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

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VIII. A Proposed Alternating Intramolecular–Intermolecular Chain Propagation[1]

BY GEORGE B. BUTLER AND RUDOLPH J. ANGELO

RECEIVED NOVEMBER 23, 1956

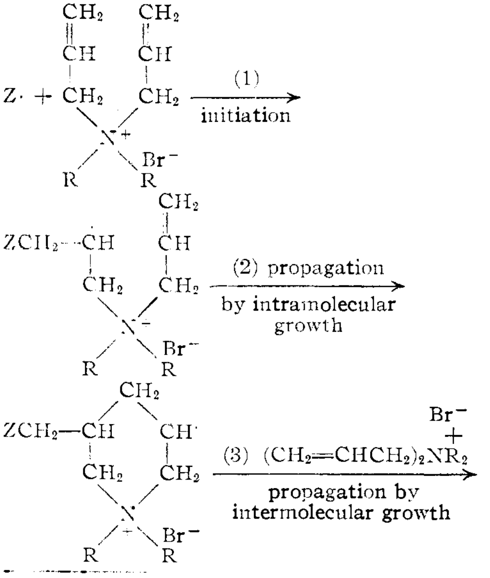
A mechanism is proposed for the polymerization of certain allyl unsaturated quaternary ammonium salts which involves an alternating intramolecular–intermolecular chain propagation leading to the formation of chains of piperidine rings. This mechanism is supported by results obtained using suitable monomers, by studies of solvent, initiator and oxygen effects and by hydrogenation evidence. An estimation of the molecular weight of the polymers has been made.

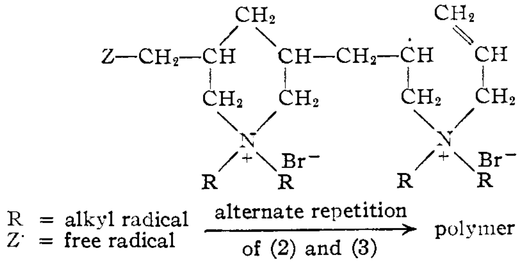
Previous work[2-6] carried out in this Laboratory on the free radical initiated polymerization of allyl or substituted allyl quaternary ammonium derivatives showed that infusible and water-insoluble polymers were obtained only from monomers containing three or more allyl groups. Polymers from monomers containing only two allyl groups were non-cross-linked, since they were completely soluble in water. Monomers containing only one allyl group did not undergo polymerization.

These results are contrary to the accepted views that monomers containing one double bond result in linear polymers possessing some degree of solubility, while monomers containing two or more double bonds result in three-dimensional, cross-linked polymers possessing little or no solubility. Since the products of the polymerization of allyl quaternary ammonium salts appear to have abnormal properties, it was decided to investigate the mechanism of this polymerization.

To explain the formation of water-soluble, non-cross-linked polymers in all cases when quaternary ammonium salts containing two allyl groups were polymerized, a chain growth mechanism is proposed as illustrated below.

PROPOSED MECHANISM FOR POLYMER CHAIN PROPAGATION





This would involve a free radical attack on one of the double bonds, followed by cyclization with the remaining favorably situated double bond within the same molecule; the resulting cyclic radical then attacks another molecule of monomer, and repetition of the process results in a growing chain.

In a somewhat related case, Simpson, *et al.*,[7] studied the structure of polydiallyl phthalate at the gel point and, by calculations from values of residual unsaturation and degree of polymerization, concluded that at the gel point about 40% of the reacted monomer units was used up in cyclization reactions and were, therefore, not available for further cross-link formation. In a later publication[8] these authors analyzed several other polydiallyl esters in a similar way, but only in the above case did cyclization appear to occur to any great extent. Such an intramolecular cyclization in the case of diallyl phthalate would lead to ten-, eleven-, twelve-membered, or even larger, rings. Such cyclizations are much less likely to occur than those we propose which lead to six-membered rings.

Through use of suitable monomers, studies of solvent, initiator and oxygen effects, hydrogenation studies and estimation of molecular weight, evidence has been obtained to support this proposed mechanism.

