Selectivity Enhancement of Silica-Supported Sulfonic Acid Catalysts in Water by Coating of Ionic Liquid

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Supporting Information

General remarks

Silica gel (60 ACC 40-63 μm , surface area: 550 m^2/g) was purchased from CARLO ERBA REACTIFS-SDS. 3-Mercaptopropyltrimethoxy silane, formalin (37%, w/w), 1-methylimidazole, bromooctane, bis(trifluoromethane)sulfonimide lithium salt, hydrogen peroxide aqueous solution (30%), 1-totyl-1-ethanol, 1-phenyl-1-propanol, 4-methylstyrene, 4-chlorostyrene, α -methylstyrene, 2-phenyl-2-propanol, 2-(4-chlorophenyl)propanol, 1-phenyl-1-cyclohexene, 1,2-dodecene oxide, 3-phenyl-1-propionaldehyde and β -methylstyrene were purchased from Aldrich Chemical Company. Styrene was purchased from TCI. 1,2-Epoxy-9-decene oxide, chloroacetaldehyde aqueous solution (45% w/w), ($\pm$)-epichlorohydrin, 1-phenyl-1-cyclohexanol, 4-chloro- α -methylstyrene and 4-*tert*-butylstyrene were purchased from Alfa Aesar Chemical Company. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 DPX 300. Chemical shifts are expressed in ppm relative to Me_4Si in CDCl_3 . IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Elemental analysis was measured on a NA 2100 Instrument. The reaction progress was monitored on a Varian 3300 GPC equipped with a BPX5 column ($12\text{m} \times 0.22\text{ mm}$; phase thickness: 0.25 μm) supplied by SGE, a Flame Detector Ionization and an injector on column. Mass was recorded over a GC/MS HP5972. Ionic liquid $[\text{C}_8\text{MIm}]\text{NTf}_2$ was synthesized using the methods described in previously published material.¹

Synthesis of covalently anchored sulfonic acid onto silica gel²

Silica was activated by an over-night heating at 150 °C. In order to remove trace amount of water, toluene was treated on typical water-carry reflux equipment under refluxed condition before use. Activated silica (2 g) and 3-mercaptopropyltrimethoxy silane (0.2-0.4 g) were added into a 200 ml of round-bottom flask containing 80-150 ml toluene. After 24 h of reflux, the 3-mercaptopropyl silica was filtered off, washed with hot toluene and dried at room temperature for 2 days. The obtained 3-mercaptopropyl silica (2 g) was then mixed with an aqueous solution of hydrogen peroxide (30%, 120 ml). The mixture was stirred at room temperature for 12 h after addition of three drops of conc. H₂SO₄. The solid was then filtered off and washed with distilled water till washings were neutral. Determination of ion exchange capacity was measured by our previous reported method.³

Procedure for Silica-SO₃H-IL Catalyst Preparation.⁴

The silica-supported sulfonic acid catalyst (50 mg) was mixed in a 10 mL flask with an acetonitrile solution of ionic liquid (25 mg ionic liquid was contained in this solution) at room temperature. The solution was stirred for 10 min, and acetonitrile was then evaporated to dryness in an evaporator under reduced pressure. Finally, the obtained solid was dried in vacuo for 20 min to give a free-flowing white powder (50 wt % of ionic liquid was coated onto the silica gel catalyst).

A typical procedure for Prins Reaction

All reactions were conducted in a 10 mL flask with equipped with magnetic stirring. In a typical reaction, Silica-SO₃H-IL (120 mg) was mixed with α -methylstyrene (90 mg, 0.77 mmol) and formalin (37% w/w, 0.25 mL, 3.1 mmol) under air. The mixture was stirred for 4 hours at 90 °C. After reaction, the mixture was extracted with a mixture of ethyl acetate and heptane (1:6 v/v, 6 mL $\times$ 2). After concentration of organic phase, the crude compounds were purified by silica column

chromatography to give 4-methyl-4-phenyl-1,3-dioxane (129 mg, 94%). The residue solid was treated under reduced pressure to removal all the volatile components, and then reused in the next run.

