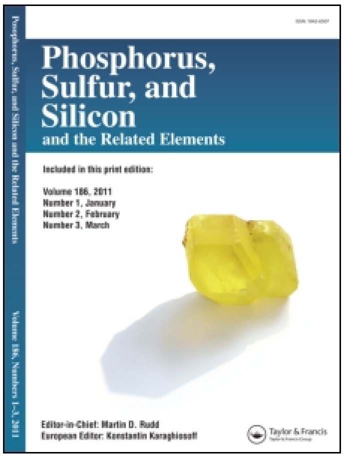

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$Al_2O_3/MeSO_3H$ (AMA) as a New Reagent for the Thia-Fries Rearrangement of Arylsulfonates to Hydroxyaryl Sulfones

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$Al_2O_3/MeSO_3H$ (AMA) as a New Reagent for the Thia-Fries Rearrangement of Arylsulfonates to Hydroxyaryl Sulfones

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A new facile method for thia-Fries rearrangement of arylsulfonates has been developed. A variety of arylsulfonates rearrange in excellent yields in the presence of $Al_2O_3/MeSO_3H$ *as a new reagent without the use of any solvent.*

Keywords Al_2O_3; $MeSO_3H$; arylsulfonates; hydroxyaryl sulfones

INTRODUCTION

Sulfones are useful intermediates in a wide range of fields such as drug and agrochemical intermediates,[1] thermographic materials,[2] polymers,[3] and effective antivirial agents.[4] The sulfonyl group is a widely used synthon for synthetic organic chemists[5] and sulfones have many industrial applications.[6] The hydroxyaryl sulfones are well known as antiseptics and also are useful as fungicides and bactricides.[7] There are several methods for synthesizing aromatic sulfones,[8] but many of these either give low yields, have serious limitations, or require special techniques. The practical method for preparing hydroxyaryl sulfones is the thia-Fries rearrangement of arylsulfonates, which provides a useful route to these compounds.[9] However, these rearrangements require drastic reaction conditions (solvent free with more than stoichiometric amounts of $AlCl_3$ at 80–160°C or in refluxing nitrobenzene) and produce very low yields (generally $<20\%$) of the desired products.[10] Supported clays such as Lewis acids give better results but the method

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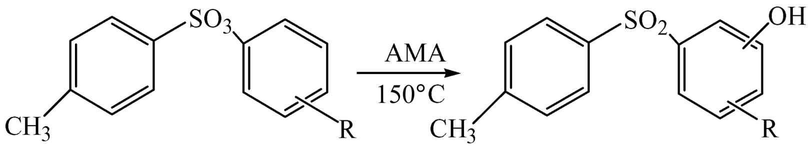
has not been applied to a wide range of arylsulfonates.[11] We recently have reported that a mixture of $Al_2O_3/MeSO_3H$ (AMA) was an effective reagent for Fries rearrangement,[12] Beckmann rearrangement,[13] conversion of nitriles into amides,[14] monoesterification of diols,[15a] and direct conversion of aromatic aldehydes to glycol monoesters.[15b]

RESULTS AND DISCUSSION

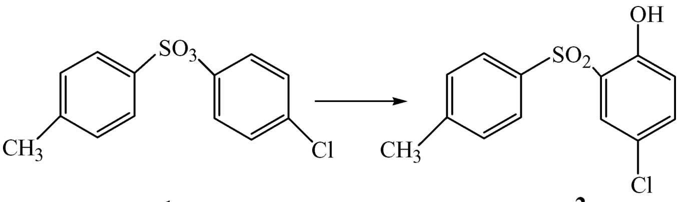
We report herein that AMA also works as a good reagent for the synthesis of hydroxyaryl sulfones. When heated with AMA, arenesulfonate rearranges to give the corresponding hydroxyaryl sulfones in a higher yield and milder condition than previously reported procedures (Scheme 1).



