form 1,2-dimethoxy-2-butene[28] or *via* hydrogen migration in the carbonium ion formed from IV by loss of OH^-.[29] Reaction through an olefin intermediate finds an analogy in the report[30] that 1,3-dimethoxy-2-butene rapidly rearranges to 4-methoxy-2-butanone in the presence of dilute sulfuric acid.

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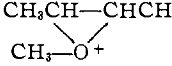
[28] This olefin might actually arise from either IV or 1,3-dimethoxy-2-butanol; in fact, in acid solution the two ethers may perhaps exist in equilibrium through a possible common intermediate



$CH_3CH{-}CHCH_2OCH_3$, $CH_3{-}O^+$

which might be formed from either ether through loss of OH with the bonding pair of electrons. Hence, VII might perhaps be formed by treatment of either IV or 1,3-dimethoxy-2-butanol with acid, and the assignment of the position of the methoxy groups in IV is based, not on this reaction, but on the iodoform test. The behavior of 1,3-dimethoxy-2-butanol toward acids is now under investigation in this Laboratory.

[29] See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 475–476.

[30] R. O. Norris, J. J. Verbanc and G. F. Hennion, THIS JOURNAL, **60**, 1159 (1938).

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

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. V. Propargyl Derivatives[1]

BY GEORGE B. BUTLER AND ROGER A. JOHNSON

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In order to determine whether or not quaternary ammonium compounds having the propargyl group as one or more of the substituents would undergo a free radical catalyzed polymerization in a manner similar to the corresponding allyl derivatives, a number of compounds containing this group were prepared and characterized. This series consisted of compounds containing, as the only unsaturated groups, one propargyl group, one propargyl and one allyl group, one propargyl and two allyl groups, one propargyl and three allyl groups, and two propargyl and one allyl groups. As intermediates for these compounds, four unsaturated tertiary amines were prepared and characterized. Polymerization studies showed that only those compounds containing two or more allyl groups produced polymers, and that the propargyl groups did not enter into the polymerization.

Previous work[2,3] has shown that unsaturated quaternary ammonium salts containing two or more allyl or chloroallyl groups undergo polymerization by a free radical catalyzed mechanism. More recent work[4] has shown that even though vinyl ethers will copolymerize with a variety of olefinic compounds by a free radical catalyzed mechanism, such groups, when present in quaternary ammonium salts, do not polymerize or copolymerize with any allyl groups which may be present.

Although data are as yet insufficient to permit wide generalizations with regard to polymerization and copolymerization of acetylenic compounds, many compounds of this type have been found to undergo these reactions. Vinylacetylene under pressure, with or without the usual catalysts such as benzoyl peroxide or sodium borate, is readily polymerized by heat to form viscous drying oils and finally hard resinous solids. Jacobs and Whitcher[5] have shown that phenoxyacetylene undergoes polymerization, quite often violently. Propargyl acetate has been shown by Ladd[6] to undergo a free radical initiated reaction with bromotrichloromethane in presence of free radical forming catalysts to give 2-bromo-4,4,4-trichloro-2-butenyl acetate. Bruson and Butler[7] have shown that 2-nitro-2-methylpropyl propargyl maleate polymerizes on heating with benzoyl peroxide.

The potential use of unsaturated quaternary ammonium salts as intermediates for strongly basic ion-exchange resins indicates the desirability of compounds of lowest possible equivalent weights. The introduction of groups containing acetylenic linkages offers the possibility of a tetrafunctional group toward polymerization or copolymerization reactions. Previous work[2,3] has shown that of the compounds studied, two allyl or chloroallyl groups are necessary for polymerization, and at least three of these groups must be present in a single molecule to cause cross-linking to occur. Because of the possibility of one propargyl group serving the purpose of two allyl groups, thus allowing a decrease in the equivalent weight, this work was undertaken. The results are recorded below in the experimental section and in the accompanying tables.

Experimental

Materials.—Allyl bromide was obtained from Dow Chemical Company and was used as received. 2,3-Dibromopropene was prepared from 1,2,3-tribromopropane,[8] and it in turn was prepared from allyl bromide.[9]

Diallylcyanamide, which was used to prepare diallylamine,[10] was obtained from American Cyanamid Company. Butylamine and diethylamine were obtained from Carbide and Carbon Chemicals Corporation and were used as received. The *t*-butyl hydroperoxide was obtained as a 60% solution from Lucidol Division, Novadel–Agene Corporation.

