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Cationic Polymerization of α-Pinene Oxide and β-Pinene Oxide by a Unique Oxonium Ion-Carbenium Ion Sequence

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ABSTRACT

The cationic polymerization of α- and β-pinene oxide has been studied. By use of boron trifluoride or phosphorus pentafluoride these monomers may be oligomerized ($DP_n \cong 6\text{-}7$). According to ^{13}C-NMR spectroscopy and other evidence, the four-membered ring present in these monomers opens or expands during reaction. The repeat structures of these polymers suggest a unique oxonium ion-carbenium ion propagation mechanism. Simultaneously with the oligomerization, these epoxides also yield large amounts of aldehydes by a related isomerization.

INTRODUCTION

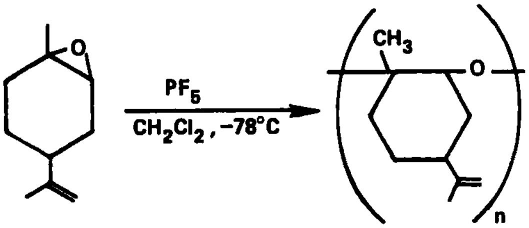
In the course of our study of the polymerization of terpenes by cationic processes we have prepared the epoxides of limonene, α-pinene and β-pinene and have studied their polymerization characteristics.

A thorough search of the patent as well as published literature revealed no pertinent articles on the polymerization of these epoxides.

This paper concerns a study of the polymerization of α- and β-pinene epoxide, the structural mers present in the polymers, and monomeric rearrangement products. A unique oxonium ion-carbenium ion propagation mechanism is suggested which explains the results obtained with α- and β-pinene epoxides .

RESULTS AND DISCUSSION

Polymerization of limonene epoxide by cationic initiation, e.g., PF_5, yields the expected 1,2-trans polyether in high yield [Eq. (1)]; there is little if any evidence for polymerization through the double bond system [1].



I

It might be predicted that α- and β-pinene oxide would polymerize to yield a similar 1,2-trans polyether; however, it became apparent that the polymerization was more complex, and structural differences from limonene oxide played a key role. Both α- and β-pinene oxide monomers possess a four-membered ring, beta to the epoxide ring, and when the epoxide is cationated to an oxonium ion the cyclobutane ring opens.

The variety of structural units in the pinene oxide polymers, the optical activity of the products, and the monomeric rearrangement products confirmed the complexity of the reaction.

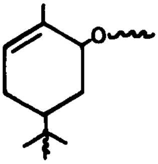
α-Pinene and β-pinene oxides were homopolymerized with boron trifluoride or phosphorus pentafluoride coinitiators by using tert-butyl chloride or presumably advantitious water initiators and nonpolar solvents (Table 1). The yield of solid poly(α-pinene oxide) ranged from 1 to 28% with dimeric oils and monomeric rearrangement products accounting for the balance. Solid poly(β-pinene oxide) yields were from 1 to 8%, with by-products similar to those encountered with α-pinene oxide.

Poly(α-pinene Oxide)

A comparison of runs 1 and 2 in Table 1 illustrates that hexane as solvent ($\epsilon = 2.0$) proved superior to methylene chloride, ($\epsilon = 14.7$) in terms of polymer yield and product molecular weight. When methylene chloride was used, only a low molecular weight oil was obtained. By contrast, limonene epoxide could be polymerized only in a polar solvent such as methylene chloride [1].

If α-pinene oxide was polymerized in methylene chloride with BF_3 and presumably advantitious water as initiator, polymer yield dropped but molecular weight increased (runs 1, 3). The use of BF_3:OEt_2/tert-BuCl, in place of BF_3/tert-BuCl, and hexane solvent increased polymer yield but lowered molecular weight (runs 1, 4), whereas PF_5/tert-BuCl proved less effective as both yield and molecular weight were reduced (runs 1, 7). Polymerizations at lower than -78° C failed to give increased resin yield or molecular weight (runs 5, 6).

