J. Org. Chem. **2001,** 66, 421−425

Acylation and Related Reactions under Microwaves. 4. Sulfonylation Reactions of Aromatics†

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Received July 7, 2000

Solvent-free sulfonylation of benzene and its activated or deactivated derivatives were carried out under microwave (MW) irradiation and a catalytic amount of iron(III) chloride, which, under these conditions, is more active than other metallic salts. With more reactive and/or nonvolatile reagents (anisole, xylenes, mesitylene) expeditious conditions (short reaction time at constant MW power without control of the temperature) were used. With less reactive and/or low-boiling reagents (benzene, toluene, halobenzenes), the rise in temperature and the increase of reaction time were controlled either by sequential MW irradiation or by a temperature order. It was shown that MWs cause preferential interactions with polar species present in the reaction, especially the aryl sulfone and its $FeCl_3$-complexed form. A MW nonthermal effect was not observed when identical temperature gradients were produced by classical heating and MW irradiation, and if reaction temperature was strictly controlled.

Among Friedel−Crafts (FC)-type reactions,[1] sulfonylation poses an important problem of catalysis.[2] The formation of a stable complex between the sulfone produced and the Lewis acid used as catalyst (traditionally $AlCl_3$ or $FeCl_3$) implies that at least a stoichiometric amount of catalyst is required. Brönsted acids, which usually are good catalysts for FC acylation,[1] poorly catalyze sulfonylation of arenes,[2a−c,3,4] for example, a procedure employing a sulfonic acid as reagent requires a large amount of polyphosphoric acid,[3] and triflic acid is a poor catalyst when a sulfonyl chloride is used.[4a] Recently, several interesting new catalysts have been reported for FC sulfonylation: cation-exchanged zeolite β (methanesulfonylation of toluene),[2d] the superelectrophilic reagent systems ($MeSO_2F/3\ SbF_5$ or $(MeSO_2)_2O/2\ TfOH-B(OTf)_3$) (methanesulfonylation of deactivated aromatics),[2e] Fe(III)-exchanged montmorillonite clay (arylsulfonylation of benzene and its methylated derivatives),[2f] Bi(III) triflate,[2g] and TfOH−Bi(III) halide systems (aryl- and alkylsulfonylation of benzene and its activated or deactivated derivatives).[2h] However, these reactions often require prolonged heating and/or a large amount of a sometimes expensive catalyst.

We have shown recently that it is possible to carry out FC acylation under MW irradiation, in solvent-free conditions and in the presence of a small amount of some metal salts.[5] Among them, $FeCl_3$, an inexpensive and eco-friendly reagent, exhibited higher catalytic activity than other metallic chlorides, in particular $AlCl_3$. It allowed acylation in short reaction times (expeditious conditions) of the more reactive arenes (ethers,[5b] alkylbenzenes, naphthalene),[5c] and under controlled MW power (sequential irradiation) the less reactive ones (benzene, toluene, halobenzenes).[5c] This previous study is now extended to the FC sulfonylation reaction.

Results and Discussion

The reactions were performed in a monomode cavity under focused MWs using an open quartz reactor fitted with a refluxing condenser. According to the reactivity and bp of reagents, three different modes of MW irradiation were used: i) a continuous MW irradiation with a constant incident power (CMWI mode); ii) a MW irradiation controlled to a maximum temperature (MWIC mode);

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† For part 3 in the series, see ref 5c.

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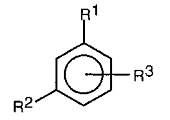
10.1021/jo0010173 CCC: $20.00

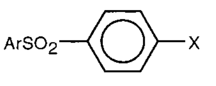
Chart 1



R^1 = Me , R^2 = H , R^3 = H(**1**), *o*-Me(**2a**), *m*-Me(**2b**), *p*-Me(**2c**) ; R^1 = R^2 = Me, R^3 = *m*-Me (**3**);
R^2 = R^3 = H , R^1 = Et(**4**), OMe(**5**), H(**6**), F(**7**), Cl(**8**), Br(**9**), I(**10**) ; R^1 = R^2 = Cl, R^3 = H(**11**)

