DOI: 10.1002/adsc.200900905

Iron(III) Chloride-Catalyzed Direct Sulfonylation of Alcohols with Sodium Arenesulfinates

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Received: December 29, 2009; Revised: June 18, 2010; Published online: August 16, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900905.

Abstract: A new protocol for the direct sulfonylation of benzylic, allylic and homoallylic alcohols with sodium arenesulfinates is described by using iron(III) chloride as a catalyst and chlorotrimethylsilane as an additive. This method requires no preactivation of alcohols. Surprisingly in the reaction with homoallyl alcohols nucleophilic addition of sulfinate anion, occurs at the terminal double bond instead of nucleophic substitution at the alcohol.

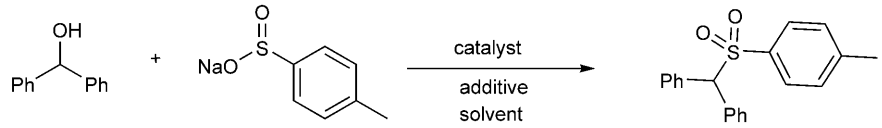
Keywords: benzylic alcohols; chlorotrimethylsilane; direct sulfonylation; homoallylic alcohols; sodium *p*-toluenesulfinate

The sulfonyl group is a well-established activating moiety that is introduced into an intermediate molecule for the construction of C–C bonds and other transformations.[1] The ability of the sulfonyl group to stabilize carbanions is one of the best known features of these compounds[2] and they also act as radical stabilizers[3] and cationic synthons.[4] Aryl alkyl sulfones have become a popular tool for the synthesis of various natural products as the α-carbanion is readily generated by reaction with a base and reacts with various electrophiles such as alkyl halides and aldehydes.[5] The allyl phenyl sulfones are also excellent sources for regio- and diasterioselective diene synthesis *via* Julia olefination procedure.[6] In this context, the direct sulfonylation of alcohols would be quite an important process to provide useful building blocks in organic synthesis. Earlier attempts to carry out the direct sulfonylation of alcohols were made using Brønsted acids such as AcOH, HCOOH and HCl to afford aryl alkyl sulfones.[7] However, in terms of functional group tolerance, side reactions, and the reaction conditions, most of these reagents may have one or more drawbacks. The direct sulfonylation of a hydroxy group in alcohols by sulfinate salts through nucleophilic substitution is generally difficult because of the inefficient leaving group ability of the hydroxy group which generally requires preactivation by transforming it into a good leaving group such as halide or mesylate.[8] Recently, the direct sulfonation of benzyl carbamates and allylic alcohols using palladium catalysts has been developed.[9] Although the above methods are encouraging, they require expensive phosphine ligands to promote the reaction which is undesirable because of their toxicity and sensitivity to air as well as moisture. Very recently Tian et al. reported a convenient protocol for the synthesis of benzylic and allylic sulfones through the reaction of alcohols with sulfinyl chlorides as well as alkylation reaction of sulfinic acids with sulfonamides *via* sp^3 C–N bond cleavage.[10]

Thus, in view of the demand for efficient, economic and ecologically valuable processes, the direct sulfonylation of alcohols with suitable salts without any stoichiometric hydroxy group activators would be an environmentally benign protocol. Since the pioneering work of Tamura and Kochi,[11] iron salts have emerged as alternative and promising catalysts for many organic transformations,[12] such as oxidation,[13] hydrogenation,[14] hydrosilylation,[15] rearrangement,[16] Michael addition,[17] carbon-carbon[18] and carbon-heteroatom bond-forming reactions;[19] also the oxidative coupling of arynes[20] has been extensively studied. In addition to that, various iron-catalyzed cross-coupling reactions including Sonogashira,[21] Heck,[22] Kumada,[23] Negishi,[24] and Suzuki[25] reactions have been developed. Moreover, iron salts have been successfully employed for the activation of alcohols towards various nucleophiles.[26]

We have recently developed a highly efficient method for the β-sulfonation of α,β-enones using $FeCl_3$/TMSCl as catalytic system.[27] As our previous research focused on the direct nucleophilic substitution of alcohols,[28] with regard to the importance of

Table 1. Optimization of reaction conditions for the direct sulfonylation.[a]



Entry	Catalyst	Additive	Solvent	Time [h]	Yield [%][b]
1	$FeCl_3$	TMSCl	CH_2Cl_2	10	96
2	$FeCl_2$	TMSCl	CH_2Cl_2	10	55
3	$Fe(acac)_2$	TMSCl	CH_2Cl_2	10	75
4	$FeSO_4$	TMSCl	CH_2Cl_2	10	30
5	Fe_2O_3	TMSCl	CH_2Cl_2	10	45
6	Fe(0)	TMSCl	CH_2Cl_2	10	65
7	$FeCl_3$	TMSCl	DMSO/DMF	10	0
8	$FeCl_3$	TMSCl	1,4 dioxane	10	35
9	$FeCl_3$	TMSCl	CH_3CN	10	10
10	$FeCl_3$	TMSCl	CH_3NO_2	10	25
11	$FeCl_3$	TBDMSCl	CH_2Cl_2	10	41
12	$FeCl_3$	TBDPSCl	CH_2Cl_2	10	23
13	$FeCl_3$	—	CH_2Cl_2	10	0
14	—	TMSCl	CH_2Cl_2	10	37
15	$FeCl_3$	TMSOTf	CH_2Cl_2	10	trace