R = CH_3, Cl, F, Br, OH

SCHEME 1

To exploit an effective reagent for the thia-Fries rearrangement of arenesulfonates, the reaction of 4-chlorophenyl 4-methyl-1-benzensulfonate (**1**) was chosen as a model and its behavior was studied under a variety of conditions via TLC and ^{1}H-NMR spectroscopy (Scheme 2). The results are summarized in Table I.



1 **2**

SCHEME 2

According to Table I, entry 3 gives 81% hydroxylsulfonate in 2 min, but the reaction required at least stoichiometric quantities of a Lewis acid, which, after quenching, afforded a lot of metal oxides. These drawbacks set a severe limit to the industrial application of the reaction because the process requires the handling and use of amounts of Lewis acids that are too large resulting in high production costs and causing

TABLE I Thia-Fries Rearrangement of 0.2 mmol of Arylsulfonate (1) Under Various Conditions

Entry	Conditions	Time (h)	Yield%[a]
1	$AlCl_3$, 150°C[6]	4	35
2	PPA, 150°C[16]	4	32[b]
3	$AlCl_3$-$ZnCl_2$/MW[8f]	0.033	81
4	Montmorilonit Clay, 120°C[11]	8	—
5	Al_2O_3 (3 mmol), 150°C	2	—
6	$MeSO_3H$ (15 mmol), 150°C	2	—
7	Al_2O_3 (3 mmol), $MeSO_3H$ (15 mmol), 100°C	2	20
8	Al_2O_3(3 mmol), $MeSO_3H$ (15 mmol), 150°C	2	70

[a] Isolated yields.

[b] 65% bis (4-methyl phenyl) sulfone was obtained (Jacobsen rearrangement).[17]

great plant damage. The problem turned more and more worrisome in recent times due to the increasingly stringent environmental legislations in developed countries during the last decade, which aimed to minimize the production of waste and pollutant materials.

The best results were obtained by a mixture of Al_2O_3 and $MeSO_3H$ in a molar ratio 3 mmol: 15 mmol, when carried out at 150°C for 2 h. The experiments also show the importance of the use of both Al_2O_3 and $MeSO_3H$, respectively.

The results show that all hydroxyaryl sulfones are prepared without a Jacobsen rearrangement.[17] We have confirmed that in AMA media (in accordance with PPA), arenesulfonates react without desulfonylation and transsulfonation reactions. Because of this initial observation, it seemed advantageous to investigate this reagent as a new and better reagent for a thia-Fries rearrangement. A typical procedure is as follows: to a mixture of alumina (0.3 g) and methanesulfonic acid 98% (1 mL, 15 mmol) at 150°C was added arenesulfonates (2 mmol). The mixture was stirred and heated in an oil bath at 150°C for 2 h. After an usual work up, hydroxyaryl sulfones were obtained in good yield. Infrared analysis of the product showed two strong absorption bonds at 1300–1350 and 1100–1150 cm^{-1}, which are characteristic of the sulfone group and also are strong absorption bonds at 3000–3400 cm^{-1} for a hydroxyl group.

To establish the generality and applicability of this method, various arenesulfonates were subjected to the same reaction conditions to furnish the corresponding hydroxyaryl sulfones in good yields. Thus, arenesulfonates with both electron-donating and -withdrawing substituents were carried out in the presence of AMA (Table II).

TABLE II Thia-Fries Rearrangement of 0.2 mmol of Arylsulfonates Using Al_2O_3 (3 mmol)/$MeSO_3H$ (15 mmol) at 150°C