R = H(**12**), Me(**13**), ^{t}Bu(**14**), OMe(**15**), F(**16**), Cl(**17**)   **18**

Chart 2



Ar = C_6H_4Me , X = H(**19**), Me(**20**), ^{t}Bu(**21**), OMe(**22**), F(**23**), Cl(**24**) ;
Ar = $C_6H_3Me_2$, X = H(**25**) ; Ar = $C_6H_2Me_3$, X = H (**26**) ;
Ar = C_6H_4Et , X = H (**27**) ; Ar = C_6H_4OMe , X = H (**28**), OMe(**29**) ;
Ar = C_6H_5 , X = H (**30**) ; Ar = C_6H_4F , X = H (**31**) ; Ar = C_6H_4Cl , X = H (**32**), Cl(**33**) ;
Ar = C_6H_4Br , X = H (**34**) ; Ar = C_6H_4I , X = H (**35**), Cl(**36**) ; Ar = $C_6H_3Cl_2$, X = H (**37**)

iii) a sequential MW irradiation (SMWI mode). Starting compounds and products are collected in Charts 1 and 2.

Sulfonylation of Toluene (1). In a model reaction, sulfonylation of toluene by benzenesulfonyl chloride was examined using various catalysts in order to determine their relative activities. Reactions were done with an excess of toluene with respect to the sulfonylating reagent (**1**/**12** = 2:1 (mol)), without added solvent and in the presence of 5 mol % of catalyst. The more typical results are reported in Table 1. The MW incident power was monitored to obtain a maximum temperature of 110 °C for 5 min (MWIC). Indeed, with a relatively volatile arene like **1**, the use of expeditious conditions (CMWI, 120 W) for a short time (1 min) provoked its vaporization, and gave a lower sulfonylation yield (entries 1, 2). Irradiation times (5 min) in MWIC experiments (entries 2−8) were voluntarily shortened in order to discriminate among the catalysts and to select the best.

The higher catalytic activity shown by iron(III) chloride in FC acylation under MW[5] is still noteworthy here. Complete conversion of **12** was obtained, and the sulfone **19** was isolated in 95% yield (Table 1, entry 2). In contrast, aluminum chloride was much less efficient and gave a yield corresponding to the stoichiometry used (entry 3). Samarium(III) chloride (entry 5) and some other metallic chlorides (not shown) appeared wholly (or nearly) inefficient. Concerning bismuth(III) salts, recent studies in our laboratories showed the high efficiency of $Bi(OTf)_3$ to catalyze sulfonylation of arenes under thermal heating, while $BiCl_3$ was much less active.[2g] Under MWs, sulfonylation of **1** with **12** led to the same discrimination (entries 4 and 7).

Another comparison was attempted between $Bi(OTf)_3$ and two other metallic triflates, $Sc(OTf)_3$, known to catalyze the FC acylation,[6] and $Fe(OTf)_3$, not previously used for a FC reaction. A major difference in activity appeared between them (Table 1, entries 6−8). Considering our earlier results about catalysis by $Bi(OTf)_3$ and other metallic triflates in the FC acylation[7] and sulfonylation[2g] reactions, the high activity of $Bi(OTf)_3$ is due to the TfO^-/Cl^- ligand exchange between this triflate and the acid chloride (RCOCl or RSO_2Cl). This exchange induces the formation of a strong electrophilic intermediate, a mixed anhydride RCOOTf or RSO_2OTf, that agrees with the first step of the catalytic cycle. The metallic triflates that do not give this TfO^-/Cl^- exchange (in particular Sc or Fe ones)[2g,7] are less efficient (or inefficient) catalysts of this reaction. The surprising difference in activity between $FeCl_3$ and $Fe(OTf)_3$ (entries 2 and 6) can be explained by a stronger affinity of the triflate toward the aryl sulfone produced (like $AlCl_3$),[2a] leading to an inhibition of the reaction.