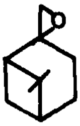
The chemical shifts obtained from ^{13}C-NMR spectra of the solid poly-(α-pinene oxide) and several structurally related terpenes are shown in Table 2. Sobrerol and ℓ-borneol are structurally related to mer units proposed to occur in the polymer of α-pinene oxide. Nine of the ten resonances indicated by asterisks in Table 2 (excluding that of $\delta = 134.8$ ppm), are within ± 0.8δc ppm in the α-pinene oxide polymer. This is evidence that some mer structures in the polymer of α-pinene oxide are of the type II



II

The ^{13}C spectra of bornane (III), bornylene (IV), and camphor (V) have been studied and the resonances assigned [2]. In these compounds

TABLE 1. Synthesis and Characteristics

Formula	Run	Concn (M)	Solvent	Initiator system	Lewis acid (mole %)
	1	1.62	Hexane	BF_3/(t-BuCl, 0.097 M)	b
	2	3.29	CH_2Cl_2	BF_3/(t-BuCl, 0.197 M)	b
	3	4.40	CH_2Cl_2	BF_3	b
$[\alpha]^{25}_{D}$ + 48.0°	4	0.816	Hexane	$BF_3:OEt_2$/(t-BuCl, 0.049 M)	3.6
	5	1.49	EtCl	PF_5	3.6
	6	1.03	Pentane	PF_5	3.6
	7	1.09	Hexane	PF_5/(t-BuCl, 0.049 M)	3.6
	8	1.09	Hexane	PF_5	3.6
	9	1.09	Hexane	PF_5	3.6
	10	2.19	CH_2Cl_2	PF_5	3.6
$[\alpha]^{25}_{D}$ + 13°	11	1.09	Hexane	$BF_3:OEt_2$	3.6
	12	1.09	Hexane	BF_3/(t-BuCl, 0.065 M)	b
	13	1.03	Pentane	PF_3	3.6

[a] Precipitatable powder. The balance between % conversion and % monomer.

[b] BF_3 added until exotherm observed.

III

IV

of Pinene Oxide Polymers

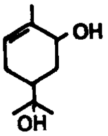
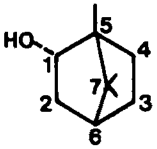
Temp. (° C)	Time (min)	Con- ver- sion (%)	Poly- mer (%)[a]	$\overline{M}_n$	Soft- ening range (° C)	$[\alpha]^{25}_{D}$ (CHCl$_3$)	Physical state
-78	2	100	20	1025	67-80	+19.5°	white powder
-78	5	–	0	219			
-78	120	100	4.6	1420	75-97	+18.8°	white powder
-78	60	100	28	512	57-70		viscous oil
-130	60	77.5	1	1000	70-82		white powder
-125	60	76	2.4	1170	78-90		white powder
-78	5	100	2.1	600	85-95	+28.1°	white powder
-78	60	100	1.1	–	62-75		white powder
-90	5	100	0.9	2360	78-90		white powder
-90	5	100	0	390			oil
-78	60	100	2.5	403	77-92	-29°	white powder
-78	5	100	5.5	552	48-65		amorphous solid
-125	10	90	8.5	780	68-80	-31°	white powder

polymer is made up by nonprecipitatable oligomers and isomerized

V

the angular bridgehead methyl group at C-10 was observed to be the most shielded carbon and was observed to resonate at 15.8, 13.4 and 9.5 δc ppm, respectively, from TMS. The angular bridgehead methyl group in ℓ-borneol was also observed farthest upfield at 13.3 δc ppm. On this basis, the most intense and also most shielded resonance line in the ^{13}C spectrum of α-pinene oxide polymer (12.6 δc ppm) may be assumed to be an angular bridgehead methyl group.

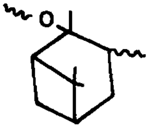
TABLE 2. Chemical Shift Data (from TMS)

	Chemical shift (ppm)	
Sobrerol	ℓ-Borneol	Poly(α-pinene oxide)
		
CH$_3$ 21.0	CH$_3$ 13.3	12.6 v. intense
CH$_3$ 26.0	CH$_3$ 18.7	19.8
CH$_2$ 27.3	CH$_3$ 20.2	20.1
CH$_3$ 27.7	CH$_2$ 26.0	20.8
CH$_2$ 32.8	CH$_2$ 28.3	21.7*
CH$_2$ 38.7	CH$_2$ 39.0	25.7
CHOH 68.0	C-6 45.2	26.6*
COH 71.5	C-5 } 48.0, 49.5	27.1*
=CH 124.6	C-7 }	27.6*
=C< 134.8	C-1 77.3	32.8*
CDCl$_3$ + 20% DMSO (76.3, 77.6, 78.9)		35.6
		38.9*
		44.3
		45.2
		47.0
		68.7*
		72.3*
		121.6
		125.3*
		?133.1
		CDCl$_3$ (75.8, 77.0, 78.3)

A typical ^{1}H-NMR spectrum of a poly(α-pinene oxide) prepared at -130° C using ethyl chloride and PF_5 is shown in Fig. 1A.

