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RHODIUM CARBENOID MEDIATED CYCLISATIONS.
SYNTHESIS AND REARRANGEMENT OF CYCLIC SULPHONIUM YLIDES

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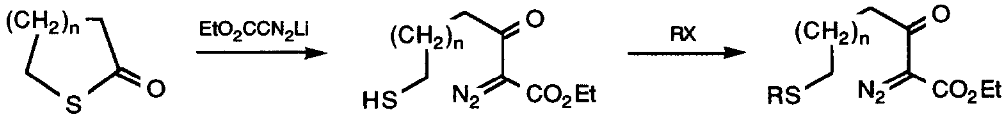
Summary: Treatment of diazo sulphides with rhodium (II) acetate in benzene gives six- and seven-membered cyclic sulphonium ylides; although the *S*-benzyl and *S*-ethyl ylides can be isolated, they rearrange, or eliminate ethylene respectively, on heating; the *S*-allyl ylides cannot be isolated since they undergo spontaneous [2,3]-sigmatropic rearrangement.

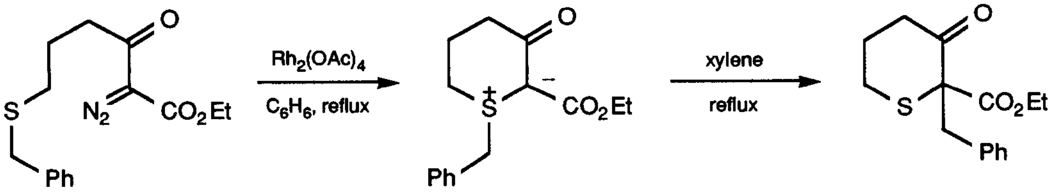
The reaction of electrophilic carbenes and carbenoids with divalent sulphur compounds to give sulphonium ylides is well described,[1-3] and provided that the carbene substituents are electron withdrawing, the ylides are stable and isolable. Stable *cyclic* sulphonium ylides are less well known, although a few have been prepared by treatment of cyclic sulphonium salts with base, rather than by a carbene route.[4] Indeed the few attempts to effect the intramolecular version of the sulphide-carbene reaction have usually resulted in products arising from rearrangement of a non-isolable cyclic ylide.[1,2] The recent report of the formation of stable cyclic sulphonium ylides by intramolecular reaction of a rhodium carbenoid with phenyl sulphides,[5] prompts us to report our own work in this area.

In continuation of our interest in rhodium carbenoid mediated cyclisations,[6,7] we investigated the rhodium (II) acetate catalysed decomposition of a series of diazo sulphides, readily prepared by ring opening of γ-thiobutyrolactone or δ-thiovalerolactone with ethyl lithiodiazoacetate,[7] followed by *in situ* alkylation of the resulting thiolate, or by alkylation (alkyl halide/Et_3N) of the isolated crude thiol (Scheme 1).



Scheme 1.

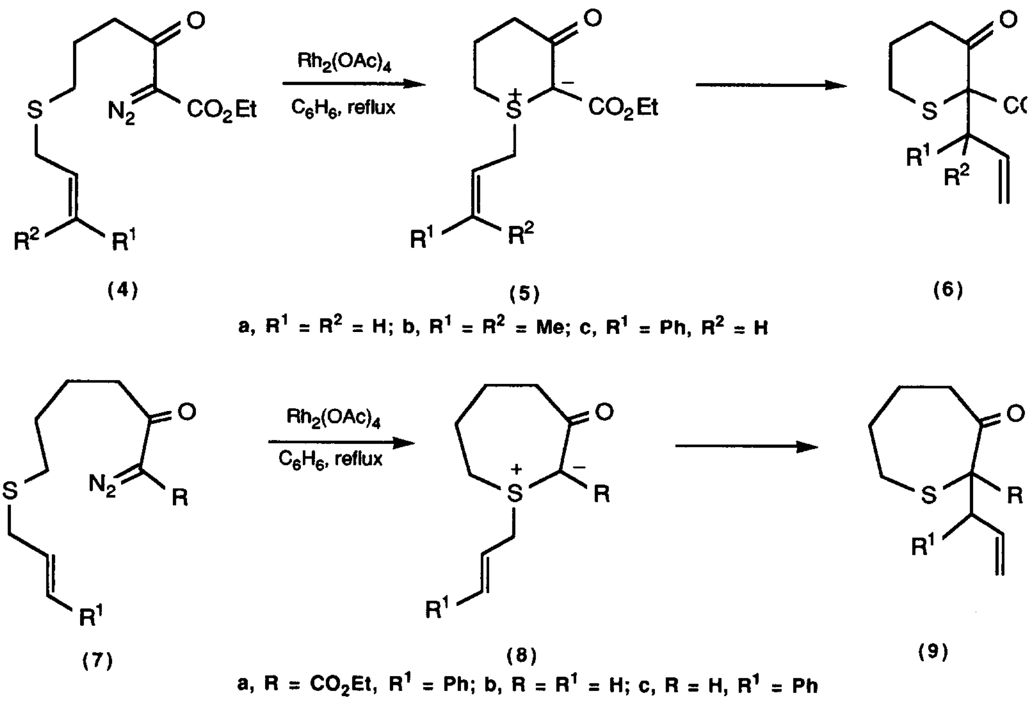
On heating in boiling benzene in the presence of a catalytic amount of rhodium (II) acetate, the diazo sulphide (**1**) gave the *S*-benzyl ylide (**2**), m.p. 134-135°C in 24% yield. Although the ylide (**2**) is stable at room temperature, it undergoes a Stevens type [1,2]-rearrangement to give (**3**) (55%) on heating in boiling xylene for 2.5 h (Scheme 2). No products resulting from alternative rearrangement pathways were detected, and this result contrasts with that obtained from a related *S*-benzyl cyclic ylide, which undergoes formal [1,4]-rearrangement to the carbonyl oxygen.[8]