Experimental

Diallyldiethylammonium Bromide.—Allyl bromide, 60.5 g. (0.5 mole), was added to 50.0 g. (0.44 mole) of N,N-diethylallylamine dissolved in 100 ml. of acetone; the N,N-diethylallylamine had a boiling point of 110° and $n^{22}D$ 1.4198; Libermann and Paal[9] report the boiling point as 110–113°. Upon addition of the bromide, the mixture became cloudy and crystals began to form. The product was washed and decanted several times with cold acetone, filtered and dried in a vacuum desiccator. White, hygroscopic crystals, 87 g. (84% yield), m.p. 155° (closed capillary), were formed and were recrystallized from acetone–absolute ethanol.

Anal. Calcd. for $C_{10}H_{20}NBr$: Br, 34.15. Found: Br, 34.12.

Diallyldimethylammonium bromide and triallylbutylam-

---

(1) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, Dallas, Texas, April, 1956.

(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, R. L. Bunch and F. L. Ingley, *ibid.*, **74**, 2543 (1952).

(5) G. B. Butler and R. L. Goette, *ibid.*, **74**, 1939 (1952); **76**, 2418 (1954).

(6) G. B. Butler and R. J. Angelo, *ibid.*, **78**, 4797 (1956).

(7) W. Simpson, T. Holt and R. Zeite, *J. Polymer Sci.*, **10**, 489 (1953).

(8) W. Simpson and T. Holt, *ibid.*, **18**, 335 (1955).

(9) C. Libermann and C. Paal, *Ber.*, **16**, 526 (1883).

monium bromide were prepared as described in previous papers.[2,5]

Polydiallyldiethylammonium Bromide.—Twenty drops of 60% *t*-butyl hydroperoxide (approximately 0.012 g./drop) was added to a solution of 8.0 g. of diallyldiethylammonium bromide and 4.0 ml. of water. The mixture was allowed to remain open to the atmosphere in an oven at 60° for 48 hr. The resulting white hygroscopic product was ground to a fine powder and dried for several days in a vacuum desiccator. Eight grams of product, melting with considerable decomposition at 346–354°, was obtained. The product was quite soluble in water and ethanol and gave an immediate halogen test when treated with $AgNO_3$ solution.

Anal. Calcd. for $C_{10}H_{20}NBr$: C, 51.30; H, 8.20; N, 5.98; Br, 34.15. Found: C, 51.35; H, 8.32; N, 5.50; Br, 33.90.

Polydiallyldimethylammonium Bromide.—Twenty-five grams of the salt, 12.5 g. of water and 20 drops of *t*-butyl hydroperoxide were mixed and allowed to stand overnight at room temperature. The solution was then placed in an oven at 70° for 72 hr. when a white opaque, brittle mass resulted. This polymer was hygroscopic and soluble in water. After grinding and drying *in vacuo*, the m.p. was 348–352°.

Polydiallylamine Hydrochloride.—Ten grams of diallylamine hydrochloride (recrystallized from acetone–ethanol three times, m.p. 164–165°) was dissolved in 5 ml. of water and treated with 25 drops of 60% *t*-butyl hydroperoxide solution. The mixture remained in an open beaker at 60° for three days. Ten grams of polymeric product was obtained which was insoluble in water and ethanol. The wash ethanol on treatment with acetone showed only a faint cloudiness which indicated there was very little unreacted diallylamine hydrochloride present. After soaking in an acetone–ethanol mixture or absorbing moisture from the atmosphere, the product exhibited elastic properties. This was the only monomer in this study with two allyl groups to show characteristics of cross-linking upon polymerization.

Hydrogenation.—An infrared absorption band at 6.10 μ indicated some degree of unsaturation in the water-soluble polymers obtained from diallyldiethyl- and diallyldimethylammonium bromides. Quantitative hydrogenation of weighed samples of polydiallyldiethylammonium bromide over Adams catalyst at atmospheric pressure resulted in an average absorption of 0.193 mole of hydrogen per mole of monomer unit in the polymer.

