

Aroma Chemicals by Direct Hydration/Etherification of Olefins: An Industrial Approach

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α -Terpineol and dimethyl phenyl carbinol are prepared in excellent yields (85 per cent) by contacting an azeotropic mixture of the corresponding olefins, limonene or α -pinene and α -methylstyrene, with a strong cation exchange resin (H⁺ form). The corresponding methyl and ethyl ethers are prepared likewise by replacing water in the reaction mixture with methanol and ethanol respectively. While the methyl ethers are obtained in 75-80 per cent yield, the ethyl ethers are accompanied by the corresponding alcohols in equal proportion, in overall yield of 60-75 per cent.

Introduction

α -Terpineol is extensively used in perfumery and flavour industry as a bulk aroma chemical, and also for preparing its esters which are valuable aroma chemicals^{1,2}. Some of the important commercial methods of its preparation include hydration of limonene (dipentene), hydroxylation of limonene hydrochloride with potassium hydroxide solution, dehydration of terpin hydrate, and hydrolysis of α -terpinyl acetate. The last two intermediates are usually derived from *alpha*-pinene. Dimethyl phenyl carbinol is one of the aromatic carbinols used in floral fragrances¹. The corresponding methyl and ethyl ethers also find application, although to a lesser extent, in perfume formulations. Mono- and di-alkyl phenyl carbinols are routinely prepared in moderate yields by reacting phenylmagnesium bromide with an appropriate aldehyde or ketone. However, the method which is industrially viable consists of two steps, viz. addition of hydrogen chloride to the respective olefins and hydrolysis or etherification of the haloderivative^{1,3}. But, the presence of halogen compounds even in trace amounts imparts harshness to the final product. An attempt has been made now to develop a direct method for these alcohols and ethers employing cationic exchange resins, which are known to give reasonably good yields in similar transformations⁴.

Materials

(+) Limonene, α -pinene, and α -methylstyrene were procured from commercial sources and rectified before

use. Isopropyl alcohol and methanol of LR grade were used as such. Commercial rectified spirit was refluxed with calcium oxide for 4 h and then distilled. The middle cut was used in the experiments.

Resins

Amberlyst 15; Dowex 50W; Tulsion; CX C - 135 (all H⁺ form) were wetted with 1N aq HCl overnight and then washed free of acid with distilled water. After draining off the water, the resin is suspended in the solvent medium used for reaction.

Methods

The two alternative methods followed for hydration were 'Column' and 'Soxhlet' methods.

Column Method - A mixture of 100 mmol of substrate and 150 ml of isopropyl alcohol containing 5-10 per cent of distilled water was passed through a bed of 50 g of resin in a column maintained at 50-60°C and eluted at different flow rates (1-5 ml/min).

Soxhlet Method - A mixture of 100 mmol of substrate and 150 ml of isopropyl alcohol containing 10 per cent of distilled water was refluxed and the vapourised (azeotropic) mixture was allowed to come in contact with cation exchange resin (25 g) in a Soxhlet apparatus for 12 to 24 h duration.

In both the cases, the reaction mixture was stirred with solid sodium bicarbonate (5 g) and filtered off. The

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Table 1 – Hydration / Etherification of olefinic hydrocarbons by Soxhlet method SI

Sl no.	Substrate	Water		Methanol		Ethanol	
		Time, h	Yield,* per cent	Time, h	Yield,* per cent	Time,h	Yield,* per cent
1	Limonene	12	85	8	80	8	75(40+35)
2	α -Pinene	16	70	20	65	20	70(30+40)
3	α -Methyl styrene	12	84	20	76	20	60(30+30)

* Isolated yields of products are based on one mol scale experiments and carried out in triplicate, they showed zero optical rotation. Individual per cent of ethyl ether and the corresponding alcohol are given in the paranthesis

filtrate was concentrated in a rotary evaporator and the residue fractionated at reduced pressure (5-10 Torr). Purity of the fractions was determined by GC.

Gas Chromatographic Analysis of Samples

GC analyses were carried out on a Hewlett-Packard (HP) 5734 gas chromatograph employing a 6' x 1/8" (O D) S S column, that was packed with 10 per cent SE-30 on Chromosorb W (60-80 mesh), under the following conditions: N_2 -30 ml/min; H_2 -FID; Inj.-200°C; Det.-250 °C; oven temperature was kept at 100°C for 2 min initially and then increased to 200°C at the rate of 8°C/min and maintained for 8 min; peak areas as well as their relative per centages were determined using a HP 3380A reporting integrator.

Results and Discussion

Four commercially branded cation resins were tried for hydration of limonene by the column method. At room temperature, none of them gave satisfactory yield of α -terpineol; only Amberlyst 15 (H form) yielded the product to a maximum extent of 40 per cent at 50°C for 12 h. This product contained, besides α -terpineol, 10 per cent terpin hydrate.

On the other hand, Soxhlet method under optimised conditions gave an improved yield of α -terpineol from the respective olefins (Table 1). Limonene was a better substrate than α -pinene as it gave α -terpineol in 85 per cent yield, whereas the latter afforded only 70 per cent, due to the formation of various isomeric alcohols as by-

products. Under similar conditions, dimethyl phenyl carbinol was obtained from *alpha*-methylstyrene in 84 per cent yield.

Limonene, α -pinene and α -methylstyrene alkyl ethers were prepared by replacing isopropyl alcohol-water solvent system by a primary alcohol. With ethanol as solvent, both alcohol and the corresponding ethyl ether were formed in 1:1 ratio. In methanolic medium, methyl ether was the only major product. Results are presented in Table 1.

Thus, α -terpinyl methyl and ethyl ethers, dimethyl phenyl carbinol and its methyl and ethyl ethers have been prepared, for the first time, using cation exchange resins. The Soxhlet method has the advantage of upscalability for industrial production of these aroma chemicals. The resin could be reused by activating it with acid, after every ten cycles. This method is economical, environment friendly and general in application. It can be applied to various olefinic substrates of natural and synthetic origin.

References

- 1 Bedoukian P Z, *Perfumery and Flavouring Synthetics* (Allured Publishing Corporation, Wheaton) 1986, 82; 393.
- 2 Thomas A F & Bessiere Y, *Nat Prod Rep*, 6 (1989) 291
- 3 Gurudutt K N, Jagan Mohan Rao L, Sanjay Rao & Srinivas P, *Indian J Chem*, 32B (1993) 468.
- 4 Nigam S C, Bannore S N, Subba Rao H N & Sukh Dev, *Proc Eleventh Int Congr Essen Oils, Frag Flav, New Delhi*, 5 (1989) 113.