Rapid Communication

Base-catalysed rearrangement of terpinolene oxide

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Terpinolene oxide, a tetrasubstituted spiro epoxide has been found to get rearranged over KOtBu in DMSO to give p-cymenol in high yields.

Due to the presence of strained ring, epoxides undergo a variety of reactions with acids, bases, nucleophiles, reducing agents etc. 1-3. Terpinolene oxide, a tetrasubstituted spiro epoxide is found to be resistant towards bases, there is only one report in the literature in which it is mentioned that with Al(OiPr)3 it gives 4-hydroxylimonene 4. Reduction using sodium, 5 LiAlH4 -AlCl3 and acid-catalysed 6 reactions of terpinolene oxide have been reported by us earlier for synthesising some useful perfumery and flavour chemicals, such as 4-terpinenol and karahanaenone.

We have now found in our laboratory that, rearrangement of terpinolene oxide takes place readily with KOtBu in DMSO under reflux to give a single compound, p-cymenol, as shown in Scheme I within 2 hr.

The reaction of terpinolene oxide was carried out with a set of bases such as, NaOEt, NaOtBu and KOtBu. The solvents employed were hexane, toluene, THF, pyridine and DMSO. The base catalysts were used at 0.5-1 mmole percent level. The reactions were first carried out at 0°C (1-6 hr) then at room temperature (24°C, 1-24 hr) and if incomplete, were examined at reflux temperature of the solvent (1-24 hr). Among the above conditions, the reaction goes to completion only with KOtBu in DMSO within 2 hr, and in all the other cases <5% reaction occurred or there was no reaction even after refluxing for 24 hr.

From the above studies it is clear that, initially the base participates in a reaction to give dienol, which may get oxidized in the presence of DMSO to give p-cymenol. A probable mechanism of the reaction is given in Scheme II.
Experimental Section

Commercial terpinolene oxide (from viking Inc, USA) was purified by column chromatography using silica gel (60-120 mesh) before use.

General procedure. A mixture of terpinolene oxide (1.52g, 10 mmole), potassium t-butoxide (0.555g, 5 mmole) in DMSO (10 mL) was refluxed at 60-65°C. The progress of the reaction was monitored by TLC (5% EtOAc : hexane). At the end of the reaction (2 hr), ether (10mL) was added and washed successively with 10% HCl (3 × 10mL), water (3 × 10mL), saturated NaHCO₃ (3 × 10mL) and extracted into ether (2 × 10mL). The combined extract was dried over anhydrous Na₂SO₄ and evaporated to remove the solvent. The product was then chromatographed over silica using 5% EtOAc: hexane to yield pure p-cymenol (1.49g, 98%). The structure of p-cymenol was confirmed by the PMR spectral analysis and by comparison on TLC with standard p-cymenol obtained by the SeO₂ oxidation of p-cymene.

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References