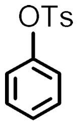
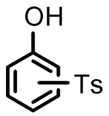
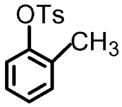
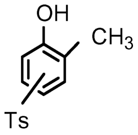
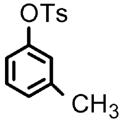
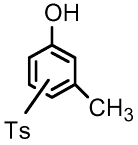
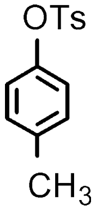
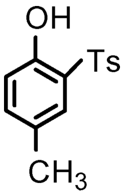
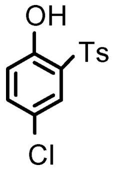
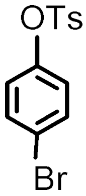
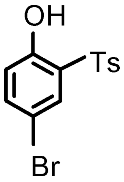
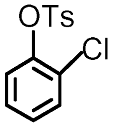
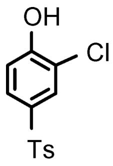
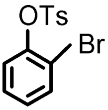
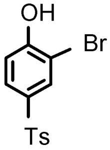
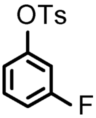
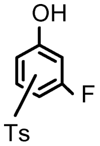
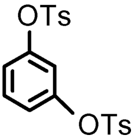
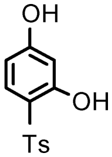
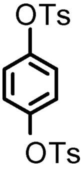
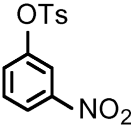
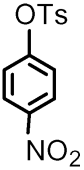
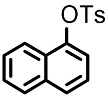
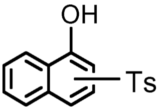
Entry	Substrate ^{a,b}	Time (h)	Products	Yield (%)^{c,d} (*ortho: para*)
1		2		80 (1:3)
2		2		75 (1:3)
3		2		88 (1:3)
4		2		75^{e}
5		2		70
6		2		65
7		2		75

TABLE III Thia-Fries Rearrangement of 0.2 mmol of Arylsulfonates Using Al_2O_3 (3 mmol)/$MeSO_3H$ (15 mmol) at 150°C *(Continued)*

Entry	Substrate [a,b]	Time (h)	Products	Yield (%)[c,d] (*ortho: para*)
8		2		68
9		2		65 (1:1)
10		2		78
11		12	No Reaction	—
12		12	No Reaction	—
13		12	No Reaction	—
14		2		85 (10:1)

[a] Ts = Tosyl.

[b] Refrences 18, 19, and 20.

[c] All yields refer to pure isolated products.

[d] The ratio of the products were determined by ^1H NMR analysis.

[e] The IPSO rearrangement product also is produced (15%). The product is 3-methyl-4-[(methylphenyl)sulfonyl]phenol.

According to Table II, activated sulfonates gave a mixture of two isomers (ortho and para) hydroxyaryl sulfones in good yields (entries 1–4, 11). *p*-Chloro and bromo sulfonates selectively gave the ortho isomer of hydroxyaryl sulfones in 70% and 65% yields, respectively (entries 5, 6). In order to increase the yields of these hydroxyaryl sulfones, the time of the reaction was increased, but no changes were observed. Special mention must be made of the rearrangement of *o*-chloro and bromo sulfonates. The corresponding para isomer selectively formed in 75% and 68% yields, respectively (entries 7, 8). In particular, *m*-ditosyl benzene undergoes the reaction to produce the corresponding sulfone in a 78% yield (entry 10) and only a monosulfonylated product has been formed. However, the reaction of *p*-ditosyl benzene did not afford the corresponding sulfone (entry 12). With more bulky naphthyl tosylate, the reaction is regioselective and the 2-isomer is the selective product (entry 14). Finally, nitro-substituted sulfonates do not rearrange to produce the corresponding hydroxyaryl sulfones. These results indicate that electrophilic substitution does not occur because an electron-withdrawing group deactivates the aromatic ring.

The relative reactivities of the aromatic substrates are consistent with a mechanism involving an attack on the aromatic ring by an electrophilic reagent. The attacking electrophile in this case must be weak and demands an electron-rich ring. The reaction mechanism in the formation of hydroxyaryl sulfones apparently involves the sulfonium cation, $ArSO_2^+$, which is very similar to the mechanism involved in the preparation of aromatic ketones (via the acyl cation, $ArCO^+$)[21] in PPA.

In conclusion, we have demonstrated that a readily available and inexpensive reagent, AMA, is very effective for the thia-Fries rearrangement of arylsulfonates. The simple procedure and work up, the lack of solvent in the reaction step, and the good yields make this method a useful addition to the present methodologies. Hence, we believe that it will find wide application in organic synthesis as well as in the industry.

