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Copper(II) tetrafluroborate-promoted Meinwald rearrangement reactions of epoxides

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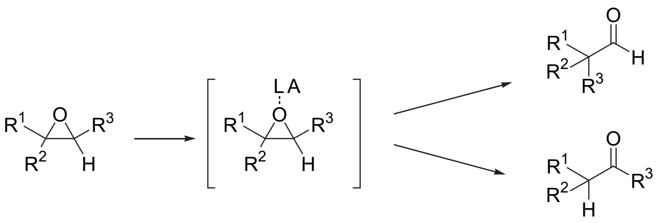
ABSTRACT

Epoxides undergo a highly efficient Meinwald rearrangement in the presence of catalytic quantities of copper(II) tetrafluoroborate to give carbonyl compounds in high yields and with excellent selectivity. The low toxicity and ease of handling of this reagent make it an attractive alternative to the more corrosive or costly Lewis acids frequently employed.

1. Introduction

Epoxides are readily available and highly versatile intermediates, which due to their high reactivity, undergo either stereospecific nucleophilic ring-opening reactions to yield valuable bifunctional compounds or rearrangement reactions to give cyclic or carbonyl compounds.[1] In particular, the rearrangement reaction of epoxides to produce carbonyl compounds, the Meinwald rearrangement, has attracted considerable recent interest given the high efficiency of this protocol and its potential for application in synthetic and industrial processes (Scheme 1).[2] These developments have concentrated on investigating and improving the regiochemical outcome of the rearrangement protocol, with the most important factors being identified as the migratory aptitude of the various epoxide substituents and the Lewis acid catalyst employed.[3] Typically, if there is no structural bias, a mixture of products is produced due to the lack of regioselectivity in the initial ring-opening process. Hence, there has been considerable interest in the development of Lewis acids that display high selectivity and which give highly efficient conversions employing catalytic quantities.



Scheme 1.

The original rearrangement protocols employed either boron trifluoride diethyletherate, lithium salts, magnesium bromide or methylaluminium bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR),[4] which all proved to be highly useful procedures; however, these reagents are toxic or require the catalyst to be employed in stoichiometric quantities. More recent protocols, employing catalytic quantities of Lewis acids, such as palladium salts, indium trichloride, iridium trichloride and both bismuth and gallium salts, have all proven to be more efficient.[5] There remain, however, limitations to these protocols, which need to be addressed, whether it be moderate product selectivity, the toxic or corrosive nature of the catalysts employed, the production of addition or polymeric products or the requirement to employ expensive rare metals. Recently, while investigating addition reactions to epoxides catalyzed by copper(II) tetrafluoroborate ($Cu(BF_4)_2 \cdot nH_2O$) under microwave irradiation, we noted that in some cases, the epoxides substrates underwent a competing Meinwald rearrangement process to produce carbonyl products in moderate yields.[6] We were somewhat surprised to discover that there had only been one previously report in the literature of the use of Cu(II) salts to catalyze epoxide rearrangement reactions[7,8] and this prompted us to initiate studies

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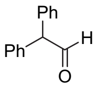
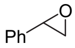
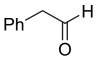
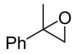
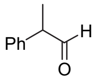
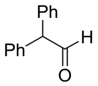
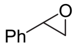
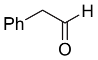
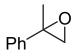
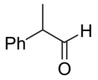
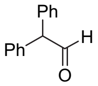
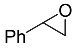
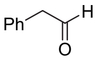
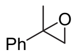
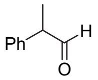
to assess their application as catalysts for the Meinwald rearrangement. In this paper we report our recent progress in the development of $Cu(BF_4)_2\cdot nH_2O$ as an efficient and highly selective catalyst for epoxide rearrangement.[9]

2. Results and discussion

We initially investigated the use of both $Cu(BF_4)_2\cdot nH_2O$ and copper(II) triflate ($Cu(OTf)_2$) under reaction conditions similar to those previously reported.[7] The rearrangement of *trans*-stilbene oxide catalyzed by $Cu(OTf)_2$ proved disappointing with low isolated yields produced, even on extending reaction times and increasing the quantity of catalyst to 10 mol % (Table 1, entry 1). Reactions employing styrene oxide and α-methylstyrene under these modified conditions, however, did proceed to give aldehyde products in high yield and with excellent regioselectivity (entries 2 and 3). Under similar reaction conditions, $Cu(BF_4)_2\cdot nH_2O$ proved to be a highly efficient catalyst (entries 4–6), providing high conversion of the epoxide to the aldehyde products with excellent selectivity. On increasing the quantity of $Cu(BF_4)_2\cdot nH_2O$ to 25 mol %, reaction times for the rearrangement reaction were significantly reduced and provided near quantitative conversions to the aldehyde (entries 7–9). Given that $Cu(BF_4)_2\cdot nH_2O$ is significantly cheaper than $Cu(OTf)_2$, we chose this catalyst for further study employing a range of structurally diverse epoxides (Table 2).