Solvent interaction during the polymerization might affect the nature of the polymer. If a chain radical could react with a solvent radical in preference to a monomer molecule, the degree of polymerization would be reduced. Thus it might be possible to have a monomer molecule containing several unsaturated groups and yet obtain a polymer of a low degree of polymerization and slight cross-linking. The following experiments were carried out varying the solvent and solvent concentration. (a) A mixture of 3.0 g. of triallylbutylammonium bromide, 3.0 ml. of water and 6 drops of 60% *t*-butyl hydroperoxide solution was heated at 60° for 76 hr. A hard, water-soluble solid was obtained. The product was dissolved in 10 ml. of water, 10 drops of initiator was added and the mixture heated for an additional week at 60°. The product was still water soluble. (b) A mixture of triallylbutylammonium bromide (2 g.), 4 drops of initiator and 2.0 ml. of water was allowed to react at 100° for 38 hr. The product was again water soluble. (c) Two grams of triallylbutylammonium bromide, 2 drops of initiator and 0.08 ml. of water were allowed to react at 100° for 38 hr. The resulting hard, glassy product was soaked in hot water, filtered and dried; 1.7 g. (85% yield) of water-insoluble product was obtained. The procedure was that of Bunch,[10] who reported a 52.5% yield. (d) Three grams of diallyldiethylammonium bromide, 10 drops of initiator and 0.3 ml. of water were allowed to react at 100° for 38 hr. The product was water soluble. (e) Three grams of diallyldiethylammonium bromide, 10 drops of initiator and 50 drops of dimethylformamide were allowed to react at 100° for 38 hr. The product was water soluble.

Initiator Effect.—Various initiators were tried with monomers containing one and two double bonds to see whether *t*-butyl hydroperoxide is unique in its property of yielding non-cross-linked polymers with monomers containing two allyl groups.

One gram each of triethylallylammonium bromide and diallyldiethylammonium bromide were dissolved in 1.0 ml. of water and reacted for one week at 60° with 0.05 g. each of *t*-butyl hydroperoxide, di-*t*-butyl peroxide and benzoyl peroxide.

The lack of cross-linking was indicated by the water solubility of the products. Polymerization took place only in the reaction of diallyldiethylammonium bromide with *t*-butyl hydroperoxide. In the other cases, the starting monomers were recovered and identified.

In an attempt to evaluate the initiating property of 2,2′-azoisobutyronitrile, this initiator was treated with hexaallylethylenediammonium dibromide, since it was thought that an easily isolated, insoluble product would be obtained if polymerization occurred. The monomer (5 g.), dissolved in 10 ml. of dimethylformamide, was allowed to react with varying amounts of initiator for two weeks at 60° in an open vessel. These results are recorded in Table I (a to f).

TABLE I

Initiator, %	Weight of H_2O insoluble product	Remarks
(a) 0.1	Soluble	Light viscous liq. after 2 wk.
(b) 0.5	Soluble	Light viscous liq. after 2 wk.
(c) 1.0	Soluble	Viscous liq. after 2 wk.
(d) 2.0	0.75 g.	Heavy viscous liq. after 2 wk.
(e) 5.0	3.28 g.	Gelatinous after 12–15 hr., flexible solid 2 wk.
(f) 10.0	4.37 g.	Gelatinous after 6 hr.; brittle solid at 2 wk.
(g) 1.0	Soluble	Hot acetone–insol. portion, m.p. 295–300°
(h) 5.0	Soluble	M.p. 305–307°
(i) 10.0	Soluble	M.p. 306–307°

The effect of this initiator on the polymerization of diallyldiethylammonium bromide was determined in a similar manner. Two grams of diallyldiethylammonium bromide, dissolved in 10 ml. of dimethylformamide, was allowed to react with varying amounts of azo initiator at 75° for fifteen days. The product was water soluble in every case. Unreacted monomer was separated from the reaction product by extraction with hot acetone. Results are given in Table I (g to i).

