Subsequently it began to drop off markedly and a band appeared at 815 cm.$^{-1}$. A plot of (100% − Σ) *versus* the absorption at this frequency was linear at low concentrations, but even at moderate concentrations there was a sharp leveling-off. Since other terpenes show linearity over large concentration ranges, it is reasonable to assume that the linear portion indicates a single compound whereas the leveling-off is caused by formation of a mixture.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD RESEARCH INSTITUTE, AND THE ETHYL CORPORATION RESEARCH LABORATORIES][1]

# Telomerization of Ethylene with Methyl Bromoacetate

BY W. A. SKINNER,[2] J. D. JOHNSTON AND MARY FISHER

RECEIVED JUNE 1, 1957

Methyl ω-bromoesters have been prepared in good yields by the telomerization of ethylene with methyl bromoacetate. The effects of variations in ethylene pressure, reaction temperature, initiator and solvent on the product distribution were studied. Conditions can be chosen so that 90–95 weight % of the total yield of telomers is composed of methyl γ-bromobutyrate and methyl ε-bromohexanoate. The thermal conversion of methyl γ-bromobutyrate to γ-butyrolactone was investigated.

Telomerization is a well known process,[3] but little commercial use has been made of it. The vast majority of the patents covering telomerization reactions are concerned with the production of telomer waxes.[4] The process described in most detail is the telomerization of ethylene with carbon tetrachloride to yield $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes.[5]

Kharasch[6] has studied the free radical addition of bromoesters to olefins. He found that good yields of the 1:1 addition product of ethyl bromoacetate and octene-1 could be obtained. The structure of the product, ethyl γ-bromocaprate, was proven by its conversion to γ-caprolactone upon heating and removal of methyl bromide. Other α-bromoesters likewise gave good yields of the 1:1 addition products with octene-1. These reactions were initiated with acetyl peroxide.

The addition reaction failed with β-bromoesters due to the increased strength of the carbon–bromine bond in the bromoesters. It was found that propylene reacted with ethyl bromoacetate to yield ethyl γ-bromoisovalerate. Styrene and ethyl acrylate yielded polymers in the presence of ethyl bromoacetate and acetyl peroxide.

## Results and Discussion

This paper is concerned with the radical polymerization of ethylene in the presence of methyl bromoacetate to form methyl ω-bromoesters. The reaction is believed to proceed as

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5CO_2\cdot \longrightarrow 2C_6H_5\cdot + 2CO_2 \quad (1)$$

$$C_6H_5\cdot + BrCH_2CO_2CH_3 \longrightarrow C_6H_5Br + \cdot CH_2CO_2CH_3 \quad (2)$$

$$\cdot CH_2CO_2CH_3 + nCH_2{=}CH_2 \longrightarrow \cdot(CH_2CH_2)_nCH_2CO_2CH_3 \quad (3)$$

$$\cdot(CH_2CH_2)_nCH_2CO_2CH_3 + BrCH_2CO_2CH_3 \longrightarrow \cdot CH_2CO_2CH_3 + Br(CH_2CH_2)_nCH_2CO_2CH_3 \quad (4)$$

$$2\cdot CH_2CO_2CH_3 \longrightarrow CH_3O_2CCH_2CH_2CO_2CH_3 \quad (5)$$

Methyl bromoacetate was chosen in place of either bromoacetic acid or ethyl bromoacetate because of higher yields of the 1:1 addition product with octene-1 and higher yields of telomers with ethylene. Kharasch[6] also reported better yields of the 1:1 addition product from octene-1 and methyl bromoacetate than those secured with the ethyl bromoester.

Attempts to telomerize ethylene with one of the telomers, methyl γ-bromobutyrate, failed to yield any higher telomers.

**The Effect of Reaction Conditions on the Product Distribution.**—The influence of such variables as ethylene pressure, reaction temperature, initiator and inert solvent on the product distribution is shown in Table I. The over-all reaction can be written thus

$$BrCH_2CO_2CH_3 + nC_2H_4 \longrightarrow Br(C_2H_4)_nCH_2CO_2CH_3 \quad (6)$$

It is evident (Table I) that increasing the ratio of ethylene in solution to the methyl bromoacetate either by increasing the ethylene pressure or by adding an inert solvent in which ethylene is quite soluble tends to shift the distribution toward higher molecular weight products. This is to be expected, since increasing the ratio of ethylene to methyl bromoacetate increases the rate of the propagation reaction, equation 3, at the expense of the transfer reaction, equation 4.

