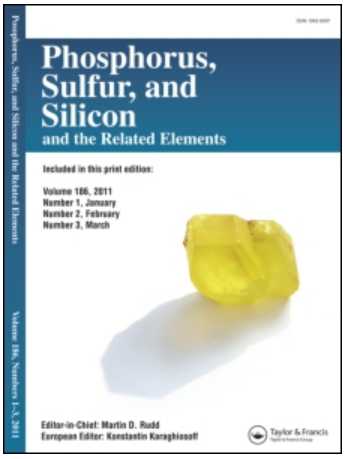


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

OXIDATIVE FLUORINATION OF SULFIDES IN PRESENCE OF $Et_3N,3HF$

Thierry Brigaud[a]; André Laurent[a]; Eliane Laurent[a]
[a] UCB-LYON I, Laboratoire de Chimie Organique 3, associé au CNRS 43, VILLEURBANNE Cedex, France

To cite this Article Brigaud, Thierry , Laurent, André and Laurent, Eliane(1991) 'OXIDATIVE FLUORINATION OF SULFIDES IN PRESENCE OF $Et_3N,3HF$', Phosphorus, Sulfur, and Silicon and the Related Elements, 59: 1, 153 — 156
To link to this Article: DOI: 10.1080/10426509108045712
URL: http://dx.doi.org/10.1080/10426509108045712

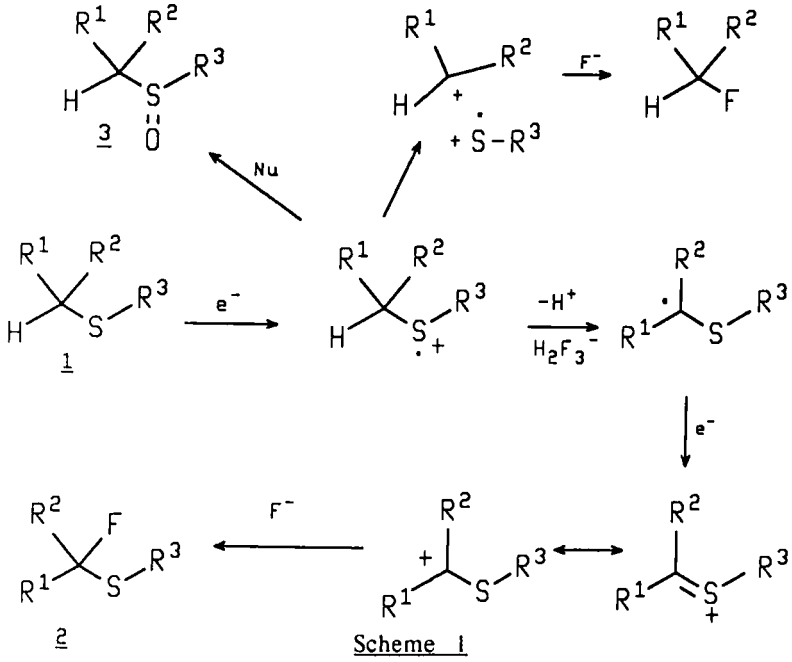
Phosphorus, Sulfur, and Silicon, 1991, Vol. 59, pp. 153–156
Reprints available directly from the publisher
Photocopying permitted by license only

OXIDATIVE FLUORINATION OF SULFIDES IN PRESENCE OF $Et_3N,3HF$

*Thierry BRIGAUD, André LAURENT and Eliane LAURENT**
UCB-LYON I, Laboratoire de Chimie Organique 3, associé au CNRS
43, Boulevard du 11 Novembre 1918 69622 VILLEURBANNE Cedex (France)

