Pergamon

Tetrahedron Letters 39 (1998) 7113–7116

TETRAHEDRON LETTERS

Reaction of Vinylcarbenoids with Cyclic Disulfides: Formation of 1,3-Insertion Products as well as 1,1-Insertion Products

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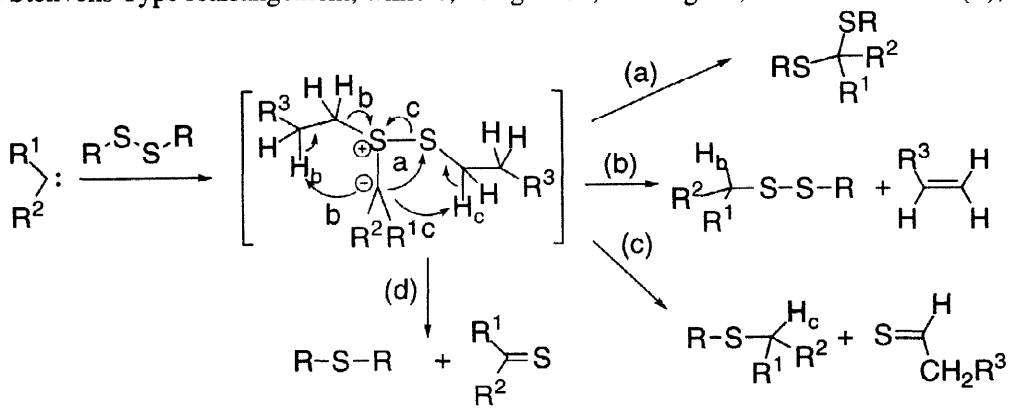
Received 1 June 1998; revised 12 July 1998; accepted 16 July 1998

Abstract: Reactions of vinylcarbenoids with cyclic disulfides were carried out. $Rh_2(OAc)_4$-catalyzed reaction of vinyldiazo compounds **1a-c** with biphenylene disulfide **6** gave 1,3-insertion adducts **7a-c** as the sole products in very good yields, while the reaction with dithiaphenanthrene **9** afforded only 1,1-insertion adducts **10a-c**.

Key words; Carbenes and Carbenoids; Diazo compounds; Disulfides; Rearrangements

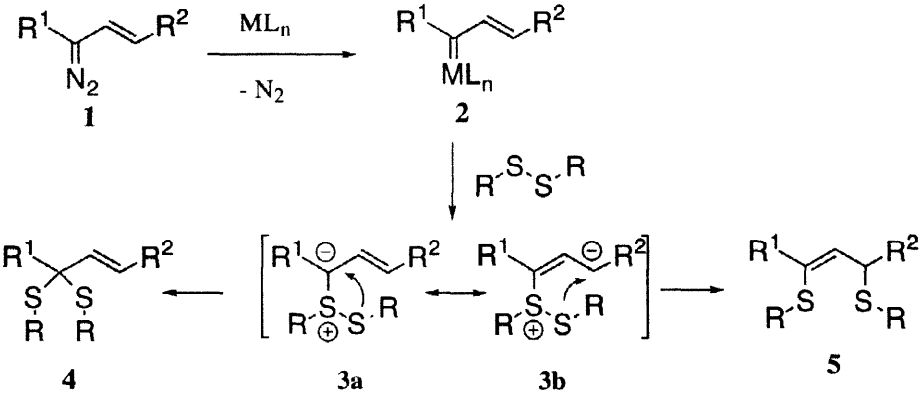
Chemistry of vinylcarbenoids has received significant attention from synthetic and mechanistic interest for the past ten years.[1] Davies et al. have found that the vinylic β-carbon of vinylcarbenoids is involved in the reaction with dienes, to give [3+4] cycloadducts via formation of *cis*-divinylcyclopropanes followed by Cope rearrangement.[2] The formation of ylides by intermolecular or intramolecular reaction of carbenes or metal carbenoids with heteroatom-bearing molecules, such as sulfides, ethers, or amines, has been widely investigated.[3] However, in spite of many studies concerning the reaction with sulfides, some examples of the reaction of carbenes with disulfides were reported,[4-12] where the formed ylides of disulfides can undergo the four types of reactions: (a) migration of thio group to the ylide carbon to give the insertion product of carbene into S-S bond,[5-8] bond formation between the ylide carbon and two types of hydrogens Hb and Hc β to the ylide sulfur atom (b) concertedly with C-S bond cleavage[9] and (c) S-S bond cleavage,[10] respectively, and (d) desulfurization.[11] The use of vinylcarbenoids (**2**) in the reaction of disulfides results in intermediary formation of sulfonium ylide (**3**) of disulfide bearing a vinyl group on the ylide carbon, which has a resonance contribution of formula **3a** and **3b**, suggesting that the C-3 as well as the C-1 of vinyl carbene can be involved in the reactions. 1,2-Migration of thio group to the ylide carbon, forming a 1,1-insertion adduct (**4**), is regarded as Stenvens Type rearrangement, while 1,4-migration, forming a 1,3-insertion adduct (**5**), can be a