This spectrum shows two types of olefinic H (5.15, 5.44 δ), two types of $\underline{H}$–C–O (3.78, 4.64δ) two types $C\underline{H}_3$–C=C (1.6, 1.7 δ) and four methyl hydrogen peaks at 1.30, 1.16, 0.97 and 0.74 δ). Assignment of these proton resonances will be developed later.

The number-average molecular weight ($\bar{M}_n$) by vapor pressure osmometry determined for a precipitated α-pinene oxide polymer was 1420 ($\overline{DP}_n$ ~ 9.3). Comparison of the vapor-pressure osmometry and gel-permeation chromatographic (GPC) data for poly(limonene oxide) and poly(α-pinene oxide) indicates that for chains of the same molecular weight the poly(α-pinene oxide) has the larger hydrodynamic size. These data strongly suggest a longer than expected polymer repeat unit.



VI

The complexity of these data and the monomeric rearrangement products to be discussed below prompted speculation on the mechanism and proposal of several structural units for the polymer. Based on our previous studies of the structure of polyterpene hydrocarbon resins [3], isomerization, and rearrangements of monomeric terpenes [4], the four types of mers were considered to be present in the poly(α-pinene oxide): a ring-opened mer, a ring closed mer, a branched mer, and a ring expanded mer.

Ring Opened Mer

It is proposed that the ring-opened mer VII is an important structural unit in poly(α-pinene oxide) and that it is formed by the mechanism shown in Eq. (2).

Initiation probably occurs by protonation and yields a strained oxonium ion. Propagation is proposed to proceed by a concerted ring-opening mechanism involving both the epoxide and the condensed four-membered ring. The unique feature of this mechanism is the simultaneous involvement of oxonium and carbenium ions in the propagating species. The relieving of the strain of the two ring systems must significantly contribute to the driving force of propagation

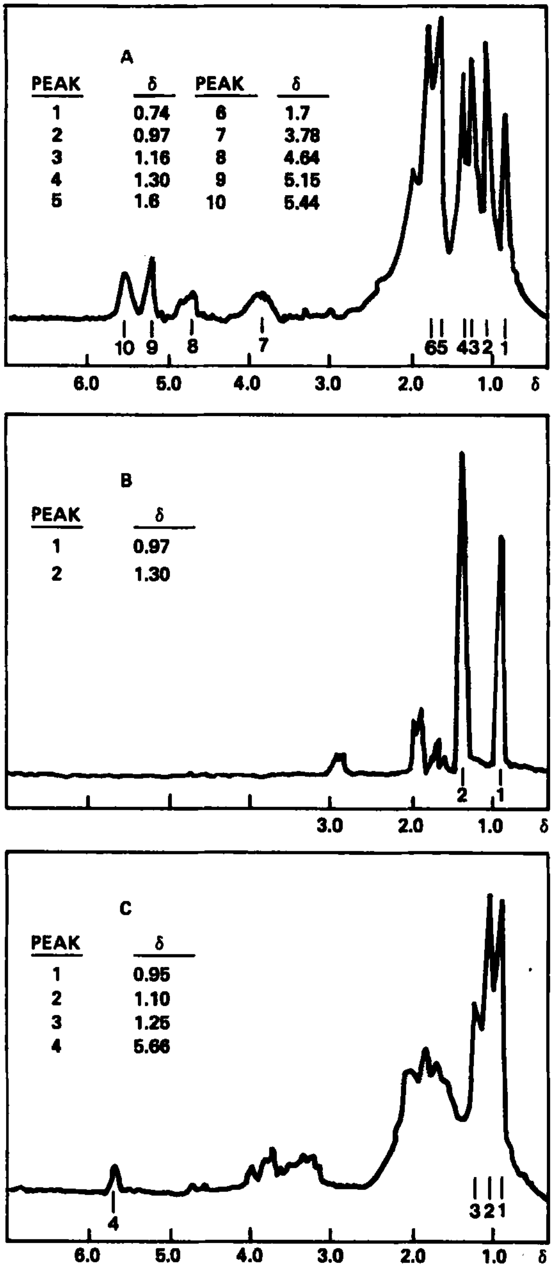
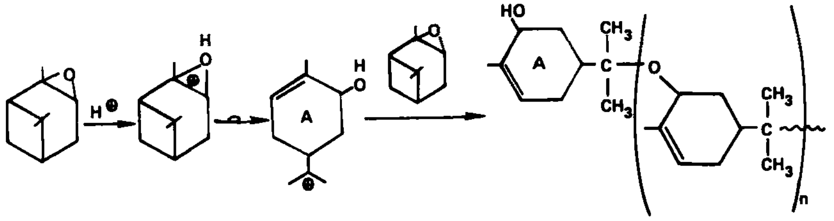


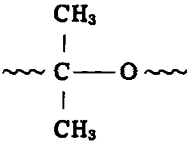
FIG. 1. ^{1}H-NMR spectra of (A) poly(α-pinene oxide); (B) α-pinene oxide; (C) poly(β-pinene oxide).



