tion was 3.5 hours, and since appearance of 5.5 hour Cs^{127} was not observed, formation of Ba^{127}, which is expected to be shortlived, did not occur in bombardment of CsCl with 96 Mev. protons.

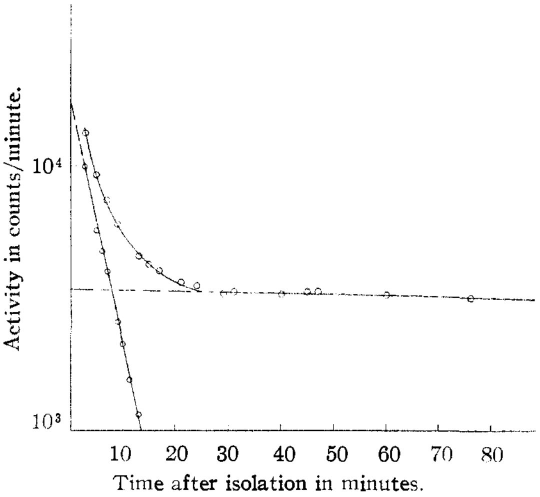

Fig. 1.

The combined yield of Cs^{128} plus Cs^{129} daughters, after subtraction of 10 day Cs^{131}, is shown in Fig. 2, where in each case the yield is that from extrapolation to instant of isolation from barium parents. On this curve, portions marked A represent the presence of 31 hour Cs^{129}, arising from 2.0 hour decay of Ba^{129}, while portion B shows only 3.13 minute Cs^{128} daughter, arising from decay of 2.4 day Ba^{128}. The genetic relationships for these activities are therefore proved.

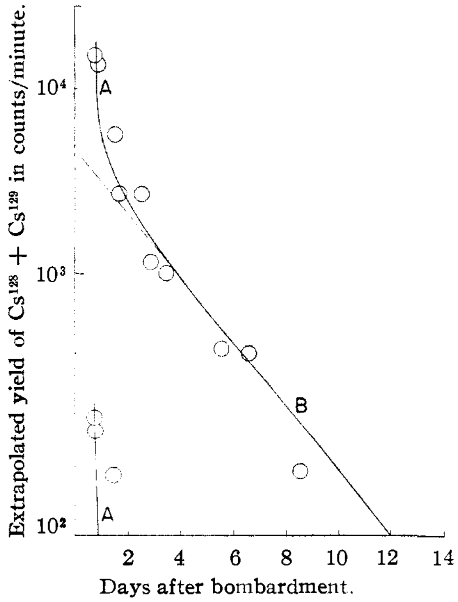

Fig. 2.

No radiations of Cs^{128} have yet been characterized, but one expects that since Ba^{128} is a long-lived even–even nuclide, Cs^{128} may be the 3 Mev. positron emitter in equilibrium with its parent, as noted in a previous communication.[3]

We are appreciative of the coöperation of Dr. Sidney W. Barnes and the crew of the 130-inch cyclotron in these experiments.

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The Partial Reduction of the Double Bond in 2-Hexenoic Acid by Lithium Aluminum Hydride[1]

BY ROBERT W. FREEDMAN AND ERNEST I. BECKER

The reduction of aliphatic unsaturated acids by means of lithium aluminum hydride has been reported to take place without saturation of the double bond.[2] However, with α,β-unsaturated acids a temperature effect has been reported in that acrylic acid is converted to allyl alcohol at room temperature and in part to *n*-propanol at 100°.[3] The reduction of cinnamic acid led to hydrocinnamyl alcohol even at room temperature[2] unless the lithium aluminum hydride was added to the acid with cooling, in which case cinnamyl alcohol was obtained.[3] The purpose of this work is to report the partial reduction of the α,β-double bond in an aliphatic acid at ordinary temperatures.

Two different samples of 2-hexenoic acid were separately reduced with lithium aluminum hydride. Quantitative bromination[4] of the product showed that 25.0–28.5% saturation of the double bond had occurred.

The mixture of alcohols was separated by adding bromine and fractionally distilling the mixture at reduced pressure. The distillate consisting of *n*-hexanol was converted to the allophanate, m.p. 160–161°, which did not depress the melting point of the authentic allophanate, m.p. 160–161°.[5]

The 2-hexen-1-ol was obtained from the dibromide by treatment with alcoholic potassium iodide[6] and zinc in dilute acetic acid. The allophanate melted at 154.4–155.5° and the 3,5-dinitrobenzoate melted at 64.5–65.5°.

Experimental

All melting points are corrected.

Reduction of 2-Hexenoic Acid.—A solution of 91.2 g. (0.80 mole) of 2-hexenoic acid (purified commercial sample m.p. 32°) in 100 ml. of ether was added dropwise to 45 g. (1.18 moles) of lithium aluminum hydride in 1500 ml. of ether with stirring. Water was added cautiously, cooling with ice, until no further reaction occurred. The mixture was poured into 1200 g. of water and ice containing 133 g. of sulfuric acid and the aqueous layer extracted with three 250-ml. portions of ether. The combined extracts were washed with saturated potassium carbonate and dried with ignited potassium carbonate. The mixture was distilled using a 20-plate, glass helix-packed column of the total reflux variable take-off type, collecting 46.2 g. (0.46 mole, 58%) of product, b.p. 94.6–100° (95 mm.), $n^{25}\mathrm{D}$ 1.4273–1.4300. The major portion distilled at 100° (95 mm.) and its refractive index varied gradually from $n^{25}\mathrm{D}$ 1.4293 to $n^{25}\mathrm{D}$ 1.4300. Two fractions were found to be 71.5 unsaturated upon titration with bromine.[4]

Isolation of *n*-Hexanol.—A solution of 24.6 g. of the partially saturated 2-hexen-1-ol in 100 ml. of carbon tetra-

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[1] This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[3] F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

[4] Ben Brae, *Anal. Chem.*, **21**, 1461 (1949).

[5] A. Béhal [*Bull. soc. chim.*, [7] **25**, 473 (1919)] reported a melting point of 165°.

[6] R. Schoenheimer, *J. Biol. Chem.*, **110**, 461 (1935).

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.

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(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).

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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.

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(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.