Attempts were made to obtain highest yields of methyl γ-bromobutyrate, $n$ = 1, and methyl ε-bromohexanoate, $n$ = 2. Conditions can be chosen (350–400 p.s.i.g., ethylene pressure, Table I) so that 94 weight % of the products is composed of these two telomers. Attempts to peak the product distribution at methyl ε-bromohexanoate or higher resulted in a spreading out of the distribution curve. This behavior is characteristic of most telomerization reactions.

The distributions were determined by vacuum distillation of the products. Bromine analyses were made on the various fractions in order to check the efficiency of the distillation.

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(1) The work reported herein was supported by the Ethyl Corporation, Baton Rouge, La., and was presented in part at the 131st meeting of the American Chemical Society in Miami, Fla., April 7–13, 1957.

(2) Stanford Research Institute, Menlo Park, California.

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TABLE I

TELOMERIZATION OF ETHYLENE WITH METHYL BROMOACETATE

| Pressure, p.s.i.g. | Initiator[a] | Time, hr. | Methyl bromo-acetate, ml. | Pentane, ml. | Temp., °C. | Products,[g] wt. % $n = 1$ | $n = 2$ | $n = 3$ | Yield, g. product/ mole initiator added |
|---|---|---|---|---|---|---|---|---|---|
| 200–250 | $Ac_2O_2$[b] | 2.25 | 250 | 500 | 70–80 | 50 | 29 | .. | 5,000 |
| 250–400 | $Ac_2O_2$ | 2.50 | 270 | 500 | 70–85 | 49 | 30 | .. | 7,000 |
| 800–950 | $Ac_2O_2$ | 2.00 | 250 | 500 | 70–88 | 16 | 22 | .. | 12,000 |
| 450–550 | $Ac_2O_2$ | 2.25 | 270 | None | 70–85 | 48 | 44 | 1 | 3,200 |
| 500–550 | $Ac_2O_2$ | 2.50 | 250 | 500 | 70–90 | 29 | 28 | 14 | 8,500 |
| 750–800 | $Bz_2O_2$[c] | 1.50 | 330 | None | 90–110 | 46 | 18 | 12 | 6,100 |
| 350–400 | $Bz_2O_2$ | 2.25 | 270 | 350 | 90–110 | 62 | 32 | 3 | 5,300 |
| 600–650 | $Bz_2O_2$ | 2.25 | 250 | 350 | 90–110 | 42 | 37 | 6 | 3,400 |
| 850–1000 | $Bz_2O_2$ | 2.00 | 250 | 500 | 85–98 | 34 | 20 | 16 | 10,000 |
| 550–600 | D.T.B.P.[d] | 2.00 | 260 | 350 | 130–140 | 43 | 32 | 4 | 4,600 |
| 550–600 | D.T.B.P. | 2.00 | 260 | None | 130–140 | 55 | .. | .. | 4,600 |
| 500–550 | $Bz_2O_2$ | 4.00 | 400[e] | None | 100–110 | .. | .. | .. | 2,500 |
| 500–550 | ABN[f] | 3.50 | 500 | None | 100–110 | 51 | 28 | .. | 2,650 |

[a] Initiators were used in 0.01 mole quantities. [b] Diacetyl peroxide. [c] Benzoyl peroxide. [d] Di-*t*-butyl peroxide. [e] Methyl bromoacetate replaced with bromoacetic acid (400 g.). Telomer mixture not separated. [f] Azobis-isobutyronitrile. [g] Difference between sum of wt. % of products and 100% is yield of higher telomers.

**Structure of the Products.**—The products were proven to be methyl ω-bromoesters by conversion to known compounds. The methyl γ-bromobutyrate was converted to γ-butyrolactone by heating at 170° for 2 hr. Methyl bromide was evolved, and the γ-butyrolactone formed was isolated by distillation and identified by its boiling point and comparison of its infrared spectra with that of commercial γ-butyrolactone. The methyl ε-bromohexanoate was converted to pimelic acid by treatment with potassium cyanide in ethanol followed by an alkaline hydrolysis of the nitrile ester to yield the dibasic acid. Methyl ε-bromohexanoate also was converted to ε-caprolactam *via* hydrolysis and ammonolysis.

**Thermal Conversion of Methyl γ-Bromobutyrate to γ-Butyrolactone.**—Methyl γ-bromobutyrate was heated under reflux and the methyl bromide liberated was trapped. An infrared spectrum of the products after heating was used to calculate the proportion of γ-butyrolactone present. The peak at 10.74 μ is characteristic of γ-butyrolactone and can be used for its determination in the presence of methyl γ-bromobutyrate. Upon heating methyl γ-bromobutyrate at 170° for 2.5 hr., a 95% yield of γ-butyrolactone is obtained.

