A first homogeneous gold(III)-catalysed epoxidation of aromatic alkenes

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The first example of a homogeneous gold(III)-catalysed epoxidation of aromatic alkenes at room temperature using sodium chlorite as the stoichiometric oxidant in a homogeneous trisolvent system of 2-methoxyethanol/acetonitrile/water (volume ratio: 1/3/1) is reported. A radical-trapping experiment suggested that the reaction might proceed via a radical pathway.

Key words: alkenes, epoxidations, homogeneous catalysis, gold, sodium chlorite

Homogeneous cationic gold-catalysed organic transformations have been a focus of attention in recent years due to their novelty and high efficiency.[1] In most cases, cationic gold acts as a soft Lewis acid to activate alkynes and allenes towards either carbon-carbon bond or carbon-heteroatom bond formation. Owing to the lower electron density in a carbon–carbon double bond,[1b] reports concerning the activation of alkenes have been limited and only appeared quite recently with the nucleophilic addition of phenols,[2,3] active methylene compounds,[4] and alcohols[5] to unactivated alkenes. Homogeneous gold-catalysed oxidation reactions have attracted interest as well,[1a] including oxidation of sulfides to sulfoxides,[6] alcohols to carbonyl compounds,[7] methane to methanol,[8] alkanes to alkyl hydroperoxides[9] and the Baeyer–Villiger oxidation of ketones.[10] Moreover, the homogeneous gold-catalysed oxidation of alkenes such as the nitrene transfer reaction[11] and the oxidative cleavage of a C–C double bond[12] have also been studied. To the best of our knowledge, the homogeneous epoxidation of alkenes using a simple gold salt as a catalyst,[13] has not been reported. Hence, we report the first example of a homogeneous gold(III)-catalysed epoxidation of aromatic alkenes with sodium chlorite ($NaClO_2$) as the stoichiometric oxidant in a trisolvent system of $CH_3OCH_2CH_2OH/CH_3CN/H_2O$ at room temperature.

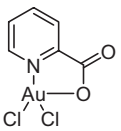
Initially, the epoxidation reaction of *trans*-stilbene was tested using gold trichloride as a catalyst and sodium chlorite[14] as an oxidant in CH_3CN/H_2O (4/1, v/v). This reaction provided *trans*-stilbene oxide in 42% yield at room temperature (Table 1, entry 1).[15] However, the background reaction (without $AuCl_3$) also gave the *trans*-stilbene oxide in 35% yield. In order to increase the catalytic activity of $AuCl_3$, various types of ligands including *N,N*-bidentate ligands such as neocuprione; *N,O*-mixed tetracoordinating ligands such as *N,N′*-bis(salicylidene)-1,2-phenylenediamine and the *O, O*-bidentate ligand, acetylacetone (acac) were tried. Of these, only acac was successful (Table 1, entry 2 *vs* entry 1).[16] With this in mind, six oxygen-containing organic solvents were screened as a third solvent along with CH_3CN/H_2O without the use of any ligands (entries 3-8). It was observed that the use of $CH_3OCH_2CH_2OH/CH_3CN/H_2O$ (volume ratio: 1/3/1) as the solvent system gave the best result, with conversion of *trans*-stilbene being 91% and the isolated yield of *trans*-stilbene oxide being 81% (entry 4). Noticeably, there was no background epoxidation reaction in this trisolvent system. This was distinct from the CH_3CN/H_2O bisolvent system where background reaction occurred to a great extent. The catalytic activity of gold trichloride in the epoxidation of *trans*-stilbene in this trisolvent system was evident. 1,2-Dimethoxyethane, ethanol and *i*-propanol were inferior solvent components to 2-methoxyethanol (entries 3, 6 and 7). Though the same yield of *trans*-stilbene oxide was obtained in a trisolvent of *t*-BuOH/CH_3CN/H_2O as that in $CH_3OCH_2CH_2OH/CH_3CN/H_2O$ (entry 4 vs. 8), only 14% epoxide yield was produced for the epoxidation of *trans*-4-chlorostilbene in *t*-BuOH/CH_3CN/H_2O. Consequently, the trisolvent of $CH_3OCH_2CH_2OH/CH_3CN/H_2O$ was the choice of solvent for further optimisation.

