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Study of regioselective methanesulfonylation of simple aromatics with methanesulfonic anhydride in the presence of zeolite catalysts

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Regioselective methanesulfonylation of simple aromatics using methanesulfonic anhydride can be achieved over zeolite catalysts. For example, methanesulfonylation of toluene over various cation-exchanged zeolite β catalysts affords higher *para*-selectivity in the synthesis of methyl tolyl sulfone than standard Friedel–Crafts methanesulfonylation utilising aluminium chloride.

Introduction

Sulfones are useful intermediates in organic synthesis[1] with applications in agrochemicals,[2] polymers[3–5] and other industrial fields.[6] Direct sulfonylation of aromatic compounds is one of the most important methods for the synthesis of sulfones.[7,8] However, relatively little detailed attention has been paid to this reaction.[9–13] In order to allow the reaction to proceed at a satisfactory rate, an activator such as $AlCl_3$ is usually needed, but $AlCl_3$ forms a 1 : 1 complex with the product and therefore has to be used in a more than stoichiometric amount.[7] Recently, several new catalytic systems have been developed for such sulfonylation reactions. These systems include the use of cation-exchanged zeolites (ZSM-5, Y, β),[14] Fe(III)-exchanged montmorillonite clay,[15,16] Bi(III) triflate,[17] TfOH–Bi(III) halide[18] and microwave irradiation in the presence of a small quantity of certain metal salts.[19–21]

Nevertheless, at the outset of the work reported here, highly selective production of alkyl aryl sulfones remained an elusive goal. We have shown that solid catalysts[22] can have advantages in alkylation,[23] acylation,[24] allylation,[25] bromination,[26] chlorination[27] and nitration[28] of aromatic compounds. Therefore, we undertook a detailed study of methanesulfonylation, to see if improvements could be made in the yield and *para*-selectivity of the reaction. We have already given a preliminary account of some of the results.[29] We now report the full details of this work.

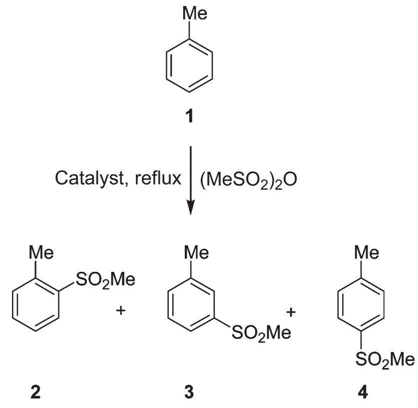
Results and discussion

Initially, different methanesulfonylating agents were tested for efficacy in the methanesulfonylation of toluene (**1**) under reflux conditions in the presence of selected solid catalysts. Methanesulfonic anhydride gave much better yields than methanesulfonyl chloride in these tests, while other reagents (acid, amide and ester) produced negligible yields of methanesulfonylated products. Methanesulfonic anhydride was therefore chosen for further study of the methanesulfonylation of toluene (**1**) in the presence of a range of heterogeneous catalysts, including large pore zeolites (Hβ, HY, HX, Naβ, NaY and H-Mordenite), a medium pore zeolite (HZSM-5), clays (K10 and KSF) and amorphous silica–aluminas (Synclyst 13 and 25). Under reflux conditions, the products of methanesulfonylation of **1** were methyl-*o*-tolyl sulfone (**2**), methyl-*m*-tolyl sulfone (**3**) and methyl-*p*-tolyl sulfone (**4**) [eqn. (1)]. The yields and selectivities obtained under a standard set of conditions are recorded in Table 1.

Table 1 Methanesulfonylation of toluene (**1**) over various solid catalysts according to eqn. (1)[a]

Entry	Catalyst (Si/Al ratio)	Yields (%)[b]	Isomer proportion (%)[c]		
			2	**3**	**4**
1	Hβ (25)	78	32	11	57
2	Hβ (25)[d]	82	35	11	54
3	HY (2.7)	6	44	10	46
4	HY (2.75)	11	41	9	50
5	HY (5.25)	34	44	10	46
6	HY (16.15)	59	47	13	40
7	HY (19.4)	56	46	14	40
8	HY (30.15)	50	47	12	41
9	HY (45)	12	46	12	42
10	HX (1.2)	—	—	—	—
11	Naβ (25)	12	10	5	85
12	NaY (12.5)	56	47	8	45
13	NaY (28)	62	48	8	44
14	H-Mordenite (10)	9	43	12	45
15	H-Mordenite (18.23)	22	47	14	39
16	HZSM-5 (38)	36	48	15	37
17	HZSM-5 (150)	6	48	14	38
18	K10	78	46	12	42
19	KSF	57	49	14	37
20	Synclyst 13	85	56	10	34
21	Synclyst 25	56	49	13	38