Preparation of 2-Bromoallylamines.—The following preparation of 2-bromoallyldiallylamine will illustrate the method used for preparation of this compound, bis-(2-bromoallyl)-butylamine, and 2-bromoallyldiethylamine: A mixture of 56.3 g. of $NaHCO_3$ with enough water to form a thin sus-

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[1] The work described in this manuscript was presented in part before the Southeastern Regional Meeting of the American Chemical Society, Wilson Dam, Alabama, October, 1951, and was abstracted from a thesis presented by Roger A. Johnson to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree Master of Science, February, 1952.

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

[3] G. B. Butler and F. L. Ingley, *ibid.*, **73**, 895 (1951).

[4] G. B. Butler and R. L. Goette, *ibid.*, **74**, 1939 (1952).

[5] T. L. Jacobs and W. J. Whitcher, *ibid.*, **64**, 2635 (1942).

[6] E. C. Ladd, U. S. Patent 2,554,533 (to U. S. Rubber Co.).

[7] H. A. Bruson and G. B. Butler, U. S. Patent 2,404,688 (to Rohm & Haas Co.).

[8] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 209.

[9] *Ibid.*, p. 521.

[10] *Ibid.*, p. 201.

TABLE I

PHYSICAL PROPERTIES OF TERTIARY AMINES

Amine	B.p. °C.	Mm.	n^{25}_D	d^{25}_4	MR_D Calcd.	Obsd.	Yield, %	Nitrogen, % Calcd.	Found
2-Bromoallyldiallyl	77–78	7.8	1.4903	1.1647	54.07	53.68	87.3	6.48	6.31
Diallylpropargyl	80–82	59.3	1.4588	0.8290	44.77	44.57	57.2	10.36	10.27
Bis-(2-bromoallyl)-butyl	112–113	2.8	1.5100	1.4063	66.92	66.32	52.2	4.50	4.32
Butyldipropargyl	81–82	13.7	1.4572	0.8480	48.32	47.95	60.8	9.39	8.72

pension and 65.4 g. of diallylamine was placed in a round-bottom, three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel, and heated on a steam-bath. While stirring and heating, 148 g. of 2,3-dibromopropene-1 was added dropwise. Heating and stirring were continued for an additional 5.5 hours. The solution was then cooled and saturated with NaOH. Separation of the amine was done mechanically, and it was dried for 12 hours over solid NaOH. Fractionation was carried out to yield 126 g. of 2-bromoallyldiallylamine, b.p. 77° (7.8 mm.).

Preparation of Propargylamines.—The method employed for dehydrohalogenation of the 2-bromoallylamines was essentially that previously described in the literature.[11,12] The following preparation of diallylpropargylamine will illustrate the method employed for the various propargylamines prepared: A solution of sodamide in liquid ammonia was prepared by the method of Vaughn, Vogt and Nieuwland[13] using 30.9 g. of sodium and diluting the resulting solution to 1.5 liters with liquid ammonia in a three-liter, round-bottom, three-necked flask equipped with a mechanical stirrer. To this solution was added dropwise, with stirring, 116.5 g. of 2-bromoallyldiallylamine over a period of two hours. After addition was complete, the volume of the solution was again brought up to 1.5 liters with liquid ammonia, and stirring was continued. When the volume of the liquid in the reaction flask had decreased to approximately 250 ml., the reaction was stopped by the addition of 250 ml. of ether followed by 250 ml. of water. Stirring was not stopped until all of the ice had melted. Separation of the amine was done mechanically, and it was dried for 12 hours over solid NaOH. Fractionation yielded 29.3 g. of diallylpropargylamine, b.p. 80–82° (59.3 mm.). From the higher boiling fraction, 34.6 g. of 2-bromoallyldiallylamine was recovered. The physical constants and analyses of the tertiary amines prepared by the above procedures are recorded in Table I.