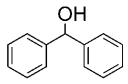
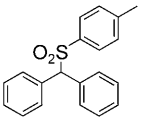
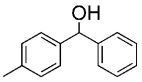
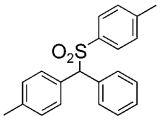
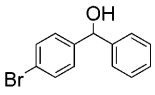
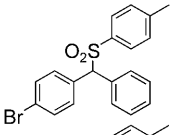
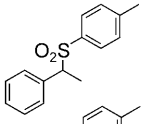
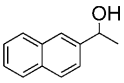
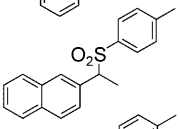
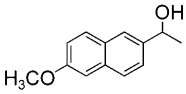
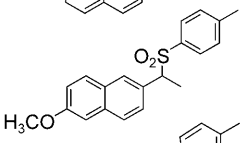
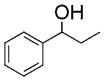
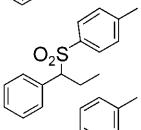
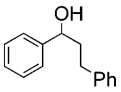
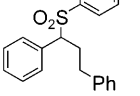
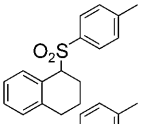
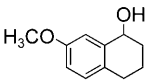
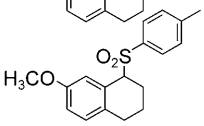
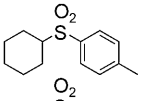
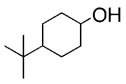
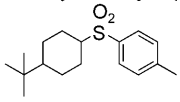
[a] *Reaction conditions:* benzhydrol (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol), catalyst (15 mol%), additive (1.2 equiv.), solvent (3 mL), 45 °C.
[b] Yield after column chromatography.

sulfones as intermediates in organic synthesis, in the present work, we report our investigations on the application of $FeCl_3$ as catalyst with TMSCl as an additive for the practical and atom economic synthesis of aryl alkyl sulfones through direct sulfonylation of benzyl, allylic and homoallylic alcohols. In our initial studies, various iron catalysts in combination with different solvents were investigated using benzhydrol and sodium *p*-toulenesulfinate as model substrates (Table 1). The reaction conditions were optimized and the best conditions were found to be 15 mol% $FeCl_3$ and 1.2 equiv. of TMSCl as shown in Table 1, entry 1. By virtue of these optimized conditions, the reaction afforded the desired product in 96% yield. Reactions with other iron catalysts such as $FeCl_2$, $Fe(acac)_2$, $FeSO_4$, Fe_2O_3 did not generate the desired product in appreciable yields (Table 1, entries 2–5). However, the reaction with Fe(0) gave the product in moderate yield (Table 1, entry 6). Subsequently, the reaction conditions were optimized by employing different solvents, wherein various polar and non-polar solvents were examined and it was found that all of them had a negative influence on the reaction to different degrees (Table 1, entries 7–10).

Having gained some crucial insights into the effect of different catalysts, further optimization was performed on exploring the effect of additives as well as temperature. Obviously, TMSCl proved to be the best additive, while other additives disfavored the reaction to different degrees (Table 1, entries 11 and 12). A control experiment with $FeCl_3$ in the absence of TMSCl was ineffective and no product was obtained, whereas TMSCl alone gave the desired product in 37% yield (Table 1, entries 13 and 14). Noteworthy is that TMSCl not only generates nucleophilic the sulfinate anion from its salts but also activates the alcohol with its Lewis acidity.[29] However, only a trace amount of the product was obtained with TMSOTf although it is more Lewis acidic, which suggests that the activity does not necessarily depend on the Lewis acidity of the silicon source (Table 1, entry 15).

Subsequently, on the basis of the optimized reaction conditions, the scope of this $FeCl_3$-catalyzed direct sulfonylation of several structurally diverse benzylic alcohols with sodium *p*-toluenesulfinate was explored and the results are summarized in Table 2. In general, the reaction proceeded efficiently with various benzylic alcohols and gave the products in good to excellent yields. Benzhydrols with both electron-donating or electron-withdrawing groups underwent the desired reaction and gave the products[30] in excellent yields. Other secondary benzylic alcohols (Table 2, entries 4–8) also underwent the reaction smoothly to give the desired products in good to ex-

Table 2. Direct sulfonylation of different secondary alcohols with sodium *p*-toluenesulfinate salt using $FeCl_3$ and TMSCl.[a]

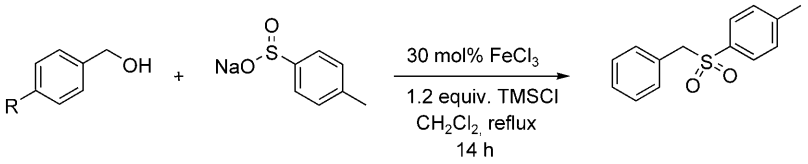
Entry	Alcohol	Product	Time [h]	Yield [%]
1			10	96
2			10	95
3			10	95
4			12	62
5			12	74
6			12	80
7			12	80
8			12	60
9			12	75
10			12	67
11			12	71
12			12	65