VII (2)

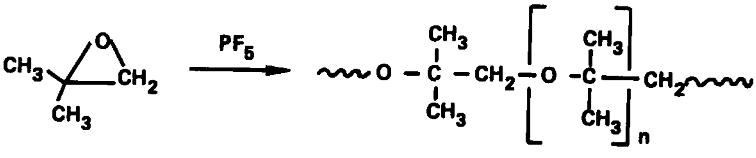
step. A somewhat similar strain-relief propagation mechanism has been proposed for the cationic polymerization of α- and β-pinenes [5].

Evidence for this conclusion comes from ^{1}H NMR spectroscopy (Fig. 1A), according to which the polymer contains units of the type:



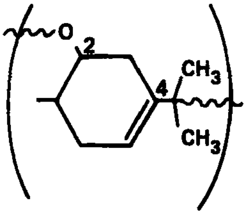
$$\sim\!\sim\!\sim \underset{CH_3}{\overset{CH_3}{C}} - O \sim\!\sim\!\sim$$

That the strong resonance at 1.16 δ is in fact due to this structure has been confirmed independently. Thus the ^{1}H NMR spectrum of poly(isobutylene oxide) exhibits a resonance at 1.14 δ due to the gem-dimethyl moiety [Eq. (3)].



(3)

In addition, GPC studies also seem to indicate a longer than expected mer unit for poly(α-pinene oxide) which would be a consequence of formation of this mer. The dual nature of the olefinic and $\underline{\text{H}}$–C–O peaks suggests occasional isomerization of repeat unit VII to VIII:

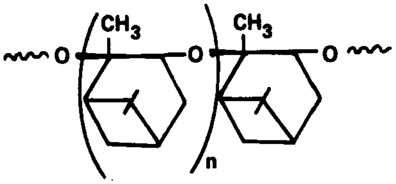


VIII

The driving force for isomerization would be the planarity of the olefinic position minimizing steric interaction at the 2 and 4 positions.

Ring Closed Mer

Such a mer has the structure IX. The ^{1}H-NMR spectrum of the α-pinene oxide polymer prepared in ethyl chloride at -130°C shows a

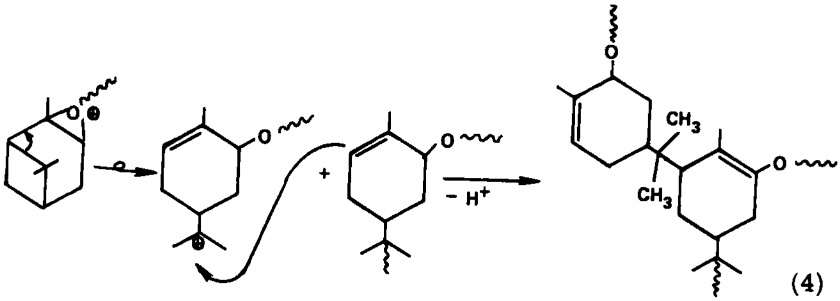


IX

nonequal pair of resonances at 0.97 and 1.30 δ which correspond to the position of the gem-dimethyl absorption in α-pinene monomer. (Figs. 1A, 1B) However, the polymer prepared in pentane at -130°C exhibits only a trace of the 1.30 δ peak and that obtained at -90°C does not show this resonance at all. An estimate of the ratio of unopened/opened cyclobutane can be determined from the ratio of absorptions: 2(1.30 δ)/[0.97 δ + 1.16 δ + 1.30 δ]. The resonance at 1.30 δ in the numerator is doubled, since the equal companion resonance at 0.97 δ for the unopened cyclobutane is masked by larger absorption at this frequency due to another type mer (see ring expanded mer). Calculation of this ratio for poly(α-pinene oxide) prepared at -130°C in ethyl chloride indicates that 7.4% of the monomer units polymerize through the epoxide without concomitant participation by the four-membered ring.

Branched Mer

A complication of the ^{1}H-NMR spectrum was the two types of $\underline{C}H_3$–C = C resonances observed at 1.6 and 1.7 δ. These can be accounted for by branching due to occasional attack by a carbenium ion on preformed polymer [Eq. (4)].

