Tetrahedron Letters, Vol.31, No.43, pp 6213-6216, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

PHTHALIMIDOSULPHENYL CHLORIDE: A SYNTHETIC EQUIVALENT OF INACCESSIBLE SULPHENYL CHLORIDES

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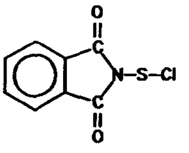
Summary. The phthalimido derivative 3a, synthesized by addition of phthalimidosulphenyl chloride 1 to 2-butyne, reacts with variuos nucleophiles (t-BuLi, MeLi, PhLi, t-Bu-C$\equiv$CLi, $(Me_3Si)_2NNa$) to give substitution of the phthalimido residue. Tri-n-butyltin hydride, in the presence of a radical initiator, also reacts with 3a and gives the tri-n-butyltin-vinylsulphide 9. The stereo and regiochemical course of the addition of 1 to several alkynes was found to be similar to that of simple alkane or arenesulphenyl chlorides.

The phthalimidosulphenyl chloride 1 was synthesized many years ago[1]; however its chemistry has been scarcely exploited[2]. It is a solid compound easy to handle and to prepare, and is storable for months in the refrigerator without any appreciable decomposition.

The phthalimidosulphenyl chloride exhibits a general reactivity very similar to that of simple alkane or arenesulphenyl chlorides. In addition it contains a nitrogen-sulphur bond that opens new reaction pathways.

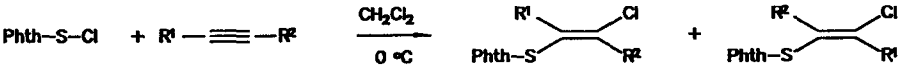


$\equiv$ Phth–S–Cl

1

In this communication we report the synthesis of the adducts of 1 to some alkynes and the reactivity of a selected adduct towards nucleophilic reagents. The reaction of 1 with alkenes has been already studied[2] whereas that with alkynes, to our knowledge, has never been described.

The reaction of 1 with the alkynes 2a and 2b has been carried out in dichloromethane at 0 °C and gave very good yields of the adducts 3a and 3b (equation 1). In the case of the reaction of 1 with the alkynes 2(c-e), carried out under the same reaction conditions, we observed by nmr a mixture of the two regioisomers 3(c-e) and 4(c-e) in a ratio of 89:11, 98:2 and 85:15 respectively (equation 1). Pure anti-Markovnikov type adducts were obtained by standard purification procedures[3].



1 2 3 4 (1)

2a, 3a, 4a; $R^1 = R^2 = Me$

2b, 3b, 4b; $R^1 = R^2 = Ph$

2c, 3c, 4c; $R^1 = n\text{-}Bu$, $R^2 = H$

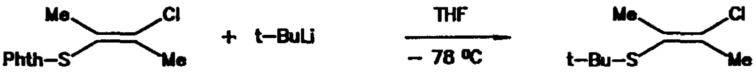
2d, 3d, 4d; $R^1 = t\text{-}Bu$, $R^2 = H$

2e, 3e, 4e; $R^1 = Ph$, $R^2 = H$

The regioselectivity observed in this reaction is very similar to that shown by other simple alkane or arenesulphenyl chlorides[4-7] in spite of the presence of the carbonyl functionalities in the phthalimido residue which might have influenced the regiochemical course of the reaction as the nitro group in the *o*-nitro-phenylsulphenyl chloride does[5]. This behaviour, like that observed in the addition of "normal" sulphenyl chlorides to alkynes, points to the presence of thiirenium ions as intermediates in this reaction too[4-6].

Many sulphenyl halides are known[5,8], others have so far escaped synthesis or trapping because of their intrinsic instability related to the nature of the substituent at sulphur. Among them *t*-butylsulphenyl chloride[9] and N,N'-bis(trimethylsilyl)aminosulphenyl chloride[10] are representative examples. The adducts 3, because of the presence of the sulphenamide functionality[11], appeared reasonable candidates for the synthesis of compounds formally derived from addition of the aforementioned sulphenyl chlorides to alkynes.

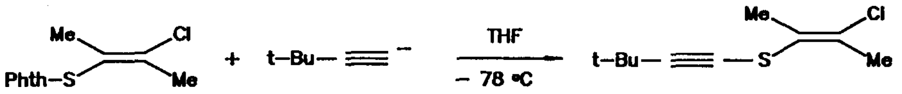
Indeed the reaction of 3a with *t*-butyllithium in THF at -78 °C allowed the isolation of the vinylsulphide 5[12] which can be regarded as the adduct of *t*-butylsulphenyl chloride to 2-butyne (equation 2)[13].



3a 5 (56%) (2)

Other organolithium reagents like methyllithium and phenyllithium react similarly with 3a and give methyl[14] or phenylsulphides[15] which were identified by comparison with samples synthesized by addition of methane or benzenesulphenyl chloride to 2-butyne.

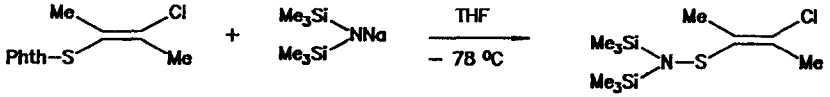
The synthetic potential of 3a is also disclosed by its reaction with the alkynide ion 6 which gave in high yield the sulphide 7[12] (equation 3). Alkynyl-alkenylsulphides of type 7 belong to an almost unknown class of compounds[16].