Table 1. Reuse of catalyst SiO₂-SO₃H-[C₈MIm]NTf₂ for Prins cyclization of α -methylstyrene

Run	1	2	3	4
Yield (%)	94	93	95	94

4-Methyl-4-phenyl-1,3-dioxane ⁵

(colorless liquid, heptane/ethyl acetate = 5/1, 94% yield) ¹H NMR δ 1.40 (s, 3H), 2.04-2.27 (m, 2H), 3.63 (td, J_a = 11.2 Hz, J_b = 2.8 Hz, 1H), 3.85-3.92 (m, 1H), 4.67 (d, J = 6.6 Hz, 1H), 4.85 (d, J = 6.5 Hz, 1H), 7.18-7.25 (m, 1H); 7.29-7.32 (m, 4H) ¹³C NMR δ 31.1, 33.9, 62.6, 74.7, 88.2, 124.8, 126.0, 127.7, 143.0.

4-Phenyl-1, 3-dioxane ⁶

(colorless liquid, heptane/ethyl acetate = 5/1, 95% yield) ¹H NMR δ 1.63 (dt, J_a = 13.5 Hz, J_b = 1.32 Hz, 1H), 2.00 (ddd, J_a = 12.8 Hz, J_b = 4.8 Hz, J_c = 1.3 Hz, 1H), 3.79 (td, J_a = 12.0 Hz, J_b = 2.5 Hz, 1H), 4.12 (dd, J_a = 11.4 Hz, J_b = 4.8 Hz, 1H), 4.57 (dd, J_a = 11.3 Hz, J_b = 2.5 Hz, 1H), 4.81 (d, J = 6.4 Hz, 1H), 5.14 (d, J = 6.3 Hz, 1H), 7.20-7.30 (m, 1H); ¹³C NMR δ 34.4, 67.3, 79.2, 94.6, 126.2, 128.2, 128.9, 141.9.

4-(4-Methylphenyl)-1, 3-dioxane ⁷

(colorless liquid, heptane/ethyl acetate = 5/1, 96% yield) ¹H NMR δ 1.68 (dt, J_a = 13.0 Hz, J_b = 1.4 Hz, 1H), 2.01 (dd, J_a = 12.2 Hz, J_b = 4.9 Hz, 1H), 2.26 (s, 3H), 3.77 (td, J_a = 11.7 Hz, J_b = 2.4 Hz, 1H), 4.10 (dd, J_a = 11.4 Hz, J_b = 4.8 Hz, 1H), 4.52 (dd, J_a = 11.2 Hz, J_b = 2.3 Hz, 1H), 4.80 (d, J =

6.3, 1H), 5.12 (d, $J = 6.3$ Hz, 1H), 7.13 (dd, $J_a = 28.8$ Hz, $J_b = 8.1$ Hz, 4H); ^{13}C NMR δ 20.1, 32.9, 65.9, 77.6, 93.1, 124.7, 128.1, 136.5, 137.5.

4-(4-Chlorophenyl)-1,3-dioxane⁸

(colorless liquid, heptane/ethyl acetate = 5/1, 92% yield) ^1H NMR δ 1.69 (dt, $J_a = 13.5$ Hz, $J_b = 0.9$ Hz, 1H), 2.02 (ddd, $J_a = 12.6$ Hz, $J_b = 4.9$ Hz, $J_c = 1.7$ Hz, 1H), 3.85 (td, $J_a = 11.9$ Hz, $J_b = 2.5$ Hz, 1H), 4.19 (dd, $J_a = 11.5$ Hz, $J_b = 4.8$ Hz, 1H), 4.62 (dd, $J_a = 11.3$ Hz, $J_b = 2.5$ Hz, 1H), 4.87 (d, $J = 6.4$ Hz, 1H), 5.20 (d, $J = 6.4$ Hz, 1H), 7.25-7.35 (m, 4H); ^{13}C NMR δ 34.3, 67.2, 78.3, 94.5, 127.5, 129.0, 133.8, 140.4.