Table 1 Optimisation of reaction components[a]

Entry	Ligand or the third solvent	Yield/%[b]	Conversion /%
1	None	42	47
2	acac[c]	66	84
3	DME[d]	59	66
4	$CH_3OCH_2CH_2OH$[e]	81	91
5	$HOCH_2CH_2OH$[e]	–	no reaction
6	EtOH[e]	34	43
7	*i*-PrOH[e]	51	61
8	*t*-BuOH[e]	81	86

[a]Unless otherwise indicated, the reaction was conducted with 1 mmol of *trans*-stilbene, 5 mol% of $AuCl_3$, 3 mmol of $NaClO_2$ in the bisolvent of CH_3CN (12 ml) and H_2O (3 ml) at room temperature for 24 hours. [b]Isolated yields. [c]20 mol% of acac was added into the reaction system illustrated in note *a*. [d]3 ml of DME was added into the reaction system illustrated in note a, correspondingly, volume of CH_3CN was reduced to 9 ml from 12 ml and volume of H_2O kept unchanged. No ligand was used. [e]All other parameters were identical to those of entry 3 except that 3 ml of alcohol was employed instead of DME.

Table 2 Screened gold catalysts[a]

Entry	Gold catalyst	Yield/%
1[b]	$(PPh_3)AuCl$	< 5
2[b,c]	$(PPh_3)AuCl/AgOTf$	< 5
3[d]	 $AuCl_3$	80
4[d]	$AuCl_3$	81

[a]Reaction conditions: 0.5 mmol of *trans*-stilbene, 0.025 mmol of gold catalyst, and 1.5 mmol of $NaClO_2$ in a trisolvent of $CH_3OCH_2CH_2OH$ (1.5 ml), CH_3CN (4.5 ml), and H_2O (1.5 ml). [b]95% of *trans*-stilbene was recovered. [c]Molar ratio of $(PPh_3)AuCl$ to AgOTf was 1:1. [d]The conversion of *trans*-stilbene was 91%.

Other gold(I) and gold(III) complexes were screened with results summarised in Table 2. Chloro(triphenylphosphine) gold(I)[17] has no catalytic activity since more than 95% of the starting material was recovered, and its catalytic activity did not improve on the addition of AgOTf (Table 2, entries 1 and 2). Dichloro(pyridine-2-carboxylato)gold(III)[18] showed equal catalytic activity to $AuCl_3$ when *trans*-stilbene was used as the substrate (entries 3 and 4). However, in the case of *trans*-4-chlorostilbene, $AuCl_3$ was more reactive since yields of the corresponding epoxide using $AuCl_3$ and dichloro(pyridine-2-carboxylato)gold(III) were 87% and 76%, respectively. Therefore, the optimal reaction system was composed of 5 mol% $AuCl_3$, 3 equivalents of sodium chlorite, and a trisolvent $CH_3OCH_2CH_2OH/CH_3CN/H_2O$ (1/3/1, volume ratio)

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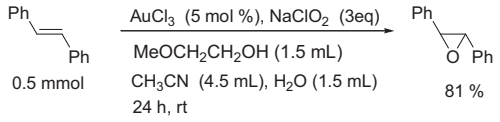

Scheme 1 Optimal epoxidation system of *trans*-stilbene.

(see Scheme 1). Under the optimal conditions, there was no precipitate of metallic gold during the course of the reaction, which supports a homogeneous gold-catalysed epoxidation reaction.

Various olefins were tested using this homogeneous gold-catalysed epoxidation reaction. The reaction of *cis*-stilbene was much slower than *trans*-stilbene as only 39% of *cis*-stilbene was transformed to give *trans*-stilbene oxide as the major epoxidation product (ratio of *trans*- *to cis*-stilbene oxide: 20/1) after 48 h (Table 3, entry 2). The nonstereospecificity of the epoxidation reaction implied that the reaction proceeds stepwise. As for mono *para*-halogen substituted *trans*-stilbenes, the yields of the corresponding epoxides decreased from excellent to poor in the order of F > Cl > Br (entries 3, 4, 6). Different solubility observed in experiments among these three halogen-substituted *trans*-stilbenes might account for the observed yield order. A trisubstituted aromatic olefin, triphenylethylene gave triphenylethylene oxide in 62% yield (entry 10). When *trans*-α-methyl stilbene and 1-phenylcyclohexene were tested, however, the oxidation products obtained were 2,2-phenyl propanal and α-phenylcyclopentanecarboxaldehyde, which derived from the rearrangement of two epoxides intermediates, *trans*-α-methyl stilbene oxide and 1-phenylcyclohexene oxide respectively.[19] A control experiment showed that *trans*-α-methyl stilbene oxide readily rearranged to 2,2-phenylpropanal in quantitative yield in the presence of 5 mol% $AuCl_3$ in dichloromethane at room temperature within 30 min. 1,2-Dialkyl-substituted alkenes and terminal olefins were poor substrates under the standard conditions. During the study of substrate scope, it was observed that metallic gold precipitated after several minutes if the epoxidation reaction proceeded poorly, whereas, if the epoxidation reaction went on well, there was no precipitated metallic gold until the completion of the reaction.

