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$Al_2O_3/MeSO_3H$ (AMA) a Useful System for Direct Sulfonylation of Phenols with *p*-Toluenesulfonic Acid

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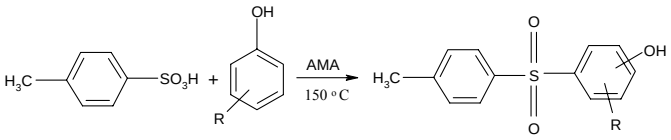
A useful method for direct sulfonylation of phenols with *p*-toluenesulfonic acid in the presence of $Al_2O_3/MeSO_3H$ system has been described.

Keywords: Hydroxyaryl sulfones, Phenols, Al_2O_3 , $MeSO_3H$, *p*-Toluenesulfonic acid

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 hydroxyaryl sulfones are well known as antiseptics and also they are useful as fungicides and bactericides [5]. Diaryl sulfones have been prepared by the reaction of arenesulfonyl chlorides with aromatic hydrocarbons under Friedel-Crafts condensations or by the condensation of an arenesulfonic acid with aromatic hydrocarbons in polyphosphoric acid [6] or solid acids [7]. However, polyphosphoric acid is a viscous liquid and is not easy to handle and also, the Jacobsen rearrangement may occur in its presence [8]. These methods have not been used for the preparation of hydroxyaryl sulfones.

We have recently reported the use of $Al_2O_3/MeSO_3H$ (AMA) system for Fries rearrangement [9], Beckmann rearrangement [10], conversion of nitriles into amides [11] and monoesterification of diols [12]. We report herein that AMA system is also applicable for the synthesis of hydroxyaryl sulfones, using *p*-toluenesulfonic acid and phenols with good yields (Scheme 1).



R = CH_3, F, Br, Cl, OH

Scheme 1.

EXPERIMENTAL

^{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 a Perkin-Elmer or FTIR-800 instruments. Mass spectra were obtained on a Shimadzu GCMS-QP1000EX at 20 and/or 70 eV.

All starting materials, *p*-toluenesulfonic acid and phenols, were used as purchased from Fluka or Merck. Alumina (Al_2O_3) type 5016A, (pH = 9.0), and methanesulfonic acid, 98%, were purchased from Fluka.

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General Procedure for Direct Sulfonylation of Phenols

Sulfonic acid (20 mmol) and phenol derivatives (20 mmol) were added to a mixture of alumina (3 g) and methanesulfonic acid (10 ml) at 150 ^{o}C and stirred for 4 h. Then the mixture was poured into water, extracted with chloroform (2 × 25 ml), washed with 5% sodium hydrogen carbonate solution (2 × 20 ml) and dried over anhydrous $CaCl_2$. The crude product was purified by silica gel column using *n*-hexane/ethyl acetate. Specific detailed data for each of the produced hydroxyaryl sulfones are given below:

2-[(4-Methylphenyl) sulfonyl] phenol [13]. White crystal, m.p: 124-5 ^{o}C (Lit. [13] 126 ^{o}C); IR (neat): 3292, 159, 1361, 1145 cm^{-1}; ^{1}H 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).

4-[(4-Methylphenyl) sulfonyl] phenol [13]. White crystal, m.p.: 143-4 ^{o}C (Lit. [13] 143 ^{o}C); IR (neat): 3375, 1585, 1284, 1144 cm^{-1}; ^{1}H 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).

2-Methyl-6-[(4-methylphenyl) sulfonyl] phenol [14]. White crystal, m.p.: 130-1 ^{o}C (Lit. [14] 130-2 ^{o}C); IR (neat): 3330, 1593, 1284, 1144 cm^{-1}; ^{11}H 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).

2-Methyl-4-[(4-methylphenyl) sulfonyl] phenol [14]. White crystal, m.p.: 117-9 ^{o}C (Lit. [14] 120 ^{o}C); IR (neat): 3367, 1590, 1283, 1147 cm^{-1}; ^{1}H 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).

5-Methyl-2-[(4-methylphenyl) sulfonyl] phenol [15]. White crystal, m.p.: 144-5 ^{o}C (Lit. [15] 145-7 ^{o}C); IR (neat): 3315, 1594, 1300, 1149 cm^{-1}; ^{1}H 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).

