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Reactive propylene oligomers

II. Propylene oligomers with primary-OH, tertiary-OH and α,β-di-OH end groups

Sándor Nemes, János Borbély, Jenö Borda, György Deák, and Tibor Kelen*

Institute of Applied Chemistry, L. Kossuth University, P.O. Box 1, H-4010 Debrecen, Hungary

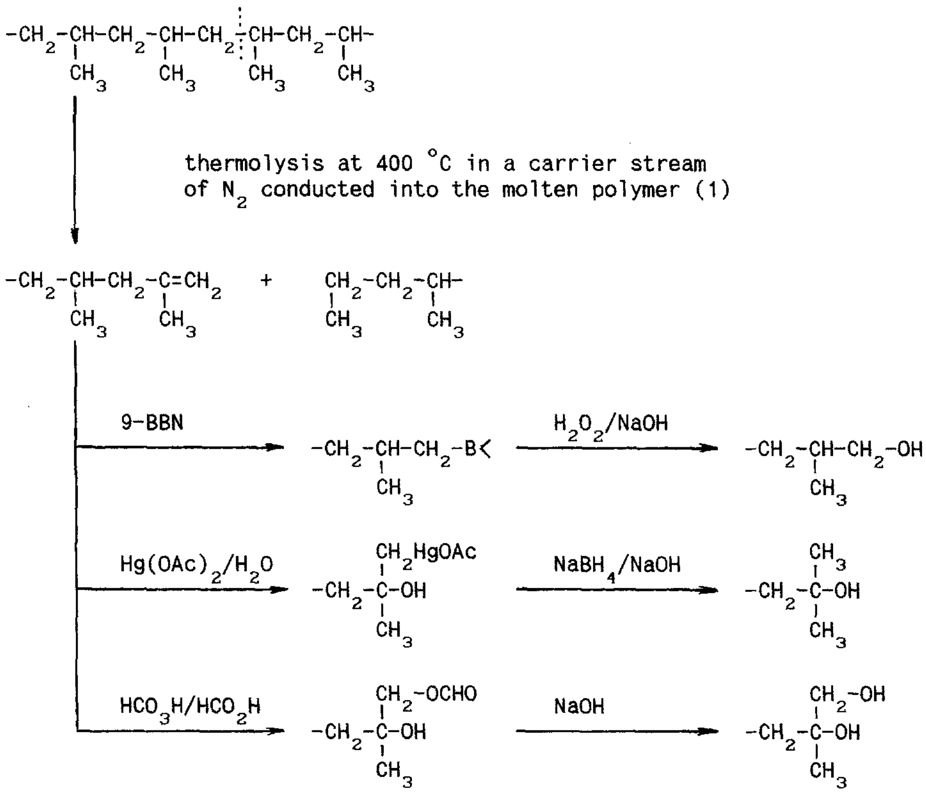
SUMMARY

Propylene oligomers with primary-OH, tertiary-OH and α,β-di-OH end groups have been prepared by converting the isopropenyl-ended oligomers with hydroboration-oxydation, oxymercuration-demercuration and performic acid hydroxylation reactions, respectively.

I. INTRODUCTION

In continuation of our work on the preparation of reactive propylene oligomers (1) we have converted the isopropenyl-ended oligomers to primary-OH, tertiary-OH and α,β-di-OH-ended derivatives by using appropriate chemical reactions.

For the preparation of reactive propylene oligomers the following reaction sequence was employed:



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*Corresponding author

Hydroboration-oxydation of olefins offers a highly convenient procedure, without evident rearrangement, for achieving the anti-Markovnikov hydration of carbon-carbon double bonds (2-4).

The reaction of olefins with mercuric acetate in aqueous tetrahydrofuran, followed by the *in situ* reduction of the oxymercurial intermediate with alkaline sodium borohydride gives the corresponding alcohol. This is a Markovnikov hydration procedure (5-6) that is complement the anti-Markovnikov hydration method, based on hydroboration-oxydation.

Performic acid is an efficient hydroxylating agent for olefins with isolated double bonds. Performic acid is prepared in solution by simply warming 30 % hydrogen peroxide with excess formic acid. The peracid attacks an olefin to form an epoxide, which is then cleaved by formic acid to afford a hydroxymonoformate. In usual practice the material is hydrolyzed with alkali to the diol (7-8).

In the present work synthetic procedures for hydroboration-oxydation, oxymercuration-demercuration and performic acid hydroxylation of isopropenyl-ended propylene oligomers are reported.

II. EXPERIMENTAL

a/ Materials

The preparation of propylene oligomers with isopropenyl end group (number-average chain end functionality, $\bar{F}_n = 1.00 \pm 0.05$) has been described (1). 9-Borabicyclo[3.3.1.]nonane (9-BBN) (0.5 M solution in tetrahydrofuran) (Aldrich), $Hg(CH_3COO)_2$ (Merck), H_2O_2 (30 wt % solution in water), $NaBH_4$ and HCOOH (98+%) (Reanal) were used as received. Tetrahydrofuran (THF) was distilled over CaH_2 and subsequently over $LiAlH_4$ before use. All other solvents and chemicals were "for analysis" grade and were used without further purification.

b/ Characterization methods

The products were characterized by NMR spectroscopy and GPC, as described previously (1). In spite of the fact that distinct shoulders and side-peaks are present on the low molecular weight side of the elution profiles, the $\bar{M}_n$'s (number-average molecular weights) were calculated. Although not highly accurate, this method gives a sufficiently good estimate of the average molecular weight for our purposes.

