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Cationic oligomerization of 3-methylene-*p*-menth-4(8)-ene and 2-methyl-3-methylene-5-isopropylbicyclo $[3.1.0^{1,5}]$ hexane

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Summary

The title monomers were synthesized via Wittig reaction from thujone and pugelone. The monomers were found to react rapidly with cationic initiators at temperatures from -15° to 22°C. The products of these reactions were found to be low molecular weight oligomers. The reaction temperature, presence of solvent or initiator type and concentration seemed to have some effect on the molecular weights of the products obtained.

Introduction

Recently, we have been investigating the synthesis of polymerizable materials from naturally occurring molecules (1,2). Obtaining such materials from renewable resources continues to be of importance considering the steady decline of petroleum based feed stocks (3,4). We have found that certain materials can be polymerized to moderate to high molecular weight materials via free radical and/or ionic initiation. In a continuation of our study we chose two readily available and relatively inexpensive substrates, thujone and pugelone (5,6).

Figure 1

A) Thujone; B)Pugelone

Both these materials have ketone functionality that is easily converted to unsaturation via a Wittig reaction. This report summarizes our initial findings concerning the two title monomers.

Experimental

General

All solvents and reagents were obtained from Aldrich and were purified by distillation from the appropriate drying agents before use. All nmr spectra were recorded with a Varian Gemini 300 FT NMR on $CDCl_3$ solutions of polymer at ambient temperature. TMS was used as an internal reference. Polymer molecular weights were measured by GPC as previously described.

Monomer Synthesis

The monomers, 3-methylene-p-menth-4(8)-ene (MME) and 2-methyl-3-methylene-5-isopropylbicyclo $[3.1.0^{1,5}]$ hexane (MMIH), were synthesized from pugelone and thujone respectively via a Wittig reaction (7). The MME and MMIH were isolated and purified by distillation. B.p. of MME = 87-88°/40 mm, b.p. of MMIH = 77-79°/35 mm.

Polymer Synthesis

Polymerizations were effected by weighing the monomer (3.0g) into a clean, dry test tube equipped with a magnetic stirring bar and rubber septum. The test tube was placed in a fluid bath at the desired temperature and the contents were allowed to thermally equilibrate with stirring, for 15 min. The initiator was added through the septum via syringe. After the desired length of time the polymerizations were terminated by injecting 5-6 ml of cold CH_3OH into the test tube. Reaction products were purified by reprecipitation from $CHCl_3$ solution into CH_3OH. The products were dried in vacuo at 30°C for 48h.

Results and Discussion

The results obtained are summarized in Table 1. In all cases the materials obtained were low molecular weight oligomers regardless of the initiator or temperature employed.

The level of initiator is high in all cases, which, it could be argued, is the reason that low molecular weight materials are produced. Experiments with lower levels of initiator were performed (1.0 wt %) however, no polymeric/oligomeric materials were formed. In order for such materials to be formed at a reasonable rate and in workable yields initiator levels of at least 3.0-4.0 wt % were necessary. In fact for THUJ4, THUJ5 and PUG4 higher levels of initiator yielded either higher conversions or greater molecular weights. Reaction temperature did have some effect on conversion and molecular weight. In most cases lower temperatures gave higher conversions and higher molecular weights. This was particularly true for the MME monomer.

TABLE 1

Polymerization Results

Polymer	Monomer	Initiator	Initiator Quantity (wt %)	Solvent	PZN Temp. (C°)	PZN Time (hr)	Conv. (wt %)	$\underline{M}_n$	$\underline{M}_w$
THUJ1	MMIH	$BF_3 \cdot OEt_2$	5.0	1,2DCE[a]	-15	3.0	4.3	620	700
THUJ2	MMIH	$BF_3 \cdot OEt_2$	5.0	-	-15	3.0	18.8	460	570
THUJ3	MMIH	$BF_3 \cdot OEt_2$	4.0	-	0	3.0	10.9	450	550
THUJ4	MMIH	$BF_3 \cdot OEt_2$	6.3	-	22	3.0	2.0	770	1500
THUJ5	MMIH	$SnCl_4$	7.0	-	22	4.5	21.3	440	500
PUG1	MME	$BF_3 \cdot OEt_2$	4.0	1,2DCE	-15	3.5	21.0	520	870
PUG2	MME	$BF_3 \cdot OEt_2$	4.0	-	-15	3.5	24.0	560	630
PUG3	MME	$BF_3 \cdot OEt_2$	4.0	-	0	3.5	14.3	550	620
PUG4	MME	$BF_3 \cdot OEt_2$	9.0	-	21	3.0	7.1	405	470
PUG5	MME	$BF_3 \cdot OEt_2$	7.0	-	21	3.0	5.7	540	670

a. 1,2DCE = 1,2-dubloroethane

For MMIH reaction temperature primarily affected conversion, with lower temperatures favoring higher conversion. Experiments at much lower temperatures (-50°C,-78°C) were performed but only trace amounts of oligomeric material were formed at -50°C and no oligomeric materials were formed at -78°C.

The structures of the resulting oligomers were examined by nmr spectroscopy. Figure 2 shows the ^{1}H-NMR spectra of THUJ2 and THUJ4.

