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Reaction of vinylcarbenoids with thioketones: formation of vinylthiocarbonyl ylides followed by ring closure to thiiranes and dihydrothiophenes

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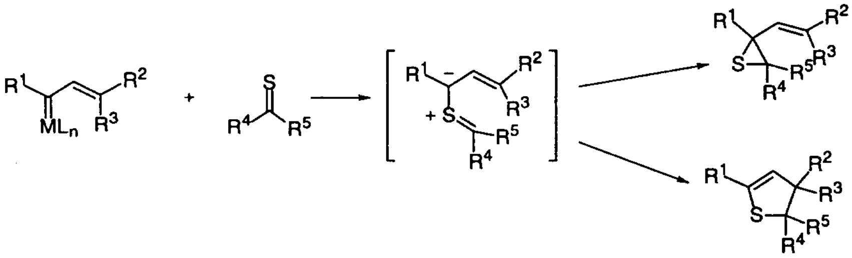
Abstract

Reactions were carried out on thioketones with vinylcarbenoids. $Rh_2(OAc)_4$-catalyzed reaction of vinyldiazo compounds **1a,b** with xanthione **2** and thiochromone **3** gave thiiranes **4b** and olefins **5** and **6**, desulfurization products from thiiranes, while the reaction of **1c** with **2** and **3** afforded dihydrothiophenes **7**, **8** and **9**. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: carbenes; carbenoids; thiocarbonyl compounds; cyclization; ylides.

Reaction of diazoalkanes with thioketones giving unstable 1,3,4-thiadiaozolines followed by extrusion of nitrogen has been widely studied by Schönberg et al. as a traditional method of generation of thiocarbonyl ylides.[1–4] The reaction of metallocarbenoids, generated from diazo compounds with thiocarbonyl compounds such as thioamides and thionesters, has recently attracted much interest from a synthetic viewpoint (Scheme 1).[5] From a synthetic and mechanistic viewpiont the chemistry of vinylcarbenoids has received significant attention over the past ten years.[6] Davies et al. have found that the vinylic β-carbon of vinylcarbenoids is involved in the reaction with dienes, giving [3+4] cycloadducts via formation of *cis*-divinylcyclopropanes followed by Cope rearrangement.[7] We have also expected the participation of the vinylic β-carbon of vinylcarbenoids in the reaction with heteroatom compounds.[8]



Scheme 1.

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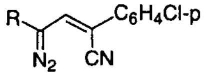
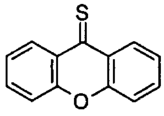
In the present communication, we report the first example of generation of novel vinylthiocarbonyl ylides by the reaction of vinylcarbenoids with thioketones. Metallovinylcarbenoids generated from $Rh_2(OAc)_4$-catalyzed decomposition of vinyldiazo compounds attack a lone pair of sulfur of thioketones to give vinylthiocarbonyl ylides, which could undergo 1,3- and 1,5-electrocyclization to thiiranes and dihydrothiophenes, respectively. We used vinyldiazo compounds **1a–c** as precursors of carbenoids, and xanthione **2** and thiochromone **3** as thiocarbonyl compounds.



