then was raised to 50° for 15 minutes and 25 ml. of ethanol was added. The precipitated manganese dioxide was removed by suction filtration and washed first with hot water, then with ethanol. The filtrate and washings were combined and flushed with carbon dioxide to bring the solution to *pH* 8 and then evaporated to dryness *in vacuo*. The organic material in the residue was extracted with hot absolute ethanol and the solution was filtered. The solvent was removed with a stream of nitrogen while gently warming the flask. There remained about 650 mg. of a colorless material. From this residue unreacted material was removed by washing three times with 3-ml. portions of anhydrous ether, leaving behind 424–486 mg. crude potassium diacetone 2-keto-L-gulonate-C^{14}. Crystallization and reoxidation of the recovered material and combination of both batches of diacetone 2-keto-L-gulonate-C^{14} gave a total yield of 651–723 mg. (about 90% yield based on diacetone-L-sorbose-C^{14} oxidized).

L-Ascorbic acid-C^{14}. In a 65-ml. flask equipped with a ground glass joint, 651 mg. of potassium diacetone 2-keto-L-gulonate-C^{14} (prepared from 500 mg. of L-sorbose-C^{14} having a specific activity of 0.18 μcuries/mg.) were covered with 30 ml. of chloroform and while cooling the flask, 1.5 ml. of concentrated hydrochloric acid was added dropwise. The flask was stoppered and the mixture was allowed to stand in the dark at room temperature for 9–10 days.[21] The resulting brown mixture was extracted three times with 30-ml. portions of 0.01 *N* hydrochloric acid and the dissolved chloroform was removed from the aqueous phase by flushing with nitrogen. The volume was adjusted to 100 ml. and an aliquot was titrated with indophenol dye,[22] which indicated the presence of 170 mg. of L-ascorbic-C^{14} acid. Then 50 mg. of carrier was added and the material was purified by an anion exchange column technique, described previously,[3, 23] except that the Amberlite IR-4B resin was used in the acetate form and 2 *N* formic acid was employed to elute the L-ascorbic-C^{14} acid from the column (resin bed 15 cm. long and 2.5 cm. in diameter). The resulting material was washed twice with 0.5-ml. portions of cold acetone. Recrystallization afforded 146 mg. of pure L-ascorbic-C^{14} acid, m.p. 190–191°, having a specific activity of 0.13 uc/mg. Correcting for unreacted diacetone L-sorbose-C^{14}, this represents a yield of C^{14} of 22% based on L-sorbose-C^{14}. Addition of carrier to the acetone washings and recrystallization of the resulting material gave less active L-ascorbic-C^{14} acid which brought the total yield to 27%.[24] Radioactive purity was established by the following criteria:[23] the specific activity remained constant on recrystallization with carrier and L-ascorbic-C^{14} acid, its 2,4-dinitrophenylosazone and dimedone[25] derivatives had the same molar specific activity.

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[21] If instead of allowing the mixture to stand, it was refluxed for 8 hours the yield was slightly lower.

[22] The Association of Vitamin Chemists, Inc., *Methods of Vitamin Assay*, Interscience Publishers, Inc., New York, N. Y., 1951, pp. 77–80.

[23] Jackel, Mosbach, and King, *Arch. Biochem.*, **31**, 442 (1951).

[24] This method has also been carried out starting with 150 mg. of L-sorbose-C^{14}.

[25] Horowitz, Doerschuk, and King, *J. Biol. Chem.*, **199**, 193 (1952).

2-Alkynyl Formals Formed During the Synthesis of 2-Alkynols[1a]

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Many times we have prepared large quantities of 1-alkynols in yields as high as 85% by reaction of alkynylmagnesium bromide with formaldehyde. In certain instances however, products boiling higher than the expected alkynol have been formed with a corresponding decrease in the yield of alkynol.

This paper deals with the elucidation of structure and the origin of the high-boiling product formed during the synthesis of 2-heptynol. Sufficient quantity of this higher-boiling material was available from a previous synthesis. The major component of this material was identified as di-2-heptynoxymethane, $(C_4H_9C{\equiv}C-CH_2O)_2CH_2$, **I**, on the basis of elemental analysis, molecular weight, infrared spectrum, hydrogenation equivalent, and identification of the hydrogenated product. An independent synthesis of **I** was also achieved by heating 2-heptynol with formaldehyde in the presence of magnesium bromide or ferric chloride.

