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Reductive Formation and Transformation of Epoxides in Neutral Aqueous Medium

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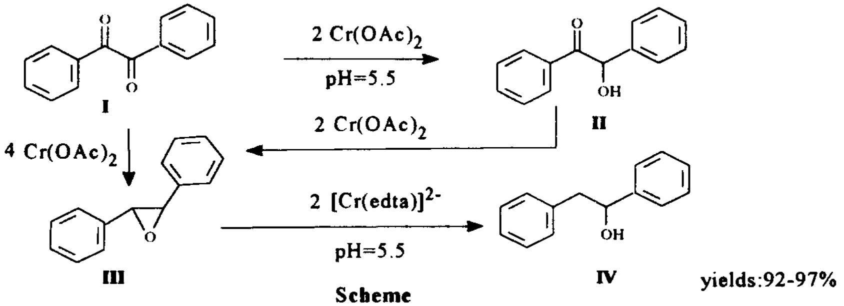
Abstract: Stoichiometrically controlled reductive epoxidation could be elaborated to transform α,β-diketones or α-hydroxy ketones to epoxides in a very good yields in neutral aqueous medium using chromium(II)acetate. Modification of the coordination sphere of Cr(II) ion with the added ligand makes the reductive ring-opening possible. © 1997 Elsevier Science Ltd.

Epoxides are one of the most important intermediates in the practical organic synthesis and can be prepared by numerous classical reactions.[1] Methods for synthesis based on epoxidation of olefins, cyclization of halohydrins, different coupling reactions of aldehydes and ketones are the daily practice in modern organic chemistry.[2a,3] "Epoxidation" seems to be the general approach to this synthetic problem and "reductive" solutions are very limited. Bimolecular coupling of aldehydes and ketones to epoxides with hexamethylphosphorus triamide[4] represents a reductive way but the combination with coupling delimits the application. Transformations of epoxides to alkenes and alcohols are performed by means of the traditional ring-opening methods as well as the hydrolysis to diols.[2b,5] Among the countless ring opening reactions low-valent metal ions such as Cr(II), V(II), Sm(II) etc. could be used for the reduction of epoxides in mild reaction medium. Especially, the $CrCl_2$[6], the $Cr(OAc)_2$[7-9] salts and the $[Cr(en)_2]^{2+}$ complex[10] were used to reach the required reactivity and selectivity.

In the course of our work we found that a reductive pathway for the synthesis of epoxides could be developed into an applicable synthetic method. As a model system our choice fell on *benzil* **I** (see Scheme) and in the reaction between **I** and 4 moles of $Cr(OAc)_2$ exclusively *trans-stilbene-oxide* **III** was formed stoichiometrically.[11a] Simultaneously, we also distinguished that the intermediate of this reaction was the *benzoin* **II** which was formed also quantitatively from **I** with 2 moles of $Cr(OAc)_2$ under standard conditions. Taking **II** as a starting material and reacting with 2 moles of $Cr(OAc)_2$ formed **III** in very good yield, too. Although, **III** is able to pick up additional electrons we didn't find any reaction between epoxide and $Cr(OAc)_2$ in spite of the fact that the reaction time was increased and $Cr(OAc)_2$ excess was applied.

Varying the reactivity of Cr(II) ion by generating $[Cr(edta)]^{2-}$ complex in aqueous, neutral medium[11b] the result was a reaction between **I** and 6 moles of complex forming 1,2-diphenyl-ethan-1-ol **IV** directly.

As the Scheme shows, applying the adequate stoichiometric amounts of reagents, different products - **II** from **I**, **III** from **II** and **IV** from **III** - can be prepared separately in good yield.



Scheme

According to our studies there are possibilities to use this method to form and transform epoxides from ketones independently upon the substituents with the appropriate selection of ligands.

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11. Typical experimental procedures: (a) $[Cr(OAc)_2 H_2O]_2$ (0.75g, 2 mmoles) was added in one portion to $45cm^3$ $H_2O/DMF=1:1$ after deoxygenation with argon. The pH was adjusted with CH_3COONa/CH_3COOH buffer to 5.5 (0.43g, 5 mmoles NaOAc and 2.31 mmoles HCl). Benzil (0.42g, 2 mmoles) dissolved in DMF was added to this magnetically stirred solution and the colour of the mixture began to turn to reddish-brown. The reaction vessel was than stoppered under argon (18 hours). After it the solution was extracted with ether (3x), the organic phase was washed with water (3x), than dried with Na_2SO_4. The solvent was evaporated under diminished pressure. The structure and the purity of the products were analyzed by ^1H-NMR spectroscopy. (b) Ethylenediaminetetra-acetate (edta) $Na_2edta\ 2H_2O$ (4.09g, 11 mmoles) with 14.1 mmoles KOH was dissolved in 35 cm^3 $H_2O/DMF=1:1$ and **III** (0.2g, 1 mmoles) was added as before (further procedures see above).

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