Table 1. Sulfonylation of Toluene (1) under Microwave Irradiation

entry	sulfonylating reagent[a]	catalyst (mol %)[b]	conditions[d] (T_{max})	product, yield[h] [*o*/*m*/*p*][i]
1	**12**	$FeCl_3$ (5)	120 W; 1 min[e] (133 °C)	**19**, 63% [38/6/56]
2	**12**	$FeCl_3$ (5)	110 °C; 5 min[f]	**19**, 95% [34/7/59]
3	**12**	$AlCl_3$ (5)	110 °C; 5 min[f]	**19**, 5%[i] [28/8/64]
4	**12**	$BiCl_3$ (5)	110 °C; 5 min[f]	**19**, 2%[i]
5	**12**	$SmCl_3$ (5)	110 °C; 5 min[f]	**19**, 0%
6	**12**	$Fe(OTf)_3$[c] (5)	110 °C; 5 min[f]	**19**, 3%[i]
7	**12**	$Bi(OTf)_3$[c] (5)	110 °C; 5 min[f]	**19**, 70% [38/6/56]
8	**12**	$Sc(OTf)_3$ (5)	110 °C; 5 min[f]	**19**, 0%[i]
9	**13**	$FeCl_3$ (5)	110 °C; 5 min[f]	**20**, 85% [6/3/91]
10	**14**	$FeCl_3$ (5)	110 °C; 10 min[f]	**21**, 76% [16/1/83]
11	**15**	$FeCl_3$ (5)	110 °C; 5 min[f]	**22**, 85% [11/3/86]
12	**16**	$FeCl_3$ (5)	300 W 15 s × 20 (45s)[g] (160 °C)	**23**, 85% [40/7/53]
13	**17**	$FeCl_3$ (5)	300 W 10 s × 20 (50s)[g] (200 °C)	**24**, 89% [38/8/54]
14	**18**	$FeCl_3$ (5)	110 °C; 10 min[f]	**20**, 76% [5/2/93]

[a] **1**/sulfonylating reagent = 20/10 mmol. [b] Catalyst/sulfonylating reagent. [c] Tetrahydrated form. [d] Applied incident power, irradiation time and period between two irradiations (bracketed) in the case of sequential irradiation. [e] Continuous MW irradiation. [f] MW irradiation controlled to a maximum temperature of 110 °C. [g] Sequential MW irradiation. [h] Yield of isolated product with respect to sulfonylating reagent. [i] GC analysis.

The action of various sulfonylating reagents, arylsulfonyl chlorides **13**−**17** and a sulfonic anhydride **18**, on toluene were studied using $FeCl_3$ as catalyst. Reactions were carried out under the same irradiation conditions as before (MWIC). Sulfones **20**−**22** were obtained in good yields using short reaction times (Table 1, entries 9−11, 14). With the weaker electrophilic sulfonyl chlorides **16** and **17**, better yields were obtained using the SMWI mode (entries 12 and 13), which allows a longer irradiation time and a higher maximum temperature while restricting the vaporization of **1** at the beginning of the irradiation.

Concerning the regioselectivity of FC reactions, it is

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Table 2. Sulfonylation of Alkylbenzenes (2−4) and Anisole (5) under Microwave Irradiation in the Presence of Iron(III) Chloride[a]

entry	aromatic	sulfonylating reagent[b]	conditions[c] (T_{max})	product, yield[e] [isomers][f,g]
1	**2a**	**12**	300 W; 45 s (170 °C)	**25**, 86% [$\mathbf{a}^1$/$\mathbf{a}^2$ = 77/23]
2	**2b**	**12**	300 W; 45 s (166 °C)	**25**, 95% [$\mathbf{b}^1$/$\mathbf{b}^2$ = 99/1]
3	**2c**	**12**	300 W; 50 s (165 °C)	[**c**] **25**, 95%
4	**3**	**12**	140 W; 1 min (130 °C)	**26**, 95%
5	**4**	**12**	135 °C; 4 min[d]	**27**, 94% [20/8/72]
6	**5**	**12**	300 W; 1 min (248 °C)	**28**, 91% [45/0/55]
7	**5**	**15**	300 W; 1 min (185 °C)	**29**, 91% [27/0/73]

