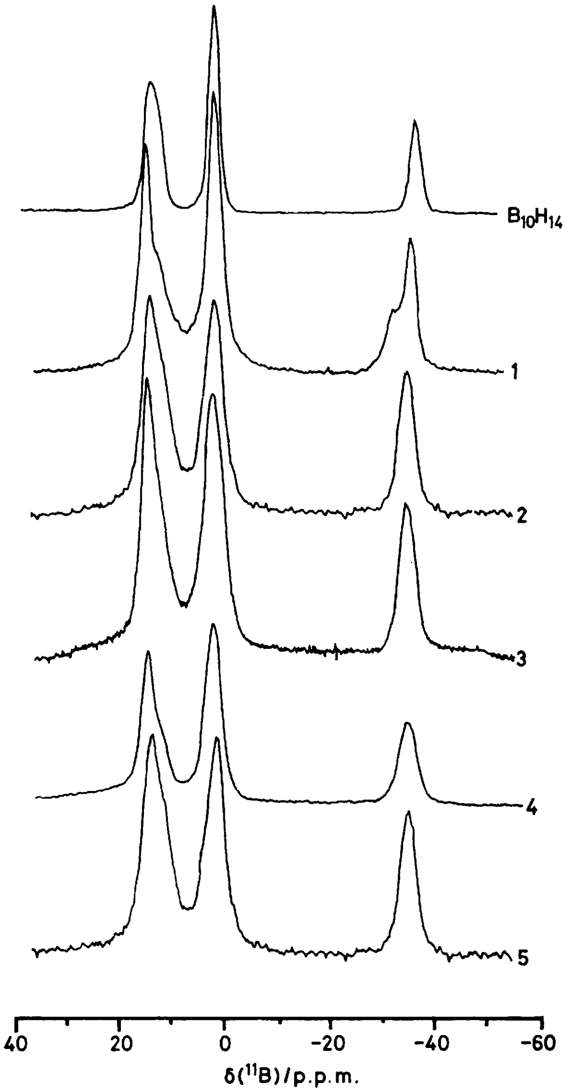


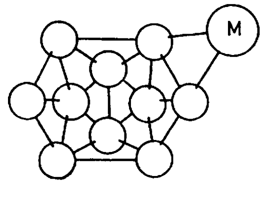
FIGURE 2 28.9-MHz{^{11}B-^{1}H(broad band)} n.m.r. spectra of $B_{10}H_{14}$ (top trace) and $B_{20}H_{26}$, isomers 1—5, in C_6D_6 solution at 25 °C. The effective spectrometer gain varies from trace to trace

DISCUSSION

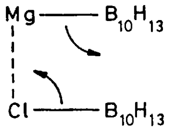
It is probable that all five isomers of icosaborane(26) reported here have the bis(*nido*-decaboranyl) structure. Certainly this is the structure to be expected from the Grignard-type reaction (1) and the similarity of the ^{11}B n.m.r. spectra (Figure 2) and mass spectra (Figure 1) for all the isomers implies that all have similar constitutions. Further, the ^{11}B n.m.r. spectra are all very similar to that of decaborane itself, and the mass spectra all show a high incidence of $[B_{10}H_n]^+$ fragments.

$$Mg(B_{10}H_{13})X + B_{10}H_{13}Cl \longrightarrow (B_{10}H_{13})_2 + MgX(Cl) \quad (1)$$

There has been considerable discussion about the constitution and structure of the so-called decaboranyl Grignard reagent $Mg(B_{10}H_{13})X$ but it is known to react to give substitution at both the 5 and 6 positions.[17] This may imply a structure such as (IV) and there is ample precedence for this type of bonding in metallodecaborane complexes.[24] In any event, reaction of $Mg(B_{10}H_{13})X$ with $B_{10}H_{13}$(Cl-6) might be expected to yield the (5,6′) and (6,6′) isomers of $B_{20}H_{26}$. An S_N2-type process for this would be sterically forbidden but a formally four-centre S_Ni process (V) initiated by electrophilic attack of magnesium on the chlorine atom would give the same result. Isomers 3 and 5 may therefore have the structures 5,6′-$(B_{10}H_{13})_2$ and 6,6′-$(B_{10}H_{13})_2$. This conclusion is however tentative since alkali- and alkaline-earth metal derivatives of more electropositive elements take part readily in halogen–metal exchange processes and one-electron transfer reactions.[25,26] Here this is illustrated by the formation of $B_{10}H_{14}$, $B_{10}H_{13}Me$, $B_{10}H_{12}Me(Et)$, $B_{10}H_{13}I$, and $B_{18}H_{21}Cl$ in the Grignard reaction mixtures. With these mechanisms the (5,5′) and (5,7′) isomers and others could easily result from the 6-chlorodecaborane reaction. This may also be the case if any contribution from an S_N1 type mechanism occurs: the equilibration behaviour of the $[B_{10}H_{13}]^+$ *nido*-decaborane cation is at present unknown.