3-Methyl-4-[(4-methylphenyl) sulfonyl] phenol [15]. White crystal, m.p.: 150-1 ^{o}C (Lit. [15] 151-2 ^{o}C); IR (neat): 3366, 1595, 1317, 1153 cm^{-1}; ^{1}H 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).

4-Methyl-2-[(4-methylphenyl) sulfonyl] phenol [13]. White crystal, m.p.: 133-4 ^{o}C (Lit. [13] 135 ^{o}C); IR (neat): 3319, 1595, 1367, 1147 cm^{-1}; ^{1}H 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).

4-Chloro-2-[(4-methylphenyl) sulfonyl] phenol [15]. White crystal (needle type), m.p.: 127-8 ^{o}C (Lit. [15] 127 ^{o}C); IR (neat): 3386, 1596, 1290, 1141, 817 cm^{-1}; ^{1}H 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).

2-Chloro-4-[(4-methylphenyl) sulfonyl] phenol [13]. White crystal (cubic type), m.p.: 174-5 ^{o}C (Lit. [13] 176 ^{o}C); IR (neat): 3327, 1584, 1303, 1132, 737 cm^{-1}; ^{1}H 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).

5-Flouro-2-[(4-methylphenyl) sulfonyl] phenol [16]. White crystal m.p.: 128-30 ^{o}C; IR (neat): 3345, 1591, 1279, 1148, 1090 cm^{-1}; ^{1}H 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).

3-Fluro-4-[(4-methylphenyl) sulfonyl] phenol [16]. White crystal, m.p.: 124-6 ^{o}C; IR (neat): 3405, 1609, 1319, 1140, 1248 cm^{-1}; ^{1}H 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).

2-[(4-Methylphenyl) sulfonyl]-1-naphthol [13]. White crystal, m.p. 128-30 ^{o}C (Lit. [13] 129 ^{o}C); IR (neat): 3150, 1570, 1120, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.37 (s, 3H), 7.3 (d, 2H), 7.6 (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).

4-[(4-Methylphenyl) sulfonyl]-1-naphthol [13]. White crystal, m.p.: 160 °C (Lit. [13] 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), 7.9 (d, 2H), 8.1 (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).

4-[(4-Methylphenyl) sulfonyl]-1,3-benzendiol [17]. White crystal, m.p.: 160-2 °C (Lit. [17] 155-7 °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 (ε = 1993).

4-Bromo-2-[(4-methylphenyl) sulfonyl] phenol [18]. White crystal (needle type), m.p.: 145-6 °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 (ε = 2909), 307.7 (ε = 1180).

2-Bromo-4-([4-methylphenyl) sulfonyl] phenol [18]. White crystal, m.p.: 170-2 °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* 21.963, 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 (ε = 2801), 301.3 (ε = 1778).

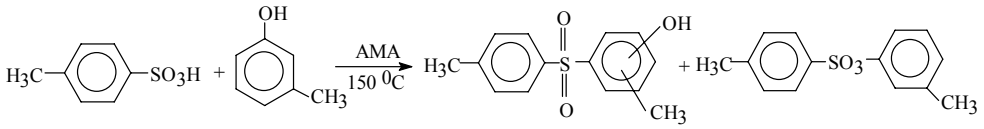
RESULTS AND DISCUSSION

As a model reaction, the condensation of *p*-toluenesulfonic acid **(1)** with *m*-cresol **(2)** was studied under different reaction conditions using diverse systems (Scheme 2). The results are summarized in Table 1.

According to Table 1, a mixture of Al_2O_3 and $MeSO_3H$ in 3:15 molar ratio gave the best results when carried out at 150 °C for 4 h. The results also show the importance of the use of both Al_2O_3 and $MeSO_3H$ respectively. Namely, in the absence of $MeSO_3H$ (entry 11) or Al_2O_3 (entry 10) the attempted phenylsulfonylation did not afford hydroxyaryl sulfone **3**. It is obvious that phenol **2** does not sulfonylated with sulfonyl chloride in presence of Lewis acids such as $AlCl_3$, $ZnCl_2$, $FeCl_3$, $SnCl_4$ and $SbCl_5$ (Table 1, entries 2, 4, 8, 10 and 13).

