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

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VI. Derivatives of 1,4-Diaminobutene-2[1,2]

BY GEORGE B. BUTLER AND ROBERT L. GOETTE

RECEIVED NOVEMBER 9, 1953

Eight unsaturated quaternary ammonium bromides and one unsaturated tertiary amine have been prepared and characterized. The quaternary ammonium bromides were polymerized by use of peroxide catalysts, and some of the properties of the polymers determined. It was shown that the double bond of the butene-2 structure did not enter into the polymerization, and that this residual double bond caused a decrease in the basic properties of the resulting polymer.

Previous work[2] has shown that certain unsaturated quaternary ammonium salts will undergo polymerization in the presence of peroxide catalysts to produce water-insoluble polymers suitable for strongly basic ion exchange resins. Investigation of unsaturated quaternary ammonium bromides containing the vinyloxyethyl group and the propargyl group,[2] respectively, has shown that these groups do not enter into the polymerization under the conditions used. A study[2] of the properties of the polymers resulting from polymerization of unsaturated quaternary ammonium salts has shown that the exchange of chloride ions for hydroxide ions is more rapid than the reverse exchange. Since conversion of the polymer from the salt form to the hydroxide form by use of sodium or potassium hydroxide depends mainly on the mass action principle, assuming that the quaternary ammonium hydroxide is comparable to these inorganic hydroxides in basic strength, a quaternary ammonium center having decreased basic properties would be desirable. From a theoretical standpoint, this could be accomplished by attaching electrophilic groups to the nitrogen to give a polymer which would lend itself to the halide-hydroxide exchange more readily. This paper describes some studies of this nature.

The use of 1,4-dibromobutene-2 or 1,4-dichlorobutene-2, compounds resulting from 1,4-addition of bromine and chlorine, respectively, to butadiene-1,3, in synthesizing tertiary amines or quaternary ammonium salts offered the possibility of two allyl-type halogens, in addition to one double bond of the allyl type. In order to determine whether or not the butene-2 double bond entered into the polymerization, compounds containing two, four and six allyl groups in addition to the butene-2 double bond were prepared and polymerized. Since it has been shown[2] that unsaturated quaternary ammonium compounds containing a maximum of two allyl groups produce water-soluble polymers on polymerization, this series of compounds affords a means of determining whether or not the butene-2 double bond enters into the polymerization.

In addition to derivatives of 1,4-diaminobutene-2, several quaternary ammonium salts of different type were prepared and characterized for comparison in properties with the 1,4-diaminobutene-2 compounds. Among these were derivatives of diaminomethane. The results of this phase of the work present additional evidence of the instability of compounds of this general structure.

The results of these studies are recorded in the Experimental section and in Tables I and II.

Experimental

Preparation of Tertiary Amines.—Triallylamine was prepared by a modification of a method previously reported.[3] The following preparation of 1,4-bis-(diallylamino)-butene-2 will illustrate the general procedure used for preparation of derivatives of 1,4-diaminobutene-2: One mole (125 g.) of 1,4-dichlorobutene-2 was dissolved in 300 ml. of dry benzene in a three-neck flask equipped with mechanical stirrer, reflux condenser and addition funnel. Diallylamine (194 g., 2 moles) was added dropwise. Stirring at room temperature was continued for 48 hours. A saturated solution of sodium hydroxide (200 g.) was added to the flask and the benzene layer then removed and dried over solid sodium hydroxide. The benzene was removed and the amine distilled at 102° under a pressure of 0.8 mm. The product weighed 167.7 g.; yield, 68%, $n^{25}{}_{\mathrm{D}}$ 1.4820, $d^{25}{}_{4}$ 0.8647. *Anal.* Calcd. for $C_{16}H_{26}N_2$: N, 11.37. Found: N, 11.45.

