chloride was treated dropwise with liquid bromine until yellow, maintaining the temperature at −10 to −3°. The slight excess of bromine and the hydrogen bromide were removed by shaking with 10% sodium carbonate solution.

The carbon tetrachloride layer was dried with ignited potassium carbonate, the solvent removed with an aspirator at room temperature and distilled at 3 mm. using an 18-cm. Vigreux column, collecting 5.6 g. of crude *n*-hexanol, b.p. 48–60° (3 mm.), $n^{25}\text{D}$ 1.4182–1.4266. Titration with bromine showed no unsaturation. It was redistilled using a vacuum-jacketed concentric tube column equipped with a total reflux, solenoid operated vapor dividing head[7] to give 2.2 g. of product, b.p. 155–156° (760 mm.), $n^{25}\text{D}$ 1.4158–1.4162. The allophanate was prepared in the usual manner, m.p. 160–161°, and did not depress the allophanate of authentic *n*-hexanol, m.p. 160–161°.[5]

Isolation of 2-Hexen-1-ol.—A solution of 10.6 g. of the mixture resulting from another reduction of 2-hexenoic acid was dissolved in carbon tetrachloride, saturated with bromine in carbon tetrachloride at 0°, washed with 10% sodium carbonate, dried over ignited potassium carbonate and concentrated at reduced pressure. Five grams of 3,5,5-trimethylhexanol[9] (b.p. 193–194° (760 mm.)) was added as a pusher and the solution distilled through the concentric tube column[10] to remove *n*-hexanol.

The residue was refluxed with 3.25 g. of sodium iodide in 20 ml. ethanol for two hours and followed by extraction with 10% sodium thiosulfate. Organic bromide was still present whereupon the solvent was stripped and the residue treated with powdered zinc (1.5 g.) and 15 ml. of glacial acetic acid for 65 hours. The reaction mixture was treated with 165 ml. of ice-cold 20% sulfuric acid. An oily layer separated and was washed with water, 10% potassium carbonate, dried over potassium carbonate, and distilled in the concentric tube column to give 2.04 g. of 2-hexen-1-ol, b.p. 101.4–101.8° (95 mm.), $n^{25}\text{D}$ 1.4336–1.4346. Titration with bromine showed 89% unsaturation.[11] The allophanate, m.p. 154.5–155.5°, and the 3,5-dinitrobenzoate, m.p. 64.5–65.5°, were prepared according to standard procedures.

Allophanate of 2-Hexen-1-ol. *Anal.* Calcd. for $C_8H_{14}N_2O_3$: C, 51.60; H, 7.58; N, 15.05. Found: C, 51.62, 51.42; H, 7.54, 7.53; N, 15.6, 15.6.

3,5-Dinitrobenzoate of 2-Hexen-1-ol.—*Anal.* Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 53.11; H, 4.91; N, 9.78.

---

[7] Obtained from M. J. Seavy and Son, 30 Church Street, New York, N. Y., and an adaptation of that described by Naragon and Lewis[8] and tested at 54 theoretical plates.

[8] E. A. Naragon and C. G. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 448 (1946).

[9] W. M. Bruner, *Ind. Eng. Chem.*, **41**, 2860 (1949).

[10] The column was adapted to vacuum operation by insertion of the necessary stopcocks to permit samples to be withdrawn without affecting the distillation. The pressure was regulated to within 0.05 mm. with a cartesian diver manostat no. 5 obtained from The Emil Greiner Company, New York, N. Y.

[11] *trans*-2-Hexen-1-ol[12] subsequently prepared by the reduction of methyl 2-hexenoate with lithium aluminum hydride showed 95% unsaturation and the following physical properties: b.p. 102.0° (95.0 mm.), $n^{25}\text{D}$ 1.4350, d^{25}_4 0.8340, $R^{25}\text{D}$ 31.12 (Calcd. $R^{25}\text{D}$ 30.97); allophanate, m.p. 154.0–154.5° (no depression with prepared allophanate).

[12] G. Smets, *Trav. lab. chim. gen. Univ. Louvain*, 1942–1947, 69 pp.; *Acad. Roy. Belg. Classe* sci. Mem, collection in 8°, **21**, 3–72 (1947); *C. A.*, **44**, 8315f (1950).

