477. *Thermochemistry of Organoboron Compounds. Part VI.* The Heats of Reaction of Diborane with Olefins.*

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The heats of addition of diborane to the olefins hex-1-ene, hept-1-ene, oct-1-ene, and oct-2-ene have been measured in an isothermal-jacket calorimeter. The heats of reaction were used in conjunction with the already-known heats of formation of diborane and of the olefins to derive values for the heats of formation of the trialkylboranes trihexylborane, triheptylborane, trioctylborane, and tri-s-octylborane.

Brown and Subba Rao[1] recently reported that diborane adds to olefins rapidly at room temperature in the presence of organic ethers to form trialkylboranes in high yields:

$$6RCH{:}CH_2 + B_2H_6 \longrightarrow 2(RCH_2{\cdot}CH_2)_3B \qquad (1)$$

The thermochemistry of this reaction provides a route to the heats of formation of the trialkylboranes since the heats of formation of diborane and of the olefins are already well established. Furthermore, the measured heats of combustion of alkylboranes are difficult to interpret accurately because of the tendency towards incomplete combustion of the boron to boric oxide. The alternative route to heats of formation through heats of hydroboronation therefore seemed well worthy of investigation.

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* Part V, *J.*, 1954, 3930.

[1] Brown and Subba Rao, *J. Org. Chem.*, 1957, **22**, 1136; *J. Amer. Chem. Soc.*, 1959, **81**, 6428.

An account of some preliminary studies by Bennett and Pedley on the heats of hydroboronation of hex-1-ene, oct-1-ene, and oct-2-ene was presented at the Symposium on Thermodynamics at Wattens in 1959.[2]

EXPERIMENTAL

Preparation of Compounds.—Diborane. This was prepared from sodium borohydride and boron trifluoride etherate in diethylene glycol dimethyl ether (" Diglyme "), as described by Brown and Rao.[1] The diborane gas was purified by low-temperature bulb-to-bulb fractional distillation in an all-glass grease-free vacuum system. Samples of diborane were freshly prepared before each hydroboronation in quantities of 100—150 ml., sufficient for a single calorimetric experiment only. The diborane samples were used immediately after preparation.

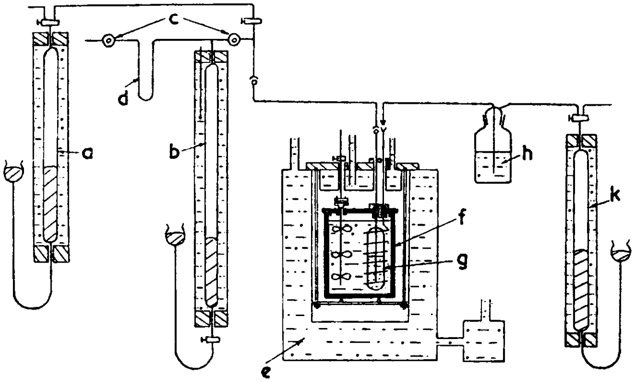
Diethylene glycol dimethyl ether. This, supplied by the Ansul Chemical Co., was purified by distillation over calcium hydride under reduced pressure (20 mm., glass-ring packed column): the main fraction was redistilled over lithium aluminium hydride and the purified product stored under dry oxygen-free nitrogen.

*Hex-*1*-ene.* The hexene was supplied by the N.C.L., D.S.I.R., Teddington, and was stated to be >99·9% pure hex-1-ene. A further sample, supplied by Light and Co., was purified as described under hept-1-ene.

*Hept-*1*-ene.* This material, supplied by Light and Co., was purified by distillation from sodium, followed by careful fractional distillation using an 18-in. gauze-packed column.

*Oct-*1*-ene and oct-*2*-ene.* These were also supplied by Light and Co. and were purified in the same manner as hept-1-ene. Measurements of the purity of the olefins were made by Mr. J. V. Davies, using the melting-point calorimeter of Brooks and Pilcher.[3] The hept-1-ene had a purity of 99·28 ± 0·1 mole %, and oct-1-ene a purity of 98·4 ± 0·2 mole %. The oct-2-ene contained both the *cis*- and the *trans*-form, but the relative proportions were not determined.