A preliminary study has been done to probe the mechanism of the present $AuCl_3$-catalysed epoxidation reaction. The fact that *cis*-stilbene yielded *trans*-stilbene oxide as the major epoxidation product implied that free radical species might be involved in the reaction. This was the case since the addition of 20 mol% of 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO), a widely used radical scavenger, inhibited the epoxidation reaction dramatically, with conversion of *trans*-stilbene being only 22% after 30 h.

In summary, the first homogeneous gold(III)-catalysed epoxidation of aromatic olefins has been developed. A novel redox catalytic reactivity of cationic gold(III) has been discovered. Further studies to understand the mechanism and develop a gold-catalysed enantioselective epoxidation reaction are underway.

Experimental

Sodium chlorite (80% purity) was purchased and used without further purification. CH_3CN, H_2O and $CH_3OCH_2CH_2OH$ were distilled before use. The known epoxide products were identified by comparison of their ^{1}H- and ^{13}C NMR spectra with those reported in literature. The ^{1}H NMR spectra were recorded at 400 MHz (^{13}C NMR at 100 MHz), using $CDCl_3$ as the solvent.

Epoxidation of trans-stilbene; typical procedure

To a stirred mixture of *trans*-stilbene (90 mg, 0.5 mmol) and gold(III) chloride (7.6 mg, 0.025 mmol) in a homogeneous solvent of CH_3CN (4.5 ml), $CH_3OCH_2CH_2OH$ (1.5 ml) and water (1.5 ml) was added sodium chlorite (170 mg, 1.5 mmol, 80% purity) at room temperature. The reaction mixture turned to yellow immediately. After 24 h, the reaction was quenched by the addition of saturated aqueous $Na_2S_2O_3$ solution (15 ml), and the mixture was extracted with EtOAc (30 ml × 3). The combined organic layers were washed with water (10 ml) and brine (10 ml) once, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (2% EtOAc in petroleum ether) on silica gel to give *trans*-stilbene oxide[14] (159 mg, 81%) as a white solid: m.p. 66–67°C (lit.[14] 63–65°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.37 (m, 10H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.07, 128.53, 128.29, 125.47, 62.80. IR (KBr) 1452, 1278, 860, 837, 745, 690 cm^{-1}; EI-MS (M^+): 196.

Table 3 Epoxidation of olefins catalysed by $AuCl_3$[a]

Entry	Olefin	Yield /%[b]	Conversion /%
1	*trans*-Stilbene	81	91
2	*cis*-Stilbene	35[c]	39
3	*trans*-4-Fluorostilbene	92	97
4	*trans*-4-Chlorostilbene	87	91
5[d]	*trans*-4-Bhlorostilbene	76	85
6	*trans*-4-Bromostilbene	56	58
7[e]	*trans*-4-Cyanostilbene	50	70
8	*trans*-4-Methylstilbene	55	92
9	*trans*-4,4′-Dimethylstilbene	50	90
10	Triphenylethylene	62	84
11	*trans*-α-Methylstilbene	56[f]	71
12	1-Phenylcyclohexene	58[g]	100
13	β-Methylstyrene	37	100

[a]Unless otherwise noted, reactions were conducted under the standard conditions shown in Scheme 1. [b]Isolated yields. [c]*trans*/*cis*-stilbene oxide = 20:1, determined by ^{1}H NMR. [d]5 mol% of dichloro(pyridine-2-carboxylato)gold(III) was used as the catalyst instead of $AuCl_3$. [e]Reaction time was 48 h. [f]The yield of 2,2-phenyl propanal. [g]The yield of α-phenylcyclopentanecarboxaldehyde.

Oxidation of 1-phenylcyclohexene

1-Phenylcyclohexene was treated with the above procedure, except that flash column chromatography was conducted with 1% EtOAc in petroleum ether on silica gel, giving 50 mg α-phenylcyclopentanecarboxaldehyde[20] in 58% yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.28–7.16 (m, 5H), 2.47–2.41 (m, 2H), 1.83–1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.59, 140.20, 128.67, 127.58, 127.08, 63.61, 32.24, 24.13. IR(KBr) 3036, 2805, 2715, 2212, 1720 1587, 1488, 754, 659 cm^{-1}. ESI-MS (M^+): 174.

trans-*4-Fluorostilbene oxide* (Table 3, entry 3)