Effect of Oxygen.—The following experiment, along with the molecular weight estimation, demonstrated the inhibiting effect of oxygen; a mixture of 8.0 g. of diallyldiethylammonium bromide, 4.0 ml. of water and 33 drops of 60% *t*-butyl hydroperoxide solution (approximately 0.012 g./drop) was allowed to react for 76 hr. at 60–65°. The reaction was carried out in an oxygen-free, dry nitrogen atmosphere. Eight grams of hygroscopic product was obtained after drying for several days in a vacuum desiccator. The product decomposed over a wide range and melted with decomposition at 355–360°, and was soluble in water but relatively insoluble in ethanol, forming some gel. The degree of solubility of this product in ethanol differed from that of the polydiallyldiethylammonium bromide, which was prepared open to the atmosphere.

Identical experiments, carried out quantitatively, open to the atmosphere, and under pure nitrogen, gave weight increments which showed that hydroxyl radical interaction from the solvent was not appreciable and could be neglected.

It was also considered that the formation of peroxide or hydroperoxide linkages might account for the utilization of some of the monomer double bonds during the polymerization. However, infrared spectra of the above products showed no absorption bands at 870 and 840 cm.$^{-1}$, which are characteristic of peroxide[11] and hydroperoxide,[12] respectively. Polarographic determinations[13] of polydiallyldiethylammonium bromide (prepared open to the atmosphere

---

[10] R. L. Bunch, Ph.D. Dissertation, University of Florida, 1949, p. 37.

[11] A. R. Philpotts and W. Thain, *Anal. Chem.*, **24**, 638 (1952).

[12] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *ibid.*, **23**, 282 (1951).

[13] A. H. Gropp and G. Long, private communication.

and under nitrogen) gave no indication of a peroxide or hydroperoxide wave.

Estimation of Molecular Weight.—A crude approximation of the degree of polymerization was obtained as shown in Table II. This estimation involves the following assumptions: (1) Only the *t*-butoxide radical is to be considered as an initiating fragment. This assumption is probably valid, considering work carried out on the decomposition of *t*-butyl hydroperoxide in the gaseous and liquid phase.[14-17] In all cases cited, fission of the O–O linkage to produce *t*-butoxide and hydroxyl radicals was proposed to account for the formation of the reaction products. (2) The increase in weight during polymerization is due only to incorporation of initiator fragments. (3) The means of chain termination is either by combination or by disproportionation.

The polymerization reaction products were freed from any unreacted monomer by extraction with hot acetone. Samples of the reaction products were extracted in a fine filter funnel until a constant weight was obtained upon vacuum drying.

TABLE II

APPROXIMATION OF THE DEGREE OF POLYMERIZATION

	Open to atm.	Under N_2
Wt. increase (assuming only init. fragment incorporation), g.	0.1545	0.1038
Moles of radical (assuming only *t*-butoxide radical as init.), g.	0.00212	0.00142
Starting weight of monomer, g.	7.9061	8.5279
Fraction converted to polymer, g.	0.949	0.969
Polymer fract. expressed as mole of monomer	0.0321	0.0353
Moles monomer/mole of radical init.	15.1	24.8
Avg. degree of polymn. (assuming chain detmn. by dispropn.)	15.1	24.8
Avg. degree of polymn. (assuming chain termn. by combination)	30.2	49.6
Avg. mol. wt. (assuming chain termn. by combination	7066	11,606

Discussion of Results

Free radical catalyzed polymerization of quaternary ammonium salts containing only two allyl groups affords only water soluble, non-cross-linked polymers.

The polymers showed some unsaturation by their infrared absorption at 6.10 μ. Quantitative hydrogenation indicated that one free double bond was left for every five monomer units in the polymer chain. Linear intermolecular chain growth would have used five double bonds per five monomer units, leaving four double bonds unaccounted for in the polymerization. It appears probable that much of the unsaturation is used up in the formation of an intramolecular cyclic structure, since cross-linking does not occur to any significant extent. Under these circumstances, the suggested mechanism appears to be the obvious mode of chain propagation.