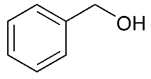
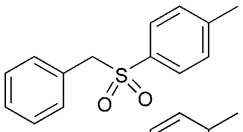
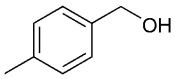
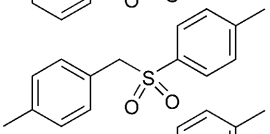
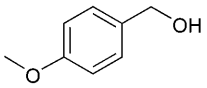
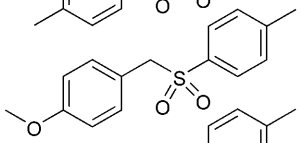
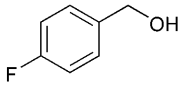
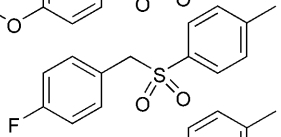
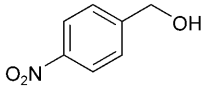
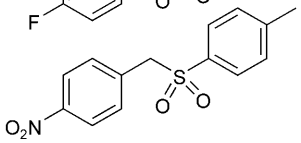
[a] *Reaction conditions:* alcohols (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol), $FeCl_3$ (15 mol%), TMSCl (1.2 mmol), dichloromethame (3 mL), 45 °C.
[b] Yield after column chromatography.

cellent yields, which can be attributed to the formation of a more stabilized carbocation intermediate.[31] The formed products were useful for the synthesis of tri- and tetrasubstituted olefins.[5d] The reaction was equally effective for the sulfonylation of cyclic benzylic alcohols and gave the expected sulfonyl ethers in good yield (Table 2, entries 9 and 10).

The present catalytic system was also found to be suitable for the direct sulfonylation of non-benzylic alcohols, such as cyclohexanol and 4-*tert*-butylcyclohexanol and the respective products obtained in good

Table 3. Direct sulfonylation of different benzyl alcohols with sodium *p*-toluenesulfinate salt using $FeCl_3$ and TMSCl.[a]



Entry	Alcohol	Product	Yield [%]
1			43
2			58
3			35
4			38
5			trace

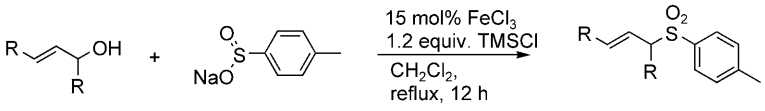
[a] *Reaction conditions:* alcohols (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol), $FeCl_3$ (15 mol%), TMSCl (1.2 mmol), dichloromethane (3 mL) at 45 °C.
[b] Yield after column chromatography average on 3 runs.

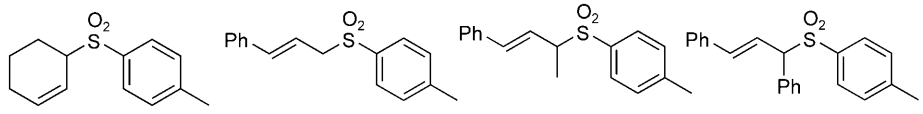
yields (Table 2, entries 10 and 11). However, the reactions with butanol, isopropyl alcohol and *tert*-butyl alcohol were not successful.

With these encouraging results in hand, we subsequently set out to explore the scope of various benzyl alcohols and the results are listed in Table 3. In this study different substituted benzyl alcohols were transformed into their corresponding benzyl aryl sulfones in moderate yields. However, only a trace amount of the product was formed with *p*-nitrobenzyl alcohol which may be attributed to the generated cation that is influenced by the electronic and steric factors of benzylic alcohols and the formed cation may be unstable.

In further experiments, with regard to the importance of allylic sulfones,[32] we investigated the sulfo-

Table 4. Direct sulfonylation of different allyl alcohols with sodium *p*-toluenesulfinate salt using $FeCl_3$ and TMSCl.[a]

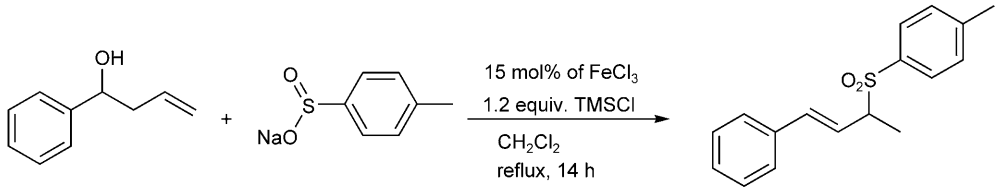


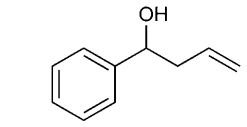
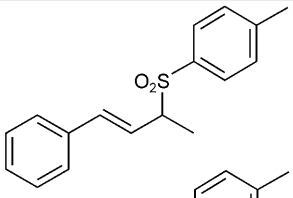
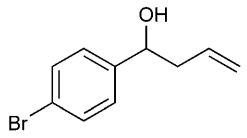
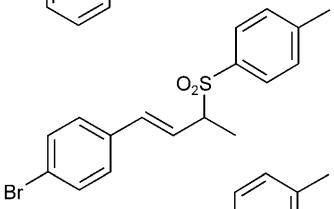
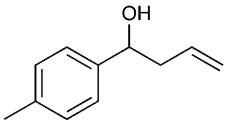
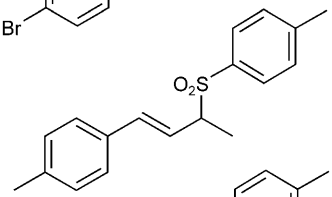
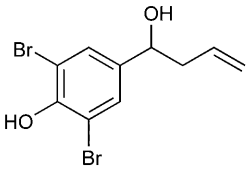
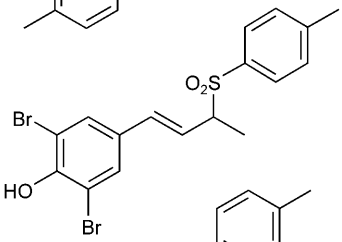
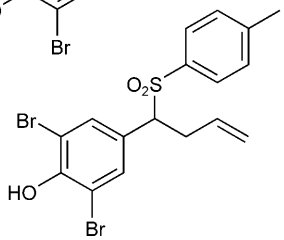