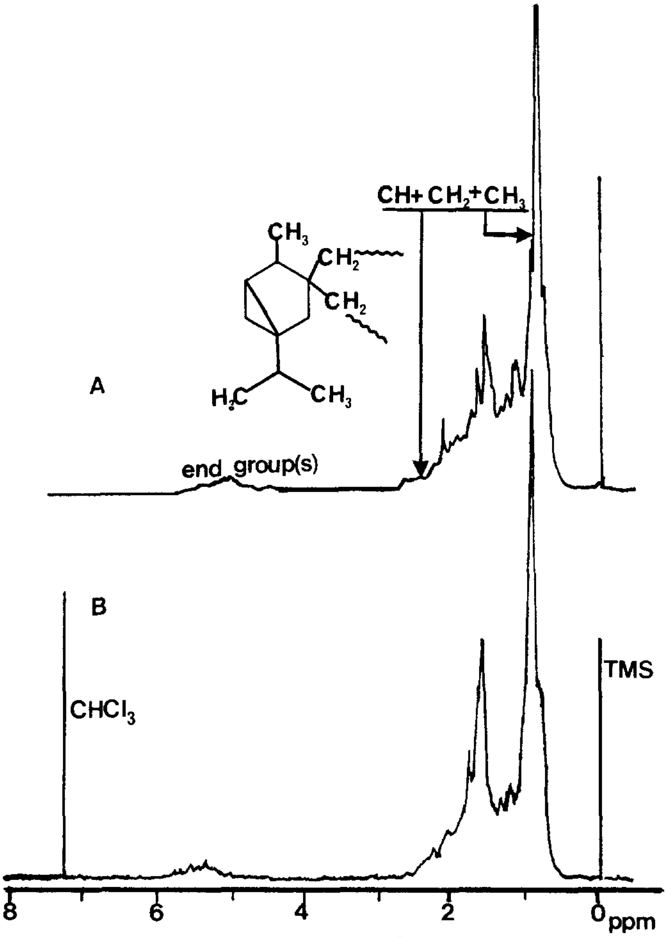

Figure 2

300 MHz ^{1}H-NMR Spectra of: A) THUJ2;
B) THUJ 4

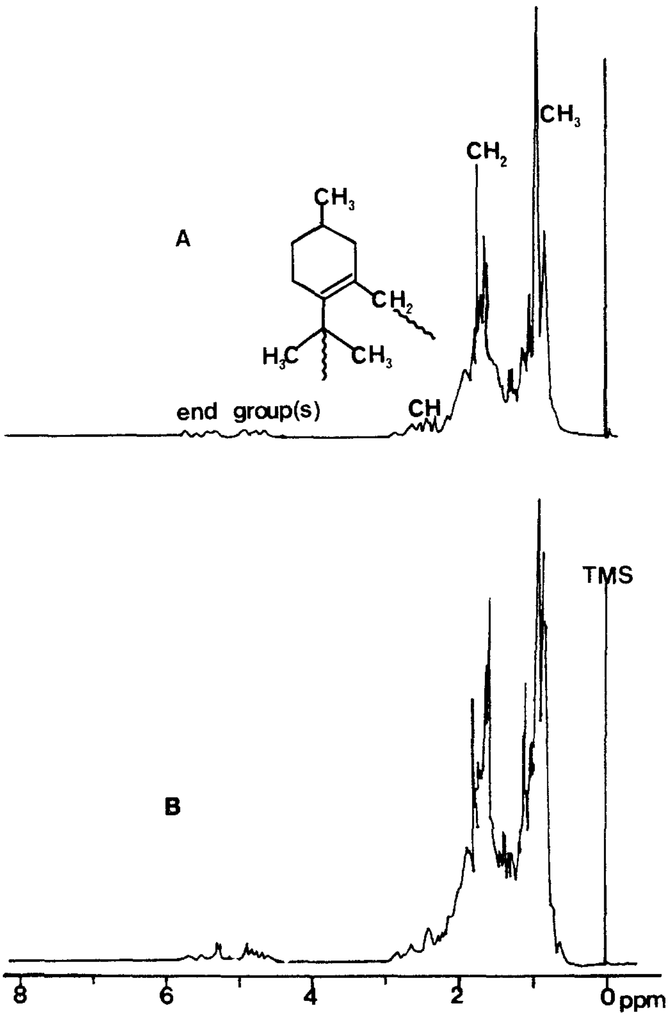

Figure 3

300 MHz ^{1}H-NMR Spectra of: A) PUG1;
B) PUG2

Figure 3 shows the ^{1}H-NMR spectra of PUG1 and PUG2. The ^{1}H-NMR spectra of all the other oligomers are virtually identical to these representative examples. While the spectra are insufficiently detailed to establish oligomer structure with certainty, the spectra are not inconsistent with the structures proposed in the Figures (8).

Conclusion

Monomers capable of being oligomerized with cationic initiators have been synthesized from two natural products, thujone and pugelone. Temperature and initiator type as well as the presence of solvent seemed to have some effect on oligomer yields and molecular weights but in all cases the effect was not dramatic. NMR spectra were consistent with the proposed oligomer structures but more spectroscopy is needed (^{13}C-NMR, IR) to establish product structures with certainty. Work is in progress on reaction conditions and initiator types and concentrations that hopefully will allow higher yields and molecular weights to be attained.

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