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$AuCl_3/AgSbF_6$-catalyzed rapid epoxide to carbonyl rearrangement

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ABSTRACT

An efficient epoxide to carbonyl rearrangement using catalytic $AuCl_3/AgSbF_6$ has been presented. The reactions are fast and high yielding. β-Hydrogen migration takes place exclusively when hydrogen and methyl or substituted methyl groups are present at β-carbon of epoxide. When phenyl/acetyl/benzoyl and hydrogen are available at same carbon atom, migration of the former is preferred over the latter.

Epoxides are versatile and valuable synthetic building blocks for the synthesis of complex organic structures due to their ready availability in both racemic and enantiomerically pure forms and their high reactivity to undergo different organic transformations. Epoxide to carbonyl rearrangement which is also called as Meinwald rearrangement is a synthetically useful protocol to obtain carbonyl compounds in an atom-economical way. Different catalytic systems have been developed which include Lewis acids and Brønsted acids for the epoxide rearrangement.[1,2] For the synthesis of various bioactive natural products, this epoxide rearrangement has been applied widely.[3] Even several tandem reactions have been reported which exploit the synthetic efficiency of Meinwald rearrangement to generate in situ aldehyde or ketone intermediates from epoxides for further transformations.[4] These tandem processes are particularly valuable when the carbonyl compounds are sensitive or unstable or difficult to handle. Mainly Lewis acid mediated epoxide rearrangement became an attractive approach for the carbon-skeletal reorganization of epoxide. The yields and regioselectivity of the rearrangement are sensitive to reaction conditions (Lewis acid employed and solvent) and migrating aptitude of substituents attached to the ring. For example, Pd,[1b–d] In,[1e] V,[1f] Bi,[1g,h] Ir,[1i] Fe,[1j–m] Er,[1n] and Cu[1o,p] favor the hydrogen migration, while Al,[1a,2a] B,[2b] Cr,[2c,d] Ga,[2e] and Si[2f] promote the alkyl migration. Among these systems only a few are both regioselective and truly catalytic in nature. However they pose poor substrate scope. Hence, there is significant scope for the development of better catalyst which would address the factors like efficiency, regioselectivity, good substrate scope, and less catalyst amount.

In recent years, several gold-catalyzed reactions have been reported, where gold in +1 or +3 oxidation states catalyzes a variety of organic transformations with high efficiency in chemo, regio, and stereoselective ways.[5] In some of the gold catalyzed reactions epoxides have been used as nucleophiles to attack gold-activated alkyne or alkene bond.[6,7] Gold can also activate oxirane ring towards nucleophiles as it possesses oxophilicity in addition to carbophilicity.[8–11] Liang et al. investigated the rearrangement of α-hydroxy epoxides into 1,5 or 1,6-diketones and monoketones where gold(III) activates oxirane ring.[8] Stratakis et al. recently reported the isomerization of epoxides into allyl alcohols mediated by TiO_2-supported gold nano particles in which cationic Au(I) is stabilized by the surface of TiO_2.[9] Hashmi et al. in the conversion of 2-alkynylaryl epoxides into 3-acylindenes, observed the gold(I) catalyzed isomerization of oxirane ring to a carbonyl compound as a minor side product.[7] In our study of opening of gold activated epoxides with acetone for subsequent transformation into cyclic acetals, we observed the epoxide to carbonyl rearrangement product in minor amount from stilbene oxide. Here the oxidation state of gold was +3.[10] Based on these reports, we became interested to study the gold-catalyzed epoxide rearrangement to carbonyl compounds. Moreover, gold being capable of promoting a variety of reactions, the intermediate or product of the reaction could be exploited for further synthetic manipulations. We wished to use gold(III) salts for this transformation because it is more oxophilic compared to gold(I).[11] The reaction is expected to proceed faster as gold does not have strong affection to oxyanion (generated during the reaction) like the other trivial Lewis acid catalysts have.[12] As believed gold(III) catalyzed oxirane rearrangement occurred with high efficiency as the reactions completed faster even with 0.1 mol % catalyst at room temperature.

