and after the reaction subsided, a temperature of 125° was maintained for one hour. The viscous yellow solution solidified on cooling. On recrystallization from a 50% aqueous alcohol solution, the product was obtained in pure form, m.p. 64–65°.

2-*n*-Amyl-2-methyl-4-*o*-toloxymethyl-1,3-dioxolane (LI).—A mixture of 91.0 g. (0.5 mole) of 3-*o*-toloxy-1,2-propanediol, 57.0 g. (0.5 mole) of methyl *n*-amyl ketone, 1.0 g. of *p*-toluenesulfonic acid and 300 ml. of toluene was refluxed in a flask fitted with a water-separating reflux condenser. After refluxing for five hours (98% of the theoretical amount of water was collected in the first two hours) the reaction mixture was cooled and extracted twice with 100 ml. of 5% sodium carbonate solution followed with 100 ml. of water. The toluene was distilled at reduced pressure and the residue yielded 119 g. (86%) of product, b.p. 164–165° (4.0 mm.).

3-*o*-Toloxy-1-(2,2-diethyl-3-hydroxypropoxy)-2-propanol (LVI). 3-Chloro-1-(2,2-diethyl-3-hydroxypropoxy)-2-propanol.—To a stirred mixture of 92.5 g. (1.0 mole) of 1-chloro-2,3-epoxypropane and 264 g. (2.0 mole) of 2,2-diethyl-1,3-propanediol heated to 40°, was added 4.3 ml. of concentrated sulfuric acid over a period of half an hour. When the reaction commenced it was necessary to cool the mixture in order to maintain the temperature at 40–50°. The mixture was kept at 100° for five hours after the spontaneous reaction had ceased. The sulfuric acid was neutralized with sodium carbonate and the product distilled directly from the reaction mixture. A forerun of 150 g. of the original diol, b.p. 91–93° (1.0 mm.), and 110 g. (49%) of product, b.p. 112–115° (0.1 mm.), were obtained. *Anal.* Calcd. for $C_{10}H_{21}O_3Cl$: C, 53.25; H, 9.36. Found: C, 53.50; H, 9.08.

A solution of 10.8 g. (0.1 mole) of *o*-cresol, 4.4 g. (0.11 mole) of sodium hydroxide and 50 ml. of water was refluxed for ten minutes. A solution of 22.5 g. (0.1 mole) of 3-chloro-1-(2,2-diethyl-3-hydroxypropoxy)-2-propanol in 30 ml. of ethanol was introduced to the stirred solution over a period of half an hour, and refluxing continued for four hours. After removal of the alcohol by distillation, the oil was taken up in 100 ml. of ether, washed with 40 ml. of a saturated sodium chloride solution, concentrated and the residue distilled, collecting the fraction, b.p. 145–158° (0.1 mm.). Refractionation gave 20.0 g. (73%) of 3-*o*-toloxy-1-(2,2-diethyl-3-hydroxypropoxy)-2-propanol, b.p. 153–155° (0.1 mm.).

NEW BRUNSWICK, NEW JERSEY

RECEIVED OCTOBER 29, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. III. Vinyloxyethyl Derivatives[1,2]

BY GEORGE B. BUTLER AND ROBERT L. GOETTE

Several new tertiary amines and unsaturated quaternary ammonium bromides containing the β-vinyloxyethyl group have been prepared and characterized. The unsaturated quaternary ammonium salts were polymerized under the influence of *t*-butyl hydroperoxide to yield water soluble polymers from those compounds containing only two unsaturated groups in addition to the β-vinyloxyethyl group, and water insoluble polymers from those compounds containing three unsaturated groups in addition to the β-vinyloxyethyl group. The water insoluble polymers were found to undergo ion exchange reactions. These polymers had a high coefficient of swelling and ion-exchange capacity equal to 88.8% of the theoretical. It was found that the β-vinyloxyethyl group did not enter into the polymerizations under the conditions used.

Polymerization of unsaturated quaternary ammonium compounds has been found[3] to produce water insoluble polymers suitable for strongly basic ion exchange resins. However, because of the low tensile strength and brittleness of these materials, apparently due to a low degree of polymerization, an effort to improve these properties seemed important. Polymerization studies of unsaturated quaternary ammonium salts containing halogenated allyl derivatives[4] resulted in the formation of improved capacities, apparently as the result of a higher coefficient of swelling, but no improvement in physical properties.