Terminal epoxides underwent an extremely facile rearrangement process at room temperature to rapidly give the aldehyde product in excellent yields (entries 1–4). The rearrangement of styrene oxide proceeded readily to give phenylacetaldehyde contaminated with trace quantities of the suspected aldol product (Table 2, entry 1). This example is noteworthy given the sensitivity of phenylacetaldehyde to acidic conditions and the difficulties encountered in previously reported procedures,[5d] and clearly demonstrates the benign nature of this catalyst. We next probed the chemoselectivity of the catalyst employing a range of substituted stilbene oxides (entries 5–8). These substrates proved to be less reactive than the terminal epoxides, and while the rearrangement did occur at room temperature, these reactions were sluggish and were therefore carried out under reflux conditions. The rearrangement of these materials has previously been used to demonstrate the selectivity of rearrangement processes, as the reaction can occur with either phenyl migration to produce diphenylacetaldehyde, or with hydrogen migration to give deoxybenzoin.[4b] Under reflux conditions, *trans*-stilbene oxide underwent regioselective rearrangement to produce diphenylacetaldehyde in excellent yield as the only product observed by ^{1}H NMR spectroscopy of the crude reaction mixture (entry 5). *cis*-Stilbene oxide produced diphenylacetaldehyde as the major product, in addition to small quantities (approximately 10%) of the deoxybenzoin product (entry 6). Interestingly, the ratio of these products was unchanged when the reaction was carried out at room temperature over extended

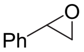
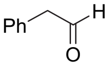
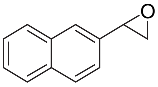
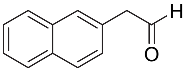
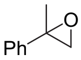
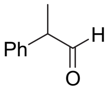
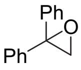
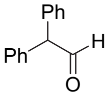
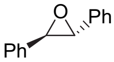
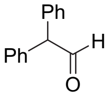
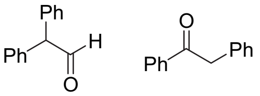
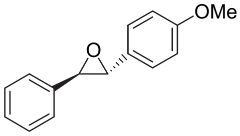
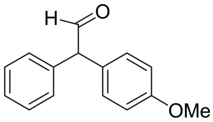
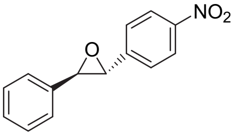
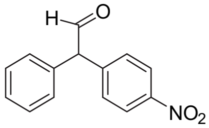
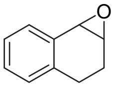
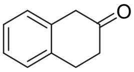
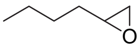
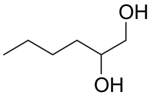
Table 1
Optimisation of the Meinwald rearrangement reaction using Cu(II) salts

Entry	Epoxide	Cu(II) salt	Quantity (mol %)	Time (h)	Products[a]	Conversion[b] (%)
1		$Cu(OTf)_2$	10	6		11
2		$Cu(OTf)_2$	10	3		90
3		$Cu(OTf)_2$	10	3		90
4		$Cu(BF_4)_2\cdot nH_2O$	10	6		62
5		$Cu(BF_4)_2\cdot nH_2O$	10	3		45
6		$Cu(BF_4)_2\cdot nH_2O$	10	3		90
7		$Cu(BF_4)_2\cdot nH_2O$	25	6		95
8		$Cu(BF_4)_2\cdot nH_2O$	25	0.5		98
9		$Cu(BF_4)_2\cdot nH_2O$	25	1		95

[a] All reactions were carried out in 10 mL of anhydrous CH_2Cl_2 at room temperature.
[b] Determined by ^{1}H NMR analysis of the crude reaction mixture.

Table 2

Rearrangements of epoxides catalyzed by $Cu(BF_4)_2 \cdot nH_2O$

Entry	Epoxide[a]	Time (h)	Product[b]	Yield[c] (%)
1		0.3		90
2		0.25		90
3		1		85
4		2		90
5		1.5		95[d]
6		4		95[d,e]
7		2.5		93[d]
8		6		10[d]
9		5		89
10		2		100[d]

[a] All epoxides were used as supplied or were synthesized using published procedures.

