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Catalytic, regioselective, and green methods for rearrangement of 1,2-diaryl epoxides to carbonyl compounds employing metallic triflates, Brønsted-acidic ionic liquids (ILs), and IL/microwave; experimental and computational substituent effect study on aryl versus hydrogen migration

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ABSTRACT

The Lewis-acid catalyzed rearrangement of parent *trans*-stilbene oxide **1** was studied with $M(OTf)_3$/DCM and $M(OTf)_3$/[BMIM][BF_4] (M = Bi, Al, Ga, Sc, and Yb; [BMIM] = butylmethylimidazolium) and $Zn(NTf_2)_2$, and with $Bi(OTf)_3$/[BMIM][X] (X = NTf_2, OTf, PF_6, and BF_4), employing 5 mol% of catalyst. Selective formation of 2,2-dipheylacetaldehyde **2** (phenyl migration product) was observed in all cases, with $Bi(OTf)_3$ proving most efficient. The rearrangement of **1** was also effected in [BMIM][X] (X = NTf_2, OTf, PF_6, and BF_4) without an added catalyst under microwave MW irradiation, and X = PF_6 gave the highest yield and selectivity. Efficient and selective rearrangement of **1**–**2** was also observed with 0.1–0.3 equiv. of [BMIM(SO_3H)][OTf] in DCM and in [BMIM][X]. A substituent effect study was performed with a series of singly substituted 1,2-diphenyl oxiranes (with X = OMe, Me, F, CN, and NO_2) with 5 mol% $Bi(OTf)_3$ in DCM and in [BMIM][NTf_2]. Notable formation of ketones was observed with the NO_2 and CN derivatives. Competing formation of ketones was also observed in [BMIM][PF_6] under MW and under Brønsted acid catalysis with [BMIM(SO_3H)][OTf] in DCM and in [BMIM][NTf_2]. The aryl versus H migration was studied computationally by DFT and MP2 methods and by including solvation effects (IEFPCM).

1. Introduction

The rearrangement of epoxides to carbonyl compounds, also referred to as "Meinwald rearrangement", is a fundamentally important transformation with significant synthetic and industrial utility, and it is therefore not surprising that a rich literature employing a wide range of catalysts is associated with this reaction, and interest in this transformation still continues.

Earlier studies employed stoichiometric (or excess) Lewis acids such as $InCl_3$, $BF_3{\cdot}Et_2O$, lithium salts, and methylaluminum bis(4-bromo-2,6-di-tert-butylphenoxide) [1–4]. With the goal to make the process catalytic and regioselective, a number of inorganic and organometallic catalysts have been employed, namely high valence vanadium complexes [5], bismuth oxide perchlorate [6], copper(II) tetrafluoroborate [7,8], iridium trichloride [9], [(η^5-C_5H_5)$Fe(CO)_2$(THF)][BF_4] [10], mixed-valent iron trifluoroacetate [11], $Ce(OTf)_3$ and $Er(OTf)_3$ [12], and $Bi(OTf)_3$ [13,14]. These reactions typically employed DCM, THF, MeCN, and Et_2O as solvent. A high-valent metalloporphyrin complex Cr(TPP)OTf in DCE solvent proved efficient in regio- and stereo-selective epoxide rearrangement to aldehydes [15,16].

Despite the significantly greater migratory aptitude of hydrogen versus aryl, a large majority of Lewis acid-catalyzed epoxide ring opening reactions of styrene oxides and stilbene oxides result in the formation of aldehydes (aryl migration) (Fig. 1), but situations where the ketone is formed, either as minor product along with the aldehyde or as a major product, have also been reported [5].

Concerning the Brønsted acid-catalyzed rearrangement, acidic zeolite HZSM-5 in solvents such as CH_2Cl_2, $CHCl_3$ and Et_2O [17], and Nafion-H/DCM [18], proved efficient for isomerization of styrene oxide and stilbene oxide with high selectivity toward the

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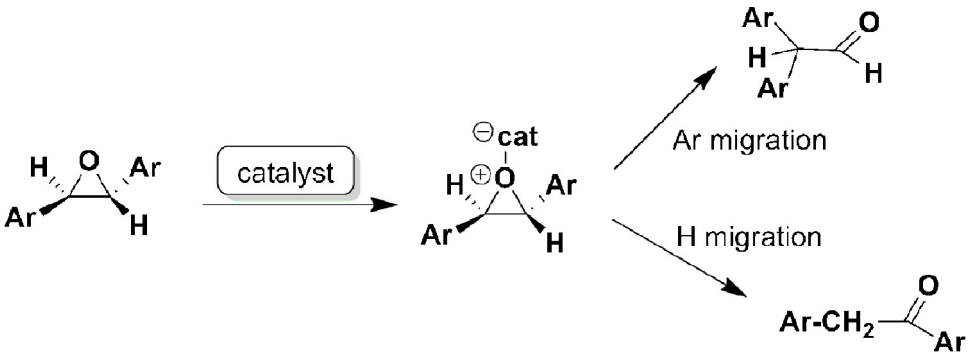


Fig. 1. 1,2-diaryl-epoxide ring opening.

aldehyde, although minor amounts of the ketone was formed from *trans*-stilbene oxide over zeolites [17].

Continuing our interest in synthesis and catalysis in ionic liquids (ILs) [19], we report here on catalytic and regioselective methods for rearrangement of stilbene oxides via (a) Lewis acid-catalysis employing a series of metallic triflates in DCM and in [BMIM][X] (X = NTf_2, OTf, PF_6, and BF_4), (b) Brønsted acid catalysis with [BMIM(SO_3H)][OTf] in DCM and in [BMIM][X] as solvents, and (c) MW irradiation in [BMIM][X] (X = NTf_2, OTf, PF_6, and BF_4) without an added catalyst, and with recycling and reuse of the IL. A substituent effect study with a series of mono-substituted 1,2-diphenyl oxiranes (with X = OMe, Me, F, CN, and NO_2) was also undertaken in DCM and in IL solvents under Lewis acid, Brønsted acid, and under MW without an added catalyst. To gain some mechanistic insight, the ring opening process was also studied computationally by density functional theory (DFT) and MP2 methods to gauge the relative energies of cationic intermediates and substituent effect on aryl/phenyl versus hydrogen shift. The ionic liquid version of this chemistry, with or without an added catalyst and with recycling and reuse of the IL, offers alternative and *green* methods to perform this synthetically important transformation.

2. Experimental

2.1. General

Butyl methyl imidazolium ionic liquids [BMIM][X] were synthesized using established literature procedures [20]. 1-Methyl-3-(4-sulfobutyl)imidazolium triflate [BMIM(SO_3H)][OTf] was synthesized following the reported methods [21,22]. $Ga(OTf)_3$ was prepared according to the literature [23]. Other metallic triflates $M(OTf)_3$ and $Zn(NTf_2)_2$ were high purity commercial samples and were used without further purification. Column chromatography was performed on silica gel (200–400 mesh). NMR spectra were recorded in $CDCl_3$ on a Varian 500 MHz NMR instrument (^{1}H: 500 MHz, ^{19}F: 470 MHz, ^{13}C: 125 MHz). GC monitoring was performed on an HP-5890 instrument. GC–MS analyses were performed on a Varian CP-3800-Saturn 2200 instrument. Microwave (MW) induced experiments were performed in 1-Point Support-Biotage Initiator 2.0, and the IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer.

