Table I. Oxidations by Potassium Permanganate in Benzene (25°)

Starting material	Product[a]	Isolated yields, %	Stoichiometry	
			Obsd	Theory[c]
trans-Stilbene	Benzoic acid	100	2.68	2.67
Cyclohexene	Adipic acid	100	2.71	2.67
α-Pinene	Pinonic acid	90		
3-Methylenecyclobutanecarboxylic acid	3-Oxocyclobutanecarboxylic acid	*b*		
1-Heptanol	Heptanoic acid	70		
Benzyl alcohol	Benzoic acid	100	1.31	1.33
Benzhydrol	Benzophenone	100	0.71	0.67
Toluene (solvent)	Benzoic acid	78		
p-Xylene (solvent)	Toluic acid	100	2.00	2.00
Benzaldehyde	Benzoic acid			

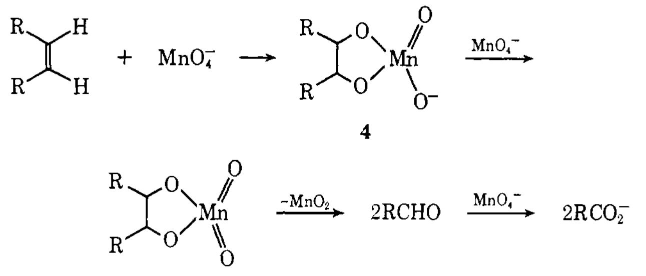
[a] The initially formed products were the potassium salts of the acids. [b] Clean but incomplete oxidation occurs. The starting material and product were precipitated by the KOH formed during the reaction. [c] Theory for corresponding aqueous oxidations.

within minutes, whereas alkylbenzenes such as toluene require up to 72 hr for complete reaction. For preparative reactions, it is more convenient to bypass prior complex formation. The crown ether is used in catalytic amounts, but efficient and abrasive stirring is needed to sustain solubilization of the oxidizing agent since the manganese dioxide formed coats the unreacted potassium permanganate. As an example, 12.2 g (68 mmol) of *trans*-stilbene, 28.6 g (181 mmol) of potassium permanganate, 2.4 g (6 mmol) of dicyclohexyl-18-crown-6, and 1.0 l. of benzene were rolled in a ball mill for 2 hr.[7] The product potassium benzoate was filtered along with manganese dioxide and then was dissolved in 5% sodium hydroxide solution. After filtration of manganese dioxide, the aqueous solution was extracted with ether to remove traces of crown ether. Acidification yielded 16.0 g (97%) of pure benzoic acid.

The mechanism of the oxidations in benzene is not known, but we speculate the reaction sequence for olefins (Scheme I) is similar to that generally accepted for aqueous systems.[8-10] In the first place the stoichiometries of the oxidations in benzene are the same as the corresponding aqueous oxidations (Table I). The reaction can be considered as initiated by [2 + 4] electrocyclic addition of permanganate ion to the olefinic π bond to form the usual manganate ester ion **4**. Attempts to observe **4** directly by ^{55}Mn and ^{1}H nmr experiments were unsuccessful, presumably because oxidation of **4** to **5** by electron transfer is rapid. The fourfold decrease in the relative rates of oxidation of cyclopentene (4.0), trimethylethylene (2.3), tetramethylethylene (2.0), and cyclohexene (1.0), which were determined by competition studies, is small but consistent with the olefin acting as an electron donor.[11]

Scheme I

$$3RCH{=}CHR + 8KMnO_4 \longrightarrow 6RCO_2K + 8MnO_2 + 2KOH + 2H_2O$$



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5

In aqueous systems at high pH, diols are formed by hydrolysis of **4**, whereas at low pH ketols result from **5**. These products are not formed under our conditions even though low concentration of water may be produced. It is postulated that **5** fragments to manganese dioxide and two molecules of aldehyde. Such a [2 + 2 + 2] cheletropic change can be visualized as a thermally allowed ground-state process. The steps leading to aldehyde and carboxylate ion are rapid compared to the initial addition of permanganate ion. Aldehyde formation could not be suppressed even when the olefin was used in large excess; and the aldehyde, unaccompanied by further oxidation to acid, was detected only at very low olefin conversion.

We are developing the scope of these oxidations since this reagent should be especially adaptable where water solubility is a major limitation of where mild conditions are necessary. Since the oxidations proceed cleanly as exemplified by the stoichiometry values, the reagent has analytical utility. In particular, the degree of end-group unsaturation in water-insoluble polymers has been demonstrated. The oxidation of olefins to diketones using potassium permanganate in acetic anhydride[12] and the oxidation of olefins to acids by phase-transfer catalysis[13] provide other recent examples of permanganate oxidations in organic solvents.