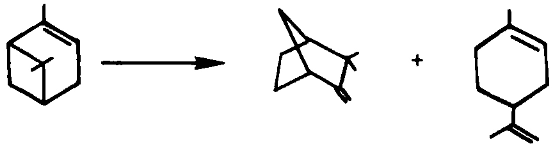


(4)

X

Ring Expanded Mer

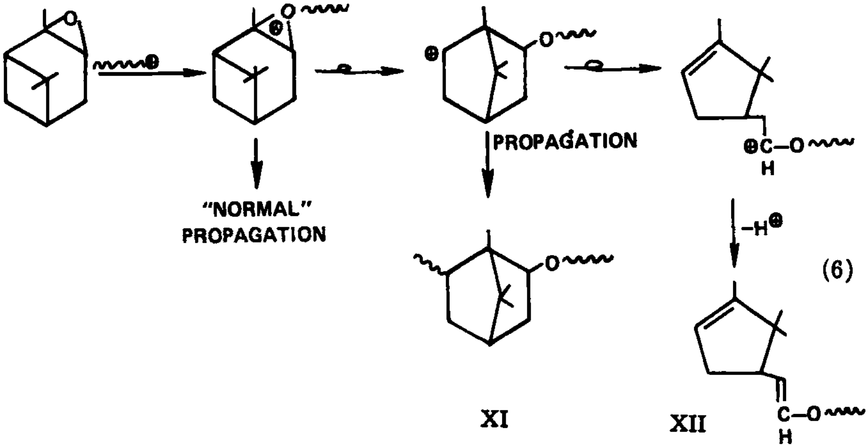
By analogy to the chemistry of monomeric terpenes and terpene hydrocarbon resins, the ring expanded mer is anticipated. The Wagner-Meerwein rearrangement [Eq. (5)] which expands the four-membered ring of α- or β-pinene to the [2:2:1] bicyclic ring system is well documented in the literature [6].



(5)

The mechanism proposed in Eq. (6) demonstrates how the ring expanded mer XI would be incorporated in the chain. Cleavage of the [2:2:1] bicyclo skeleton as will be described later for campholene aldehyde, could lead to a mer having structure XII.

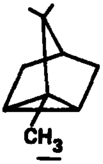
The ^{1}H-NMR spectra of several model compounds were recorded to explain the methyl resonance at 0.74 δ in the resin. Tricyclene (XIII) and one of the gem-dimethyl groups in campholene aldehyde (XIV) have resonance frequencies in this region.



XI

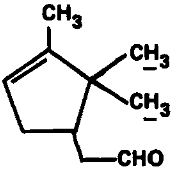
XII

(6)



0.80δ

XIII



0.78δ, 1.0δ

XIV

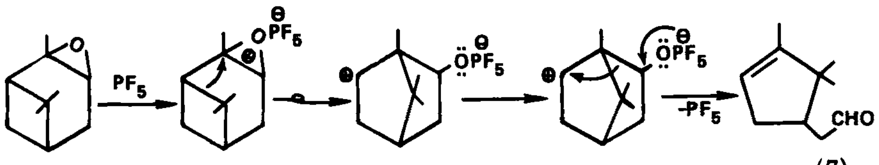
Therefore, either of the structures shown (XI, XII) resulting from the ring expansion pathway could be responsible for the methyl resonance observed at 0.74 δ; XI contains a bridgehead methyl, as does tricyclene (XIII), while the end unit derived from XII contains a gem-dimethyl group as in campholene aldehyde (XIV).

Polymerization By-Products

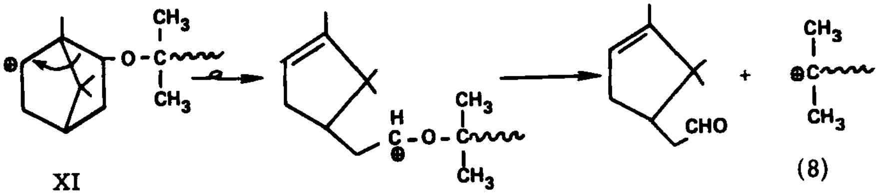
The α-pinene oxide in most cases was converted completely to polymer, dimer oils, and monomeric rearrangement products. The nonpolymeric products can be explained by mechanisms similar to those proposed for polymer formation.

The major nonpolymeric product isolated (about 50%) is a mixture of dimers, $\overline{M}_n \sim 300$. The GLC generally showed three or four distinct peaks of approximately equal intensity. Attempts to minimize dimer formation have failed. Even at -130°C (Table 1, run 5) dimers are the principal product. The overriding amount of dimer indicates that propagation from dimer to trimer is less favorable than rearrangement and/or transfer.