Diallylmethylamine, 1,4-bis-(dimethylamino)-butene-2 and 1,4-bis-(diethylamino)-butene-2 were prepared by methods previously described or slight modifications thereof.[4,5]

Attempts to prepare 1,4-bis-(diallylamino)-butane and 1,4-bis-(diethylamino)-butane by this method were unsuccessful, although the hydrobromides of these amines were isolated in yields of 75% and 65%, respectively. 1,4-Bis-(diallylamino)-butane dihydrobromide, m.p. 58°. *Anal.* calcd. for $C_{16}H_{30}N_2Br_2$: Br, 38.95. Found: Br, 38.70. 1,4-Bis-(diethylamino)-butane dihydrobromide, m.p. 80°. *Anal.* Calcd. for $C_{12}H_{30}N_2Br_2$: Br, 44.13. Found: Br, 43.92.

Tetraallylmethylenediamine and tetramethylmethylenediamine were prepared by the method of Henry.[6]

Preparation of Quaternary Ammonium Salts.—Two general procedures were used for preparation of the quaternary ammonium salts required for this work: **Method I.**—The following preparation of 1,4-bis-(triallylammonium)-butene-2 dibromide will illustrate this method: one-half mole (123.2 g.) of 1,4-bis-(diallylamino)-butene-2 was dissolved in 150 ml. of dry acetophenone, and allyl bromide (121 g., 1 mole) was added dropwise with stirring. The reaction flask was cooled, as necessary, in ice-water. After the addition of the allyl bromide was complete, the reaction was stirred for one hour. Diisopropyl ether was added and the white, hygroscopic solid filtered and washed twice with dry diisopropyl ether. The product, after drying in a vacuum desiccator for several hours, weighed 244.2 g. The yield was quantitative.

Method II.—The following preparation of 1,4-bis-(triallylammonium)-butene-2 dibromide will illustrate this method: Eight grams (0.0373 mole) of 1,4-dibromobutene-2 was dissolved in 10 ml. of dry acetone and triallylamine (10.2 g., 0.0746 mole) was added dropwise with stirring. After a short time a viscous liquid separated. Within an hour, the viscous liquid had turned to a fine, white, hygroscopic solid. This solid was washed well with dry diiso-

---

[1] An abstract of a dissertation presented by Robert L. Goette to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The most recent paper of this series appeared in THIS JOURNAL, **76**, 713 (1954).

[3] G. B. Butler and B. M. Benjamin, *J. Chem. Educ.*, **28**, 191 (1951).

[4] R. Willstätter and T. Wirth, *Ber.*, **46**, 537 (1913).

[5] A. Partheil and H. von Broich, *ibid.*, **30**, 819 (1897).

[6] L. Henry, *ibid.*, **26**, 934 (1893).

TABLE I

UNSATURATED QUATERNARY AMMONIUM BROMIDES

Bromide	Formula	M.p., °C.	Bromine, % Calcd.	Bromine, % Found	Yield, %
Triallylmethylammonium	$C_{10}H_{18}NBr$	89–91	34.42	34.44	91.5
Triallyl-2-hydroxyethylammonium	$C_{11}H_{20}NOBr$	[a]	30.50	30.10	[b]
Diallyldimethylammonium	$C_8H_{16}NBr$	[a]	38.68	39.08	100.0
Dibromide					
1,4-Bis-(triallylammonium)-butene-2	$C_{22}H_{36}N_2Br_2$	155–157	32.72	32.47	100.0
1,4-Bis-(allyldiethylammonium)-butene-2	$C_{18}H_{36}N_2Br_2$	172–173	36.29	36.31	89.3
1,4-Bis-(allyldimethylammonium)-butene-2	$C_{14}H_{28}N_2Br_2$	183–184	41.60	41–57	92.7
Bis-(triallylammonium)-methane	$C_{19}H_{32}N_2Br_2$	[a]	35.65	35.40	[b]
Bis-(allyldimethylammonium)-methane	$C_{11}H_{24}N_2Br_2$	[a]	46.42	46.85	[b]

[a] The compound was not obtained in crystalline form. [b] No yield was calculated because the compound was obtained in the form of a viscous liquid.

propyl ether and dried in a vacuum desiccator. The dry product weighed 15.5 g.; yield 85.3%.

