

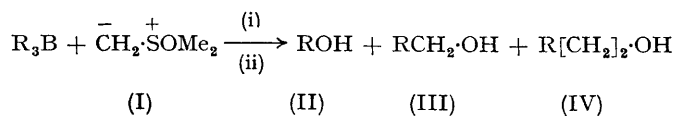
## The Reaction of Organoboranes with Dimethylsulphonium Methylide

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THE recently reported<sup>1</sup> reaction of equimolar amounts of trialkylboranes and dimethyloxosulphonium methylide (I) to afford homologated

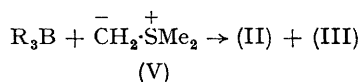
methylide<sup>2</sup> gives a high yield of the corresponding homologated alcohol after alkaline hydrogen peroxide oxidation of the product organoborane.



Reagents: (i) tetrahydrofuran at 0°, (ii) [O].

organoboranes signals a potentially important method of chain extension. A disadvantage of this method is the formation of substantial quantities of doubly homologated alcohol (*i.e.*, IV) upon oxidation of the organoborane reaction mixture. Thus in the reaction of tri-*n*-hexylborane with (I), 19% of the mixture of homologated alcohols [(III) + (IV)] consisted of the doubly-homologated alcohol, octan-1-ol.

We now find that the reaction of an organoborane with the more reactive dimethylsulphonium



Reagents: (i) dimethyl sulphoxide at -10°; (ii) [O].

The yields recorded in the Table are generally good for a variety of trialkylboranes as well as triphenylborane. Only trace amounts of doubly homologated alcohol (*i.e.*, IV) could be detected in the cases tabulated.

TABLE

*Product distribution from the reaction of organoboranes with dimethylsulphonium methylide<sup>a</sup>*

Borane, R <sub>3</sub> B	Product distribution <sup>b</sup> (mole %)		Migration, % of theoretical <sup>c</sup>
	(II)	(III)	
Tri-n-hexylborane	70	30	91
Tri-(2,4,4-trimethylpentyl)borane	74	26	78
Tri-(4-methylpentyl)borane	68	32	96
Tri-(2-norbornyl)borane	76	24	73
Triphenylborane	69	31	94

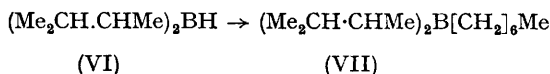
<sup>a</sup> In dimethyl sulphoxide-tetrahydrofuran at  $-10^{\circ}$ .

<sup>b</sup> The overall yields of alcohol are  $90 \pm 10\%$  by v.p.c. analysis.

<sup>c</sup> The theoretical yield of homologated alcohol (*i.e.*, III) is based on  $\frac{1}{3}[R_3B]$ ; thus, a theoretical yield of (III) would be  $33\frac{1}{3}$  mole per cent of the product alcohols in each case. Excess of ylid was used as this can also be consumed by reactions (*ref.* 2) which do not involve the organoborane.

The presence of boron-hydrogen bonds in the reaction mixture has an adverse effect on the yield of homologated alcohol. Mono- and di-alkylboranes react with either ylid, (I) or (V), to

homologated alcohols, 2,3-dimethylbutan-1-ol and octan-1-ol, derived from the two different boron-bound groups is *ca.* 2 : 1, respectively. This ratio is *ca.* 4 : 1 in the case of the reaction involving the



afford low yields, after oxidation, of the corresponding homologated alcohol. Thus, oxidation of the di-(1,2-dimethylpropyl)borane<sup>3</sup> (VI)-dimethylsulphonium methylide reaction mixture results in the production of only 24% of the theoretical yield of 2,3-dimethylbutan-1-ol.

In the reaction of di-(1,2-dimethylpropyl)-n-heptylborane<sup>4</sup> (VII) with (I), the molar ratio of the

sulphonium ylid. Thus, after correction for the statistical predominance of the 1,2-dimethylpropyl group, it can be seen that both groups migrate extensively. Small amounts of doubly homologated products are formed in both reactions.

(Received, March 29th, 1967; Com. 306.)

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<sup>2</sup> E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **1965**, **87**, 1353.

<sup>3</sup> H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **1962**, **84**, 1478.

<sup>4</sup> H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, 1962, p. 191.