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Epoxidation of olefins with peracid at low temperature with copper catalysis

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Abstract

Treatment of a wide range of olefins with *m*-chloroperbenzoic acid (MCPBA) at low temperature in the presence of copper(I) and (II) catalysts in methylene chloride provides epoxides in good to excellent yields. © 2000 Elsevier Science Ltd. All rights reserved.

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While various transition metals have been employed with great success,[1] epoxidations with copper are rare. Iodosylbenzene with copper(II) nitrate and triflate with stilbenes,[2] silylalkyl peroxybenzoate with Cu(II) trifluoroacetate[3] and binuclear trisamino complexes have been reported.[4] Substrates are limited to electron rich olefins where low yields and isomerization of *cis*-alkenes to *trans* products are typically found. As copper has recently gained in prominence as a catalyst for numerous transformations,[5] it became useful to investigate various oxidants for low temperature epoxidation with a wide range of substrates as a prelude to ligand identification.

Initial attempts were disappointing. Use of $Cu(CH_3CN)_4PF_6$[6] or $Cu(SbF_6)_2$ as catalysts with stoichiometric oxone or iodosylbenzene at −40°C gave no product even after 2 d (Fig. 1). Yet, remarkably when MCPBA (2 equiv., 60–80% Aldrich) was used the reaction with 5 mol% copper(I) was complete after 10 h at −78°C giving the epoxide from allylbenzene in 92% isolated yield. Without added copper, MCBPA gave no product after 2 d at −78°C.[7] The catalyst–oxidant system was then employed with a range of electron-rich and deficient olefins to explore the scope of the process (Table 1).[8]

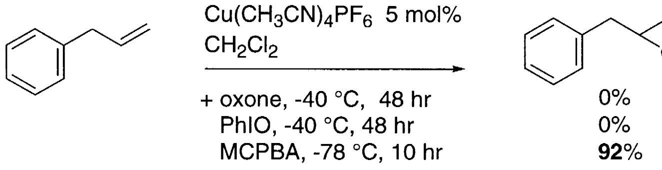

Fig. 1. Epoxidation at low temperature with copper catalysis

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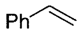
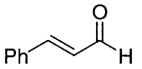
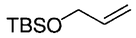
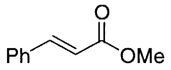
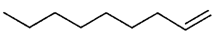
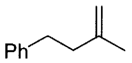
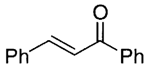
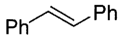
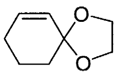
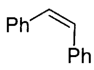
Table 1

Epoxidation of olefins with MCPBA (2 equiv.) and $Cu(CH_3CN)_4PF_6$ (5 mol%) in CH_2Cl_2

	temp. °C	time, h	yield(%)		temp. °C	time, h	yield(%)
	-20	10	60		-78	8	67
	-20	48	60[a]		-20	96	50[c]
	-78	8	77		-40	36	25
	-20	48	70		-20	48	63
	-40	10	70		-40	10	51
	-78	5	90[b]				

All yields are for isolated, chromatographed products identified with ^1H and ^{13}C NMR, IR, and MS characterization. [a]1.5 equiv. of $NaHCO_3$ added. [b]1:2 *cis/trans* ratio obtained. [c]10 mol% catalyst used.

The temperature needed to be adjusted to −20°C in some cases to ensure a reasonable rate as with styrene, methyl cinnamate and chalcone. Bicarbonate was added in the case of the TBS silylether to prevent protecting group removal by the benzoic acid by-product. Cinnamaldehyde was epoxidized at −78°C for 8 h in 67% yield. Other electron deficient substrates reacted with lower yields requiring 10 mol% catalyst in the case of cinnamate. Use of $Cu(SbF_6)_2$ at −78°C for 10 h with allylbenzene also gave epoxide in high yield (90%). Cu(II) had a similar effect with the stilbenes. The *cis* isomer gave *trans* product predominantly suggestive of a step-wise radical or a reversible copper–oxetane process.[9] With an efficient low temperature system, efforts can now proceed to identify suitable asymmetric ligands.

Acknowledgements

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7. MCPBA without copper catalysis requires 50°C for 10 h with stilbene. At rt MCPBA alone shows only 20% yield after 3 d. Lynch, B. M.; Pausacker, K. H. *J. Chem. Soc.* **1955**, 1525. At higher temperatures acid sensitive substrates undergo acid mediated decomposition.
8. Representative experimental: A dry, sealed flask with $Cu(CH_3CN)_4PF_6$ (5 mol%), MCPBA (2 equiv.) and CH_2Cl_2 (0.2 M) was degassed with N_2, stirred for 5 min and cooled to −78°C. The olefin was added and stirring continued. Aqueous $NaHCO_3$ quench, methylene chloride extraction, $MgSO_4$ drying, and flash chromatography (EtOAc/hexanes) gave the pure epoxide.
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