Attention was also directed to determining the origin of **I** during a conventional synthesis of 2-heptynol. Conant, *et al.*[2] noted that formals are byproducts of the synthesis of saturated primary alcohols when a considerable excess of gaseous formaldehyde is passed into the Grignard reagent. Isolation of the product in the usual way (which in their case was hydrolysis with sulfuric acid followed by steam-distillation) converted as much as two-thirds of the alcohol to the formal.[2]

Addition of excess formaldehyde to hexynylmagnesium bromide followed by conventional (rapid) hydrolysis did not give **I** however. No higher-boiling products were formed if the reaction mixture was kept cool as excess formaldehyde was being added but if the reaction mixture was allowed to become warm, a higher-boiling product having a double bond rather than an acetylenic

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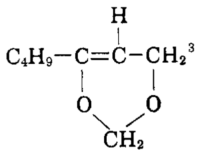
[1a] Contribution No. 990, Department of Chemistry, University of Pittsburgh.

[1b] Abstracted from the thesis of J. A. W. presented in partial fulfillment of the requirements for the degree of Master of Science, University of Pittsburgh, 1956. The author wishes to thank the Dow Corning Fellowship at the Mellon Institute for the use of their facilities.

The authors wish to thank Dr. James F. Miller and James Kerns of Mellon Institute for elemental analyses and Dr. Foil A. Miller and co-workers, also at Mellon Institute, for infrared analyses.

[2] J. B. Conant, C. N. Webb, and W. C. Mendum, *J. Am. Chem. Soc.*, **51**, 1246 (1929); **51**, 3677 (1929).

bond was formed, as shown by infrared analysis. A possible structure for this product could be



The formation of I as a by-product was found to occur during the hydrolysis of 2-heptynoxymagnesium bromide in the presence of unreacted excess formaldehyde if the hydrolysis was carried out gradually over a period of several hours. The reaction of the formed heptynol with the formaldehyde is catalyzed by some of the salts present in the hydrolysis mixture.

EXPERIMENTAL

The identification of 2-heptynyl formal, I. The higher-boiling by-product formed during the synthesis of 2-heptynol was collected and stored at 0° for as long as 10 years. Redistillation gave a major fraction with the following properties: b.p. 137–138° at 1.5 mm., n^{25}_{D} 1.4610, d^{25}_{4} 0.911.

Anal. Calc'd for $C_{15}H_{24}O_2$: C, 76.2; H, 10.3; M. W. 236; Hydrogenation Equivalent 59. Found: C, 75.7; H, 10.4; M. W. (cryoscopic, benzene, average) 222; Hydrogenation Equivalent (semimicro, Adams' catalyst catalyst in ethanol, average value) 56.

The infrared spectrum shows characteristic bands at 2240 cm.$^{-1}$ (triple bond) 1040 and 1100 cm.$^{-1}$ (ether or acetal), and the absence of bands at 3200 cm.$^{-1}$ (hydroxyl), 1620 cm.$^{-1}$ (double bond).

Hydrogenation and hydrogenolysis of I. A sample (6.4 g.) of I was exposed to hydrogen at 40 p.s.i. in the presence of Adams' catalyst until the uptake of hydrogen ceased. Distillation yielded 3.3 g. of heptanol (b.p. 95° at 34 mm., n^{25}_{D} 1.4221, phenylurethan m.p. 59–60°, no depression of melting point when mixed with an authentic sample) and 1.9 g. of heptyl formal (b.p. 140–145° at 5 mm., n^{25}_{D} 1.4289, d^{25}_{4} 0.839).

I *as by-product in the synthesis of 2-heptynol.* 2-Heptynol was prepared as previously described,[4] in yields as high as 83%. Hydrolysis with saturated ammonium chloride or with dilute hydrochloric acid, followed by washing with sodium bisulfite, produced various amounts of I. When a several-fold excess of formaldehyde was introduced and hydrolyzed by a rapid addition of acid, a product (b.p. 94–97° at 2 mm., n^{25}_{D} 1.4979, d^{25}_{4} 1.26) was isolated which was not I. Other higher-boiling fractions had refractive indices too high to be I.

