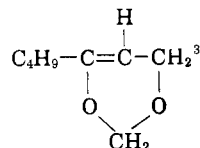


bond was formed, as shown by infrared analysis. A possible structure for this product could be



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_D²⁵ 1.4610, d₄²⁵ 0.911.

Anal. Calc'd for C₁₅H₂₄O₂: 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 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_D²⁵ 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_D²⁵ 1.4289, d₄²⁵ 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_D²⁵ 1.4979, d₄²⁵ 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_D²⁵ 1.4613, d₄²⁵ 0.913.

Authentic I. Formaldehyde (from the thermal decomposi-

tion 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_D²⁵ 1.4608, d₄²⁵ 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_D²⁵ 1.4269, d₄²⁵ 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_D²⁵ 1.4270, d₄²⁵ 0.8367, R_D 0.307 (Calc'd 0.307).

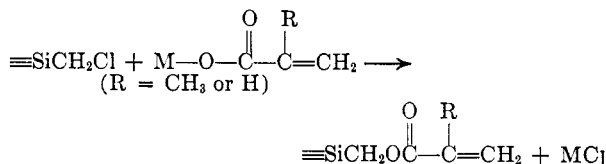
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH 13, PENNSYLVANIA

Methacryloxymethyl and Acryloxymethyl Silicones

R. L. MERKER AND J. E. NOLL

Received August 7, 1956

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.



The methods used for the syntheses of such monomers were modifications of a reaction reported by Whitmore and Sommer³ 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-isobutyronitrile or benzoyl peroxide to yield high molecular weight polymers. The results of a comprehensive study of the monomer reactivity ratios⁴ for one of the moro-

(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).

(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).

mers prepared, methacryloxymethylpentamethyl-disiloxane, with methyl methacrylate, acrylonitrile, styrene, vinyl acetate, etc., will be published in the near future. A few of the physical properties of copolymers of methyl methacrylate (MMA) and methacryloxymethylpentamethyl-disiloxane (SMA) are shown in Table I. Copolymerizations were carried out in bulk using monomer compositions as shown in Table I.

benzene, the excess methacrylic acid and dimethylformamide were removed by washing with water followed by dilute sodium bicarbonate. After drying over sodium sulfate, 5 g. of hydroquinone was added and the product was distilled on a still of approximately ten plates to give 141 g. (68% yield) of 1,3-bis(methacryloxymethyl)tetramethyl-disiloxane b.p. 127° at 3 mm.; n_D^{25} 1.4472; d_4^{25} 0.996.

Anal. Calc'd for $C_{14}H_{26}O_3Si_2$: R_D ,⁶ 0.2671; Si, 16.95. Found: R_D , 0.2676; Si,⁷ 16.80.

In another run commercial sodium methacrylate (Matheson, Coleman & Bell, 118 g., 1.1 moles) was added in the

TABLE I
PROPERTIES OF SMA-MMA COPOLYMERS

Copolymer No.	Wt.-% SMA	Mole-% MMA	Ratio		Hardness Rockwell "R"	Sp. Gr.* 25/25	Contact Angle θ^{**}
			MMA Units	SMA Units			
1	0	100	∞		121	1.185	58°
2	20	90.8	9.86		120	1.152	—
3	40	78.7	3.70		113	1.112	—
4	60	62.1	1.64		91	1.075	91°
5	80	38.1	0.62		28	1.040	—
6	100	0	0		***	0.983	101°

* The densities (d_4^{25}) for methyl methacrylate and methacryloxymethylpentamethyl-disiloxane monomers are 0.938 and 0.903, respectively. ** Contact angle for water droplets on films deposited on glass from acetone solution. *** Too soft to measure.

It can be seen that copolymers possessing an MMA/SMA ratio of 3.7/1 or greater are nearly comparable in hardness to polymethylmethacrylate. Thus copolymers Nos. 2 and 3 could be machined and polished by the same methods commonly employed for polymethylmethacrylate, Nos. 4 and 5 were too soft for normal machining operations and No. 6 was soft enough to mill on slightly heated rolls on a conventional rubber mill. It will be noted that the approximate density change on polymerization for methyl methacrylate (+ 0.247 g./cc.) is about three times as great as that observed for methacryloxymethylpentamethyl-disiloxane (+0.080 g./cc.).

The striking difference in the hydrophobic properties of polymethylmethacrylate and polymethacryloxymethylpentamethyl-disiloxane is evident from the data in Table I. Indeed, the later polymer possesses water repellancy characteristics comparable to those of dimethylpolysiloxanes ($\theta = 110^\circ$).⁵