(IV)



(V)

The problems of structural assignment are compounded for isomers 1, 2, and 4 obtained from the photolytic and thermolytic processes since the mechanistic bases of these reactions both with and without catalysts are still undetermined. In this regard, however, it is known that compounds[27] such as $B_{10}H_{12}(SMe_2)_2$ give monoligand adducts $B_{10}H_{12}(SMe_2)$ on being heated[15,28] and that the *arachno*-nonaborane analogue $B_9H_{13}(SMe_2)$ gives $B_{18}H_{22}$ as a major product on thermolysis.[29,30] We found that heating $B_{10}H_{12}(SMe_2)_2$ or $B_{10}H_{12}(SMe_2)$ under a variety of conditions did not yield $B_{20}H_{26}$; the only identified higher boranes produced in significant quantities were $B_{18}H_{22}$ and, when the reactions were carried out in the presence of oxygen, $B_{20}H_{26}O$. The effectiveness of thioethers compared to amines in catalysing the formation of $B_{20}H_{26}$ from decaborane is similar to that found in the thermolysis of $B_9H_{13}L$ compounds to give $B_{18}H_{22}$.[30] With L = SMe_2 and SEt_2, the adducts produced $B_{18}H_{22}$ readily but with L = pyridine or *p*-toluidine they did not. This was related to the observation of the free reactive intermediate B_9H_{13} from the former compound but not the latter.[30]

The photolytic reaction to produce icosaborane(26) may occur *via* initial homolysis of a B–H bond in decaborane [equation (2a)] followed by hydrogen abstraction from a second decaborane molecule to form a second $B_{10}H_{13}^{\bullet}$ radical [equation (2b)]; $B_{20}H_{26}$ would then be formed by the combination of two $B_{10}H_{13}^{\bullet}$

$$B_{10}H_{14} \xrightarrow{h\nu} B_{10}H_{13}^{\bullet} + H^{\bullet} \tag{2a}$$

$$H^{\bullet} + B_{10}H_{14} \longrightarrow H_2 + B_{10}H_{13}^{\bullet} \tag{2b}$$

$$B_{10}H_{13}^{\bullet} + B_{10}H_{13}^{\bullet} \longrightarrow B_{20}H_{26} \tag{2c}$$

$$2B_{10}H_{14} \xrightarrow{h\nu} B_{20}H_{26} + H_2 \tag{3}$$

radicals [equation (2c)] which would therefore have to be relatively stable. This is a non-chain process and therefore overall quantum yields would be low since abstraction of hydrogen from the solvent would regenerate decaborane itself. Further evidence for the non-chain process is that heating of decaborane solutions with free-radical initiators such as dibenzoyl peroxide failed to produce $B_{20}H_{26}$, although it should also be pointed out that a bimolecular u.v.-catalysed direct reaction as in equation (3) cannot be excluded on present evidence. However, analogous reactions to (2a) and (2c) have been postulated in studies of the photochemical syntheses of B_4H_{10} from B_2H_6 [31] and of 2,2′-$(B_5H_8)_2$ from B_5H_9.[32] Evidence for the boranyl radical $B_{10}H_{13}^{\bullet}$ has been obtained in pulse-radiolysis experiments on $B_{10}H_{14}$ in both hydrocarbon and hydroxylic solvents.[33] This study suggested that the radical was formed *via* a radical anion $[B_{10}H_{14}]^{-\bullet}$ which has also been considered as a possible species in an e.s.r. study of products from γ-irradiation of $B_{10}H_{14}$.[34]

It may be worth noting at this point that component 1, which is one of the major photolysis products, is the only isomer isolated which shows significant deviation in its 28.9-MHz ^{11}B n.m.r. spectrum from that of decaborane itself [35] (Figure 2). Line-narrowing experiments indicated that the spectrum of isomer 1 consisted of resonance peaks at $\delta(^{11}B)$ −34.5, −31.5, +1.1, +11.1, and +14.1 p.p.m. of approximate relative intensity 3 : 1 : 8 : 1 : 7 respectively. These intensity comparisons will have limited meaning, but, on the assumption that the nuclei of those boron atoms which have had terminal B–H bonds replaced by direct B–$B_{10}H_{13}$ linkages will show most change in chemical shift, comparison with the $B_{10}H_{14}$ spectrum [35] implies a structure of isomer 1 which involves 1, 2, or 6 substitution. However, this conclusion is also tentative since the factors which affect small changes in ^{11}B shielding in cage compounds are not understood. It is also known [36] that antipodal effects of substituents on polyhedral boron skeletons can produce changes in chemical shift much larger than those observed here.[*]

