[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID COMPANY]

Liquid Phase Catalytic Isomerization of α-Pinene[1]

BY V. P. WYSTRACH, L. H. BARNUM AND M. GARBER

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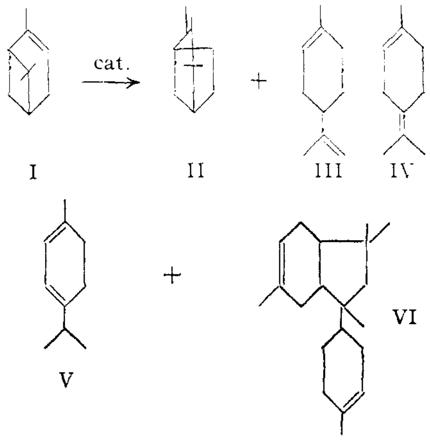
α-Pinene was isomerized at the reflux temperature in the presence of about 1% of calcined Attapulgus clay or cobalt molybdite–alumina catalyst. The progress of the reaction was followed by infrared analysis. Camphene and dipentene were found to be primary products formed directly from α-pinene by relatively fast reactions. Other monocyclic terpenes and terpene dimers and polymers were shown to be formed by relatively slow secondary reactions, principally from the dipentene. A mechanism is proposed to account for the formation of camphene as the chief product under conditions of heterogeneous acid catalysis, whereas dipentene and other monocyclic terpenes result from the homogeneous acid-catalyzed isomerization. The isomerization is pictured as a concerted reaction involving exchange of hydrogen between the catalyst surface and the α-pinene while the latter is held in a rather fixed configuration on the surface.

Introduction

The liquid phase isomerization of α-pinene (I) by heterogeneous catalysis was reported in 1915 by Gurvich.[2] The reaction produces camphene (II), monocyclic terpenes such as dipentene (III), terpinolene (IV) and α-terpinene (V), as well as terpene dimers (VI) and polymers.



Subsequently, a large variety of acidic substances, primarily clays, minerals and inorganic salts, have been studied as catalysts, the objectives having been to increase the yield of camphene and reduce polymer formation.[3] The technology of this process is well known, but very little has been published on the mechanism of the rearrangement of α-pinene to camphene.

During a study of this reaction, several types of catalysts were compared for camphene yield, product distribution and degree of polymer formation. The infrared technique, which was found to be particularly adaptable to the problem, gave a considerable amount of additional information about the isomerization beyond that required for the catalyst evaluation. The experiments reported in this paper have established the sequence of reactions that take place in this complex system and have afforded some speculations on the difference between the homogeneous and heterogeneous catalytic isomerizations of α-pinene.

It was not within the scope of the present study to investigate the nature of the monocyclic terpenes. Moreover, it was not convenient to identify the constituents of the monocyclic terpene mixture by infrared examination; a different region of the spectrum was used from that employed by O'Connor and Goldblatt[4] and reference samples of the likely products were not readily available.

Discussion

Figure 1 is a plot of the change in composition of α-pinene isomerized at 130° using 1.09% of calcined Attapulgus clay. Two conclusions seem evident from these curves. First of all the camphene and dipentene are formed simultaneously and independently from α-pinene by rapid processes. Each reaches a maximum at about the same time, although the rate of camphene formation is appreciably faster. Secondly, it appears that the other monocyclic terpenes, as well as the terpene dimers and polymers, are secondary products derived predominantly from the dipentene by relatively slow reactions.

The data plotted in Fig. 2 were obtained with 0.9% of Attapulgus clay at the reflux temperature of 156 to 172°. They show more clearly that the formations of monocyclic terpenes and polymers are secondary reactions. It also appears that in the later stages of the reaction the camphene as well as the dipentene and other monocyclic terpenes contribute to polymer formation. During the last 2 hr. the total decrease of camphene, dipentene and monocyclic terpenes was 14.1% while polymer formation amounted to 15%.

Essentially the same reaction pattern may be deduced from the data plotted in Fig. 3, obtained by conducting the isomerization at the reflux temperature in the presence of 0.96% cobalt molybdite–alumina cracking catalyst.[5] For the present purpose this material may be considered as an acidic solid catalyst comparable with clay. At equivalent temperature, time and concentration the rate of polymerization with cobalt molybdite catalyst was considerably less, and the extent of polymerization was less than one-third of that obtained with clay. These results show again that dipentene is a definite intermediate in the formation

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[1] Presented at the Naval Stores Symposium, Division of Paint, Plastics, and Printing Ink Chemistry, 131st National A.C.S. Meeting, Miami, Florida, April 7–12, 1957.

