



PER FORMIC ACID: EFFECTIVE REAGENT FOR PREPARATION OF CARENE DIOL FROM Δ^3 -CARENE

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Abstract

In the natural product, terpenoids are important because of its valuable importance in various sectors. The terpenoids occur only in the volatile oils and they are normally colourless liquids or solids with pleasant smell and insoluble in water. They are soluble in organic solvents, alcohol and fixed oils. These terpenoids are very sensitive to prepare its various different derivatives. Terpenes are one of that terpenoids which can give oxygenated derivatives like alcohols, ketones, aldehydes etc. Monoterpene is one of the terpenoids having molecular formula $C_{10}H_{16}$ used to prepare various derivatives. (+)- β -Carene is one of the monoterpene which on oxidation by using oxidising agent performic acid which gives epoxide as intermediate product, (epoxidation of carene). Which on hydrolysis, it gives carene diol as final product.

Keyword: terpenoids, volatile oils, Δ^3 -Carene, α - pinene, carene diol.

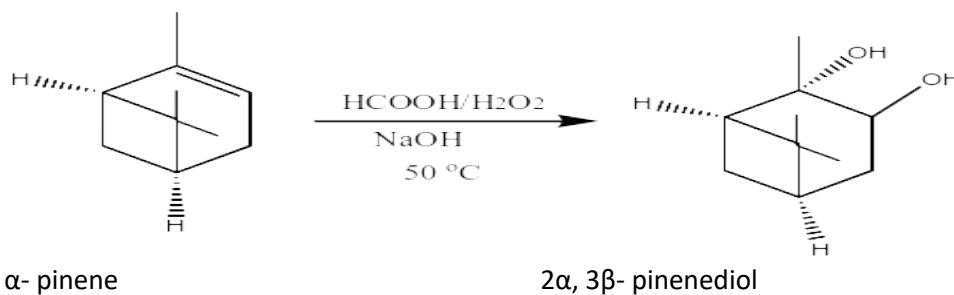
1. Introduction:

In the natural product, terpenoids are valuable natural product because of its importance in various sectors. The terpenoids occur only in the volatile oils they are normally colourless liquids [1] or solids with pleasant smell and are insoluble in water. They are soluble in, organic solvents, alcohols and fixed oils. Terpenoids normally contains one or more double bonds and forms additive compounds with halogens[2-3], nitrosyl chloride[4], and nitrosyl bromide. They are readily volatilise in steam and most of them are optically active [5]. Then get oxidized by oxidizing agent. Terpene [No. of isoprene units two, M.F. $C_{10}H_{16}$] by virtue of their pleasant flavour the compounds of terpene [6] used in several industries

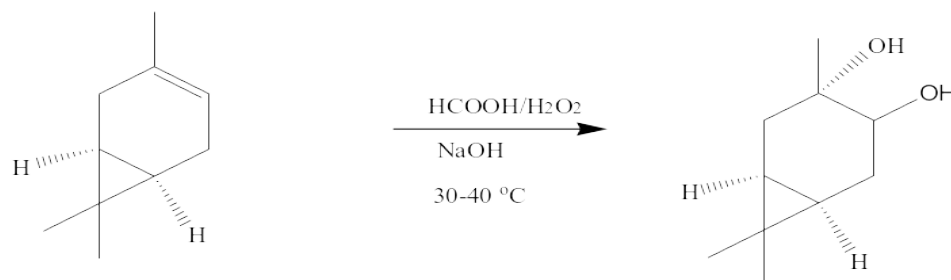


insecticides, pesticides and deodorant [9] Antibacterial and Antifungal Properties [10]. Therapeutically they owe their action due to several compounds and find applications as antiseptic [11], stimulant, and diuretic, analgesic [12] and for several other purposes. Terpenoids are classified on the basis of no. of isoprene units (C_5H_8). In that monoterpenes or terpene contains two units of isoprene ($C_{10}H_{16}$). Terpene or carene is present in (+) and (-) form. (-) form is isolated from root oil of kaempferia galangal [13-14] and from cedrus deodar oil and (+) form is wide spread plant product found specially in abies, citrus and janipenus oil with pleasant odor B.P.₂₀₀=123-124°C and $\{\alpha\}_D^{30}=5.72$, The (+) form of Δ^3 -Carene is obtained from geranyl diphosphate [15]. Already recorded reaction of peracid such as Performic acid on terpene such as α -pinene epoxidation [16] takes place and epoxide of α -pinene is obtained. Which on hydrolysis, This epoxide is converted into 2 α , 3 β -pinenediol [17]. The present work was done as same procedure given above on Δ^3 -Carene which gives final product is 3 α , 4 β -carenediol.