1a R = H
b R = CH_3
c R = C_6H_5



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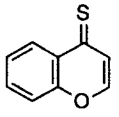
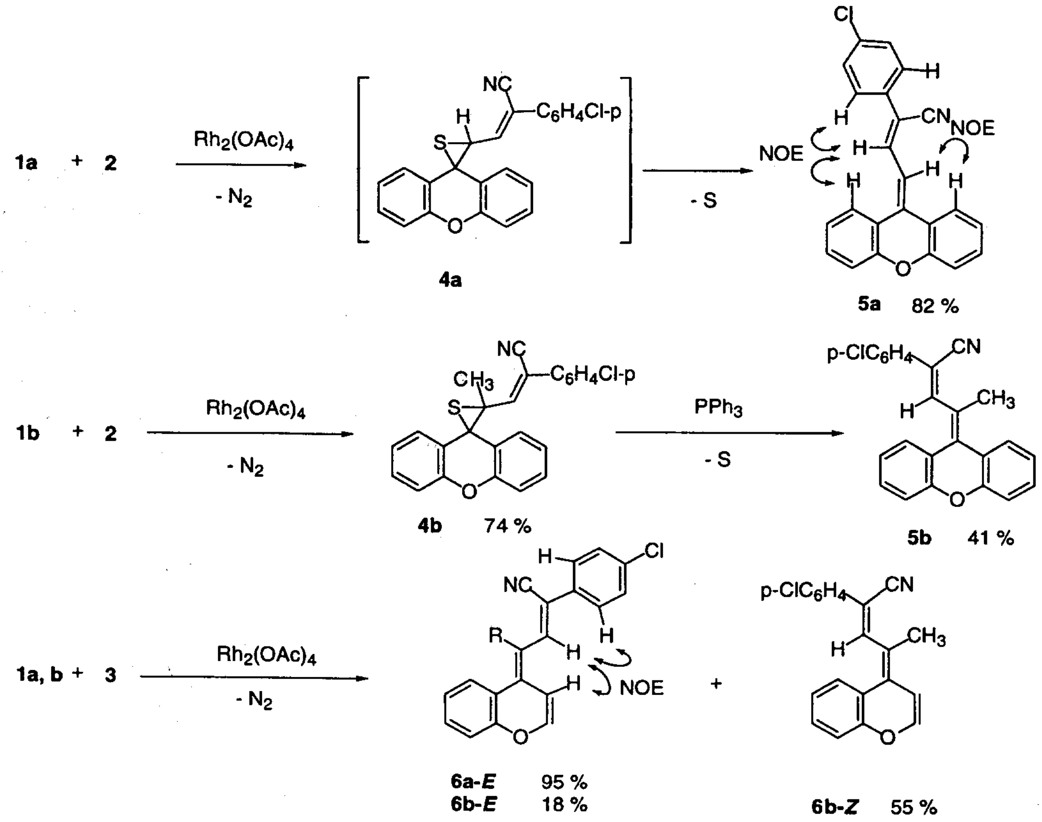