[a] A mixture of catalyst (0.6 g), $(MeSO_2)_2O$ (1.22 g, 7 mmol) and dry toluene (15 ml) was refluxed for 18 h. [b] Isolated yield based on anhydride. [c] Measured by quantitative GC and ^1H NMR (400 MHz). [d] Product extracted with toluene (2 × 15 ml).



(1)

The results in Table 1 show that Synclyst 13 (Entry 20) produced the highest yield of sulfones **2**–**4** (85%), based on the methanesulfonic anhydride added. The yield could be raised to 91% by the use of a dry bag during transfer of the anhydride

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Table 2 Methanesulfonylation of toluene (**1**) according to eqn. (1)[a] over various quantities of Naβ (Si/Al = 25) under various reaction conditions

Entry	Naβ/g	*t*/h	Yields (%)[b]	Isomer proportions (%)[c] 2	3	4
1	0.6	18	12	10	5	85
2	1	8	34	13	6	81
3	1[d]	8	31	12	5	83
4	1	18	40	13	5	82
5	1	24	42	15	6	79
6	1	48	47	17	8	75
7	2	18	31	10	4	86
8	2	24	32	11	5	84
9	2	30	37	12	5	83
10	3	18	18	13	6	81
11	3	24	20	14	6	80
12	3	48	24	17	7	76

[a] A mixture of Naβ, $(MeSO_2)_2O$ (1.22 g, 7 mmol) and dry toluene (15 ml) was refluxed for the indicated reaction time. [b] See footnotes *b* and *c* to Table 1. [c] See footnotes *b* and *c* to Table 1. [d] Toluene (25 ml) was used.

Table 3 Methanesulfonylation of toluene (**1**) according to eqn. (1) over partially exchanged Naβ solution[a]

Entry	NH_4Cl solution/M[b]	Yields (%)[c]	Isomer proportion (%)[d] 2	3	4
1	1.0	77	39	12	49
2	0.5	68	39	11	50
3	0.25	54	21	7	72
4	0.125	42	20	7	73
5	0.0625	19	17	4	79

[a] See footnote *a* to Table 1. [b] The standard procedure for cation exchange is: Naβ (1 g) was stirred in a refluxing aqueous NH_4Cl solution (10 ml) for 1 h, then filtered, washed with water (10 ml), subjected to a second exchange, washed with water until halide-free, and then calcined at 400 °C. No attempt was made to estimate the degree of cation exchange in individual cases. Partial exchanges were carried out on Naβ received from the supplier. [c] See footnotes *b* and *c* to Table 1. [d] See footnotes *b* and *c* to Table 1.

and by the addition of a very small amount of phosphorus pentoxide to the reaction mixture. Unfortunately, although the yield was excellent, the regioselectivity was unexceptional (**2**:**3**:**4** = 56:10:34). Synclyst 25 (Entry 21), K10 (Entry 18) and KSF (Entry 19) were also reactive and gave better *para*-selectivities (37–42%), but the overall yields of products **2**–**4** were lower (56–78%) with these catalysts.

The results also indicate that H-Mordenite and HZSM-5 (Entries 14–17) are not good catalysts for the methanesulfonylation of toluene (**1**). The poor yields (9–22%) obtained on use of H-Mordenite may be due to the limited one-dimensional entry to the pores of this solid, which causes statistical disadvantage in comparison to a catalyst with two- or three-dimensional entry. In the HZSM-5 case, reaction within the restricted pores of the catalyst is highly unlikely, so that any reaction that took place was probably catalysed at external sites.