EXPERIMENTAL

General

^{1}H NMR and ^{13}C NMR spectra were measured on Bruker Advance DPX FT 250 and 62.9 MHz spectrometry with TMS as an internal standard. IR spectra were obtained on Perkin-Elmer or FTIR-800 instruments. Mass spectra were obtained on a Shimadzu GCMS0QP 1000EX at 20 and 70 ev, or both.

All starting materials, *p*-toluenesulfonic acid and phenols, were purchased from Fluka or Merck. Alumina (Al_2O_3) type 5016A, (pH = 0.9) and methanesulfonic acid 98% were purchased from Fluka.

Typical Procedure

General Procedure for Thia-Fries Rearrangement of Arylsulfonates

To a mixture of alumina (3 g) and methansulfonic acid (10 mL) at 150°C, arylsulfonate (20 mmol) was added and stirred for 2 h. Then the mixture was poured into water, extracted with chloroform (2 × 25 mL), washed with 5% sodium hydrogen carbonate solution (2 × 25 mL), dried over anhydrous $CaCl_2$, and evaporated. The crude product was isolated in a pure state by silica gel column with *n*-hexane/ethyl acetate. The produced hydroxyaryl sulfones were known. Specific detailed data for each of the compounds are given below:

(a) 2-[(4-Methylphenyl)sulfonyl]phenol[8f]

White crystal, m.p.: 124–125°C (Lit.[8f] 126°C); IR (neat): 3292, 159, 1361, 1145 cm^{-1};^1H NMR ($CDCl_3$, 250 MHz) δ 2.42 (s, 3H), 7.00 (m, 2H), 7.30 (d, 2H), 7.45 (d, 1H), 7.65 (d, 1H), 7.84 (d, 2H), 9.26 (s, 1H); MS (*m/e*) = 248 (M^+, 59.6), 172 (23.5), 94 (58.2), 65 (100, base peak).

(b) 4-[(4-Methylphenyl)sulfonyl]phenol[8f]

White crystal, m.p.: 143–144°C (Lit.[8f] 143°C); IR (neat): 3375, 1585, 1284, 1144 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.38 (s, 3H), 6.30 (s, 1H), 6.90 (d, 2H), 7.37 (d, 2H), 7.79 (d, 4H); MS (*m/e*) 249(M^+, 100, base peak), 141 (45.8), 108 (43.4), 91 (32.6), 65 (66.2), 43 (54.7).

(c) 2-Methyl-6-[(4-methylphenyl)sulfonyl]phenol[22]

White crystal, m.p.: 130–131°C (Lit.[22] 130–132°C); IR (neat): 3330, 1593, 1284, 1144 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.45 (s, 3H), 2.58 (s, 3H), 6.80 (t, 1H), 7.35 (d, 3H), 7.85 (d, 2H), 9.30 (s, 1H); MS (*m/e*) 262 (M^+, 100, base peak), 195 (17.6), 155 (64.6), 107 (93.0), 65 (41.3), 43 (68.5).

(d) 2-Methyl-4-[(4-methylphenyl)sulfonyl]phenol[22]

White crystal, m.p.: 117–119°C (Lit.[22] 120°C); IR (neat): 3367, 1590, 1283, 1147 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.25 (s, 3H), 2.38 (s, 3H), 5.40 (s, 1H), 6.80 (d, 1H), 7.25 (d, 2H), 7.66 (d, 2H), 7.78 (d, 2H); MS (*m/e*) 262 (M^+, 0.2), 247 (98.2), 155 (11.0), 139 (100, base peak), 107 (11.1), 91 (32.7), 65 (35.9), 43 (15.1).