M.p. 75–76°C (lit.[21] 76–77°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.04 (m, 9H), 3.85 (d, J = 2.4 Hz, 1H), 3.83 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72 (d, J = 244.9 Hz), 136.82, 132.81, 128.55, 128.37, 127.14 (d, J = 8.2 Hz), 125.44, 115.55 (d, J = 21.5 Hz), 62.76, 62.18. IR(KBr) 3062, 3033, 2987, 1602, 1509, 1459, 1430, 1234, 1093, 829, 775, 738, 694, 563, 520 cm^{-1}. ESI-MS (M^+): 214.

trans-*4-Chlorostilbene oxide* (Table 3, entry 4)

M.p. 99–100°C (lit.[21] 100.4–101.5°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 9H), 3.85 (d, J = 2.4 Hz, 1H), 3.82 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.67, 135.69, 134.01, 128.70, 128.55, 128.41, 126.79, 125.44, 62.82, 62.09. IR(KBr) 3046, 2979, 2917, 1650, 1589, 1488, 1457, 1274, 1087, 1010, 817, 748, 696, 516 cm^{-1}. ESI-MS (M^+): 230.

trans-*4-Bromostilbene oxide* (Table 3, entry 6)

M.p. 83–85°C (lit.[22] 83–85°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.21 (m, 9H), 3.84 (d, J = 2.4 Hz, 1H), 3.82 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.63, 136.11, 131.63, 128.55, 128.42, 127.09, 125.43, 122.12, 62.79, 62.13. IR(KBr) 3045, 2985, 1671, 1587, 1484, 1457, 1423, 1105, 1068, 1006, 815, 748, 698, 617, 514 cm^{-1}. ESI-MS (M^+): 274.

trans-*4-Cyanostilbene oxide* (Table 3, entry 7)

M.p. 76–77°C (lit.[21] colourless oil, in view of our other evidence we believe the literature description to be in error). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.70–7.26 (m, 9H), 3.92 (d, *J* = 1.6 Hz, 1H), 3.83 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.40, 136.11, 132.33, 128.62, 126.08, 125.46, 125.35, 118.53, 111.95, 63.16, 61.74. IR(KBr) 3041, 3010, 2225, 1602, 1494, 1459, 1423, 1280, 1170, 1091, 825, 759, 725, 694, 611, 551 cm^{-1}. ESI-MS (M^+): 221.

trans-*4-methylstilbene oxide* (Table 3, entry 8) [21]
M.p. 59–61°C (lit.[21] 59–60°C).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.18 (m, 9H), 3.85 (d, *J* = 2.4 Hz, 1H), 3.83 (d, *J* = 2.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.11, 137.19, 134.06, 129.21, 128.50, 128.20, 125.43, 62.83, 62.71, 21.19. IR(KBr) 3049, 2984, 1494, 1457, 1427, 1218, 1108, 1049, 817, 732, 696, 607, 509 cm^{-1}. EI-MS (M^+): 210.

trans-*4,4'-Dimethylstilbene oxide* (Table 3, entry 9)
M.p. 80–82°C (lit.[14] 75–77°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.18 (m, 9H), 3.82 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.01, 134.19, 129.18, 125.39, 62.74, 21.18. IR(KBr) 3032, 2896, 1608, 1523, 1278, 1010, 882, 839, 801 cm^{-1}. EI-MS (M^+): 224.

Triphenylethylene oxide (Table 3, entry 10)
M.p. 75–76°C (lit.[14] 75–77°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–6.93 (m, 15H), 4.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.92, 135.73, 135.40, 129.13, 128.66, 128.56, 128.30, 127.79, 127.73, 127.65, 127.59, 127.50, 126.70, 126.28, 68.62, 67.98. IR (KBr) 3027, 1605, 1460, 1394, 1280, 756, 690 cm^{-1}. EI-MS (*m/z*) (M^+): 272.

2,2-diphenyl propanal (Table 3, entry 11)[19a]
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.35–7.25 (m, 10H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.48, 141.74, 128.68, 128.11, 127.17, 59.78, 22.53. IR(KBr) 3046, 2980, 1720, 1605, 1491, 1450 860, 832, 741, 693 cm^{-1}. ESI-MS (M^+): 210.

trans-β-*methylstyrene oxide* (Table 3, entry 13)[14]
Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 3.57 (d, *J* = 1.6 Hz, 1H), 3.03 (dq, *J* = 4.8, 1.6 Hz, 1H), 1.45 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.67, 128.35, 127.94, 125.47, 59.43, 58.94, 17.84. IR(KBr) 3033, 2924, 1691, 1447, 1246, 1067, 687 cm^{-1}. EI-MS: *m/z* 134 (M^+).

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