**Thermally Induced Condensation of Methyl ε-Bromohexanoate.**—Methyl ε-bromohexanoate is considerably more thermally stable than methyl γ-bromobutyrate. At its boiling point, approximately 200°, methyl ε-bromohexanoate slowly liberates methyl bromide under nitrogen purge. The resulting product is composed of dimers, trimers, etc., formed as

$$2Br(CH_2)_4CH_2CO_2CH_3 \longrightarrow CH_3Br + Br(CH_2)_4CH_2CO_2(CH_2)_4CH_2CO_2CH_3 \quad (7)$$

Very little dehydrohalogenation occurs under these conditions.

## Experimental

**Materials.**—**Methyl bromoacetate** was from Matheson-Coleman-Bell, b.p. 59–60° (20 mm.). **Bromoacetic acid** was also from Matheson-Coleman-Bell, m.p. 48–50°. **Ethylene** was from Matheson, C.P. grade. **Diacetyl peroxide** was from Becco Chemical Division, 25% solution in dimethyl phthalate. **Benzoyl peroxide** was from Lucidol Division, fine powder. **Di-*t*-butyl peroxide** was obtained from the Shell Chemical Corporation.

**Process.**—The telomerization reactions were carried out in a 2-liter, stainless steel, Magnadash autoclave. The autoclave was installed at the bottom of a pit in the ground, 10 feet deep and 4 feet in diameter. This method of protection is more economical to install than the conventional concrete barricade and affords adequate protection for the operator who controls the reaction from outside the pit. The following procedure was used for all runs

(a) The telogen, solvent and initiator were added by gravity flow through the dip-tube into the autoclave.

(b) After the valve through which the liquids enter the dip-tube was closed, the air was purged from the reactor by alternately pressurizing the reactor to 250 p.s.i.g. with ethylene and then venting the gases. This procedure was repeated three times.

(c) The reactor was then pressurized with ethylene and the stirrer was started to assist in dissolving the ethylene.

(d) The reactor was then heated and controlled in the proper temperature range by means of a Brown controller and two variacs. The reaction temperature used was dependent upon the decomposition temperature of the initiator.

(e) Temperature control was assured by the use of an internal, stainless steel, cooling coil through which water could be circulated in case of a sudden temperature rise.

(f) The reaction was run for 2–3 hr. or until the initiator was essentially exhausted.

(g) The reactor was cooled by means of the cooling coil, and the products were forced out through the dip-tube, using the residual ethylene pressure.

(h) During the course of the reaction, the ethylene pressure was maintained essentially constant by adding more ethylene from the tank as it was utilized in the reaction.

(i) This solvent and unreacted telogen were removed under vacuum in a 2-foot Vigreux column.

(j) The telomer products were isolated by vacuum distillation in a glass, vacuum-jacketed column, 8 mm. i.d., packed with 50-mesh Monel screen twisted at right angles to give a spiral-like packing.[7]

**Product Analysis and Boiling Point Data.**—The purified methyl ω-bromoesters gave the analyses tabulated.

**Preparation of ε-Caprolactam from Methyl-ε-Bromohexanoate.**—ε-Hydroxyhexanoic acid (9.2 g.) obtained by alkaline hydrolysis of methyl-ε-bromohexanoate, was dissolved in 50 ml. of concentrated ammonium hydroxide solution. Seventy ml. of xylene and 1 g. of urea were added and the mixture was refluxed with stirring until all the water present was distilled through a water separator. After refluxing for an additional 4 hr., the mixture was cooled and the solid filtered. The filtrate was washed w.th ether and

(7) J. R. Bower and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

| Compound | $n^{22}D$ | B.p. °C. | B.p. Mm. | Bromine, % Calcd. | Bromine, % Found | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|
| Methyl γ-bromobutyrate | 1.4582 | 40 | 1 | 44.2 | 42.0 | 33.2 | 32.7 | 4.97 | 4.45 |
| | | 78 | 10 | | | | | | |
| | | 105 | 40 | | | | | | |
| Methyl ε-bromohexanoate | 1.4635 | 72 | 1 | 38.5 | 38.5 | 40.2 | 39.2 | 6.22 | 6.04 |
| | | 100 | 5 | | | | | | |
| | | 112 | 10 | | | | | | |

extracted with 95% ethanol. The ethanol-insoluble product was washed with water and dried. The dry product, 2.5 g., was polymeric. The ethanol-soluble material was separated by concentrating the solution and was recrystallized from absolute ethanol. The yield was 4.3 g., m.p. 68–69° (literature for ε-caprolactam, 69°).

