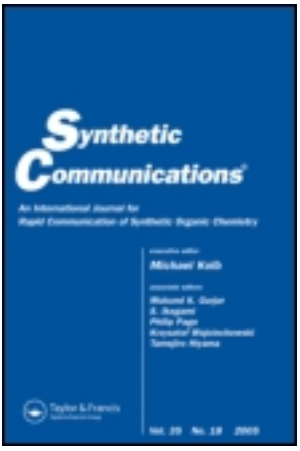

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ZINC-MEDIATED FAST SULFONYLATION OF AROMATICS

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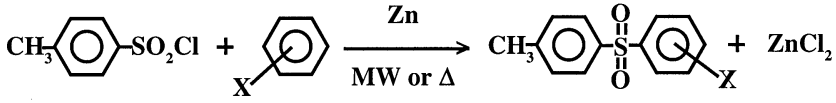
ABSTRACT

Zn dust-mediated Friedel-Crafts sulfonylation of aromatic compounds with p-toluenesulfonyl chloride was carried out to give corresponding sulfones in good yields. Isolation of pure products by simple filtration and evaporation is an important feature of this method.

We report here the selective synthesis of diaryl sulfones using microwaves and zinc dust under solvent-free conditions, as well as using a



conventional heating mode. Results are summarized in the Table. Activated as well as deactivated aromatics underwent smoother and faster sulfonylation under microwave irradiation than under conventional heating mode.

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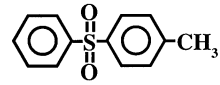
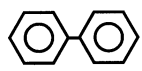
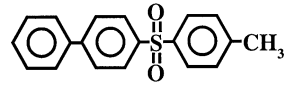
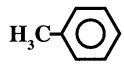
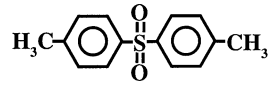
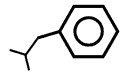
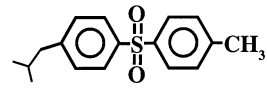
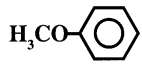
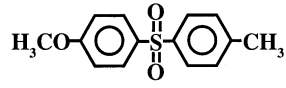
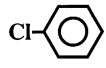
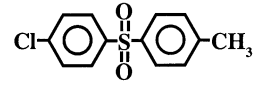
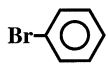
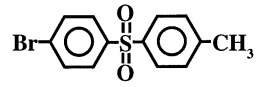
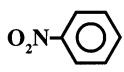
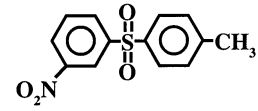
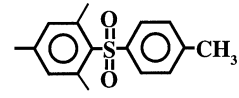
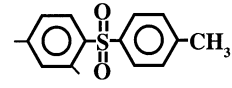
Table. Zinc-Mediated Sulfonylation of Aromatics

Sr. No.	Arene	Product[8]	Reaction Time		Yield[a,b]	
			Conv.Δ (min.)	M.W. (sec.)	Conv.Δ (%)	M.W. (%)
1			60	70	69	72
2			60	60	86	89
3			45	45	72	86[c]
4			60	90	62	70
5			30	15	75	77[d]
6			45	60	72	70
7			45	60	82	77
8			50	20	78	91
10			60	45	52	62
11			60	45	58	62

[a]Yields are of isolated products; [b]Products were characterized by their physical constants[8] IR, ^{1}H NMR, and mass; [c]ortho : para = 1:3; [d]ortho : para = 1:4.

Zn-mediated sulfonylation using even conventional mode of heating is fast (30–60 min), compared with sufonylation using Fe(III)-exchanged montmorillonite[6] (3–12 h). It is also important to note that the p-selectivity of sulfonylation is impressive with this method. On the other hand, aluminium chloride yields mixture of ortho : meta : para products. The synthesis of diphenyl sulfone, an intermediate for DIPSONE (4,4′-diaminodiphenyl sulfone)[7] effective for leprosy treatment and synthesis of similar drug intermediates using Zn dust offers a commerciably feasible route with control of effluents. The products obtained by this method are in good yields with essentially pure form.

In conclusion, we have developed novel method for the synthesis of useful sulfone intermediates for drug industry. Isolation pure products by simple filtration and evaporation is an important feature of this method.

EXPERIMENTAL

IR spectra were recorded on a Bomem MB104 FT-IR spectrometer, whereas ^{1}H NMR spectra were recorded on a Perkin-Elmer 90 MHz spectrometer.

Typical Procedure for Sulfonylation of Toluene

A mixture of toluene (5 mmol), p-toluenesulfonyl chloride (5 mmol), and Zn dust (5 mmol) was exposed to microwaves for 45 s or heated at 110°C for 60 min (Table). After completion of reaction (TLC), the product was extracted with ether (3×10 mL). Removal of the solvent under reduced pressure gave product in good yield and in pure form. In most of the cases, the reaction works very well on 25 mmol scale.

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REFERENCES

1. Olah, G.A.; Lin, H.C. Synthesis **1974**, 342.
2. Truce, W.E.; Vriesen, C.W. J. Am. Chem. Soc. **1953**, *75*, 5032.
3. Buehler, C.A.; Masters, J.E. J. Org. Chem. **1939**, *4*, 262.

4. Huismann, T. U.S. Patent 2,224,964 (*Chem. Absr.* **1941**, *35*, P2159).
5. Baliah, V.; Matheu, A. J. Ind. Chem. Soc. **1957**, *34*, 434.
6. Choudary, B.M.; Sreenivasa Choudhary N.; Laxmi Kantam M.; Kannan R. Tetrahedron Lett. **1999**, *40*, 2859.
7. Weijlard, J.; Messerly, J.P. U.S. Patent 2,385,899, Oct. 2, 1945. (*Chem. Abstr.* **1946**, *40,* P180)
8. *Dictionary of Organic Compounds*; 6th Ed., Chapman and Hall: London, **1995**.

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