Metal-free epoxidation of internal and terminal alkenes with tert-butyl hydroperoxide/isobutyraldehyde/oxygen system

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Abstract: The epoxidation of several alkenes was studied using oxygen as green oxidant, isobutyraldehyde as co-reagent and tert-butyl hydroperoxide (TBHP) as radical initiator at mild conditions (333 K, atmospheric pressure with an oxygen balloon). TBHP could accelerate the production of carbonyl radical and its peroxidation, without using a metal catalyst. The factors influencing the conversion of the substrates and selectivity of the epoxides have been well investigated. Under optimized reaction conditions, the epoxidation of linear terminal, cyclic and aromatic alkenes was evaluated. Most performed reactions were high selectivity for production of the corresponding epoxides.

Keywords: Alkene epoxidation, Metal free, Molecular oxygen.

1. Introduction (11-point boldface)

Epoxyethylbenzene is an important raw material for the manufacturing of phenethyl alcohol, tetramisole, levamisole and phenylacetaldehyde, which have found extensive applications in the petrochemical industry, fine chemicals, medicines, perfumery and polymers. Traditionally, epoxyethylbenzene was obtained by the epoxidation of styrene with oxyhalides (or alternatively from chlorohydrins and bromohydrins via dehalogenation/dehydration under basic conditions); however, these procedures produce a vast amount of environmentally undesirable waste. It is highly preferential to develop an environmentally benign procedure by using green oxidants such as molecular oxygen. Styrene epoxidation bear low or non-selectivity (0-47%) due to the uncontrolled over-oxidation of the initially formed epoxide to phenylacetaldehyde and benzaldehyde [1-3]. We envision that the use of oxygen without any metal catalyst at mild conditions with short reaction time is one of the most attractive protocols for the epoxidation reaction.

2. Experimental (or Theoretical)

The epoxidation reaction was carried out under aerobic conditions. Typically, a 25 mL round-bottom flask equipped with a condenser was used. An amount of 0.5 mmol TBHP, 4 mmol isobutyl aldehyde and 3 mL acetonitrile were added in the flask and the mixture was stirred for 30 min at 308 K using an oxygen balloon. Dodecane was used as internal standard. After the experiment temperature reached 333 K, 0.11 mL (1 mmol) styrene was introduced into the reaction system and stirred for 5 h. Afterwards, the resulting solution was analyzed through GC-MS for qualitative and quantitative analyses.

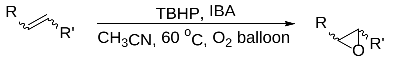
3. Results and discussion

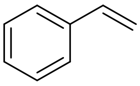
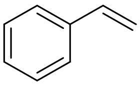
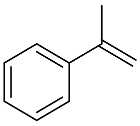
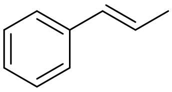
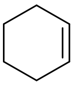
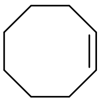
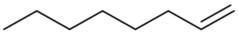
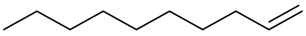
To explore the scope of this metal-free catalytic system with TBHP/aldehyde/oxygen for the epoxidation of alkenes, the epoxidation of styrene was carried out in an open vessel, and it still showed good results (Table 1, entries 2). The conversion of styrene was lower in comparison to when the O_2 balloon was used, which is due to the low concentration of molecular oxygen in the air. However, the selectivity towards the epoxide remained completely the same (63%). The oxidation reaction in the air makes the developed method much more convenient and economical. Encouraged by the obtained results, the generality of this catalytic system was further investigated in the epoxidation of other alkenes such as trans-β-methylstyrene, α-methylstyrene, cyclohexene, cyclooctene, 1-octene and 1-decene under the optimized epoxidation conditions. As seen in Table 1, endocyclic alkenes such as cyclooctene and cyclohexene participated well in this epoxidation reaction. Full conversion of cyclooctene was achieved in 10 h without any byproduct (Table

1, entry 6). Cyclohexene shows 89% conversion to form cyclohexene oxide as the major product with 92% selectivity. In addition, 2-cyclohexen-1-ol was generated, owing to allylic C-H oxidation.

Furthermore, terminal linear alkenes are generally considered as inert olefins towards epoxidation. Interestingly, they were also oxidized in decent yields and with excellent selectivities (Table 1, entries 7 and 8). In case of terminal olefin α-methylstyrene the selectivity was not encouraging. Both steric and electronic factors affect the conversion and time of the epoxidation. For instance, the electron-rich substrates such as α-methylstyrene, trans-β-methylstyrene and styrene are more reactive than cyclohexene and cyclooctene for the epoxidation by the system. Moreover, 1-octene and 1-decene as linear alkenes with inherent steric properties displays lower activity in this alkene series.

Table 1. Variation of substrates in the epoxidation reaction utilizing the TBHP/isobutyl aldehyde/oxygen oxidation system [a].



Entry	Substrate	t (h)	Conversionb (%)	Epoxide Selectivityb (%)	Epoxide Yieldb (%)
1		5	100	63	63
2 [c]		5	51	63	32
3		5	88	37	33
4		7	92	80	74
5		8	89	92	82
6		10	100	100	100
7		8	73	100	73
8		8	64	100	64

[a] Reaction conditions: Substrate 1 mmol, TBHP 0.5 mmol, IBA 4 mmol, Temperature 333 K, O2 balloon.

[b] Determined by GC-MS.

[c] In an open vessel without balloon.

4. Conclusions

This epoxidation process has three advantages compared with other reported epoxidation processes. The first one is that the reaction can be carried out at lower temperature, within a short reaction time and with high selectivity. The second is that air can be used as efficient oxidant compared to costly oxidants, such as H_2O_2 and TBHP, which were reported in the literatures for the epoxidation processes. And the third advantage is that this oxidative system could work very well in the absence of metal catalyst, which could reduce economy cost and metallic pollution.

References

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