[a] FeCl$_3$/sulfonylating reagent = 5% (mol). [b] Aromatic/sulfonylating reagent = 20/10 mmol. [c] Continuous MW irradiation: applied incident power and irradiation time. [d] MW irradiation controlled to a maximum temperature of 135 °C. [e] Yield of isolated product with respect to sulfonylating reagent. [f] GC analysis. [g] 3,4- (**25a**^{1}), 2,3- (**25a**^{2}), 2,4- (**25b**^{1}), 2,6- (**25b**^{2}), and (2,5-dimethylphenyl) phenyl sulfone (**25c**); mesityl phenyl sulfone (**26**); **27**−**29**: *o*/*m*/*p*.

well established that the reacting electrophilic species are more active and less selective in the sulfonylation than in the corresponding acylation.[2a] Effectively, under similar MW irradiation conditions, we observed that the required amount of catalyst (FeCl$_3$) was less for the sulfonylation of toluene than for its benzoylation.[5c] The sulfonylation reaction time was also shorter. Moreover, the para-selectivity of FC-aryl sulfones is generally lower (Table 1) than that of the corresponding FC-aryl ketones.[5c]

Sulfonylation of Alkylbenzenes (2−4) and Anisole (5). Benzene derivatives having methyl or methoxy substituents are among the most reactive in the presence of an electrophilic reagent (σ_p^+ (Me) = −0.31, σ_p^+ (OMe) = −0.78).[8] Sulfonylation of a series of activated aromatics, alkylbenzenes **2**−**4** and anisole **5**, in the presence of FeCl$_3$ was examined. The MW irradiation mode was changed to CMWI because of the higher boiling points of **2**−**5** with excellent results (Table 2). However, for ethylbenzene (**4**) MWIC conditions to a maximum temperature of 135 °C for 4 min were necessary for a very high yield (entry 5). For all sulfonylations subjected to expeditious conditions (entries 1−4, 6, 7), almost complete conversions were obtained in short reaction times (45 s to 1 min), and sulfones **25**, **26**, **28**, and **29** were isolated in high yields. With the highly reactive mesitylene (**3**), an irradiation MW power of only 140 W was sufficient to give a complete reaction within 1 min (entry 4).

Sulfonylation of Benzene (6) and Its Halogenated Derivatives (7−10). Benzene (**6**) is a volatile and poor reactive substrate. Its sulfonylation carried out under MW irradiation controlled to a maximum of 78 °C (MWIC) for 20 min gave a yield of only 39% (Table 3, entry 1). An SMWI mode was obviously preferable (entries 2 and 3). This irradiation mode limits the vaporization of **6** at the beginning of the irradiation, allows **6** to exceed its bp, and allows a slow rise in temperature, leading to a convenient yield of the sulfonylation.

Table 3. Sulfonylation of Benzene (6) and Halobenzenes (7−11) under Microwave Irradiation in the Presence of Iron(III) Chloride[a]

entry	aromatic	sulfonylating reagent[b]	conditions[c] (T_{max})	product, yield[g] [isomers[h,i]]
1	**6**	**12**	78 °C; 20 min[d]	**30**, 39%
2	**6**	**12**	300 W; 15 s × 6 (45s);[e] (160 °C)	**30**, 88%
3	**6**	**13**	300 W; 15s × 4 (45 s);[e] (254 °C)	**19**, 80% [*para*]
4	**7**	**12**	80 °C; 20 min[d]	31, 41% [3/0/97]
5	**7**	**12**	300 W; 15 s × 8 (45s);[e] (150 °C)	**31**, 72% [3/0/97]
6	**8**	**12**	300 W; 4 min[f] (202 °C)	**32**, 74% [2/0/98]
7	**8**	**17**	300 W; 4 min[f] (220 °C)	**33**, 82% [1/0/99]
8	**8**	**17**	144 °C; 20 min[d]	**33**, 95% [2/0/98]
9	**9**	**12**	300 W; 4 min[f] (204 °C)	**34**, 76% [0/0/100]
10	**10**	**12**	300 W; 2 min[f] (197 °C)	**35**, 95% [2/0/98]
11	**10**	**17**	180 °C; 20 min[d]	**36**, 72% [3/0/97]
12	**11**	**12**	300 W; 2 min + 1 min × 8 (1 min)[e] (204 °C)	**37**, 50% [**a**/**b** = 97/3]

