One-Step Synthesis of Primary Alkyl- and Aralkyl-*N,N*-disulfonimides

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An improved synthesis of primary alkyl- and aralkyl-*N,N*-disulfonimides is reported. Reaction of 2 equiv of sulfonyl chloride with 1 equiv of amine and 2 equiv of NaH in THF produces 40–85% isolated yields of the title compounds.

Substitution and elimination reactions of compounds containing the sulfonimide leaving group, $-N(SO_2R)_2$, have recently aroused considerable attention (*1*, *2*). Published two-step procedures for the preparation of alkyl- and aralkyl-*N,N*-disulfonimides (**1**) by Baumgarten and co-workers (*3*) and by Pan and Fletcher (*5*) require isolation of the intermediate sulfonamides. A one-step synthesis of benzyl- and *n*-hexyl-*N,N*-di(trifluoromethane)sulfonimides has been reported (*4*), but experimental details are almost completely lacking and extension of the method to less reactive sulfonating agents is uncertain.

We wish to describe an efficient, one-step general synthesis of primary alkyl- and aralkyl-*N,N*-disulfonimides, **1** (eq 1).

$$RNH_2 + 2R'SO_2Cl + 2NaH \xrightarrow{THF} \underset{\mathbf{1}}{RN(SO_2R')_2} \qquad (1)$$

Two equivalents of the sulfonyl chloride in THF are slowly added to a cooled and vigorously stirred mixture of 1 equiv of the amine and 2 equiv of NaH in THF. Foaming of the reaction mixture during the addition and subsequent reflux is controlled by small amounts of the Union Carbide Corp. antifoaming agent SAG-100 (dimethylpolysiloxane). During workup, a major portion of the THF is recovered by distillation and may be used in succeeding synthesis.

Yield (mostly 55–86%) and melting point data for nine primary alkyl and aralkyl-*N,N*-disulfonimides are presented in Table I. Assignment of structures **1a–i** is supported by C, H elemental, infrared spectral (*3*), and proton magnetic resonance spectral (*3*) analyses.

For a given primary alkyl- or aralkylamine, the yield of *N,N*-di(*p*-toluene)sulfonimide is always somewhat higher than that of the *N,N*-dimethanesulfonimide. Compounds **1b** and **1c** were previously reported by Baumgarten and co-workers using a two-step method (*3*). Yields of these compounds from the current one-step procedure compare favorably with those obtained from the two-step synthesis.

Experimental Section

Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz. For all new compounds, carbon and hydrogen analyses agree with the theoretical values within ±0.4%.

General Synthetic Method. Into a 1000-mL three-necked flask equipped with a nitrogen atmosphere, reflux condenser, addition funnel, and magnetic stirrer is placed 10.0 g of NaH (52% oil dispersion, 0.217 mol). Mineral oil is removed from the NaH by washing (3 × 25 mL) with pentane. To the dry NaH is added 200 mL of THF and 6.4 mL of a 0.05% solution of SAG-100 in THF. The amine (0.10 mol) is added with stirring and the reaction flask is then cooled in an ice-salt bath. With maximum stirring, 0.20 mol of the sulfonyl chloride in 100 mL of THF is slowly added at such a rate that foaming is controlled. After addition of the sulfonyl chloride, the ice–salt bath is removed and the mixture is slowly heated to a gentle reflux. After 24 h, the apparatus is modified and most of the THF is distilled into a receiver (but not to dryness). The reaction flask is cooled in an ice–salt bath and residual NaH is destroyed by careful addition of wet CH_2Cl_2. Approximately 300 mL of water is added, the mixture is extracted (3 × 75 mL) with CH_2Cl_2 or $CHCl_3$, and the combined extracts are in turn washed with 300 mL of water. The organic layer is dried over $MgSO_4$ and filtered, and the solvent is removed in vacuo. The crude residue is purified by recrystallization.

Literature Cited

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Table I. Yield and Melting Point Data for Primary Alkyl- and Aralkyl-*N,N*-disulfonimides[a]

Compd	Registry no.	R	R′	Yield,[b] %	Mp, °C	Recryst solvent
1a		$CH_3(CH_2)_5$	CH_3	66	42–43	MeOH
1b	24332-41-0	$CH_3(CH_2)_5$	*p*-$CH_3C_6H_4$	81	118–118.5[c]	MeOH
1c	52374-07-9	$CH_3(CH_2)_5$	*m*-$NO_2C_6H_4$	70	113.5–114[d]	EtOH–acetone (4:1)
1d		$PhCH_2$	CH_3	40	117–117.5	MeOH
1e		$PhCH_2$	*p*-$CH_3C_6H_4$	57	162–163	Acetone
1f		$PhCH_2CH_3$	CH_3	68	70–71	MeOH
1g		$PhCH_2CH_2$	*p*-$CH_3C_6H_4$	78	103–104	MeOH
1h		Furfuryl	CH_3	67	122–122.5	MeOH
1i		Furfuryl	*p*-$CH_3C_6H_4$	86	139–140	MeOH

[a] Elemental analyses (for these compounds) in agreement with theoretical values were obtained. [b] Yield of recrystallized product. [c] Reference 3 reports mp 114.9–115.2 °C and 97% yield. [d] Reference 3 reports mp 113.0–114.5 °C and 47% yield.