[2] L. G. Gurvich, *J. Russ. Phys. Chem. Soc.*, **47**, 827 (1915); *C. A.*, 3005 (1915). *Cf.* A. Deschamps, *Verre silicates ind.*, **13**, 57, 86 (1948).

[3] The literature and patent references to specific catalyst systems are numerous, but apparently no review of this subject has been published. The works cited in this article are perhaps the most significant in the field; however, only their relation to the over-all problem of α-pinene isomerization has been considered.

[4] R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

[5] *Cf.* H. R. Arnold and J. E. Carnahan, U. S. Patent 2,571,997 (du Pont) (Oct. 23, 1951).

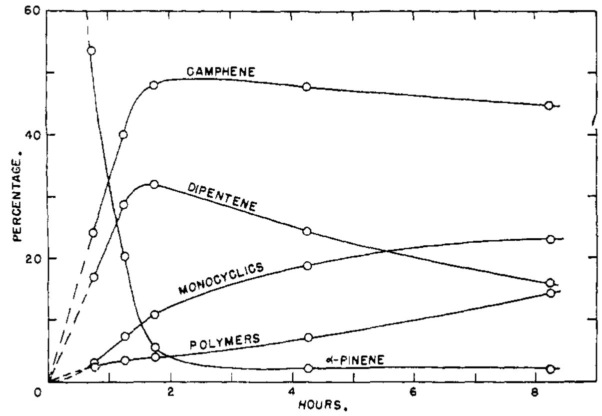


Fig. 1.—Isomerization of α-pinene; 1.09% Attapulgus clay; 130°

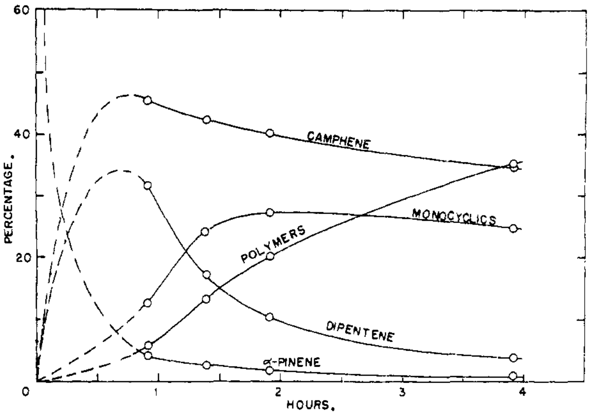


Fig. 2.—Isomerization of α-pinene; 0.9% Attapulgus clay; 156–170°.

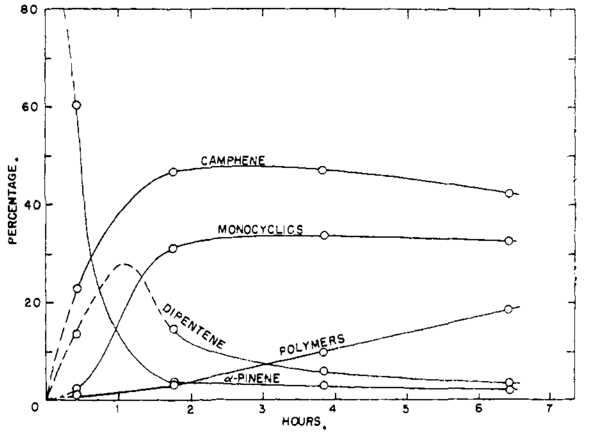
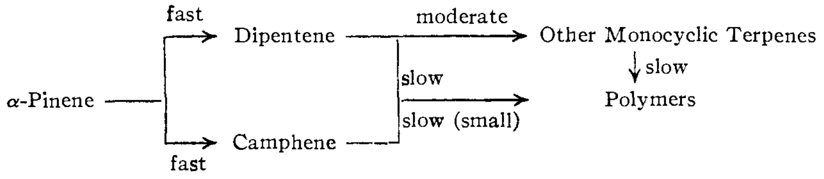


Fig. 3.—Isomerization of α-pinene; 0.96% cobalt molybdite catalyst; 156–169°.

of other monocyclic terpenes, and it is indicated that the polymers are formed to a considerable extent as tertiary products from monocyclic terpenes.