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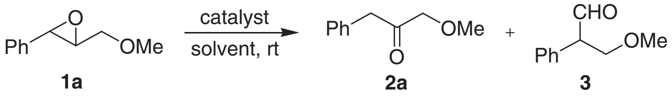
Optimization of the reaction was carried out using the substrate **1a** which has both H and alkyl groups available for migration. Several reactions were carried out using $AuCl_3$ by changing the solvent and adding co-catalyst $AgSbF_6$. Our first attempt with 2 mol % of $AuCl_3$ in CH_2Cl_2 resulted in 56% of ketone **2a**, formed by hydrogen migration and 13% of aldehyde **3** resulting from alkyl migration along with 31% of the unreacted starting material in the crude mixture. In fact there was no progress in the reaction after 15 min due to the catalyst precipitation (Table 1, entry 1). Since the aldehyde **3** decomposed during the silica gel column purification of the crude mixture, the isolated yield of **3** could not be presented in Table 1. When 2 mol % of $AuCl_3$ in combination with 6 mol % of $AgSbF_6$ was used in CH_2Cl_2, 82% of **2a** and 18% of **3** were obtained with complete consumption of the starting material **1a** (entry 2). In dioxane, while there was no reaction with $AuCl_3$ alone (entry 5), the reaction proceeded nicely when $AgSbF_6$ was used along with $AuCl_3$ (entry 6). The reaction was fast and completed in less than 15 min resulting the product **2a** in 92% along with 8% of **3**. Then the reaction was carried out with 1 mol % of $AuCl_3/3AgSbF_6$ which was found to be equally efficient as that of the reaction with 2 mol % of $AuCl_3/3AgSbF_6$ (entry 7). These results led us to perform the reaction with a mixture of 0.1 mol % of $AuCl_3$ and 0.3 mol % of $AgSbF_6$. The reaction worked well and completed in 20 min to yield **2a** in 93% (entry 8). Interestingly, there was no reaction when $AuCl_3$ or $AgSbF_6$ alone were used as catalysts in dioxane. Perhaps the cationic gold species generated in $AuCl_3/AgSbF_6$ mixture might be the active catalyst responsible for the reaction in dioxane. Also $NaAuCl_4$ in dioxane did not catalyze the reaction (entry 11). Other solvents like CH_3CN, toluene, and THF were not found to be suitable solvents.