[a] FeCl$_3$/sulfonylating reagent = 5% (mol), except for entries 8 and 9:10%. [b] Aromatic/sulfonylating reagent = 20/10 mmol . [c] Applied incident power, irradiation time and period between two irradiations (bracketed) in the case of sequential MW irradiation. [d] MW irradiation controlled to a maximum temperature. [e] Sequential MW irradiation. [f] Continuous MW irradiation. [g] Yield of isolated product with respect to sulfonylating reagent. [h] GC analysis. [i] **31**−**36**: *o*/*m*/*p*; 2,4- (**37a**) and (2,6-dichlorophenyl) phenyl sulfone (**37b**).

Fluorobenzene (**7**) is a practically nonactivated aromatic (σ_p^+ (F) = −0.07),[8] and its bp is close to that of **6**. The search for proper MW irradiation conditions for sulfonylation of **7** resulted in the same conclusion as that for **6** (entries 4, 5). Other halobenzenes **8**−**10** are deactivated aromatics (σ_p^+ (Cl) = +0.11, σ_p^+ (Br) = +0.15, (σ_p^+ (I) = +0.14)[8] but are much less volatile than **7**. Different MW irradiation modes can be used to obtain their sulfonylation: MWIC to a maximum temperature near the bp of the aromatic (entries 8 and 11), expeditious conditions (CMWI) (entries 6, 9, 10), or a SMWI (entry 12) for the very deactivated *m*-dichlorobenzene (**11**) which requires a longer reaction time.

Behavior under MW Irradiation of Various Chemical Species Involved in the Sulfonylation of Mesitylene (3). Previously, we have shown that the MW energy absorbed during the benzoylation of anisole and *p*-xylene differs strongly according to the chemical species involved.[5b,c] We report here a similar study, limited to an analysis of one reaction, that of the sulfonylation of mesitylene (**3**) by **12** using an identical ratio of reagents: **3**/**12**/FeCl$_3$ = 40/10/0.5 mmol. The thermal profile of the reaction, carried out under a MW power of 300 W for 1 min (83% yield), showed a strong increase of temperature (ΔT = 118 °C) after 30 s of irradiation (Figure 1). To identify the chemical species that induced this strong *T*-gradient, the behavior under MWs of various species involved in the reaction was investigated.

Three mixtures, representative of the reaction, were irradiated at 300 W for 1 min: **A** (**3**/**12** = 40/10 mmol), **B** (**3**/**26** = 30/10 mmol), and **C** (**3**/**26**/FeCl$_3$ = 30/10/0.5

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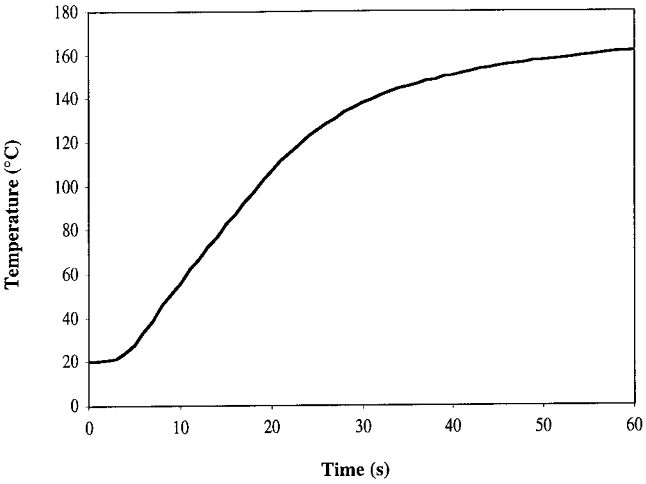

Figure 1. Thermal behavior of the benzenesulfonylation of mesitylene (**3**) (**3**/**12** = 40/10 mmol) in the presence of $FeCl_3$ (0.5 mmol) under MW irradiation of 300 W for 1 min.