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Received February 16, 1972

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(7) Although we have experienced no hazards from ball milling potassium permanganate, benzene, and organic substrates, caution should be exercised in such experiments.

(8) K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

(9) G. Wagner, *J. Russ. Chem. Soc.*, **27**, 219 (1895).

(10) J. Boeseken, *Recl. Trav. Chim. Pays-Bas*, **41**, 199 (1922); **47**, 638 (1928).

(11) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(12) K. B. Sharpless, R. F. Lauer, O. Repic, A. Y. Teranishi, and D. R. Williams, *ibid.*, **93**, 3303 (1971).

(13) C. M. Starks, *ibid.*, **93**, 195 (1971); N. A. Gibson and I. W. Hoskings, *Aust. J. Chem.*, **18**, 123 (1965).

Monomeric Dialkylboranes

Sir:

We wish to report the first identification of monomeric dialkylboranes with characteristic infrared ab-

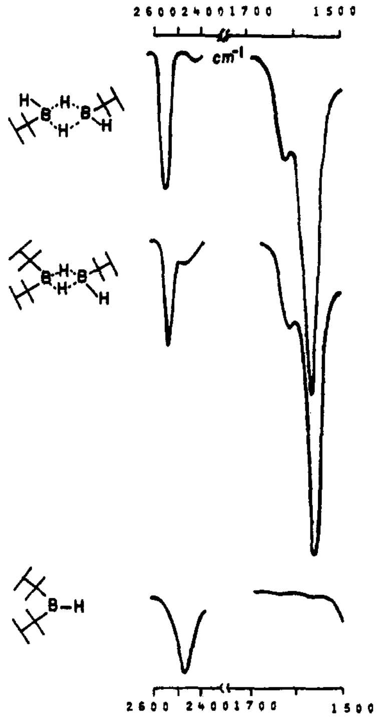
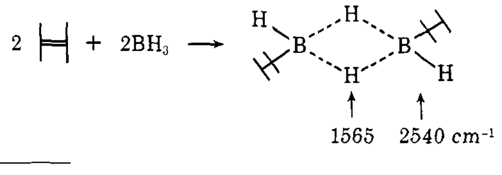


Figure 1. Infrared spectra of dithexyldiborane, trithexyldiborane, and dithexylborane.

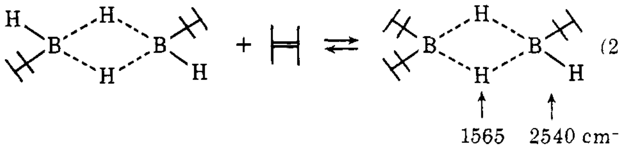
sorption at 2470 cm^{-1} and the essential absence of the usual boron–hydrogen bridge absorption in the 1600–1500-cm^{-1} region exhibited by tetraalkyldiboranes.

All dialkylboranes studied previously exist as the dimers, *i.e.*, as the tetraalkyldiboranes, either under neat conditions or in various solvents, such as cyclohexane and tetrahydrofuran. Thus, pure dialkylboranes, such as dimethylborane,[1] di-*n*-butylborane,[2] diisobutylborane,[2] disiamylborane,[3] dicyclohexylborane,[3] bis(2-methylcyclohexyl)borane,[3] diisopinocampheylborane,[3] borinane,[4a] 3,5-dimethylborinane,[4b] and 9-borabicyclo[3.3.1]nonane,[5] all exhibit the strong absorption characteristic of the B- - -H- - -B stretching in the 1600–1500-cm^{-1} region and no absorption characteristic of the terminal B–H stretching in the 2600–2400-cm^{-1} region.[6]

The hydroboration of tetramethylethylene (TME) with borane in the 1:1 molar ratio produces 1,2-dithexyldiborane rapidly and cleanly at 0° (eq 1).[3] In the presence of an excess of TME, further hydroboration takes place.[7] When the thexyl to boron ratio in the product is 3:2,[8] the ir features are basically the same as those of 1,2-dithexyldiborane, except that the intensity of the 2540-cm^{-1} band has diminished and a very minor band appears at 2470 cm^{-1}. No noticeable change in intensity of the 1565-cm^{-1} band is observed (Figure 1). These observations indicate[7] that the product exists essentially as 1,1,2-trithexyldiborane[9] (eq 2).

