

Dipolarophilic Behaviour of Propadienyl Sulfides towards 3,5-Dichloro-2,4,6-trimethylbenzonitrile Oxide

Gianluigi Broggin, Giorgio Molteni and Gaetano Zecchi*

Dipartimento di Chimica Organica e Industriale dell'Università, Via Golgi 19, 20133 Milano, Italy

J. Chem. Research (S),
1993, 398–399
J. Chem. Research (M),
1993, 2649–2662

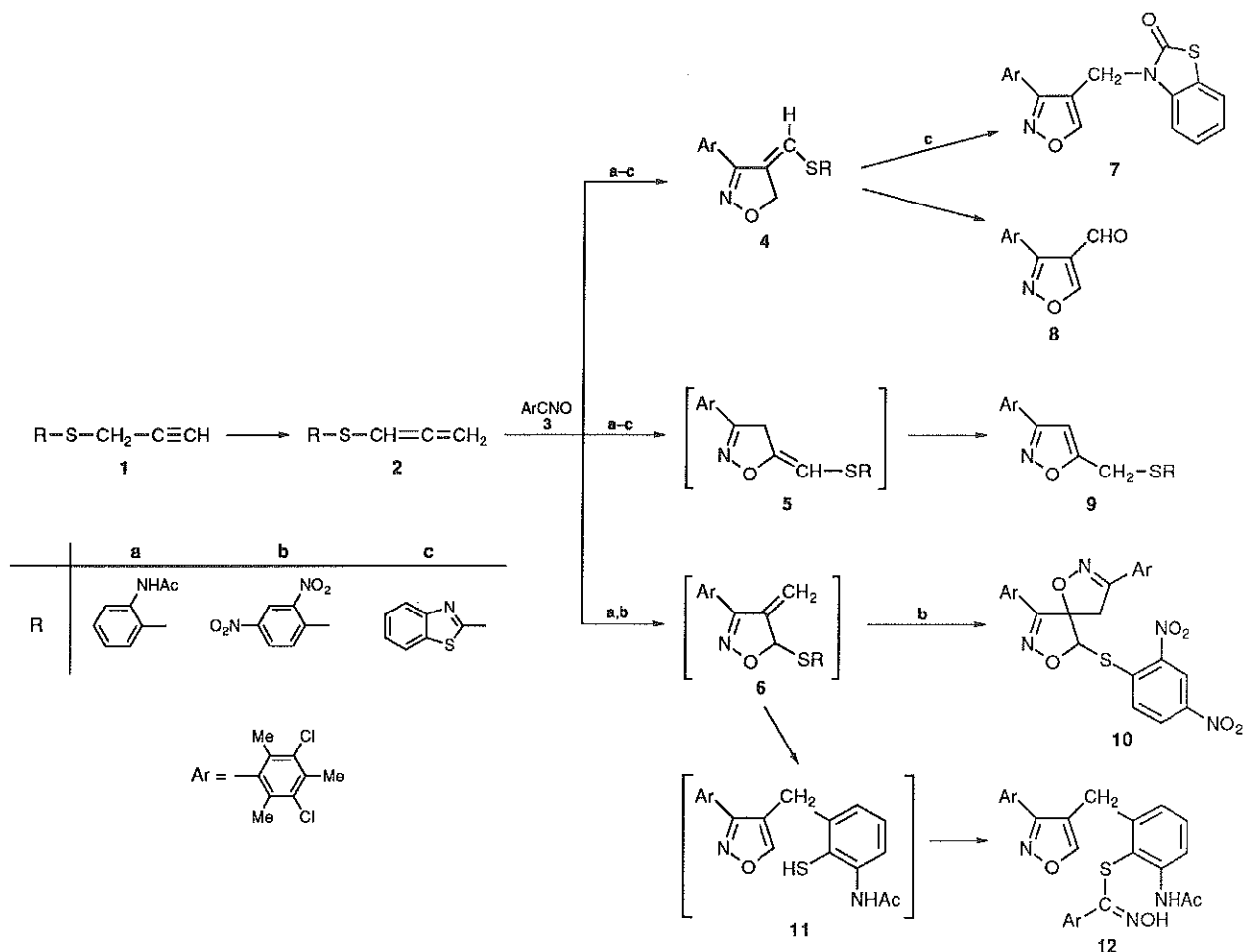
We report an exploratory study aimed at shedding light on the site selectivity and regioselectivity of nitrile oxide cycloadditions to propadienyl sulfides.