After finding that the rearrangement is highly efficient at room temperature using 0.1 mol % of $AuCl_3/3AgSbF_6$ in dry dioxane, the generality of $AuCl_3/3AgSbF_6$ catalytic system was examined in the reactions of various substituted and structurally diverse epoxides. Table 2 represents the outcome of these experiments. As explicit from Table 2, the reactions were faster and clean. For comparison, selected best literature data available for the conversion are presented along the corresponding entries in Table 2. 1-Aryl substituted epoxides rearranged exclusively by β-hydrogen migration to give the corresponding aryl-substituted acetaldehydes or arylmethyl ketones. In the case of *trans*-stilbene oxide **1d** which is a 1,2-diaryl substituted epoxide, phenyl migration dominated exclusively over hydrogen migration which lead to the formation of diphenylacetaldehyde **2d** as the sole product (entry 4). However, *cis*-stilbene oxide **1d** resulted in a mixture of rearranged products due to both phenyl and hydrogen migrations. Still, diphenylacetaldehyde **2d** was the major product and the hydrogen migrated product, phenylacetophenone was being 11% only from ^1H NMR of the mixture (entry 5). The reactions of epoxides bearing electron withdrawing groups were also studied. β-Acetyl styrene oxide **1e** and β-benzoyl styrene oxide **1f** lead to the formation of acetyl and benzoyl migrated products, respectively, **2e** and **2f** (entries 6 and 7). Same migration pattern has been reported in the reactions involving $InCl_3$[1e] or $Bi(OTf)_3{\cdot}xH_2O$.[1h] Even, the substituent $-CO_2Me$ on epoxide ring did not affect the reaction as it yielded the hydrogen migrated product, as observed with BF_3 in the rearrangement of ethyl β-phenylglycidate.[13] As we were unable to isolate the pure product due to its decomposing nature in silica gel,[14] the crude reaction mixture was treated with $NaBH_4$ to reduce the keto group to get the hydroxyl ester derivative **4** (entry 8). It is interesting to note that $InCl_3$ did not promote the rearrangement in this case but cleaved the epoxide ring to result in the formation of chlorohydrin by nucleophilic attack of Cl^- from $InCl_3$.[1e] However epoxides bearing cyano or nitro group at β-carbon are resistant to the reaction conditions as the starting materials were recovered. It is worth mentioning that these substrates do not undergo rearrangement with other Lewis acid catalysts also. When there is competition between hydrogen and methyl or substituted methyl, selectively hydrogen migration is preferred to produce methyl ketones (entries 1, 9–14, and 16). In the case of silyl (TBS) protected epoxy alcohol **1h**, reaction worked well and resulted in the product **2h** corresponding to hydrogen migration without damaging the silyl protection (entry 9). Aryl epoxides attached to propyl, isopropyl, and tertiary butyl group were also treated with gold catalyst (entries 11–14). In all the cases reaction worked through hydrogen migration selectively. Only when tertiary butyl group is attached to oxirane ring, very small amount (3%) of alkyl group migrated product was observed (entry 14). If there are two methyl groups attached to the same carbon of the epoxide ring as seen in **1n**, methyl migration occurred because of unavailability of hydrogen for migration (entry 15). It is pleasing to note that epoxide derived from cinnamyl alcohol **1o** resulted in the hydrogen migrated product **2o** in 76% yield in just 10 min (entry 16). The same conversion took 60 h with $Pd(PPh_3)_4$ and heating in toluene at 140 °C.[1b]

Table 1

Catalyst and solvent screening for the epoxide rearrangement

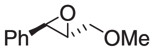
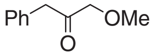
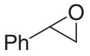
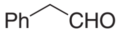
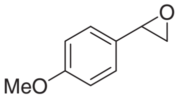
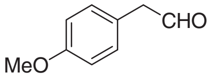
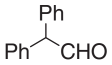
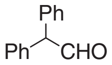
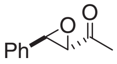
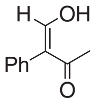
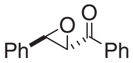
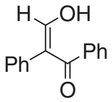
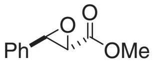
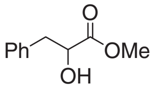
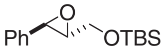
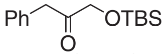
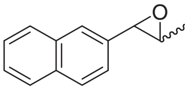
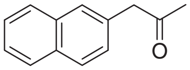
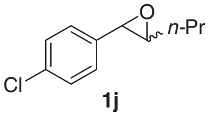
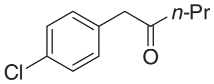
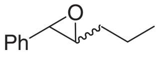
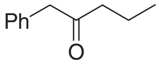
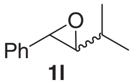
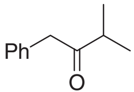
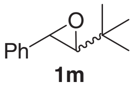
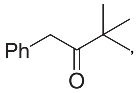
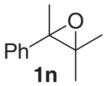
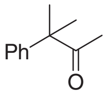


Entry	Catalyst	Solvent	Time	Yield (%)[h]		
				2a[i]	**3**	**1a**[i]
1	$AuCl_3$[a]	CH_2Cl_2	24 h[g]	56(48)	13	31(27)
2	$AuCl_3$[a]/$AgSbF_6$[b]	CH_2Cl_2	15 min	82(74)	18	0
3	$AuCl_3$[a]	CH_3CN	24 h	No reaction		
4	$AuCl_3$[a]/$AgSbF_6$[b]	CH_3CN	24 h	No reaction		
5	$AuCl_3$[a]	Dioxane	24 h	No reaction		
6	$AuCl_3$[a]/$AgSbF_6$[b]	Dioxane	15 min	92(84)	8	0
7	$AuCl_3$[c]/$AgSbF_6$[d]	Dioxane	15 min	92(83)	8	0
8	$AuCl_3$[e]/$AgSbF_6$[f]	Dioxane	20 min	93(83)	7	0
9	$AuCl_3$[a]	THF	30 min	42(41)	9	49(47)
10	$AuCl_3$[a]/$AgSbF_6$[b]	Toluene	24 h	No reaction		
11	$NaAuCl_4$[a]	Dioxane	24 h	No reaction		
12	$AgSbF_6$[b]	Dioxane	24 h	No reaction		