EXPERIMENTAL

1,3-Bis(methacryloxymethyl)tetramethyl-disiloxane. Potassium methacrylate (145 g., 1.17 moles) was added to an agitating mixture of dimethylformamide (150 g.), methacrylic acid (150 g.), and hydroquinone (10 g.) at the reflux temperature, the rate of addition of potassium methacrylate being slow enough so that rapid solution of the salt was effected. 1,3-Bis(chloromethyl)tetramethyl-disiloxane (125 g., 0.54 mole) then was added over a period of one-half hour and the mixture was heated at reflux for another two hours. The potassium chloride was removed by filtration and after dilution of the reaction mixture with an equal volume of

same manner as described above to a mixture of glacial methacrylic acid (219 g., 2.5 moles) and hydroquinone (10 g.). 1,3-Bis(chloromethyl)tetramethyl-disiloxane (116 g., 0.5 mole) was added over a half hour period to the refluxing mixture. Refluxing was continued for another two hours. The sodium chloride formed (found 54 g.; theory, 58.5 g.) was removed by filtration and the acid was removed after dilution of the reaction mixture with an equal volume of benzene by washing with water and dilute sodium bicarbonate. The residue after drying over sodium sulfate was found to be fairly pure 1,3-bis(methacryloxymethyl)tetramethyl-disiloxane (found 150 g.; theory 166 g.), n_D^{25} 1.4484; d_4^{25} 1.003. This material was used directly to prepare methacryloxymethylpentamethyl-disiloxane.

Methacryloxymethylpentamethyl-disiloxane. 1,3-Bis(methacryloxymethyl)tetramethyl-disiloxane (116 g., 0.35 mole) from the above preparation was mixed with hexamethyl-disiloxane (146 g., 0.9 mole) to give a homogeneous solution. Ten grams each of hydroquinone, concentrated sulfuric acid, and trifluoroacetic acid was added and the mixture was allowed to stand three days before the acid was removed by washing with water. The product after drying over sodium sulfate followed by the addition of 5 g. hydroquinone was distilled at 10 mm. in a still of approximately ten plates to give, in addition to hexamethyl-disiloxane, methacryloxymethylpentamethyl-disiloxane, 74 g. (0.3 mole), and a residue (50 g., 0.15 mole) of 1,3-bis(methacryloxymethyl)tetramethyl-disiloxane. Methacryloxymethylpentamethyl-disiloxane is a clear, sharp-smelling liquid b.p. 86.5° at 10 mm.; n_D^{25} 1.4202; d_4^{25} 0.903.

Anal. Calc'd for $C_{16}H_{22}O_3Si_2$: R_D , 0.2803; Si, 22.73. Sap. equiv., 246.2; Bromine No., 64.7.

Found: R_D , 0.2790; Si, 21.85; Sap. equiv., 247.8; Bromine No., 64.6.

Bulk polymerization of the above monomer yielded an optically clear, tough, gummy polymer which was soluble in acetone or benzene. The molecular weight from osmotic pressure measurements was found to be 600,000-700,000.

Methacryloxymethyltrimethylsilane. Sodium methacrylate

(6) E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

(5) M. J. Hunter, M. S. Gordon, A. J. Barry, J. F. Hyde, and R. D. Heidenreich, *Ind. Eng. Chem.*, **39**, 1389 (1947).

(7) J. L. Speier, B. F. Daubert, and R. R. MacGregor, *J. Am. Chem. Soc.*, **76**, 1117 (1948).

(123 g., 1.15 moles) was added in the same manner as described previously to a mixture of glacial methacrylic acid (150 g.), dimethylformamide (150 g.), and hydroquinone (5 g.). At the reflux temperature of the solution, chloromethyltrimethylsilane (123 g., 1 mole) was added slowly over a period of one hour. After refluxing for an additional two hours, the solids were filtered off (Wt. 62 g.; theory for NaCl 58.5 g.). The filtrate was washed first with water and then with dilute sodium bicarbonate solution. The product was dried over sodium sulfate. After the addition of hydroquinone (5 g.), distillation yielded methacryloxymethyltrimethylsilane, b.p. 98° at 75 mm.; n_D^{25} 1.4282; d_4^{25} 0.883; in 62% yield.

Anal. Calc'd for $C_8H_{16}O_2Si$: R_D , 0.2905; Si, 16.30. Found: R_D , 0.2915; Si, 16.10.

The monomer was polymerized to give a clear, hard acetone-soluble polymer which in appearance was very similar to polymethylmethacrylate.

Methacryloxymethyldimethylphenylsilane. Chloromethyldimethylphenylsilane⁸ (92.3 g., 0.5 mole), sodium methacrylate (59 g., 0.55 mole), methacrylic acid (70 g., 0.82 mole), hydroquinone (7 g.), and dimethylformamide (150 g.) were heated at 60–70° for 18 hours and refluxed for one-half hour. Filtration yielded 27 g. of solids (theory for NaCl, 29 g.). The filtrate after dilution with benzene was washed with water until neutral and distilled in a still of ten plates to give 23 g. (0.13 mole) of chloromethyldimethylphenylsilane (26% recovery) and methacryloxymethyldimethylphenylsilane, b.p. 103° at 10 mm.; n_D^{25} 1.5045; d_4^{25} 0.991, in 84% yield based on unrecovered chloromethyl compound.

Anal. Calc'd for $C_{13}H_{18}O_2Si$: R_D , 0.2984; Si, 11.99. Found: R_D , 0.2990; Si, 11.86.

Polymerization yielded a hard, slightly yellow polymer which was insoluble in both acetone and benzene.