Mechanism.—Tishchenko and Rudakov[6] have already shown that terpene polymers are derived from terpenes other than camphene in the liquid phase isomerization of α-pinene. Moreover, Levsuk and co-workers[7] have published a plot of camphene and terpene polymer formation *versus* time from which it is evident that polymer formation is a secondary process with respect to that portion of the original α-pinene which does not become camphene. The present work has corroborated these findings. In addition, it has confirmed the position of dipentene as a primary product and has established that dipentene is the precursor of the other monocyclic terpenes as well as most of the terpene polymers formed in the over-all process.

The sequence of reactions that takes place in this complex system may be summarized as



This sequence is compatible with the carbonium ion mechanisms advanced by Kharasch and Reynolds[8] for the analogous conversion of α-pinene to borneol esters and by Mosher[9] for the acid-catalyzed isomerization of α- and β-pinene to monocyclic terpenes. An adaptation of these mechanisms to the present situation is shown. If the clay or catalyst were simply a source of protons analogous to a Brønsted acid, there should be little difference between the course of the homogeneous and heterogeneous acid-catalyzed isomerizations. However, the homogeneous acid-catalyzed isomerization of α-pinene gives monocyclic terpenes and practically no camphene[10,11] (Path 1), whereas the heterogeneous reaction gives predominantly camphene. In the latter case other factors must be involved which direct the course of the isomerization along Path 2.

An obvious possibility is an interaction between the α-pinene and the surface which holds an early reaction intermediate in a position more sterically favorable for the rearrangement of the electron pair in the direction of camphene formation. In addition it appears from the rapid rate of camphene formation that a concerted mechanism is involved, *i.e.*, the steps of Path 2 take place essentially simultaneously. The following scheme, suggested by the "Hydrogen Switch" mechanism of Turkevich and Smith,[12] is proposed. It is assumed that the clay or catalyst surfaces have hydrogen available

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[6] V. E. Tishchenko and G. A. Rudakov, *J. Applied Chem. (U.S.S.R.)*, **6**, 691 (1933).

[7] M. Levsuk, *et al.*, *ibid.*, **13**, 1178 (1940).

[8] M. S. Kharasch and W. B. Reynolds, *J. Org. Chem.*, **9**, 148 (1944).

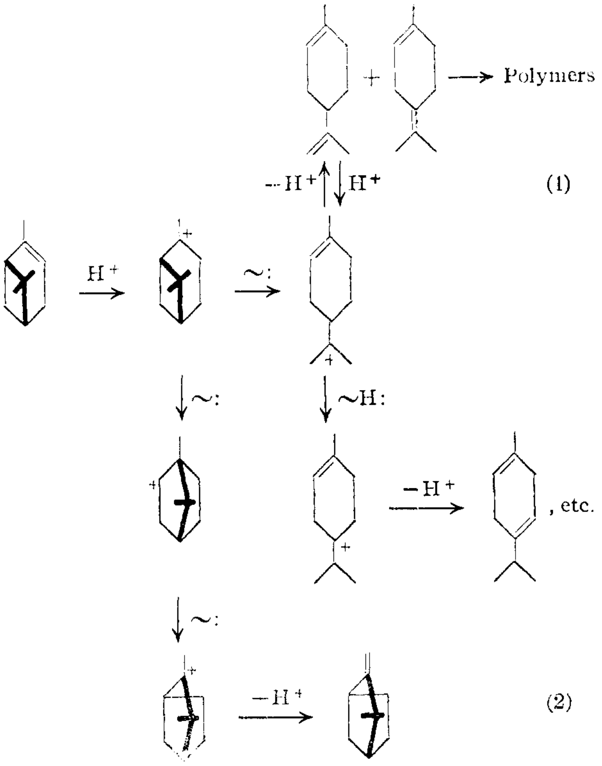
[9] W. A. Mosher, THIS JOURNAL, **69**, 2139 (1947); *cf.* G. Swann, *Ind. Chemist*, **24**, 141 (1948), on formation of bicyclic and tricyclic terpenes as minor products.

[10] J. Reisman, *Bull. soc. chim.*, **41**, 94 (1927).