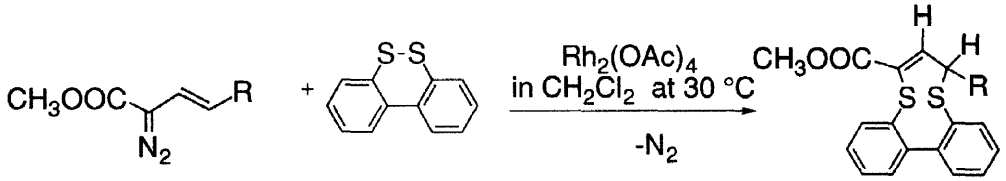
PII: S0040-4039(98)01510-X

symmetry-allowed process including 6-electron system.

In this paper, we report formation of 1,3-insertion adducts (**5**) as well as 1,1-insertion adducts (**4**) in the reaction of metallovinylcarbenoids with cyclic disulfides.



We first examined the reaction using dimethyl diazoglutaconate (**1a**) and biphenylene disulfide (**6**)[13] as test materials. $Rh_2(OAc)_4$-catalyzed reaction of **1a** in the presence of 2.5 molar equiv. of **6** at 30 °C for 1 hr in CH_2Cl_2 was carried out. Afster removal of the solvent *in vacuo* the reaction mixture was subjected to silica gel column chromatography with benzene as eluent to give the 1,3-insertion product (**7a**) as the sole product nearly quantitatively. The similar reaction of methyl 2-diazo-4-*p*-nitrophenyl-3-butenate **1b** and

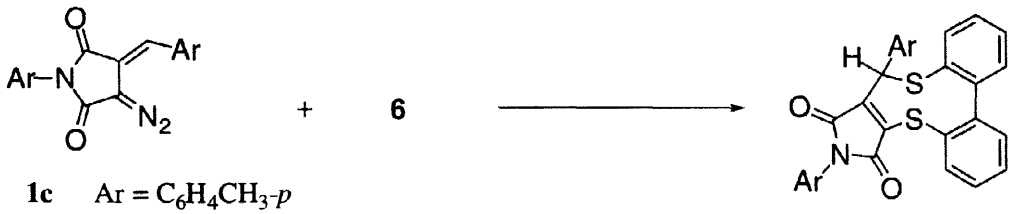


1a R = $COOCH_3$

1b R = $C_6H_4NO_2$-*p*

7a (99%)

7b (84%)



1c Ar = $C_6H_4CH_3$-*p*

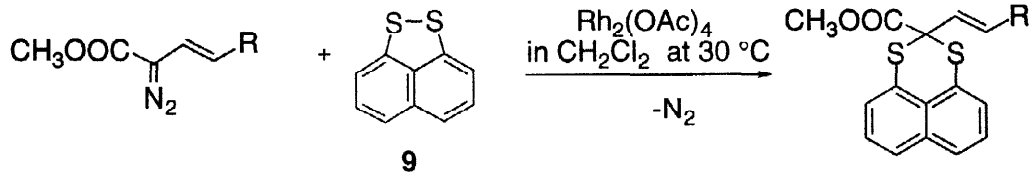
7c (99%)

8a,b **8c**

p-tolylmethylene-*N*-tolyldiazosuccinimide **1c** with **6** also afforded the corresponding 1,3-adducts **7b** and **7c** in good yields respectively. These 1,3-adducts **7a** and **7b** showed very similar NMR spectra, in which the olefinic protons appeared at low fields (δ 6.67 and 6.73), coupling, with J = 11.2 and 11.8 Hz, to the methine protons at δ 4.40 and 4.86 ppm, respectively. Two phenyl rings of **7a-c** were nonequivalent. The 1,1-

adducts **8a-c** were not observed in the NMR of the reaction mixtures.

On the contrary, use of 1,2-dithiaphenanthrene **9**[14] in place of **6** in the reaction with vinylcarbenoids gave different results. Reaction of **1a** and **1b** with 1,2-dithiaphenanthrene was carried out in the presence of a catalytic amount of $Rh_2(OAc)_4$, giving 1,1-adduct **10a** and **10b** in the yields of 96 and 67 %, respectively. Diazosuccinimide **1c** also gave only 1,1-adduct **10c**. The NMR spectra of **10a-c** showed symmetric naphthalene moiety.