FIG. 1. a, Nitrogen burette; b, Diborane burette; c, Springham valves; d, U-Tube; e, Thermostat jacket; f, Calorimeter can; g, Reaction vessel; h, Acetone-filled trap; k, Exit-gas burette.



Calorimeters. A calorimetric experiment was carried out by measuring the temperature change of the calorimeter when a carefully measured volume of diborane gas was passed into a solution of olefin in Diglyme solvent contained in a Pyrex-glass vessel inside the calorimeter. The calorimeter was of the constant-temperature environment type, and is shown schematically in Fig. 1. The calorimeter can (polished copper; capacity 1·4 l.) was placed centrally in the well of a surrounding jacket thermostat, maintained at 25·0°. The roof of the thermostat well was closed by a thermostatted lid, also maintained at 25°.

The calorimeter can was fitted with a propeller stirrer, an electric heater for calibration purposes, and a shielded thermistor element (Stantel F/2311) acting as resistance thermometer. In each experiment the can was charged with 1200 g. of water, and sealed with a close-fitting copper lid. This was slotted to take the inlet and exit tubes of the glass reaction vessel, and to support the vessel firmly in position inside the can.

The experimental procedure was as follows: the reaction vessel (capacity 50 ml.) was

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[2] Skinner, Bennett, and Pedley, Symposium on Thermodynamics, Paper 3: Wattens, Aug. 1959.
[3] Brooks and Pilcher, *J.*, 1959, 1535.

cleaned, thoroughly swept out with pure dry nitrogen, and charged with 35 ml. of " Diglyme " solvent. The vessel was fitted in position inside the calorimeter can, which, in turn, was placed centrally in the thermostat jacket. The calorimeter stirrer was set in motion, and the inlet and exit tubes to the reaction vessel were connected through ball-and-socket joints to the inlet and exit gas lines. Nitrogen from a storage burette was passed *via* the inlet gas line into the reaction vessel, escaping *via* the exit gas line to an acetone-filled trap backing the calorimeter, and thence to a gas burette. The nitrogen was passed for several minutes in order thoroughly to sweep trapped air from the system.

Diborane from the preparative apparatus was transferred by vacuum distillation to a U-tube, cooled by liquid air, and the frozen diborane subjected to high-vacuum pumping for several minutes to remove traces of hydrogen gas impurity. The sample was then cut off from the vacuum-line and preparative apparatus by closing a Springham greaseless valve in the connecting-line (Springham valves were found to be satisfactory for work with diborane). The diborane was allowed to warm and expand as a gas into the storage gas-burette.

At this stage the solvent in the calorimeter reaction vessel was *pretreated* with diborane by forcing a measured volume of the gas from the burette into it. This pretreatment was very necessary to remove traces of moisture and other hydroxylic impurities (*e.g.*, glycol residues) present in the diethylene glycol dimethyl ether. Diborane escaping from the reaction vessel was absorbed in the acetone trap; the hydrogen gas formed by reaction of the diborane with impurities in the solvent passed the trap to be collected in a gas-burette on the exit side. A slight evolution of hydrogen gas indicated a clean dry sample of solvent; a moist sample, on the other hand, required an extensive pretreatment before hydrogen evolution ceased. After the diborane pretreatment the solvent was swept out with nitrogen to remove diborane from the system.

The inlet to the reaction vessel was now opened at the ball-joint, and 6—7 ml. of olefin was introduced into the solvent from a micropipette. The acetone trap was removed and replenished with fresh acetone. The joints were re-made, and the system was swept out once more with dry nitrogen.

The calorimeter was allowed to approach the desired starting temperature and to reach a steady thermal state. Measurements of the thermistor resistance were then taken at regular time intervals to establish the pre-rating characteristics. A measured volume of diborane was now slowly forced through the reaction mixture, and the thermistor resistance recorded throughout the reaction period. At the end of the reaction (after passage of *ca.* 80 ml. of diborane), the system was swept out with a measured volume of nitrogen to clear the inlet lines of diborane, following which the thermistor resistance was recorded for a further period of *ca.* 20 min. to establish the after-rating characteristics.