The results show that all hydroxyaryl sulfones are prepared without Jacobsen rearrangement [8]. We have confirmed that in AMA media (in accordance with PPA) *p*-toluenesulfonic acid reacts without desulfonylation and trans-sulfonation reactions. Because of this initial observation, it seemed advantageous to investigate this method as a new and better way to synthesize hydroxyaryl sulfones.

A typical experimental procedure is as follows: *p*-toluenesulfonic acid **1** (2 mmol) and phenol **2** (2 mmol) were added to a mixture of $MeSO_3H$ (1 ml, 15 mmol) and Al_2O_3 (0.3 g, 3 mmol). The mixture was stirred and heated in an oil bath at 150 °C for 4 hrs. After a usual work up, hydroxyaryl sulfones were obtained in 75% yield. Infrared analysis of the products showed two strong absorption bonds at 1300-1350 and 1100-1150 cm^{-1}, which are characteristic of the sulfone group, and also a strong bond at 3000-3400 cm^{-1} for hydroxyl



1 **2** **3** **4**

Scheme 2

group.

To establish the generality and applicability of this method, various phenols were subjected to the same reaction conditions to furnish the corresponding hydroxylaryl sulfones in good yields. Thus phenols with both electron-donating and withdrawing substituents were carried out in the presence of

Table 1. Sulfonylation of Phenol **2** under Various Reaction Conditions

.Entry	Conditions	Time (h)	Yield (%)[a]	
			3 (*ortho: para*)	**4**
1	$AlCl_3$, 80 °C [19] , Sulfonic acid **1**	2	-	-
2	$AlCl_3$, 80 °C, *p*-tosyl chloride, nitrobenzene [19]	2	-	-
3	$ZnCl_2$, $POCl_3$, 80 °C, Sulfonic acid **1** [20]	24	-	-
4	$ZnCl_2$, 80 °C [20], *p*-tosyl chloride, nitrobenzene	24	-	-
5	PPA, 150-60 °C [21] , Sulfonic acid **1**	8	40 (3:1)[b]	-
6	P_2O_5, CH_3SO_3H, 150 °C [22], Sulfonic acid **1**	24	25 (0:1)	-
7	$FeCl_3$, 80 °C [7], Sulfonic acid **1**	4	-	-
8	$FeCl_3$, 80 °C, *p*-tosyl chloride, nitrobenzene [7]	4	-	-
9	$SnCl_4$, 80 °C [7] , Sulfonic acid **1**	4	-	-
10	$SnCl_4$, 80 °C, *p*-tosyl chloride, nitrobenzene [7]	4	-	-
11	Montmorillonit Clay (Fe^{3+}), 100 °C [7], Sulfonic acid **1**	24	-	-
12	$SbCl_5$, 60 °C [23], Sulfonic acid **1**	2	-	10
13	$SbCl_5$, $60^{\circ 0}$C, *p*-tosyl chloride, nitrobenzene [23]	2	-	-
14	Triflic acid, 80 °C [24,25], Sulfonic acid **1**	8	-	60
15	CH_3SO_3H, 150 °C, Sulfonic acid **1**	4	-	-
16	Al_2O_3, 150 °C, Sulfonic acid **1**	4	-	-
17	Al_2O_3 (3 mmol), $MeSO_3H$ (15 mmol), 150 °C, Sulfonic acid **1**	4	75 (1:3) [c]	-
18	Al_2O_3 (2 mmol), $MeSO_3H$ (15 mmol), 150 °C , Sulfonic acid **1**	4	50 (1: 3)	-
19	Al_2O_3 (3 mmol), $MeSO_3H$ (30 mmol), 150 °C, Sulfonic acid **1**	4	45 (1:3)	-
20	Al_2O_3 (3 mmol), $MeSO_3H$ (15 mmol), 150 °C[d]	4	-	-

[a] Isolated yields. [b] 40% bis (4-methyl phenyl) sulfone was obtained (Jacobsen rearrangement).
[c] The ratio of the products were determined by ^{1}H NMR integration. [d] In the absence of *p*-toluenesulfonic acid.