The yield of 2-heptynol was 60% when 0.55 equivalent of ethyl magnesium bromide reacted with 0.67 mole of hexyne-1, followed by 0.7 equivalent of formaldehyde. An excess of dilute hydrochloric acid was used for the conventional (rapid) hydrolysis. There was no product boiling higher than the heptynol.

In a similar experiment a 120% excess of formaldehyde was used and the addition of hydrochloric acid was over a period of two hours while the heterogeneous mixture was vigorously agitated. The yield of heptynol was only 36% and I was isolated in 24% yield, b.p. 139–140° at 3 mm., n^{25}_{D} 1.4613, d^{25}_{4} 0.913.

Authentic I. Formaldehyde (from the thermal decomposition of 0.33 equivalent of paraformaldehyde) was passed into a solution of 10 g. (0.09 mole) of 2-heptynol and 0.5 g. (0.0003 mole) of anhydrous (by heating the hydrated salt under a vacuum) magnesium bromide in 100 ml. of ether. The product was washed with three 20-ml. portions of 40% sodium bisulfite and dried over Drierite. Distillation yielded 2 g. (20% recovery) of 2-heptynol, and 6.4 g. (70% yield) of I, b.p. 135° at 2 mm., n^{25}_{D} 1.4608, d^{25}_{4} 0.907, R_D 0.303. The compound was also obtained in a 63% yield using ferric chloride as catalyst. The hydrogenation of 9.0 g. (0.038 mole) of I in ethyl alcohol using Adams' catalyst produced 7.3 g. (78% yield) of heptyl formal, b.p. 135–138° at 5 mm., n^{25}_{D} 1.4269, d^{25}_{4} 0.840, R_D 0.306.

An authentic sample of heptyl formal was prepared in 70% yield by heating 17.4 g. (0.15 mole) of heptyl alcohol 2.3 g. (0.075 equivalent) of paraformaldehyde and 0.2 g. of ferric chloride on a steam-bath for one hour, b.p. 135° at 5 mm., n^{25}_{D} 1.4270, d^{25}_{4} 0.8367, R_D 0.307 (Calc'd 0.307).

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[3] M. J. Beets and L. G. Heeringa, *Rec. trav. chim.*, **74**, 1085 (1955).

[4] M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

Methacryloxymethyl and Acryloxymethyl Silicones

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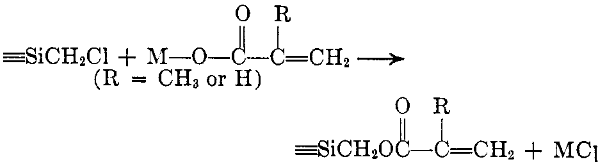
The difficulties encountered in attempts to achieve high molecular weight additon type polymers or copolymers from vinylsilicon compounds[1,2] stimulated an interest in the preparation of several methacryloxymethyl and acryloxymethylsilicone monomers utilizing the reaction of an alkali salt of an unsaturated acid with chloromethyl silanes or chloromethylsiloxanes.



$$\equiv SiCH_2Cl + M{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}{=}CH_2 \longrightarrow \equiv SiCH_2O\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}{=}CH_2 + MCl$$
$$(R = CH_3 \text{ or } H)$$

The methods used for the syntheses of such monomers were modifications of a reaction reported by Whitmore and Sommer[3] in which they reacted chloromethyltrimethylsilane with potassium acetate in glacial acetic acid to yield acetoxymethyltrimethylsilane and potassium chloride.

In contrast to vinylsilicon compounds, these new monomers were found to be readily polymerizable in bulk using conventional polymerization initiators such as α,α'-azodi-iso-butyronitrile or benzoyl peroxide to yield high molecular weight polymers. The results of a comprehensive study of the monomer reactivity ratios[4] for one of the mono-

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[1] G. H. Wagner, *et al.*, *Ind. Eng. Chem.*, **45**, 367 (1953).

[2] B. R. Thompson, *J. Polymer Sci.*, 19, 373 (1956).

[3] F. C. Whitmore and L. H. Sommer, *J. Am. Chem. Soc.*, **68**, 481 (1946).

[4] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).