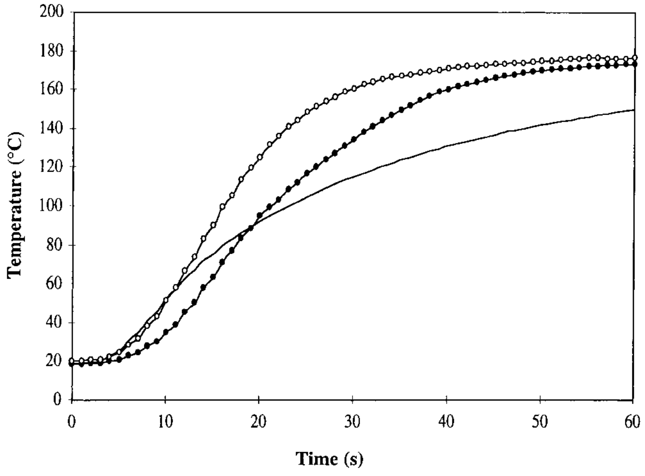

Figure 2. Thermal behavior of various mixtures **A** (**3**/**12** = 40/10 mmol), **B** (**3**/**26** = 30/10 mmol), and **C** (**3**/**26**/$FeCl_3$ = 30/10/0.5 mmol) under MW irradiation of 300 W for 1 min.

mmol). The mixture **A** corresponds to the initial conditions (without catalyst) of the reaction, mixture **B** to the final ones (without catalyst), and mixture **C** to the true final conditions (with catalyst). Whereas **A** heated (ΔT_{25s} = 86 °C) with a T-gradient $\delta T_{0-25s} = 3.4$ °C·s^{-1}, **B** and especially **C** gave the highest gradients: $\Delta T_{25s} = 99$ °C, $\delta T_{0-25s} = 3.9$ °C·s^{-1} and $\Delta T_{25s} = 129$ °C, $\delta T_{0-25s} = 5.2$ °C·s^{-1}, respectively (Figure 2). Despite the low proportion of the complex **26**−$FeCl_3$ in the mixture **C** (1.25 mol %), which contains a great part of the nonpolar compound **3**, it seems reasonable to us that the sulfone **26**, and particularly its complex with $FeCl_3$, are the species responsible for the thermal behavior of the reaction medium. Since the formation of the product **26** increases progressively in proportion as the reaction occurs, a strong T-gradient appeared (Figure 1).

Comparison between Classical and MW Heatings. In the first place, the two heatings, thermal (TH) and MW, were applied to the $FeCl_3$-catalyzed benzenesulfonylation of a reactive aromatic, mesitylene (**3**), and of a less reactive one, chlorobenzene (**7**). The apparatus used offers the possibility of reproducing a temperature increase obtained beforehand by conventional heating.

Table 4. Sulfonylation of Mesitylene (3) and Chlorobenzene (7) under Microwave and Thermal Heatings

entry	aromatic[a]	heating mode[b,c] T_{max} (°C)	reaction time (min)	product and conversion[d] (%)
1	**3**	TH; 110	3	**26**, 36
2	**3**	MW; 110	3	**26**, 40
3	**3**	TH; 110	5	**26**, 58
4	**3**	MW; 110	5	**26**, 62
5	**3**	TH; 110	30	**26**, 78
6	**3**	MW; 110	30	**26**, 80
7	**7**	TH; 130	20	**31**, 45
8	**7**	MW; 130	20	**31**, 40
9	**7**	TH; 144	20	**31**, 55
10	**7**	MW; 144	20	**31**, 95

[a] Sulfonylating reagent: **12**; aromatic/**12**/$FeCl_3$ = 20/10/0.5 mmol. [b] TH: immersion of the reactor into an oil bath first heated and kept at the indicated temperature with recording of the T-evolution by the computer; MW: controlled microwave irradiation with reproduction of the TH-profile of temperature up to the indicated temperature. [c] Experiments have been carried out with (entries 1−6, 7, 9) or without (entries 8, 10) mechanical stirring. [d] GC analysis.

Thus, the TH-temperature profile of the reaction was recorded and monitored under suitable MW irradiation.

At first, sulfonylation of **3** was carried out using an oil bath thermostated at 110 °C, with mechanical stirring and the temperature rise reproduced by MW irradiation. After 3, 5, and 30 min, the conversions into sulfone **26** were unrelated to the heating mode (Table 4, entries 1−6). In the same way, the sulfonylation of **7** at 130 °C gave similar results under TH or MW heatings (not shown).