The second major (~30%) nonpolymeric product, campholene aldehyde, was identified by ^{1}H-NMR. This aldehyde could form either from monomer [Eq. (7)] or from a rearrangement and loss of a terminal active mer of structure XI [Eq. (8)].



(7)

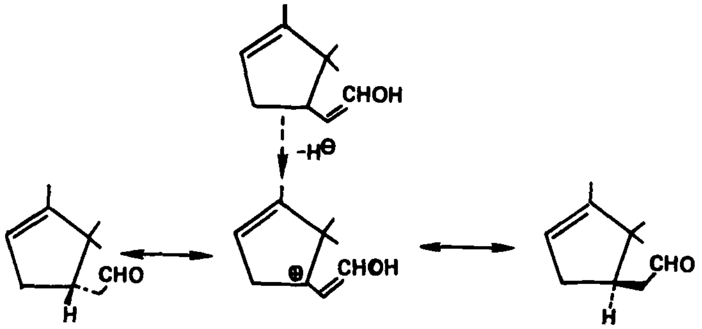


XI

(8)

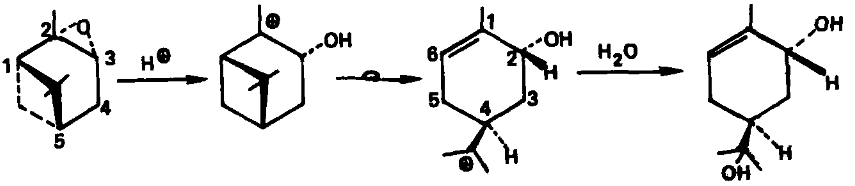
Campholene aldehyde produced from α-pinene oxide has previously been reported [7] and results from one of a relatively small group of reactions involving cleavage of a bicyclo[2:2:1]heptane skeleton. Inhibition of this facile rearrangement by conducting polymerizations at -130° C using either pentane or ethyl chloride and PF$_6$ were unsuccessful. Substantial amounts of campholene aldehyde were formed in all polymerizations.

The campholene aldehyde isolated was optically inactive. Presumably the allylic hydrogen of the enolic tautomer is mobilized in the strongly acidic media and can rearrange as illustrated in Eq. (9).



(9)

Polymerization in a "wet" system yielded sobrerol, and it was found to be predominantly, if not exclusively, the (+) trans isomer; $[\alpha]_D^{25}$ = +169 (CHCl$_3$); mp 142-145°C; m/e 170.



(10)

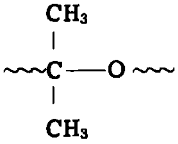
Schench et al. [8] report the following physical constants for (+) trans-sobrerol: mp 146-148° C, $[\alpha]_D^{20}$ = +141 (C$_2$H$_5$OH). These above physical data indicate that the configuration of the C-3 and C-5 centers of α-pinene oxide is retained after opening of the epoxide and cyclobutane ring systems. The retention of configuration at C-4 (of sobrerol) indicates the absence of hydride transfer involving the C-4 tertiary hydrogen and the pendant C-4 isopropyl carbenium ion and that the reaction with water is so fast that configuration is retained.

Retention of configuration in the related acidic hydration of α-pinene was also observed using a heterogeneous cationic catalyst [4].

Poly(β-pinene Oxide)

Polymer Structure

The polymerization of β-pinene oxide produced a lower yield of polymer than α-pinene oxide. The best yield of polymer was 8.5% (Table 1, run 13). The ^{1}H-NMR spectrum of this polymer (Fig. 1c) shows olefinic H (5.66 δ), large areas of $OC\underline{H}_2$ (3-4 δ) and ring $C\underline{H}_2$ (1.4 to 2.4 δ) plus several types of methyl hydrogen resonances (.95 δ, 1.10 δ and 1.25 δ). Integration shows the correct proton ratio of 6.5 for ($C\underline{H}_2$ and $C\underline{H}_3$)/$OC\underline{H}_2$, however, the olefinic proton resonance is only about 30% of that expected. The resonance at 1.10 δ can be assigned to the group



$$\sim\!\sim C(CH_3)_2 - O \sim\!\sim$$

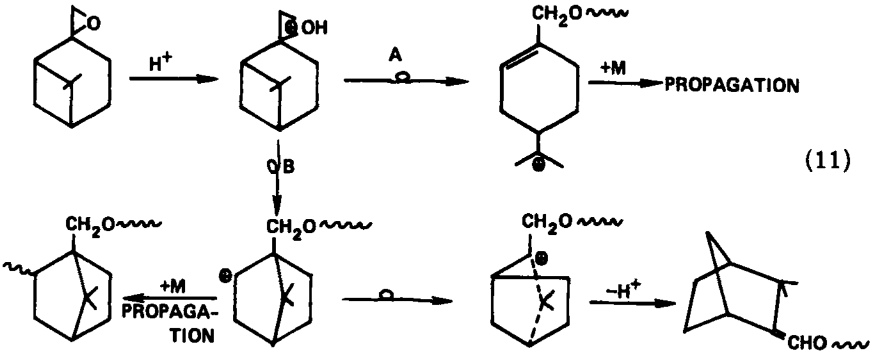
previously observed at 1.16 δ and 1.14 δ in poly(α-pinene oxide) and poly(isobutylene oxide), respectively.