In addition, we found that zeolite HX (Entry 10) gave no reaction, presumably because its acidic sites are not strong enough. Similarly, samples of HY zeolites with low Si/Al ratios gave only low yields of sulfones. However, a moderate yield (34–59%) of sulfones **2**–**4** could be achieved with some HY zeolite samples (Entries 5–8). For example, the use of HY (Si/Al = 5.25, Entry 5) led to a 34% yield of sulfones **2**–**4** with a better *para*-selectivity (**2**:**3**:**4** = 44:10:46) than standard Friedel–Crafts methanesulfonylation utilising $AlCl_3$ as the Lewis acid. Similar yields and selectivities were achieved by the use of NaY catalysts (Entries 12 and 13).

Zeolite Hβ (Si/Al = 25, Entries 1 and 2) was the most active zeolite tried, giving an 82% yield of sulfones **2**–**4** with an isomer distribution of 35:11:54. Increasing the quantity of Hβ gave the same or a slightly lower yield. The sample of zeolite Hβ that was recovered from the reaction depicted in eqn. (1) was regenerated by calcination at 400 °C and reused up to three times. The yield and selectivity were virtually the same.

To our surprise, Naβ (Si/Al = 25, Entry 11) produced only a low yield (12%) of methanesulfonylated products **2**–**4**, but with high *para*-selectivity (**2**:**3**:**4** = 10:5:85). Therefore, we undertook a more detailed study of the methanesulfonylation of toluene (**1**) with Naβ as a catalyst in the hope of enhancing the production of sulfones **2**–**4** while retaining the higher *para*-selectivity.

Initially, to determine if there was any benefit to gained by varying the amount of Naβ catalyst and the duration of the reaction, the amount of Naβ was varied from 0.6 to 3.0 g and the duration of the reaction was varied from 8 to 48 h. The results obtained are given in Table 2.

It was found that for reactions carried out under reflux over 18 h, increasing the amount of Naβ from 0.6 g to 1 g increased the overall yield of sulfones **2**–**4** by 28% (Entry 4) without affecting the isomer distribution significantly. However, doubling the amount of Naβ to 2 g showed only a little improvement in *para*-selectivity (86%) but a reduction in overall yield by 9% (Entry 7). A further reduction in yield was observed when the amount of catalyst was increased to 3 g (Entry 10). Therefore, it was concluded that the most suitable quantity of Naβ is 1 g.

The general trend on increasing the reaction time was an increase in the overall yield of sulfones **2**–**4** with little variation in the isomer distribution. The yield of **2**–**4** was increased from 34 to 40% with no significant changes in the isomer distribution on increasing the reaction time from 8 to 18 h when Naβ (1 g) was used (Entries 2 and 4). Clearly, the majority of the reaction occurred within 8 h and only an extra 9% overall yield was obtained in the next 10 h. Also, the yield increased only by 16% when the reaction time was increased form 18 h to 48 h but the *para*-selectivity was lower in this case (Entry 6). Therefore, it was decided to standardise the reaction time as 18 h.

As Hβ gave a good yield (82%) with *para*-selectivity of 54%, while Naβ gave a low yield (12%) but with a high *para*-selectivity (85%), partially exchanged zeolite β catalysts were introduced. Partial exchanges were carried out on Naβ with various concentrations of aqueous NH_4Cl solution (1.0–0.0625 M). These partially exchanged β catalysts (0.6 g) were then used in the methanesulfonylation of toluene (**1**) under reflux conditions [eqn. (1)] for 18 h. The yields and selectivity of sulfones **2**–**4** obtained are recorded in Table 3.

The first batch of Naβ, which was treated with 1 M NH_4Cl solution (Entry 1, Table 3), gave results that were very similar to those of Hβ (Entry 1, Table 1) in both yield and *para*-selectivity. It is therefore fair to assume that this batch was essentially completely exchanged from Naβ to Hβ. The second batch of Naβ, which was treated with 0.5 M NH_4Cl solution (Entry 2, Table 3), showed no improvement in selectivity towards the desired isomer **4** but a reduction in overall yield by 9%, compared to Hβ. The third batch of Naβ, which was treated with 0.25 M NH_4Cl solution (Entry 3, Table 3), suffered another reduction in yield by a further 14%, but the *para*-selectivity improved to 72%. The fourth and fifth batches of Naβ (Entries 4 and 5) resulted in still lower yields of sulfones **2**–**4**, but the *para*-selectivity increased further to only a small extent. It was clear that the sulfone **4** could be produced in 79% selectivity but in low overall yield (19%) (Entry 5). These results suggested that there is a tradeoff in yield for *para*-selectivity. The catalyst loses activity but becomes more geometrically constrained due to the presence of larger sodium cations.