2.2. Synthesis of benzyldimethylsulfonium hydrogensulfate

Preparation of benzyldimethylsulfonium hydrogensulfate was essentially carried out by the procedure reported by Forrester et al. [24] with a slight modification in the workup. When benzyldimethylsulfonium hydrogensulfate was produced according to the Forrester's method, the lower layer containing the sulfonium salt was washed repeatedly with diethyl ether and dried in vacuo in order to remove the unreacted benzyl alcohol and dimethyl sulfide. Benzyldimethylsulfonium hydrogensulfate was obtained as a pure colorless oil in 85% yield; ^{1}H NMR (500 MHz, d_6-DMSO), δ 7.52 (s, 5H); 4.65 (s, 2H); 2.80 (s, 6H); ^{13}C NMR (125 MHz, d_6-DMSO), δ 131.2, 130.0, 129.7, 128.8, 45.9, 24.1.

2.3. General procedure for the synthesis of the singly substituted stilbene oxides

Following the literature procedure [25] *para*-substituted benzaldehyde (10.0 mmol), benzyldimethylsulfonium hydrogensulfate (12.0 mmol), and 0.2 g of BTEAC were suspended in 10 mL of CH_2Cl_2. The solution was stirred and cooled in an ice bath and 10.0 mL of 50% NaOH was added drop-wise. After the addition was completed the reaction mixture was allowed to warm to room temperature and stirred until completion (monitored by TLC). It was diluted with 10 mL of water and extracted three times with 20 mL of DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated to yield a crude solid which was purified by column chromatography with ethyl acetate/*n*-hexane (10%).

2.3.1. Preparation of 2-(4-nitrophenyl)-3-phenyl-oxirane **1e** (typical procedure)

4-Nitrobenzaldehyde (1.51 g, 10.0 mmol), benzyldimethylsulfonium hydrogensulfate (3.0 g, 12.0 mmol) and 0.2 g of BTEAC were suspended in 10 mL of CH_2Cl_2. The solution was stirred and cooled in an ice bath and 10 mL of 50% NaOH was added drop-wise. After the addition was completed the brownish reaction mixture was allowed to warm to room temperature and stirred for 3 h. It was then diluted with 10.0 mL of water and extracted three times with 20.0 mL of DCM. The combined organic extracts were dried over $MgSO_4$, the solvent was evaporated, and the crude brownish solid was recrystallized from CH_3CN/H_2O (70%). A mixture of *cis* and *trans* isomers was obtained in 85% yield (*cis: trans* 2:3). The *trans* isomer was separated by column chromatography with ethyl acetate/*n*-hexane (10%) as the eluent. The yield of pure *trans*-2-(4-nitrophenyl)-3-phenyl-oxirane **1e** [26] was 1.1 g (46%): light yellow crystals; m.p. 125–127 °C (lit. [27] 125–128 °C); IR (CH_2Cl_2) 3055, 2985, 1604, 1523, 1346, 1265, 1111 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 2H) 7.52 (d, J = 8.0 Hz, 2H) 7.41–7.35 (m, 5H), 3.98 (d, J = 2.0 Hz, 1H), 3.86 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 144.4, 136.1, 128.8, 128.8, 126.3, 125.6, 123.9, 63.4, 61.7; GC–MS *m*/*z* 241 (M^+), 196 (100%).

Trans-2-(4-methylphenyl)-3-phenyl oxirane **1a** [27], (crude yield 70%, isolated yield 48%); white solid; m.p. 55–57 °C (lit. [26] 59–60 °C); IR (CH_2Cl_2) 3047, 2985, 2306, 1604, 1519, 1458, 1265, 1111 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 5H), 7.25–7.19 (m, 4H), 3.86 (d, J = 2.0 Hz, 1H), 3.85 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.3, 134.1, 129.3,

128.6, 128.5, 125.5, 125.5, 62.9, 62.8, 21.2; GC–MS *m/z* 210 (M^+), 165 (100%), 181 (60%).

Trans-2-(4-methoxyphenyl)-3-phenyl oxirane **1b** [28] (crude yield 56%, isolated yield 37%); white solid; m.p. 80–82 °C (lit. [26] 80–81 °C); IR (CH_2Cl_2) 2998, 2836, 1613, 1172, 1111 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.33 (m, 5H), 7.31–7.23 (m, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.84 (d, J = 1.5 Hz, 1H), 3.80 [s, 1H and 3H(OMe)]; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 137.3, 129.1, 128.6, 128.3, 126.8, 125.5, 114.0, 62.8, 62.7, 55.4; GC–MS *m/z* 226 (M^+), 197 (100%).

Trans-2-(4-fluorophenyl)-3-phenyl oxirane **1c** [28], (crude yield 75%, isolated yield 54%); white solid; m.p.72–73 °C (lit. [7] 76–77 °C); IR (CH_2Cl_2) 3056, 2965, 2306, 1604, 1512, 1419, 1265, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 7H), 7.07 (t, J = 8.5 Hz, 2H), 3.90 (d, J = 2.0, 1H), 3.80 (d, J = 2.0, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, J = 245.0 Hz), 136.8, 132.9 (d, J = 2.8 Hz), 128.5 (d, J = 22.0 Hz), 127.2 (d, J = 8.0 Hz), 125.5, 115.6 (d, J = 22.0 Hz), 62.8, 62.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.6 (s, 1H); GC–MS *m/z* 214 (M^+), 165 (100%).

Trans-2-(4-cyanophenyl)-3-phenyl oxirane **1d** [29] (crude yield 78%, isolated yield 47%); white solid; m.p. 67–68 °C; IR (CH_2Cl_2) 3066, 2989, 2225, 1924, 1813, 1612, 1496, 1458, 1427,1276, 1111 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H) 7.42–7.34 (m, 5H), 3.92 (d, J = 2.0 Hz, 1H), 3.83 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 136.5, 132.7, 129.1, 129.0, 126.5, 125.8, 119.1, 112.3, 63.6, 62.2; GC–MS *m/z* 221 (M^+), 165 (100%).

2.4. $Bi(OTf)_3$ catalyzed isomerizations in DCM – general procedure (Table 8)

The diaryl-epoxide was added to 5 mol% of $Bi(OTf)_3$ dissolved in dry DCM (2 mL) in a 5 mL round bottom flask and the reaction mixture was stirred at r.t. and monitored by GC until completion. It was then diluted with DCM (5 mL) and washed with water (5 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum. The corresponding product was purified by column chromatography with ethyl acetate/n-hexane (10%).

2.4.1. $Bi(OTf)_3$ catalyzed isomerization of ***1a*** in DCM solvent – typical procedure (Table 8, entry 1)

Compound **1a** (0.053 g) was added to 5 mol% of $Bi(OTf)_3$ (0.008 g) dissolved in 2 mL of dry DCM in a 5-mL round bottom flask. The reaction mixture was stirred at r.t. for 5 min, diluted with dry DCM (5 mL) and washed with water (5 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under vacuum. The crude 2-(phenyl)-2-(4-methylphenyl)-acetaldehyde **2a** was purified by column chromatography using ethyl acetate/n-hexane (10%), and pure 2-(4-methylphenyl)-2-(phenyl)acetaldehyde **2a** was obtained in 90% yield (0.048 g).

2-(4-Methylphenyl)-2-(phenyl)acetaldehyde **2a** [30], yellow oil, IR (CH_2Cl_2) 3028, 2920, 2816, 1716, 1600, 1512, 1454, 1114 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.00 (d, J = 2.0 Hz, 1 H), 7.46–7.20 (m, 9H), 4.93 (d, J = 2.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 137.6, 136.8, 133.5, 130.0, 129.4, 129.3, 129.2, 127.8, 64.0, 21.3; GC–MS *m/z* 210 (M^+), 181 (100%).