It appears that the solvent affects the polymerization to some extent, since the attempted polymerizations of triallylbutylammonium bromide at 60 and 100° indicated that the amount of water as solvent is rather critical in obtaining an insoluble product. Diallyldiethylammonium bromide did not yield a water-insoluble product under any circumstances, again showing that at least three allyl groups per molecule of quaternary ammonium salt are required to produce an insoluble product. Diallylamine hydrochloride was the only monomer with two double bonds that produced a water-insoluble product upon polymerization. This compound, however, is not a quaternary ammonium salt and steric considerations suggest that it would be less likely to favor cyclizations of the type proposed.

It was found that *t*-butyl hydroperoxide or 2,2′-azoisobutyronitrile would initiate the polymerization of allyl quaternary ammonium derivatives. Table I indicates that the effective amount of azo initiator is between 5 and 10%, which is higher than the effective initiator ratio of *t*-butyl hydroperoxide.

The polymerization appeared to be somewhat sensitive to oxygen, since the degree of polymerization of the product polymerized under nitrogen was higher than that prepared open to the atmosphere; this greater degree of polymerization also was evident from the different solubilities in ethanol. Chemical, infrared and polarographic analyses did not however, show the presence of peroxide linkages. It is likely that oxygen affects the rate of initiation rather than the formation of different polymers.

Since the soluble polymers are polyelectrolytes, a molecular weight determination of the products, as such, was very difficult. The usual molecular weight determinations, which are dependent on the colligative properties of polymer molecules in solution, were not useful since the degree of ionic dissociation of the polyelectrolytes was unknown. An attempt was made to convert polydiallyldiethylammonium bromide to the polyhydroxide form, degrade this product by the loss of ethylene and water and measure the molecular weight of the resulting polytertiary amine. Although the polyelectrolyte was degraded, a molecular weight determination of the product obtained could not be carried out because of the extreme insolubility of the product. A crude approximation of the molecular weight was obtained by polymerizing accurately weighed amounts of monomer and catalyst, determining weight increments, extracting unreacted monomer and by various assumptions arriving at a degree of polymerization. By assuming that the chain termination process is by disproportionation or combination, the data indicate the degree of polymerization to be from 15 to 30 for the product polymerized open to the atmosphere and 25 to 50 for the product polymerized under nitrogen.

This low degree of polymerization agrees with the results of Bartlett and Altschul[18] who found the degree of polymerization of allyl acetate to be

---

(14) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

(15) M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *ibid.*, **17**, 207 (1952).

(16) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *ibid.*, **16**, 1556 (1951).

(17) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughn, *Faraday Soc. Discn.*, **10**, 246 (1951).

(18) P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 812 (1945); **67**, 816 (1945).

from 13 to 14 and attributed this low degree of polymerization to resonance stabilization of the monomer by transfer of the α-hydrogen atom to a chain radical. Later work by these authors[19] showed that this was the case.

Consideration of the proposed cyclic intramolecular polymerization of diallyl phthalate by Simpson, Holt and Zeite[7] and the degradative chain transfer in the polymerization of allyl acetate by Bartlett and co-workers[18,19] leads to the belief that the polymerization of allyl quaternary derivatives is affected by both factors. Cyclic intramolecular polymerization, greatly influenced by chain termination caused by α-hydrogen transfer, could account for the soluble, non-cross-linked, low molecular weight and unsaturated polymers obtained in this work.

This study has provided evidence that a suggested alternating intramolecular–intermolecular chain propagation occurs when unsaturated quaternary ammonium salts are polymerized and shows that a polymer of average degree of polymerization of approximately 25 or 50 is obtained when diethyldiallylammonium bromide is polymerized under nitrogen with *t*-butyl hydroperoxide as catalyst. It also shows that this chain propagation mechanism is followed by an average of four-fifths of the monomer units entering the chain, leaving an average degree of unsaturation in the polymer equivalent to one-fifth double bond per monomer unit in the chain.

Acknowledgment.—We wish to express our appreciation to the Atomic Energy Commission who supported this work under terms of Contract No. AT-(40-1)-1353. Thanks are also due to Dr. C. S. Marvel of the University of Illinois for reading the original manuscript and to Dr. Alan Crawshaw of this Department for many helpful suggestions.