Finally, it is of interest to note that although many products other than the $B_{20}H_{26}$ isomers were identified in our reaction mixtures, there was no evidence for the formation of icosaborane(16), $B_{20}H_{16}$. This is surprising since it is quite stable and is formed [18,37,38] in processes which might be expected to have mechanistic similarities to the reactions reported here. It has a characteristic mass spectrum [37,38] and the only incidence of this compound in fact noted in the present work was as an impurity [1] in the technical-grade decaborane(14) from which the pure samples of $B_{10}H_{14}$ were prepared.

EXPERIMENTAL

Decaborane(14) was purified by repeated sublimation (60—80 °C, 0.01 mmHg) [†] before use to remove any icosaboranes and other trace impurities.[1] Bis- and mono-ligand adducts of decaborane, $B_{10}H_{12}L_2$ and $B_{10}H_{12}L$, were made by previously reported routes,[15,28] as were $B_{10}H_{13}$-(Cl-2) and $B_{10}H_{13}$(Cl-6).[39,40] Solvents were distilled before use. Reactions were carried out under anaerobic conditions except where stated; other manipulations were generally carried out in air. Products and intermediate mixtures were stored *in vacuo* or under nitrogen, generally at 0 °C. Melting points were determined in open capillary tubes.

Chromatographic Experiments.—(*a*) *Thin-layer chromatography* (*t.l.c.*). Analytical t.l.c. plates were made in the laboratory as required from silica gel G, type 60 (Merck), and developed using hexane–benzene (75 : 25) to which *ca.* 1% (w/w) glacial acetic acid was added to reduce 'tailing.' Component detection after drying in air was by exposure to iodine vapour whereupon a brown colouration occurred with polyborane species. Typical retention values R_F are given in the Table, although it should be noted that these are particularly susceptible to small changes in eluant composition. Relative yields of components were estimated by comparison of relative 'spot' intensities after prolonged exposure to iodine vapour. Preparative t.l.c. plates were made from the same materials, but with a thickness of *ca.* 1 mm and on a plate of dimensions 20 × 20 cm. The same developing medium was used. Component positions were located either by spraying the peripheral areas of the plate with a solution of I_2 in $CHCl_3$, followed by interpolation, or by brief exposure of the whole plate to iodine vapour until the component positions were just visible. Under these latter conditions the iodine colouration was quickly reversible and the polyboranes of interest remained unchanged. The

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[*] *Note added at proof:* Subsequent work in this laboratory has conclusively established the structures of three isomers of $B_{20}H_{26}$ and some of this work has already appeared in print elsewhere. A single-crystal structure determination by *X*-ray analysis has shown that isomer 1 (photolysis) is 2,2′-$(B_{10}H_{13})_2$ (N. N. Greenwood, J. D. Kennedy, W. S. McDonald, J. Staves, and D. Taylorson, *J.C.S. Chem. Comm.*, 1979, 17) and that isomer 4 obtained by catalytic thermolysis in solution is 2,6′-$(B_{10}H_{13})_2$ (W. S. McDonald, personal communication). Furthermore, the suspected seventh isomer (from catalytic thermolysis in solution) has been shown to be 6,6′-$(B_{10}H_{13})_2$ (S. K. Boocock, N. N. Greenwood, J. D. Kennedy, and D. Taylorson, *J.C.S. Chem. Comm.*, 1979, 16).

[†] Throughout this paper: 1 mmHg ≈ 13.1 × 9.8 Pa, 1 eV ≈ 1.60 × 10^{-19} J.

components were then isolated by shaking with benzene followed by filtration and evaporation.

(b) *Column chromatography*. This was carried out on a column of area 12 cm^2 and length 30 cm using untreated silica gel (100—200 mesh) (*ca.* 200 g) as the stationary phase and hexane–benzene (95 : 5) as eluant. The course of the elution was monitored by t.l.c. (see above) and the components isolated by removal of the solvent in a rotary evaporator at $\leqslant 50$ °C. The order of elution observed was as for the t.l.c. experiments (for typical t.l.c. R_F values see Table), and in a typical experiment $B_{20}H_{26}$ isomer 1 was first detected after *ca.* 3 l of eluting medium had passed at a flow rate of 10—20 cm^3 min^{-1}.