2.5. $Bi(OTf)_3$ catalyzed isomerization reactions in $[BMIM][NTf_2]$ – general procedure (Table 9)

The diaryl-epoxide (0.25 mmol) was added to $Bi(OTf)_3$ dissolved in 1 mL of $[BMIM][NTf_2]$ in a small schlenk tube. The reaction was performed under sonication at ambient temperature and monitored by GC. After completion, the reaction mixture was extracted repeatedly with diethyl ether. The combined organic extract was washed with water, dried over $MgSO_4$, and the solvent was evaporated under vacuum and the crude product was purified by column chromatography with ethyl acetate/n-hexane (10–20%).

2.5.1. $Bi(OTf)_3$ catalyzed isomerization in $[BMIM][NTf_2]$ – typical procedure (Table 4, entry 1)

Compound **1** (0.050 g, 0.25 mmol) was added to $Bi(OTf)_3$ (0.008 g, 5 mol%) dissolved in 1.0 mL of $[BMIM][NTf_2]$ in a schlenk tube. The reaction was performed under sonication at ambient temperature and monitored by GC. After 5 min, the reaction mixture was extracted with 3 × 5 mL of Et_2O. The combined ether extracts was washed with water and dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude mixture was purified by column chromatography with ethyl acetate/n-hexane (10%) to give **2** (0.040 g; 80%).

2,2-Diphenylacetaldehyde **2** [31], clear light yellow liquid, IR (CH_2Cl_2) 3060, 3030, 1724, 1657, 1599, 1495, 1278 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.83 (d, J = 3.0 Hz, 1H), 7.28–7.26 (t, J = 16.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.11 (t, J = 8.5 Hz, 1H), 4.77 (d, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 136.4, 129.2, 129.1, 127.7, 64.1; GC–MS *m/z* 196 (M^+), 167 (100%).

2.6. Rearrangement in [BMIM][X] under MW irradiation (Tables 6 and 12)

The diaryl-epoxide (0.25 mmol) was added to a MW vial containing [BMIM][X] (1 mL) and the reaction mixture was subjected to MW irradiation in sealed vials at 100 W until the vial temperature reached 200 °C (45–140 s depending on the sample), at which point the reaction was stopped, the reaction mixture was cooled to r.t. and extracted repeatedly with 5 mL portions of Et_2O. The combined ether extracts was concentrated under vacuum to give the crude product mixtures which were purified by chromatography with ethyl acetate/n-hexane (10%). Chromatographic separation of **2b/4b** mixture was only partially successful.

2-(4-Methoxyphenyl)-2-(phenyl)acetaldehyde **2b** [8] ^1H NMR (500 MHz, $CDCl_3$) (in a mixture with **4b**): δ 9.92 (d, J = 2.5, 1H), 7.37 (d, J = 7.5, 2H), 7.31 (d, J = 7.5, 1H), 7.21 (d, J = 9.5 Hz, 2H), 7.14 (d, J = 9.5 Hz, 2H), 6.92 (d, J = 9.5), 4.84 (d, J = 2.5, 1H), 3.80 (s, 3H).

2-(4-Methoxyphenyl)-phenyl-ethanone **4b** [32] (present as minor component together with **2b**) ^1H NMR (500 MHz, $CDCl_3$) δ 8.01–8.02 (m, 2H), 7.55 (m, 1H), 7.47–7.43 (m, 2H), 7.17 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 4.23 (s, 2H), 3.78 (s, 3H).

1-(4-Nitrophenyl)-2-phenyl ethanone **3e** [33], yellow solid, m.p. 156–157 °C; IR(CH_2Cl_2) 1693, 1527, 1350 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 2H), 7.36–7.24 (m, 5H), 4.33 (s, 2H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 152.2, 141.3, 130.0, 129.7, 129.3, 127.7, 124.24, 121.9, 46.4.

2-(4-Nitrophenyl)-2-phenylacetaldehyde **2e**, IR (CH_2Cl_2) 2306, 1732 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$) (from crude product mixture) δ 9.96 (d, J = 2.5 Hz, 1H), 8.33 (d, J = 8.5, 2H), 7.94 (d, J = 8.5, 2H), 7.81–7.79 (m, 2H), 7.64 (d, J = 8.5, 2H), 7.53 (t, 2H), 7.33 (t, 2H), 5.05 (s, 1H).

2.7. $[BMIM(SO_3H)][OTf]$ catalyzed isomerization in $[BMIM][NTf_2]$ – general procedure (Table 11)

The diaryl-epoxide (0.25 mmol) was added to a pre-sonicated homogeneous mixture of $[BMIMSO_3H][OTf]$ (10 mol%) and $[BMIM][NTf_2]$ (1 mL). The reaction was performed under sonication at ambient temperature and monitored by GC. After completion, the reaction mixture was repeatedly extracted with Et_2O and the combined ether extracts was washed with water and dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography with ethyl acetate/n-hexane (10–20%).

*2.7.1. Rearrangement of trans-2-4-(cyanophenyl)-3-phenyl oxirane **2d** catalyzed by [BMIM(SO_3H)][OTf] in [BMIM][NTf_2] – typical procedure (Table 11 entry 4)*

To a pre-sonicated homogeneous mixture of [BMIM(SO_3H)][OTf] (10 mol%) and [BMIM][NTf_2] (1 mL) was added 0.25 mmol (0.055 g) of 2-(4-cyanophenyl)-3-phenyl oxirane **1d**. The reaction was performed under sonication at ambient temperature and monitored by GC. After completion, the reaction mixture was extracted repeatedly with diethyl ether and the combined ether extracts was washed with water, dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product mixture consisting of **2d** (major) and **3d** (minor) was purified by column chromatography with ethyl acetate/n-hexane (20%).

4'-Cyano-2-phenylacetophenone **3d** [8], white solid, m.p. 97–99 °C, IR (CH_2Cl_2) 2225, 1693; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 7.0 Hz, 2H), 7.21–7.15 (m, 3H), 4.22 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 139.8, 133.8, 132.9, 129.7, 129.4, 129.3, 127.7, 118.2, 116.8, 46.2.

2-(4-Cyanophenyl)-2-phenyl acetaldehyde **2d**, [931426–36–7], ^{1}H NMR (500 MHz, acetone-d_6) δ 10.0 (d, J = 1 Hz, 1H), 7.82 (d, J = 8.5, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.36–7.35 (m, 5H), 5.3 (s, 1H).

2.8. [BMIM(SO_3H)][OTf] catalyzed isomerization reactions in DCM as solvent – general procedure (Table 10)

The diaryl-epoxide (0.25 mmol) was added to a solution of 10 mol% [BMIM(SO_3H)][OTf] in 2 mL of dry DCM. The reaction mixture was stirred at room temperature and monitored by GC. After completion, the reaction was quenched by adding 5 mL of water. The two layers were separated and the aqueous layer was washed with 2 × 5 mL of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated under vacuum and the residue was purified by column chromatography with ethyl acetate/n-hexane (10–20%).

