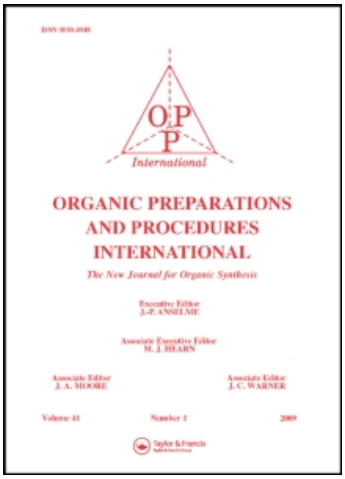


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A SIMPLE SYNTHESIS OF THE HETEROCYCLIC S,S-DIPHENYLSULFILIMINES

Olga G. Vlasova[a]; Oleg A. Rakitin[a]; Lenor I. Khmelnitski[a]
[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, RUSSIA

To cite this Article Vlasova, Olga G. , Rakitin, Oleg A. and Khmelnitski, Lenor I.(1994) 'A SIMPLE SYNTHESIS OF THE HETEROCYCLIC S,S-DIPHENYLSULFILIMINES', Organic Preparations and Procedures International, 26: 3, 331 — 335
To link to this Article: DOI: 10.1080/00304949409458430
URL: http://dx.doi.org/10.1080/00304949409458430

ORGANIC PREPARATIONS AND PROCEDURES INT., 26 (3), 331-335 (1994)

A SIMPLE SYNTHESIS OF THE HETEROCYCLIC S,S-DIPHENYLSULFILIMINES

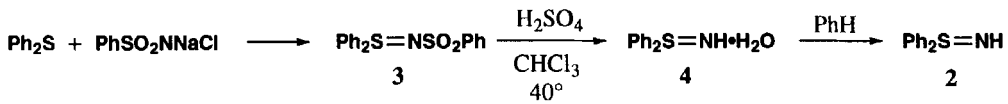
Olga G. Vlasova, Oleg A. Rakitin* and Lenor I. Khmelnitski

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences
Leninsky Prospect 47, 117334 Moscow B-334, RUSSIA

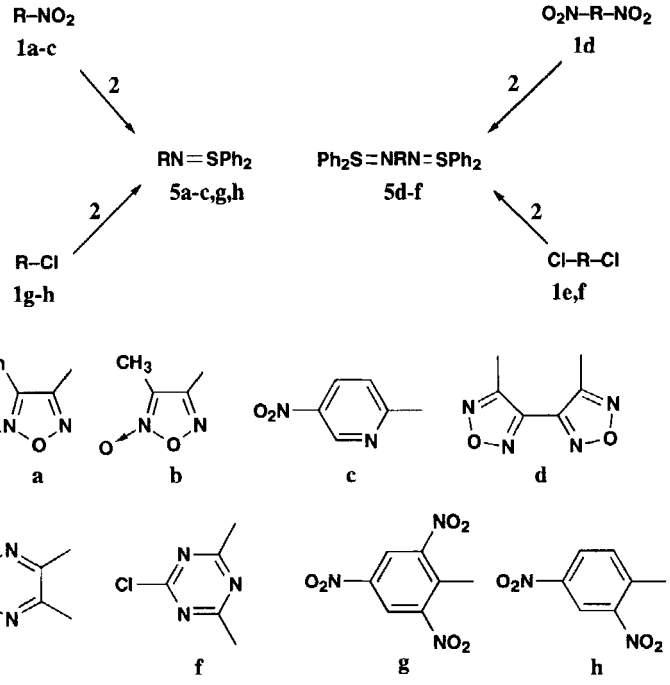
Sulfilimines are important intemediates for the synthesis of various heterocyclic compounds. The sensitivity of the S=N bond to both nucleophilic and electrophilic reagents make sulfilimines important reagents in organic synthesis.[1,2] Furthermore,, some sulfilimine derivatives show herbicidal, bactericidal and pharmacological activity. [1,3-6] Heterocyclic sulfilimines could also find a similar utilization, should effective methods of their preparation be available. All known methods of synthesis of sulfilimines are based on condensation reactions of amines with activated dimethyl sulfide[7-9] or DMSO.[3,10,14] However, these methods are not always successful,[15] especially for the preparation of polysulfilimines.[12] The synthesis of sulfilimines by nucleophilic substitution of chloro or nitro groups by sulfilimino functions seems to be most convenient, especially in cases where chloro or nitro derivatives are more accessible than the corresponding amines. N-Unsubstituted sulfilimines may be used as nucleophilic reagents in these reactions. The synthesis of heterocyclic sulfilimines by this method could not be found in the literature.