entry 1, 65% entry 2, 53% entry 3, 82% entry 4, 82%

[a] All reactions were performed on a 1.0 mmol scale in the presence of 15 mol% $FeCl_3$, 1.2 equiv. of TMSCl in Dichloromethane at 45 °C.
[b] Yields are the average of 3 runs.

Table 5. Direct sulfonylation of different homoallyl alcohols with sodium *p*-toluenesulfinate salt using $FeCl_3$ and TMSCl.[a]



Entry	Homoallylic alcohol	Product	Yield [%]
1			55
2			60
3			58
4			8
			52

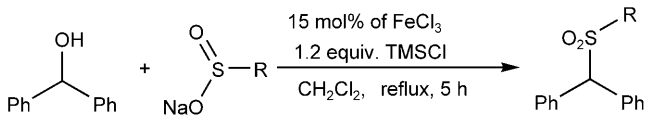
[a] All reactions were performed on a 1.0 mmol scale in the presence of 15 mol% of $FeCl_3$, 1.2 equiv. of TMSCl in dichloromethane at 45 °C.
[b] Yields are the average of 3 runs after column chromatography.

nylation of four different allylic alcohols which showed similar reactivity as benzhydrols and the desired products were obtained in good yields (Table 4). In the case of cinnamyl alcohol, the product was obtained in moderate yield along with some unidentified by-products (Table 4, entry 2).

During our investigation of the $FeCl_3$-catalyzed direct sulfonylation of homoallylic alcohols (Table 5), we were surprised to find that nucleophilic addition of sulfinate anion occurs at the terminal double bond instead of nucleophic substitution at the alcohol, resulting in the formation of allylic sulfones instead of homoallylic sulfones with double bond migration.

To the best of our knowledge, this represents the first example of an $FeCl_3$-catalyzed addition of sulfinate anion to the unactivated double bond. Also, this reaction broadens the scope of Li et al.'s work on the isomerization of the double bond that occurs with ruthenium catalysts in water.[33] To further evaluate the scope of this reaction, different homoallylic alcohol derivatives were subjected to the optimized reaction conditions and the results are shown in Table 5.

Table 6. Direct sulfonylation of benzhydrol with different sulfinate sodium salts.[a]



Entry	1	2	3
R	CH_3	Ph	p-NO_2-C_6H_4
Yield [%][b]	72	90	85

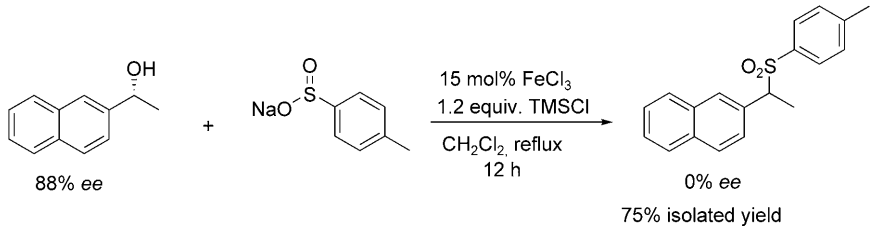
[a] All reactions were performed on a 1.0 mmol scale in the presence of 1.2 equiv. of sulfinate sodium salt, 1.2 equiv of TMSCl in dichloromethane at 45 °C.
[b] Yields after column chromatography.

With bromo- or methyl-substitution at the *para* position or without any substitution on the phenyl ring, the allylic sulfones were obtained in good yields along with trace amounts of homoallylic sulfones (entries 1–3). On the other hand, with 2,6-dibromo-4-(1-hydroxybut-3-enyl)phenol we observed the formation of homoallylic sulfones along with trace amounts of allylic sulfones (Table 5, entry 4). On the other hand, the reaction with simple homoallylic alcohols afforded allylic and homoallylic sulfones in 10% yield as inseparable mixtures in the ratio of 1:1.[34]

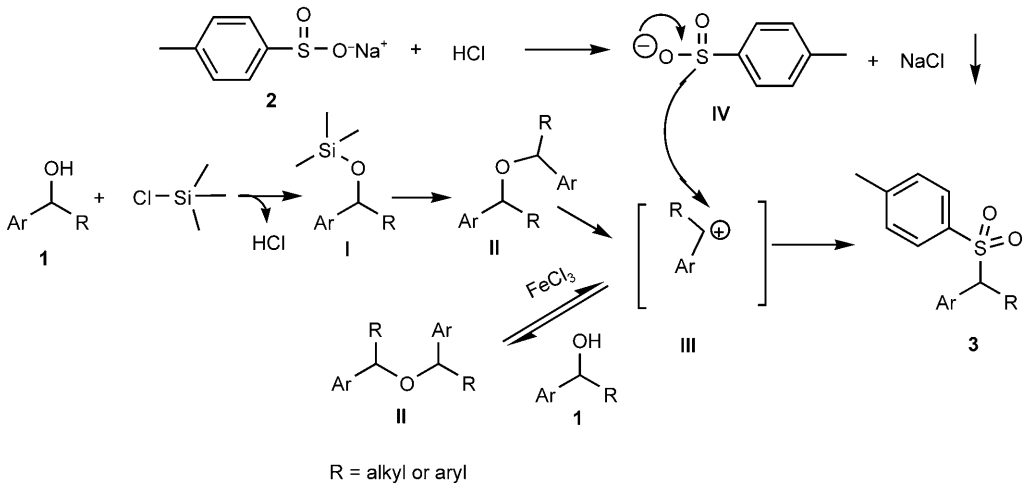
Furthermore, the scope of the reaction with respect to sulfinate sodium salt substrate was also examined and the results are given in Table 6. Both electron-donating as well as electron-withdrawing substituents gave the corresponding sulfonyl ethers were obtained in good yields within 12 h (entries 1–3).

