Tetrahedron Letters,Vol.29,No.46,pp 6009-6012,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

RHODIUM CARBENOID MEDIATED CYCLISATIONS. SYNTHESIS AND X-RAY STRUCTURES OF CYCLIC SULPHOXONIUM YLIDES

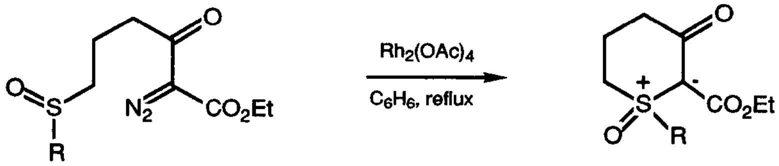
**Christopher J. Moody,* Alexandra M. Z. Slawin, Roger J. Taylor,
and David J. Williams**

*Department of Chemistry, Imperial College of Science, Technology & Medicine,
London SW7 2AY, U.K.*

Summary: Rhodium (II) acetate catalysed decomposition of the diazo sulphoxides (1) and (3) gives the cyclic sulphoxonium ylides (**2**) and (**4**); the structures of (**2c**) and (**4a**) were confirmed by *X*-ray crystallography.

The reaction of electron deficient nitrenes with sulphoxides is a general route to nitrogen-sulphoxonium ylides (sulphoximides).[1] Carbenes also react with sulphoxides,[2] although the reaction is not widely used as a route to sulphoxonium ylides, since, firstly, it is complicated by competing attack of the carbene on oxygen resulting in deoxygenation of the sulphoxide,[3] and secondly, simple versions of such ylides can usually be prepared from the versatile Corey ylide, dimethylsulphoxonium methylide.[4] In the previous *Letter* we described the intramolecular interception of rhodium carbenoids by sulphides to give cyclic sulphonium ylides,[5] and we now report the first examples of the *intramolecular* carbene-sulphoxide reaction to give 5- and 6-membered cyclic sulphoxonium ylides.

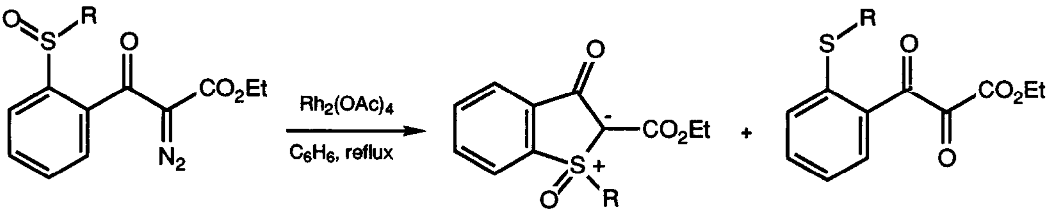
The precursors to the 6-membered cyclic sulphoxonium ylides are the diazo sulphoxides (**1**), prepared by oxidation of the corresponding diazo sulphides[5] with 3-chloroperbenzoic acid (mCPBA). On heating in boiling benzene in the presence of a catalytic amount of rhodium (II) acetate the diazo sulphoxide (**1a**) gave the cyclic ylide (**2a**), m.p. 174-177°C, in 78% yield. Similarly the ylides (**2b**) (m.p. 175-177°C), (**2c**) (m.p. 128-130°C), and (**2d**) (m.p. 143-144°C) were prepared from the corresponding diazo compounds in 76, 84, and 54% yield respectively. Since cyclic sulphoxonium ylides are a relatively rare class of compound,[6] the ylide (**2c**) was studied by *X*-ray crystallography.[7] The *X*-ray structure shows the pyramidal nature of the ylidic sulphur atom, and that the sulphoxide oxygen is axial (Figure).