c/ Preparative procedures

Synthesis of propylene oligomers with primary-OH end group

A 2 wt % solution of the isopropenyl-ended propylene oligomer mixture (10 mmol) in anhydrous THF was placed in a three-neck flask with a pressure equalization dropping funnel, and 30 ml of 9-BBN (1.5 mol excess, 0.5 M solution in THF) was dropwise added at 0°C over 30 minutes under dry N_2 atmosphere. The reaction mixture was kept at room temperature (25 °C) for a period of 6 h. The oligomer solution was then cooled in an ice-water bath and 0.30 ml of water was added to decompose excess 9-BBN, followed by the addition of a required amount of aqueous 6 M NaOH solution (1.5 mol/mol of borane) into the stirred oligomer solution. A 30 wt % aqueous solution of H_2O_2 (4.5 mol/ mol of borane) was added dropwise to the oligomer solution, while the temperature was kept below 25 °C. The solution was allowed to warm up to room temperature and was maintained at 25 °C for 2 h. Cyclohexane was added to the flask and stirring was continued for a few minutes. Then the reaction mixture was extracted with a saturated K_2CO_3 solution. After phase-separation the organic layer was washed several times with distilled water, separated, and dried over anhydrous $MgSO_4$. After filtration the solvent was evaporated and the product dried in vacuum at ambient temperature. Yield: $\geq$90%.

Synthesis of propylene oligomers with tertiary-OH end group

In a 250 ml flask, equipped with a magnetic stirrer and an addition funnel, was placed 6.38 g (20 mmol) of mercuric acetate ($Hg(OAc)_2$). To this was added 20 ml of water (in which the salt dissolved), followed by 20 ml of THF. Then 10 mmol of the propylene oligomer dissolved in 10 ml THF was added. The reaction mixture was stirred for 60 minutes at room temperature to complete the oxymercuration stage. Then 20 ml of 3.0 M sodium hydroxide was added, followed by 20 ml of a solution of 0.50 M sodium borohydride in 3.0 M sodium hydroxide, while the temperature was maintained below 25 °C. The reaction mixture was constantly stirred at this temperature for 10 minutes to complete the reaction. Mercury was allowed to settle and sodium chloride was added to saturate the water layer. The upper layer of THF was separated, dried over $MgSO_4$, then THF was evaporated, and the product dried in vacuum at ambient temperature. Yield: $\geq$ 90 %.

Synthesis of propylene oligomers with α,β-di-OH end group

To a mixture of 7.5 ml (200 mmol) of 98+ % formic acid, 0.10 g of concentrated sulfuric acid and 5.2 ml (50 mmol) of 30 % hydrogen peroxide in a 100 ml flask, equipped with a magnetic stirrer, condenser and an addition funnel was added 10 mmol of the propylene oligomer. The immiscible layers were stirred together and the suspension became homogeneus at 40 °C, where it was held for 4 hours, and an additional 1 hour at 75 °C in a water bath. Formic acid was removed by washing with water and the residue was heated for 2 hrs with an excess of 3 M of sodium hydroxide at 75 °C. On cooling, the solution was neutralized with 3 M of hydrochloric acid. After washing several times with distilled water, the product was separated, dissolved in $CHCl_3$, dried over $MgSO_4$, then $CHCl_3$ evaporated and the product was dried in vacuum at ambient temperature. Yield: $\geq$ 85 %.

III. RESULTS AND DISCUSSION

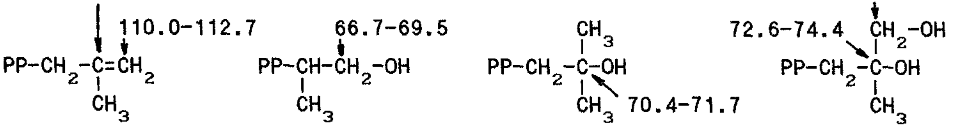
The isopropenyl-ended propylene oligomers can be converted to primary-OH, tertiary-OH and α,β-di-OH-ended oligomers by modifying the standard hydroboration-oxydation (2-4), oxymercuration-demercuration (5-6) and performic acid hydroxylation (7-8) reactions, respectively.

The synthetic procedures were adapted to oligomer mixtures with a number-average molecular weight of $\bar{M}_n$ = 200-500.

After the oxymercuration-demercuration reactions we have found detectable amount of the unreacted olefin; when this reaction was adapted to oligomer mixtures with $\bar{M}_n \geq 400$. This is most likely due to the inaccessibility of the isopropenyl chain end in the water-tetrahydrofuran medium.

In the performic acid hydroxylation reaction we observed that the relatively vigorous oxydative reaction conditions were deleterious to a small extent for the $-CH_2CH(CH_3)-$ backbone.

The quantitative conversion was substantiated by the disappearance of the ^{13}C NMR resonances characteristic of the isopropenyl end group, with the simultaneous appearance of ^{13}C NMR resonances characteristic of primary-OH, tertiary-OH and α,β-di-OH end groups, respectively:



$PP-CH_2-C(CH_3)=CH_2$ $\quad$ $PP-CH(CH_3)-CH_2-OH$ $\quad$ $PP-CH_2-C(CH_3)_2-OH$ $\quad$ $PP-CH_2-C(CH_3)(CH_2-OH)-OH$

The chemical shift assignments were made by comparing the assignments of model compounds, and using known additivity parameters and substituent effects (9-13). Assignments are given in ppm's, on the TMS (tetramethylsilane) scale.

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