It has been shown by a number of workers[5,6] that vinyl ethers can be polymerized by a cationic mechanism to give polymers of high molecular weight. It has also been shown[7] that vinyl ethers of unsaturated alcohols such as allyl alcohol can be made to undergo a two-stage polymerization in which the ether is converted to an unsaturated linear polymer through the vinyl groups by a cationic mechanism and this polymer cross-linked through the unsaturated linkages by a free radical catalyzed mechanism. Also, in this work, cross-linked polymers were obtained by a free radical catalyzed polymerization of ethylene glycol vinyl allyl ether, indicating that the vinyloxy group undergoes copolymerization with the allyl group. Many other examples of copolymerization of vinyloxy groups may be cited. It has been shown[8] that 2-alkoxy-1,3-butadienes, compounds which are both vinyl and allyl ethers, undergo polymerization as the result of peroxide catalysis, as well as by light, heat and other catalysts. Divinyl ether[9,10] has been used as a cross-linking agent for vinyl acetate and methyl methacrylate. Vinyl chloride copolymerizes with the trivinyl ether of glycerol[11] in ratios of 0.1–10% in presence of benzoyl peroxide catalyst to produce a brittle copolymer decomposing from 174–200° depending on the amount of cross-linking agent used. Vinyl ethers have been copolymerized with maleic anhydride and related compounds in presence of per-

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(1) An abstract of a thesis presented by Robert L. Goette to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science.

(2) This material was presented before the Meeting-in-Miniature, Florida Section, American Chemical Society, Orlando, Florida, May, 1951.

(3) G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

(4) G. B. Butler and Francis L. Ingley, *ibid.*, **73**, 895 (1951).

(5) I. G. Farbenindustrie, A. G., French Patent 734,129 (March 24, 1932).

(6) I. G. Farbenindustrie, A. G., British Patent 443,978 (March 11, 1936).

(7) G. B. Butler and J. L. Nash, Jr., THIS JOURNAL, **73**, 2538 (1951).

(8) H. B. Dykstra, *ibid.*, **57**, 2255 (1935).

(9) R. G. W. Norrish and E. F. Brookman, *Proc. Roy. Soc.* (*London*), **A163**, 205 (1937).

(10) K. G. Blaikie and R. N. Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

(11) I. P. Losev and S. M. Zhivukhin, *Trudy Konferentsii Vysoko molekulyar. Soedineniyam, Akad. Nauk S. S. S. R., Otdel. Khim. Nauki, Otdel. Friz. Mat. Nauk*, **1**, 23 (1943).

TABLE I

UNSATURATED TERTIARY AMINES

Amine	Formula	B.p., °C.	Mm.	d^{25}_4	n^{25}_D	*MR*D Calcd.	Theory	Nitrogen, % Theory	Found	Yield, %
β-Vinyloxyethylmorpholine	$C_8H_{15}NO_2$	53–54	0.9	0.9954	1.4658	43.73	43.86	8.91	8.76	54.8
β-Vinyloxyethylpiperidine	$C_9H_{17}NO$	72.3–73	7.5	.9117	1.4639	46.97	46.84	9.02	8.95	90.2
Dibutyl-β-vinyloxyethyl-	$C_{12}H_{25}NO$	59–60.5	0.2	.8321	1.4378	62.85	62.89	7.02	7.00	30.1
Diallyl-β-vinyloxyethyl-	$C_{10}H_{17}NO$	47–48	1.4	.8666	1.4567	52.53	52.72	8.38	8.42	26.9
Dimethallyl-β-vinyloxyethyl-	$C_{12}H_{21}NO$	43	0.5	.8680[a]	1.4572	61.50	61.96	7.17	7.07	29.4
Allylbutyl-β-vinyloxyethyl-	$C_{11}H_{21}NO$	51.3	0.4	.8523	1.4470	57.46	57.81	7.64	7.60	57.9

[a] d^{20}_4.

oxide catalysts.[12-17] This information led us to believe that quaternary ammonium compounds containing both the vinyloxy group and the allyl group could possibly be made to form linear polymers first through the vinyloxy group and the unsaturated linear polymer cross-linked by means of the allyl groups. Such a polymerization would be expected to lead to polymers of a higher degree of polymerization which should result in improved physical properties.

Since no unsaturated tertiary amines containing the β-vinyloxyethyl group have been reported, it was necessary to prepare several of them as intermediates for the preparation of the unsaturated quaternary ammonium compounds. These amines were prepared by a modification of the procedure outlined in the first two papers of this series.[3,4] Since vinyl-2-chloroethyl ether was very reluctant to form quaternary ammonium compounds, it was necessary to prepare tertiary amines containing the β-vinyloxyethyl group. Also, since reaction of the halide with secondary amines was very slow, a large excess was usually employed in preparing the tertiary amines.