**Thermal Condensation of Methyl ε-Bromohexanoate.**—Thirty ml. of methyl ε-bromohexanoate was heated at 200° under a nitrogen purge for 6 hr. During this time 7.0 ml. of methyl bromide was liberated (theoretical, 9.6 ml.). Only 0.001 mole of hydrogen bromide was evolved. The final product was a dark viscous oil. Upon distillation, 5 g. of a clear liquid (b.p. 62–129° (1 mm.)) was removed. The dark residue contained 17.0% bromine. The distillate which was clear and contained 24.0% bromine was largely the dimer, $Br(CH_2)_5CO_2(CH_2)_5CO_2CH_3$.

**Preparation of Methyl ε-Cyanohexanoate from Methyl ε-Bromohexanoate and Alkali Cyanides.**—Forty-one grams (0.2 mole) of methyl-ε-bromohexanoate, 15 g. (0.23 mole) of potassium cyanide and 300 ml. of anhydrous ethanol were refluxed while being stirred in a 3-necked flask for 16 hr. After the precipitated salts were filtered off, the solution was distilled to yield 12.54 g. of the nitrile ester (b.p. 119–125° (3 mm.)). Calcd. for $C_8H_{13}O_2N$: N, 9.04. Found: N, 9.04. Only 7.5 g. of unreacted bromoester was recovered.

When this reaction was repeated with only an 8-hr. reflux time, 8.6 g. of the nitrile ester was recovered and 17.3 g. of unreacted bromoester was recovered.

When sodium cyanide was used in place of potassium cyanide, after a 16-hr. reflux, 11.2 g. of nitrile ester and 17.9 g. of unreacted bromoester were obtained.

When potassium cyanide was used and the alcohol was replaced with dioxane as solvent, after a 16-hr. reflux no nitrile ester was obtained and 40 g. of unreacted bromoester was recovered.

**Acknowledgments.**—The authors wish to express appreciation to Mr. Oliver D. Smith, who carried out the bromine analyses, Mr. Wiley Crawford for the infrared analyses, Dr. Zoila Reyes for the synthesis of ε-caprolactam, Mr. Ernest Bishop for assistance in the telomerization runs, and to Drs. Bruce Graham, C. M. Himel and O. F. Senn of Stanford Research Institute and Drs. A. P. Giraitis and W. E. Foster of the Ethyl Corporation for valuable suggestions during the course of the work.

MENLO PARK, CALIF.

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[CONTRIBUTION NO. 1401 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

# Electron Exchange Polymers. X. A General Method for the Preparation of Phenolic Polystyrenes[1a]

BY ROBERT STERN[1b] JAMES ENGLISH, JR., AND HAROLD G. CASSIDY

RECEIVED OCTOBER 24, 1956

A general method for the preparation of phenolic polystyrenes and the corresponding monomers is described. Vinylhydroquinone bis-methoxymethyl ether (V) was obtained in 60% yield from hydroquinone in a three-step synthesis; catechol gave similarly 3-vinylcatechol bis-methoxymethyl ether (VI), and *p,p'*-biphenol afforded *p,p'*-biphenol bis-methoxymethyl ether (X). The structure of these monomers was verified. All three monomers could be polymerized; the molecular weights of the macromolecules were determined osmometrically. Mild hydrolysis of the acetal groups afforded, for the first time, analytically pure polyvinylhydroquinone, 3-polyvinylcatechol and 3-polyvinyl-*p,p'*-biphenol.

**Introduction.**—Among the numerous investigations devoted to styrene derivatives,[2] vinylphenols and particularly dihydric vinylphenols are but rarely represented, probably because few, if any, of the pertinent synthetic methods[3] can be applied successfully to their formation. In the category of styrenes of dihydric phenols the formation of both 4-vinylcatechol[4] and 4-vinylresorcinol[5] has been claimed, but neither compound has been characterized and structurally authenticated. On the other hand, vinylhydroquinone (II) has been synthesized by two independent four-step processes,[6] the over-all yield in both methods being rather low. Because hydroxylated polystyrenes have attracted attention as electron exchangers[6,7] and novel polyelectrolytes, we wish to report a general method for the synthesis of these macromolecules and their monomers.

**Synthetic Results.**—Even though a carbanion would be unstable in the presence of as powerful an oxidizing agent as *p*-benzoquinone, it seemed

(1)(a) Abstracted from Part I of the dissertation submitted by Robert Stern in February, 1956, to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Part of the material of this paper was first presented before the Division of Organic Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, Abstracts of Papers, p. 102-O. (b) Department of Chemistry, Wesleyan University, Middletown, Conn.

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