The higher *para*-selectivity using Naβ than using other catalysts suggests that there must be some active sites present within the network of pores and channels of the zeolite. It was then supposed that the supplied Naβ contained some proton-

Table 4 Methanesulfonylation of toluene (**1**) according to eqn. (1) over various quantities of completely exchanged Naβ[a,b]

Entry	Quantity of Naβ zeolite used/g		Yields (%)[c]	Isomer proportion (%)[d]		
	Initial/g	Added (g) at time (h)		**2**	**3**	**4**
1	0.6	—	6	4	2	94
2	1.0	—	18	3	2	95
3	2.0	—	11	5	3	92
4	1.0	(1.5) 0.50 × 3 (4)	15	2	1	97
5	1.0	(1) 0.25 × 4 (2)	11	6	4	90
6	1.0	(1) 0.50 × 2 (4)	9	6	4	90
7	1.0	(1) 0.25 × 4 (4)	11	6	4	90

[a] A mixture of Naβ (1 g) and NaCl (1 M, 10 ml) was refluxed for 1 h. [b] Naβ, $(MeSO_2)_2O$ (1.22 g) in toluene (15 ml) was refluxed for 18 h. [c] See footnotes *b* and *c* to Table 1. [d] See footnotes *b* and *c* to Table 1.

exchanged sites and that if subjected to exchange with aqueous NaCl solution then the *para*-selectivity might be improved even further. Therefore, a series of experiments was conducted to determine the effect on yield and selectivity of using various quantities of completely exchanged Naβ zeolite in the methanesulfonylation of toluene (**1**) under reflux conditions [eqn. (1)] for 18 h. Various modes of addition of catalyst were made in a bid to optimise the yield and *para*-selectivity. The results are recorded in Table 4.

It was found that the use of fully exchanged Naβ (0.6 g) gave an overall yield of only 6% of sulfones **2**–**4**, of which 94% was the *para*-isomer **4** (Entry 1). Increasing the amount of catalyst to 1 g improved the yield to 18%, of which 95% was isomer **4** (Entry 2). When the amount of catalyst was increased to 2 g, however, the yield was reduced to 11%, with *para*-selectivity of 92% (Entry 3). A very high *para*-selectivity (**2** : **3** : **4** = 2 : 1 : 97) could be achieved, but in only 15% yield, when an extra three additional portions of fresh Naβ (0.5 g each) were added into the reaction mixture at 4 h intervals (Entry 4). The small amounts of *ortho*-isomer **2** (2%) and *meta*-isomer **3** (1%) are most likely produced from reaction at the external surface. Other variations in the mode of catalyst addition did not improve either the yield or selectivity (Entries 5–7). Therefore, this seems to be the limit to the yield, but these reactions are nevertheless highly *para*-selective.

The results suggested that zeolite Naβ offered the best *para*-selectivity (97%). Therefore, a range of cation-exchanged forms of zeolite β were prepared and then tested as catalysts (0.6 g) in the methanesulfonylation of toluene (**1**) under reflux conditions [eqn. (1)] for 18 h. The results are reported in Table 5.

Several features of interest emerge from the results recorded in Table 5. Within Group 1 (Entries 1–6) the yields decrease down the group as the cations become larger. The larger cations presumably block entry to the pore system of the zeolite, spoiling its potential as a catalyst. However, the restriction of the pore size might also be expected to lead to an increase in *para*-selectivity, which is apparent with sodium but tails off thereafter. With the larger cations it may be that a substantial proportion of the product arises from reaction at the external surface, thereby reducing the regioselectivity and also limiting the yield because of the relatively small number of available sites.

For Group 2 (Entries 7–11) the yields are higher than their Group 1 counterparts (Entries 1–6). Presumably the smaller divalent cations allow easier entry into the pore network, which would be consistent with the increased yields. There is also a general increase in *para*-selectivity going down the group as the cations get larger, but again at the expense of overall yield. $Be^{2+}\beta$ (Entry 7) appears to be an exception, giving a lower yield and higher selectivity than $Mg^{2+}\beta$ analogue (Entry 8).