1,3-Bis(acryloxymethyl)tetramethyldisiloxane. Dry sodium acrylate (71 g., 0.75 mole) prepared from glacial acrylic acid practical grade, was dissolved, as described previously, in a mixture of practical glacial acrylic acid (200 g.) and hydroquinone (5 g.). Over a period of one half hour 1,3-bis(chloromethyl)tetramethyldisiloxane (77 g., 0.33 mole) was added at the reflux temperature of the reaction mixture. Refluxing was maintained for three hours. After cooling, the reaction mixture was mixed with an equal volume of benzene and then washed with water and sodium bicarbonate solution until neutral. The benzene solution was dried over sodium sulfate and the benzene was evaporated to give a residue of 97 g. (theory for product is 99.6 g., 0.33 mole).

The residue was distilled on a still of about ten plates at 1–2 mm. pressure using hydroquinone as an inhibitor; 56 g. of distillate was obtained in five cuts. The two middle cuts were combined, washed with sodium hydroxide to remove the hydroquinone that had distilled over, and dried over sodium sulfate to yield 1,3-bis(acryloxymethyl)tetramethyldisiloxane, b.p. 123° at 1 mm.; n_D^{25} 1.4418, d_4^{25} 1.008.

Anal. Calc'd for $C_{12}H_{22}O_8Si_2$: R_D , 0.2615; Si, 18.57. Found: R_D , 0.2624; Si, 18.24.

Acryloxymethylpentamethyldisiloxane. This was prepared in the manner previously described for its methacrylate analog using a 6.5/1 molar ratio of hexamethyldisiloxane to 1,3-bis(acryloxymethyl)tetramethyldisiloxane. Acryloxymethylpentamethyldisiloxane was obtained by distillation at reduced pressure b.p. 113° at 50 mm.; n_D^{25} 1.4165; d_4^{25} 0.906.

Anal. Calc'd for $C_9H_{20}O_3Si_2$: R_D , 0.2758; Si, 24.15. Found: R_D , 0.2772; Si 24.48.

Polymerization yielded a clear, elastic high polymer which was soluble in acetone or benzene.

Polymerization. The monomers were polymerized in bulk by heating the sample at 70° using as a catalyst 0.05 to

0.1% by wt. of α, α' -azodi-iso-butyronitrile or benzoyl peroxide. A nitrogen atmosphere was maintained over the sample during the polymerization which required from 4 to 24 hours. Copolymerizations of methyl methacrylate (MMA) and methacryloxymethylpentamethyldisiloxane (SMA) corresponding to the monomer compositions shown in Table I were carried out at 70° under a nitrogen atmosphere for a period of 16 hours using 0.1% by wt. of α, α' -azodi-iso-butyronitrile.

Acknowledgment. The authors wish to thank Dr. O. K. Johannsen for the molecular weight determination of polymethacryloxymethylpentamethyldisiloxane.

CORNING GLASS AND DOW CORNING MULTIPLE FELLOWSHIP

MELLON INSTITUTE
PITTSBURGH, PENNA.

Reactions of *unsym*-Dimethylhydrazine with Acrylonitrile and with Chloroacetamide

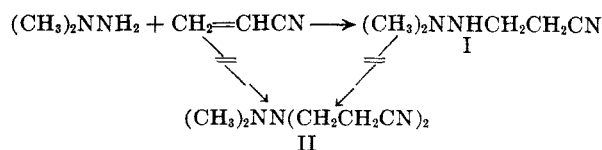
RICHARD L. HINMAN AND JAMES ROSENE

Received August 10, 1956

1,1-Dimethyl-2,2-hydrazino-diacetic and -dipropionic acids were desired for study as possible chelating agents. This paper reports two approaches, which, though unsuccessful, are of some interest in their own right.

The method selected for the preparation of 1,1-dimethyl-2,2-hydrazinodipropionic acid was cyanoethylation of *unsym*-dimethylhydrazine, followed by hydrolysis of the nitrile group. Monocyanoethylation of *unsym*-dimethylhydrazine was readily effected by refluxing an aqueous solution of the reactants for two hours. The product, 1,1-dimethyl-2-(β -cyanoethyl)hydrazine (I) was isolated in 87% yield. It is particularly interesting that the reaction occurred only when water was present. In another experiment the reactants were recovered unchanged from refluxing in wet ether which contained a few pellets of sodium hydroxide.

Various attempts were made to introduce two cyanoethyl groups into *unsym*-dimethylhydrazine. However, 1,1-dimethyl-2-(β -cyanoethyl)hydrazine (I) was the only product isolated from reactions in which the following sets of conditions were employed: (1) 4:1 molar ratio of acrylonitrile to dimethylhydrazine; (2) 4:1 molar ratio of acrylonitrile to hydrazine at 170° and 300 p.s.i.; (3) use of sodium hydroxide as a catalyst; (4) use of acetic acid as a solvent.



(8) J. E. Noll, J. L. Speier, and B. F. Daubert, *J. Am. Chem. Soc.*, **73**, 3867 (1951).