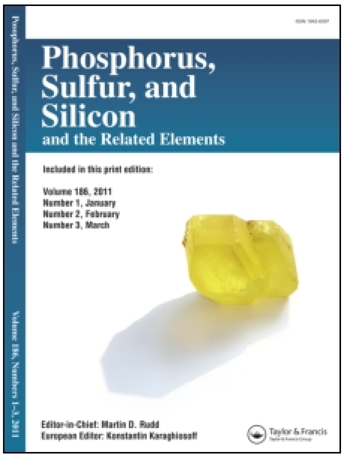


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Internal 1,2-Aryl Migration in the Thermolyses of *N*-Unsubstituted *S-p*-and *S-o*-Nitrophenylsulfilimines

Kunihiko Akutagawa[a]; Naomichi Furukawa[a]; Shigeru Oae[ab]
[a] Department of Chemistry, The University of Tsukuba, Ibaraki, Japan [b] Okayama University of Sciences, Okayama, Japan

To cite this Article Akutagawa, Kunihiko , Furukawa, Naomichi and Oae, Shigeru(1984) 'Internal 1,2-Aryl Migration in the Thermolyses of *N*-Unsubstituted *S-p*-and *S-o*-Nitrophenylsulfilimines', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 2, 255 — 257

To link to this Article: DOI: 10.1080/03086648408077586

URL: http://dx.doi.org/10.1080/03086648408077586

Phosphorus and Sulfur, 1984, Vol. 19, pp. 255–257
0308-664X/84/1902-0255/$18.50/0

SHORT COMMUNICATION
Internal 1,2-Aryl Migration in the Thermolyses of *N*-Unsubstituted *S*-*p*- And *S*-*o*-Nitrophenylsulfilimines

KUNIHIKO AKUTAGAWA, NAOMICHI FURUKAWA* and SHIGERU OAE*[a]

Department of Chemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

(*Received September 23, 1983; in final form November 8, 1983*)

o- or *p*-Nitroaniline was obtained when thermolysis of *N*-unsubstituted *S*-*o*-nitrophenyl- or *p*-nitrophenyl-*S*-phenylsulfilimine was carried out at 50–100°C without solvent.

Earlier, Oae *et al.*, reported a convenient method to prepare *N*-unsubstituted sulfilimines.[1] The reactions of *N*-unsubstituted sulfilimines with various electrophiles are important for syntheses of various sulfilimine derivatives.[1,2] Although *N*-unsubstituted dialkylsulfilimines are known to be rather unstable, decomposing even at room temperature,[3] *N*-unsubstituted diarylsulfilimines, e.g., diphenyl derivative, are thermally stable and do not decompose even in refluxing benzene for 24 h, and decompose on heating in neat form at above 100°C to afford the corresponding diaryl sulfide, nitrogen and ammonia which are assumed to arise by disproportionation of unstable free nitrene formed as an intermediate.[1a] In the thermolysis of *S*-benzyl- or *S*-methyl-*S*-phenyl-(*N*-*p*-tolylsulfonyl)sulfilimine in DMF[4] and also in the reaction of *S*-methyl-*S*-phenyl-(*N*-*p*-tolylsulfonyl)sulfilimine with halide ion[5] or *N*-*N*-dimethylaniline[6] in aprotic solvents, 1,2-benzyl or methyl migration from a sulfur atom to a nitrogen atom was observed, affording *S*-benzyl or *S*-methyl *p*-toluenesulfenamide. Both reactions were shown to involve two consecutive steps, namely the initial nucleophilic attack of either halide ion or *N*, *N*-dimethylaniline on the carbon atom of methyl or benzyl group and the subsequent nucleophilic attack of the sulfenamide anion on the intermediate, benzyl or methyl halide or ammonium salt. However, thermolyses of *N*-unsubstituted *S*-*o*-nitrophenyl-(**1a**) and *S*-*p*-nitrophenyl-(**1b**)-*S*-phenylsulfilimines have been found to give a rearrangement product in this case, an internal 1,2-aryl migration product, i.e., *o*- and *p*-nitroaniline (**2a, b**) together with the corresponding sulfide in moderate yields.

This paper describes the results of the thermolyses of the sulfilimines **1a** and **1b**.

Thermolyses of the sulfilimines (**1a, 1b**) were carried out under reduced pressure with no solvent at 50–100°C for 1 h, although the reactions did not take place in refluxing benzene for 60 min. The major products thus obtained were *o*- and *p*-nitroaniline (**2a, b**) together with the corresponding reduced sulfides. The results

---

[a] Present Address; Okayama University of Sciences, Ridai-cho, 1-1, Okayama 700, Japan.

