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LETTERS

$Mo(CO)_6$-promoted facile deoxygenation of α,β-epoxy ketones and α,β-epoxy esters

Asit Patra, Mausumi Bandyopadhyay and Dipakranjan Mal*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

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Abstract—Deoxygenation of α,β-epoxy ketones and α,β-epoxy esters is accomplished in high yields under mild and neutral conditions by the use of $Mo(CO)_6$. © 2003 Published by Elsevier Science Ltd.

Deoxygenation of epoxides is an important synthetic transformation in organic chemistry. It can be achieved by a number of methods, which have been comprehensively reviewed by Larock.[1] The scope of the reagents are limited in nature as few functional groups can be tolerated and the reaction conditions are harsh. In certain cases, the reagents required are expensive. Methods known for the deoxygenation of α,β-epoxyketones and α,β-epoxy esters are scanty in the literature. These include $Cr(OAc)_2$,[2] sodium cyclopentadienyldicarbonylferrate,[3] dimethyl diazomalonate,[4] and Cp_2TiCl_2–Zn.[5] Recently, thiourea dioxide[6] has been introduced as a new reagent for deoxygenation of α,β-epoxy ketones which necessitates alkaline THF as reaction medium. Alternatively, $Fe(CO)_5$,[7] among metal carbonyls, has been reported to be useful under neutral conditions. However, its success has been restricted to the use of two uncommon solvents namely, tetramethylurea and *N*,*N*-dimethylacetamide. The reactions fail in refluxing tetrahydrofuran as the medium. In an earlier occasion, the reactivity of $Mo(CO)_6$ towards various substituted epoxides in 1,2-dimethoxyethane was thoroughly examined by Alper et al.[8] The general trend with regard to product formation was rearrangement to the corresponding aldehydes. Tungsten hexacarbonyl was found to be an ineffective catalyst for such reactions. Most recently, samarium iodide has been reported to effect *E*-selective deoxygenation of α,β-epoxy esters in high yields.[9]

In connection with our on-going research program on the total synthesis[10] of fused ring isocoumarin natural products through thermal rearrangement of epoxides, we had the opportunity to investigate the reactivity of indenone epoxides towards metal carbonyls. This study has yielded the finding that deoxygenation of α,β-epoxy ketones and α,β-epoxy esters can be smoothly performed with the use of an equimolar amount of $Mo(CO)_6$ in benzene or toluene under mild conditions.

The epoxides studied were prepared by epoxidation of the corresponding unsaturated ketones and esters using 30% H_2O_2 in the presence of sodium ethoxide,[11] and submitted for deoxygenation under the conditions described below. The results are presented in Table 1. A variety of functional groups tolerate the reaction. These are ketones, esters, sulfones and olefins. The deoxygenation of epoxy esters is stereoselective. The first example examined was epoxy furoindanone (entry 1) which underwent smooth deoxygenation to yield the corresponding indenone in an excellent yield. The epoxide derived from indenone, when submitted to similar conditions, furnished a small amount of indenone along with a large amount of polymeric material which might have arisen due to the instability of indenone. With other epoxy ketones (entries 2–5), the reactions gave the desired products in high yields. This method is equally applicable to epoxy esters (entries 6–7). The most striking feature of the reaction, in addition to its mildness, is its *E* stereoselectivity. It may be noted that there are very few deoxygenation methods which are stereoselective.[9,12] When a 6:4 mixture of *trans*- and *cis*-ethyl α,β-epoxy-β-phenylpropionate was subjected to the reaction with $Mo(CO)_6$, *trans* ethyl cinnamate was obtained as the sole product. Similar was the result with a *trans* sulfone substituted epoxy ester (entry 6) and the acetate (entry 8). The *cis* isomers of the product were not traceable by ^1H NMR.

Keywords: molybdenum hexacarbonyl; deoxygenation; epoxides; enones.

* Corresponding author.