(e) 5-Methyl-2-[(4-methylphenyl)sulfonyl]phenol[23]

White crystal, m.p.: 144–145°C (Lit.[23] 145–147°C); IR (neat): 3315, 1594, 1300, 1149 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz δ 2.30 (s, 3H), 2.38 (s, 3H), 6.65 (s, 1H), 6.78 (d, 1H), 7.31 (d, 2H), 7.47 (d, 2H), 7.77 (d, 2H), 9.16 (s, 1H); MS (*m/e*) 262 (M^+, 45.4), 246 (33.4), 228 (25.7), 180 (37.9), 139 (100, base peak), 107 (21.5), 91 (91.4), 65 (83.1).

(f) 3-Methyl-4-[(4-methylphenyl)sulfonyl]phenol[23]

White crystal, m.p.: 150–151°C (Lit.[23] 151-2°C); IR (neat): 3366, 1595, 1317, 1153 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.32 (s, 3H), 2.40 (s, 3H,), 6.41(s, 1H), 6.65 (s, 1H), 6.79 (d, 1H), 7.26 (d, 2H), 7.69 (d, 2H), 8.04 (d, 1H); MS (*m/e*) 262 (M^+, 24.7), 244 (25.0), 227 (12.1), 196 (100, base peak), 153 (50.0), 107 (26.4), 77 (99.8).

(g) 4-Methyl-2-[(4-methylphenyl)sulfonyl]phenol[23]

White crystal, m.p.: 133–134°C (Lit.[23] 135°C); IR (neat): 3319, 1595, 1367, 1147 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.26 (s, 3H), 2.4 (s, 3H), 6.9 (d, 1H), 7.25 (d, 3H), 7.34 (s, 1H), 7.83 (d, 2H), 9.08 (S, 1H); MS (*m/e*) 262 (M^+, 26.0), 186 (51.9), 107 (100, base peak), 77 (73.8), 51 (22.5).

(h) 4-Chloro-2-[(4-methylphenyl)sulfonyl]phenol[8f]

White crystal (needle type), m.p.: 127–128°C (Lit.[8f] 127°C); IR (neat): 3386, 1596, 1290, 1141, 817 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.32 (s, 3H), 6.68 (d, 1H), 7.13 (d, 2H), 7.24 (s, 1H), 7.73 (d, 2H), 9.10 (s, 1H); MS (*m/e*) 282 (M^{+2}, 63.5), 215 (26.1), 126 (14.5), 108 (15.8), 92 (100, base peak), 65 (54.9), 41 (23.4).

(i) 2-Chloro-4-[(4-methylphenyl)sulfonyl]phenol[23]

White crystal (cubic type), m.p.: 174–175°C (Lit.[23] 176°C); IR (neat): 3327, 1584, 1303, 1132, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.33 (s, 3H) 6.07 (s, 1H), 7.02 (d, 1H), 7.23 (d, 2H), 7.69 (d, 3H), 7.85 (s, 1H); MS (*m/e*) 282 (M^{+2}, 82.3), 175 (40.7), 139 (77.1), 108 (91.7), 9 (100, base peak), 65 (98.6), 41 (53.7).

(j) 5-Flouro-2-[(4-methylphenyl)sulfonyl]phenol[24]

White crystal m.p.: 128–130°C; IR (neat): 3345, 1591, 1279, 1148, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz)δ 2.35 (s, 3H), 6.60 (d, 1H), 7.19 (s, 1H), 7.24 (d, 2H), 7.58 (t, 1H), 7.72 (d, 2H), 9.35 (s, 1H); MS (*m/e*)266 (M^+, 98.4), 202 (20.1), 155 (22.6), 139 (22.2), 108 (47.1), 91 (100, base peak), 65 (65.6).

(k) 3-Flouro-4-[(4-methylphenyl)sulfonyl]phenol[24]

White crystal, m.p.: 124–126°C; IR (neat): 3405, 1609, 1319, 1140, 1248 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.34 (s, 3H, $-CH_3$), 6.50 (d, 1H), 6.68 (s, 1H), 7.07 (s, 1H), 7.26 (d, 2H), 7.76 (d, 3H); MS (*m/e*) 266 (M^+, 44.7), 159 (26.8), 139 (37.4), 108 (65.8), 91 (57.5), 65 (50.1), 43 (100, base peak).