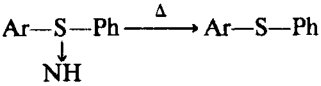
TABLE I

Internal 1,2-aryl migration products in the thermolysis of *N*-unsubstituted *S*-*o*-, or *S*-*p*-nitrophenyl-phenylsulfilimine

Substrate	Condition	Product	Yield (%)[a]
$\mathrm{Ph{-}\underset{\underset{NH}{\downarrow}}{S}{-}C_6H_4{-}NO_2}$-*o* **(1a)**	80°C 1 h	*o*-$\mathrm{O_2N{-}C_6H_4{-}NH_2}$ **(2a)**	33
$\mathrm{Ph{-}\underset{\underset{NH}{\downarrow}}{S}{-}C_6H_4{-}NO_2}$-*p* **(1b)**	60°C 1 h	*p*-$\mathrm{O_2N{-}C_6H_4{-}NH_2}$ **(2b)**	27

[a] Isolated yield.

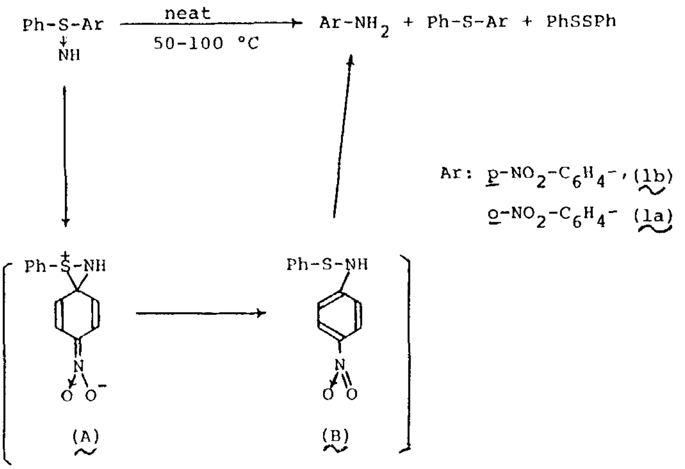
are shown in Table I. Other *N*-unsubstituted diarylsulfilimines, e.g., diphenyl-, *p*-chlorophenyl-phenyl-, phenyl-*p*-tolyl-, phenyl-*m*-tolyl-, *p*-bromophenyl-phenyl, and phenyl-(2-pyridyl) did not decompose under the present reaction conditions. The product obtained by thermolyses of these *N*-unsubstituted diarylsulfilimines at an elevated temperature, i.e., 150°C, was only the diaryl sulfide as shown below.



$$\mathrm{Ar{-}\underset{\underset{NH}{\downarrow}}{S}{-}Ph} \xrightarrow{\Delta} \mathrm{Ar{-}S{-}Ph}$$

Ar: $p\text{-}\mathrm{ClC_6H_4}$—, $p\text{-}\mathrm{BrC_6H_4}$—, *m*- or $p\text{-}\mathrm{CH_3C_6H_4}$—, $\mathrm{C_6H_5}$—, $2\text{-}\mathrm{C_5H_4N}$

Both anilines (**2a, b**) are considered to be formed through the mechanistic paths as shown in the following scheme. Namely, the imino nitrogen atom in **1a** or **1b** may attack intramolecularly the carbon atom on the nitrophenyl group to form a Meisenheimer-type intermediate (**A**) which then collapses to the sulfenamide (**B**) from which upon thermolysis **2a** or **2b** would be obtained. On the other hand,



SCHEME Internal 1,2-aryl migration in the thermolyses of *N*-unsubstituted *o*- or *p*-nitrophenyl-phenylsulfilimine.

S,S-diaryl- (*N*-*p*-tolylsulfonyl)sulfilimines are thermally stable, and decompose only upon heating at 300°C.[7] When *S*-*o*-nitrophenyl or *S*-*p*-nitrophenyl-*S*-phenyl- (*N*-*p*-tolylsulfonyl)sulfilimine was heated at 300°C for 2 h, decomposition took place but no rearranged product was obtained. The products thus obtained in major yields were the corresponding sulfide and *p*-toluenesulfonamide. Since the imino group is deactivated by the electron-withdrawing sulfonyl group in *N*-*p*-tolylsulfonylsulfilimine, it is no longer basic enough to undergo nucleophilic attack which is essential for this rearrangement in **1a** or **1b**.

