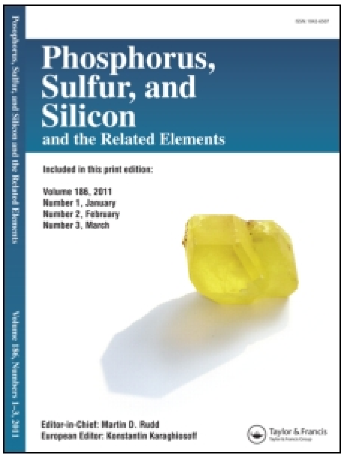
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

A Novel Light Induced Oxygen Shift from Sulfur to Nitrogen in Saccharine Derived Sultams

Dietrich Döpp[a]; Peter Lauterfeld[a]; Markus Schneider[a]; Dietmar Schneider[a]; Uwe Seidel[a]
[a] Fachgebiet Organische Chemie, Gerhard-Mercator-Universität - GH Duisburg, Duisburg, Federal Republic of Germany

To cite this Article Döpp, Dietrich , Lauterfeld, Peter , Schneider, Markus , Schneider, Dietmar and Seidel, Uwe(1994) 'A Novel Light Induced Oxygen Shift from Sulfur to Nitrogen in Saccharine Derived Sultams', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 481 — 482

To link to this Article: DOI: 10.1080/10426509408034283

URL: http://dx.doi.org/10.1080/10426509408034283

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 481–482
Reprints available directly from the publisher
Photocopying permitted by license only

Published under license by Gordon and Breach Science Publishers SA
Printed in the United States of America

A NOVEL LIGHT INDUCED OXYGEN SHIFT FROM SULFUR TO NITROGEN IN SACCHARINE DERIVED SULTAMS

DIETRICH DÖPP, PETER LAUTERFELD, MARKUS SCHNEIDER,
DIETMAR SCHNEIDER and UWE SEIDEL
Fachgebiet Organische Chemie, Gerhard-Mercator-Universität - GH Duisburg,
D-47048 Duisburg, Federal Republic of Germany

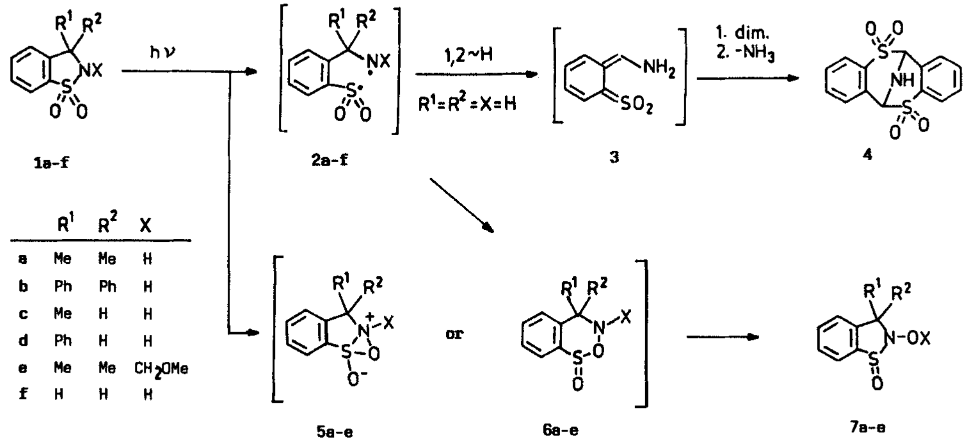
Abstract 2,3-Dihydrobenzo-1,2-thiazole-1,1-dioxides **1a-e** bearing at least one alkyl or aryl group at C-3 undergo a smooth photoisomerization into the isomeric N-hydroxy sulfinamides **7a-e**. These represent a new thermodynamically instable functional group, i. e. the sulfine hydroxamic acid moiety. The mode of formation probably involves initial S-N homolysis followed by a sequence of steps.

According to current knowledge[1] photochemical activation of sulfonamides $R-SO_2-NH-R'$ may result in homolysis of the $R-SO_2$, SO_2-N and $N-R'$ bonds. The resulting radicals in turn undergo typical reactions open to them, among others loss of SO_2 from $R-\dot{S}O_2$. The light induced reactions of sultams, being cyclic sulfonamides, have received so far comparatively little attention.

In methanol or acetonitrile solution upon 254 nm irradiation, sultams **1a-d** undergo a smooth and efficient (the quantum yields for formation of **7a** and **7b** are 0.51 and 0.36, respectively) into the cyclic sulfine hydroxamic acids **7a-d**[2]. The sulfine hydroxamic acid is a hithertho unknown functional group. Its thermodynamic instability with respect to the sulfonamide moiety may have prevented its detection as a product in reactions of sulfinyl chlorides with hydroxylamines[3].

Crystalline **7a-d** is perfectly stable, in solution, especially under the influence of added mineral acid, the labile functionality tends to revert rapidly to the thermodynamically more stable starting materials **1a-d**. Two pathways (**1**→**2**→**6**→**7**) and (**1**→**5**→**7**) are conceivable. Since **1f** does not give rise to a product of type **7** but forms the dimerization/condensation product **4**, S−N bond rupture is regarded as the most likely primary event, followed by formation of **6a-e** or, as the case of **2f**, by rearrangement to **3** and dimerization/condensation of the latter to form compound **4**, the structure of which has been unambiguously confirmed by an X-ray structural analysis[4].

The proton on nitrogen in **1a-d** (X = H) may be replaced by electrophilic carbon (e.g. X = CH_2-O-CH_3 as in **1e**) but not by alkyl groups. For four wavelengths the absorbancy difference diagrams[5] are strictly linear, thus no spectroscopically detectable intermediate is accumulating.



	R^1	R^2	X
a	Me	Me	H
b	Ph	Ph	H
c	Me	H	H
d	Ph	H	H
e	Me	Me	CH_2OMe
f	H	H	H

Racemic **1c** is photoisomerized to a 72:28 trans/cis mixture of **7c**. The geometrical isomers could not be interconverted thermally, instead, **7c** is reverted into **1c**. This process is accompanied by some dehydration of **7c**. Inversion at sulfur does not noticeably compete with re-isomerization below 60°C in solution.

The benzo[e]- and [g]-homologues of **1a** undergo analogous light induced transformations.

Acknowledgement: Generous support by Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. F. Golpasphin, B. Weiss and H. Dürr, Arch. Pharm. 317 (1984), 906.
2. The structure of **7a** has been unambiguously confirmed by an X-ray crystal structure analysis: D. Döpp, C. Krüger, P. Lauterfeld and E. Raabe, Angew. Chem. Int. Ed. Engl. 26 (1987), 146.
3. H. F. Whalen and L. W. Jones, J. Am. Chem. Soc. 64, 1356 (1925).
4. D. Döpp, G. Henkel and U. Seidel, to be published.
5. H. Mauser, Z. Naturforschg. 23b (1968), 1025; H.-D. Scharf and J. Fleischhauer, Methoden der Organischen Chemie, 4th. ed., Vol. IV/5a, edited by E. Müller, pt. 1, (Thieme, Stuttgart, 1975) p. 21.