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, N. Y.
RECEIVED JANUARY 13, 1951

The Determination of Silanols with the Karl Fischer Reagent[1]

BY HENRY GILMAN AND LEWIS S. MILLER

During some experiments in which silanol solutions were being titrated for water with the Karl Fischer reagent[2] it was found that most silanols and silanediols, themselves, can be titrated quantitatively with this reagent. The data obtained are given in Table I.

The reaction is analogous to that described[3] for orthoboric acid, which consumes Fischer reagent equivalent to three moles of water per mole of boric acid and yields trimethyl borate. Thus the reaction with silanols can be formulated as

$$R_3SiOH + I_2 + SO_2 + 2CH_3OH \longrightarrow R_3SiOCH_3 + 2HI + CH_3HSO$$

After the titration of tri-*p*-xenylsilanol, tri-*p*-xenyl-[4] methoxysilane was actually isolated from the reaction products. The Fischer reagent or its modifications using other alcohols in place of methanol thus offers an alternate preparative method for certain alkoxy silanes. Further studies of this method are now being conducted.

The only silanols which did not react rapidly with the Fischer reagent were the two highly hindered compounds, tri-1-naphthylsilanol[4a] and tri-*o*-tolylsilanol.[4b] The former silanol would decolorize a slight amount of Fischer reagent on standing several hours.

Evidence of steric hinderance in these and several other silanes has been reported.[4a,b,c] For example, tri-1-naphthylchlorosilane was found to be quite resistant to hydrolysis by water and relatively forced conditions were required to effect hydrolysis by alcoholic base.

The carbon compounds analogous to the silanols, *i.e.*, tertiary alcohols, do not react with the Fischer reagent. *t*-Butyl alcohol solutions have been titrated for water content without interference[5] and triphenylcarbinol was tested and found not to decolorize the Fischer reagent. As expected, hydroxy compounds of the heavier group IVB elements

TABLE I

TITRATION OF SILANOLS WITH THE KARL FISCHER REAGENT

Silanol[a]	Millimoles taken	Millimoles of apparent water	
		Found	Found per mmole silanol
(1) $(C_6H_5)_3SiOH$	4.52	4.47	0.99
(2) $(C_6H_5)_2Si(OH)_2$	0.927	1.84	1.98
(3) $(p\text{-}C_6H_5C_6H_4)_3SiOH$	.398	0.393	0.99
(4) $(p\text{-}C_6H_5C_6H_4)_2Si(OH)_2$	.272	.483	1.78[b]
(5) $(C_6H_5)_2(p\text{-}CH_3C_6H_4)SiOH$	.690	.680	0.99
(6) $[p\text{-}(CH_3)_2NC_6H_4]_3SiOH$	.358	.356	0.99
(7) $(C_2H_5)_3SiOH$	1.60	1.60	1.00
(8) $(p\text{-}ClC_6H_4)_3SiOH$	0.375	0.377	1.00

[a] Compound 2 was prepared by H. N. Benedict and compounds 3, 4, 5 and 6 were prepared by G. E. Dunn in the course of studies from these laboratories. Compound 7 was obtained from the Anderson Laboratories, Adrian, Mich. [b] This silanediol presumably contained some condensation products.

---

[1] Paper LXVIII in the Series "The Relative Reactivities of Organometallic Compounds"; the preceding paper with Beel is in THIS JOURNAL, **73**, 774 (1951).

[2] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[3] J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 257; E. G. Almy, W. E. Griffin and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940); J. Mitchell, D. M. Smith and W. N. D. Bryant, THIS JOURNAL, **62**, 4 (1940).

[4] (a) H. Gilman and G. G. Brannan, *ibid.*, **73**, (1951). See further references to steric effects in this paper. (b) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950). (c) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946); V. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2876 (1948); H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947); F. P. Price, *ibid.*, **69**, 2600 (1947); W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949).

[5] *Cf.* p. 117 in Mitchell and Smith, ref. 3,

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, $C_6H_5B(OH)_2$.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED NOVEMBER 1, 1950

---

[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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.

RECEIVED JANUARY 13, 1951

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