*2.8.1. [BMIM(SO_3H)][OTf] catalyzed isomerization reactions of trans-2-(4-fluorophenyl)-3-phenyl oxirane **1c** in DCM as solvent – typical procedure (Table 10 entery 3)*

Trans-2-(4-fluorophenyl)-3-phenyl oxirane **1c** (0.25 mmol, 0.054 g) was added to a solution of [BMIM(SO_3H)][OTf] (10 mol%) in 2 mL of dry DCM and the reaction mixture was stirred at room temperature and monitored by GC. After completion (5 min), the reaction was quenched by adding 5 mL of water, the aqueous layer was washed with 2 × 5 mL of CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$. The solvent was evaporated under vacuum to give the crude products. Column chromatography with ethyl acetate/n-hexane (10%) furnished the pure fluorinated aldehyde **2c** in 92% yield.

2-(4-Fluorophenyl)-2-phenylacetaldehyde ***2c***, [496880–72–9], pale yellow liquid, IR (CH_2Cl_2) 1659, 1270 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 7.0 Hz, 2H), 7.23–7,17 (m, 5H), 7.07 (t, J = 9.0 Hz, 2H), 4.91 (d, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 162.5 (J = 245.2 Hz), 136.0, 132.6 (J = 19.4), 132.0 (J = 2.9), 130.7 (J = 8.2 Hz), 129.1 (J = 4.6 Hz), 127.8, 116.2 (J = 21.2 Hz), 63.6; GC–MS m/z 214 (M^+), m/z 165 (100%).

3. Computational methods

Calculations were carried out with the Gaussian 09 package [34]. Structures were fully optimized by the DFT-B3LYP [35] functional, and at the MP2 [36] level, using the 6-31G(d,p) basis set at both levels. Stationary points were characterized as minima (no imaginary frequencies) or transition states (only one imaginary frequency) by harmonic vibrational frequency calculations. In order to get accurate activation and reaction energies, single-point calculations with the MPWB1K [37] functional and the 6-311+G(d,p) basis set were performed at the B3LYP/6-31G(d,p) optimized geometries. Solvation effects were included by performing SCRF-polarized continuum model (IEFPCM) [38] energy minimizations in CH_2Cl_2 (dielectric constant ε = 8.93).

4. Results and discussion

4.1. Catalysis by Lewis acids in DCM and in ionic liquids

At the onset a series of control experiments were performed with *trans*-stilbene oxide **1** by using 5% and 10% Bi($OTf)_3$ in DCM as solvent and the reactions were monitored by GC (Fig. 2, Table 1). These studies showed that in line with earlier reported studies [13,14], 5% Bi($OTf)_3$ was sufficient for near quantitative conversion to diphenylacetaldehyde **2** after just 5 min at r.t.

In the next step, Al($OTf)_3$, Ga($OTf)_3$, Sc($OTf)_3$, and Yb($OTf)_3$ were tested along with Zn($NTf_2)_2$ for their relative efficiency by using 5 mol% of catalyst, and the reactions were allowed to continue for 30 min. The data (Table 2) shows that conversion to **2** with Al, Ga, and Sc triflates were in the 81–86% range with up to 19% side products (heavy, aldol condensation derived products), with Yb($OTf)_3$ and Zn($NTf_2)_2$ exhibiting significantly lower activity. It is noteworthy that all systems proved to be highly regio-selective (no deoxybenzoin **3** was observed).

With the goal to substitute volatile organic solvents with ionic liquid solvents (ILs), and with the added prospect for recycling and reuse, the Lewis acid assay was repeated in [BMIM][BF_4] using 5 mol% catalyst and the results are summarized in Table 3. In a blank experiment no rearrangement was observed in [BMIM][BF_4] alone after 30 min r.t., and subsequently 5 mol% catalyst was employed. GC monitoring of the progress of the reaction indicated slower conversion in ILs compared to DCM, and this is attributed to solubility and mixing issues in a more viscous environment (in comparison to DCM) and in the presence of a very small quantity of catalyst. For short reaction times (up to 30 min), Bi($OTf)_3$ produced the best results in terms of efficiency and chemo-selectivity. It is noteworthy that despite a sluggish start, Al($OTf)_3$ proved worthy under longer reaction times, reaching high conversion (89%) with no side reactions.

In an effort to select an optimal [BMIM][X] for this transformation, rearrangement of **1** was studied in three other ILs with X = NTf_2, OTf, and PF_6 for comparison with X = BF_4, by using 5 mol% Bi($OTf)_3$ at room temperature, and the reactions were monitored

Table 1
Rearrangement of *trans*-stilbene oxide in the presence of different amounts of Bi($OTf)_3$ in dry DCM at r.t.

Entry	Molar ratio of *t*-stilbene oxide to Bi($OTf)_3$	GC yield (%) [**1: 2: 3: SP**][a]		
		5 min	10 min	30 min
1	1–0.05	[0: 96: 0: 4]	[0: 96: 0: 4]	[0: 93: 0: 7]
2	1–0.1	[0: 94: 0: 6]	[0: 93: 0: 7]	[0: 93: 0: 7]

[a]SP, side products.

Table 2
Rearrangement of *t*-stilbene oxide in the presence of 5 mol% catalyst in DCM at r. t. after 30 min.

Entry	Lewis acid	GC yield (%) [**1: 2: 3: SP**][a]
1	Al($OTf)_3$	[0: 81: 0: 19]
2	Ga($OTf)_3$	[0: 86: 0: 14]
3	Sc($OTf)_3$	[0: 84: 0: 16]
4	Yb($OTf)_3$	[42: 54: 0: 4]
5	Zn($NTf_2)_2$	[65: 32: 0: 3]

[a] SP: side products

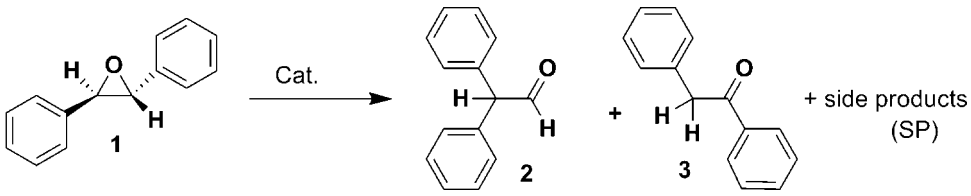


Fig. 2. Rearrangement of *trans*-stilbene oxide.

Table 3
Rearrangement of *t*-stilbene oxide in the presence of 5 mol% of different Lewis acids in [BMIM][BF_4] at r.t.

Entry	Lewis acid	GC yield (%) [**1: 2: 3: SP**][a]				
		5 min	10 min	30 min	60 min	90 min
1	$Al(OTf)_3$	[85: 15: 0: 0]	[74: 26: 0: 0]	[70: 30: 0: 0]	[35: 65: 0: 0]	[11: 89: 0: 0]
2	$Ga(OTf)_3$	[65: 32: 0: 0]	[55: 45: 0: 0]	[50: 50: 0: 0]	[47: 53: 0: 0]	[44: 56: 0: 0]
3	$Sc(OTf)_3$	[91: 9: 0: 0]	[86:14: 0: 0]	[70: 21: 0: 0]	[57: 43: 0: 0]	[56: 44: 0: 0]
4	$Yb(OTf)_3$	[84: 7: 0: 9]	[85: 7: 0: 8]	[84: 8: 0: 8]	[80: 10: 0: 10]	[81: 9: 0: 10]
5	$Bi(OTf)_3$	[45: 55: 0: 0]	[43: 57: 0: 0]	[34: 65: 0: 0]	–	–
6	$Zn(NTf_2)_2$	[86: 14: 0: 0]	[83: 17: 0: 0]	[76: 24: 0: 0]	[58: 42: 0: 0]	–

[a] SP: side products.

Table 4
Rearrangement of *t*-stilbene oxide in [BMIM][X] the presence of 5 mol% of $Bi(OTf)_3$ at r.t.