The amount of diborane reacting during the reaction period in the calorimeter was determined from the volume of diborane added, less that escaping the reaction zone, subsequently to be absorbed in the exit acetone trap. This latter was determined by hydrolysing the contents of the trap at the end of the reaction, and estimating the boric acid produced. Generally, less than 2% of the added diborane escaped unchanged from the reaction zone.

In addition to the heats of hydroboronation, measurements were also made of the heats of solution of products and reactants in diethylene glycol dimethyl ether. A small Dewar vessel calorimeter (150 ml. capacity), fitted with a flange and closed by a brass headpiece, through which passed a rotary stirrer, thermistor element, calibration heater, and solution pipette, was used to measure the heats of mixing of the olefins with the solvent. This calorimeter was not suitable for measuring heats of solution of the alkylboranes, which, because of their extremely ready oxidation by air, had to be handled in a completely sealed, nitrogen-filled system. The calorimeter used is shown in Fig. 2. The Pyrex reaction vessel (200 ml. capacity) contained a stainless-steel stirrer, fitting through a greased ball-joint, an ampoule-holder and breaking-device, and a central well to accommodate the thermistor element.

The solution vessel was placed centrally in a copper can and surrounded completely by a thermally insulating polyurethane foam (formed in *situ* and allowed to set hard).

In a measurement of the heat of solution, a glass ampoule containing a known weight of pure alkylborane was broken under the surface of 200 ml. of solvent in the solution vessel, and the resulting change in resistance of the thermistor element recorded. Before the bulb was broken, the solvent was pretreated with a small amount of diborane gas in order to destroy traces of peroxidic material or of dissolved oxygen, and then thoroughly swept out with pure nitrogen. This pre-treatment was necessary—otherwise the mixing (which is actually an endothermic process) was masked by spurious exothermic oxidation side-reactions.

Calibration.—The reaction calorimeter (Fig. 1) was calibrated electrically by the substitution method. The mean value (9 calibration experiments) of the calibration constant, k, was 94·22 ± 0·15—where $k \log R_i/R_f$ = heat evolved in calories, and R_i, R_f are the initial and final resistances of the thermistor ($\log R_i/R_f \propto \Delta T$ = corrected temperature rise of the calorimeter). The heat exchange between calorimeter and jacket was evaluated from the resistance–time curves by applying Regnault and Pfaundler's method.

The solution calorimeters were also calibrated electrically.

Units and Assumed Data.—Heat quantities are given throughout in thermochemical calories, defined by 1 cal. ≡ 4·1840 abs. joules. All measurements were made so that the final calorimeter temperature was 25° C.

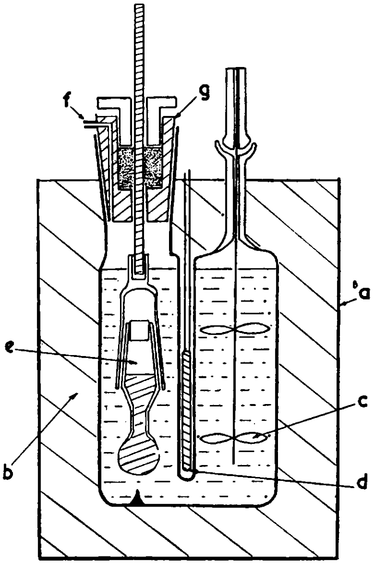

FIG. 2. a, Copper can; b, Foam insulation; c, Steel stirrer; d, Thermistor; e, Ampoule and holder; f, Nitrogen inlet; g, Brass cone valve.

To calculate the mass of diborane from the volume used, it was assumed that 1 mole of *pure* diborane occupies 22·15 l. at N.T.P. The purity of the diborane samples used in each experiment was not measured, but analyses were made of selected diborane samples (by hydrolysing a measured volume, and estimating the boric acid produced) which indicated a purity range of 99—99·5%. We have assumed, somewhat arbitrarily, that 1 mole of diborane was contained in 22·4 l. (at N.T.P.) of the gas taken from the diborane burette.

The value adopted for the standard heat of formation of diborane is that reported by Prosen, Johnson, and Pergiel [4] from measurements of the heat of decomposition into amorphous boron and hydrogen gas, ΔH_f° (B_2H_6, gas) = 6·73 ± 0·52 kcal./mole.