Tetraallylammonium bromide and triallylbenzylammonium bromide were prepared as described previously.[2]

Preparation of Polymers and Copolymers.—The general procedure described in the second paper of this series[2] was followed in these peroxide-catalyzed polymerizations. The samples were allowed to remain for 24 hours in an oven set at 65°. The resins were treated with hot distilled water, and if insoluble were broken down to small particles. The particles were then washed with hot distilled water until the filtrate did not give a test for the halide ion. The resin was dried at 65° and then ground to 20–60 mesh material. All of the water-insoluble resins were passed through one cycle of bromide to hydroxide to bromide, as previously described in the fourth paper in this series.[2] Polymers from 1,4-bis-(allyldiethylammonium)-butene-2 dibromide, diallyldimethylammonium bromide, bis-(diallylmethylammonium)-methane dibromide and bis-(allyldimethylammonium)-methane dibromide were water-soluble. All other polymers or copolymers from the quaternary ammonium salts studied were water-insoluble. The water-soluble polymers were not studied further.

Ion Exchange Capacity of Resins.—The general procedure described in the fourth paper of this series[2] was followed in the determination of the ion exchange capacity of the resins mentioned in this investigation. Several modifications of this general procedure were made. The bromide form of the resin, after one complete cycle, was thoroughly dried at 65° and then cooled in a desiccator before weighing out a 2.0000-g. sample into a 400-ml. beaker. One hundred ml. of 4% sodium hydroxide solution was added to the resin. After about 24 hours the solution was filtered and the resin washed at least four times with distilled water. Another 100 ml. of 4% sodium hydroxide solution was added to the resin. This process was continued until there were no more than 10 parts of Br^- per million in the solution above the resin after the sodium hydroxide solution had stood over the resin for 24 hours. When the bromide ion concentration reached the desired level, the hydroxide form of the resin was washed free of excess hydroxyl ions. The titration was carried out, as mentioned previously, after addition of 100 ml. of 0.1 *N* potassium bromide solution to the beaker containing the hydroxide form of the resin. Approximately 0.2 *N* hydrobromic acid was used in the titration. The capacities and other properties of a number of polymers and copolymers are shown in Table II.

A portion of the copolymer of diallyldimethylammonium bromide and tetraallylammonium bromide was converted to the chloride form and then treated in exactly the same manner as described above. The titration curves of the bromide and chloride forms of this copolymer are shown in Fig. 1 for comparison. Curves for other polymers studied are essentially like those shown except for displacements along the abscissa.

Exchange Rate Studies.—In the fourth paper of this series a procedure was described for comparing the rates of exchange of chloride ion for hydroxide ion and the reverse exchange. This procedure was used for the rate studies reported here with the exceptions that bromide ion was used exclusively and flow rates of both solutions were 5 ml. per minute. The results of these studies are shown in graph form in Fig. 2.

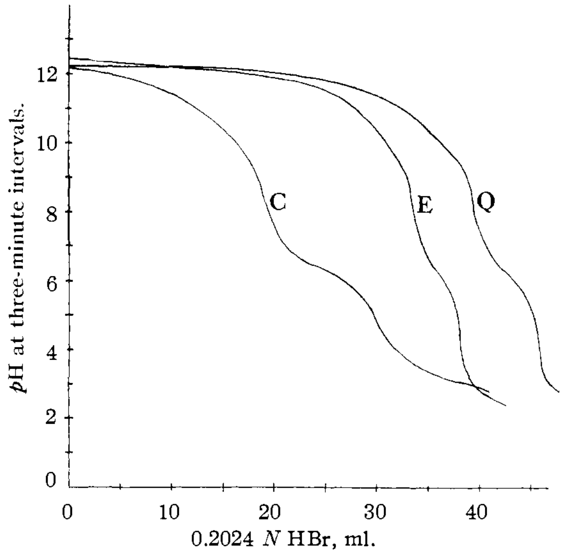


Fig. 1.—Typical titration curves of the polymers.

It is evident from the regeneration curve (dotted curve) that copolymer L, which contains 0.143 mole fraction of butene-2 groups, 0.343 mole fraction of methyl groups, and swelling coefficient of 2.48, has a higher regeneration rate (exchange of hydroxyl ion for bromide ion) than copolymer P, which contains no residual double bonds, 0.300 mole fraction of methyl groups, and swelling coefficient of 2.62. Plots of the two regeneration curves on two cycle semilog paper, bromide ion concentration *vs.* time, shows that the exchange follows approximately first-order reaction rates, and that the time required for exchange of one-half of the bromide ion originally present at flow rates as described above, was found to be 12 minutes for copolymer L, and 24 minutes for copolymer P.