(l) 2-[(4-Methylphenyl)sulfonyl]-1-naphthol[25]

White crystal, m.p. 128–130°C (Lit.[25]134°C); IR (neat): 3150, 1570, 1120, 1350 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.37 (s, 3H), 7.30 (d, 2H), 7.60 (m, 4H), 7.65 (d, 1H), 7.85 (d, 2H), 8.40 (d, 1H), 10.46 (s, 1H, OH); MS (*m/e*) 298 (M^+, 91.9), 191 (19.8), 162 (10.4), 139 (57.9), 115 (50.2), 91 (42.6), 59 (47.5), 43 (100, base peak).

(m) 4-[(4-Methylphenyl)sulfonyl]-1-naphthol[8f]

White crystal, m.p.: 160°C (Lit.[8f] 163°C); IR (neat): 3200, 1600, 1110, 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.38 (s, 3H), 6.93 (m, 4H), 7.26 (d, 2H), 7.85 (d, 1H), 7.90 (d, 2H), 8.10 (s, 1H), 8.21 (d, 1H); MS (*m/e*) 298(M^+, 100, base peak), 265 (11.5), 234 (23.1), 206 (22.7), 142 (73.2), 114 (64.6), 91 (47.4), 65 (48.2), 43 (43.5).

(n) 4-[(4-Methylphenyl)sulfonyl]-1,3-benzendiol[18]

White crystal, m.p.: 160–162°C (Lit.[18] 155–157°C); IR (neat): 3358, 1595, 1334, 1136 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.33 (S, 3H), 5.62 (s, 1H), 6.37 (d, 2H), 7.20(d,2H), 7.43 (d, 1H), 7.71 (d, 2H), 9.20 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) *d* 22.01, 105.02, 109.34, 126.95, 127.25, 130.42, 131.49, 132.82, 149.50, 154.32; MS (*m/e*) 264(M^+, 100, base peak) , 199 (21.1), 157(22.1), 125(14.31), 108 (33.8), 91 (60.0), 65 (57.3); UV ($CHCl_3$) λ_{max} 308.4 ($\varepsilon = 1993$).

(o) 4-Bromo-2-[(4-methylphenyl)sulfonyl]phenol[26]

White crystal (needle type), m.p.: 145–146°C; IR (neat): 3388, 1469, 1290, 1141, 131 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.43 (s, 3H), 6.89 (d, 1H), 7.34 (d, 2H), 7.51 (d, 1H), 7.73 (s, 1H), 7.81 (d, 2H), 9.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) *d* 22.05, 121.12, 125.47, 125.95, 127.42, 129.81, 130.67, 134.80, 138.33, 145.83, 145.66; MS (*m/e*) 328(M^{+2}, 46.9), 261(12.2), 181(10.5), 139 (28.0), 108 (16.4), 92 (100, base peak), 65 (58.4), 43 (47.6); UV ($CHCl_3$) λ_{max} 251 ($\varepsilon = 2909$), 307.7 ($\varepsilon = 1180$).

(p) 2-Bromo-4-([4-methylphenyl)sulfonyl]phenol[26]

White crystal, m.p.: 170–172°C; IR (neat): 3327, 1593, 1299, 1110, 723 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.41(s, 3H), 6.85 (t, 1H), 7.31 (d, 2H), 7.64 (d, 2H), 7.82 (d, 2H), 9.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) *d* 21.96, 111.06, 117.07, 127.89, 129.38, 130.42, 132.31, 135.30, 138.93, 144.75, 156.82; MS (*m/e*) 326 (M^{+2}, 6.4), 155 (38.5), 108 (12.4), 91 (82.0), 69 (42.3), 43 (100, base peak); UV ($CHCl_3$) λ_{max} 257.6 ($\varepsilon = 2801$), 301.3 ($\varepsilon = 1778$).

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