GAINESVILLE, FLORIDA

[19] P. D. Bartlett and F. A. Tate, This Journal, **75**, 91 (1953).

[Contribution from the Departments of Biological Chemistry and Chemistry of the University of Utah]

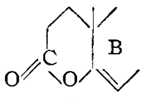
Rearrangement in the Addition of Grignard Reagents to Enol Lactones

By Kenneth D. Zwahlen,[1] W. J. Horton and George I. Fujimoto

Received December 6, 1956

Grignard reagents add to the acyl portion of enol lactones with rearrangement of this acyl carbon to the β-olefinic carbon atom. Further addition of Grignard reagent is subject to steric considerations. Such rearrangements were found in the case of a model steroid enol lactone and also in the addition of Grignard reagents to vinyl acetate and isopropenyl acetate.

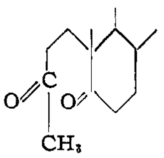
The addition of methylmagnesium halide to enol lactones derived from steroids (I) has been a useful method for the synthesis of Δ^4-3-keto steroids containing C^{14} at position 4[2] and for the closure of the A ring in the synthesis of steroids.[3]



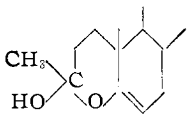
I

An intermediate in this process has been assigned various structures (II,[2a] III,[2c] with phenylmagnesium bromide IV).[4] Structure II for the intermediate from the enol lactone derived from cholestenone, however, is not identical with II from an independent source.[2c,5]

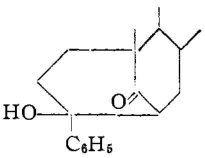
The present investigation was undertaken in order to test whether a structure of type IV would satisfy the requirements for the intermediate obtained when the enol lactone from cholestenone was combined with methylmagnesium halide.[6] For this purpose a model V of a steroid enol lactone was studied.



II



III



IV

Model V, when treated with methylmagnesium iodide or phenylmagnesium bromide, gave VI and VII, respectively. The structure of VII was confirmed by an independent synthesis (formulas V–X). Reduction of VII with lithium aluminum hydride gave VIII, thus adding support for VII. This diol formed a cyclic sulfite ester IX which enables the assignment of an $8\beta,11\alpha$-configuration. These reactions are not easily explainable on the basis of the hemiketal structure (type III).

The reaction of V to yield VI (or VII) involves the migration to an olefinic carbon atom. Such migrations occur when Grignard reagents are added to the simplest enol esters. Methylmagnesium iodide, added to isopropenyl acetate (XI), gave 2,4-dimethyl-2,4-pentanediol (XIII), identical with material prepared as reported.[7] Similarly, ethyl-

---

[1] From the Doctoral Dissertation of K. D. Zwahlen, Eastman Kodak Fellow, 1955–1956.

[2] (a) G. I. Fujimoto, This Journal, **73**, 1856 (1951); (b) G. I. Fujimoto and J. Prager, *ibid.*, **75**, 3259 (1953); (c) R. D. H. Heard and P. Ziegler, *ibid.*, **73**, 4036 (1951).

[3] (a) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *ibid.*, **74**, 4223 (1952); (b) P. Wieland, H. Ueberwasser, G. Anner and K. Miescher, *Helv. Chim. Acta*, **36**, 1231 (1953); (c) L. B. Barkley, *et al.*, This Journal, **76**, 5014 (1954); **78**, 4111 (1956).

[4] S. A. Julia, A. Eschenmoser, H. Heusser and N. Tarköy, *Helv. Chim. Acta*, **36**, 1885 (1953).

[5] H. Schmid and K. Kagi, *ibid.*, **33**, 1582 (1950).

[6] The part of this work which was carried out on steroids is to be the material in a separate paper.

[7] (a) P. H. Hermans, *Z. anorg. Chem.*, **142**, 101 (1925); (b) J. English, Jr., and F. V. Brutcher, Jr., This Journal, **74**, 4279 (1952); (c) J. Lemaire, *Rec. trav. chim.*, **29**, 22 (1910).