4-(Chlorophenyl)-4-methyl-1,3-dioxane⁹

(white solid, heptane/ethyl acetate = 5/1, 94% yield) ^1H NMR δ 1.37 (s, 3H), 2.00-2.18 (m, 2H), 3.59 (td, $J_a = 10.2$ Hz, $J_b = 3.1$ Hz, 1H), 3.83-3.90 (m, 1H), 4.62 (d, $J = 6.6$ Hz, 1H), 4.83 (d, $J = 6.6$ Hz, 1H), 7.17-7.28 (m, 4H); ^{13}C NMR δ 30.6, 33.8, 62.4, 74.3, 88.0, 126.2, 127.8, 131.8, 141.8.

4-[4-(1,1-Dimethylethyl)phenyl]-1,3-dioxane¹⁰

(colorless liquid, heptane/ethyl acetate = 6/1, 92% yield) ^1H NMR δ 1.31 (s, 9H), 1.70 (dt, $J_a = 13.5$ Hz, $J_b = 0.8$ Hz, 1H), 2.14 (ddd, $J_a = 25.3$, $J_b = 11.9$ Hz, $J_c = 4.8$ Hz, 1H), 3.86 (td, $J_a = 11.9$ Hz, $J_b = 2.4$ Hz, 1H), 4.20 (dd, $J_a = 11.4$ Hz, $J_b = 4.8$ Hz, 1H), 4.62 (dd, $J_a = 11.3$ Hz, $J_b = 2.4$ Hz, 1H), 4.88 (d, $J = 6.3$ Hz, 1H), 5.20 (d, $J = 6.3$ Hz, 1H), 7.34 (dd, $J_a = 24.6$ Hz, $J_b = 8.3$ Hz, 4H); ^{13}C NMR δ 31.8, 34.1, 35.0, 67.4, 79.1, 94.6, 125.8, 126.0, 138.8, 151.2.

Hexahydro-8a-phenyl-4H-1,3-dioxane¹¹

(white solid, heptane/ethyl acetate = 5/1, 90% yield) ^1H NMR δ 1.18-1.31 (m, 2H), 1.34-1.47 (m, 1H), 1.60-1.70 (m, 2H), 1.75-1.80 (m, 2H), 2.10 (dt, $J_a = 12.1$ Hz, $J_b = 2.2$ Hz, 1H), 2.29 (ddd, $J_a = 25.4$ Hz, $J_b = 17.4$ Hz, $J_c = 4.7$ Hz, 1H), 3.48 (d, $J = 11.1$ Hz, 1H), 3.77 (dd, $J_a = 11.1$ Hz, $J_b = 2.1$ Hz, 1H), 4.77 (dd, $J_a = 24.4$ Hz, $J_b = 6.3$ Hz, 1H), 7.16-7.25 (m, 1H), 7.30 (d, $J = 4.3$ Hz, 4H); ^{13}C NMR δ 20.9, 24.4, 25.0, 34.9, 42.4, 67.4, 76.3, 88.5, 124.8, 125.8, 127.7, 144.0.

5-Methyl-4-phenyl-1,3-dioxane ¹²

(colorless liquid, heptane/ethyl acetate = 5/1, 89% yield) ^1H NMR δ 0.47 (d, $J = 6.8$ Hz, 1.8 H), 0.80 (dd, $J_a = 7.0$ Hz, $J_b = 0.3$ Hz, 1.2 H), 1.68-1.76 (m, 0.4 H), 1.96-2.07 (m, 0.6 H), 3.23 (t, $J = 11.1$ Hz, 0.6 H), 3.81-4.01 (m, 2 H), 4.70-4.77 (m, 1.4 H), 5.08-5.14 (m, 1H), 7.11-7.27 (m, 5 H); ^{13}C NMR δ 10.1, 11.4, 33.8, 35.4, 71.9, 71.9, 79.4, 85.1, 93.0, 93.5, 124.0, 125.9, 126.3, 127.1, 127.2, 127.3, 138.5, 139.5.

A typical procedure for tandem dehydration/Prins Reaction

In a typical reaction, Silica-SO₃H-IL (120 mg) was mixed with 2-phenyl-2-propanol (105 mg, 0.77 mmol) and formalin (37% w/w, 0.25 mL, 3.1 mmol) under air. The mixture was stirred for 4.5 hours at 90 °C. After reaction, the mixture was extracted with a mixture of ethyl acetate and heptane (1:6 v/v, 6 mL $\times$ 2). After concentration of organic phase, the crude compounds were purified by silica column chromatography to give 4-methyl-4-phenyl-1,3-dioxane (126 mg, 92%).