Discussion of Results

Polymers of Derivatives of 1,4-Diaminobutene-2.—Results of polymerization studies of 1,4-diaminobutene-2 derivatives containing two, four and six allyl groups in addition to the butene-2 double bond show that those compounds containing only two double bonds, *e.g.*, bis-(allyldimethylammonium)-butene-2 dibromide, produce water-soluble polymers, while those containing four or six double bonds result in the formation of water-insoluble polymers. Since previous results have shown that water-insoluble polymers result from those compounds containing three or more double bonds, the failure of bis-(allyldimethylammonium)-butene-2 dibromide to produce a water-insoluble polymer is conclusive evidence that the butene-2

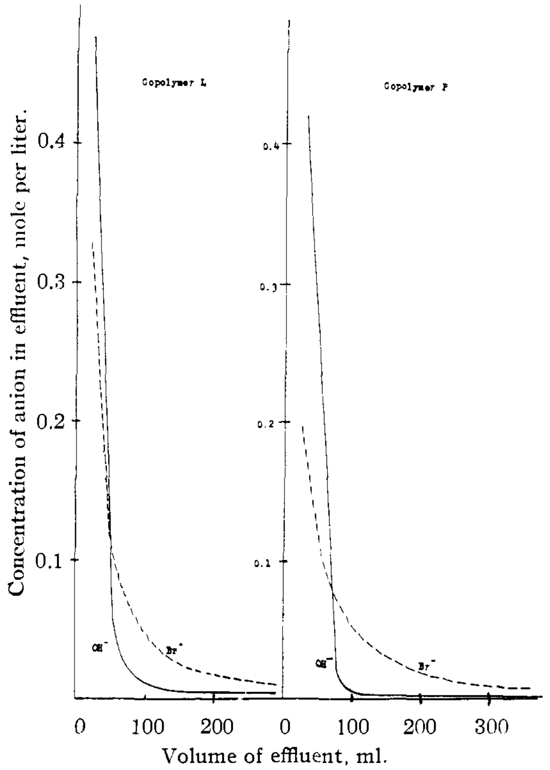


Fig. 2.—Exchange rates of hydroxyl ion for bromide ion and bromide ion for hydroxyl ion in copolymer L (left, 0.023 molar equivalent of bromide ion originally present), and copolymer P (right, 0.022 molar equivalent of bromide ion originally present).

double bond did not enter into the polymerization. This is substantiated by the pronounced effect of this double bond on the regeneration rates of the resulting polymers as discussed below. Even though those monomers containing only two allyl groups would not produce water-insoluble polymers suitable for further study alone, their copolymers with monomers containing three or more allyl groups were prepared.

TABLE II

PROPERTIES OF ION EXCHANGE RESINS

Resin	Yield, %	Swelling coeff.	Capacity Theor., meq./g.	Capacity Experimental, meq./ml.	Capacity Experimental, meq./g.	Theor., %	Wt. per ml. wet (Br form)
A	83.5	1.52	4.31	0.87	3.04	70.5	0.28
B	86.0	1.38	4.09	.76	2.26	55.4	.33
C	80.0	3.46	4.46	.35	1.94	43.5	.18
D	100.0	1.48	3.88	.71	1.92	49.5	.37
E	84.3	2.58	4.56	.87	3.37	73.9	.26
F	83.3	2.60	4.36	.76	3.09	71.0	.25
G	83.2	2.04	4.20	.85	2.76	65.7	.31
H	61.0	12.3	3.38	.15	2.48	73.4	.06
I	85.0	2.60	5.07	.96	3.89	76.7	.25
J	50.8[a]	3.46	4.94	.69	3.58	72.5	.19
K	50.5[a]	3.12	4.81	.70	3.40	70.7	.21
L	55.0[a]	2.48	4.69	.81	3.18	67.8	.26
M	74.3	10.4	4.80	.22	3.69	76.9	.06
N	71.7	6.97	4.74	.38	3.71	78.3	.10
O	78.0	3.22	4.56	.75	3.43	75.2	.22
P	76.5	2.62	4.41	.84	3.28	74.5	.26

[a] Catalyst to monomer ratio one-half of the value used in synthesizing the other resins.