When the optically active (*R*)-1-(naphthalen-2-yl)-ethanol, which was prepared by the oxazaborolidine-catalyzed asymmetric borane reduction of the 1-(naphthalen-2-yl)ethanone, reacted with sodium *p*-toluenesulfinate salt, only the racemic product was obtained (Scheme 1). This suggests a reaction mechanism in which a carbenium intermediate is formed.

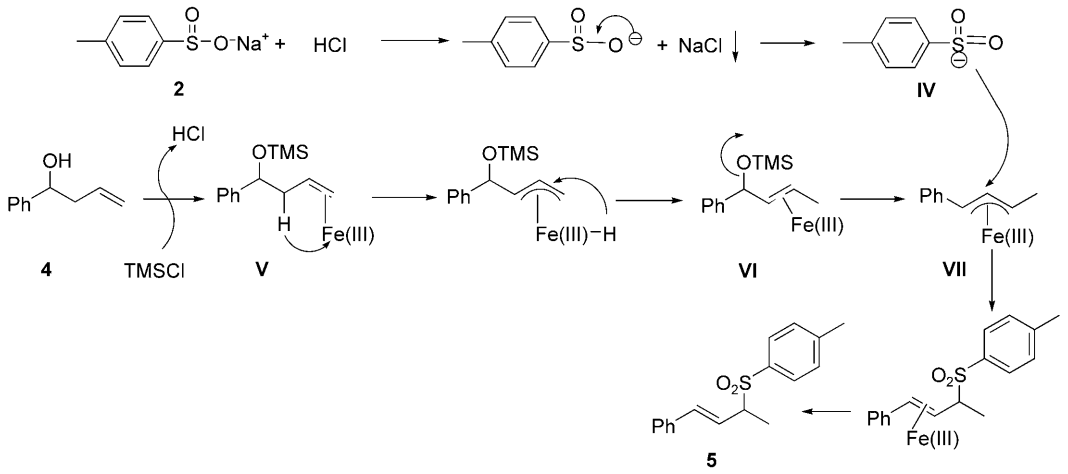
To get an insight into the mechanism, we performed several experiments to confirm the possibilities of the best reaction system. Scheme 2 shows possible pathways for the $FeCl_3$-catalyzed sulfonylation reaction using TMSCl as an additive. In this reaction, TMSCl plays a crucial role by dual activation of both alcohol and sodium *p*-toluenesulfinate. First it reacts with an alcohol to give trimethylsilyl ether **I** of an alcohol and generates HCl, which can convert an alcohol or its TMS ether to a dimeric ether **II**. It is also known that with a catalytic amount of Lewis acids,



Scheme 1. Direct sulfonylation of an optically active alcohol with sodium *p*-toluenesulfinate salt.



Scheme 2. Proposed mechanism for the direct sulfonylation of alcohols with sulfinate sodium salts using $FeCl_3$ and TMSCl.



Scheme 3. Proposed mechanism for the direct sulfonylation of homoallylic alcohols with sodium *p*-toluenesulfinate using $FeCl_3$ and TMSCl

benzylic and allylic alcohols rapidly convert into dimeric form by eliminating water,[35] which was confirmed by NMR and mass spectroscopy. The formed HCl in the above process converts sulfinate salt **2** to sulfinic acid nucleophile **IV**. Presumably, in the presence of a nucleophile, the ether is polarized by both $FeCl_3$ and/or HCl and generates an incipient benzylic carbocation **III**. The stability of the intermediate, benzylic carbocation is well-documented and has been the subject of theoretical and experimental studies.[29] The nucleophilic attack of the sulfinate anion onto the benzylic carbocation generates the desired sulfonyl ether **3**.

On the other hand, in the case of homoallylic alcohols, a plausible reaction course is proposed as shown in Scheme 3. The silylation of homoallylic alcohol **4** with TMSCl takes place as the first step and gives the intermediate trimethylsilyl ether **V** and hydrochloric acid. The coordination of iron to the double bond of the homoallyl alcohol transfers it from a terminal position to an internal position through migration of hydride[36] from the C-2 position to the C-4 of the chain **VI**. Then, the structure of π-allyl-iron **VII**[37] is built-up through the departure of the trimethylsilyl-protected hydroxy group. Attack of the π-allyl-iron complex with sulfinate anion **IV**, which was generated from the reaction of sulfinate salt and HCl, gives the final product allylic sulfones **5.**

In summary, we have developed a new and efficient $FeCl_3$-catalyzed direct sulfonylation of benzylic, allylic and homoallylic alcohols with high atom economy using TMSCl as an additive. The new catalytic reactions presented in this paper could be a meaningful addition to the existing methods with preformed or activated electrophiles and the use of stoichiometric amounts of base and/or metal salts. Additionally, a first example of the $FeCl_3$-catalyzed direct sulfonylation of homoallyl alcohols through nucleophilic addition of sulfinate anion at the terminal double bond instead of nucleophic substitution at the alcohol has been described.