Entry	Solvent	GC yield (%) [**1: 2: 3: SP**][a]		
		5 min	10 min	30 min
1	[BMIM][NTf_2]	[0: 85: 0:15]	[0: 83: 0:17]	[0: 82: 0: 18]
2	[BMIM][OTf]	[0:91: 0: 9]	[0: 91: 0: 9]	[0: 80: 0: 20]
3	[BMIM][PF_6]	[0: 95: 0: 0]	[0: 73: 0: 36]	[0: 65: 0: 35]
4	[BMIM][BF_4]	[45: 55: 0: 0]	[43: 57: 0: 0]	[34: 65: 0: 0]

[a] SP: side products.

by GC at intervals. The data summarized in Table 4 shows that initially [BMIM][OTf] and [BMIM][PF_6] exhibited high conversion and good selectivity but overtime they produced more side products and on balance [BMIM][NTf_2] performed better. The reactions were noticeably slower in [BMIM][BF_4] but selectivity was excellent.

4.2. Catalysis by Brønsted acidic IL

Compared to significant literature on the Lewis-catalyzed epoxide rearrangements fewer studies have dealt with catalytic Brønsted acid-catalyzed version of this transformation [17,18]. We previously employed [BMIM(SO_3H)][OTf]/IL systems in a number of transformations such as the Schmidt reaction of aldehydes [19f] and Rupe rearrangement [19a].

As summarized in Table 5 the [BMIM(SO_3H)][OTf]/IL systems also proved useful in the present study, employing catalytic amounts of Brønsted acidic IL, and with little side products being formed and with no ketone detected.

Table 6
Rearrangement of *t*-stilbene oxide in [BMIM][X] under MW condition with no added catalyst.

Entry	Ionic liquid[a]	GC yield (%) [**1: 2: 3**]
1	[BMIM][PF_6]	[10: 90: 0]
2	[BMIM][NTf_2]	[13: 75: 12]
3	[BMIM][BF_4]	[23: 65: 12]
4	[BMIM][OTf]	[46: 47: 7]

[a] 45 s reaction time.

4.3. Reactions in IL solvents under microwave MW with no added catalyst

Our attention was next turned to IL/MW reactions without an added catalyst. We reasoned that the Lewis-acidity of the IL's cationic core may be adequate in conjunction with MW irradiation and very short reaction times to bring about this rearrangement with high selectivity, thus eliminating the need for an added catalyst altogether. Rearrangement of **1** was studied in four different [BMIM][X] with X = PF_6, NTf_2, BF_4, and OTf, and the results are summarized in Table 6. Among the ILs examined [BMIM][PF_6] with 90% conversion and no side-reactions (GC analysis) proved most promising. It is noteworthy that with the other ILs minor amounts of deoxybenzoin **3** (hydrogen shift derived product) was produced.

The prospects for recycling and reuse of the IL was examined next by using [BMIM][PF_6] (Table 7), and the reaction was repeated five time with no significant decrease in the conversions (GC).

4.4. Substituent effect study – the aryl versus hydrogen shift

Having identified the most efficient and selective Lewis and Brønsted acidic systems and solvents for isomerization of parent

Table 5
Rearrangement of *trans*-stilbene oxide catalyzed by [BMIM(SO_3H)][OTf] in [BMIM][X] and in DCM at r.t.

Entry	BMIM(SO_3H)[OTf] (equiv.)	Solvent	GC yield (%) [**1: 2: 3: SP**][a]		
			5 min	10 min	30 min
1	0.1	[BMIM][NTf_2]	[20: 73: 0: 7]	[18: 75: 0: 7]	[17: 75: 0: 8]
2	0.2	[BMIM][NTf_2]	[14: 72: 0: 14]	[14: 72: 0: 14]	[11: 75: 0: 14]
3	0.3	[BMIM][NTf_2]	[15: 74: 0: 11]	[13: 74: 0: 13]	[13: 75: 0: 12]
4	0.1	[BMIM][PF_6]	[15: 73: 0: 12]	[12: 78: 0: 20]	[4: 65: 0: 31]
5	0.1	DCM	[1: 92: 0: 7]	[0: 93: 0: 7]	[0: 90: 0: 10]

[a] SP: side products.

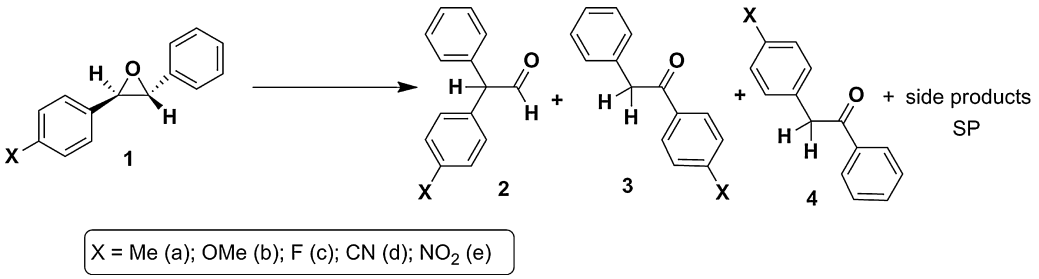


Fig. 3. Catalytic stilbene oxide ring opening with singly substituted derivatives.

Table 7
Recycling and reuse of [BMIM][PF_6] in catalyst-free reaction under MW.

Number of runs	GC Yield (%) [**1: 2**]
1	[10: 90]
2	[10: 90]
3	[10: 90]
4	[12: 88]
5	[10: 90]

trans-stilbene oxide, and since the hydrogen migration product **3** was not observed under these conditions, except as a minor product in the MW assisted reactions, we sought to explore the effect of activating and deactivating substituents on product distribution and the possibility to form more ketones, and to that end the singly substituted stilbene oxides **1a**–**1e** were synthesized for this purpose (Fig. 3).

*4.4.1. $Bi(OTf)_3$-catalyzed isomerization of the singly substituted derivatives **1a**–**1e** in DCM and in [BMIM][NTf_2]*

Epoxides **1a**–**1e** were allowed to react with 5 mol% $Bi(OTf)_3$ in DCM at r.t. and the reactions were monitored by GC (Table 8). The *p*-Me and *p*-F derivatives reacted cleanly and selectively to produce **2** with minimal side products and no ketones were observed. With the *p*-OMe derivatives the yield of **2** was lower and a number of unidentified side products were observed by GC. With the *p*-CN and *p*-NO_2 derivatives significant amounts of the ketones **3** were formed, with **3** becoming the major product in the case of *p*-NO_2. Absence of ketone **4** implies that the direction of hydrogen shift is rather specific and occurs from the benzylic position that bears the electron withdrawing substituent.

The isomerization reactions were repeated by using 5 mol% $Bi(OTf)_3$ in [BMIM][NTf_2] as solvent and the reactions were monitored by GC as before (Table 9). As was observed with parent **1**, the reactions were slower in the IL, and in some cases led to increased side product formation. The *p*-Me and *p*-OMe derivatives gave no ketones. Small quantities of the ketone **3** were formed in the case of *p*-F derivative, whereas none was detected in DCM. The % ketone formed in the case of the *p*-CN derivative was lower than that in DCM. Compound **3** was formed as a major product with the *p*-NO_2 derivative. For comparison, isomerization of the *p*-OMe with

Table 8
Rearrangement of singly substituted stilbene oxides **1a**–**1e** in the presence of 5 mol% of $Bi(OTf)_3$ in DCM at r.t.

