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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON
T. D. PARSONS
D. M. RITTER

RECEIVED FEBRUARY 8, 1954

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[1] A. A. Morton, *et al.*, THIS JOURNAL, **72**, 3785 (1950).

[2] E. A. Baude, J. A. Coles and C. J. Timmons, *J. Chem. Soc.*, 2000 ff (1950).

[3] F. L. McKennon, Dissertation, University of Chicago Libraries, 1936.

[4] H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938); R. L. Letsinger and I. H. Sksog, *J. Org. Chem.*, **18**, 895 (1953).

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).

TABLE I

SPECIFIC ACTIVITIES OF REACTANTS AND PRODUCTS (μc. PER MMOLE) IN THE IODOFORM REACTION

Reaction	Acetone used × 0.5	Derivative	Iodoform	Acetic acid	Derivative	Procedure
1	0.741 ± 0.004	2,4-Dinitrophenyl	0.738 ± 0.006	...	...	*a*
2	2.898 ± 0.002	Hydrazone	2.881 ± 0.007	2.863 ± 0.003	S-1-Naphthylmethylthiuronium salt	*b*
3	5.60 ± 0.03	Semicarbazone	5.57 ± 0.08	5.63 ± 0.08	*p*-Nitrobenzyl ester	*c*
4	5.60 ± 0.03	...	5.55 ± 0.06	...	...	*d*

[a] Acetone (0.200 ml.) in aqueous base was treated with excess iodine in potassium iodide solution as originally described.[1] The yield of iodoform was 80%. Acetic acid was not recovered. [b] Acetone (2.00 ml.) was added to water (200 cc.) containing iodine (14.4 g., 10% excess) and sodium iodide (20 g.); 10% sodium hydroxide solution was added dropwise until the iodine color disappeared. The iodoform was filtered, the filtrate was acidified, and sodium hydroxide was added until the solution became colorless. The additional iodoform which separated was filtered, and the process was repeated until no more iodoform separated. The total yield of iodoform was 90%. Residual iodine was destroyed with sodium bisulfite. The slightly basic filtrate was evaporated to dryness and sodium iodide was removed by acetone extraction. The acidified solution of the remaining salts was steam distilled to recover acetic acid. [c] To 2.00 ml. of acetone in 400 ml. of 2 *N* sodium hydroxide solution, 600 ml. of iodine solution (containing 15 g. of iodine and 22 g. of sodium iodide, enough for reaction of 70% of the acetone) was added. The iodoform yield was 95% based on iodine. The acetic acid was isolated in a manner similar to that described under (*b*) except that sodium acetate was extracted from the acetone-insoluble salts with hot ethanol. A 55% recovery of sodium acetate resulted. [d] Reaction was run with just enough reagent to react with only 5% of the acetone present.

TABLE II

SPECIFIC ACTIVITIES OF REACTANTS AND PRODUCTS (μc. PER MMOLE) IN THE SCHMIDT REACTION

Reaction	Acetone used × 0.5	Unreacted acetone recovered × 0.5	Methylamine	Acetic acid	Acetone reacted, %
1	1.034 ± 0.007	...	1.015 ± 0.010	1.021 ± 0.006	85–100
2	1.496 ± 0.020	...	1.443 ± 0.010	1.483 ± 0.015	50
3	1.464 ± 0.009	1.495 ± 0.002	1.423 ± 0.005	1.472 ± 0.002	30

reed electrometer for radioactivity assay. Two different samples of acetone-1-C^{14} which were used in these reactions were prepared by different synthetic methods. Both samples were carefully fractionated. One sample was subsequently distilled from calcium oxide to eliminate the possibility that it might contain acetic acid.

Table I presents the results of the four independent experiments. All samples were assayed for radioactivity using Van Slyke solution in the usual wet-combustion procedure.[4] The carbon dioxide resulting was counted in a stainless steel ion chamber. For all assays from a given reaction, the same ion chamber was used.

The data of Table I indicate that no measurable *intramolecular* or *intermolecular* isotope effect accompanies the iodoform reaction of acetone-1-C^{14}. Several sets of reaction conditions were employed including the reaction conditions originally reported.[1]

Since the Schmidt reaction of acetone-1-C^{14} has also been reported to involve a reverse *intramolecular* isotope effect,[2,3] three runs have been made in attempt to repeat this work. As Table II reveals, the data fail to confirm the reverse effect previously reported; instead, small *intramolecular* and *intermolecular* isotope effects in the usual direction are indicated. Experimental conditions used were those described in "Organic Reactions," Vol. III.[5] The reactions were carried out in benzene solution at 0 to 5° and the percentage reaction was in each case controlled by the amount of hydrazoic acid solution used. Acetic acid product was converted to the *p*-nitrobenzyl ester, methylamine was converted to the phenylthiourea derivative, and acetone was converted to the 2,4-dinitrophenylhydrazone. These derivatives were carefully purified and radioassayed in the same manner[4] as were the iodoform reaction products.

Further studies of these reactions of labeled acetone and related ketones are in progress in attempt to correlate any observed isotope fractionation factors with reaction mechanisms.

GUS A. ROPP
OAK RIDGE NATIONAL LABORATORY WILLIAM A. BONNER
OAK RIDGE, TENNESSEE[6] MARION T. CLARK
VERNON F. RAAEN

RECEIVED MARCH 1, 1954

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[4] O. K. Neville, THIS JOURNAL, **70**, 3501 (1948); V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953); for wet combustion of derivatives containing nitrogen, a lead dioxide trap at 180° was included in the line.

[5] Hans Wolff, "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, pp. 327–329.

[6] This paper is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

CHROMATOGRAPHY OF PROTEINS ON CELLULOSE ION-EXCHANGERS

Sir:

Previous studies in this Laboratory[1] with an egg-white protein mixture and a bovine plasma albumin–hemoglobin mixture on a strong cation-exchange resin, as well as the experiments of other workers[2] with relatively stable, low molecular weight crystalline proteins on a weak cation-exchanger, were performed with commercial resins.

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