Experimental Section

Typical Experimental Procedure for the Direct Sulfonylation of Alcohols

To a solution of alcohol (1 mmol), sodium arenesulfinates (1.5 mmol) and $FeCl_3$ (15 mol%) in dichloromethane (3 mL), TMSCl (1.2 mmol) was added. The reaction mixture was stirred at 45 °C and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with $NaHCO_3$ solution. The aqueous layer was extracted with ethyl acetate (3×20 mL), and the combined organic phases were dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by column chromatography on silica gel to afford the pure product. All products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopic techniques.

Acknowledgements

MAR and PSR thank the Council of Scientific and Industrial Research (CSIR), India, for Senior Research Fellowships.

References

[1] a) E. S. Patai, Z. Rappoport, C. Stirling, *The Chemistry of Sulphones and Sulphoxides*, John Wiley & Sons, Chichester, **1988**; b) N. S Simpkins, *Sulphones in Organic Synthesis*, Pergamon Press, Oxford, **1993**; c) J. E. Bäckvall, R. Chinchilla, C. Najera, M. Yus, M. *Chem. Rev.* **1998**, *98*, 2291; d) T. G. Back, *Tetrahedron* **2001**, *57*, 5263; e) F. Chemla, *J. Chem. Soc. Perkin Trans. 1* **2002**, 275.