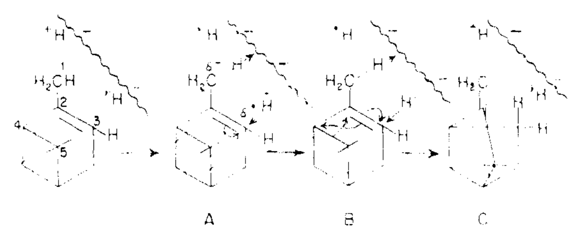
[11] R. W. Charlton and A. R. Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

[12] J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 466 (1948).

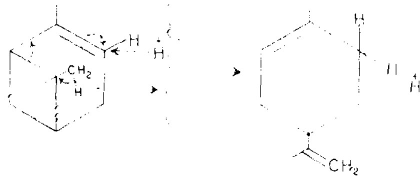
as protons or chemisorbed hydrogen, and it is implied that the hydrogen atoms are conveniently distributed and spaced on the surface in relation to the distance between the hydrogen atoms on 1- and 3-carbon atoms of α-pinene. No pertinent information on proton distribution on attapulgite has been found in the literature.



The catalyst surface interacts with the α-pinene on the side away from the *gem*-dimethyl group because of its bulkiness. As a hydrogen atom from the surface approaches the 3-position, a second hydrogen atom begins its elimination from the 1-position (A). It is suggested that due to the close proximity of the 1- and 3-positions to the surface, adsorption of the α-pinene on the catalyst holds the 1-carbon atom away from the *gem*-dimethyl group. This condition, as seen with molecular models, tends to inhibit the formation of the 2,4-double bond, which would result in the isomerization taking Path 1. Moreover, the fixation of the methyl group in that particular position would facilitate the formation of the 3,4-bond by assisting the necessary inversion of the hydrogen atom on the 4-carbon. The 1-carbon remains favorably situated for the ultimate formation of the 1,2-double bond. It should be reiterated that the process is conceived as one in which all the shifts indicated in B occur at the same time. Completion of the reaction results in a buckling of the camphene molecule (C) toward the catalyst which may aid its recession from the surface.



The less favorable reaction, dipentene formation, can be conceived as occurring when the α-pinene molecule approaches the surface with the *gem*-dimethyl group forward. A hydrogen atom from the surface again attacks the 3-position while a hydrogen atom from one of the methyl groups on the 5-carbon is released to the surface. After appropriate migration of electron pairs, the cyclobutane ring is opened giving rise to the isopropenyl group of dipentene.



The subsequent isomerizations of dipentene into terpinolene, α-terpinene, etc., may be considered to proceed by essentially the same process. These transformations only require a 1,3 shift (or exchange) of a hydrogen atom.

Intermediate A suggests the possibility of α-pinene isomerizing to β-pinene by a heterogeneous reaction. However, this transformation has been shown to be thermodynamically unfavorable.[13]

The formation of terpene dimers and polymers as secondary (or tertiary) products is consistent with Ritter's[14] observation that essentially the same dimer is obtained from either α-pinene or *d*-limonene. Samples of the present polymer fractions were distilled and found to be primarily dimers, probably of the structural type (VI) recently reported by Mosher.[15]

Experimental Part

α-Pinene.—α-Pinene which assayed 99+% was obtained from the Arizona Chemical Company and used without further purification.

Calcination of Clay.—Attapulgus Fuller's Earth (Sample #SO 564-53; Grade: low V.M.; 100/up mesh) was charged into a 4-liter stainless steel beaker fitted with a flat anchor type agitator and a thermometer. The beaker was fitted with a Transite cover, which accommodated the agitator, a thermometer and a water vapor outlet. With slow agitation the clay was heated with a gas burner at 260° for 0.5 hr. The calcined clay was allowed to cool to 180°, whereupon it was transferred to air-tight containers for storage.

Cobalt Molybdite Catalyst.—This material was an experimental cracking catalyst having the composition: 3.6% CoO, 10% MoO_3 and 5.4% SiO_2 on alumina.

Isomerization.—α-Pinene (850–2200 g.) was charged into a three-necked Morton flask of proper size fitted with a reflux condenser, a stirrer and a thermometer. In most instances the charge was heated to the reflux temperature (156°). The catalyst was added portionwise as rapidly as the ensuing exothermic reaction would permit. In certain cases the required amount of catalyst was added in one charge at room temperature and the stirred reaction mixture heated as rapidly as possible to reflux. Samples of 150–250 g. were withdrawn periodically for the analysis of their

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(13) J. E. Hawkins and W. T. Eriksen, This Journal, **76**, 2669 (1954).