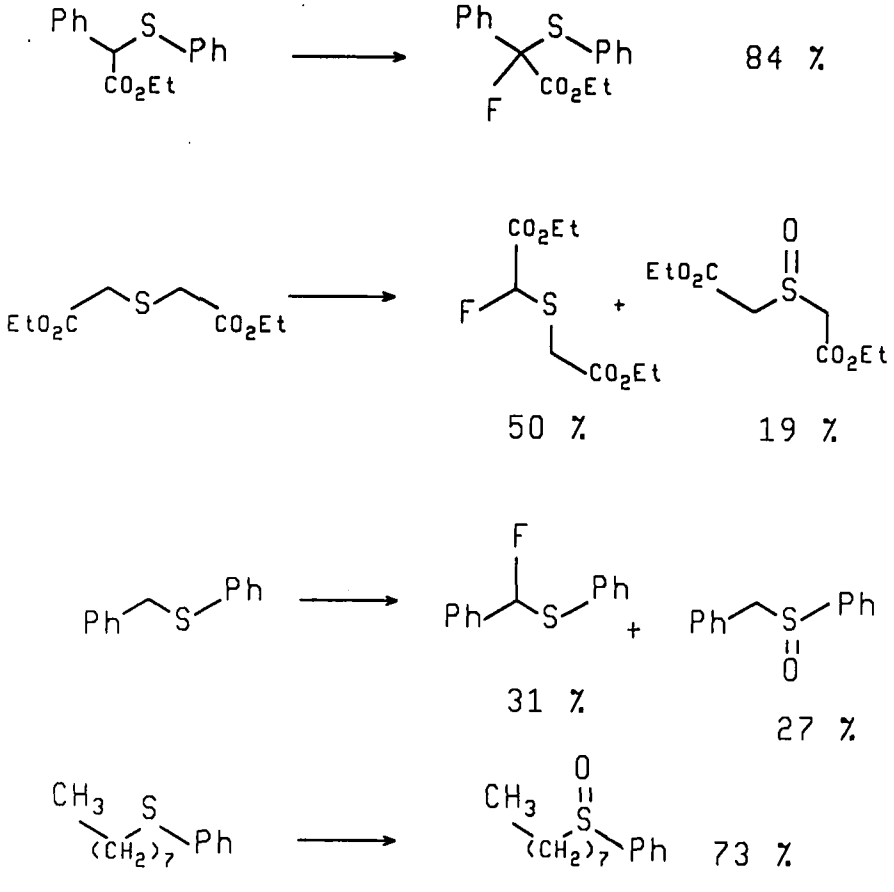
Summary Electrochemical oxidation of sulfides produces sulfonium ions. The reactivity of these ions versus fluoride anions is described.

Synthesis of α-fluorothioethers is particularly interesting because these compounds have a biological potentiality (1). Previously these compounds were prepared by the reaction of DAST on sulfoxides (2), which proceeds by addition of fluoride on a sulfonium ion. Such ion can also be obtained by electrochemical oxidation of sulfides (3). If this reaction is carried out in the presence of nucleophilic fluorides, the formation of α-fluorothioethers can be expected (scheme 1 ; 1 --> 2). As fluorinating reagent, we used $Et_3N.3HF$, which is not very toxic and easy to handle.



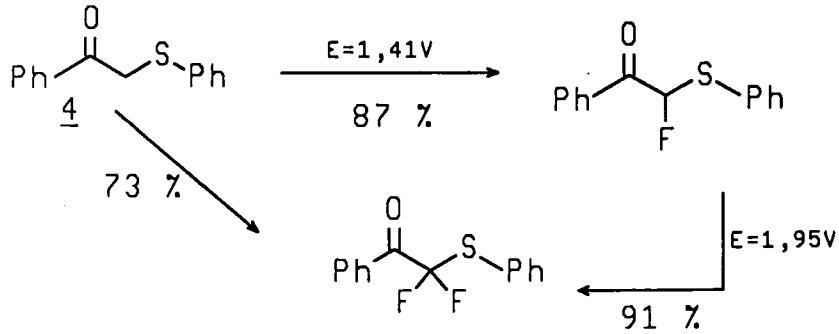
Scheme 1

We report our results on the electrochemical oxidation of different sulfides and thioketals. In electrochemical oxidation, constant potential electrolysis of sulfides (2.25 mmoles) was carried out on a platinum electrode in acetonitrile (30 ml) containing $Et_3N.3HF$ (4.5 ml) at room temperature. The formation of the sulfonium ion is conditioned by the deprotonation of the intermediate radical cation to form a radical. So substrates with an electron withdrawing group in the α-position of sulfur, produces a captodative radical and the fluorothioether is formed in a good yield (scheme 2). When the radical is not a captodative one, a nucleophilic addition reaction takes place on the radical cation to form a sulfoxide 3 (schemes 1 and 2, compound 3).