We investigated the possible use of N-unsubstituted sulfilimines R_2S=NH (R= Me, Ph) for the nucleophilic substitution of chloro or nitro groups in heterocycles. S,S-Dialkylsulfilimines are known to be unstable solids.[16] Therefore, we attempted to carry out the reaction of 3-nitro-4-phenylfuroxan (**1a**) with S,S-dimethylsulfilimine[16] in dichloromethane. However, the latter reagent was too unstable in solution and decomposition occurred before reaction with **1a**.

While S,S-diphenylsulfilimine (**2**) is a stable compound,[22] the known methods of its preparation are inconvenient because of high cost and difficult access to starting compounds.[16-21] We now report the development of a convenient procedure for the synthesis of **2** in good yield from commercially available materials: sodium N-chlorobenzensulfonamide (Chloroamine B) and diphenyl sulfide. First, S,S-diphenyl-N-phenylsulfonylsulfilimine (**3**) was prepared by the method of Tsujihara *et al.*[26] Then, the N-sulfonyl group was eliminated by sulfuric acid at 40° in chloroform. Finally, the S,S-diphenylsulfilimine hydrate (**4**) obtained was dehydrated by azeotropic distillation in benzene.



We have found that chloro- or nitroheterocycles [furazans, furoxans, pyridines, pyrazines and 1,3,5-triazoles (**1a-f**)] give diphenylsulfilimino derivatives (**5a-f**) by treatment with **2**. If two chloro or nitro groups prone to substitution are present as in **1d-f**, *bis*-diphenylsulfilimines (**5d-f**) were formed. Unlike nitrofuroxans **1a,b**, mildly activated nitroheterocycles such as 4-methyl- and 4-phenyl-3-nitrofurazans do not react with **2**. This method also enabled us to obtain the aromatic sulfilimines **5g,h**. It should be pointed out that S,S-diphenylsulfilimine hydrate (**4**) does not react with 2,4-dinitrochlorobenzene (**1b**)[17] and, consequently, is a weaker nucleophile than **2**.



In summary, a simple procedure for the synthesis of **2**, mild reaction conditions and high yields of products **5** make this method a useful contribution to the synthesis of heterocyclic sulfilimines.

EXPERIMENTAL SECTION

The melting points are determined on a Boetius apparatus and are uncorrected. The ^{13}C NMR spectra were obtained on an AM-300 Bruker at 75.5 MHz in $CDCl_3$ solution with TMS as internal standard, δ ppm. The IR spectra were recorded on a Specord spectrometer in KBr tablets. Microanalyses were carried out by the Analytical Laboratory of the Institute.

S,S-Diphenyl-N-phenylsulfonylsulfilimine (3).- Diphenyl sulfide (18 mL, 0.1 mol) and Chloroamine-B (sodium N-chlorobenzensulfonamide) (35 g, 0.11 mol) were dissolved in 200 mL of methanol. To this solution, acetic acid (5.0 mL) in 25 mL of methanol was added dropwise at 20-30°. The mixture was allowed to stand at room temperature for 1 hr and was then poured into a cold solution of NaOH (5g) in 450 mL of water. The resulting precipitate formed was collected, washed with water, and dried to yield 32.2 g (83%) of **3** a colorless solid, mp. 126-128°. IR: 945 (S=N) cm^{-1}.