Moreover, no product, formed by "Vicarious" substitution[8] of hydrogen in aromatic nitro compounds, was detected. Thus, the product, *N*-unsubstituted *S*-3-amino-4-nitrophenyl-*S*-phenylsulfilimine which may be formed by nucleophilic attack of imino nitrogen of **1b** on the 3-position of nitrophenyl ring of another one was not obtained. Indeed, *N*-unsubstituted *S,S*-diphenylsulfilimine did not react at all with nitrobenzene, 1-nitronaphthalene or quinoline which are reported to react with dimethyloxosulfonium methylylide, methyl sulfinyl carbanion or hydroxylamine under "Vicarious" substitution conditions to afford *o*-, or *p*-nitrotoluene, 1-nitro-4-aminonaphthalene or 4-methylquinoline, respectively.

Thus, the 1,2-rearrangement of *o*- or *p*-nitrophenyl group in **1a** or **1b** upon thermolysis may proceed *via* an intramolecular nucleophilic substitution on the aromatic carbon atom. However, a mechanism for the Stevens-type rearrangement of the isoelectronic sulfonium ylide[9] cannot be ruled out. Further experiments to clarify the mechanism for this thermolysis of **1a** or **1b** are undergoing in this laboratory.

REFERENCES

1. (a) T. Yoshimura, T. Omata, N. Furukawa and S. Oae, *J. Org. Chem.*, **41**, 1728 (1976); (b) M. Moriyama, T. Yoshimura, N. Furukawa, T. Numata and S. Oae, *Tetrahedron*, **32**, 3003 (1976); (c) M. Moriyama, N. Furukawa, T. Numata and S. Oae, *J. Chem. Soc., Perkin-2*, **1977**, 1783.
2. (a) N. Furukawa, M. Fukumura, T. Nishio and S. Oae, *J. Chem. Soc., Perkin-1*, **1977**, 96; (b) N. Furukawa, M. Fukumura, T. Nishio and S. Oae, *Bull. Chem. Soc., Jpn.*, **51**, 3599 (1978); (c) N. Furukawa, M. Fukumura, T. Nishio and S. Oae, *Phosphorus and Sulfur*, **5**, 231 (1978); (d) Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi and M. Ikeda, *J. Org. Chem.*, **38**, 4324 (1973); (e) Y. Tamura, H. Matsushima, M. Ikeda and K. Sumoto, *Tetrahedron*, **32**, 431 (1976); (f) Y. Tamura, T. Miyamoto, J. Eiho, H. Taniguchi, T. Nishimura and Y. Kita, *J. Chem. Soc. Perkin-1*, **1974**, 105; (g) T. L. Gilchrist, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin-1*, **1975**, 1964; (h) N. Furukawa, T. Yoshimura, M. Ohtsu, T. Akasaka and S. Oae, *Tetrahedron*, **36**, 73 (1980); (i) R. Appel and W. Buchner, *Chem. Ber.*, **95**, 2220 (1962).
3. (a) R. Appel and W. Buchner, *Chem. Ber.*, **95**, 849, 855 (1962); (b) J. B. Lambert, C. E. Mixan and D. S. Bailey, *J. Am. Chem. Soc.*, **94**, 208 (1972).
4. T. Aida, N. Furukawa and S. Oae, *J. Chem. Soc., Perkin-2*, **1976**, 1431.
5. N. Furukawa, T. Aida and S. Oae, *Int. J. Sulfur Chem.*, **A2**, 181 (1972).
6. T. Aida, *PhD Dissertation, Osaka City University*, **1974**.
7. (a) K. Goldhahn, *J. Prakt. Chem.*, **156**, 315 (1940); (b) G. A. Russell and A. Weiner, *J. Org. Chem.*, **31**, 248 (1966); (c) V. J. Traynelis and S. J. V. McSweeney, *J. Org. Chem.*, **31**, 243 (1966); (d) P. A. Argabright, J. E. Hofmann and S. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965); (e) E. T. McBee, E. P. Wesseler and T. Hodgins, *J. Org. Chem.*, **36**, 2907 (1971); (f) M. Makosza and J. Winiarski, *J. Org. Chem.*, **45**, 1534 (1980).
8. W. Ando, T. Yagihara and T. Migita, *Tetrahedron Lett.*, **1969**, 1983; (b) U. Schöllkopf, G. Ostermann and J. Schossing, *Tetrahedron Lett.*, **1969**, 2619; (c) U. Schöllkopf, U. Ludwig, G. Ostermann and M. Patsh, *Tetrahedron Lett.*, **1969**, 3415.
9. (a) R. C. Atkins and C. M. Lentz, *J. Org. Chem.*, **43**, 773 (1978); (b) K. Akutagawa, *Ph.D. Dissertation, University of Tsukuba*, **1983**.