Entry	X	GC yield (%) [**1: 2: 3: 4: SP**][a]		
		5 min	10 min	30 min
1	Me (a)	[0: 96: 0: 0: 4]	[0: 86: 0: 0:14]	[0: 84: 0: 0: 16]
2	OMe (b)	[17: 53: 0: 0: 30]	[16: 52: 0: 0: 32]	[16: 52: 0: 0: 32]
3	F (c)	[0: 97: 0: 0: 3]	[0: 96: 0: 0: 4]	[0: 95: 0: 0: 5]
4	CN (d)	[10: 60: 30: 0: 0]	[3: 65: 32: 0: 0]	[0: 55: 35: 0: 10]
5	NO_2 (e)	[17: 19: 57: 0: 7]	[2: 26: 63: 0: 9]	[2: 20: 59: 0: 19]

[a] SP: unidentified side products.

Table 9
Rearrangement of singly substituted stilbene oxides **1a–1e** in the presence of 5 mol% of $Bi(OTf)_3$ in [BMIM][NTf_2] at r.t.

Entry	X	GC yield (%) [**1: 2: 3: 4: SP**][a]		
		5 min	10 min	30 min
1	Me (a)	[10: 66: 0: 0: 24]	[0: 62: 0: 0: 38]	[0: 62: 0: 0: 38]
2	OMe (b)	[36: 52: 0: 0: 12]	[25: 58: 0: 0:17]	[24: 51: 0: 0: 25]
3	F (c)	[13: 65: 7: 0: 15]	[0: 70: 10: 0: 20]	[0: 70: 10: 0: 20]
4	CN (d)	[14: 56: 12: 0: 18]	[9: 60: 13: 0: 18]	[0: 67: 15: 0: 18]
5	NO_2 (e)	[10: 27: 66: 0: 0]	[4: 26: 70: 0: 0]	[0: 22: 70: 0: 8]

[a] SP: unidentified side-products.

$Cu(BF_4)_2{\cdot}nH_2O$ [7] was reported to give the corresponding aldehyde in 93% yield after 24 h, whereas isomerization of the *p*-NO_2 derivative with this catalyst gave only a 10% yield of the *aldehyde* after 6 h reflux in DCM.

*4.4.2. [BMIM(SO_3H)][OTf] catalyzed isomerization of the singly substituted derivatives **1a**–**1e** in DCM and in [BMIM][NTf_2]*

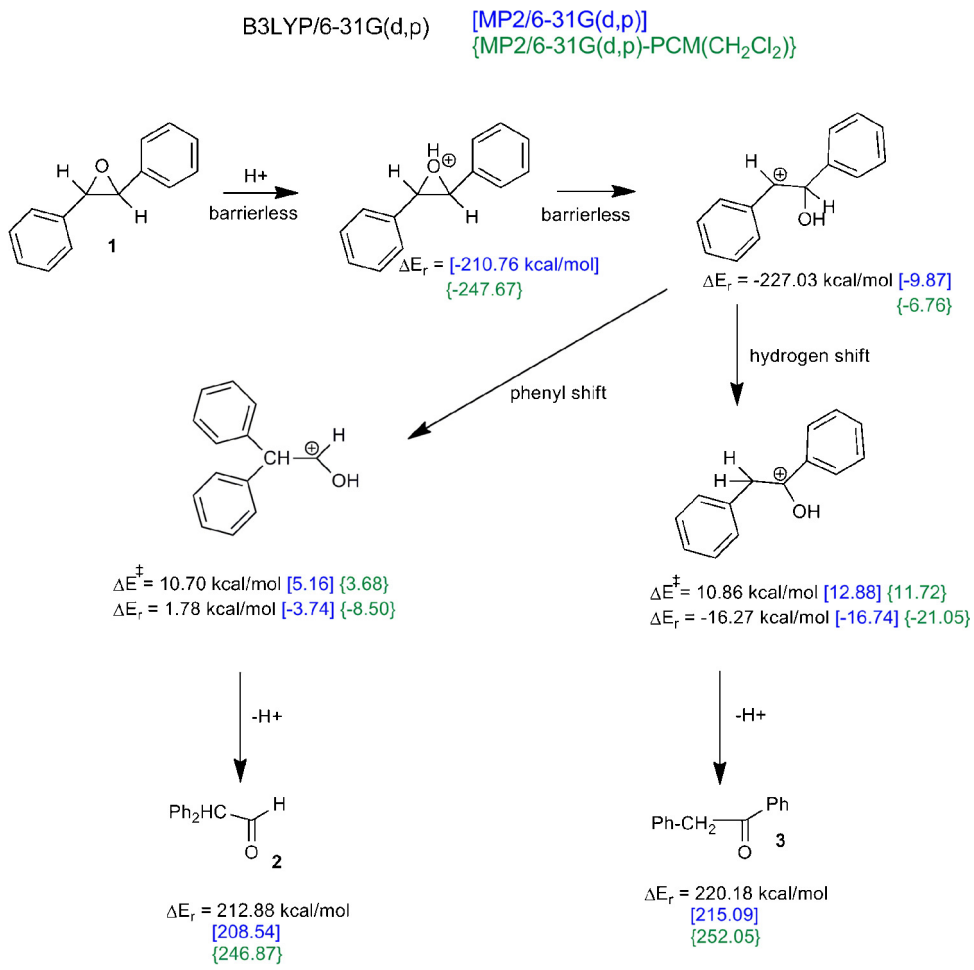
Epoxides **1a**–**1e** were allowed to react with 10% [BMIM(SO_3H)][OTf] in DCM at r.t. and the reactions were monitored by GC (Table 10). The *p*-Me and *p*-F derivatives reacted cleanly and selectively to produce **2** with minimal formation of side products, and no ketones were observed. The reaction did not work well with the *p*-OMe derivatives and side-product formation was extensive. The *p*-CN and *p*-NO_2 derivatives were rather cleanly converted to give a mixture of **2** and **3** (ketone **4** was not detected), and with the *p*-NO_2 derivative near equivalent amounts of **2e** and **3e** were formed.

As in earlier described cases, isomerization reactions progressed slower in the IL solvent as compared to DCE (Table 11), but the selectivity trends were somewhat similar with **1a** reacting most cleanly, and **1b** producing extensive side products. Isomerization of the *p*-F derivative **1c** was less selective in the IL than in DCM (side-products were formed in IL). Formation of ketone **3** was observed with the *p*-CN and *p*-NO_2 derivatives but the conversions were lower.

Table 10
Rearrangement of singly substituted stilbene oxides with 10 mol% [BMIM(SO_3H)][OTf] in DCM at r.t.

Entry	X	GC yield (%) [**1: 2: 3: 4: SP**][a]		
		5 min	10 min	30 min
1	Me (a)	[9: 83: 0: 0: 8]	[4: 85: 0: 0: 11]	[4: 84: 0: 0: 12]
2	OMe[b] (b)	[13: 38: 0: 0: 49]	[12: 37: 0: 0: 51]	[10: 37: 0: 0: 53]
3	F (c)	[0: 100: 0: 0: 0]	[0: 100: 0: 0: 0]	[0: 92: 0: 0: 8]
4	CN (d)	[10: 68: 19: 0: 3]	[0: 74: 23: 0: 3]	[0: 70: 23: 0: 7]
5	NO_2 (e)	[17: 29: 37: 0: 17]	[0: 41: 42: 0: 17]	[0: 40: 42: 0: 18]

[a] SP: side-products.
[b] In the case of 2-(4-MeO-phenyl)-3-phenyl oxirane **1b** in addition to the corresponding aldehyde several unidentified products were produced.