[a] 2 mol %.
[b] 6 mol %.
[c] 1 mol %.
[d] 3 mol %.
[e] 0.1 mol %.
[f] 0.3 mol %.
[g] After 15 min there was no progress in reaction.
[h] % derived from ^1H NMR spectrum of crude reaction mixture.
[i] Value in parenthesis refers to isolated yield.

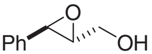
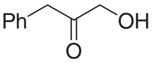
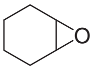
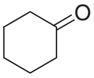
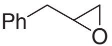
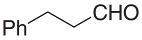
The rearrangement of non-aromatic epoxides was also checked with the present catalytic system. Compared to aromatic epoxides, these required longer reaction times and comparatively more catalyst (2 mol % of $AuCl_3/3AgSbF_6$). Cyclohexene oxide **1p** rearranged by hydrogen migration and resulted in cyclohexanone **2p** in good yield although it has to proceed via the formation of secondary carbocation which does not form as readily as benzylic/tertiary carbocation (entry 17). This observation is special as the reaction of cyclohexene oxide with $IrCl_3{\cdot}xH_2O$ yielded only 4% of cyclopentene carboxaldehyde,[1i] with $InCl_3$ resulted in chlorohydrin by the nucleophilic attack of Cl^-,[1e] with $BiOClO_4{\cdot}xH_2O$,[1g] or $Bi(OTf)_3{\cdot}x\text{-}H_2O$[1h] there were no reaction and with mixed-valent iron catalyst polymerization happened.[1m] These results show the superiority of gold catalyst over other catalysts known for epoxide rearrangement. Epoxide **1q** derived from allyl benzene on treatment with $AuCl_3/3AgSbF_6$ resulted in the formation of hydrocinnamaldehyde **2q** (entry 18). In this case also the reaction proceeded through a secondary carbocation intermediate.

Table 2
Applicability of gold catalyst in epoxide rearrangement[a] (see below-mentioned references for further information)

