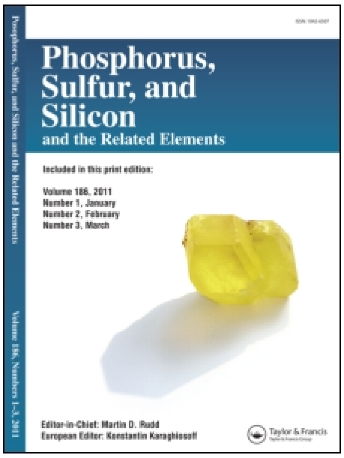
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

1*H*-2-Benzothiopyrans and 1*H*-2-Benzothio-Pyrylium Salts Based On Bis(Arylmetylthio)Acetylenes

Egon Fanghänel; Nasser Yehia; Thomas Klein

To cite this Article Fanghänel, Egon , Yehia, Nasser and Klein, Thomas(1999) '1*H*-2-Benzothiopyrans and 1*H*-2-Benzothio-Pyrylium Salts Based On Bis(Arylmetylthio)Acetylenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 433 — 434

To link to this Article: DOI: 10.1080/10426509908546507

URL: http://dx.doi.org/10.1080/10426509908546507

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, 1999, Vol. 153-154, pp. 433-434
Reprints available directly from the publisher
Photocopying permitted by license only

© 1999 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

1*H*-2-Benzothiopyrans and 1*H*-2-Benzothio-Pyrylium Salts Based On Bis(Arylmetylthio)Acetylenes

EGON FANGHÄNEL, NASSER YEHIA and THOMAS KLEIN

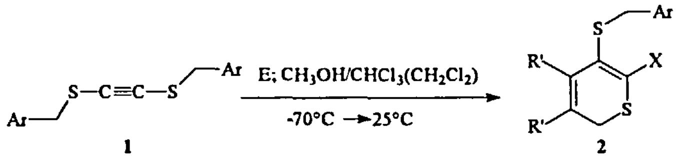
Department of Chemistry, Martin Luther University Halle-Wittenberg, D-06099 Halle, Germany

Downloaded At: 14:16 28 January 2011

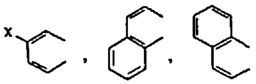
The intramolecular cyclization of bis(arylmethylthio)acetylenes by electrophiles like ICl, Br_2, $POCl_3$, and $Ph_3C^+BF_4^-$ to substituted 1*H*-2-benzothiopyrans, -thiopyrylium salts and in a specific case to a 2-thiaspiro[5,4]-deca-3,6,9-trien-8-one is described.

Keywords: Bis(arylmethylthio)acetylene; 1*H*-2-benzothiopyran; 1*H*-2-benzothiopyrylium salt; electrophilic cyclization; *ypso*-substitution

Substituted 1*H*-2-benzothiopyrans find applications as biological active compounds or 1*H*-2-benzothiopyrylium salts in particular as synthons for more complex sulfur heterocycles.[1,2] New derivatives of 1*H*-2-benzothiopyrans are available in a one-pot synthesis from bis(arylmethylthio)acetylenes 1 and electrophiles like ICl[3], Br_2[3] and $POCl_3$, respectively.

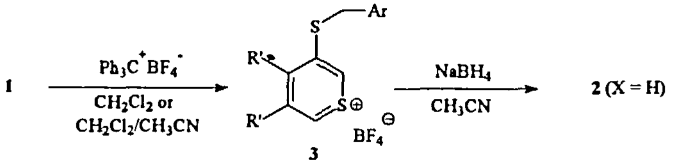


Ar: 4-Y-C_6H_4 (Y = H, OCH_3, CH_3); 1-naphthyl, 2-naphthyl

R', R':


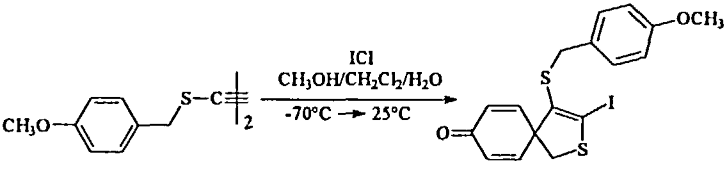
; E: ICl, Br_2, $POCl_3$; X: I, Br, H

With tritylium tetrafluoroborate the acetylenes **1** react in a one-pot synthesis to the fused 1*H*-2-arenothiopyrylium salts in high yields (80-90%). Similar results were obtained with tri(4-bromophenyl)aminium-hexachloroantimonate. The thiopyrylium salts **3** were reduced to the corresponding thiopyrans **2** (yields: 70-85%), which are on this way easily available.



3

From bis(4-methoxybenzylthio)acetylene and ICl the reaction can be regioselectively directed to an *ypso*-substitution and formation of a spiro-substituted cyclohexadienone **4** by adding a small amount of water to the reaction medium.



4

4 reacts in an acid induced ring transformation to the corresponding 6-hydroxybenzothiopyran. Benzothiopyrano[4,3-c]-2-benzothiopyrans are available from **2** (X = I) via a radical induced cyclization. Substitution of the iodine in **2** by phenylacetylene in a Heck-like reaction and subsequent iodine monochloride induced cyclization provides 1*H*-thieno[3,2-c]-2-benzothiopyrans.

ACKNOWLEDGEMENT
Generous support by Deutscher Akademischer Austausch Dienst, and Kultusministerium of Sachsen-Anhalt is gratefully acknowledged.

References

[1] A. H. Ingall, *Compr. Heterocycl. Chem. II*, **5**, 501 (1996).
[2] Shimizu; S. Miyazaki ; T. Kataoka, *Tetrahedron*, **53**, 4611 (1997).
[3] T. R. Klein, M. Bergemann, N. A. M. Yehia, E. Fanghänel, *J. Org. Chem.*, in press.

Downloaded At: 14:16 28 January 2011