The heats of formation of the liquid olefins were obtained from heat of combustion and heat of vaporization data given in the A.P.I. Tables (Project 44), published by the Carnegie Institute of Technology, Pittsburgh:

ΔH_f° (hex-1-ene, liq.) = −17·30 kcal./mole
ΔH_f° (hept-1-ene, liq.) = −23·41 kcal./mole
ΔH_f° (oct-1-ene, liq.) = −29·52 kcal./mole

The heat of formation values for *cis-* and *trans*-oct-2-ene were estimated on the basis of the known values for hept-2-ene and hex-2-ene,

ΔH_f° (*cis*-oct-2-ene, liq.) = −31·12 kcal./mole
ΔH_f° (*trans*-oct-2-ene, liq.) = −32·12 kcal./mole

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[4] Prosen, Johnson, and Pergiel, *J. Res. Nat. Bur. Stand.*, 1958, **61**, 247.

The error limits associated with the ΔH_f° values of the olefins are of the order of $\pm 0{\cdot}2$—$0{\cdot}3$ kcal./mole.

Test of the Calorimeter.—A test of the calorimeter was made by measuring the heat of hydrolysis of diborane gas. The reaction vessel was filled with 40 ml. of water, and a measured volume of diborane passed through it. About 80% of the diborane was hydrolysed in the reaction vessel, the remainder being carried away by the hydrogen evolved, subsequently to be absorbed outside the calorimeter in two acetone-filled traps. The amount of diborane hydrolysed in the calorimeter was determined by estimating the boric acid formed in the reaction vessel. The measured heat of hydrolysis (based on the amount of boric acid formed in the calorimeter) was $\Delta H = -112{\cdot}5 \pm 1{\cdot}5$ kcal./mole, which is in very fair agreement with the more precise measurements made by Prosen, Johnson, and Pergiel[5] and by Gunn and Green.[6]

RESULTS

Hex-1-ene.—The reaction occurring in the calorimeter was assumed to follow the equation:

$$B_2H_6(\text{gas}) + (m + 6)C_6H_{12} \text{ ("Diglyme" soln.)} \longrightarrow 2B(C_6H_{13})_3 + mC_6H_{12} \text{ ("Diglyme" soln.)} \quad . \quad . \quad (2)$$

The observed heat of reaction, $\Delta H_{\text{obs.}}$, refers to this system; in most experiments an approximately twofold excess of hexene was used.

The amount of reaction in each experiment was determined from the amount of diborane consumed in the reaction vessel. Reaction (2) is rapid, and only a small fraction of the diborane added escaped the reaction zone. As already stated, the "Diglyme" solvent was pretreated with diborane before the calorimetric experiment proper in order to remove impurities particularly water, which would otherwise compete with reaction (2). As a check on this, any hydrogen formed during the reaction period and escaping from the reaction vessel and backing acetone trap was collected in the exit gas-burette. Since 1 ml. of diborane produces 6 ml. of hydrogen on hydrolysis, the volume of gas evolved during the reaction periods gave a sensitive indication of the extent of competing hydrolysis reactions. In the event of a copious evolution of gas, the experiment was discounted; small corrections were made to $\Delta H_{\text{obs.}}$ to allow for the thermal effect of the competing side-reactions, if necessary (based on $\Delta H = -112$ kcal. per 6 moles of hydrogen evolved). The adjusted values are listed as $\Delta H_{\text{corr.}}$.

Separate measurements were made of the heats of solution of hexene and of trihexylborane in "Diglyme." From the measured heats of solution, adjustments were made to $\Delta H_{\text{corr.}}$ in order to derive the heat of the idealised reaction, ΔH_2:

$$B_2H_6 \text{ (gas)} + 6C_6H_{12} \text{ (liq.)} \longrightarrow 2B(C_6H_{13})_3 \text{ (liq.)} \quad . \quad . \quad . \quad . \quad (3)$$

A representative selection from the experimental results is presented in Table 1.