Scheme 1. Ring opening of parent **1**.

Table 11
Rearrangement of singly substituted stilbene oxides **1a–1e** with 10 mol% of [BMIM(SO_3H)][OTf] in [BMIM][NTf_2] at r.t.

Entry	X	GC yield (%) [**1: 2: 3: 4: SP**][a]		
		5 min	10 min	30 min
1	Me (a)	[56: 40: 0: 0: 4]	[44: 51: 0: 0: 5]	[44: 49: 0: 0: 7]
2	OMe (b)	[21: 45: 0: 0: 34]	[15: 49: 0: 0: 36]	[14: 48: 0: 0: 38]
3	F (c)	[22: 55: 0: 0: 23]	[20: 56: 0: 0: 24]	[12: 62: 0: 0: 26]
4	CN (d)	[16: 57: 15: 0: 12]	[10: 60: 16: 0:14]	[6: 56: 18: 0: 20]
5	NO_2 (e)	[68: 24: 8: 0: 0]	[65: 26: 9: 0: 0]	[44: 40: 16: 0: 0]

[a] SP: unidentified side-products.

4.4.3. *Rearrangement of singly substituted stilbene oxides in [BMIM][PF_6]/MW with no added catalyst*

Epoxides **1a**–**1e** were cleanly isomerized in [BMIM][PF_6] under MW irradiation without an added catalyst (Table 12). In this mode, despite reaching rather high temperatures, short contact times must prevent side-product formation since the usual side-products were not detected by GC. Stilbene oxides **1a** and **1c** gave their corresponding aldehydes **2a** and **2c** in high yields and no ketones were observed. Competitive formation of ketones was observed with **1d** and **1e** and to a less extent with **1b**. The observed high chemoselectivity in IL solvent without using an added catalyst, and taking into account the possibility of recycling and reuse of the IL makes the IL/MW method promising as a synthetic method for epoxide isomerization to carbonyl compounds.

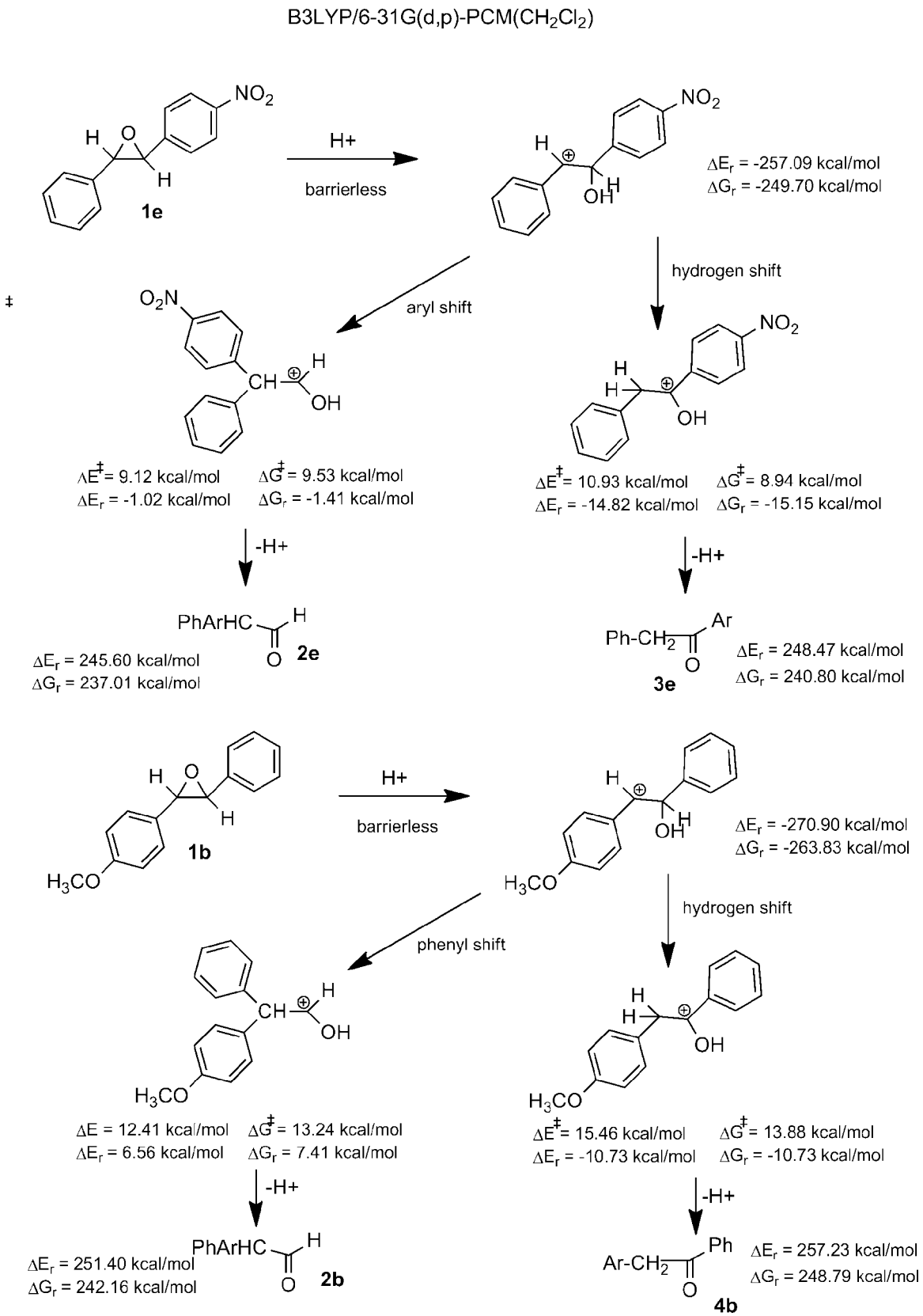
Table 12
Rearrangement of singly substituted stilbene oxides **1a–1e** in [BMIM][PF_6]/MW with no added catalyst.

Entry	X	Max. temperature (°C)	Reaction time (s)	GC yield (%) [**1: 2: 3: 4**]
1	Me (a)	216	120	[7: 93: 0: 0]
2	OMe (b)	217	67	[0: 72: 0: 28]
3	F (c)	203	120	[4: 96: 0: 0]
4	CN (d)	216	140	[0: 41: 59: 0]
5	NO_2 (e)	213	118	[0: 59: 41: 0]