(**1**) (**2**) (**3**)

Scheme 2.

The symmetry allowed [2,3]-sigmatropic rearrangement of *S*-allyl sulphonium ylides is generally quite facile,[1-3] and because of this, *S*-allyl sulphonium ylides cannot usually be isolated since they rearrange under the conditions of their generation. However the intramolecular capture of carbenes or carbenoids by allyl sulphides to give cyclic *S*-allyl sulphonium ylides is rare, although the intermolecular reaction is well known.[2] Therefore we prepared a series of *S*-allyl diazo sulphides, and investigated their rhodium catalysed decomposition. Catalytic decomposition of the diazo allylsulphide (**4a**) in boiling benzene gave the rearrangement product (**6a**) directly (59%). That the thiopyran (**6a**) was formed by a [2,3]-rearrangement rather than by a [1,2]-shift of the allyl group, was shown by the formation, with allylic inversion, of the thiopyrans (**6b**) (66%) and (**6c**) (mixture of diastereomers) (78%) from the *S*-prenyl- and cinnamyldiazo compounds (**4b**) and (**4c**) respectively (Scheme 3). Decomposition of the diazo sulphide (**7a**) gave the cyclic sulphide (**9a**) (29%), presumably *via* the seven-membered ring *S*-ylide (**8a**). In this case the [2,3]-rearrangement supervenes over the facile ring fragmentation by elimination of the β-hydrogen that occurs with the corresponding seven-membered *S*-phenyl ylide.[5] Since the yield of the seven-membered sulphide (**9a**) was low, we also investigated the decomposition of the diazo sulphides (**7b**) and (**7c**) which lack the ester group (Scheme 3). These were prepared from 5-mercaptopentanoic acid by *S*-alkylation, conversion into the acid chloride, and reaction with diazomethane. Rhodium (II) acetate catalysed decomposition of the diazo sulphides (**7b**) and (**7c**) gave the rearranged cyclic sulphides (**9b**) and (**9c**) in 42 and 64% yield respectively.



(4) (5) (6)

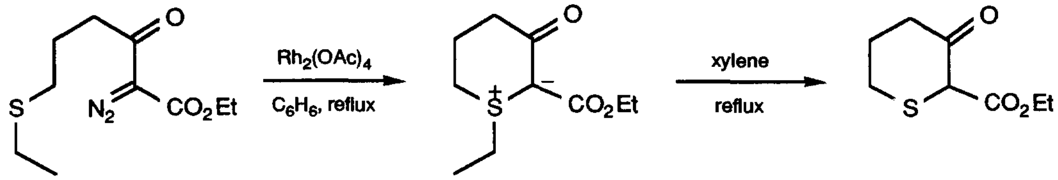
a, $R^1 = R^2 = H$; b, $R^1 = R^2 = Me$; c, $R^1 = Ph$, $R^2 = H$

(7) (8) (9)

a, $R = CO_2Et$, $R^1 = Ph$; b, $R = R^1 = H$; c, $R = H$, $R^1 = Ph$

Scheme 3.

In addition to [1,2]- and [2,3]-rearrangements, the other major reaction pathway for acyclic sulphonium ylides is β-elimination,[1] and since we did not observe elimination reactions involving the *endocyclic* β-hydrogen atoms of our cyclic ylides, we prepared the ylide (11) containing *exocyclic* β-hydrogens. Decomposition of the *S*-ethyl diazo sulphide (10) in boiling benzene in the presence of rhodium (II) acetate gave the ylide (11) (62%) (Scheme 4), which on further heating in xylene eliminated ethylene to give ethyl 3-oxothiane-2-carboxylate (12). Alternatively heating the diazo compound (10) and rhodium acetate in boiling toluene (or xylene) gave (12) directly in excellent yield (92%).



(10) (11) (12)

Scheme 4.

The formation of cyclic sulphoxonium ylides by the intramolecular interception of rhodium carbenoids by sulphoxides is described in the following paper.

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