Polymerization by pathway B [Eq. (11)] would explain the lower than expected amount of olefin anticipated if pathway A were the sole route.

The amount of olefin observed suggests that 30% of the mers are formed via pathway A; 70% via pathway B. The gem-dimethyl group formed from pathway A could account for the resonance at 1.10 δ and 1.25 δ. (Fig. 1C)

Polymerization By-Products

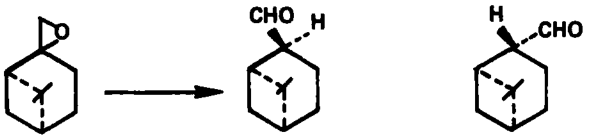
Again, as was the case with α-pinene oxide, polymerization of β-pinene oxide resulted in complete conversion of monomer to polymer, dimer oils and rearranged monomer, with the nonpolymer by-products



(11)

predominating. About 7.5% of the by-product consisted of aldehydes, bp 89-92 °C/10 Torr and the remainder dimer oils. ^{1}H-NMR showed the presence of at least two aldehydic components.

The aldehyde products were anticipated from our experience with α-pinene oxide and from the published literature. Coxon et al. [9] have described epimeric aldehydes as products of the boron trifluoride-etherate catalyzed reaction of β-pinene oxide in ether [Eq. (12)].



(12)

We presume that the aldehydes produced during polymerization with PF_5 arise by a similar route.

EXPERIMENTAL

Equipment and Source of Chemicals

Gas-liquid chromatographic (GLC) analyses were made with a Wilkens Aerograph Model 1520 gas chromatograph coupled with a Hewlett-Packard Model 3373B Electronic Integrator. The analyses were made on a 16 ft × 1/8 in. stainless steel column packed with 15% Carbowax 20M on Anakrom AB 70/80.

The ^{1}H-NMR spectra were obtained on a Varian HA-100 nuclear magnetic resonance spectrometer at room temperature using carbon tetrachloride as solvent. The ^{13}C-NMR spectra were obtained with a Varian XL-100 spectrometer operating in the pulse FT mode with deutereochloroform as solvent.

Gel-permeation chromatographic (GPC) analysis was made with a Waters Associates gel-permeation chromatograph, Model 200, equipped with five 4 ft × 3/8 in. columns packed with gels having pore sizes as follows: 10^5 Å, 8.5×10^3 Å, 10^3 Å, 150-350 Å, and 50-80 Å. The first three columns were packed with Styrogel and the latter two with Porogel.

The molecular weights were determined by vapor-pressure osmometry with a Model 301 A Mechrolab instrument with chloroform as solvent at 37° C.

Hexane, pentane, and methylene chloride (J. T. Baker Company) were dried over Linde 4Å Molecular Sieves prior to use. Ethyl chloride and boron trifluoride (Matheson Co.) were used as received. Isobutylene oxide (Research Organic Inorganic Chemical Corporation) was purified by distillation prior to use, bp 52° C/760 Torr.

α-Pinene Oxide

This procedure was obtained as a personal communication [10].

To a stirred mixture of 100 g α-pinene (as Acintine A, assay ca. 96% α-pinene) and 67 g sodium carbonate was added dropwise 61 g 40% peracetic acid at 25° C. The slight exotherm was easily controlled by ice water cooling. After stirring the mixture at 25° C for 2.5 hr it was drowned in a mixture of cracked ice and water and the organic layer allowed to separate. After washing the organic layer with sodium carbonate solution and with water until neutral, it was dried over anhydrous sodium sulfate and fractionated at 10 Torr pressure. Unreacted α-pinene distilled at 42° C and α-pinene oxide at 61-62° C. The yield of α-pinene oxide was 44 g, (90% of theory based on the peracetic acid utilized); $[\alpha]_D^{25} = +48.0°$ (c = 1.76, $CHCl_3$) GLC showed it to be 99% pure. The column temperature for GLC should not be higher than 150° C, otherwise α-pinene oxide will rearrange to carveol and pinocamphone [11].