The results of these studies are recorded below in the Experimental section and in the accompanying tables.

Experimental

Materials.—Piperidine, practical grade, was obtained from Eastman Kodak Company and used as received. The dibutylamine, morpholine and vinyl 2-chloroethyl ether were obtained from Carbide and Carbon Chemicals Corporation and used without further treatment. The dimethallylamine was obtained from Shell Development Company. It was fractionated and the fraction boiling between 57–58° at 26 mm. was recovered for use. Some of the dimethallylamine used was made from methallyl chloride obtained from Shell Development Company. The diallyl cyanamide which was hydrolyzed to make the diallylamine used in this research project was obtained from American Cyanamid Company and utilized without further purification. The allyl bromide was obtained from Dow Chemical Company and the fraction boiling between 70.0–70.2° was recovered for use. The *t*-butyl hydroperoxide was obtained as a 60% solution through the courtesy of Union Bay State Company.

Preparation of Tertiary Amines.—Because of the inertness of the halogen atom in vinyl 2-chloroethyl ether, poor yields of tertiary amines were obtained by the procedure previously employed.[3,4] Satisfactory yields of these amines were obtained by a modification of the above procedure in which a two molar excess of the halide was used, and the reaction time extended to an average of 15 hours. The excess of vinyl 2-chloroethyl ether was recovered during the distillation process. The compounds were purified by fractionation through a heated column 2 × 40 cm., packed with 1/4" Berl saddles. The properties, analyses and yields of these amines are recorded in Table I.

Preparation of Quaternary Ammonium Bromides.—Procedures similar to those described previously in this series were employed for preparing the unsaturated quaternary ammonium compounds containing the 2-vinyloxyethyl group. Because of the pronounced hygroscopicity of these compounds and their reluctance to crystallize, purification was rather difficult. By repeated solution of these compounds in dry chloroform or ethylene chloride and precipitation with dry ether, four of the salts were obtained as solids. Allyldimethallyl-β-vinyloxyethylammonium bromide and allyl-β-vinyloxyethyldibutylammonium bromide were obtained only as viscous oils. After drying for an average time of four days at 1 mm. pressure and 56°, the compounds were analyzed for bromine. The results of these analyses are recorded in Table II.

TABLE II

QUATERNARY AMMONIUM BROMIDES

Bromide	Formula	Bromine, % Theory	Found
N-Allyl-N-β-vinyloxyethyl-morpholinium	$C_{11}H_{20}BrNO_2$	28.72	28.53
N-Allyl-N-β-vinyloxyethyl-piperidinium	$C_{12}H_{22}BrNO$	28.93	28.93
Triallyl-β-vinyloxyethyl-ammonium	$C_{13}H_{22}BrNO$	27.72	27.65
Diallylbutyl-β-vinyloxy-ethylammonium	$C_{14}H_{26}BrNO$	26.27	26.64
Allyldibutyl-β-vinyloxy-ethylammonium	$C_{15}H_{30}BrNO$	24.95	24.64
Allyldimethallyl-β-vinyloxy-ethylammonium	$C_{15}H_{26}BrNO$	25.26	25.57

Cationic-Catalyzed Polymerization Studies.—Fourteen grams of N-allyl-N-β-vinyloxyethylmorpholinium bromide was placed in a three-necked flask equipped with a stirrer, water separator and reflux condenser, and 120 ml. of dry benzene was added. The benzene was refluxed for several hours to thoroughly dry the salt. After this time, 5 g. of the addition compound of BF_3 and diethyl ether was added while stirring was continued. The insoluble salt, although most of it adhered to the walls of the flask rather than remain suspended in the liquid, slowly changed to dark brown in color. Heating at reflux temperature was continued for 2.5 hours. After cooling, the benzene was decanted and the solid residue was found to be almost completely soluble in water; however, a small amount of water-insoluble material remained. This residue was washed thoroughly and dried. It was found to be free of nitrogen and bromine.

Five grams of N-allyl-N-β-vinyloxyethylmorpholinium bromide was dissolved in 40 ml. of acetic acid and 10 ml. of acetic anhydride added to remove any water which may have been present. Five grams of the BF_3–diethyl ether addition compound was added causing a slight rise in temperature. The solution was heated on a steam-bath with stirring for 5 hours. After cooling, it was added to an equal volume of water. The material appeared to be completely soluble; however, after standing for several hours, a small amount of a dark solid separated. This was removed,

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[12] A. Voss and E. Dickhauser, U. S. Patent 2,047,398 (July 14, 1936).