AMA (Table 2).

According to Table 2, activated phenols gave a mixture of two isomers (*ortho* and *para*) hydroxyaryl sulfones in good yields (entry 1-4). *Para* chloro and *para* bromo phenols, selectively gave *ortho* isomer of hydroxyaryl sulfones in with yields of 68% and 60%, respectively (entries 5, 6). In order to

Table 2. Sulfonylation of Phenols Using a 1:5 Mixture of Al_2O_3 and $MeSO_3H$ (AMA) at 150 ^oC

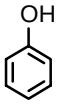
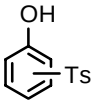
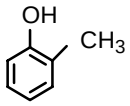
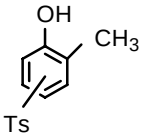
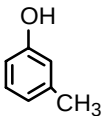
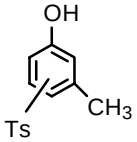
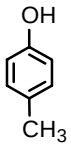
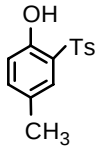
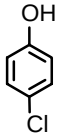
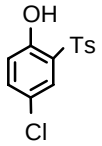
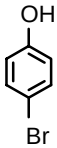
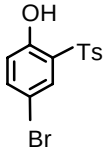
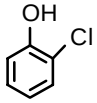
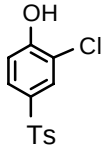
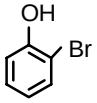
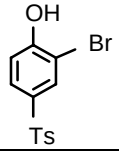
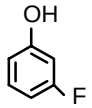
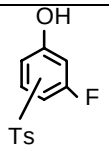
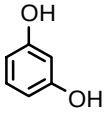
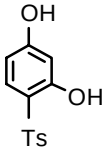
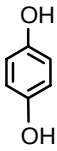
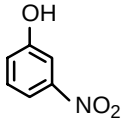
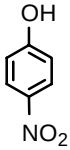
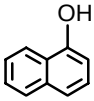
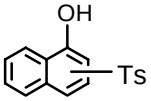
Entry	Phenols	Time (h)	Products [a]	Yield (%) [b, c] (*ortho: para)*
1		4		70 (1:5)
2		4		68 (1:3)
3		4		75 (1:3)
4		4		60 [d]
5		4		68
6		4		60
7		4		70
8		4		62

Table 2. Continued

Entry	Phenols	Time (h)	Products [a]	Yield (%) [b, c] (*ortho: para)*
9		4		68 (1:1)
10		4		70
11		12	no reaction	-
12		12	no reaction	-
13		12	no reaction	-
14		4		80 (10:1)

[a] Ts = Tosyl, [b]All yields refer to pure isolated products.[c]The ratio of the products were determined by ^{1}H NMR analysis. [d]IPSO rearrangement product, 3-methyl-4-[(methylphenyl) sulfonyl] phenol, is also produced (15%).

increase the yields of these hydroxyaryl sulfones, the reaction mixture was heated for a longer periodes, but changes in the yields were not occurred. Special mention must be made of the sulfonation of *ortho* chloro and bromo phenols. The corresponding *para* isomers selectively formed in with yields of 70% and 62%, respectively (entries 7,8). In particular, *m*-dihydroxy benzene undergoes the reaction to produce the corresponding sulfone in 70% yield (entry 10) and only monosulfynated product has been formed. However, the reaction of *p*-dihydroxy benzene was not afforded the corresponding sulfone (entry 11). With more bulky naphthol, the reaction is regioselective and the 2-isomer is the selective product (entry 14). Nitro substituted phenols do not react with *p*-tolounesulfonic acid to produce the corresponding hydroxyaryl sulfones. These results indicate that electrophilic substitution does not occur because electron-withdrawing group deactivates the aromatic ring. The relative reactivities of the aromatic substrates are consistent with a mechanism involving attack on the aromatic ring by 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, $ArCO^+$) in PPA [26].

In conclusion, we have demonstrated that a readily available and inexpensive reagent, AMA, is very effective for direct sulfonylation reaction of phenol and naphthol derivatives with *p*-toluenesulfonic acid. The simple procedure and work-up, the lack of solvent in the reaction step, and the high 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 industry.

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