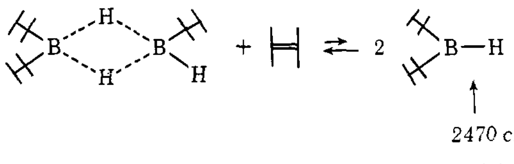


(1)



(2)

A dramatic change in ir spectra takes place as the reaction proceeds beyond the formation of 1,1,2-trithexyldiborane. The two original bands at 1565 and 2540 cm^{-1} diminish and the minor band at 2470 cm^{-1} increases. When the ratio of TME to borane is 16:1, the ir spectrum of the reaction mixture (0.5 *M* in B) at 3 hr and 25° shows only the 2470-cm^{-1} band in the 2600–2400-cm^{-1} region and practically no absorption is observed in the 1600–1500-cm^{-1} region (Figure 1). The amount of residual hydride corresponds to the formation of a dialkylborane (active hydride:B = 1.01), and glpc examination of the oxidation product indicates the formation of 1.96 mol of thexyl alcohol[10] per mole of borane. These observations are consistent only with the formation of monomeric dithexylborane (eq 3).



(3)

Treatment of the 16:1 reaction mixture with a 100% excess of methanol followed by evaporation of the volatile substances at 25° and 0.5 mm provides ~95% pure[11] methoxydithexylborane in 95% yield, purified by distillation (85% yield by isolation): bp 50–52° (0.25 mm); $n^{20}D$ 1.4515; pmr (CCl_4, TMS) δ 0.79 (d, J = 7 Hz, 24 H), 1.70–2.30 (septet, J = 7 Hz, 2 H), and 3.96 ppm (s, 3 H); ir (neat) 1310 (s), 980 cm^{-1} (s). *Anal.* Calcd for $C_{13}H_{29}BO$: C, 73.58; H, 13.78; B, 5.10. Found: C, 73.77; H, 13.76; B, 5.28. Oxidation of 1 mmol of the distilled product yielded 1.98 mmol of thexyl alcohol.[10]

The assignment of the band at 2470 cm^{-1} was further confirmed by treating tetramethylethylene with deuterioborane, BD_3, in THF, to produce the deuterium analogs of 1,2-dithexyldiborane (**1**) and dithexylborane (**2**) and observing the infrared shifts produced by the introduction of the deuterium atoms. The shift

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(1) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961), and references cited therein.

(2) H. C. Brown and S. K. Gupta, *J. Organometal. Chem.*, **32**, C1 (1971).

(3) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(4) (a) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971); (b) H. C. Brown and E. Negishi, *ibid.*, **28**, C1 (1971).

(5) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

(6) The ir spectrum of tetramethyldiborane reported in the literature shows a *minor absorption* at 2500 cm^{-1}. However, the authors have concluded that it is due to trimethyldiborane present as an impurity: W. J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro, *Advan. Chem. Ser.*, **No. 32**, 139 (1961).

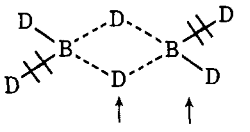
(7) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **84**, 1478 (1962).

(8) It was necessary to react TME and borane in the 2:1 molar ratio in order to observe the thexyl to boron ratio of 1.5 in the product.

(9) Glpc examination (2 ft, SE-30) of the methanolyzed product derived from 20 mmol of borane indicated the presence of 10.1 mmol of dimethoxythexylborane and 9.4 mmol of methoxydithexylborane.

(10) A trace quantity (<1 ~2%) of 2,3-dimethyl-1-butanol was observed.

(11) By pmr. The crude product contained ~5% of dimethoxythexylborane.



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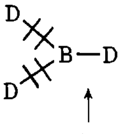

2

from 2540 cm^{-1} for the terminal B–H stretching to 1870 cm^{-1} for the corresponding B–D stretching is in agreement with the predicted effect of the heavier isotope.[1] The similar shift, from 2470 cm^{-1} for dithexylborane to 1820 cm^{-1} for the corresponding deuterium derivative **2**, supports the assignment of these absorptions to the stretching frequencies for the monomeric species. The monomeric nature of dithexylborane was further established by ^{11}B nmr, which exhibits a doublet centered at 81.3 ppm (J = 110 Hz) downfield relative to $BF_3 \cdot OEt_2$.

That dithexylborane exists as an unassociated monomer rather than the THF complex was established by its synthesis in the absence of THF. The reaction of TME with preformed neat dithexyldiborane in the 30:1 molar ratio (TME:B = 16:1) produced slowly (24 hr) at 25° dithexylborane which exhibits the same ir features in the 2600–2400- and 1600–1500-cm^{-1} regions as the sample prepared in THF. The molecular weight of the product in TME, determined by osmometry, was 185, in excellent agreement with the theoretical value 182 for the monomer.

