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### PHTHALIMIDOSULPHENYL CHLORIDE: ADDITION TO ALKYNES AND GENERAL REACTIVITY

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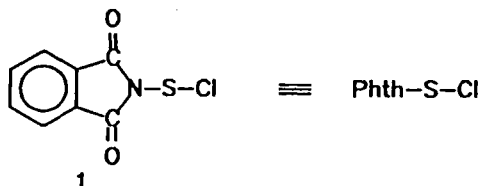
## PHTHALIMIDOSULPHENYL CHLORIDE: ADDITION TO ALKYNES AND GENERAL REACTIVITY

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**Abstract** The regiochemistry of the adducts of phthalimidosulphenyl chloride to alkynes and their reactivity with nucleophiles is described.

Albeit the phthalimidosulphenyl chloride **1** has been synthesized many years ago<sup>1</sup>, its chemistry has been scarcely exploited. It exhibits a general reactivity very similar to that of simple alkane or arenesulphenyl chlorides and, in addition, it contains a nitrogen-sulphur bond that opens new reaction pathways.



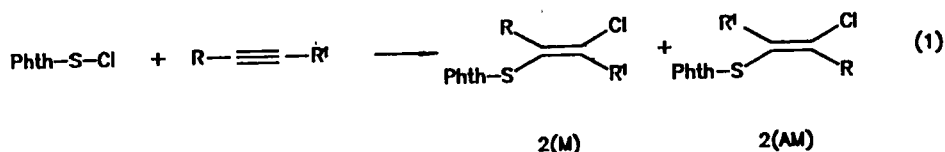
The reaction of **1** with alkenes has been already studied<sup>2</sup> whereas that with alkynes, to our knowledge, has never been described.

In this communication we shall report a brief study on the regiochemistry of the addition of **1** to unsymmetrically substituted alkynes including 1-alkynes and some synthetic applications of the addition products.

### Regiochemical Study

It has been reported<sup>3</sup> that in the addition of arenesulphenyl chloride to 1-alkynes the effect of a nitro group in the *ortho* position increases the Markovnikov to *anti*-Markovnikov ratio of the adducts because of several reasons like the destabilization of the three-membered ring intermediate thirenium ion. We investigated the addition of **1** to several alkynes to verify whether the presence of the phthalimido residue in the sulphenyl chloride **1** might have a similar effect (equation 1).

The regiochemistry of the reaction was proved by nmr using also bidimensional techniques. The results are summarized in the Table. The regiosomeric distribution of the products obtained in the addition of other sulphenyl chlorides to the same alkynes are reported in the Table as well.



Table

| Alkynes                      | Sulphenyl Chlorides                                 | Adducts<br>AM/M Ratio |
|------------------------------|---|-----------------------|
| $\text{Et} \equiv \text{H}$  | 4-ClC <sub>6</sub> H <sub>4</sub> SCl               | 90/10 <sup>4</sup>    |
|                              | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SCl | 67/33 <sup>3</sup>    |
| $\text{nBu} \equiv \text{H}$ | Phth-S-Cl   | 89/11                 |
|                              | 4-ClC <sub>6</sub> H <sub>4</sub> SCl               | 80/20 <sup>4</sup>    |
| $\text{tBu} \equiv \text{H}$ | Phth-S-Cl   | 100/0                 |
|                              | 4-ClC <sub>6</sub> H <sub>4</sub> SCl               | 100/0 <sup>4</sup>    |
| $\text{Ph} \equiv \text{H}$  | Phth-S-Cl   | 85/15                 |
|                              | 4-ClC <sub>6</sub> H <sub>4</sub> SCl               | 70/30 <sup>5</sup>    |
|                              | 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SCl | 45/55 <sup>3</sup>    |
| $\text{Ph} \equiv \text{Me}$ | Phth-S-Cl   | 0/100                 |
|                              | 4-ClC <sub>6</sub> H <sub>4</sub> SCl               | 33/67 <sup>6</sup>    |

Inspection to the data shows that a similar or even higher regiospecificity with respect to other "normal" sulphenyl chlorides is observed from the addition of 1 to 1-alkynes.