The growing interest towards 1,3-dipolar cycloadditions to allenes arises from the fact that the resulting cycloadducts still contain an ethylenic bond susceptible to a variety of further transformations.^{1–4} However, the site and regiochemical outcomes of these cycloadditions depend on the complex interplay of several factors, which are far from being thoroughly elucidated. Hence, we devised the opportunity of studying the behaviour of propadienyl sulfides **2a–c** towards 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide **3** (Scheme 1). To our knowledge, the only previous report on this kind of allene deals with the reaction of phenylthiopropadiene with 2,6-dichlorobenzonitrile oxide.⁵

Table 1 Reaction of allenes **2a–c** with nitrile oxide **3**

Allene	Time (t/h)	Eluant	Products ^a	Yields (%)
2a	21	Et ₂ O	12	10
			9a	5
			8	5
			4a	12
2b	20	light petroleum ^b -EtOAc (1:1)	4b	20
			10	5
			9b	13
2c	24	PhMe-EtOAc (1:1)	4c	41
			9c	24
			8	4

^aIn order of elution. ^bB.p. 45–60 °C.



Scheme 1

The allenes **2a–c**, which were readily available upon base-promoted isomerisation of the corresponding propargyl derivatives **1a–c**, were treated with an equimolar amount of **3** in boiling tetrachloromethane. Reaction times, products and yields are reported in Table 1.

The lack of isolation of the primary cycloadducts **5** can be accounted for by the pronounced acidity of the isoxazolinic

hydrogens in position 4, which facilitates the prototropic rearrangement to **9**. On the other hand, the lability of **6** is not surprising, since 4-methylene-4,5-dihydroisoxazoles are known to be good dipolarophiles generating spiro di-adducts.^{1,4,6–8} However, the conversion of **6** into **12** must be stressed as a peculiar example of a thio-Claisen rearrangement followed by a 1,3-addition of the so-formed thiol group onto the nitrile oxide dipole.

In conclusion, the above results demonstrate that nitrile oxides cycloadd preferably (or exclusively) to the external

*To receive any correspondence.

double bond of propadienyl sulfides. The degree of regioselectivity of this cycloaddition is rather modest, but favours the formation of 4-alkylidene- over 5-alkylidene-4,5-dihydroisoxazoles.

The authors are grateful to MURST (Rome) for financial support.

Techniques used: IR, ^1H NMR, ^{13}C NMR, MS, elemental analysis

Schemes: 2

References: 12

Table 1: Reaction of allenes **2a-c** with nitrile oxide **3**

Table 2: Elemental analyses of new compounds

Table 3: Physical and spectral data for compounds **4**, **9**, **10** and **12**

Received, 13th April 1993; Accepted, 17th June 1993
Paper E/3/02085A

References cited in this synopsis

- 1 H. F. Schuster and G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, 1984, p. 317.
- 2 W. R. Dolbier, Jr., *Adv. Detailed React. Mech.*, 1991, **1**, 127.
- 3 A. Padwa, W. H. Bullock, B. H. Norman and J. Perumattam, *J. Org. Chem.*, 1991, **56**, 4252.
- 4 G. Brogginì, L. Bruché, G. Zecchi and T. Pilati, *J. Chem. Soc., Perkin Trans. 1*, 1990, 533.
- 5 E. Arlandini, M. Ballabio, L. Da Prada, L. M. Rossi and P. Trimarco, *J. Chem. Res.*, 1983, (S) 170; (M) 1575.
- 6 G. Brogginì, G. Molteni and G. Zecchi, *J. Chem. Res.*, 1993, (S) 203; (M) 1263.
- 7 M. Ballabio, P. Dalla Croce, V. Massari, D. Pocar, A. Riva and P. Trimarco, *J. Chem. Res.*, 1983, (S) 140; (M) 1317.
- 8 P. Beltrame and G. Gelli, *J. Heterocycl. Chem.*, 1986, **23**, 1539.