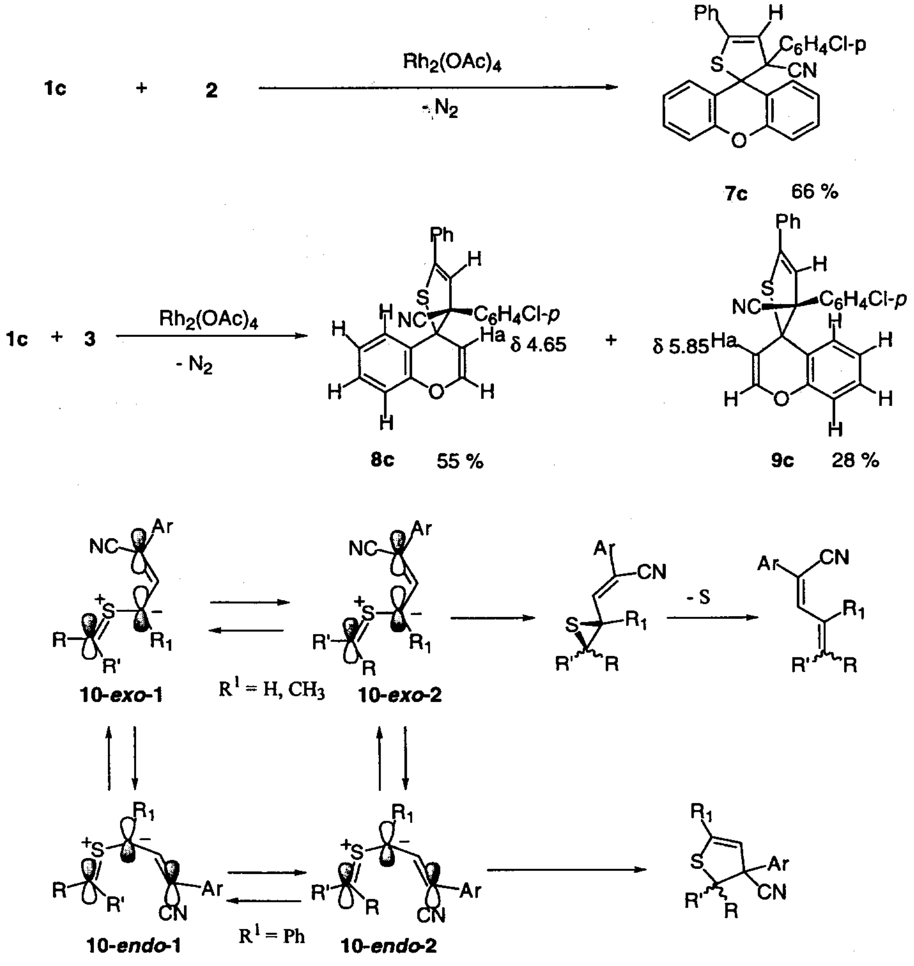
3

2-(*p*-Chlorophenyl)-4-diazo-*cis*-2-butenenitrile (**1a**) in dichloromethane was added over 6 hours to a solution of an equimolar amount of xanthione **2** and a catalytic amount of $Rh_2(OAc)_4$ at room temperature and the reaction mixture was separated by chromatography over silica gel to give the diene **5a** in the yield of 82% (Scheme 2). The thiirane **4b** was isolated in the yield of 74% in the reaction of 2-(*p*-chlorophenyl)-4-diazo-*cis*-2-petenenitrile (**1b**) with **2** in the presence of $Rh_2(OAc)_4$. Treatment of **4b** with triphenylphosphine in refluxing THF gave the diene **5b**. The reaction of **1a** with thiochromone **3** afforded the diene **6a**-*E* in the yield 95%, while **1b** reacted with **3** to yield two isomeric dienes **6b**-*E* and **6b**-*Z* in the yields of 18 and 55%, respectively.[9] Stereochemistry of the dienes **6a**-*E*, **6b**-*E* and **6b**-*Z* was determined by NOE experiments. Thus, both **1a** and **1b** gave dienes or a thiirane in the reaction with xanthione **2** and thiochromone **3**.



Scheme 2.

However, phenylvinyldiazomethane derivative **1c** reacted with **2** to give only dihydrothiophene **7c** (66%) (Scheme 3). Two isomeric spirocyclic dihydrothiophene **8c** and **9c** were obtained in a ratio of 2:1 in the reaction with **3**. The structures of **8c** and **9c** were assigned on the basis of the appearance of an Ha proton (δ 4.65) of **8c** at 1.20 ppm higher field due to the shielding effect of chlorophenyl group *syn* to Ha comparing with that of **9c** (δ 5.85).[10]



Scheme 3.

Vinylcarbenoids attack either of the lone pairs of sulfur of the thioketones to give vinylthio-carbonyl ylides. In the reaction of **1a** with **2**, only sterically favorable vinylthiocarbonyl ylide **10**-*exo* (R=R′), in which a cyanostyryl group is located at *exo*-position, could be formed and cyclized in a conrotatory fashion to the thiirane **4a** followed by extrusion of sulfur, yielding the diene **5a**. The reaction of **1a** with **3** would produce two isomeric vinylthiocarbonyl ylides **10**-*exo*-**1** and **10**-*exo*-**2**, which would undergo cyclization to isomeric thiiranes and subsequent desulfurization would give **6b**-*E* and **6b**-*Z*. The vinylcarbenoid from **1c** attacks either of sulfur lone pairs of **3** to give two isomeric vinylthiocarbonyl ylides **10**-*endo*-**1** and **10**-*endo*-**2**, in which a larger phenyl group is located at the *exo*-position and a smaller cyanostyryl group at the *endo*-position. The ylides **10**-*endo*-**1** and **10**-*endo*-**2** could undergo 6-electrons cyclization to dihydrothiophene derivatives **8c** and **9c**.

In conclusion, novel vinylthiocarbonyl ylides, generated from the reaction of vinylcarbenoids with thioketones, undergo 1,3-electrocyclization to a thiirane or 1,5-electrocylization to a dihydrothiophene depending on the properties of substituents of the ylides.

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9. As the *trans* structure of α-cyanostyryl group was confirmed by NOE experiments, the suffixes *E*, *Z* are used to denote the stereochemistry of another double bond of the dienes.
10. ^{1}H NMR ($CDCl_3$) data for **8c**: δ 4.65 (1H, J=6.3 Hz), 5.99 (s, 1H), 6.36 (d, 1H, J=6.3 Hz), 6.97 (dd, 1H, J=8.2, 1.4 Hz), 7.18–7.24 (m, 1H), 7.25–7.39 (m, 5H), 7.44–7.48 (m, 2H), 8.28 (dd, 1H, J=7.9, 1.6 Hz). ^{1}H NMR ($CDCl_3$) data for **9c**: δ 5.85 (d, 1H, J=6.3 Hz), 5.96 (s, 1H), 6.68 (dd, 1H, J=8.5, 1.4 Hz), 6.80–6.86 (m, 1H), 6.89 (d, 1H, J=6.3), 7.05–7.14 (m, 5H), 7.30 (dd, 1H, J=7.9, 1.3 Hz), 7.45–7.48 (m, 3H), 7.62–7.66 (m, 2H).