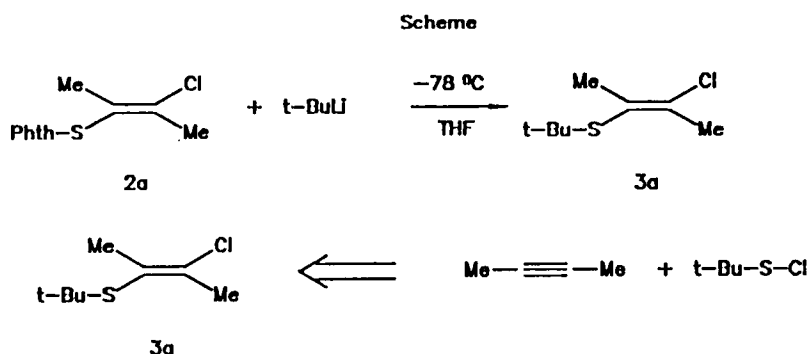
#### Synthetic Applications

Many functionalized sulphenyl halides are known<sup>7</sup>, others have so far escaped synthesis or trapping because of their intrinsic instability related to the nature of the new functionality introduced into the molecule. Among them *t*-butylsulphenyl chloride and N,N'-

bis(trimethylsilyl)aminosulphenyl chloride are representative examples.

The adducts **2** because of the presence of the sulphenamide functionality, appeared reasonable candidates for obtaining compounds formally derived from addition of the aforementioned sulphenyl chlorides to alkynes.

The presence of an electrophilic sulphur in **2**, in principle, allows the substitution of the phthalimido residue with a suitable nucleophile. Indeed the reaction of **2a** with *t*-butyllithium in THF at  $-78^{\circ}$  allowed the isolation of the vinylsulphide **3a** which can be regarded as the adduct of *t*-butylsulphenyl chloride to 2-butyne (Scheme).



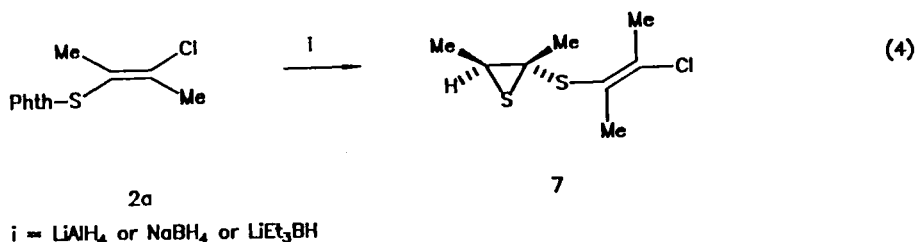
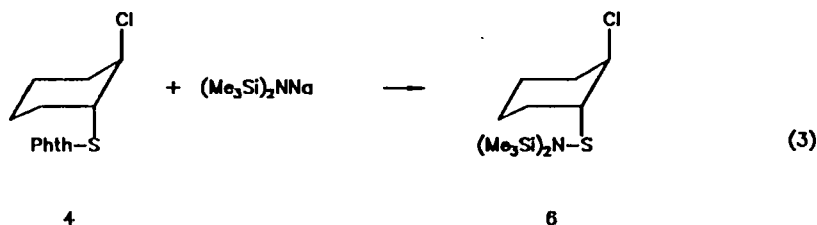
The same reaction on the adducts **2b** ( $\text{R} = \text{R}^1 = \text{Ph}$ ) and **2c** ( $\text{R} = t\text{-butyl}$ ,  $\text{R}^1 = \text{H}$ ) gave the corresponding *t*-butylvinylsulphides **3b** and **3c** which maintain the same stereo and regiochemistry of the reagents.



Other organolithium reagents like methyl and phenyllithium react similarly with **2a-c** and give methyl or phenyl vinyl sulphides.

Another sulphenyl derivative which escaped trapping is the bis(trimethylsilyl)-aminosulphenyl chloride. We synthesized products formally derived from the addition of this sulphenyl chloride to alkynes and alkenes by nucleophilic displacement of the phthalimido moiety in **2a** and **4** by bis(trimethylsilyl)sodium amide (equations 2 and 3). The evaluation of the synthetic potentiality of this new highly functionalized species is currently in progress.

The versatility of the phthalimido derivatives is also shown by the reaction of **2a** with hydrides like  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$  or  $\text{LiEt}_3\text{BH}$  (Super-Hydride). We isolated in this case the thirano derivative **7** very difficult to synthesize by other methods (equation 4).



In conclusion we have shown that the phthalimidosulphenyl chloride 1 can be really regarded as a synthetic equivalent of many known and unknown sulphenyl derivatives, and moreover that the reactivity of the adducts of 1 to alkynes may open new channels for the synthesis of interesting sulphur compounds.

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