Some New Silicon-Containing Secondary and Tertiary Acetylenic Alcohols

JOHN SAMUEL ADAMS, JR.[1]
Monsanto Research Corp., Boston Laboratory, Everett, Mass. 02149

Five new silicon-containing secondary and tertiary acetylenic alcohols were synthesized and characterized. Elemental analyses, infrared data, per cent yields, and melting and boiling points are given for these compounds.

By THE PROCEDURE of Shikhiev and Aslanov (*1*), five new secondary and tertiary acetylenic alcohols containing organosilyl groups have been synthesized in these laboratories. The reaction route is illustrated below for 1-[β-(dichloromethyldimethylsilyl)ethynyl]-cyclohexanol:

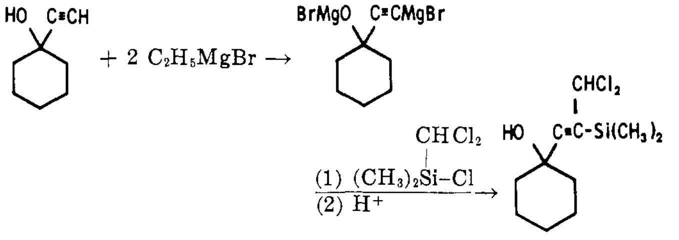
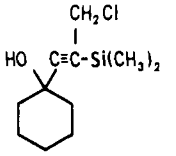
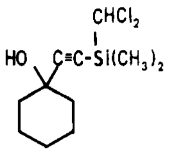
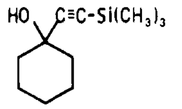
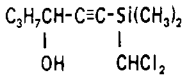
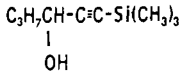


Table I lists the compounds prepared, together with their melting points, boiling points, per cent yields, and elemental analyses. Table II gives infrared absorption data for each material. In all cases, compounds exhibited characteristic absorptions consistent with the proposed structures.

EXPERIMENTAL

The acetylenic alcohols used in this work were obtained from Columbia Organic Chemical Co., the chlorosilanes from Dow Corning Corp., and the ethylmagnesium bromide from Arapahoe Chemical Co. All reagents were used without purification. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained as cast films from chloroform for solids and between rock salt plates with neat liquids.

Table I. Characterization of Acetylenic Alcohols

Compound	Structure	Yield, %	M.P., ° C. B.P., ° C./Mm.	Analysis Calcd.	 Found
1-[β-(Chloromethyldimethylsilyl)-ethynyl]cyclohexanol		56	55.8–56.8 88–89/0.3	C, 57.2 H, 8.3 Si, 12.2	C, 57.6 H, 8.3 Si, 12.0
1-[β-(Dichloromethyldimethyl-silyl)ethynyl]cyclohexanol		47	55.0–58.5 101–102/0.3	C, 49.8 H, 6.9 Si, 10.6	C, 50.1 H, 7.1 Si, 10.3
1-[β-(Trimethylsilyl)ethynyl]-cyclohexanol		26	68–70 69–70/0.1	C, 67.3 H, 10.2 Si, 14.3	C, 67.8 H, 10.3 Si, 14.0
1-(Dichloromethyldimethylsilyl)-1-hexyn-3-ol	 $\underset{OH}{C_3H_7CH}-C\equiv C-\underset{CHCl_2}{Si(CH_3)_2}$	54	. . .	C, 45.2 H, 6.7 Si, 11.7	C, 45.3 H, 6.6 Si, 11.0
1-(Trimethylsilyl)-1-hexyn-3-ol	 $\underset{OH}{C_3H_7CH}-C\equiv C-Si(CH_3)_3$	47[a]	. . .	C, 63.5 H, 10.6 Si, 16.5	C, 61.6 H, 10.0 Si, 15.9

[a] 94.5% pure by vpc.

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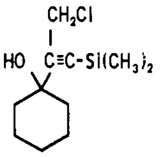
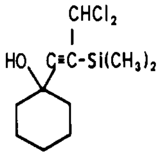
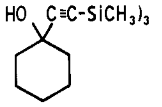
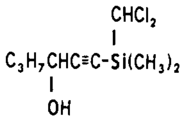
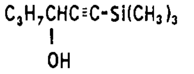
[1] Present address, Horizons, Inc., Cleveland, Ohio 44104

Table II. Characteristic Infrared Absorption Bands for Silyl Acetylenic Alcohols

Compound	Wavelengths, μm. -OH Stretch	—C—H Stretch	—C≡C—	—Si—CH_3 Deformation	—Si—CH_3 Stretch and Rock
	3.1–3.18 (strong)	3.42 3.51 (strong)	4.63 (med.)	8.06 (strong)	11.70 11.9–12.0 (strong) 12.65 (med.)
	3.15 (strong)	3.48 3.55 (strong)	4.69 (med.)	8.10 (strong)	11.71 11.95 12.68 (strong)
	3.10 (strong)	3.44 3.52 (strong)	4.64 (med.)	8.09 (strong)	11.60 11.95 13.21 (strong)
 $C_3H_7CH(OH)C\equiv C\text{-}Si(CHCl_2)(CH_3)_2$	3.00 (strong)	3.41 3.51 (strong)	4.62 (med.)	8.07 (strong)	11.59 11.80 12.61 (strong)
 $C_3H_7CH(OH)C\equiv C\text{-}Si(CH_3)_3$	3.00–3.05 (strong)	3.40 3.43 3.50 (strong)	4.62 (med.)	8.01 (strong)	11.50–12.00 13.15–13.20 (strong)

The experimental procedure followed did not differ substantially in any case from that of Shikhiev and Aslanov (*1*). However, the synthetic details for 1-[β-(chloromethyldimethylsilyl)ethynyl]cyclohexanol are cited here as an example.

A 500-ml. reaction flask equipped with stirrer, condenser (protected with a calcium chloride drying tube), thermometer, and dropping funnel was charged with 233 ml. of 3*M* ethereal ethylmagnesium bromide. To the Grignard solution was added, with stirring and cooling, 43.5 grams (0.35 mole) of 1-ethynylcyclohexanol. The mixture was stirred for 2 hours at room temperature following the addition and then, with an ice bath in place for cooling, was treated dropwise with 50 grams (0.35 mole) of chloromethyldimethylsilane. The resulting complex was decomposed with 200 ml. of 10% hydrochloric acid. The ethereal solution was separated, dried over anhydrous magnesium sulfate, concentrated, and distilled to yield 44.5 grams, b.p. 88°–89° C./0.3 mm., solidifying on cooling to a white solid, m.p. 55.8°–56.8° C.

ACKNOWLEDGMENT

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. The work was supported by the U. S. Army Biological Laboratories at Fort Detrick, Frederick, Md.

LITERATURE CITED

(1) Shikhiev, I. A., Aslanov, I. A., *J. Gen. Chem. USSR, Eng. Transl.* 33, 369 (1963).

RECEIVED for review May 16, 1969. Accepted October 8, 1969.