(*c*) *Gas-phase chromatography* (*g.l.p.c.*). A Perkin-Elmer model F30 B was used with a hot-wire detector. Dexsil 300 (3% on Chromosorb W/W) columns (length 2 m, outside diameter 0.25 in) and hydrogen as carrier gas: flow rate 20 ml min^{-1}, oven temperature 190 °C.

Preparative Reactions.—(*a*) *Photolytic reactions*. The u.v. radiation source was a 125-W medium-pressure mercury lamp (Baird and Tatlock Ltd.) contained in a double-walled quartz vessel through which cooling water was passed. This was inserted into the solution containing the reactants in a Pyrex vessel designed so that an inert atmosphere could be maintained over the solution, and so that the outer quartz wall was in contact with the solution. The standard solution volume was 175 cm^3 and this was stirred magnetically throughout the irradiation using a polytetrafluoroethylene-coated follower. A typical experiment was as follows.

Irradiation of a solution of $B_{10}H_{14}$ in cyclohexane (0.05 mol dm^{-3}, 175 cm^3) for 8 h followed by removal of the solvent and remaining $B_{10}H_{14}$ under reduced pressure yielded a waxy off-white solid (*ca.* 0.1 g). The mass spectrum of this had a high-mass limit at *m/e* 246 ($^{11}B_{20}{}^{1}H_{26}$) and analytical t.l.c. showed three major components and three compounds present in trace amounts. Small amounts of the major components were isolated by preparative t.l.c. and all had similar mass spectra (Figure 1) with a high-mass limit within the range *m/e* 246.390 ± 0.003 ($^{11}B_{20}{}^{1}H_{26}$ requires 246.3895); other properties are summarised in the Table. Of the minor components, one eluted rapidly and was isolated by column chromatography; high-resolution mass spectrometry identified it as $B_{10}H_{13}(C_6H_{13})$. The second had a t.l.c. R_F value close to that of $B_{10}H_{14}$ but exhibited the characteristic (Figure 1) $B_{20}H_{26}$ fragmentation pattern. The third component remained uneluted under the t.l.c. conditions used.

(*b*) *Thermolytic reactions: sealed-tube experiments*. Pyrex glass tubes with restricted necks were ' flamed out ' *in vacuo*, filled to atmospheric pressure with nitrogen, and charged with $B_{10}H_{14}$ (*ca.* 0.1 or *ca.* 4.0 g samples in 6 cm^3 or 50 cm^3 tubes respectively) together with the appropriate amounts of catalyst if used; the tubes were then sealed, with the part containing the reactants being maintained at -196 °C, using standard vacuum-line techniques. The tubes were then placed in protective canisters and heated in a thermostatted oven. After completion of the reaction, the tubes were opened (with care, since considerable pressure of H_2 had been generated) and the orange gummy product analysed and separated by t.l.c. and/or column chromatography; a typical procedure was as follows.

Decaborane(14) was removed by sublimation from the product from a pyrolysis carried out at 180—185 °C for 5 d; mass spectrum of the crude residue showed the presence of $B_{20}H_{26}$, and t.l.c. revealed three major components together with a ' tail ' extending from the point of application. The residue was extracted with hexane–benzene (95 : 5) in which the three components were preferentially soluble. Small samples of each of these were isolated by preparative t.l.c. (Table) of the extract, and shown by high-resolution mass spectrometry to be isomers of $B_{20}H_{26}$; they appeared to have identical t.l.c. and g.l.c. properties to the three isomers obtained from the photolytic reactions. The mass spectra of samples of the ' tail ' isolated by preparative t.l.c. showed trace amounts of $B_{20}H_{26}$ and also characteristic borane envelopes in the *m/e* 360 region.

Solution experiments. Decaborane(14) and the appropriate quantity of catalyst were heated under reflux in toluene or xylene solution under nitrogen as discussed in the results section. The product mixture was analysed and separated as in the sealed-tube experiments above. The thermolytic solution reactions of $B_{10}H_{12}(SMe_2)_2$ and $B_{10}H_{12}(SMe_2)$ were conducted similarly.