[b] Reactions were carried out using 25 mol % of catalyst in 10 mL CH_2Cl_2 at room temperature.

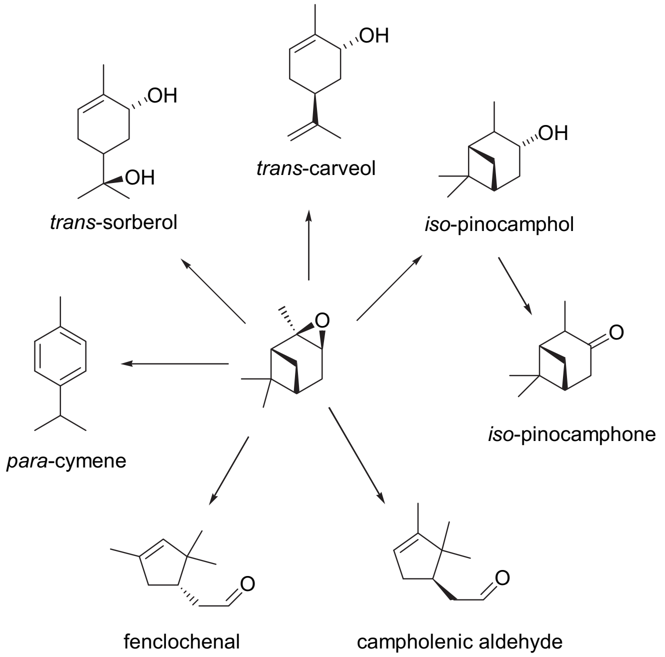
[c] All products gave satisfactory spectroscopic data.

[d] Carried out at reflux.

[e] Isolated as a 90:10 mixture of diphenylacetaldehyde: deoxybenzoin.

reaction times. *para*-Methoxy stilbene oxide underwent efficient rearrangement to give the substituted diphenylacetaldehyde (entry 7), whereas the *para*-nitro analogue gave only low conversions even after extended reaction times at reflux temperatures (entry 8). Disappointingly, the rearrangement of cyclohexene oxide provided only trace amounts of cyclohexanone even after prolonged heating in chloroform, although the starting material was recovered unchanged in contrast to previous reports where halohydrins are produced.[5b] Dihydronaphthalene oxide did, however, produce the expected β-tetralone in high yield when extended reaction times were employed (entry 9). Finally, we investigated the rearrangement of alkyl substituted epoxides, which gave low conversions of the aldehyde product (~10%) due to the efficient catalysis of the hydration of the epoxide to give the diol as the major product in high yield (entry 10).

We further investigated the selectivity of Cu(II) salts employing a more challenging substrate, in this case, α-pinene oxide. This rearrangement reaction is a well documented transformation in the literature due to its industrial importance and is particularly demanding in terms of selectivity given that a number of potential products can be formed during the rearrangement process (Scheme 2). The initially formed cation, produced on ring-opening of the epoxide, can undergo several competing rearrangement processes typical of terpenoids with Lewis acid catalysts typically favouring the formation of cyclopentenic aldehydes and Brönsted acids, typically favouring the formation of menthyl derivatives.[10]

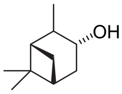
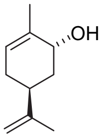
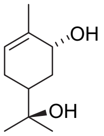
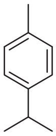
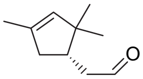
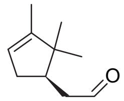


Scheme 2. Major products arising from the acid catalyzed rearrangement of α-pinene oxide.

We assessed the ability of both $Cu(OTf)_2$ and $Cu(BF_4)_2 \cdot nH_2O$ to catalyze the rearrangement of α-pinene oxide (Table 3), and determined the selectivity of the rearrangement process using ^1H NMR and GC–MS analysis. We were gratified to observe that while $Cu(OTf)_2$ gave approximately equal quantities of *trans*-carveol and campholenic aldehyde (entry 1), $Cu(BF_4)_2 \cdot nH_2O$ rapidly catalyzed an efficient and highly selective rearrangement reaction to give campholenic aldehyde in excellent overall yield and with excellent selectivity as determined by ^1H NMR and GC–MS analysis of the crude reaction mixture.