3a 6 7 (80%)

(3)

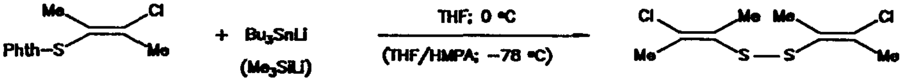
Another sulphenyl derivative which escaped trapping is the bis(trimethylsilyl)amino sulphenyl chloride. We synthesized the silylsulphenamide 8[12], a products formally derived from the addition of the above mentioned sulphenyl chloride to 2-butyne, by nucleophilic displacement of the phthalimido moiety of 3a by bis(trimethylsilyl)sodium amide (equations 4).



3a 8 (55%)

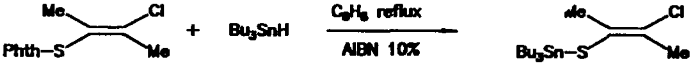
(4)

Finally we attempted to substitute the phthalimido residue of 3a with a trimethylsilyl or a tri-*n*-butyltin group by reaction of 3a with trimethylsilyllithium or tri-*n*-butyltinlithium. In both cases we isolated the disulphide 9[12] (equation 5). The tri-*n*-butyltin-vinylsulphide 10[12] was eventually synthesized in 70% yields by reaction of 3a with tri-*n*-butyltin hydride in the presence of AIBN as radical initiator (equation 6).



3a 9 (70%)

(5)



3a 10 (68%)

(6)

Preliminary results indicate that the substitution of the phthalimido residue by the nucleophiles studied is a general reaction of all the adducts 3.

In conclusion we have shown that the phthalimidosulphenyl chloride 1 can be regarded as a synthetic equivalent of many other known and unknown sulphenyl derivatives. By simple reactions it is possible to access to new classes of vinylsulphides and vinylsulphenamides whose chemistry is currently under investigation in this laboratory.

This work has been carried out with the contribution of 'Progetto Finalizzato del C.N.R. per la Chimica Fine e Secondaria.'

References and notes

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2) M. U. Bombala, and S. V. Ley, *J. Chem. Soc. Perkin I*, 1979, 3013.
3) All the adducts **3** were purified by column chromatography on silica gel and recrystallized from the appropriate solvent (isolated yields ranged from 80 to 95%); they gave correct elemental analysis and ^{1}H and ^{13}C nmr spectra in agreement with the proposed structures.
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9) An old reference to the synthesis of *t*-butilsulphenyl chloride is present in the literature: W. A. Schulze U.S. 2,123,082 (*C. A.*, 32, 6667-6).
10) Only alkyl(trimethylsilyl)aminosulphenyl chlorides are known; see for example: R. Neidlein, and W. Lehr, *Chem. Ber.*, 1981, 114, 80.
11) For examples of reactivity of phthalimidosulphenamides see: a) D. N. Harpp and B. A. Orwig, *Tetrahedron Letters*, 1970, 2691; b) D. N. Harpp, D. K. Ash, T. G. Back, J. G. Gleason, B. A. Orwig, and W. F. VanHorn,*ibid*, 1970, 3551; c) K. Boustany, and J. P. Vander Kooi, *ibid*, 1970, 4983; d) D. N. Harpp, and T. G. Back, *ibid*, 1971, 4953; e) J. S. Grossert, and P. K. Dubey, *J.Chem.Soc.,Chem.Commun.*, 1982, 1183.
12) The ^{1}H nmr data, recorded at 200 MHz in $CDCl_3$, for **5** and for the other new thiovinyl derivatives **7**, **8**, **9**, and **10** are reported below: **5**: 2.43 (3 H, q, J = 1.575 Hz), 2.15 (3 H, q), 1,34 (9 H, s) δ. **7**: 2.23 (3 H, q, J = 1.348 Hz), 2.20 (3 H, q), 1.24 (9 H, s) δ. **8**: 2.18 (3 H, q, J = 1.480 Hz), 1.95 (3 H, q), 0.18 (18 H, s) δ. **9**: 2.34 (6 H, q, J = 1.500), 2.20 (3 H, q) δ. **10**: 2.33 (3 H, q, J = 1.520 Hz), 2.10 (3 H, q), 1.62-1.42 (6 H, m), 1.40-1.20 (6 H, m), 1.14 (6 H, t, J = 7.060 Hz), 0.90 (9 H, t, J = 7.080 Hz) δ.
13) The same reaction carried out on the adducts **3b** and **3d** gave the corresponding *t*-butylsulphides albeit in lower yields.
14) G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *J.Chem.Soc., Chem. Commun.*, 1975, 248.
15) Addition of phenylsulphenyl chloride to 2-butyne gave *E*-2-(phenylthio),3-chloro-but-2-ene; ^{1}H nmr: 7.20-7.35 (5 H, m), 2.44 (3 H, q, J = 1.536 Hz), 2.06 (3 H, q) δ.
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(Received in UK 3 September 1990)