

Cycloaddition Reactions of Thiophene S,N-Ylides. A Novel Route to Thionitroso Compounds

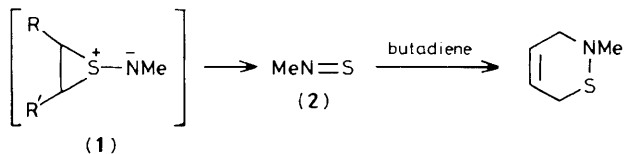
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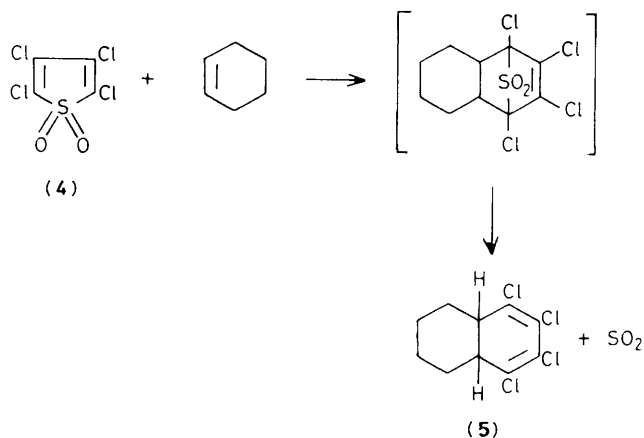
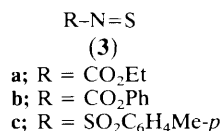
Thiophene S,N-ylides readily react with electron-rich dienophiles yielding adducts formed by the efficient extrusion of acyl- and sulphonyl-thionitroso-compounds, themselves readily trapped by Diels–Alder or ene reactions; similar but slower cycloadditions occur with the analogous S,C-ylides, a potential source of thiocarbonyl derivatives.

Thionitroso compounds are rare and those known are unstable. Thus two *N*-thionitrosamines have been isolated as purple or blue compounds of limited stability.¹ Several routes to thionitrosoarenes have been elaborated and in general the products showed transient existence, being trapped as Diels–Alder adducts.² Thionitrosomethane (2) has been trapped by fragmentation of the ylides (1)³ (generated *in situ*) (Scheme 1). Calculations suggest that electron-donor substituents should stabilise a thionitroso compound while electron-withdrawing groups should destabilise them.⁴ Similar effects

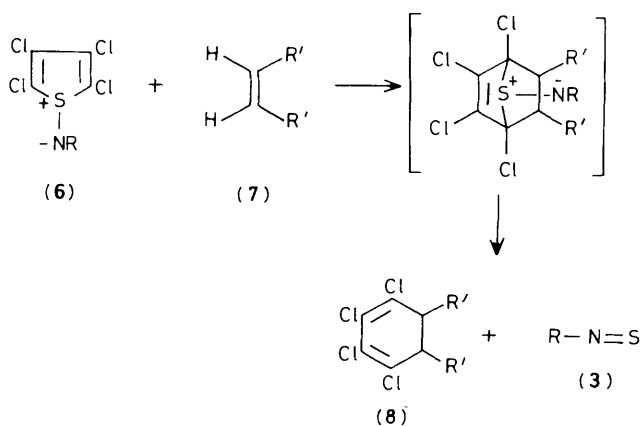
in the chemistry of analogous thioaldehydes⁵ and nitroso-compounds⁶ have recently been reported, these transient systems having been trapped as Diels–Alder adducts. We herein report the first examples of highly reactive acyl- and sulphonyl-thionitroso compounds (3), conveniently trapped as ene adducts or as Diels–Alder adducts.



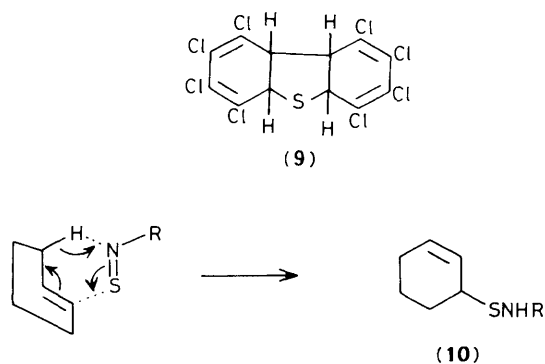
Scheme 1



Scheme 2

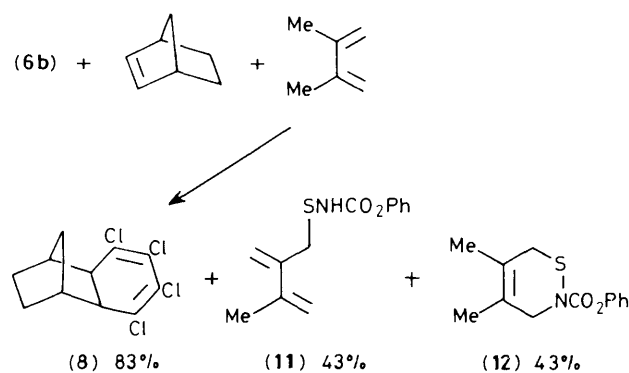


Scheme 3. [a—c as for (3)].