TABLE 1. *Reaction of diborane with hex-1-ene.*

	1	2	3	4
Diborane added (mmoles)	3·569	3·226	3·690	3·801
Diborane escaping reaction	0·069	0·024	0·027	0·027
Diborane consumed	3·500	3·202	3·663	3·774
Hexene added (mmoles)	47	32	28	33
Hexene excess	26	13	6	10
Gas evolved (ml.)	nil	nil	nil	nil
$\Delta H_{\text{obs.}}$, kcal./mole B_2H_6	−138·7	−136·6	−135·3	−136·6
$\Delta H_{\text{corr.}}$, kcal./mole of B_2H_6	−138·7	−136·6	−135·3	−136·6
$\Delta H_{\text{soln.}}$, kcal./6 moles of hexene	3·8	4·1	4·2	4·1
$\Delta H_{\text{soln.}}$, kcal./2 moles of BHx_3	3·8	3·8	3·8	3·8
ΔH_2, kcal./mole of B_2H_6	−138·7	−136·3	−134·9	−136·3

Mean $\Delta H_2 = -136{\cdot}6$ kcal./mole. Standard deviation of mean = $\pm 0{\cdot}8$ kcal./mole.

Hept-1-ene, Oct-1-ene, and Oct-2-ene.—Selected results on the hydroboration of hept-1-ene, oct-1-ene, and oct-2-ene are presented in Table 2. The oct-2-ene used in these experiments was a purified commercial sample, containing the *cis*- and the *trans*-isomer in proportions that were not determined.

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[5] Prosen, Johnson, and Pergiel, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 43.
[6] Gunn and Green, *J. Phys. Chem.*, 1960, **64**, 61.

Individual corrections to heats of solutions are not listed in Table 2. The measurements on trihexylborane and hexene in " Diglyme " showed that $\Delta H_{\text{soln.}}$ of trihexylborane is approximately equal to $\Delta H_{\text{soln.}}$ of three moles of hexene—so that, in effect, the corrections to the heats of solution needed to obtain ΔH_2 from $\Delta H_{\text{obs.}}$ cancel out. A cancellation of the corrections has been *assumed* for the examples listed in Table 2.

TABLE 2. *Reaction of diborane with hept-*1*-ene, oct-*1*-ene, and oct-*2*-ene.*

	Hept-1-ene			Oct-1-ene		
Diborane added (mmoles)	3·703	4·015	4·033	3·547	3·641	3·609
Diborane escaping	0·040	0·050	0·060	0·025	0·026	0·030
Diborane consumed	3·663	3·965	3·976	3·522	3·615	3·579
Olefine added (mmoles)	32	34	34	38	33	34
Olefin excess	10	10	10	16	11	12
Gas evolved (ml.)	—	3	1	6	—	12
$\Delta H_{\text{obs.}}$ (kcal./mole of B_2H_6)	−135·5	−135·8	−134·8	−134·5	−136·6	−135·3
$\Delta H_{\text{corr.}}$	−135·5	−135·9	−134·8	−134·8	−136·6	−135·8
ΔH_2, mean value		−135·4			−135·7	
Standard deviation		±0·4			±0·5	

	Oct-2-ene				
Diborane added (mmoles)	3·922	3·806	2·323	3·788	3·739
Diborane escaping	0·044	0·047	0·010	0·045	0·050
Diborane consumed	3·878	3·759	2·314	3·743	3·689
Olefine added (mmoles)	32	35	30	33	33
Olefin excess	9	12	16	10	11
Gas evolved (ml.)	12	22	—	—	12
$\Delta H_{\text{obs.}}$ (kcal./mole of B_2H_6)	−116·0	−116·0	−118·4	−115·4	−115·4
$\Delta H_{\text{corr.}}$	−116·1	−116·2	−118·4	−115·4	−115·5
ΔH_2, mean value			−116·3		
Standard deviation			±0·55		

DISCUSSION

The ΔH_2 values in Tables 1 and 2, together with the accepted heats of formation of diborane and of the olefins, provide the data needed to calculate the heats of formation of the alkylboranes through the thermochemical equation appropriate to the idealized hydroboronation reaction, *viz*:

$$\Delta H_f^\circ \text{ (trialkylborane, liquid)} = \tfrac{1}{2}\Delta H_f^\circ \text{ } (B_2H_6\text{, gas}) + 3\Delta H_f^\circ \text{ (olefin, liquid)} + \tfrac{1}{2}\Delta H_2 \quad . \quad . \quad . \quad (4)$$

