This article was downloaded by:

On: 28 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

Formation of T*TF* Derivatives V*IA* the Phosphonate Way: A Mechanistic Study Leading to an Improved Procedure

H. J. Cristau^a; F. Darviche^a; M. T. Babonneau^a; M. Taillefer^a; J. M. Fabre^a; E. Torreilles^a Laboratoire de Chimie Organique, E. N. S. CM. ESA 5076 du CNRS, Montpellier Cedex 5, France

To cite this Article Cristau, H. J., Darviche, F., Babonneau, M. T., Taillefer, M., Fabre, J. M. and Torreilles, E.(1999) 'Formation of T*TF* Derivatives V*IA* the Phosphonate Way: A Mechanistic Study Leading to an Improved Procedure', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 395

To link to this Article: DOI: 10.1080/10426509908053677 URL: http://dx.doi.org/10.1080/10426509908053677

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.

ary 2011

Formation of TTF Derivatives VIA the Phosphonate Way: a Mechanistic Study Leading to an Improved Procedure

H.J. CRISTAU, F. DARVICHE, M.T. BABONNEAU, M. TAILLEFER, J.M. FABRE and E. TORREILLES

Laboratoire de Chimie Organique, E. N. S. C M. ESA 5076 du CNRS, 8, rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

Until now, the only efficient method for the selective preparation of unsymmetrically substituted tetrathiafulvalenes (TTF), precursors of organic conductor materials, has been the condensation of an $\alpha\text{-metalated}$ phosphonate with an iminium salt. The major limitations of this method are the low yields (0-50%). Our goal was to investigate the mechanism of this reaction in order to improve the yields.

i) AcOH / toluene, 20°C

We have shown 2 that the acetic acid has two main roles in this reaction : as a donor of proton and as a nucleophile.

The best results are obtained in an "one pot" procedure, using 10 equivalents of acetic acid for the olefination, with a concentration of adduct equal or higher than $2.3\ 10^2\ \text{mol}\ / 1$.

This general procedure has been extended to various unsymmetrical TTF analogs, leading in all cases to better yields than those described in the literature (table).

	СН3	(s)—	$\left\langle \begin{array}{c} S \\ \\ S \end{array} \right\rangle_{R_3}$		\	S R ₃	S	_S	$\left\langle \begin{array}{c} R_2 \\ R_3 \end{array} \right\rangle$
	R ₂	R ₃	Yield	R ₂	R ₃	Yield	R ₂	R ₃	yield (%)
- 1			(%)			(%)			50 (25) A
- 1	Н	Н	48 (0)*	Н	Н	76	H	Н	50 (35)*
- [Н	CH ₃	63 (40)*	Н	CH ₃	68	Н	CH_3	57 (25)*
	-S-(C	H ₂) ₂ -S-	18 (15)*	CH ₃	CH ₃	80	CH ₃	CH_3	74 (10)*
	-S-(CH ₂) ₂ -O-		40 (38)*	-S-(CH ₂) ₂ -S-		45	-S-(CH ₂) ₂ -O-		17 (0)*
					H ₂) ₂ -O-	40 (28)*			

* yield in the literature.

It is to notice that the phosphonate carbanion is unstable when R¹=H (even at low temperature, -78°C). Further investigations will be necessary to control the syntheses in this care.

References

- [1] K. Lerstrup, M. Joergensen, I. Johannsen, Synth. Met., 1988, 27, B9-B13.
- [2] H.J. Cristau, F. Darviche, E. Torreilles, J.M. Fabre, Tetrahedron Letters, 1998, 39, 2103-2106.