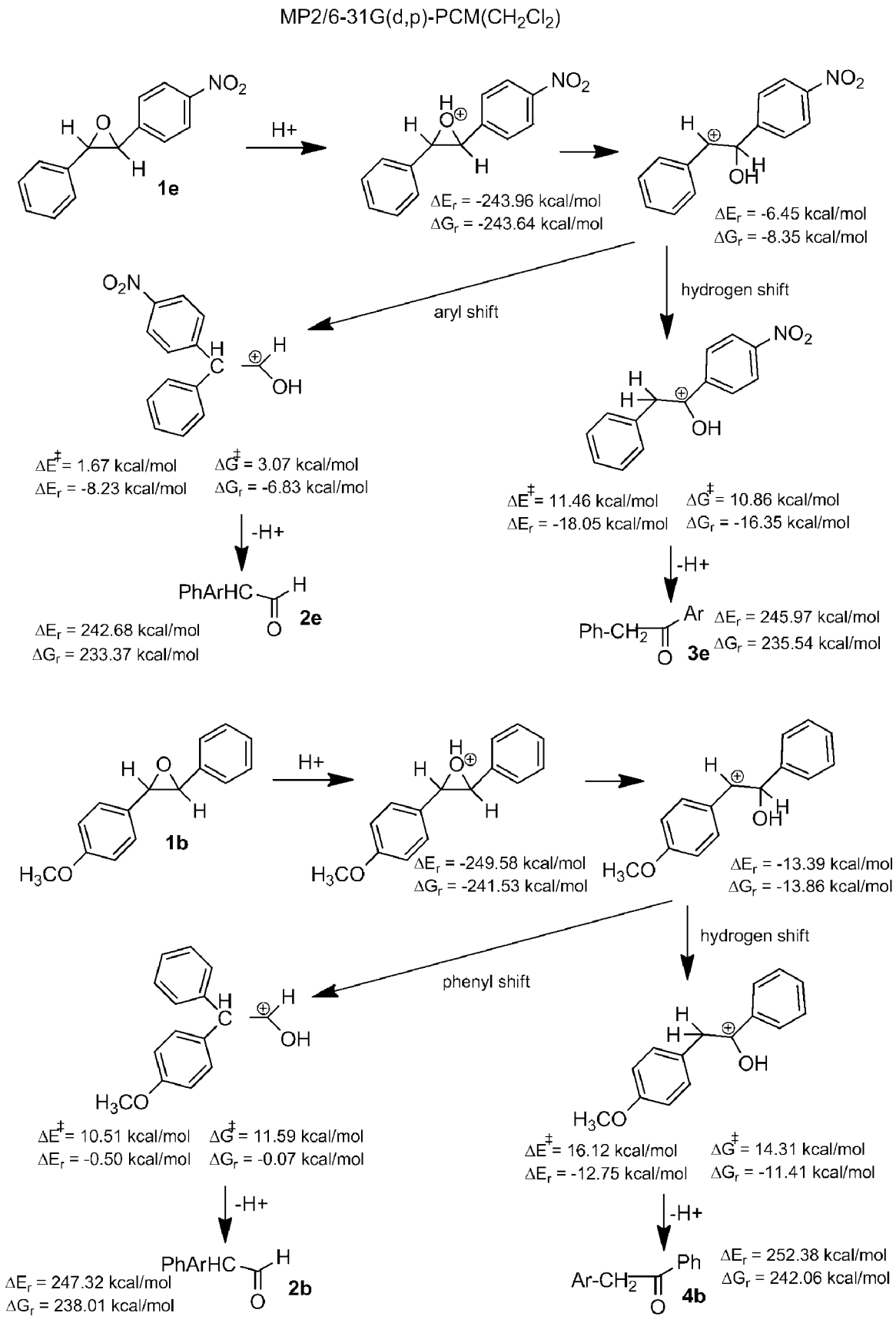
4.5. *Computational study of aryl versus hydrogen shift*

It has been shown [28] that regio-selectivity of nucleophilic capture by bromide ion in ring opening of singly substituted 2,3-diaryl oxiranes with LiBr/Amberlyst 15 (leading to bromohydrins) correlates with relative benzylic carbocation stabilities. Thus with *p*-NO_2 or *p*-CF_3 derivatives nucleophilic attack occurred on the beta-carbon and with *p*-OMe bromide ion captured the alpha-carbon. The computed relative energies for the two possible benzylic carbocations (with *p*-NO_2 and *p*-OMe) were in concert with the observed experimental regio-selectivity. In the context of the present study, with the goal to address aryl versus hydrogen migration, ring opening of parent *trans*-stilbene oxide **1**, the *p*-OMe **1b** and *p*-NO_2 **1e** were studied computationally by DFT at various basis sets and with MP2 level of theory, and by including solvation effect (IEFPCM).

Protonation of **1** is highly exothermic. With B3LYP, protonation and ring opening of the protonated epoxide take place in a single barrierless step with $\Delta E = -227$ kcal/mol (Scheme 1).



Scheme 2. Ring opening of **1e** and **1b** by B3LYP.



Scheme 3. Ring opening of **1e** and **1b** by MP2.

Table 13
Computed energies and free energies of reaction, and activation barriers for the migration processes by different methods.

Method	*H* shift (kcal/mol)		Ph shift (kcal/mol)	
	$\Delta E^{\neq}$ ($\Delta G^{\neq}$)	ΔE_r (ΔG_r)	$\Delta E^{\neq}$ ($\Delta G^{\neq}$)	ΔE_r (ΔG_r)
B3LYP/6-31G(d,p)	10.86 (9.35)	−16.27 (−17.41)	10.70 (11.28)	1.78 (2.22)
B3LYP/6-31G(d,p)-PCM(CH_2Cl_2)	9.82 (8.25)	−20.41 (−19.35)	4.56 (5.34)	−2.86 (−2.01)
MPWB1K/6-311+G(d,p)[a]	8.70	−17.44	7.26	−1.50
MPWB1K/6-311+G(d,p)-PCM(CH_2Cl_2)[a]	7.70	−21.54	0.98	−6.08
MP2/6-31G(d,p)	12.88 (11.19)	−16.74 (−17.40)	5.16 (6.00)	−3.74 (−3.22)
MP2/6-31G(d,p)-PCM(CH_2Cl_2)	11.72 (9.81)	−21.05 (−21.00)	3.68 (4.53)	−8.50 (−8.21)

[a] Single points at B3LYP/6-31G(d,p) optimized geometries.

By contrast, with MP2 the oxonium ion is a minimum with a formation $\Delta E = -211$ kcal/mol. Subsequent ring opening step presents $\Delta E = -10$ kcal/mol, which gives a total exothermicity of −221 kcal/mol for the whole process. Solvation effect (PCM) further facilitates oxonium ion formation ($\Delta E = -247$ kcal/mol; Scheme 1). The benzylic carbocation via hydrogen migration has a lower energy as compared to the carboxonium ion via phenyl migration. This is consistently the case at various levels of theory and basis sets and by including solvation effects (see Table 13). However, the phenyl migration process presents lower activation energy, thus pointing to the aldehyde as the kinetically favored product.

For the substituted derivatives (Schemes 2 and 3), the electronic nature of the *p*-substituent determines the relative stability of the carbocations that originate from epoxide ring opening. With the *p*-NO_2 and *p*-OMe the benzylic carbocations leading to $PhCH_2COAr$ (**3e**) and $ArCH_2COPh$ (**4b**) respectively are more stable than the corresponding phenyl shift carbocations leading to the aldehydes. According to the computed activation barriers, hydrogen migration and phenyl/Aryl migration were identified as feasible reactions, although a preference for migration of the aromatic groups was indicated by the MP2 results.

5. Conclusion

The present study has identified new methods and reagents for catalytic and regioselective conversion of 1,2-diaryl-epoxides to carbonyl compounds. Whereas the $M(OTf)_3$/[BMIM][X] and [BMIM(SO_3H)][OTf]/[BMIM][X] systems are highly efficient methods for Lewis acid and Brønsted acid catalyzed epoxide ring openings, the [BMIM][X]/MW requires no added catalyst. The recycling and reuse of the IL provides an added advantage for the described methods. In a substituent effect study with singly substituted 1,2-diarylepoxides significant ketone formation (hydrogen migration product) was only observed with the *p*-NO_2 and *p*-CN derivatives, except in the MW-induced reaction where ketone formation was also observed with *p*-OMe. Computational study of acid-induced ring opening of parent *trans*-stibene oxide pointed to the aldehydes as the kinetically favored product. Formation of **3e** and **4b** as hydrogen shift-derived ketones agrees with the computational results.

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