Gas-phase pyrolysis. Decaborane(14) vapour was passed through a heated region at low pressures in an apparatus similar to that described by other workers for the thermolytic dehydrogenation of $B_9H_{11}S$.[41] A small amount of $B_{20}H_{26}$ condensed on the wall of the tube above the furnace and was shown by t.l.c. analysis to have the same isomer content and proportion as that produced *via* a sealed-tube method (see above). Yields under a variety of temperature and pressure conditions were however very small, and never greater than *ca.* 1%; considerable amounts of dark intractable solids were also produced.

(*c*) *Coupling reactions with Grignard-type reagents.* These were all conducted similarly (see Results section). That giving the best yield of $B_{20}H_{26}$ is described. The decaboranyl Grignard reagent $Mg(B_{10}H_{13})I$ was made essentially according to the literature [17] by the addition of $B_{10}H_{14}$ (1.84 g, 0.015 mol) in diethyl ether (20 cm^3) to a solution of a methyl Grignard reagent, maintained at 0 °C, prepared from methyl iodide (2.13 g, 0.015 mol), magnesium (0.36 g, 0.015 mol), and diethyl ether (20 cm^3). Immediately after gas evolution had ceased (*ca.* 2 min), a solution of 6-chlorodecaborane (2.35 g, 0.015 mol) was quickly added to the solution at 0 °C and the mixture maintained for another 4 h at 0 °C with stirring. Exhaustive removal of the most volatile components *in vacuo* (0.01 mmHg, room temperature $< \theta_c < 40$ °C, 12 h) gave a yellow viscous oil of which the mass spectrum showed the characteristic fragmentation pattern of $B_{20}H_{26}$ (Figure 1).

Analysis of the mixture by t.l.c. (Table) showed three major and three minor eluted components, together with a ' tail ' extending from the point of application. The mass spectra of samples scraped from the t.l.c. plates in this ' tail ' area exhibited peaks up to *m/e ca.* 360. There was also a substantial uneluted spot at the point of application. Preparative t.l.c. and high-resolution mass spectrometry identified the three major components as $B_{10}H_{14}$ and two isomers of $B_{20}H_{26}$ which were numbered 3 and 5. Two of the minor components were similarly identified as $B_{10}H_{13}Me$ and $B_{10}H_{12}(C_3H_8)$ [$B_{10}H_{12}Me(Et)$?]. The third component was present in trace amounts and gave a very weak mass spectrum which was otherwise similar to the other $B_{20}H_{26}$ isomers (*e.g.* Figure 1). Some EtI at *m/e* 156 was also present in the crude reaction product. When the reaction was carried out for longer periods, or (and especially) at higher temperatures, the yields of $B_{20}H_{26}$ were reduced and $B_{18}H_{22}$ was produced preferentially. Use of $B_{10}H_{13}$(Cl-2) instead of $B_{10}H_{13}$(Cl-6) in the above procedure produced no icosaboranes, although preparative t.l.c. and high-resolution mass spectrometry showed that $B_{10}H_{13}Me$, $B_{10}H_{13}I$, and $B_{18}H_{21}Cl$ were present.

Spectroscopic Measurements. (*a*) *Mass spectra.* These were generally recorded on an A.E.I. MS30 instrument at an ionising voltage of 70 eV. The samples were introduced *via* the solid introduction probe. Source temperatures were usually in the range 100—150 °C and probe temperatures 50—100 °C. Molecular formulae were confirmed by high-resolution mass measurement and by intensity comparison with their isotopomers using a presumed $^{11}B : ^{10}B$ ratio of 4 : 1. Some work on isomer 4 was carried out on an A.E.I. MS9 instrument using a DS50 data-system.

(*b*) *N.m.r. spectra.* 28.9-MHz ^{11}B and ^{11}B-{^{1}H(broad band)} spectra were recorded at 25 °C in the pulsed (Fourier-transform) mode using a modified Bruker HX90 spectrometer; C_6D_6 was used as solvent and also provided the lock signal. Generally a 90° pulse was used and a pulse repetition time of *ca.* 0.2 s. Other conditions were chosen so that the digital resolution was *ca.* 6 Hz and the smoothing functions used did not significantly alter the natural linewidths. With the small quantities of solute available, typically $>$20 000 free-induction decay signals were collected to produce the signal-to-noise ratios exhibited by the spectra in Figure 2. Boron-11 chemical shifts are quoted in p.p.m. to high frequency (low field) of $OEt_2{\cdot}BF_3$, and it should be noted that in this sign convention the nuclear shielding and chemical shifts are of opposite sign.

(*c*) *U.v. spectra.* U.v. spectra were recorded in cyclohexane solution in cells of 1 cm pathlength using a Unicam SP 8000 instrument.

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