[13] H. L. Gerhart, U. S. Patent 2,230,240 (Feb. 4, 1941).

[14] F. E. Condo, C. J. Krister and W. E. Lundquist, U. S. Patent 2,286,062 (June 9, 1942).

[15] G. F. D'Alelio, U. S. Patent 2,340,110 (July 3, 1942).

[16] G. F. D'Alelio, U. S. Patent 2,340,111 (July 3, 1942).

[17] W. E. Hanford, U. S. Patent 2,378,629 (June 19, 1945).

washed and dried. It was found to be free of nitrogen and bromine.

Peroxide-Catalyzed Polymerization Studies.—The general procedure described in the second paper of this series[4] was followed in the peroxide-catalyzed polymerization studies of these salts. The samples were allowed to remain for 24 hours in an oven set at 60°. The polymers were treated with hot distilled water, and if insoluble were crushed to particles of approximately 40 mesh. Conversion to the hydroxide form and demonstration of ion exchange were accomplished as previously described. Water-insoluble polymers were obtained only from triallyl-β-vinyloxyethylammonium bromide and allyldimethallyl-β-vinyloxyethylammonium bromide. Some of the properties of polytriallyl-β-vinyloxyethylammonium bromide are recorded in Table III. Because of the small amount of the other water insoluble polymer available, it was not studied beyond demonstration of its ion-exchange ability. For comparison, similar data are recorded for two polymers of different constitution prepared in an earlier study.[4]

TABLE III

PROPERTIES OF ION-EXCHANGE POLYMERS

Ammonium bromide polymer		Triallyl-β-vinyloxyethyl-	Triallyl-2-chloroallyl-	Tetrallyl-
Coefficient of swelling		5.08	1.83	1.17
Yield, %		53.8	43.0	65.5
Capacity	meq./ml.	0.308	0.405	0.450
	meq./g.	3.08	2.08	1.53
Theoretical capacity, %		88.8	61.0	39.4
Dry bromide, form. per ml. wet, g.		0.10	0.195	0.289

Discussion of Results

Successful polymerization of the vinyl group of ethylene glycol vinyl allyl ether and related compounds[7] by a cationic mechanism to linear polymers and subsequent cross-linking of these polymers through the allyl groups by a free radical catalyzed mechanism indicates that the compounds prepared in this work should lend themselves to similar treatment. However, since these compounds are ionizable salts, and insoluble in the relatively nonpolar type of solvent in which cationic polymerization is usually effected, it is not surprising that polymerization by this method was not accomplished. Polymerization conditions in the experiments reported were such that cross-linked and water-insoluble polymers would have resulted, since under similar conditions cross-linked polymers were obtained from the vinyl allyl ethers mentioned above. As a result of these experiments, it can only be assumed that these quaternary ammonium salts do not polymerize under these conditions.

Of the quaternary ammonium salts studied, only those containing more than two unsaturated groups in addition to the vinyloxyethyl group polymerized by peroxide catalysis to produce water-insoluble compounds. Previous work[3,4] showed that compounds containing only two allyl groups produced water-soluble polymers, while those containing three or more allyl groups produced cross-linked and water-insoluble polymers. Since in this work, only compounds containing three allyl groups in addition to the vinyloxyethyl group resulted in water-insoluble polymers, we were led to believe that the vinyl group took no part in the polymerization. In order to verify this belief, diallylbutyl-β-vinyloxyethylammonium bromide, a compound containing only two allyl groups, was prepared and studied. Polymerization of this compound produced a water-soluble polymer. Triallylbutylammonium bromide[3] produces a water-insoluble polymer under similar conditions. These results show that the vinyloxyethyl group is not polymerized under the conditions used. This conclusion is substantiated by the fact that the coefficient of swelling is quite high, indicating a lower degree of cross-linking. The low yield also supports this conclusion.

The results of this investigation support those previously obtained[4] that the higher the coefficient of swelling, the higher the ion-exchange capacity of the resin. A higher ratio of the ions associated with the quaternary nitrogen center in the highly swollen polymer are available for exchange than in the more highly cross-linked tetrallylammonium and triallyl-2-chloroallylammonium polymers. For comparison, properties of these two polymers are included in Table III.

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RECEIVED JULY 20, 1951