Then, complementary experiments were obtained for the latter reaction. In a first step, two reactions of **7** (bp 132 °C) with benzenesulfonyl chloride **12** (**7**/**12**/$FeCl_3$ = 20/10/0.5 mmol), mechanically stirred, were performed using one oil bath at 130 °C and a second at 144 °C. The sulfone **31** was obtained in almost similar yields, 45% and 55%, respectively (Table 4, entries 7 and 9).

In a second series, the same experiments (*without* mechanical stirring) were conducted by reproducing under MWs the temperature profiles obtained as a function of time for conventional heating. A 40% yield in sulfone was obtained for a reaction at 130 °C (Table 4, entry 8), while it reached 95% for a reaction at 144 °C (entry 10). These results show a strong increase in the rate of the second reaction by MW heating. A specific activation might be postulated for this experiment carried out in homogeneous conditions, but the observed effect can be explained more simply by the NLBP of **7**.[9] Superheating at 144 °C occurred without boiling and without variation in the chlorobenzene concentration in the liquid. Under such conditions the rate was strongly increased.

Conclusion

Friedel−Crafts sulfonylations were done under MW radiation and in solvent-free conditions. After showing

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(9) In the MW cavity, organic solvents superheat by 13−26 °C above their conventional bp at atmospheric pressure and without stirring: Baghurst D. R.; Mingos P. *J. Chem. Soc., Chem. Commun.* **1992**, 674. Chlorobenzene (**7**) is an aromatic that undergoes a significant MW heating: the reported NLBP (Nucleation Limited Boiling Point) of **7** (bp 132 °C) is 150 °C (150 mL under a MW power of 650 W). We have measured almost the same value (147 °C) with our apparatus (10 mL of **7** with full power of 300 W).

that $FeCl_3$ is a catalyst able to give a convenient sulfonylation of toluene in a short reaction time, a search of optimal MW irradiation conditions were undertaken with benzene and various of its derivatives. Three different MW irradiations were undertaken: CMWI or MWIC, with the more reactive and/or nonvolatile reagents, and SMWI, with the less reactive and/or low boiling ones. Yields were good and reaction times often very short (CMWI).

Under solvent-free conditions, an excess of aromatic is necessary to achieve a homogeneous medium, but this excess must be limited to allow MW-absorbent species, in proportionately small amounts, to induce a fast enough temperature rise. Effectively, the study of the interaction between a MW radiation and chemical species involved in the reaction showed that the most absorbent species is the reaction product, the aryl sulfone, and especially its $FeCl_3$ complex. However, the MW absorbed energy is completely converted into thermal energy. Indeed, nonthermal activation was not observed. A noticeable increase in rate of sulfonylation of chlorobenzene was observed under MWs relative to thermal heating. This activation is not due to a nonthermal effect, but to a specific effect of MW heating, resulting in the superheating of liquid chlorobenzene that, without stirring, delays its boiling (NLBP). These observations are in agreement with our previous results relating to the FC acylation[5b,c] and recent publications concerning the kinetics of organic reactions under MWs in homogeneous media.[10]

Among the technological aspects are the following: (1) recent progress in the design of MW apparatus, in particular the control of reaction mixture temperature, has allowed open reactors to be used, thereby avoiding thermal degradation of products; and (2) owing to the different modes of irradiation, MW heating can be adapted to each reaction according to the reactivity and bp of the starting compound.

Microwave heating is no longer a laboratory curiosity of questionable use; its broad potential has already been clearly demonstrated, sometimes in solvent-free conditions,[11] an aspect of particular importance for reactions on a scaled-up industrial process. We are exploring this.

Experimental Section

General Methods. All starting materials, including metallic salts, with the exception of bismuth(III) and iron(III) trifluoromethanesulfonates, were commercially available (from Aldrich). Bismuth(III) trifluoromethanesulfonate was prepared as previously described from triphenylbismuth and triflic acid.[12,13] The experimental procedure of MW heating using a monomode MW oven, equipped with an IR pyrometer, have been previously described.[5b,c] The diaryl sulfones being solid products, the use of an excess of the starting aromatic compound permitted the retention of a homogeneous liquid medium during the reaction.