A typical procedure for cycloaddition of formaldehyde to epoxide

In a typical reaction, Silica-SO₃H-IL (120 mg) was mixed with 1,2-dodecene oxide (198 mg, 1.1 mmol) and formalin (37% w/w, 0.25 mL, 3.1 mmol) under air. The mixture was stirred for 4 hours at 90 °C. After reaction, the mixture was extracted with a mixture of ethyl acetate and heptane (1:6 v/v, 6 mL $\times$ 2). After concentration of organic phase, the crude compounds were purified by silica

column chromatography to give 4-Decyl-1,3-dioxolane (212 mg, 90%). When chloroacetaldehyde was used, 0.25 mL of the aqueous solution was charged for 1.1 mmol of reaction. In case of 3-phenylpropionaldehyde, 1.1 mmol of aldehyde and 0.30 mL of distilled water were used as solvent. For the reaction between epichlorohydrin and 3-phenylpropionaldehyde, the epoxide was used in excess amount (1.5 equiv relative to the aldehyde).

4-Decyl-1,3-dioxolane¹³

(colorless liquid, heptane/ethyl acetate = 4/1, 90% yield) ¹H NMR δ 0.81 (t, J = 6.4 Hz, 3H), 1.19-1.61 (m, 18H), 3.35 (t, J = 20 Hz, 1H), 3.87-3.96 (m, 2H), 4.75 (s, 1H), 4.95 (s, 1H), ¹³C NMR δ 13.1, 21.7, 24.8, 28.3, 28.5, 28.5, 28.6, 30.9, 32.0, 68.6, 75.3, 93.8.

2-(Chloromethyl)-4-decyl-1,3-dioxolane¹⁴

(colorless liquid, heptane/ethyl acetate = 4/1, 92% yield) ¹H NMR δ 0.81 (t, J = 6.5 Hz, 3H), 1.19-1.63 (m, 18H), 3.42-3.52 (m, 3H), 3.92-4.09 (m, 2H), 5.07 (t, J = 4.0 Hz, 0.8 H), 5.19 (t, J = 4.1 Hz, 0.2H), ¹³C NMR δ 14.5, 23.1, 26.0, 26.1, 29.7, 29.9, 30.0, 30.0, 32.3, 33.2, 33.2, 45.1, 45.2, 78.1, 102.5, 102.9.

2-(2-Phenylethyl)-4-decyl-1,3-dioxolane

(colorless liquid, heptane/ethyl acetate = 5/1, 93% yield) ¹H NMR δ 0.80 (t, J = 6.4 Hz, 3H), 1.18-1.60 (m, 18H), 1.84-1.99 (m, 2H), 2.58-2.72 (s, 2H), 3.32-3.43 (m, 1H), 3.83-4.00 (m, 2H), 4.88 (dt, J_a = 21.9 Hz, J_b = 4.7 Hz, 1H), 7.10-7.23 (m, 5H), ¹³C NMR δ 13.1, 21.7, 24.7, 28.3, 28.5, 28.6, 28.6, 29.0, 29.1, 31.0, 32.3, 32.5, 34.7, 34.8, 68.7, 69.6, 75.2, 75.9, 102.0, 102.7, 124.8, 127.3, 127.4, 140.7, 140.7; MS (EI) m/z (relative intensity) 91, 55, 69, 83, 213, 111, 240, 317[M⁺ - 1], 318[M⁺]; IR: 2923.6, 2853.9, 1455.6, 1136.9, 1030.3, 695.5 cm⁻¹; Anal. Calcd for C₂₁H₃₄O₂: C, 79.19; H, 10.76; O, 10.05. Found: C, 78.92, H, 10.54; O, 10.13.