COMPOSITION OF POLYMERS AND COPOLYMERS STUDIED

A. Polymer of triallylmethylammonium bromide
B. Polymer of 1,4-bis-(triallylammonium)-butene-2-dibromide
C. Polymer of bis-(triallylammonium)-methane dibromide
D. Polymer of tetraallylammonium bromide
E. Copolymer of diallyldimethylammonium bromide (3 moles) and tetraallylammonium bromide (1 mole)
F. Copolymer of 1,4-bis-(allyldiethylammonium)-butene-2 dibromide (2.04 moles) and tetraallylammonium bromide (1.16 moles)
G. Copolymer of triallylmethylammonium bromide (3 moles) and tetraallylammonium bromide (1 mole)
H. Copolymer of triallylbenzylammonium bromide (3 moles) and tetraallylammonium bromide (1 mole)
I. Copolymer of 1,4-bis-(triallylammonium)-butene-2 dibromide (1 mole) and 1,4-bis-(allyldimethylammonium)-butene-2 dibromide (9 moles)
J. Copolymer of 1,4-bis-(triallylammonium)-butene-2 dibromide (2 moles) and 1,4-bis-(allyldimethylammonium)-butene-2 dibromide (8 moles)
K. Copolymer of 1,4-bis-(triallylammonium)-butene-2 dibromide (3 moles) and 1,4-bis-(allyldimethylammonium)-butene-2 dibromide (7 moles)
L. Copolymer of 1,4-bis-(triallylammonium)-butene-2 dibromide (4 moles) and 1,4-bis-(allyldimethylammonium)-butene-2 dibromide (6 moles)
M. Copolymer of triallylmethylammonium bromide (1 mole) and diallyldimethylammonium bromide (9 moles)
N. Copolymer of triallylmethylammonium bromide (2 moles) and diallyldimethylammonium bromide (8 moles)
O. Copolymer of triallylmethylammonium bromide (1 mole) and diallyldimethylammonium bromide (1 mole)
P. Copolymer of triallylmethylammonium bromide (4 moles) and diallyldimethylammonium bromide (1 mole)
Q. Copolymer of diallyldimethylammonium bromide (3 moles) and tetraallylammonium bromide (1 mole) converted in an ion exchange column to the chloride form

Polymers of Derivatives of Methylenediamine.—Although some of the quaternary ammonium compounds of tetraalkyl methylenediamines were prepared[7] quite early, no information was made available concerning the stability of these compounds. It has been reported[6] that the salts of the tetraalkyl methylenediamines are not stable, but decompose to give formaldehyde and the salt of the secondary amine. In view of the possibility of producing quaternary ammonium polymers of low equivalent weight from tetraallylmethylenediamine, and in order to compare these products with the butene-2 derivatives, these compounds were prepared and studied. Polymerization studies have shown that bis-(triallylammonium)-methane dibromide produced a water-insoluble polymer, whereas bis-(methyldiallylammonium)-methane dibromide and bis-(allyldimethylammonium)-methane dibromide produced water-soluble polymers. Predictions based on previous results indicate that bis-(methyldiallylammonium)-methane dibromide should produce a water-insoluble polymer, unless some further change occurs. The failure of this monomer to produce a polymer having the expected properties together with the information available[6] concerning the salts of these tetraalkyl methylenediamines has led to the conclusion that, during the polymerization in aqueous

---

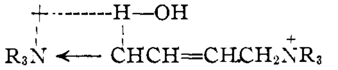
(7) J. von Braun and E. Rover, *Ber.*, **36**, 1196 (1903).

solution, the following reaction has occurred

$$[R_3NCH_2NR_3]^{++}\,2Br^- + H_2O \longrightarrow 2[R_3NH]^+\,Br + HCHO \text{ or}$$
$$[R_3NH]^+\,Br^- + [R_3NCH_2OH]^+\,Br^-$$

An inspection of the titration curve for polymer C, Fig. 1, which is the polymer of bis-(triallylammonium)-methane dibromide, indicates that the above hydrolysis has occurred to some extent, since the curve shows a second break, indicative of considerable amine capacity. However, since the *p*H remained in the range of 9–12 for a considerable portion of the curve, it is evident that hydrolysis, if by the first equation above, is not complete. Results reported in the fourth paper of this series have shown that the curve for an amine resin drops off very rapidly from *p*H 9.5 to the range of 4–5. The curve for polymer C indicates the presence of approximately equal quantities of quaternary ammonium and amine groups, resulting in convincing evidence that the second equation above was followed in the hydrolysis reaction.