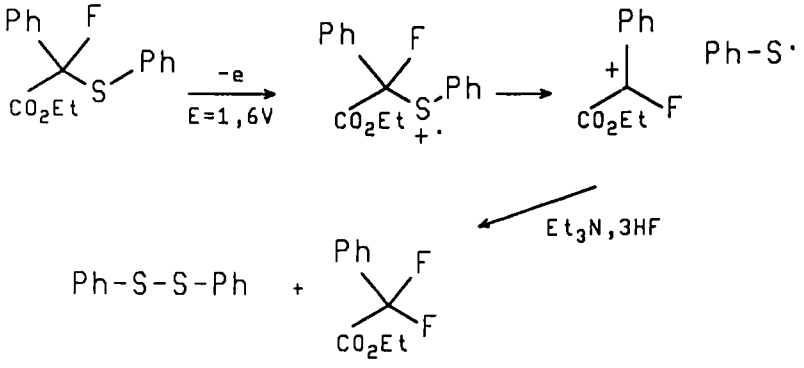
Scheme 2

The substitution of the two hydrogens of 4 (scheme 3) can be selectivity obtained because the potential of oxidation of the monofluorosulfure is higher than the potential of the starting material.



Scheme 3

An another way is the cleavage of the carbon sulfur bond (scheme 1). This reaction works well when the carbocation formed is stabilized. A typical example is the formation of the *gem* difluoroacetate 5 (scheme 4).

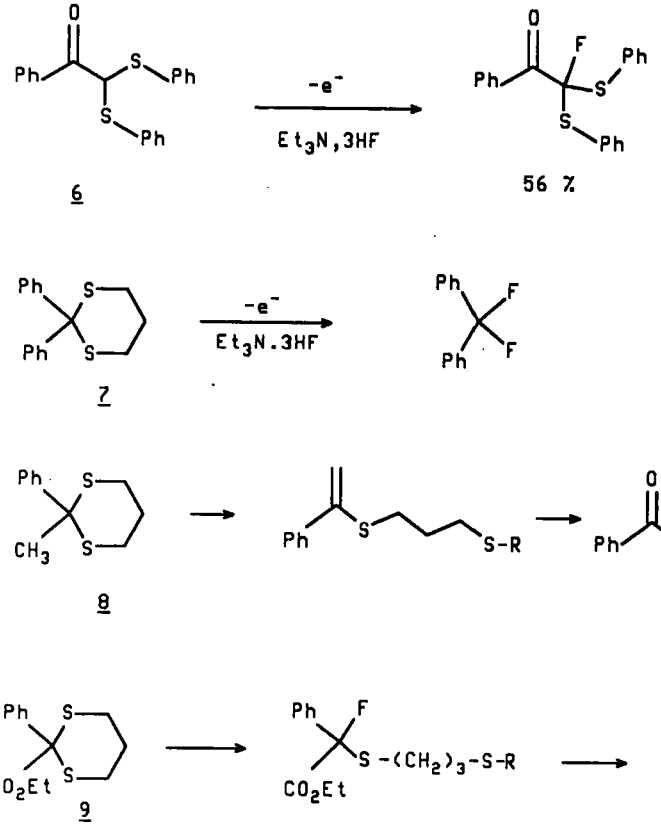


5 75 %

Scheme 4

From thioketal 6 (scheme 5), the monofluoroketal is obtained. But by oxidation of dithiane 7 the two carbon-sulfur bonds are cleaved and a *gem* difluoro compound is isolated in a good yield (4). Oxidation of only one sulfur of dithiane 8 or 9 is observed, and the preliminary compound formed is quantitatively transformed in a carbonyl group. It's well known that the deprotection (5) of dithianes possessing in

their vicinity a strong electron withdrawing group is difficult to realise. So this reaction can be useful for this purpose.



6 7 8 9

Scheme 5

REFERENCS AND NOTES

1 - a) Filler R. and Kobayashi Y., "Biomedical Aspects of Fluorine Chemistry", Kodansha Ltd, Tokyo, 1982.
b) Welch J.T., Tetrahedron, 1987, 43, 3123.
2 - Mc Carthy J.R., Peet N.P, Le Tourneau M.E. and Muthiah I., J. Am. Chem. Soc., 1985, 107, 735.
3 - Kimura M., Koie K., Matsubara S., Sawaki Y. and Iwamura H., JCS Chem. Comm., 1987, 122.
4 - Similar difluorination was obtained by chemical way, in using DBH and Olah's reagent. Sondy S.C. and Katzenellenbogen J.A., J. Org. Chem., 1986, 51, 3508.
5 - Martre A.M., Mousset G., Rachid Bel Rhlid and Veschambre H., Tetrahedron Letters, 1990, 31, 2599.