4-(Chloromethyl)-2-(2-phenylethyl)-1,3-dioxolane¹⁵

(colorless liquid, heptane/ethyl acetate = 5/1, 89% yield) ^1H NMR δ 1.85-1.95 (m, 2H), 2.61-2.69 (m, 2H), 3.32-3.57 (m, 2H), 3.62-3.68 (dd, $J_a = 8.6$ Hz, $J_b = 6.4$ Hz, 0.5H), 3.84-3.89 (m, 1H), 4.10-4.36 (m, 1.5H), 4.92 (dt, $J_a = 33.7$ Hz, $J_b = 4.7$ Hz, 1H), 7.10-7.22 (m, 5H), ^{13}C NMR δ 30.3, 30.4, 35.9, 44.6, 44.9, 68.7, 69.2, 75.5, 75.8, 104.8, 105.3, 126.4, 128.8, 128.9, 141.7, 141.8.

4-(7-Octenyl)-1,3-dioxolane

(colorless liquid, heptane/ethyl acetate = 5/1, 94% yield) ^1H NMR δ 1.27-1.68 (m, 10H), 2.01-2.08 (m, 2H), 3.38-3.45 (m, 1H), 3.93-4.03 (m, 2H), 4.87-5.01 (m, 4H), 5.74-5.87 (m, 1H), ^{13}C NMR δ 26.2, 29.2, 29.3, 29.8, 33.4, 34.1, 70.0, 76.7, 95.2, 114.6, 139.4; MS (EI) m/z (relative intensity) 55, 81, 67, 61, 95, 123, 185 [$\text{M}^+ + 1$]; IR: 2928, 2856, 1464, 1259, 1089, 1012, 910, 794 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$: C, 71.70; H, 10.94; O, 17.36. Found: C, 71.47; H, 10.86; O, 17.14.

2-(Chloromethyl)-4-(7-octenyl)-1,3-dioxolane

(colorless liquid, heptane/ethyl acetate = 5/1, 95% yield) ^1H NMR δ 1.17-1.65 (m, 10H), 1.93-2.00 (m, 2H), 3.36-3.54 (m, 3H), 3.90-4.16 (m, 2H), 4.83-4.85 (m, 0.4 H), 4.87-4.90 (m, 1H), 4.92-4.95 (m, 0.6 H), 5.07 (t, $J = 4.0$ Hz, 0.8 H), 5.16 (t, $J = 4.1$ Hz, 0.2 H), 5.66-5.79 (m, 1H), ^{13}C NMR δ 24.6, 24.6, 27.8, 27.9, 28.4, 31.8, 31.8, 32.7, 43.7, 43.8, 69.1, 69.7, 76.0, 76.7, 101.1, 101.5, 113.3, 138.0; MS (EI) m/z (relative intensity) 95, 81, 55, 67, 183, 231 [$\text{M}^+ - 1$]; IR: 2928, 2857, 1430, 1141, 1044, 1009, 909, 763 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{ClO}_2$: C, 61.92; H, 9.09; O, 13.75. Found: C, 61.66; H, 8.74; O, 13.83.

4-(7-Octenyl)-2-(2-phenylethyl)-1,3-dioxolane

(colorless liquid, heptane/ethyl acetate = 5/1, 93% yield) ^1H NMR δ 1.19-1.57 (m, 10H), 1.84-1.99 (m, 4H), 2.63-2.70 (m, 2H), 3.32-3.45 (m, 1H), 3.82-4.07 (m, 2H), 4.84-4.95 (m, 3H), 5.66-5.80 (m, 1H), 7.06-7.22 (m, 5H), ^{13}C NMR δ 24.7, 27.8, 27.9, 28.4, 29.0, 29.1, 32.3, 32.4, 32.7, 34.7, 34.8,

68.7, 69.6, 75.1, 75.8, 102.0, 102.7, 113.2, 124.8, 127.3, 127.4, 138.0, 140.6, 140.7; MS (EI) m/z (relative intensity) 95, 81, 55, 67, 183, 210, 287 [$M^+ - 1$], 288 [M^+]; IR: 2927, 2856, 1455, 1135, 1030, 994, 908, 747, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2$: C, 79.12; H, 9.78; O, 11.09. Found: C, 78.84, H, 9.57; O, 10.85.