(1) (2)

a, R = Et; **b**, R = CH_2Ph; **c**, R = $CH_2CH{=}CH_2$; **d**, R = $CH_2CH{=}CHPh$

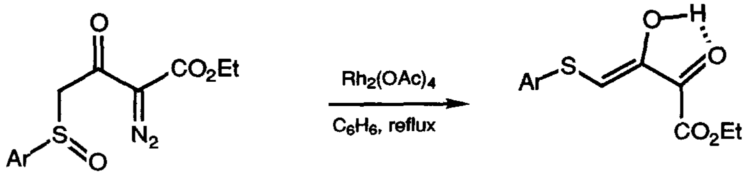
5-Membered cyclic sulphoxonium ylides (**4**) can also be prepared by rhodium carbenoid mediated cyclisation. Thus decomposition of the diazo sulphoxides (**3a**) and (**3b**), prepared in three steps (*ca.*60% overall) from 2-(benzylthio)- or 2-(phenylthio)-benzaldehyde by addition of ethyl lithiodiazoacetate, oxidation of the alcohol with barium manganate, and oxidation of the sulphide with mCPBA, gave the sulphoxonium ylides (**4a**), m.p. 168-172°C, (58%) and (**4b**), m.p. 175-176°C, (70%), together with smaller amounts of the tricarbonyl compounds (**5a**) (6%) and (**5b**) (19%), formed by deoxgenation of the sulphoxide by the rhodium carbenoid. The structure of the ylide (**4a**) was confirmed by *X*-ray crystallography (Figure).[7]



(3) (4) (5)

a, R = CH_2Ph; **b**, R = Ph

In an attempt to prepare a 4-membered cyclic sulphoxonium ylide, the diazo sulphoxide (**6**) was decomposed in boiling benzene in the presence of a catalytic amount of rhodium (II) acetate. However in this case, deoxygenation of the sulphoxide by the carbenoid was the predominant reaction, and the tricarbonyl compound (**7**), m.p. 113-117°C, was the only product isolated. In the solid state,[7] the diketo ester (**7**) exists exclusively in the enol form. There are two conformationally identical, crystallographically independent molecules in the crystal, with, in both cases, the O(3) hydroxyl proton involved in intra- (2.67, 2.65 Å) and intermolecular (2.75, 2.84 Å) hydrogen bonding to the ketone carbonyl group, O(4).