The values calculated from eqn. (4) are listed below: the limits of error recorded represent the uncertainty intervals taking into account the spread in the experiment results, the standard deviation in calibration experiments, and the uncertainties in assumed data on heats of formation.

	kcal./mole		kcal./mole
ΔH_f° (trihexylborane, liq.)	−116·83 ± 2·2	ΔH_f° (trioctylborane, liq.)	−153·04 ± 1·8
ΔH_f° (triheptylborane, liq.)	−134·56 ± 1·7	ΔH_f° (tri-s-octylborane, liq.)	−149·25 ± 3·5

The value calculated for boron tri-s-octylborane is based on the assumption that the oct-2-ene contained equal amounts of the *cis*- and the *trans*-form: the uncertainty interval makes allowance for this lack of knowledge of the true composition.

Measurements of the heats of combustion of triethylborane and of tributylborane have been reported in a preliminary communication by Prosen and Johnson.[7] The combustion data lead to $\Delta H_f^\circ = -83{\cdot}9$ kcal./mole for liquid tributylborane, and $\Delta H_f^\circ = -46{\cdot}8$ kcal./mole for liquid triethylborane. Accepting the constant heat of combustion increment per methylene group obtained from combustion studies on liquid hydrocarbons containing six or more carbon atoms, and adding this to Prosen and Johnson's combustion data on tributylborane, yields an estimated $\Delta H_f^\circ = -120{\cdot}5$ kcal./mole for liquid trihexylborane.

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[7] Prosen and Johnson, reported by Wagman, Munson, Evans, and Prosen, *N.B.S. Report*, No. 3456, 1954.

Prosen and Johnson have not stated the error limits attached to their preliminary combustion studies on tributylborane: they may be substantial, however, because of the difficulties of complete analysis of the products of combustion, and a figure as large [8] as ±3 kcal./mole is possible. The estimated ΔH_f° for trihexylborane can, in this event, be said to agree (within the combined error limits of both investigations) with the value reported here. A more detailed comparison must await the complete account of the measurement of heats of combustion.

Haseley, Garrett, and Sisler [9] have recently reported measurements of the heat of combustion in a bomb calorimeter of liquid tri-s-butylborane, from which they derived ΔH_f° [B(s-butyl)$_3$, liq.] $= -75 \pm 6$ kcal./mole. From the difference between this and the heat of formation of tributylborane given by Prosen and Johnson, the isomerization process

$$\mathrm{BBu^n_3} \longrightarrow \mathrm{BBu^s_3} \qquad (5)$$

is calculated to be endothermic, $\Delta H = 8{\cdot}9$ kcal./mole: the uncertainty in ΔH, however, is possibly as large as ΔH itself. The present investigation leads to a similar conclusion in respect of the isomerization

$$\mathrm{BOct^n_3} \longrightarrow \mathrm{BOct^s_3} \qquad (6)$$

for which ΔH is calculated to be 3·8 kcal./mole—but once again, the uncertainty is as large as ΔH itself. Nevertheless, the possibility that chain branching in alkylboranes leads to diminished thermochemical stability relative to the n-alkylboranes is interesting. Brown and Subba Rao [10] have already drawn attention to the ready isomerization of branched-chain alkylboranes to form, as they say, the " more stable " tri-n-alkylboranes (*i.e.*, with boron at the terminal position in the alkyl chain).

An isomerization process of paraffin hydrocarbons similar to scheme (5) from the steric point of view is the change:

$$\text{4-}n\text{-propylheptane} \longrightarrow \text{2,4-dimethyl-3-isopropylpentane} \qquad (7)$$

In this case, the available data on heats of formation indicate that the isomerization is exothermic, $\Delta H = -1{\cdot}6$ kcal./mole (reactants in the liquid state). Hence, in so far as similar isomerization processes of trialkylboranes are *endothermic*, this would not seem to be due simply to steric factors.

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[8] W. H. Johnson, personal communication.

[9] Haseley, Garrett, and Sisler, *J. Phys. Chem.*, 1956, **60**, 1136.

[10] Brown and Subba Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 6434.