Anal. Calcd. for $C_{18}H_{15}NO_2S_2$: C, 69.88; H, 4.89; N, 4.53; S, 10.36

Found: C, 69.62; H, 4.84; N, 4.21; S, 10.11

TABLE 1. Preparation and Spectral Data of Diphenylsulfilimines (**5**)

Cmpd	Time	Yield(%)	mp. (°C)	IR $\nu_{S=N}(cm^{-1})$
5a	5 hrs	74	144-146	960
5b	5 hrs	70	138-140	980
5c	45 min	69	152-154	960
5d	3.5 hrs	90	249-251	980
5e	30 min	95	229-231	980
5f	3 hrs	68	249-253	980
5g	15 min	85	136-137	950
5h	48 hrs	87	133-134	940

TABLE 2. Elemental Analysis of Diphenylsulfilimines (**5**)

Cmpd	Formula	Calcd				Found			
		C	H	N	S	C	H	N	S
5a	$C_{20}H_{15}N_3O_2S$	66.48	4.16	11.63	8.86	66.51	4.15	11.41	8.83
5b	$C_{15}H_{13}N_3O_2S$	60.20	4.35	14.05	10.70	60.13	4.59	13.51	10.91
5c	$C_{17}H_{13}N_3O_2S$	63.16	4.02	13.00	9.91	62.98	3.70	13.08	10.05
5d	$C_{28}H_{20}N_6O_2S_2$	62.69	3.73	15.67	11.94	62.70	3.90	15.25	12.00
5e	$C_{28}H_{20}N_6OS_2$	64.62	3.85	16.15	12.31	64.57	3.84	16.14	12.40
5f	$C_{27}H_{20}ClN_5S_2$[a]	63.10	3.89	13.63	12.46	62.99	3.82	13.12	12.23
5g	$C_{18}H_{12}N_4O_6S$	52.43	2.91	13.59	7.77	52.52	3.00	13.68	7.76
5h	$C_{18}H_{13}N_3O_4S$	58.86	3.54	14.44	8.72	58.80	3.46	14.56	8.72

a) *Anal.* Calcd. for $C_{27}H_{20}N_5OS_2Cl$ (%): Cl 6.91; found Cl 6.78.

S,S-Diphenylsulfilimine (2).- To conc. H_2SO_4 (70 mL) and $CHCl_3$ (60 mL) at 30°was added S,S-diphenyl-N-phenylsulfonylsulfilimine (**3**) (122 g, 65 mmol) under vigorous stirring at such a rate that the reaction temperature did not rise above 40°. The mixture was then refluxed for 1 hr, cooled to room temperature, and poured into 600 mL of ice water. After separation of the chloroform layer, the aqueous layer was washed with $CHCl_3$ (4 x 100 mL), and made alkaline (pH 10-11) with 20%

NaOH. The precipitate of $Ph_2S{=}NH{\bullet}H_2O$ (**4**) was collected by suction, dried and dissolved in 60 mL of hot benzene. After filtration of inorganic salts and removal of water by azeotropic distillation with benzene, **2** was crystallized from hexane to yield 10.4 g (80%), mp. 59-61°, lit.[22] mp. 58-60°.

Sulfilimines 5a-h. General Procedure.- To a stirred solution of **1a-h** (1 mmol) in CH_2Cl_2 (10 mL), **2** (0.6 g, 3 mmol for **1a-c,g,h** (or 1.2 g, 6 mmol for **1d-f**) in CH_2Cl_2 (5 mL) was added at room temperature. The reaction times are shown in Table 1. At the end of the reaction,[23] the mixture was washed with a 5% solution of acetic acid and water (2 x 5 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel column; $CHCl_3$ was used as eluent. The yields, elemental analysis data and spectral characteristics are given in Tables 1, 2 and 3.