(6) **(7)**

Ar = 2-MeO$_2$C-C$_6$H$_4$-

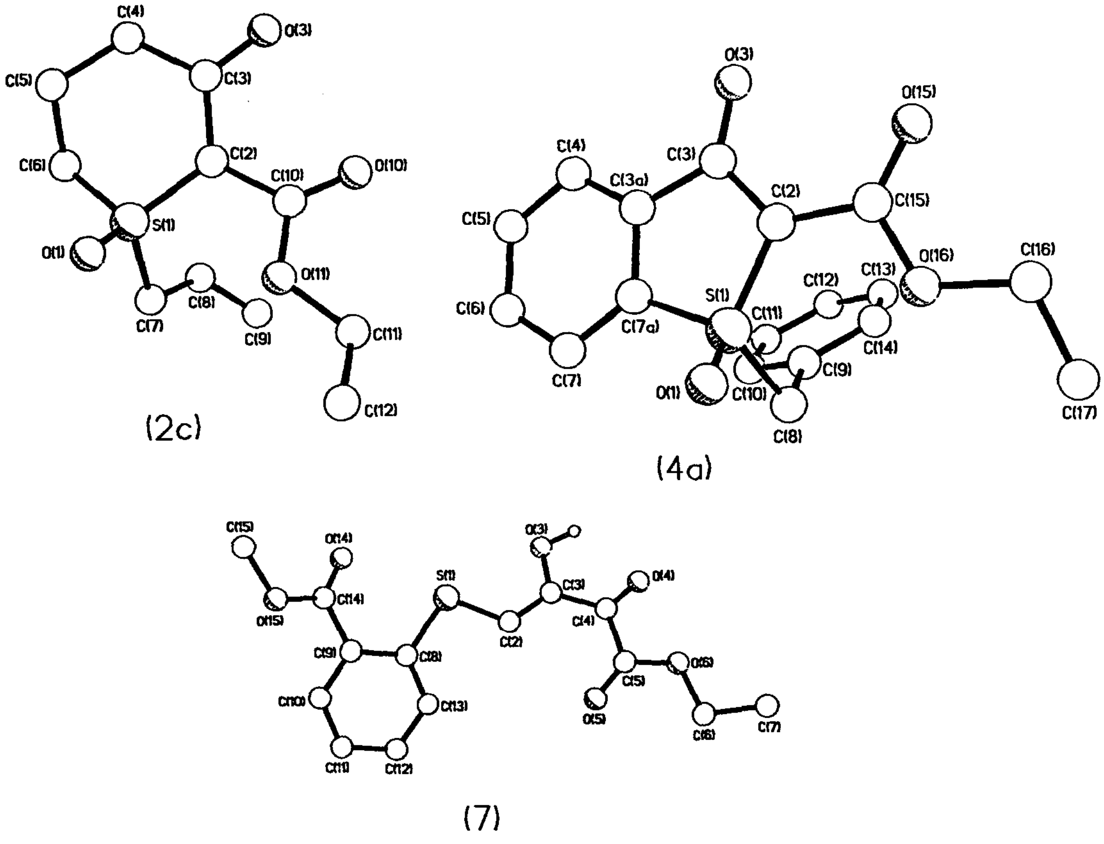


Figure. *X*-Ray crystal structures of compounds **(2c)**, **(4a)**, and **(7)** showing the crystallographic numbering scheme

We thank the S.E.R.C. for a studentship (to R.J.T.), and the Royal Society of Chemistry for a Hickinbottom Fellowship (to C.J.M.).

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7 Compound (**2c**): crystal data: $C_{11}H_{16}O_4S$, $\underline{M}$ = 244.3, monoclinic, $\underline{a}$ = 7.334 (3), $\underline{b}$ = 7.770 (3), $\underline{c}$ = 20.298 (5) Å, β = 94.19 (3)°, $\underline{U}$ = 1154 Å^3, space group $\underline{P}2_1/\underline{n}$, $\underline{Z}$ = 4, $\underline{D}_c$ = 1.41 gcm^{-3}, Cu radiation, λ = 1.54178 Å , μ(Cu-K$_\alpha$) = 24 cm^{-1}, $\underline{F}$(000) = 520. Compound (**4a**): crystal data: $C_{18}H_{16}O_4S$, $\underline{M}$ = 328.4, triclinic, $\underline{a}$ = 7.359 (3), $\underline{b}$ = 8.617 (4), $\underline{c}$ = 13.445 (6) Å, α = 97.90 (4), β = 95.97 (4), γ = 105.36 (3)°, $\underline{U}$ = 806 Å^3, space group $\underline{P}1$, $\underline{Z}$ = 2, $\underline{D}_c$ = 1.35 gcm^{-3}, Cu radiation, λ = 1.54178 Å , μ(Cu-K$_\alpha$) = 19 cm^{-1}, $\underline{F}$(000) = 344. Compound (**7**): crystal data: $C_{14}H_{14}O_6S$, $\underline{M}$ = 310.3, monoclinic, $\underline{a}$ = 15.906 (3), $\underline{b}$ = 11.106 (2), $\underline{c}$ = 16.514 (2) Å, β = 96.76 (2)°, $\underline{U}$ = 2897 Å^3, space group $\underline{P}2_1/\underline{a}$, $\underline{Z}$ = 8 (two crystallographically independent molecules), $\underline{D}_c$ = 1.42 gcm^{-3}, Cu radiation, λ = 1.54178 Å , μ(Cu-K$_\alpha$) = 22 cm^{-1}, $\underline{F}$(000) = 1296.

All three structures were solved by direct methods and refined anisotropically to give for (**2c**) R = 0.044, R_w= 0.054, for (**4a**) R = 0.050, R_w= 0.062, and for (**7**) R = 0.040, R_w = 0.042 for respectively 1500, 2084, and 2540 independent observed reflections [$|F_o| \geq 3\sigma(|F_o|)$, $\theta \leq$ 58, 58, and 50°]. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

(Received in UK 22 September 1988)