[2] C. Najera, J. M. Sansano, *Recent Res. Dev. Org. Chem.* **1998**, *2*, 637.
[3] L. A. Paquette, *Synlett* **2001**, 1.
[4] R. Chinchilla, C. Najera, *Recent Res. Dev. Org. Chem.* **1997**, *1*, 437.
[5] Recent examples: a) C. M. Adams, I. Ghosh, Y. Kishi, *Org. Lett.* **2004**, *6*, 4723; b) B. M. Trost, H. C. Shen, J.-P. Surivet, *J. Am. Chem. Soc.* **2004**, *126*, 12565; c) Q. Wang, N. A. Sasaki, *J. Org. Chem.* **2004**, *69*, 4767; d) D. A. Alonso, M. Fuensanta, C. Najera, *Eur. J. Org. Chem.* **2006**, 4747.
[6] a) B. M. Trost, M. R. Ghadiri, *J. Am. Chem. Soc.* **1984**, *106*, 7260; b) B. M. Trost, N. R. Schmuff, M. J. Miller, *J. Am. Chem. Soc.* **1980**, *102*, 5979; c) M. Julia, M. Nel, L. Saussine, *J. Organomet. Chem.* **1979**, *181*, 17.
[7] a) P. Jerkeman, B. Lindberg, *Acta. Chem. Scand.* **1964**, *18*, 1477; b) A. Fischli, H. Mayer, W. Simon, H. J. Stoller, *Helv. Chim. Acta* **1976**, *59*, 397; c) B. Koutek, *Collect. Czech. Chem. Commun.* **1976**, *41*, 2250–2255; d) S. E. Forzelious, P. Zerkman, B. Lindberg, *Acta Chem. Scand.* **1963**, *17*, 1470; e) L. Castedo, J. Delamano, C. Lopez, M. B. Lopez, G. Tojo, *Heterocycles*, **1994**, *38*, 495; f) M. R. Attwood, B. R. Brown, S. G. Lisseter, C. L. Torrero, P. M. Weaver, *J. Chem. Soc. Chem. Commun.* 1984, 177.
[8] a) T. Murakami, K. Furusawa, *Synthesis* **2002**, 479; b) Y. Ju, D. Kumar, R. S. Varma, *J. Org. Chem.* **2006**, *71*, 6697.
[9] a) S. Chandrasekhar, V. Jagadeshwar, B. Saritha, C. Narsihmulu, *J. Org. Chem.* **2005**, *70*, 6506; b) R. Kuwano, Y. Kondo, T. Shirahama, *Org. Lett.* **2005**, *7*, 2973.
[10] a) H. H. Li, D. J. Dong, Y. H. Jin, S. K. Tian, *J. Org. Chem.* **2009**, *74*, 9501; b) C. R. Liu, M. B. Li, D. J. Cheng, C. F. Yang, S. K. Tian, *Org. Lett.* **2009**, *11*, 2543.
[11] a) M. Tamura, J. K. Kochi, *J. Am. Chem. Soc.* **1971**, *93*, 1487; b) M. Tamura, J. K. Kochi, *Synthesis* **1971**, 303; c) M. Tamura, J. K. Kochi, *J. Organomet. Chem.* **1971**, *31*, 289.
[12] For a general overview on iron catalysis in organic chemistry, see: B. Plietker, *Iron Catalysis in Organic Chemistry*, Wiley-VCH, Weinheim, **2008**.
[13] a) M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 861; b) W. D. Kerber, B. Ramdhanie, D. P. Goldberg, *Angew. Chem.* **2007**, *119*, 3792; *Angew. Chem. Int. Ed.* **2007**, *46*, 3718; c) F. Shi, M. K. Tse, Z. Li, M. Beller, *Chem. Eur. J.* **2008**, *14*, 8793–8797; d) C. Pavan, J. Legros, C. Bolm, *Adv. Synth. Catal.* **2005**, *347*, 703; e) J. Legros, C. Bolm, *Chem. Eur. J.* **2005**, *11*, 1086–1092; f) J. Legros, C. Bolm, *Angew. Chem.* **2004**, *116*, 4321; *Angew. Chem. Int. Ed.* **2004**, *43*, 4225; g) J. Legros, C. Bolm, *Angew. Chem.* **2003**, *115*, 5645; *Angew. Chem. Int. Ed.* **2003**, *42*, 5487; h) Z. Li, L. Cao, C. J. Li, *Angew. Chem.* **2007**, *119*, 6625; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505; i) Z. Li, R. Yu, H. Li, *Angew. Chem.* **2008**, *120*, 7607; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497.
[14] a) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2007**, *129*, 5816; b) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360; c) S. Gaillard, J. L. Renaud, *ChemSusChem* **2008**, *1*, 505; d) S. Enthaler, B. Hagemann, G. Erre, K. Junge, M. Beller, *Chem. Asian J.* **2006**, *1*, 598; e) S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794.
[15] a) H. Nishiyama, A. Furuta, *Chem. Commun.* **2007**, 760; b) N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497; c) A. M. Tondreau, E. Lobkovsky, P. J. Chirik, *Org. Lett.* **2008**, *10*, 2789; d) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem.* **2007**, *119*, 7431; *Angew. Chem. Int. Ed.* **2007**, *46*, 7293; e) N. S. Shaikh, K. Junge, M. Beller, *Org. Lett.* **2007**, *9*, 5429; f) A. Furuta, H. Nishiyama, *Tetrahedron Lett.* **2007**, *48*, 110.
[16] G. Zhang, Q. Liu, L. Shi, J. Wang, *Tetrahedron* **2008**, *64*, 339- 344.
[17] a) C. M. Chu, W. J. Huang, C. Lu, P. Wu, J. T. Liu, C. F. Yao, *Tetrahedron Lett.* **2006**, *47*, 7375; b) M. Kawatsura, Y. Komatsu, M. Yamamoto, S. Hayase, T. Itoh, *Tetrahedron Lett.* **2007**, *48*, 6480; c) J. Christoffers, *Chem. Commun.* **1997**, 943; d) J. Christoffers, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3141.
[18] For general reviews on iron catalysis, see: a) A. Correa, O. G. Mancheno, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317;. For recent papers on iron catalysis, see: c) T. Hatakeyama, M. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 9844; d) Z. Li, L. Cao, C. J. Li, *Angew. Chem.* **2007**, *119*, 6625; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505; e) Z. Li, R. Yu, H. Li, *Angew. Chem.* **2008**, *120*, 7607; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497; f) C. M. Rao Volla, P. Vogel, *Angew. Chem.* **2008**, *120*, 1325; *Angew. Chem. Int. Ed.* **2008**, *47*, 1305; g) S. K. Xiang, L. H. Zhanga, N. Jiao, *Chem. Commun.* **2009**, 6487; h) C. C. Kofink, B. Blank, S. Pagano, N. Gçtz, P. Knochel, *Chem. Commun.* **2007**, 1954; i) I. Sapountzis, W. Lin, C. Kofink, C. Despotopoulou, P. Knochel, *Angew. Chem.* **2005**, *117*, 1682; *Angew. Chem. Int. Ed.* **2005**, *44*, 1654; j) G. Cahiez, S. Marquais, *Tetrahedron Lett.* **1996**, *37*, 1773; k) G. Cahiez, S. Marquais, *Pure Appl. Chem.* **1996**, *68*, 53. For iron-catalyzed reactions reported by the group of Bolm, see: l) J. Legros, C. Bolm, *Angew. Chem.* **2003**, *115*, 5645; *Angew. Chem. Int. Ed.* **2003**, *42*, 5487; m) J. Legros, C. Bolm, *Angew. Chem.* **2004**, *116*, 4321; *Angew. Chem. Int. Ed.* **2004**, *43*, 4225.
[19] a) For a review on iron-catalyzed carbon-heteroatom bond formation reactions, see: A. Correa, O. G. Mancheno, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; b) A. Correa, M. Carril, C. Bolm, *Angew. Chem.* **2008**, *120*, 2922; *Angew. Chem. Int. Ed.* **2008**, *47*, 2880; c) O. Bistri, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 596; *Angew. Chem. Int. Ed.* **2008**, *47*, 586; d) A. Correa, M. Carril, C. Bolm, *Chem. Eur. J.* **2008**, *14*, 10919; e) A. Correa, S. Elmore, C. Bolm, *Chem. Eur. J.* **2008**, *14*, 3527; f) for iron-catalyzed carbon-heteroatom bond formation contaminated by copper, see: S. L. Buchwald, C. Bolm, *Angew. Chem.* **2009**, *121*, 5694; *Angew. Chem. Int. Ed.* **2009**, *48*, 5586.
[20] For reviews on iron-catalyzed oxidative coupling, see: a) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730–2744; b) K. Wang, M. Lü, A. Yu, X. Zhu, Q. Wang, *J. Org. Chem.* **2009**, *74*, 935.