Entry	Epoxide (**1**)	Time (min)	Product (**2**)	Yield[b] (%)	Selected literature data for comparison and comments
1	 **1a**	15	 **2a** (ref 1e)	83	InCl$_3$ (1.0 equiv, 65%[b])[1e]
2	 **1b**	5	 **2b**	98	Cu(BF$_4$)$_2$·nH$_2$O (25 mol %, 90%[b]);[1o,1p] Bi(OTf)$_3$·xH$_2$O (0.1 mol %, 73%[b]);[1h] InCl$_3$ (0.6 equiv, 85%[b]);[1e] VO(OR)Cl$_2$ (0.5 equiv, 90%[b]);[1f] IrCl$_3$·xH$_2$O (1 mol %, 100% conversion)[1i]; LPDE (1.0 equiv, 85%[b]);[1q] mesoporous aluminosilicates (100% conversion, 5% polymeric material)[1s]
3	 **1c**	10	 **2c** (ref. 1e)	89	InCl$_3$ (0.6 equiv, 90%[b]);[1e] VO(OR)Cl$_2$ (0.5 equiv, 90%[b])[1f]
4	 *trans*-**1d**	5	 **2d**	98	Cu(BF$_4$)$_2$·nH$_2$O (25 mol %, 95%[b]);[1o,1p] Bi(OTf)$_3$·xH$_2$O (0.1 mol %, 92%[b]);[1h] BiOClO$_4$·xH$_2$O (20 mol %, 90%[b]);[1g] IrCl$_3$·xH$_2$O (1 mol %, 100% conversion);[1i] InCl$_3$ (0.6 equiv, 90%[b]);[1e] Mesoporous aluminosilicates (65% conversion);[1s] LPDE (1.0 equiv, 60%[b]);[1q] Mixed-valent iron (2 mol %, 86%[b])[1m]
5	 *cis*-**1d**	5	 **2d**	98[c]	Bi(OTf)$_3$·xH$_2$O (0.1 mol %, 89%[b]);[1h] BiOClO$_4$·xH$_2$O (20 mol %, 90%[b]);[1g] IrCl$_3$ xH$_2$O (1 mol %, 100% conversion);[1i] Cu(BF$_4$)$_2$·nH$_2$O (25 mol %, 95%[b])[1p]
6	 **1e**	10	 **2e** (ref. 1h)	89	Bi(OTf)$_3$·xH$_2$O (0.1 mol %, 89%[b]);[1h] 5 mol dm^{-3} LiClO$_4$-diethylether (78%[b]);[1r] InCl$_3$ (1.0 equiv, 72%[b])[1e]
7	 **1f**	5	 **2f** (ref. 1h)	95	Bi(OTf)$_3$·xH$_2$O (0.1 mol %, 89%[b]);[1h] No reaction with 5 mol dm^{-3} LPDE and along with 10% Yb(OTf)$_3$ resulted in 73% yield[1r]
8	 **1g**	10	 **4** (ref. 15)	76[d]	InCl$_3$ (1.0 equiv, No rearrangement; resulted in chlorohydrin)[1e]
9	 **1h**	15	 **2h** (ref. 1j)	93	Fe(tpp)ClO$_4$ (2 mol %, 99%[b])[1j]
10	 **1i**	5	 **2i** (ref. 1d)	96	Pd(OAc)$_2$/3PBu$_3$ (5 mol %, 98%[b]):[1d] InCl$_3$ (0.6 equiv, 88%[b])[1e]
11	 **1j**	5	 **2j**	92	
12	 **1k**	5	 **2k** (ref. 16)	83	
13	 **1l**	5	 **2l** (ref. 17)	88	
14	 **1m**	5	 **2m** (ref. 17)	95[e]	
15	 **1n**	10	 **2n** (ref. 18)	89	No reaction with Pd(OAc)$_2$/PPh$_3$ or PBu$_3$[1d]

(*continued on next page*)

Table 2 (*continued*)

Entry	Epoxide (**1**)	Time (min)	Product (**2**)	Yield[b] (%)	Selected literature data for comparison and comments
16	 **1o**	10	 **2o** (ref. 1b)	76	$Pd(PPh_3)_4$ (4 mol %, 62%[b])[1b]
17	 **1p**	75[f]	 **2p**	88	$IrCl_3$ (1 mol %, 4% of cyclopentane carboxaldehyde);[1i] $BiOClO_4{\cdot}xH_2O$ (no reaction);[1g] $Bi(OTf)_3{\cdot}xH_2O$ (no reaction);[1h] $InCl_3$ (1.6 equiv, no rearrangement: resulted in cholohydrin);[1e] $LiClO_4$ (no reaction);[1q] Mixed-valent iron (2 mol %, polymerization)[1m]
18	 **1q**	180[f]	 **2q**	73	Fe(tpp)OTf (2 mol %, 94%[b])[1k]

[a] All the reactions were carried out with 0.1 mol % $AuCl_3$ and 0.3 mol % $AgSbF_6$ in dioxane at rt unless otherwise stated.[19]

[b] Yields refer to pure isolated products.

[c] ~11% of hydrogen migrated product also present as revealed from ^1H NMR of the column purified material.

