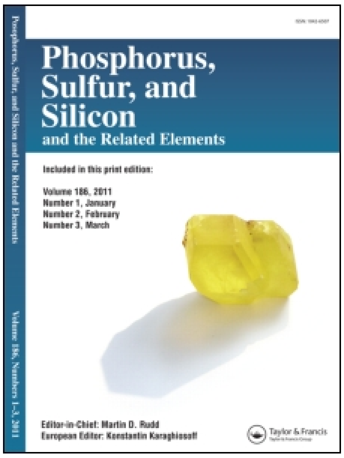
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Reduction and Sulfonylation of Olefins by Solutions of Diisopropylethylamine and Sulfur Dioxide

Fabrice Eugene[a]; Bernard Langlois[a]; Eliane Laurent[a]
[a] Laboratoire de Chimie Organique 3, associé au CNRS, Univ. Claude Bernard-Lyon I, Villeurbanne, France

To cite this Article Eugene, Fabrice , Langlois, Bernard and Laurent, Eliane(1993) 'Reduction and Sulfonylation of Olefins by Solutions of Diisopropylethylamine and Sulfur Dioxide', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 377 — 378

To link to this Article: DOI: 10.1080/10426509308038123

URL: http://dx.doi.org/10.1080/10426509308038123

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, 1993, Vol. 74, pp. 377–378
Reprints available directly from the publisher
Photocopying permitted by license only

© 1993 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded At: 14:00 29 January 2011

REDUCTION AND SULFONYLATION OF OLEFINS BY SOLUTIONS OF DIISOPROPYLETHYLAMINE AND SULFUR DIOXIDE

FABRICE EUGENE, BERNARD LANGLOIS and ELIANE LAURENT
Univ. Claude Bernard-Lyon I, Laboratoire de Chimie Organique 3, associé au CNRS, Villeurbanne, France

Abstract Solutions of diisopropylethylamine and SO_2 deliver sulfones from acrylates and reduce olefins substituted by two carbonyl moieties in α and β positions.

INTRODUCTION

The growing concentration of sulfur dioxide in the atmosphere induces questions about the biological behaviour of this compound, mainly towards aminated substrates. Though interactions between sulfur dioxide and some simple tertiary amines, like Me_3N[1] or N-benzyl-1,4-dihydronicotinamide[2], a model of the biologically important NADH, have been reported, little is known about the reactivity of branched tertiary amines, like diisopropylethylamine (DIEA), towards SO_2.

REACTION OF SOLUTIONS OF DIISOPROPYLETHYLAMINE AND SO_2 WITH OLEFINS BEARING ONE CARBONYL GROUP

Ethyl acrylate (**1a**), crotonate (**1b**) and cinnamate (**1c**), as well as benzylidene acetone (**1d**) and carvone (**1e**), were opposed to solutions of DIEA and SO_2 in dimethylacetamide (DMAc) at 80°C.

No reaction was observed from **1b-e** at 80°C after 7 hours. Only **1a**, which is a terminal olefin, reacted completely in 2 hours at 80°C to deliver a symetric sulfone as the main product:

$$CH_2{=}CH\text{-}E \xrightarrow[\text{DMAc - 80°C - 2h}]{\text{DIEA-SO}_2\text{ (1.1 eq.)}} (ECH_2\text{-}CH_2)_2S_n + (ECH_2\text{-}CH_2)_2SO_2$$

n= 1,2

(E= CO_2Et)

conv.= 100% 9% 53%

Downloaded At: 14:00 29 January 2011

This reaction seemed to be very sensitive to steric hindrance and could be consistent with a 1,4 nucleophilic addition of a SO_2 derivative.

REACTION OF SOLUTIONS OF TERTIARY AMINES AND SO_2 WITH OLEFINS BEARING TWO CARBONYL GROUPS IN α AND β POSITIONS

With such substrates, like diethyl fumarate (**4a**) and maleate (**4b**) or (E)-dibenzoyl (**4c**) and diacetyl ethylene (**4d**), the reaction with solutions of DIEA and SO_2 in DMAc proceeded completely differently. The reduction of the double bond, though sluggish at 20°C, occured rapidly at 80°C:

$$\underset{(E=CO_2Et,COPh,Ac)}{E-CH=CH-E} \xrightarrow[\text{DMAc - 80°C}]{\text{DIEA-}SO_2\text{ (1.1 eq.)}} E-CH_2-CH_2-E$$

4a	conv= 100%	1.25 h	65%	(58% isolated)
4b	76%	2.50 h	55%	(+10% **4a**)
4c	>90%	1.25 h		(31% isolated)
4d	100%	0.25 h		(43% isolated)

In solution, the Et_3N-SO_2 complex is more stable than the DIEA-SO_2 one. However, solutions of Et_3N and SO_2 in DMAc were less reactive, at 80°C, than those with DIEA (**4a** conv= 72% after 23.25 h) but became useful at 120°C (**4a** conv= 95% in 2 h). Thus, the R_3N-SO_2 complex itself did not seem to be the reductive species.

In that case too, the results were consistent with a 1,4 nucleophilic addition of a reduced form of SO_2: in such a reaction, a second carbonyl group in β position favours the orbital overlapping and maleates are less reactive than fumarates. A reversible addition could also explain the partial isomerization of maleate.

In conclusion, solutions of DIEA and SO_2 reduce α,β-unsaturated-γ-dicarbonylated compounds or deliver sulfones from acrylates through Michaël type additions. The search of the reactive species in under investigation.

REFERENCES

1. J.E. Douglas, P.A. Kollman, J. Am. Chem. Soc., 100, 5226 (1978).
2. W.F. Jarvis, D.C.Dittmer, J. Org. Chem., 48, 2785 (1983).