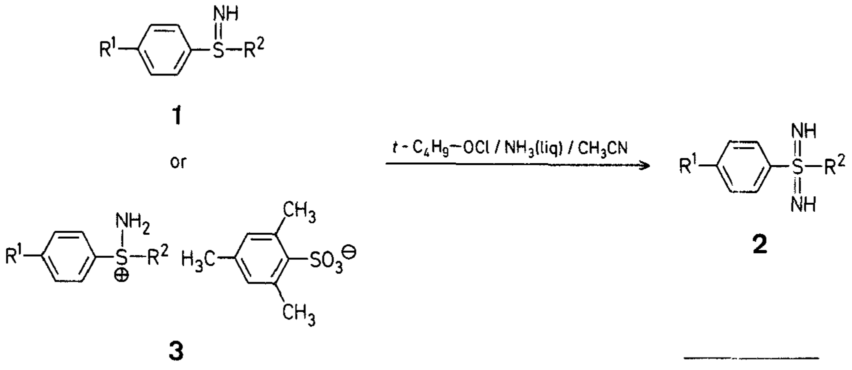
A New Method for the Synthesis of Diaryl Sulfone Diimides and *sec*-Alkyl Aryl Sulfone Diimides

Gunda GEORG, Manfred HAAKE

Institut für Pharmazeutische Chemie, Universität Marburg, Marbacher Weg 6, 3550 Marburg, Federal Republic of Germany

Sulfone diimides possess several properties which resemble those of the sulfones and sulfoximides[1]. They are usually synthesized by oxidation of sulfides with chloramine, using either a chloramine/ammonia gas mixture[2] or chloramine generated in *situ* from *t*-butyl hypochlorite and ammonia at low temperature[3]. By these methods, dialkyl sulfone diimides can be obtained in good yields. The yields of alkyl aryl sulfone diimides are generally lower. The methods fail for the synthesis of *sec*-alkyl aryl and diaryl sulfone diimides. Diaryl sulfone diimides can be obtained by reacting diarylsulfilimines with chloramine T, to form *N*-tosyl sulfone diimides; acidic hydrolysis then affords the free sulfone diimides[4]. We have now developed a new one-step synthesis of diaryl sulfone diimides and *sec*-alkyl aryl sulfone diimides **(2)**. Treatment of the corresponding sulfilimines **(1)** with *t*-butyl hypochlorite/ammonia in dry acetonitrile at −20°C gives directly the sulfone diimides **(2)**.



1

3

2

The method is limited to diaryl derivatives with electron-donating substituents at the phenyl rings. Attempts to synthesize diaryl sulfone diimides with electron-withdrawing groups ($R^1 = NO_2$, —NH—Ac, Br, Cl) were not successful. Our method also failed for $R^1 = NO_2$, $R^2 = CH_3$.

The sulfilimines **1** are readily available via electrophilic amination of thioethers with *O*-(mesitylenesulfonyl)-hydroxylamine and basification of the resultant *S*-aminosulfonium mesitylenesulfonates **(3)**[5]. The sulfone diimide syntheses reported in the present communication can also be performed with the *S*-aminosulfonium mesitylenesulfonates **(3)** as starting materials, the yields being comparable those obtained with the free sulfilimines **(1)**.

A similar method has been used for the conversion of sulfilimines into sulfoximides[6].

The melting points (HM-Lux, Leitz Heiztisch-Mikroskop) are uncorrected. The C,H analyses were carried out with a CH-apparatus Salzer, Labormatic/Wosthoff, the N analyses with a 185-CHN autoanalyzer Hewlett Packard, and the S analyses by the Schöninger method. The I.R. data were obtained with a Perkin-Elmer IR spectrometer PE 257.

Sulfone Diimides (2); General Procedure:

The sulfilimine (**1**; 20 mmol) or the *S*-aminosulfonium mesitylenesulfonate (**3**; 20 mmol) is dissolved in dry acetonitrile (100 ml) and this solution is cooled to −20°C. Liquid ammonia (15 ml) is added with stirring, followed by the dropwise addition of a solution of *t*-butyl hypochlorite (0.929 g, 50 mmol) in acetonitrile (15 ml). Stirring is continued overnight. The mixture is then filtered and the filtrate evaporated in vacuo. The residual oily product **2** can be crystallized from the solvent given in the Table.

Received: May 27, 1983

Table. Sulfone Diimides **(2)** prepared from Sulfilimines **(1)** or Salts **(3)**

2	R^1	R^2	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a] or *m.p. [°C] reported*	I.R. (KBr) ν [cm^{-1}]
a	H	C_6H_5	53[b]	88° (benzene/hexane)	92°[4]	3170, 1300, 1160, 1130, 1095, 1065, 925
b	H_3CO—	—C_6H_4—OCH_3(4)	57[b]	125° (ligroin)	$C_{14}H_{16}N_2O_2S$ (276.4)	3170, 1300, 1250, 1160, 1115, 1095, 1025, 925
c	CH_3	C_6H_5	36[b]	89° (hexane)	92°[4]	3115, 1300, 1160, 1125, 1090, 925
d	H	*c*-C_6H_{11}	60[c]	103° (hexane)	$C_{12}H_{18}N_2S$ (222.4)	3210, 1310, 1180, 1140, 1110, 1085, 1065, 925
e	H	*i*-C_3H_7	21[c]	57° (hexane)	$C_9H_{14}N_2S$ (182.3)	3140, 1300, 1180, 1150, 1110, 1090, 1065, 995, 930, 915

[a] The microanalyses were in good agreement with the calculated values: C, ±0.24; H, ±0.07; N, ±0.11; S, ±0.21.

[b] From **1**.

[c] From **3**.

---

[1] M. Haake, in: *Topics in Sulfur Chemistry*, A. Senning, Ed., Vol. 1, Georg Thieme Verlag, Stuttgart, 1976, p. 187.
C. R. Johnson, in: *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, Ed., Vol. 3, Pergamon Press, Oxford 1979, p. 237.

[2] J. A. Cogliamo, G. L. Braude, *J. Org. Chem.* **29**, 1397 (1964).

[3] M. Haake, *Tetrahedron Lett.* **1970**, 4449.

[4] N. Furukawa et al., *Synthesis* **1979**, 289.

[5] Y. Tamura, K. Sumoto, I. Mimimakawa, M. Ikeda, *Tetrahedron Lett.* **1972**, 4137.
Diphenyl sulfilimine is commercially available.

[6] N. Furukawa, K. Akutagawa, T. Yoshimura, S. Oae, *Synthesis* **1982**, 77.