Preparation of Quaternary Ammonium Salts.—The method previously employed[2–4] for preparation of quaternary ammonium salts involved use of a solvent of the ketone series for the tertiary amine. Due to difficulty of removing the solvent and obtaining the extremely hygroscopic salts in a pure state, attempts were made to prepare the quaternary ammonium salts without use of a solvent. The following preparation of triallylpropargylammonium bromide will illustrate the general method used to prepare this compound and the other quaternary ammonium salts used in this work: One gram of allyl bromide was weighed directly into a test-tube containing one gram of diallylpropargylamine. It was quite often necessary to cool the amine to zero before adding the allyl bromide, due to the exothermic nature of the reaction. The solution became cloudy immediately, indicating formation of the insoluble salt. The test-tube was stoppered and sealed with paraffin. After standing 24 hours at room temperature, the entire mass had been converted to a hard, white, crystalline material which had a melting point of 101–104°. The various propargyl derivatives prepared are summarized in Table II.

TABLE II

UNSATURATED QUATERNARY AMMONIUM BROMIDES

Compound	Formula	Bromine, % Calcd.	Found	M.p., °C.	Yield, %
Triallylpropargyl	$C_{12}H_{18}NBr$	31.20	31.11	101–104	Quant.
Ethyldiallylpropargyl	$C_{11}H_{18}NBr$	32.73	33.04	[a]	Quant.
Diethylallylpropargyl	$C_{10}H_{18}NBr$	34.42	34.33	[a]	Quant.
Methyldiethylpropargyl	$C_8H_{16}NBr$	38.76	38.88	[a]	Quant.
Butyllallyldipropargyl	$C_{13}H_{20}NBr$	29.56	29.76	87–91	Quant.

[a] Too hygroscopic to determine.

Polymerization of Quaternary Ammonium Salts.—The following procedure used for polymerization of triallylpropargylammonium bromide will illustrate the general procedure used for these compounds: One gram of triallylpropargylammonium bromide was dissolved in one drop of distilled water in a 5-ml. beaker. To this solution was added 0.012 g. of 60% *t*-butyl hydroperoxide. The solution was placed in an oven at 65° for 24 hours. The water insoluble polymer obtained was washed with distilled water until bromide ions could no longer be detected in the wash water. In order to demonstrate the ion-exchange properties of the polymer, it was treated with an excess of 4% sodium hydroxide solution. The resulting solution, after removal by filtration, was found to contain halogen by neutralizing with halogen-free nitric acid and adding silver nitrate. Results of the polymerization studies are recorded in Table III.

TABLE III

RESULTS OF POLYMERIZATION STUDIES

Quaternary ammonium bromide	No. of allyl groups	No. of propargyl groups	Nature of polymer
Methyldiethylpropargyl	0	1	No polymerization
Diethylallylpropargyl	1	1	No polymerization
Ethyldiallylpropargyl	2	1	Soluble polymer
Butylallyldipropargyl	1	2	No polymerization[a]
Triallylpropargyl	3	1	Insoluble polymer

[a] The m.p. of the recovered material was 88–92°.

Discussion of Results

Results of polymerization studies of quaternary ammonium salts containing the propargyl group have led to the conclusion that this group does not enter into the polymerization. This conclusion is based on results obtained in this study as well as results previously obtained. Previous work[2–4] has shown that compounds of this type containing only one allyl group per molecule do not polymerize under the conditions employed, and that compounds containing two allyl groups per molecule produce water soluble polymers. Those compounds containing three or more allyl groups produce cross linked, water insoluble polymers. Since no polymerization occurred in those compounds containing as the only unsaturated groups (1) one propargyl group, (2) one propargyl group and one allyl group, and (3) two propargyl groups and one allyl group, yet a water-soluble polymer was obtained from a compound containing two allyl groups and one propargyl group, and a water insoluble polymer was obtained from the compound containing three allyl groups and one propargyl group, it can be concluded that the propargyl group does not take part in the polymerization reaction.

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(11) Bourguel, *Ann. chim.*, [10] **3**, 225, 228 (1925).

(12) C. B. Pollard and R. F. Parcell, THIS JOURNAL, **73**, 895 (1951).

(13) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *ibid.*, **66**, 2120 (1934).