With an efficient protocol developed for the solution phase rearrangement of epoxides, we next studied the possibility of supporting Cu(II) salts on a heterogeneous support material. There has been considerable interest in the development of such heterogeneous systems, which catalyze the rearrangement of α-pinene oxide with high selectivity, given the importance of campholenic aldehyde as an intermediate for the fragrance industry.[11] We recently reported the synthesis and efficient rearrangement of epoxides catalyzed by nanoporous aluminosilicate materials, which gave campholenic aldehyde in good yield and with good selectivity,[12] and were intrigued as to the possibility of employing such a nanoporous support in combination with Cu(II) salts to further improve selectivity. With this aim in mind, we synthesized a small series of nanoporous silicates (S-0) and aluminosilicates (AS-(250) and AS-(150)) using our evaporation-induced supramolecular assembly (EISA) approach.[12] We have previously demonstrated that materials with moderate aluminium loadings perform as excellent catalysts for the rearrangement process, while materials with very low aluminium loadings and the unmodified silica material display low Lewis acidity and display no catalytic activity.[12] The corresponding Cu(II) modified nanoporous materials (S-0$_{Cu}$, AS(250)$_{Cu}$ and AS-(150)$_{Cu}$), which were prepared using an post-synthetic incipient wetness impregnation approach. In this protocol, the nanoporous silica or aluminosilicate was stirred in an aqueous solution of $Cu(BF_4)_2 \cdot nH_2O$ followed by drying and calcination to afford the Cu(II) supported materials as green powders, which were characterized using a range of standard techniques to assess surface area and metal content (Table 4).[13] All of the materials produced displayed the expected large surface areas typical of nanoporous silicas and absorbed Cu(II) ions in similar quantities to previous literature reports.[14]

Table 3
Product distribution from the Cu(II) catalyzed rearrangement of α-pinene oxide

Catalyst[a]	% Composition[b]						
							Yield (%)
$Cu(OTf)_2$[c]	—	38	—	8	10	43	95
$Cu(BF_4)_2$[c]	5	5	—	—	5	85	65
$Cu(BF_4)_2$[d]	2	2	—	—	1	95	88

[a] Reactions were carried out using 1 mmol epoxide in 10 mL CH_2Cl_2 at room temperature.
[b] Determined by ^1H NMR and/or GC–MS analysis of the crude reaction mixture.
[c] Catalyst (10 mol %), 3 h.
[d] Catalyst (25 mol %), 20 min.

Table 4
Physical characteristics of nanoprous catalysts

Catalyst	Si/Al (nominal)	Si/Al (EDX)[a]	Copper concentration (mmol g^{-1})[a]	Surface area (m^2 g^{-1})[b]	Conversion of styrene oxide to phenyacetaldehyde[c,d] (%)
S-0	—	—	—	697	0
S-0$_{Cu}$	—	—	0.1	704	0
AS-(250)	135	171	—	646	10
AS-(250)$_{Cu}$	135	210	0.09	672	7
AS-(150)	81	91	—	606	25
AS-(150)$_{Cu}$	81	84	0.07	598	20

[a] Determined by EDX analysis.
[b] Surface areas were obtained by the BET method.
[c] Reactions were carried out using 1 mmol of epoxide in 10 mL CH_2Cl_2 under reflux conditions for 2 h.
[d] Determined by ^1H NMR analysis of the crude reaction mixture.

Our initial studies assessed the ability of these materials to catalyze the rearrangement of styrene epoxide as a model reaction, and we were disappointed to observe that none of these modified materials functioned as effective catalysts, giving poor conversions to phenylacetaldehyde (Table 4). Only the AS-(150) and AS-(150)$_{Cu}$ materials provided significant conversions to the aldehyde product although, in all cases, styrene oxide was recovered unchanged. Similarly, reactions involving α-pinene oxide also gave poor conversions to campholenic aldehdye with the epoxide again being recovered unchanged. This lack of reactivity may reflect the relatively low loadings of Cu(II) present in these catalysts, that the metal exists in a chemically inert state, or indeed an inability of the substrate to access the active catalytic sites. Our studies are currently on-going to understand and to develop efficient Cu(II) doped nanoporous silicate materials.

3. Conclusions

In conclusion, we have demonstrated that $Cu(BF_4)_2 \cdot nH_2O$ is a highly efficient and reagent, which catalyzes the Meinwald rearrangement of a range of epoxides to produce carbonyl compounds in high yields under mild reaction conditions. The reagent displays excellent regioselectivity, as demonstrated by the rearrangement of stilbene oxide and α-pinene oxide, which gave high yields of campholenic aldehyde with excellent selectivity. The material is commercially available, and its benign nature, in addition to its low cost and ease of use, offers a highly attractive alternative to established methodologies. Disappointingly, attempts to develop novel, selective catalysts by supporting this reagent onto a high surface area silicate support generated materials that gave only disappointing conversions of epoxides.