With the exception of $In^{3+}\beta$ (Entry 27), all trivalent (Entries 12, 13, 15, 16, 18, 25, 26 and 28) and tetravalent (Entries 14 and 29) cation cases produced reasonable yields (typically 60–70%) and *para*-product distributions in the range of 40–50%. This is consistent with the idea that small cations allow more space for reaction and the results are fairly similar to those obtained with cations of the first transition series (Entries 17 and 19–22). Yields were typically 70% and *para*-proportions typically 50%.

Table 5 Methanesulfonylation of toluene (**1**) over various cation-exchanged zeolite β according to eqn. (1)[a,b]

Entry	Zeolite	Yields (%) of **2**–**4**[c]	Proportion (%) of **4**[d]
1	$H^+\beta$	78	57
2	$Li^+\beta$	51	55
3	$Na^+\beta$	18	95
4	$K^+\beta$	12	53
5	$Rb^+\beta$	3	79
6	$Cs^+\beta$	1	67
7	$Be^{2+}\beta$	52	67
8	$Mg^{2+}\beta$	69	43
9	$Ca^{2+}\beta$	62	61
10	$Sr^{2+}\beta$	33	62
11	$Ba^{2+}\beta$	50	71
12	$La^{3+}\beta$	62	46
13	$Ti^{3+}\beta$	72	44
14	$Zr^{4+}\beta$	75	43
15	$Ce^{3+}\beta$	68	50
16	$Cr^{3+}\beta$	73	50
17	$Mn^{2+}\beta$	68	45
18	$Fe^{3+}\beta$	46	54
19	$Co^{2+}\beta$	77	55
20	$Ni^{2+}\beta$	72	45
21	$Cu^{2+}\beta$	65	55
22	$Zn^{2+}\beta$	66	48
23	$Cd^{2+}\beta$	—	—
24	$Hg^{2+}\beta$	28	77
25	$Al^{3+}\beta$	69	47
26	$Ga^{3+}\beta$	60	45
27	$In^{3+}\beta$	1	71
28	$Ti^{3+}\beta$	66	43
29	$Sn^{4+}\beta$	77	40

[a] The standard procedure for cation exchange is: the supplied Hβ (1 g) following calcination at 550 °C to remove the template, was stirred in a refluxing aqueous solution of the corresponding metal chloride (1 M, 10 ml) for 1 h, then filtered, washed with water (10 ml), subjected to a second exchange, washed with water until halide-free, and then calcined at 400 °C. No attempt was made to estimate the degree of cation exchange in individual cases. [b] A mixture of catalyst (1 g), $(MeSO_2)_2O$ (1.22 g, 7 mmol) and dry toluene (15 ml) was refluxed for 18 h. [c] See footnotes *b* and *c* to Table 1. [d] See footnotes *b* and *c* to Table 1.

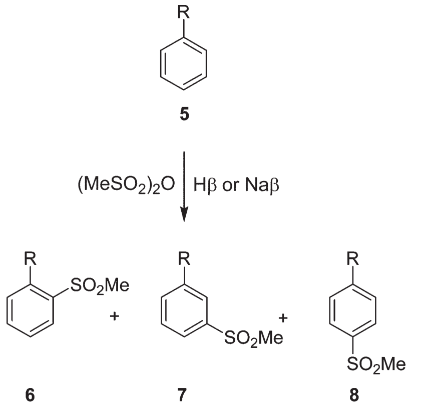
The cases which provided results that were out of line may have arisen from poor exchange, impurities or pore-blocking; however, the benefits to be gained from more careful scrutiny of them could not justify the amount of work involved in such study. It is clear that overall there is a broad correlation between cation size and both yield and selectivity. Unfortunately, there is a trade-off between the two, with those cases providing highest *para*-selectivity also giving rather poor yields.

In order to explore the scope of the reaction, similar conditions were applied to a range of mono-substituted benzenes **5** over Hβ or Naβ zeolites according to eqn. (2). The yields of methanesulfonylated products **6**–**8** and the selectivity are recorded in Table 6.

