COMMUNICATIONS TO THE EDITOR

ALKENYLMETHYLBORINES

Sir:

Several newly prepared alkenylmethylborines display unusual stability against disproportionation compared with the corresponding saturated derivatives. The new compounds have been obtained by treating solid sodium vinyl[1] or lithium propenyl[2] with dimethylboron bromide[3] at low temperature. Preliminary analytical results and tentative values for physical constants are given in Table I for substances separated from the reaction mixtures by fractional condensation.

The structures were confirmed by reaction with ammoniacal silver hydroxide.[4] From methyldipropenylborine (0.29 mmole) were obtained, methane and hydrogen (0.22 mmole), ethane (0.09 mmole, v.p. −111.8°, 165 mm.; recorded 168 mm.) and $\Delta^{2,4}$-hexadiene (0.05 mmole, extrap. b.p. 82–84°; recorded 82°). From trivinylborine (0.048 mmole) were obtained ethylene (0.022 mmole, v.p. −145° 28 mm.; recorded 28 mm.) and $\Delta^{1,3}$-butadiene (0.008 mmole, v.p. −80°, 9 mm.; recorded 9.7 mm.). In comparison trimethylborine (0.67 mmole) reacted to give methane (0.42 mmole) and ethane (0.52 mmole, v.p. −111.8° 167 mm.; recorded 168 mm.). Similarly from the reaction with bis-(dimethylboro)-ethylene (0.156 mmole) were recovered methane (0.10 mmole, molecular weight by vapor density 15.3), ethane (0.044 mmole, v.p. −111.8°, 164 mm.; recorded 168 mm.), ethylene (0.009 mmole, v.p. −145°, 27 mm., recorded 28 mm.) and propylene (0.030 mmole, v.p. −111.8°, 9 mm.; recorded 9.3 mm.).

Dimethylvinylborine disproportionates slowly at room temperature into trimethylborine, methyldivinylborine and trivinylborine. The other mixed derivatives disproportionate less rapidly. It is in this respect that the alkenyl borine derivatives differ remarkably from the corresponding saturated borines. For example, efforts to synthesize dimethylethylborine and dimethylpropenylborine have succeeded to the extent that preparations of appropriate volatility have been obtained tensiometrically pure as observed between −40° and −20°. Above these temperatures rapid disproportionation has been observed.

The differences in reactivity are currently ascribed to resonance in the alkenyl borine, depicted in part by canonical forms involving a shift in the unsaturation from Δ^{C-C} to Δ^{C-B}, restraining the alkenyl borine in planar configuration. If the activated complex for disproportionation be considered a bridge-bonded dimer with tetrahedral configuration about the boron atoms the activation energy for the alkenyl derivatives should be higher than for the saturated compounds. Also, a diminished Lewis acidity is to be expected. These considerations, refinement of the physical data and improved synthesis are being investigated.

TABLE I

DATA ON ALKENYL BORINES

Borine	Carbon, % Found	Carbon, % Calcd.	Boron, % Found	Boron, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Mol. wt. Found	Mol. wt. Calcd.	Vap. p., mm. at 0°C.
Dimethylvinyl	...	...	...	...	...	...	73	68	126
Methyldivinyl	73.45	75.12	13.60	13.54			83.5	80	109.5
Trivinyl	77.75	78.4	11.93	11.79	9.76	9.86	93.2	92	67
Bis-(dimethylboro)-ethylene	66.21	66.85	21.50	20.08			114	108	21
Dimethylpropenyl	73.8	73.3	13.14	13.21	13.32	13.52	85	82	76.5
Methyldipropenyl	77.97	77.84	10.17	10.02	11.99	12.13	109	108	12.5

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EXAMINATION OF THE IODOFORM AND SCHMIDT REACTIONS OF ACETONE-1-C^{14} FOR ISOTOPE EFFECTS

Sir:

The "reverse isotope effect" reported[1] for the iodoform reaction of acetone-1-C^{14} has appeared to be an exception to the general rule that C^{12}—C^{14} bonds break less rapidly than C^{12}—C^{12} bonds. Partly on the basis of this exceptional result, a new theory has been stated.[2,3] Because of the extreme importance of these developments to the field of isotope effect studies, attempts have now been made to repeat the original experimental work. The present authors have carefully carried out the iodoform reaction with acetone-1-C^{14}, but have observed no measurable isotope effect of any kind. Four different runs at room temperature were performed at three levels of radioactivity by different chemists working independently at different seasons of the year. In addition, alternative modes of mixing the reactants were employed. The only item common to all four runs was the vibrating

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[1] A. Roe and E. L. Albenesius, THIS JOURNAL, **74**, 2402 (1952).

[2] Abstracts of Papers, 124th Meeting of the American Chemical Society in Chicago, Illinois, September 6–11, 1953, Pages 65-O, 66-O, 67-O.

[3] *Chemical and Engineering News*, **31**, 3980 (1953).