(14) J. J. Ritter and J. G. Sharefkin, *ibid.*, **62**, 1508 (1940); J. J. Ritter and V. Bogert, *ibid.*, **62**, 1509 (1940).

(15) W. A. Mosher, A. P. Stuart and W. D. Coder, First Regional Meeting, Delaware Valley Section, A.C.S., Philadelphia, Pa., February 16, 1956.

TABLE I

ISOMERIZATION OF α-PINENE WITH ATTAPULGUS FULLER'S EARTH CATALYST

Catalyst concn., 0.9% by weight

Time,[a] min.	Temp., °C.	α-Pinene Infrared, %	α-Pinene Distn., %	Camphene Infrared, %	Camphene Distn., %	Dipentene Infrared, %	Dipentene Distn., %	Polymers, %	Monocyclics, %[b]
0	156.0	..	..	..	..	..	..	..	..
55	169.5	4.3	<3	45.6	42.3	31.6	31.2	5.8	12.7
85	170.5	2.6	..	42.5	41.3	17.4	26.2	13.3	24.2
115	169.7	1.9	..	40.1	39.5	10.5	19.5	20.2	27.3
235	169.0	1.0	..	35.0	36.0	3.9	16.1	35.2	24.9

[a] Catalyst added in increments of 0.1% as rapidly as possible starting at zero time. [b] By difference from infrared values and polymers.

compositions by fractional distillation or infrared technique. In withdrawing the samples an attempt was made to remove a proportionate amount of catalyst in an effort to maintain a constant catalyst concentration throughout the entire reaction period.

After removal of the catalyst from the various samples by filtration, a 100-g. portion of each was exhaustively steam distilled. A typical steam distillate was collected in a tared separatory funnel, and after settling and removal of the water the organic layer was weighed. The difference between the weight and 100 was used as the estimate of the total dimer and polymer. Because of the viscous nature of the polymer as well as the large amount of water remaining in the still-pot, it was impossible to weigh the polymer directly without resorting to an extraction procedure and its concomitant losses.

The fractional distillations were carried out in a one-inch vacuum jacketed column five-feet long filled with 0.25-inch stainless steel Cannon packing. One hundred gram-portions of the dried steam distillates were fractionated at 100 mm. pressure at a reflux ratio of 15 to 1. Table I summarizes the change in composition of the reaction mixture with time for α-pinene isomerized with Attapulgus clay at reflux temperatures of 155 to 175°. It includes a comparison of the analyses for the principal components by the infrared method (described below) and by distillation. Concordance with respect to α-pinene and camphene is very good over the total time interval. The increasing discrepancy with time in the case of dipentene arises from the inability to separate it cleanly from other monocyclic terpenes of approximately the same boiling point with the distillation apparatus available. It seems not unreasonable to assume that the infrared method of analysis is also reliable for dipentene.

An experiment conducted with Attapulgus clay at 130° is summarized in Table II, and an experiment with cobalt molybdite catalyst at the reflux temperature is summarized in Table III. These data are plotted as Figs. 1 and 3, respectively.

TABLE II

ISOMERIZATION OF α-PINENE WITH ATTAPULGUS CLAY CATALYST

Catalyst concn., 1.09% by weight; temperature, 130°

Time,[a] min.	α-Pinene (infrared), %	Camphene (infrared), %	Dipentene (infrared), %	Polymers, %	Monocyclics, %[b]
45	53.6	24.2	17.0	2.5	2.7
75	20.5	40.1	28.7	3.4	7.3
105	5.4	48.0	31.8	4.0	10.8
225	2.0	47.9	24.4	7.0	18.7
465	2.0	45.0	15.9	14.2	22.9

[a] Catalyst added in increments of 0.1%. Zero time is the manifestation of an exotherm after one-third of catalyst had been added. [b] By difference from infrared values and polymers.