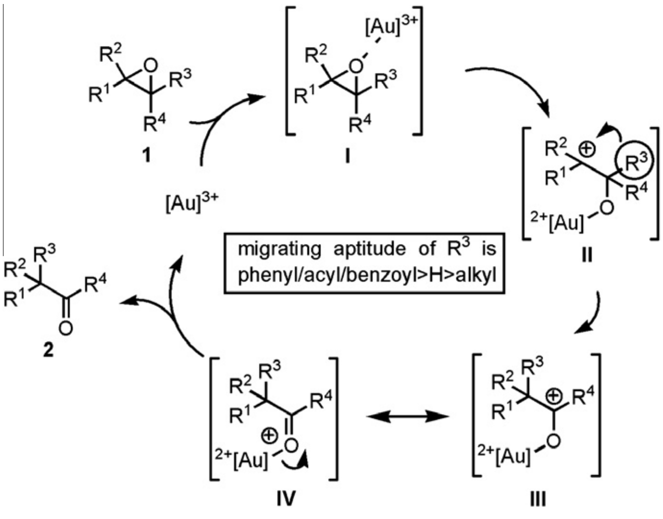
[d] After $NaBH_4$ reduction of crude reaction mixture.

[e] ~3% *tert*-butyl migrated product was also observed in ^1H NMR of crude reaction mixture.

[f] 2 mol % of $AuCl_3$ and 6 mol % of $AgSbF_6$ were used.

This study reveals that the gold-catalyzed rearrangement of substituted epoxides is regioselective through C–O bond cleavage which will lead to the formation of more stable carbocation. Also the rearrangement follows hydrogen migration mainly, that is, if there are two groups at β-position, hydrogen migration is preferred over methyl or substituted methyl group. However, when there is a competition between phenyl/acetyl/benzoyl and hydrogen the migration of phenyl/acetyl/benzoyl is preferred.

Based on these results a plausible mechanism for this epoxide rearrangement could be drawn as shown in Scheme 1. Cationic gold species coordinates to oxygen of oxirane **1**, which leads to the C–O bond cleavage to generate stable carbocation intermediate **II** regioselectively. Migration of R^3 generates carbocation **III**. When phenyl is in the β-position as in stilbene oxide, it will migrate preferentially through well-established phenonium ion. The intermediate **III** is stabilized when R^4 is alkyl by hyperconjugation effect. In the case of substrates **1e** and **1f** which bear, respectively, acetyl and benzoyl groups at the β-position, intermediate **III** is destabilized if hydrogen migration takes place. This could be the reason for the preference of acetyl or benzoyl migration over hydrogen migration. In the reaction of substrate **1g**, the ester group might not destabilize the intermediate **III** to the extent that a carbonyl group of acetyl and benzoyl could do. Eventually hydrogen migration is preferred in **1g**. The intermediate **III** which is stabilized by the lone pair on oxygen as depicted in oxonium ion **IV** generates final carbonyl compound **2** by releasing gold catalyst back into the catalytic cycle.



Scheme 1. Plausible mechanism.

$AuCl_3/3AgSbF_6$ catalyzed epoxide to carbonyl rearrangement takes place very efficiently in dioxane to result carbonyl compounds in high yields in a short span of time. Unlike other promoters used for the epoxide to carbonyl rearrangement, this catalytic system has wider substrate scope. The migrating aptitude of different substituents has been evaluated. Since gold catalysts can perform a variety of conversions, this rearrangement can be coupled with such reactions to find new tandem reactions. Studies in this direction are currently under process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.07.056.

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19. *Representive procedure for the rearrangement of **1a***: To a solution of the epoxide **1a** (100 mg, 0.61 mmol) in dry dioxane (3 mL) freshly prepared $AuCl_3$ (0.2 mg, 0.1 mol %) and $AgSbF_6$ (0.6 mg, 0.3 mol %) solutions in dry dioxane were added and the reaction mixture was allowed to stir at room temperature. The reaction was monitored by TLC and found to complete in 20 min. Dioxane was evaporated. The residue was loaded on a silica gel column and was eluted with EtOAc/hexanes (7/93) mixtures to obtain pure compound **2a** in 83% yield as colorless liquid. $R_f = 0.27$ in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 3H), 3.75 (s, 2H), 4.06 (s, 2H), 7.22–7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.0, 59.1, 76.8, 127.0, 128.6, 129.3, 133.3, 205.7.