4. Experimental

4.1. Typical procedure for the copper(II) tetrafluoroborate catalyzed Meinwald rearrangement of epoxides: 2-phenylpropionaldehyde[12]

Copper tetrafluoroborate (59 mg, 0.25 mmol, 25 mol %) was added to a solution of α-methylstyrene oxide (127 mg, 0.95 mmol) in dry dichloromethane (10 mL) at room temperature. Upon completion of the reaction (TLC) the mixture was diluted with dichloromethane (30 mL) and washed with water (3×40 mL). The organic phase was dried over magnesium sulfate, and the solvent removed to give an oil that was purified by chromatography (1:10 ethyl acetate/hexane) to give 2-phenylpropionaldehyde (108 mg, 85%) as a colourless oil; ν_{max}/cm^{-1} (neat) 1718, 1493, 1452, 1267, 1020, 759, 697; ^1H NMR (400 MHz; $CDCl_3$) δ=9.62 (1H, d, J=1.5 Hz), 7.40–7.20 (5H, m), 3.55 (1H, qd, J=7 and 1.5 Hz), 1.45 (3H, d, J=7 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ=201.6, 138.1, 129.5, 128.7, 127.5, 53.4, 15.0; MS (EI) m/z, 134 $(M)^+$; HRMS calculated for $C_9H_{14}NO$ $(M+NH_4)^+$ 152.1070, found 152.1070.

4.2. Preparation of nanoporous silicate catalyst S-0 by an EISA approach

Cetyltrimethylammonium bromide (4.0 g, 11.0 mmol) was dissolved in an aqueous solution of hydrochloric acid (2.5 mL, 0.1 M) and ethanol (17.5 mL) and tetraethylorthosilicate (25 mL, 112.0 mmol) was then added and the mixture stirred for 10 min at 40 °C. The solution was then cooled to room temperature and stirred for 20 min and left to age at room temperature for 1 week. The resultant material was crushed into a fine powder, dried overnight at 90 °C and then calcined in air at 550 °C for 12 h to remove the organic template. The resulting white mesoporous aluminosilicate catalyst was characterized by EDX and ^{29}Si MAS NMR analysis. Surface area measurements were obtained from BET experiments.

4.3. Typical procedure for the preparation of nanoporous aluminosilicate catalysts by an EISA approach: AS-(150) catalyst

Cetyltrimethylammonium bromide (4.0 g, 11.0 mmol) was dissolved in an aqueous solution of hydrochloric acid (2.5 mL, 0.1 M) and ethanol (17.5 mL). Tetraethylorthosilicate (25 mL, 112.0 mmol) was then added and the mixture stirred for 10 min at 40 °C. The solution was cooled to room temperature and aluminium nitrate nonahydrate (0.31 g, 0.83 mmol) was added in one portion. The mixture was stirred for 20 min and then left to age at room temperature for 1 week. The resultant orange solid was crushed into a fine powder, dried overnight at 90 °C and then calcined in air at 550 °C for 12 h to remove the organic template. The resulting white mesoporous aluminosilicate catalyst was characterized by EDX and MAS NMR (^{27}Al and ^{29}Si) analysis. Surface area measurements were obtained from BET experiments.

4.4. Preparation of Cu(II) modified nanoporous catalysts

The nanoporous material (500 mg) was added to a stirred solution of copper tetrafluoroborate (1.0 g) in water (10 mL) at room temperature. After this time the catalyst was filtered from the solution using a Büchner funnel with minimal washing and dried for 24 h at 70 °C. The dry powder was then calcined for 5 h in a furnace at 550 °C.

4.5. Typical procedure for the supported copper nanoporous silicate catalyzed Meinwald rearrangement of epoxides

The nanoporous catalyst (50 mg) was added to a solution of styrene oxide (1 mmol) in dichloromethane (10 mL) and the mixture stirred for 2 h under reflux conditions. After this time, the reaction mixture was cooled to room temperature and the catalyst removed by filtration through a Celite plug, which was washed with further quantities of dichloromethane (2×5 mL). The combined solvents were removed under reduced pressure and the resulting oil was analyzed by ^1H NMR and/or GC–MS.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.08.078. These data include MOL files and InChIKeys of the most important compounds described in this article.

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