Determination of Camphene, Dipentene and α-Pinene.—Infrared spectra were obtained on high purity samples of camphene, dipentene and α-pinene in the NaCl region (4000–650 cm.$^{-1}$) and the KBr region (800–400 cm.$^{-1}$) using a Perkin-Elmer Model 21 Infrared Spectrophotometer. Subsequently a Perkin-Elmer Model 12C instrument was employed for the quantitative work. The frequencies selected were

	Freq., cm.$^{-1}$	Cell, mm.	Optics
Camphene	667 (15.0 μ)	0.1	KBr
Dipentene	910 (11.0 μ)	.05	NaCl
α-Pinene	785 (12.7 μ)	.01	NaCl

A set of calibration curves at these frequencies was made up for camphene, dipentene and α-pinene whereon the densitometer readings (absorption) as the ordinates were plotted against concentration as the abscissas. Dipentene was used as solvent for camphene and, in making measurements over a range of camphene concentrations at 667 cm.$^{-1}$, the background was set by using dipentene in the reference cell. Similarly the curve for dipentene was obtained using toluene as solvent at 910 cm.$^{-1}$, and the curve for α-pinene was obtained using methylcyclohexane as solvent at 785 cm.$^{-1}$. The plots were linear over a wide concentration range in obedience to Beer's law.

TABLE III

ISOMERIZATION OF α-PINENE WITH COBALT MOLYBDITE CATALYST[a]

Catalyst concn., 0.96% (by weight)

Time,[b] min.	Temp., °C.	α-Pinene (infrared), %	Camphene (infrared), %	Dipentene (infrared), %	Polymers, %	Monocyclics,[c] %
0	156.0	..	..	..	..	..
25	161.0	60.2	22.8	13.6	1.0	2.4
105	168.8	4.1	46.8	14.6	3.2	31.3
230	168.0	3.1	47.0	6.0	10.0	33.9
385	166.5	2.1	42.5	3.9	18.7	32.8

[a] 3.6% CoO, 10% MoO_3, 5.4% SiO_2 on alumina. [b] Catalyst addition started at 0 min. time; complete at 25 min. [c] By difference from infrared values and polymers.

Analysis of a typical sample of the terpenes recovered by steam distillation was conducted as follows:

1. From the densitometer reading obtained at the camphene frequency of 667 cm.$^{-1}$, the camphene content was read off the camphene calibration plot. Dipentene and α-pinene have negligible absorptions at this frequency.
2. The densitometer reading taken at the dipentene frequency, 910 cm.$^{-1}$, was corrected for camphene absorption and the dipentene content read off the dipentene calibration plot. The absorption of α-pinene is negligible at 910 cm.$^{-1}$.
3. The densitometer reading at the α-pinene frequency, 785 cm.$^{-1}$, was corrected for camphene and dipentene and the α-pinene content, represented by the residuum, obtained from the α-pinene calibration chart.
4. The camphene, dipentene and α-pinene values were corrected for the fraction of the total reaction mixture represented by the steam distillate. The total composition of the reaction mixture is given by the expression

$$100 - \left[\frac{\text{g. steam dist.}}{100}(\%\ \text{camphene} + \%\ \text{dipentene} + \%\ \alpha\text{-pinene}) + \%\ \text{polymers}\right] = \%\ \text{other monocyclic terpenes}$$

The sum, Σ, of the camphene, dipentene and α-pinene in the first sample of the various runs was approximately 100%.

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.

STAMFORD, CONNECTICUT

[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

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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

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

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

$$\cdot CH_2CO_2CH_3 + nCH_2{=}CH_2 \longrightarrow (CH_2CH_2)_n\text{-}CH_2CO_2CH_3 \qquad (3)$$

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

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

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

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

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.

(3) W. E. Hanford and R. M. Joyce, U. S. Patent 2,440,800 (May 4, 1948); W. E. Hanford, U. S. Patent 2,418,832 (April 15, 1957); U. S. Patent 2,373,561 (April 10, 1945).

(4) M. D. Peterson and A. G. Weber, U. S. Patent 2,395,292 (February 19, 1946); W. E. Hanford and J. R. Roland, U. S. Patent 2,402,137 (June 18, 1946); S. L. R. Scott, U. S. Patent 2,407,181 (September 3, 1946).

(5) R. M. Joyce, W. E. Hanford and J. Harmon, THIS JOURNAL, **70**, 2529 (1948); M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947); F. M. Lewis and F. R. Mayo, *ibid.*, **76**, 463 (1954).

(6) M. S. Kharasch, P. S. Skell and P. Fisher, *ibid.*, **70**, 1055 (1948).