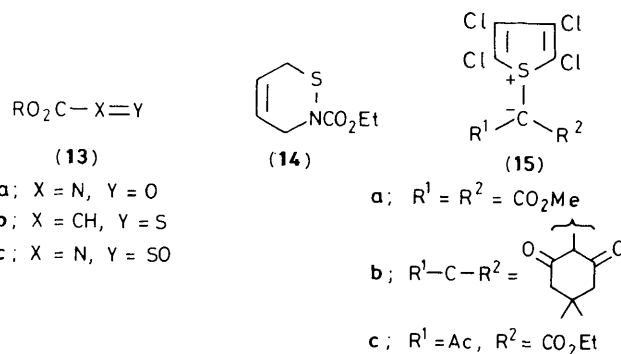
Scheme 4. R = CO₂Ph, 72%; R = SO₂C₆H₄Me-*p*, 64%.

Tetrachlorothiophene 1,1-dioxide (4) is known to be a versatile Diels–Alder diene and reacts particularly with electron-rich alkenes by cycloaddition with concomitant extrusion of sulphur dioxide.⁷ Thus with cyclohexene, the hexahydronaphthalene (5) is produced (Scheme 2). We have found that the analogous S,N-ylides (6) (easily prepared from tetrachlorothiophene and the appropriate azide⁸) undergo similar cycloadditions at almost comparable rates to give the same adducts (8) in good yield (Scheme 3). The moiety extruded in this process is a carboxy-, (3a) or (3b), or sulphonyl-thionitroso compound, (3c). In the absence of a trap, these highly reactive systems give a multitude of products. However, in the presence of an ene or diene the trapped species is conveniently isolated in good yield. Reactions are generally best conducted at ambient temperature for optimum yields and some typical reaction conditions and yields of (8) are as follows, the initial cycloaddition being rate-determining: indene (24 h, 20 °C, 69%), cyclohexene (3 h, reflux, 95%), norbornene (48 h, 20 °C, 93%), benzofuran (72 h, 20 °C, 50%), and acenaphthylene (1 h, 20 °C, 100%). Even unreactive dienophiles such as thiophene react (96 h, reflux, 17%) to give the bis-adduct (9).

When the dienophile (7) can also behave as an ene (e.g. cyclohexene or indene) then the thionitroso compound (3) is efficiently trapped (e.g. Scheme 4). With other dienophiles (e.g. norbornene and acenaphthylene) an ene or diene trap may be used separately. Thus with norbornene and dimethylbutadiene the ylide (6b) gave the expected adduct (8) and a 1:1 ratio of the ene and diene adducts (11) and (12) (Scheme 5). When the reaction was conducted with norbornene and



Scheme 5



isoprene a similar ratio of ene to diene adducts was formed, in quantitative total yield, both of the regioisomeric diene adducts being formed in equal amounts. The lack of periselectivity of the thionitroso compounds (3) is in marked contrast to that of the analogous nitroso-esters (13a),⁶ thio-esters⁵ (13b), sulphonylamines⁹ (13c), or other analogues (3, R = Me, aryl, or NMe₂) which all give solely Diels–Alder adducts with dimethylbutadiene. When the ylide (6a) was treated with acenaphthylene and butadiene (1 h, 20 °C, CHCl₃ solution) both of the expected adducts were formed quantitatively.

The most efficient and high-yielding mode of generation of the thionitroso-compounds (3) is the reaction with acenaphthylene since it is rapid (10 min to 1 h), self-indicating since the dienophile is yellow and its adduct (8) is colourless and highly crystalline, cheap, and convenient.† As it appears that some of the adducts of the thionitroso-compounds are labile (thus allowing the possibility of thionitroso-transfer), the use of acenaphthylene also allows isolation of metastable products. Thus using cyclohexene and the ylide (6a) low yields of the ene adduct were formed under reflux. Using acenaphthylene and cyclohexene at 20 °C for 1 h the adducts (8) and (10) were formed quantitatively.

In conclusion a versatile new approach to the generation of highly reactive functions such as thionitroso-compounds, by extrusion from thiophene ylide adducts, is now available. That other related intermediates such as thioketones are similarly available is indicated by the similar cycloaddition (though much slower) of dienophiles to tetrachlorothiophene S,C-ylides¹⁰ (15) [e.g. (15a) with norbornene (64 h, reflux in MeCN) gives the adduct (8) (43%) and tetramethyl ethyl-

† The reactions were performed using 0.5 g of the ylide and an equimolar amount of acenaphthylene and trapping agent in 2 ml of chloroform or in an excess of the trapping agent.

enetetracarboxylate (97%), a known thermal derivative of a thiocarbonyl compound¹¹].

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