TABLE 3. ^{13}C NMR Data of Compounds **5**[a]

Cmpd	Chemical shifts, δ (ppm)
5a	124.64, 126.90, 136.80, 129.46 (Ph-C), 111.56 (C-Ph), 161.87 (C-N), 136.80, 126.95, 129.61,128.23 (Ph-S).
5b	7.32 (Me), 111.16 (C-Me), 162.86 (C-N), 127.31,129.72, 132.05, 136.71 (Ph).
5c	113.63, 131.54, 135.02, 145.96, 168.59 (Py), 127.55, 129.80, 131.96, 136.39 (Ph).
5g	118.31,124.44, 143.98, 148.79 (Ph-N), 127.72, 131.25, 133.83, 137.97 (Ph-S).
5h	117.80, 127.69, 135.58, 141,13, 155.44 (Ph-N), 127.17, 130.41,132.82, 136.56 (Ph-S).

a) Disulfilimines **5d-f** are practically insoluble in water and organic solvents.

REFERENCES

1. T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, **77**, 409 (1977).
2. I. V. Koval, *Usp. Khim.*, **59**, 1409 (1990).
3. G. D. Hartmann, EP Pat. No 111,151 (1984); *Chem. Abstr.*, **101**, 171286f (1984).
4. R. Shapiro and C.-P. Tseng, EP Pat. No 117,014 (1984); *Chem. Abstr.*, **102**, 6533x (1984).
5. K. H. Mueller, W. Roy, L. Eue, H. J. Santel and R. R. Schmidt, DE Pat. No 3,510,794 (1986), *Chem. Abstr.*, **106**, 33130c (1987).
6. K. Kono, M. Kasai, Y. Saito, M. Morimoto and T. Ashizawa, JP Pat. No 6354380 (1988); *Chem. Abstr.*, **109**, 149231r (1988).
7. P. K. Claus, W. Rieder, P. Hofbauer and E. Vilsmaier, *Tetrahedron*, **31**, 505 (1975).
8. E. C. Taylor, C.-P. Tseng and J. B. Rampal, *J. Org. Chem.*, **47**, 552 (1982).
9. D. T. Hurst, *Australian J. Chem.*, **36**, 2119 (1983).

10. H. Labaziewicz, K. R. Lindfors and T. H. Kejonen, *Heterocycles*, **29**, 2327 (1989).

11. T. L. Gilchrist, C. J. Harris, C. J. Moody and C. W. Rees, *Chem. Comm.*, 486 (**1974**).

12. M. D. Coburn, H. H. Hayden, C. L. Coon and A. R. Mitchell, *Synthesis*, 490 (**1986**).

13. M. D. Coburn, *J. Heterocycl. Chem.*, **23**, 421 (1986).

14. I. E. Filatov, Iu. V. Kulikov, G. L. Rusinov and K. I. Pashkevich, *Khim. Geterotsikl. Soedin.*, 1423 (**1989**).

15. O. A. Rakitin, O. G. Vlasova, L. I. Khmelnitski, I. F. Faljakhov and T. N. Sobachkina, *ibid.*, 1536 (**1990**).

16. T. Yoshimura, T. Omata, N. Furukawa and S. Oae, *J. Org. Chem.*, **41**, 1728 (1976).

17. Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi and M. Ikeda, *ibid.*, **38**, 4324 (1973).

18. R. Appel and W. Büchner, *Chem. Ber.*, **95**, 849 (1962).

19. R. Appel and W. Büchner, *ibid.*, **95**, 2220 (1962).

20. K. Tsujihara, N. Furukawa, K. Oae and S. Oae, *Bull. Chem. Soc. Jpn*, **42**, 2631 (1969).

21. J. Drabowicz, P. Lyzwa and M. Mikolajczyk, *Synthesis*, 890 (**1981**).

22. Y. A. Franz and J. C. Martin, *J. Amer. Chem. Soc.*, **97**, 583 (1975).

23. Disulfilimines **5d-f** were precipitated, filtered, washed with CH_2Cl_2 and dried.

(Received July 21, 1993)