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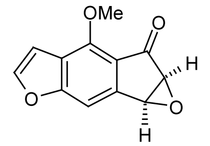
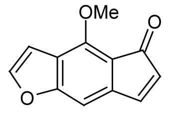
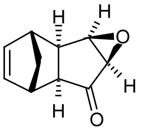
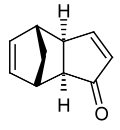
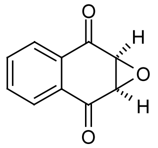
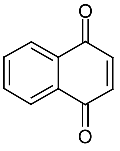
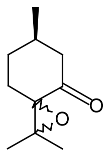
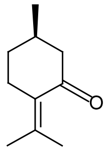
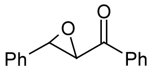
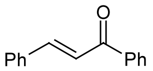
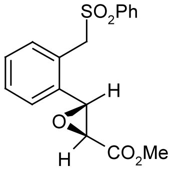
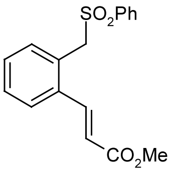
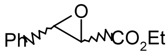
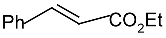
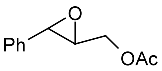
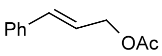
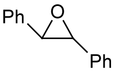
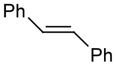
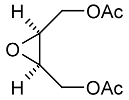
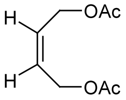
Table 1. Deoxygenation of epoxides with $Mo(CO)_6$

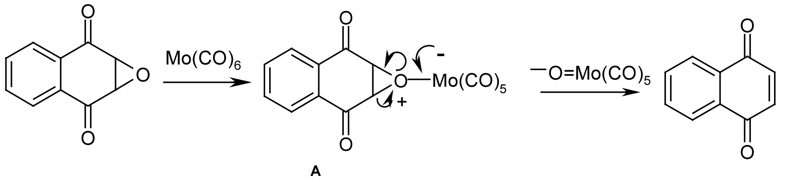
Entry	Substrate	Product[a]	time (hr)	Yield (%)
1.			4	90
2.			4	96
3.			7.5	95
4.			1	93
5.			6	70
6.			6	96
7.			3	90
8.			2.5	88
9.			3	84[b]
10.			2	0 [c]

a. Entries 1, 2, 3, 7 were carried out in refluxing toluene and 4, 5, 6, 8, 9, 10 in refluxing benzene.

b. $(Ph)_2CHCHO$ was obtained in 14% yield. When the reaction was performed in 1,2-dimethoxyethane, *trans* PhCH=CHPh and $(Ph)_2CHCHO$ were formed in 28% and 66%, respectively.

c. A complex mixture was obtained.

It appears that the deoxygenation becomes successful if the epoxides contain a π-conjugative group like carbonyl, ester and aryl. For the *cis* epoxy-diacetate (entry 10), the reaction with $Mo(CO)_6$ afforded an inseparable mixture of products, which did not contain any of the expected deoxygenation product. For *trans* stilbene oxide (entry 9), the major product was *trans* stilbene (84%), accompanied by diphenylacetaldehyde (14%) as the minor component. When the same reaction was performed in 1,2-dimethoxyethane,[8] the product distri-



(1)

bution was entirely the opposite, diphenylacetaldehyde was formed in 66% yield and *trans* stilbene in 28% yield.

Of many plausible mechanisms by which the deoxygenation can take place, the one with a simple formalism is presented below. The reaction is probably initiated by loss of CO, followed by complexation of the epoxide oxygen to the Mo center of $Mo(CO)_6$ forming the complex **A** (Eq. (1)), which subsequently collapses to form the olefin. The greenish-black residue of the reaction, as judged by its IR spectrum, appears to contain an arene complex of a molybdenum oxo species.

In conclusion, we have demonstrated that molybdenum hexacarbonyl is an efficient reagent for deoxygenation of a variety of epoxides under neutral and mild conditions. Further studies on solvent effects and scope of the reaction are in progress.

Typical experimental procedure: To a well-stirred solution of an epoxy enone or epoxy ester (2.0 mmol) in benzene or toluene (5.0 mL) is added molybdenum hexacarbonyl (2.0 mmol). The mixture is heated at reflux till no starting material is detected by TLC. The resulting **dark colored** mixture is concentrated and the residue is chromatographed on silica gel using mixtures of ethyl acetate-petroleum ether as eluents. The products are characterized by comparison of IR and ^{1}H NMR data with those of authentic materials.

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