Table 6 Methanesulfonylation of simple aromatics (**5**) over Hβ or completely exchanged Naβ according to eqn. (2)[a]

Entry	Catalyst	R	Yields (%)[b]	Isomer proportion (%)[c] 6	7	8
1	Hβ	H	38	—	—	—
2	Naβ	H	3	—	—	—
3	Hβ	Me	78	32	11	57
4	Naβ	Me	18	3	2	95
5	Hβ	Et	53	15	11	74
6	Naβ	Et	13	14	10	76
7	Hβ	^{i}Pr	74	13	20	67
8	Naβ	^{i}Pr	5	2	8	90
9	Hβ	Ph	66	—	—	100
10	Naβ	Ph	2	—	—	100
11	Hβ	OMe	54	26	—	74
12	Naβ	OMe	43	17	—	83
13	Hβ	F	12	4	11	85
14	Naβ	F	2	—	—	100
15	Hβ	Cl	23	—	12	88
16	Naβ	Cl	—	—	—	—
17	Hβ	Br	33	—	—	100
18	Naβ	Br	—	—	—	—

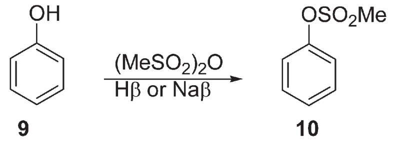
[a] A mixture of Hβ (0.6 g) or Naβ (1 g), $(MeSO_2)_2O$ (1.22 g) in toluene (15 ml) was refluxed for 18 h. [b] See footnotes *b* and *c* to Table 1. [c] See footnotes *b* and *c* to Table 1.



(2)

The results recorded in Table 6 indicated that in all cases the proton-exchanged zeolite β was considerably more active than Naβ. Anisole was the only substrate that afforded a reasonable yield (43%) of the corresponding sulfones employing Naβ as a catalyst (Entry 12). The methoxy group is a more highly activating *ortho*/*para*-director than alkyl-substituted benzenes. The high reactivity of anisole to electrophilic substitution may be the reason for the relatively high yield over Naβ. Also the substitution will favour higher *para*-selectivity. Ethylbenzene (Entries 5 and 6) and cumene (Entries 7 and 8) showed good reactivity similar to toluene. The higher *para*-selectivity achieved with cumene (Entries 7 and 8), biphenyl (Entries 9 and 10) and halobenzenes (Entries 13–15 and 17) may have been because steric hindrance was an added factor. Bromo- and chloro-benzenes did not show any reaction with Naβ (Entries 16 and 18), suggesting that they were not sufficiently reactive. Benzene was also relatively unreactive (Entry 1), as were fluorobenzene (Entry 13) and chlorobenzene (Entry 15). Hence low yields were achieved over Hβ.

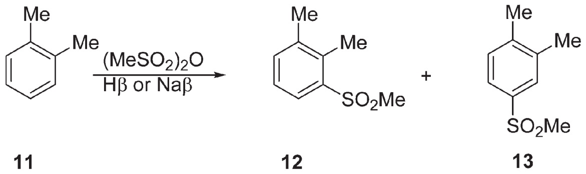
Phenol (**9**) reacted with methanesulfonic anhydride under similar conditions over Hβ and Naβ zeolites to produce the corresponding sulfonate ester **10** [eqn. (3)] in 75 and 31% isolated yields, respectively, despite the hydroxy group being highly *ortho*/*para*-directing.



(3)

In order to investigate the scope of this reaction, we planned to study methanesulfonylation reactions of disubstituted benzene derivatives using methanesulfonic anhydride as the reagent over Hβ and Naβ zeolites.

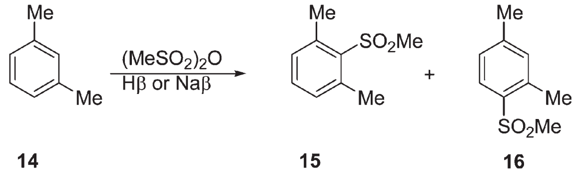
Studies were carried out on compounds having substituents with a modest influence on reactivity (methyl substituents). We first examined the methanesulfonylation of 1,2-dimethylbenzene (**11**) with methanesulfonic anhydride (1.22 g) over large pore zeolites Hβ (0.6 g) and Naβ (1 g) under reflux conditions for 18 h. The reaction produced the corresponding methanesulfonylated products **12** and **13** in which reaction took place at positions 3 and 4 [eqn. (4)].



(4)

Compounds **12** and **13** were obtained in 75% overall yield with a **12**:**13** ratio of 38:62 when reaction was carried out over Hβ, while the yield was only 6% with an isomer proportion of 34:66 when the reaction was carried out over Naβ.

