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NOTES

Application of Perkin's Reaction to Terpene Aldehyde β-Cyclocitral

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Perkin's reaction has been successfully applied to β-cyclocitral. It appears Perkin's reaction could be applied to the above terpene aldehyde because of high electron density round π bonds in conjugation with aldehyde group making it more electronegative.

Work on various organic reactions is going on in this laboratory for a long time[1,2]. Application of Perkin's reaction to β-cyclocitral has now been reported herewith. Perkin synthesised coumarin by the action of acetic anhydride on salicylaldehyde in presence of potassium acetate[3]. Cinnamic acid was then prepared from benzaldehyde by the action of acetic anhydride in presence of fused potassium acetate[3]. The method was then applied to other aromatic aldehydes and to indolylaldehyde and furfural. It was then known as Perkin's reaction. Various other bases e.g. triethylamine potassium carbonate etc. were also used. In all the above compounds one thing is in common i.e. aldehyde group is in conjugation with π bonds. The reaction has now been applied to β-cyclocitral. Perkin's reaction gives very low yields of reaction products when applied to straight chain saturated aldehydes (and by analogy to saturated cyclic aldehydes) acetals being the major products. Straight chain aldehydes with π bonds in conjugation prefer polymerisation or cyclisation. It appears that Perkin's reaction could be applied to β-cyclocitral because it has also π-bonds in conjugation with aldehyde group, increasing electronegativity of aldehyde group favouring Perkin's reaction that is carried out in presence of bases. Methyl group in β-cyclocitral further increase electronegativity of aldehyde group.

Citral (Wilson & Beckmann), sodium hydroxide, sulphuric acid, sodium sulphate, acetic anhydride, potassium acetate, carbon tetrachloride etc. B.D.H. quality were used.

β-Cyclocitral was prepared from citral by the method reported in literature[4]. β-Cyclocitral (2 gm, pure acetic anhydride (10 ml) and fused potassium acetate (4 gm) were added to the round bottom flask and was refluxed for 18 hrs. Distilled water (200 ml) was added and acetic acid was removed by steam distillation. The residue was treated with sodium hydroxide (0.5 N) till complete extraction and filtered. Filtrate was acidified with hydrochloric acid (1 : 4 dilution) to Precipitate perkin's acid. The precipitate was filtered. The residue was washed 2–3 times with distilled water and dried. Yield 1 gm m.pt. 125°C equivalent wt. by potentiometric titration is found to be 197. The above Perkin's acid (1 gm pure ethyl alcohol (25 ml), concentrated sulphuric acid (0·5 ml) was refluxed for 8–9 hrs. Alcohol was evaporated on water bath and the concentrate was extracted with ether. Ethereal layer was washed with saturated and ice-cold sodium bicarbonate solution and water. The ethereal layer separated and dried over anhydrous sodium sulphate. Ether was evaporated on water bath and the residue was extracted with hot carbon tetrachloride. All the acid was separated. It was cooled and filtered. Clear carbon terachloride solution was concentrated to obtain the ester.

PMR ($CdCl_3$;) : 1.1 (S, 6H of 2 CH_3, C_{10} and C_{11}), 1.2 (t, 3H of CH_3 of C_2'), 1.5 (s, 3H of CH_3 of C_{12}), 2.5 to 2.8 (m, 6H of CH_2 of C_1, C_7, C_8), 6.25 (t, CH_2 of C_6). 7.75 (d, 2H of 2 CH at C_2 and C_3).

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