Effect of Butene-2 Group on Properties of Polymers.—As discussed above, evidence has been obtained that the butene-2 double bond takes no part in the polymerization. It might be expected that this residual double bond would have an effect on the basic properties of the quaternary ammonium center due to its electrophilic nature. This effect appears to be analogous to that which results in a decrease in the ionization constant of an amine when, *e.g.*, a propyl group is replaced by an allyl group. Dipropylamine has $K_b = 1.02 \times 10^{-3}$ at 25°, and diallylamine has $K_b = 3.12 \times 10^{-6}$ at 25°. This effect could conceivably be the result of one or both of two mechanisms: (1) the electrophilic group decreases electron density in the immediate vicinity of the nitrogen atom, thus increasing the electropositive nature of this atom, resulting in decreased mobility of the hydroxyl ion, or (2) the C–N bond between the allyl group and the nitrogen may possess a certain degree of ionic character, as the result of resonance, thus increasing the electropositive nature of the nitrogen center. This latter effect would result in a more complete distribution of the positive charge over the entire ion, and likewise decrease the mobility of the hydroxyl ion. Since a quaternary ammonium hydroxide, according to present accepted ideas of structure, cannot exist in a non-ionized state except by hydrogen bonding through some mechanism such as that suggested below, this observed decrease in basic properties in polymers containing the butene-2 double bond must be attributed to the presence of this double bond. This decrease must be explained either on the basis of decreased mobility of the hydroxyl ion by one of the above mechanisms, or by hydrogen bonding. Since the quaternary ammonium structure has no proton attached directly to the nitrogen atom as in the ammonium and alkyl ammonium ions, hydrogen bonding could result only between the oxygen of the hydroxyl ion and a hydrogen atom attached through carbon. Since it has been shown that compounds such as allylbenzene react to produce an ionic sodium derivative,[8] it is likely that hydrogen bonding could be a factor in the manner



$$\begin{array}{l}+\cdots\cdots\text{H—OH}\\ \vdots\qquad\quad\vdots\\ R_3N \longleftarrow \text{CHCH}{=}\text{CHCH}_2\overset{+}{N}R_3\end{array}$$

Further evidence is available for the partial ionic character of the methylene hydrogen atoms in allyl groups in the extensive work on allylic arrangements.[9]

Since it has previously been shown in the fourth paper of this series[2] that the swelling coefficient is an important factor in the ion exchange rates of quaternary ammonium polymers, this factor was considered in these studies. For comparison, samples of polymers were selected which had approximately equal swelling coefficients, the polymer containing the butene-2 double bond having a slightly lower value. The polymer having the higher swelling coefficient, all other factors being equal, would be expected to have the higher exchange rate; however, in these studies, the reverse was true by two-fold. Another factor which would be expected to affect the exchange rate is the mole fraction of strong electron-releasing groups, *e.g.*, methyl. The polymers selected for comparison were approximately equal in this capacity, the polymer containing the butene-2 group having the larger mole fraction (0.343 as compared to 0.300) of methyl groups, which effect alone would be to decrease the rate of regeneration, giving this polymer a slight disadvantage in the comparison.

Acknowledgment.—The authors wish to express their appreciation to Miss Ester P. Jorolan who ran the experiments and analyses for the exchange rate studies, and to the Atomic Energy Commission which sponsored this portion of the work under Contract No. AT-(40-1)-1353.

GAINESVILLE, FLORIDA

---

[8] H. Levy and A. C. Cope, THIS JOURNAL, **66**, 1684 (1944).

[9] W. G. Young, *et al.*, *ibid.*, **73**, 1958 (1951), and previous papers.