Scheme I



Scheme II





2. General Experimental Procedure:

In the 150 ml three necked round bottom flask, equipped with a mechanical stirrer and dropping funnel was placed formic acid (90% 26 ml) and freshly distilled Δ^3 -Carene (10gm) was added with stirring through a dropping funnel H_2O_2 (30% 15ml) was then added drop wise maintaining the temperature of the reaction mixture between 30-40 °C (2hrs) stirring was continued at that temperature for 6 hrs. And reaction was allowed to stand overnight. The solution of sodium hydroxide (8 gm in 20 ml H_2O) was added slowly to the mixture under stemming keeping the temperature around 25 °C (1hrs) the reaction mixture was transpired to 150 ml separating funnel and the layers were allowed to separate the upper oily layer approximately 13 gm was transferred back to the reaction flask and further amount of solution of sodium hydroxide (2 gm in 40 ml H_2O) was added slowly under vigorous stemming maintaining the temperature at 25 °C to 30 °C. After stemming of one half hours and cooling to 5 °C to 10 °C the solid diol separate out. It was filtered the residue washed with cold water and dried yield was 7 gm (64%) melting point 68 °C. The crude diol was crystallized from pet ether + 5% ethyl acetate to give about 4 gm of diol (45%). the melting point was 87 °C to 88 °C

2.1 Spectral data of obtained compound:

3,4-Hydroxy-3,7,7-Trimethyl-1- Bicyclo-(4,1,0)-Heptane.

IR(KBr): 3448, 2900, 1460, 1375, 1058, 945 & 815 cm^{-1}

3. Result and Discussion:

Already recorded reaction of peracid such as Performic acid with terpene such as α - pinene epoxidation of reactant was takes place and epoxide of α - pinene is obtained as intermediate. Which on hydrolysis, This epoxide is converted into 2 α , 3 β - pinenediol of yield 40% . When such reaction is carried out on Δ^3 -Carene by using same reagent. i.e. performic acid which is obtained from formic acid (90%, 26 ml) and with constant stirring through a dropping funnel H_2O_2 (30% 15 ml) was then added drop wise maintaining the temperature of the reaction mixture between 30-40 °C (2 hrs) stirring was continued at that temperature for 6 hrs. And reaction was allowed to stand overnight. Then solution of sodium hydroxide (8 gm in 20 ml H_2O) was added slowly to the mixture. This mixture then cooling to 5 °C to 10 °C



the solid diol separate out dried yield was 7 gm (64%) melting point 68°C. crude diol was crystallized from petroleum ether + 5% ethyl acetate to give about 4 gm of diol (45%). the melting point was 87 °C to 88 °C

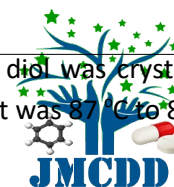


Table- 1

Sr. No.	Terpene	Yield (%)
1	α - pinene	40
2	Δ^3 -Carene	45

In the present study preparation of carene diol from Δ^3 -Carene by using simple & same procedure, Per formic acid in presence of base as same reagent and maintaining temperature between 30 to 50 °C. Which is used for preparation of diol of α - pinene. The yield of product is also nearly equal in rang i.e. between 40 to 45 %.

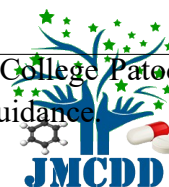
4. Conclusion:

I have been able to introduce an efficient procedure for preparation of terpene diol by using easily preferable, more efficient catalyst which gives good yield, easy to work up, purification of compounds by simple method are the key advantages of this method.

5. Acknowledgement:



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