9

1a R = $COOCH_3$

1b R = $C_6H_4NO_2$-*p*

10a (96%)

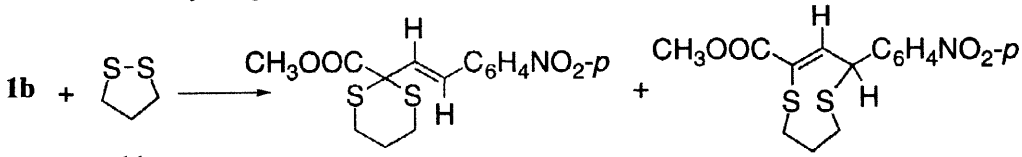
10b (67%)

1c Ar = $C_6H_4CH_3$-*p*

10c (55%)

The reaction of **1b** with 1,2-dithiapentane (**11**) gave 1,1-addduct **12** and 1,3-adduct **13** in a ratio of 65 : 35.

Predominant formation of 1,3-adducts in the reaction of biphenylene disulfide **6** with the vinylcarbenoids and preferential formation of 1,1-adducts from five-membered disulfides **9** or **11** suggest that product determining factors are flexibility, ring strain and stability of an intermediate ylide of disulfide and products.



11

12 (44 %)

13 (27 %)

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[15] ^{1}HNMR($CDCl_3$) data for compounds. **7a**: δ 7.71 (dd, J=6.3, 1.3 Hz, 2H), 7.57-7.20 (m, 6H), 6.67 (d, J=11.2, 1H), 4.40 (d, J=11.2, 1H), 3.85 (s, 3H), 3.72 (s, 3H). **7b**: δ 8.12 (d, 2H, J = 8.6 Hz), 7.80 (dd, 1H, J = 8.6, 1.3 Hz), 7.56-7.30 (m, 9H), 6.73 (d, 1H, J = 11.8Hz), 4.86 (d, 1H, J = 11.8 Hz), 3.66 (s, 3H). **7c**: δ 7.57 (dd, 1H, J = 7.9, 1.3 Hz), 7.72 (td, 1H, J = 7.3, 1.3 Hz), 7.30 - 7.23 (m, 4H), 7.15 (dd, 1H, J = 7.6, 1.7 Hz), 7.10 - 7.05 (m, 3H), 6.93 - 6.76 (m, 5H), 6.55 (dd, 1H, J = 7.9, 1.0 Hz), 5.79 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H). **10a**: δ 7.72 (dd, 2H, J = 8.3, 1.0 Hz), 7.51 (dd, 2H, J = 8.3, 1.0 Hz), 7.40 (t, 2H, J = 8.3 Hz), 7.16 (d, 1H, J = 15.5 Hz), 6.13 (d, 1H, J = 15.5 Hz), 3.84 (s, 3H), 3.65 (s, 3H). **10b**: δ 8.13 (d, 2H, J = 8.9 Hz), 7.72 (dd, 2H, J = 8.3, 1.0 Hz), 7.54 (dd, 2H, J = 8.3, 1.0 Hz), 7.36- 7.45 (m, 4H), 6.98 (d, 2H, J = 15.8 Hz), 6.78 (d, 2H, J = 15.8 Hz), 3.77 (s, 3H). **10c**: δ 8.10 (s, 1H), 8.08 (d, 2H, J = 8.6 Hz), 7.80 (dd, 2H, J = 8.6, 1.3 Hz), 7.52 (dd, 2H, J = 8.6, 1.3 Hz), 7.45 (t, 2H, J = 7.9 Hz), 7.23-7.18 (m, 6H), 2.38 (s, 3H), 2.33 (s, 3H). **12**: δ 8.20 (d, 2H, J = 8.6 Hz), 7.57 (d, 2H, J = 8.6 Hz), 7.09 (d, 1H, J = 15.8 Hz), 6.70 (d, 1H, J = 15.8 Hz), 3.86 (S, 3H), 3.39- 3.29 (m, 2H), 2.84- 2.76 (m, 2H), 2.23- 1.94 (m, 2H). **13**: δ 8.23 (d, 2H, J = 8.9 Hz), 7.62 (d, 2H, J = 8.9 Hz), 7.49 (d, 1H, J = 9.9 Hz), 5.82 (d, 1H, J = 9.9 Hz), 3.85 (S, 3H), 3.03- 2.86 (m, 3H), 2.64- 2.56 (m, 2H), 2.34- 2.16 (m, 1H).