A typical procedure for etherification of secondary alcohols

In a typical reaction, Silica- SO_3H -IL (120 mg) was mixed with distilled water (0.4 mL) and 1-totyl-1-ethanol (136 mg, 1.0 mmol) under air. The mixture was stirred for 5 hours at 80 °C. After reaction, the mixture was extracted with a mixture of ethyl acetate and heptane (1:6 v/v, 8 mL $\times$ 2). After concentration of organic phase, the crude compounds were purified by silica column chromatography to give 1,1'-(Oxydiethylidene)bis[4-methylbenzene] (244 mg, 96%).

1,1'-(Oxydiethylidene)bis[4-methylbenzene] ¹⁶

(colorless liquid, heptane/ethyl acetate = 10/1, 96% yield) ^1H NMR δ 1.27 (d, J = 6.5 Hz, 3.5H), 1.35 (d, 6.4 Hz, 2.5 H), 2.22 (s, 2H), 2.26 (s, 4H), 4.12 (dd, J_a = 13.0 Hz, J_b = 6.5 Hz, 1.2H), 4.40 (dd, J_a = 12.7 Hz, J_b = 6.4Hz, 0.8H), 6.99-7.14 (m, 8H); ^{13}C NMR δ 20.1, 20.1, 21.9, 23.7, 72.9, 73.2, 125.1, 125.2, 127.9, 128.1, 135.6, 135.9, 140.1, 140.3.

Bis(1-phenylpropyl) ether ¹⁷

(colorless liquid, heptane/ethyl acetate = 10/1, 91% yield) ^1H NMR δ 0.70 (t, J = 7.4 Hz, 3.3 H), 0.77 (t, J = 7.4 Hz, 2.7 H), 1.44-1.59 (m, 0.6 H), 1.61-1.84 (m, 1.4 H), 3.86 (t, J = 6.6 Hz, 0.6 H), 4.40 (t, J = 6.2 Hz, 0.4 H), 7.07-7.26 (m, 5 H) ^{13}C NMR δ 10.2, 10.9, 30.2, 31.8, 80.4, 81.0, 127.2, 127.4, 127.6, 127.8, 128.4, 128.7, 143.3, 143.4.

References

- 1 Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3, 156.
- 2 Gupta, R.; Paul, S.; Gupta, R. *J. Mol. Catal. A: Chem.* **2007**, 266, 50.
- 3 Gu, Y.; Ogawa, C.; Kobayashi, S.; *Org. Lett.* **2007**, 9, 175.
- 4 Gu, Y.; Ogawa, C.; Kobayashi, J.; Mori, C.; Kobayashi, S. *Angew. Chem, Eng. Ed*, **2006**, 45, 7217.
- 5 Chandrasekhar, S.; Reddy, B. V. S. *Synlett*, **1998**, 851.
- 6 Shortridge, R. W. *J. Am. Chem. Soc.* **1948**, 70, 873.
- 7 Bach, T.; Lobel, J. *Synthesis*, **2002**, 2521.
- 8 Sreedhar, B.; Swapna, V.; Sridhar, C.; Saileela, D.; Sunitha, A. *Synth. Commun.* **2005**, 35, 1177.
- 9 Tateiwa, J.; Hashimoto, K.; Yamauchi, T.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1996**, 69, 2361.
- 10 Bomhard, A.; Schaefer, M.; Markert, T.; Porrmann, V. *Ger. Offen.* DE 4404632, **1995**.
- 11 Lippi, G.; Macchia, B.; Pannocchia, M. *Gazzetta Chimica Italian*, **1970**, 100, 14.
- 12 Delmas, M.; Gaset, A. *J. Mol. Catal.* **1982**, 17, 51.
- 13 Rosenthal, I.; Elad, D. *J. Org. Chem.* **1968**, 33, 805.
- 14 Bailey, W. J.; Wu, S. R.; Ni, Z. *J. Macromol. Sci. Chem.* **1982**, A18, 973.
- 15 Mattay, J.; Thuenker, W.; Scharf, H. D. *Liebigs Annalen der Chemie*, **1981**, 1105.
- 16 Miller, K. J.; Abu-Omar, M. M. *Eur. J. Org. Chem.* **2003**, 1294.
- 17 Mukaiyama, T.; Kuwahara, M.; Izawa, T.; Ueki, M. *Chem. Lett.* **1972**, 287.