The ^{1}H- and ^{13}C-NMR spectra of α-pinene oxide agree with that expected.

β-Pinene Oxide

β-Pinene oxide monomer was prepared by the procedure described by Newhall [12]. An 85% conversion of β-pinene to oxide was realized at 30° C. Distillation on a spinning band column produced 95% pure β-pinene oxide. Refractionation on a Nester-Faust annular still increased the purity to 99%; bp 83° C/12 Torr [13], $[\alpha]_D^{25} = +13°$ (c = 1.84, $CHCl_3$). To prevent isomerization, GLC analysis of β-pinene oxide was performed at or below 110° C.

Preparation of Polymers

Poly(α-pinene Oxide)

Hexane (40 g), α-pinene oxide (15 g, assay 99%), and 0.64 ml (0.55 g) tert-butyl chloride were added to a three-necked round-bottomed flask equipped with stirrer, thermometer, and a gas inlet. This mixture was cooled to -78° C under a stream of dry nitrogen and BF_3 gas introduced beneath the liquid surface. Polymerization commenced with an abrupt temperature rise to -68° C and the simultaneous appearance of a pale yellow color. At this stage, BF_3 introduction was stopped, and after 2 min of stirring 10 ml methanol was added to deactivate the catalyst. The temperature was raised to 0° C, 50 ml 5% $NaHCO_3$ added, and the organic phase separated and washed with bicarbonate solution, followed by 50-ml portions of water until the aqueous wash was neutral.

The bulk of the solvent was distilled off and the viscous oily residue dissolved in 10 ml methylene chloride. This solution was then added dropwise to 250 ml methanol to precipitate the poly(α-pinene oxide). A white powder was collected by filtration and dried in vacuo to 3.0 g corresponding to 20% yield.

Molecular weight was 1025, indicating a $\overline{DP}_n \sim 6.7$. The softening range was 67-80° C. The polymer was optically active: $[\alpha]_D^{25} = +19.5°$ (c = 1.07, $CHCl_3$).

An 8-g yield of a mixture of α-pinene oxide dimer and rearranged monomer (campholene aldehyde) was isolated by removing volatile solvents from the precipitation liquors.

The substitution of methylene chloride solvent for hexane yielded only rearranged monomer and dimers. No precipitatable polymer was obtained.

Poly(β-pinene Oxide)

Dry pentane (40 g) and β-pinene oxide (10 g) were charged to a three-necked round-bottomed flask with stirrer, thermometer, and a gas inlet. The monomer solution was cooled to -125° C under a stream of dry nitrogen. Phosphorus pentafluoride was generated by the controlled thermal decomposition of 0.75 g recrystallized [14] Phosfluorogen A (p-chlorobenzenediazonium hexafluorophosphate, Ozark Mahoning Co., Tulsa, Okla.).

The PF_5 generator consisted of a 50-ml two-necked flask, one neck fitted with a N_2 inlet to sweep out the PF_5 initiator as generated. The rate of PF_5 generation was controlled by heating with an adjustable 160° C bath.

The PF_5 was passed into the cold monomer solution; the rate of PF_5 addition was adjusted so as to maintain -120 to -125° C.

Following completion of PF_5 addition, the reaction mixture was stirred at -78° C for 10 min, and 15 ml methanol was added to deactivate the catalyst. Subsequent workup as described for the poly(α-pinene oxide) polymer yielded 8.5% of polymer.

VPO gave $\overline{M}_n = 780$ or $\overline{DP}_n \sim 5.8$; the softening range was 65-80° C. The polymer was optically active $[\alpha]_D^{25} = -31°$ (c = 1.67, $CHCl_3$); β-pinene oxide monomer had a rotation $[\alpha]_D^{25} = +13°$ (c = 1.84, $CHCl_3$).

A mixture of 8.4 g of low molecular weight oil and rearranged aldehydic monomers was isolated by removing volatile solvents from precipitation mother liquors, while 0.7 g of a waxy material was isolated from the water washes. Material balance was thus 99.5%.

As with α-pinene oxide, the use of methylene chloride as solvent yielded only β-pinene oxide dimer and rearranged monomer.

Poly(isobutylene Oxide)

Isobutylene oxide 10 g, (GLC assay 99.5%) was dissolved in 80 g methylene chloride, cooled to -78° C, and 3.6 mole % PF_5 added as described above. The mixture was stirred for 1 hr at this temperature prior to workup. The solvent-free polymer, 6.2 g of a waxy material, had a $\overline{M}_n = 345$ or $\overline{DP}_n = 4.8$.

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