which were available could be titrated with the Fischer reagent. Samples of triphenyltin hydroxide and triphenyllead hydroxide, on titration, gave 1.01 and 1.02 moles of apparent water found per mole hydroxide, respectively. Both compounds decolorized additional reagent on standing several hours. A sample of phenylboric acid, $C_6H_5B(OH)_2$, which had been freshly crystallized from water gave on titration 1.96 moles apparent water per mole of acid. On standing in the air or drying at 70° for several hours, the oxide $(C_6H_5BO)_3$, was formed which analyzed 0.99 mole apparent water per mole of oxide. Although organic hydroxy derivatives of germanium and arsenic have not yet been tested, it is probable that they, as well as the more basic organometallic hydroxides, can be determined by this method.

Other compounds tested which do not react with the Fischer reagent at all or do not react rapidly enough to be titrated are hexamethyldisiloxane, hexaphenyldisiloxane, ethyltriethoxysilane, tris-(*p*-chlorophenyl)-ethoxysilane, triphenylchlorosilane and tris-(*p*-dimethylaminophenyl)-silane.

Experimental

Five milliliters of pyridine or methanol was pipetted into a dry 50-ml. glass-stoppered volumetric flask and this solvent was titrated to the iodine end-point with Fischer reagent from a 10-ml. automatic buret. The weighed sample of silanol was then added quickly. (Liquid samples were weighed in a platinum boat). After washing down the neck with a little Fischer reagent, the flask was stoppered and shaken a few seconds to complete solution. This solution was then titrated to the same iodine end-point as that obtained with the solvent. The apparent millimoles of water found was calculated from the amount of Fischer reagent consumed by the silanol.

Tri-*p*-xenylmethoxysilane.—The solution remaining after the titration of tri-*p*-xenylsilanol (m.p. 200–201°) was diluted with water and filtered. The residue, 0.19 g. (91%), after washing with water and drying 1 hour at 120°, melted at 157–158°. This material would not react with the Fischer reagent. A portion of this residue was warmed with a solution of potassium hydroxide in ethanol–dioxane for 5 minutes, diluted with water, and filtered. The residue from this latter filtration melted at 200–202° and its mixed melting point with tri-*p*-xenylsilanol showed no depression. A sample of tri-*p*-xenylmethoxysilane was prepared by refluxing 0.23 g. of tri-*p*-xenylsilanol with 2.0 g. of anhydrous zinc chloride in 10 ml. of methanol for 40 hours.[6] The product was filtered and the residue was washed with methanol and acetone to leave 0.1 g. (42%) of white needles, m.p. 158°. A mixed melting point with the above compound isolated from the Fischer titration showed no depression.

Anal. Calcd. for $C_{37}H_{30}OSi$: Si, 5.42. Found: Si, 5.49.

Triphenyllead Hydroxide, Triphenyltin Hydroxide and Phenylboric Acid.—The samples of triphenyltin hydroxide, m.p. 122–124°, triphenyllead hydroxide and phenylboric oxide, m.p. 219°, had been prepared in these laboratories by C. E. Arntzen, R. K. Abbott and B. A. Hunter, respectively. A sample of the phenylboric oxide was recrystallized from water and the product was dried overnight at 70°. Titration of 0.120 g. (0.00115 mole) of the dried material required 18.94 ml. of Fischer reagent equivalent to 0.001144 mole of water or 99 mole per cent. calculated as $(C_6H_5BO)_3$. Another sample of the oxide was crystallized from water and dried 30 minutes at room temperature and 20 mm. pressure. Titration of 0.00755 mole of this product took 24.60 ml. of Fischer reagent, equivalent to 0.00148 mole or 98 mole per cent. calculated as phenylboric acid, $C_6H_5B(OH)_2$.

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[6] See reference (4b) for a related procedure for like compounds.

Isotopic Exchange between D_2O and $NaBH_4$

BY PETER R. GIRARDOT AND ROBERT W. PARRY

The observation that $NaBH_4$ is appreciably soluble in cold water has been previously recorded.[1] If it were dissolved in D_2O, any isotopic exchange between D and H would be apparent on subsequent evaporation of the solution and hydrolysis of the $NaBH_4$.

We have recently observed the mass spectrum of the hydrogen evolved on hydrolysis after such a procedure, with the results shown below. Approximately 1.5 molal solutions of $NaBH_4$ were prepared in evacuated systems using 99.8% D_2O as the solvent. Hydrolysis of the $NaBH_4$ was reduced to a negligible amount by saturating the solution with $Ca(OD)_2$ (*p*H about 12). After standing 17.5 hours at 20–25°, the D_2O was distilled off, dry oxalic acid was added to the alkaline $NaBH_{4-x}D_x$ residue, the system was re-evacuated and hydrolysis effected by adding distilled water to the acid mixture. The reaction is

$$Na(BH_{4-x}D_x) + 2H_2O \xrightarrow{H^+} NaBO_2 + xHD + (4 - x)H_2$$

The resulting H_2, HD mixture was analyzed in a Consolidated Isotope Ratio Mass Spectrometer. The upper limits for the HD:H_2 ratio are found in Table I.

TABLE I

Sample	Ratio HD:H_2 × 10^4
Blank using H_2O only	2.2
No. 1	7.4
No. 2	5.0
No. 3	8.0

Although the exact constant of the instrument converting these values to absolute ratios has not yet been determined, it is known that the constant will lie somewhere between 0.6 and 1.0; thus these values may be set as upper limits to the amount of exchange.

Natural abundance gives a D:H ratio reported variously as 1.45×10^{-4}[(2)] and 1.61×10^{-4}.[(3)] It is then apparent that the values found in this experiment do not indicate formation of significant amounts of HD, and we conclude that the hydrogen of sodium borohydride does not exchange with hydrogen of water.

(1) Albert E. Finholt, Ph.D. Dissertation, The University of Chicago, June, 1946.

(2) J. A. Swarthout and M. Dole, THIS JOURNAL **61**, 2025 (1939).

(3) A. J. Edwards, R. P. Bell and J. H. Wolfenden, *Nature*, **135**, 793 (1935).

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Nopadiene

BY LELAND J. KITCHEN

The conjugated diene 2-vinyl-6,6-dimethylbicyclo[3.1.1]-2-heptene was prepared by dehydration of nopol. Because of its derivation from nopinene and nopol, the diene is designated nopadiene.

Nopadiene acted as a retarder in copolymerization experiments. Retardation probably is due