Typical Procedure for the CMWI Mode: Benzenesulfonylation of *m*-Xylene (2b) (Table 2, Entry 2). *m*-Xylene (**2b**) (2.12 g, 20 mmol)), benzenesulfonyl chloride (**12**) (1.77 g, 10 mmol), and iron(III) chloride (80 mg, 0.5 mmol) were introduced together in the quartz reactor of the MW apparatus fitted with a refluxing condenser (dry ice/acetone) and a calcium chloride tube. The reaction mixture, mechanically stirred (Teflon paddle), was irradiated under an incident power of 300 W for 50 s. At the end of irradiation, a maximum temperature of 166 °C was indicated by the IR pyrometer. After the reaction mixture was cooled, the conversion rate was determined by analyzing an aliquot of the reaction mixture by GC, using tetradecane as an internal standard: 99%. The reaction mixture was quenched with 20 mL of a saturated sodium carbonate aqueous solution. The aqueous layer was extracted with 3 × 10 mL of dichloromethane. After drying and concentration under reduced pressure of the organic phase, the crude product (white solid) was analyzed by GC (125 °C to 300 °C; 20 °C/min; 2 peaks, $t_R = 6.89$ and 7.16 min, 1:99) and identified as a mixture of (2,6-dimethylphenyl) phenyl sulfone (**25b^2**) and (2,4-dimethylphenyl) phenyl sulfone (**25b^1**) by comparison with pure samples.[14] Mass obtained: 2.34 g (95% yield from **12**). A crystallization from methanol gave **25b^1** *[4212−74−2]*: mp 87 °C (lit.[14] mp 87 °C).

Typical Procedure for the MWIC Mode: Benzenesulfonylation of Ethylbenzene (4) (Table 2, Entry 5). Ethylbenzene (**4**) (2.12 g, 20 mmol), benzenesulfonyl chloride (**12**) (1.77 g, 10 mmol), and iron(III) chloride (80 mg, 0.5 mmol) were placed in the reactor. Under stirring, the mixture was irradiated for 4 min with a maximum temperature controlled to 135 °C. After treatment similar to that used before, the crude product (white solid) was analyzed by GC (125 °C to 300 °C; 20 °C/min; 3 peaks, $t_R = 8.03$, 8.21 and 8.51 min, 20/8/72) and identified as a mixture of isomers of the (ethylphenyl) phenyl sulfone (**27**).[15] Mass obtained: 2.32 g (94% yield from **12**).

Typical Procedure for the SMWI Mode: Benzenesulfonylation of Benzene (6) (Table 3, Entry 2). Benzene (**6**) (2.12 g, 20 mmol), benzenesulfonyl chloride (**12**) (1.77 g, 10 mmol), and iron(III) chloride (80 mg, 0.5 mmol) were put into the reactor, and the mixture was stirred. A MW irradiation of 300 W applied power was programmed using the computer according to a sequential process of irradiation in which the sample was exposed to MWs for periods of 15 s separated by periods of 45 s. This sequence was repeated six times. At the end of the irradiation, a maximum temperature of 160 °C was indicated by the IR pyrometer. The same workup as before gave a crude product (white solid) identified as the diphenyl sulfone (**30**) *[127−63−9]* by comparison with a pure sample.[16,17] Mass obtained: 1.92 g (88% yield from **12**): mp (from ethanol): 123 °C [lit.[16] mp 122−123 °C].

Acknowledgment. Support of this work by the Centre National de la Recherche Scientifique and Rhodia Organique Fine is gratefully acknowledged. We thank Professor M. Onyszchuk (McGill University) for his assistance in the preparation of the manuscript. We thank also Dr. C. Le Roux (Paul-Sabatier University) for a gift of iron(III) triflate.

Supporting Information Available: Gas chromatographic, GC−MS, and ^{1}H NMR analyses of sulfones **19**−**37**; *T* and *P* (MW incident power) = *f*(MW irradiation time) curves for each irradiation mode (Figures SI.1−3). This material is available free of charge via the Internet at http://pubs.acs.org.

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