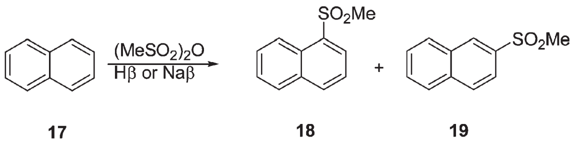
Similarly, methanesulfonylation of 1,3-dimethylbenzene (**14**) in the presence of Hβ and Naβ gave the corresponding methanesulfonylated products **15** and **16**, indicating that reaction took place at positions 2 and 4 [eqn. (5)].



(5)

Compounds **15** and **16** were obtained in 77% overall yield with a **15**:**16** ratio of 16:84 when reaction was carried out over Hβ (0.6 g), while the yield was only 3% with an isomer distribution of 15:85 when reaction was carried out over Naβ.

Finally, our attention was turned to the methanesulfonylation of naphthalene (**17**) using methanesulfonic anhydride (1.22 g) under reflux conditions for 18 h over Hβ (0.6 g) and Naβ (1 g) zeolites. The reaction took place at positions 1 and 2 to produce the corresponding methanesulfonylated products **18** and **19** [eqn. (6)].



(6)

The overall yield of **18** and **19** was 44% with a **18**:**19** ratio of 74:26 when reaction was carried out over Hβ, while the yield was 12% with an isomer ratio of 69:31 when reaction was carried out over Naβ.

Conclusion

Methanesulfonylation of toluene is less *para*-selective than arylsulfonylation, but quite high selectivity has been achieved in reactions that are relatively low yielding. The sodium-exchanged zeolite β offers the possibility of very high *para*-selectivity if the yield based on the anhydride is not critical (methanesulfonic acid can be recovered after work-up). Alternatively, reasonable *para*-selectivity can be achieved in quite good yield by use of proton-, calcium-, barium- or cobalt(II)-exchanged forms of zeolite β. All of these cases provide much better *para*-selectivity than the published reaction with aluminium chloride and methanesulfonyl chloride and in most cases the yield is substantially improved too. With the easy additional advantages of easy recovery and the lack of a metal-containing waste stream, this approach should prove attractive for sulfonylation reactions of simple aromatics.

Experimental

A Hewlett Packard HP 5890 (Series II) or PU 4400 gas chromatograph, fitted with a Carbowax capillary column (30 m, 0.32 mm ID) was used to analyse reaction mixtures. The GC conditions used for analysis were: the initial temperature was 100 °C followed by a ramp rate at 20 °C min^{-1} to 220 °C with helium as the carrier gas and nitrogen as a make-up gas. The injector temperature was 300 °C and the flame ionisation detector temperature was 350 °C. Further to GC analysis the isomer distributions were verified by ^{1}H NMR, which was carried out on a Bruker AC 400 MHz instrument. All samples were dissolved in $CDCl_3$ and TMS was the standard.

Chemicals

Methanesulfonic anhydride (98%) was obtained from Lancaster Research Chemicals. Other chemicals were obtained from Aldrich Chemical Company and were used directly without further purification. Toluene was distilled and stored over 3 Å molecular sieves.

Zeolites

Commercial zeolites were purchased from Aldrich Chemical Company or provided as gifts by Zeolyst International. Zeolites and Synclyst were freshly calcined at 400 °C and clays at 110 °C for a minimum of 6 h prior to use.

Typical experimental procedure for methanesulfonylation of toluene

Quantities are recorded in the footnotes of the appropriate tables. All reactions were carried out in a 50 ml round bottomed flask fitted with a magnetic bar and a condenser. Methanesulfonic anhydride (98%; 1.22 g, 7 mmol) was weighed into a flame-dried 50 ml round bottomed flask containing freshly calcined solid catalyst. Dry toluene (15 ml) was added to the mixture and then the reaction mixture was heated on an oil bath under reflux conditions for 18 h. The hot reaction mixture was filtered and the filtrate was immediately quenched with cold iced water (25 ml). The layers were separated and an additional extraction was carried out on the aqueous layer using toluene (15 ml). The catalyst recovered from the filtration was refluxed with CH_2Cl_2 (25 ml) for 30 min and the solid was then filtered. The toluene and dichloromethane extracts were combined and washed with Na_2CO_3 solution (1 M, 25 ml), then water (25 ml) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the residue was purified by Kugelrohr distillation (133–141 °C, 3 mm). The products were analysed by GC.

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