Existence in monomeric form appears to be a general phenomenon for dialkylboranes containing bulky alkyl groups. Thus, thexylmonoalkylboranes, derived from hydroboration of bulky olefins with thexylborane,[12] exhibit the ir band attributable to monomeric dialkylboranes at 2470 cm^{-1} in varying intensities. The ratio of intensities of the band at 2470 cm^{-1} to that in the 1600–1500-cm^{-1} region increases in the following order and seems to correlate with the steric requirements of olefins: isobutylene < cyclopentene < 2-butene < 1-methylcyclopentene < norbornene < 2-methyl-2-butene. These results strongly support the conclusion that the large steric requirements of the two alkyl groups are primarily responsible for the existence of such monomeric dialkylboranes. We are currently exploring the consequences of the monomeric nature of these dialkylboranes.

Acknowledgment. We are grateful to Professor J. B. Grutzner and Mr. R. Carlsen for the ^{11}B nmr spectroscopic measurement and to Dr. C. S. Yeh for the molecular weight determination.

(12) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963).

(13) Postdoctoral Research Associate on Grant No. DA 31–124 ARO(D) 453, supported by the U. S. Army Research Office, Durham, N. C.

(14) Graduate Research Assistant on Grant No. GM 10937, supported by the National Institutes of Health.

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Received February 26, 1972

Nonequivalent Tin Coupling to Anisochronous Protons

Sir:

We have been interested in the anisochronous behavior exhibited by chemically equivalent protons in dissymmetric environments. In many cases involving a chiral tin atom, the expected anisochronous behavior fails to occur.[1,2] However, in certain of these cases we have observed a measurable asymmetry in the tin satellite spectrum of methylene groups bonded to the chiral tin atom. Thus, the upfield satellite component is somewhat broader than the downfield component. A close examination of the nmr spectrum of *tert*-butylphenylneophyltin(IV) iodide has shown that this asymmetry is due to nonequivalent geminal coupling between the tin atom and the anisochronous protons.

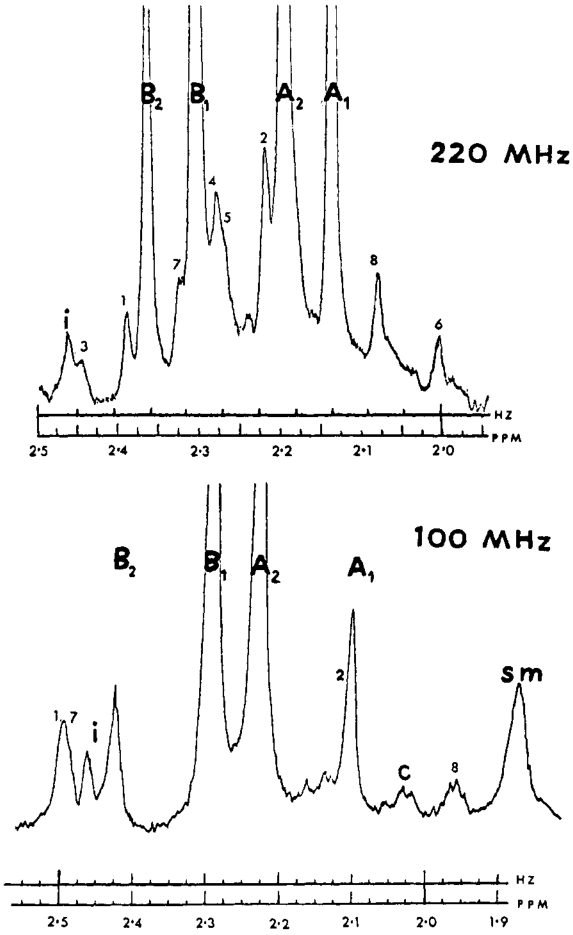

Figure 1. Neophyl methylene proton resonance spectra: sm = starting material, i = impurity, C = downfield ^{13}C satellite of *tert*-butyl protons.

The compound was prepared by a method developed elsewhere.[3] The analytically pure starting material, *tert*-butyldiphenylneophyltin(IV), was carefully cracked with iodine at 0°. The resulting solution in carbon tetrachloride was eluted through a short alumina column and concentrated by evaporation. Spectra were obtained on a Varian HA-100 using a TMS lock signal and reference, all shifts reported being downfield. The *tert*-butyl methyl peaks were found at 1.12 ppm with J_{Sn-H} couplings of 87.0 (117) and 91.0 (119). Neophyl methyl groups appeared as a doublet, as in some other dissymmetric tin complexes,[1,2] at 1.40 and 1.43 ppm with J_{Sn-H} coupling approximately 3–4 Hz. All phenyl peaks were found in the usual region (7.0–7.3 ppm). Small amounts of impurity plus some

(1) G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, **92**, 365 (1970).

(2) D. V. Stynes and A. L. Allred, *ibid.*, **93**, 2666 (1971).

(3) S. A. Kandil and A. L. Allred, *J. Chem. Soc. A*, 83 (1970).