[21] a) M. Carril, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 4940; *Angew. Chem. Int. Ed.* **2008**, *47*, 4862; b) W. M. Czaplik, M. Mayer, J. Cvengros, A. Jacobi von Wangelin, *ChemSusChem* **2009**, *2*, 396; c) B. D. Sherry, A. Furstner, *Acc. Chem. Res.* **2008**, *41*, 1500.
[22] R. Loska, C. M. Rao Volla, P. Vogel, *Adv. Synth. Catal.* **2008**, *350*, 2859.
[23] a) A. Fürstner, R. Martin, H. Crause, G. Seidel, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 8773; b) G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, *Angew. Chem.* **2007**, *119*, 4442; *Angew. Chem. Int. Ed.* **2007**, *46*, 4364; c) R. B. Bedford, D. W. Bruce, R. M. Frost, M. Hird, *Chem. Commun.* **2005**, 4161; d) M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 3686.
[24] a) R. B. Bedford, M. Huwe, M. C. Wilkinson, *Chem. Commun.* **2009**, 600; b) G. Cahiez, L. Foulgoc, A. Moyeux, *Angew. Chem.* **2009**, *121*, 3013; *Angew. Chem. Int. Ed.* **2009**, *48*, 2969.
[25] D. Bezier, C. Darcel, *Adv. Synth. Catal.* **2009**, *351*, 1732.
[26] For iron-catalyzed activation of alcohols, see: a) S. Biswas, S. Maiti, U. Jana, *Eur. J. Org. Chem.* **2009**, 2354; b) U. Jana, S. Biswas, S. Maiti, *Eur. J. Org. Chem.* **2008**, 5798; c) H. H. Li, Y. H. Jin, J. Q. Wang, S. K. Tian, *Org. Biomol. Chem.* **2009**, *7*, 3219; d) S. K. Xiang, L. H. Zhang, N. Jiao, *Chem. Commun.* **2009**, 6487; e) X. Zhang, W. Rao, S. Wai Hong Chan, P. Wai Hong Chan, *Org. Biomol. Chem.* **2009**, *7*, 4186; f) J. Wang, L. Zhang, Y. Jing, W. Huang, X. Zhou, *Tetrahedron Lett.* **2009**, *50*, 4978; g) J. Kischel, K. Mertins, D. Michalik, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2007**, *349*, 865; h) Z. P. Zhan, J. L. Yu, H. J. Liu, Y. Y. Cui, R. F. Yang, W. Z. Yang, J. P. Li, *J. Org. Chem.* **2006**, *71*, 8298; i) I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 3981; *Angew. Chem. Int. Ed.* **2005**, *44*, 3913.
[27] B. Sreedhar, M. A. Reddy, P. S. Reddy, *Synlett* **2008**, 1949.
[28] a) B. Sreedhar, P. S. Reddy, V. R. Krishna, *Tetrahedron Lett.* **2007**, *48*, 5831; b) B. Sreedhar, P. S. Reddy, M. A. Reddy, B. Neelima, R. Arundhathi, *Tetrahedron Lett.* **2007**, *48*, 8174.
[29] T. Saito, Y. Nishimoto, M.; Yasuda, A. Baba, *J. Org. Chem.* **2006**, *71*, 8516.
[30] For the utility of the diarylmethyl sulfones in organic synthesis, see: T. Niwa, H. Yorimitsu, K. Oshima, *Tetrahedron* **2009**, *65*, 1971.
[31] The stability of benzylic carbocation is well-documented and has been a subject of theoretical and experimental studies: Y. Liu, S. Zhou, G. Li, B. Yan, S. Guo, Y. Zhou, H. Zhang, P. Wang, *Adv. Synth. Catal.* **2008**, *350*, 797, and references cited therein.
[32] a) J. Clayden, M. Julia, *J. Chem. Soc. Chem. Commun.* **1994**, 1905; b) L. A. Paquette, *Synlett* **2001**, 1; c) R. Chinchilla, C. Najera, *Recent Res. Dev. Org. Chem.* **1997**, *1*, 437; d) C. Najera, M. Yus, *Tetrahedron* **1999**, *55*, 10547.
[33] C. J. Li, D. Wang, D. L. Chen, *J. Am. Chem. Soc.* **1995**, *117*, 12867.
[34] Both allylic and homoallylic sulfones formed as inseparable mixture and the ratio given is based on ^{1}H NMR.
[35] a) M. Noji, Y. Konno, K. Ishii, *J. Org. Chem.* **2007**, *72*, 5161; b) T. Saito, M. Nishimoto, M. Yasuda, A. Baba, *J. Org. Chem.* **2006**, *71*, 8516.
[36] For an example of hydride transfer by iron: D. Schröder, H. Schwarz, *Angew. Chem.* **1990**, *102*, 925; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 910.
[37] a) T. A. Jenny, L. Ma, *Tetrahedron Lett.* **1991**, *32*, 6101; b) M. C. P. Yeh, J. X. Ho, P. Y. Hsueh, *J. Chin. Chem. Soc.* **2003**, *50*, 833; c) B. Plietker, A. Dieskau, K. Mows, A. Jatsch, *Angew. Chem.* **2008**, *120*, 204; *Angew. Chem. Int. Ed.* **2008**, *47*, 198; d) B. D. Sherry, A. Furstner, *Chem. Commun.* **2009**, 7116; e) R. Trivedi, J. A. Tunge, *Org. Lett.* **2009**, *11*, 5650.

