## PALLADIUM(0)-CATALYZED INTRA- AND INTERMOLECULAR CYCLIZATION REACTIONS OF ALLENE EPISULFIDES

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Summary: Palladium(0) catalyzed reaction of allene episulfide with DMAD yielded sulfur containing medium ring compounds. Allyl substituted allene episulfide afforded an intramolecular cyclization product, [2.1.1] thiahexane derivative via  $\eta^3$ -thioallyl complex.

The reactions of methylenecyclopropane with transition metal complex have been the object of considerable interest in the formation of trimethylenemethane (TMM) complexes and its catalytic reactions.<sup>1</sup>

Recently, Trost and Kemmitt<sup>1f-i</sup> reported that bifunctional conjunctive reagent such as 2-acetoxymethyl-3allyltrimethylsilane served as a TMM equivalent and explored for the stoichiometric and catalytic reaction of TMM, respectively. A theoretical calculation, by both Albright<sup>1j</sup> and Trost<sup>1k</sup>, shows that d<sup>8</sup>-metal complexes adopt a stable ( $\eta^4$ -TMM)ML<sub>3</sub> structure (1), but [3+2] cycloaddition does not occur.With d<sup>10</sup>-metal complexes, TMM ligand is coordinated in unsymmetrical geometry, i.e. ( $\eta^3$ -TMM)ML<sub>2</sub> (2) and the catalytic cycloaddition proceeds via zwitter ionic intermediate which causes a nucleophilic attack to electron deficient alkenes and imines.



We have previously reported that allene episulfides<sup>2</sup>, sulfur analogues of methylene cyclopropanes, with  $d^8$ -metal carbonyls provided a stable  $\eta^4$ -thioallyliron tricarbonyl.<sup>3</sup> However no cycloaddition reactions were observed in  $\eta^4$ -thioallyliron tricarbonyl with alkynes such as dimethyl acetylenedicarboxylate (DMAD). Now,we report here the inter- and intramolecular reaction of allene episulfide in the presence of  $d^{10}$ -metal, palladium(0).

Treatment of a benzene solution of **1a** (0.2 mmol) and DMAD (1.0 mmol) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (10-13 mol%) under argon atmosphere (80°C, 18 hr) afforded a monoadduct  $3^4$  (27% yield) and a diadduct  $4^5$  (18% yield), respectively. In the presence of 20 times excess DMAD, only adduct 4 was yielded in 32 % yield. The reasonable lower-chemical shift of methine protons of 3 and 4 (d 5.62 and 5.97 ppm) not only confirmed the structure, shown in scheme 1, but also make the intermediary of  $\eta^3$ -thioallyl complex unlikely in this reaction. The reaction can be understood in terms of direct cycloorigomerization of allene episulfide with Pd-(DMAD)<sub>n</sub><sup>6</sup> complex to give metallacycles and reductive elimination of palladium shown in scheme 2. No reactions have been observed in methyl acrylate or phenylacetylene with **1a** under the same conditions.

5b

5c



The investigation was extended to intramolecular reaction of allyl substituted allene episulfides in the presence of Pd(0). A benzene solution of 1c was heated with stirring in the presence of 10-13 mol % Pd(PPh<sub>3</sub>)<sub>A</sub> at 80°C for 24h to afford bicyclo[2.1.1]thiahexane derivatives  $6c^7$  and a corresponding allene  $7c^8$  with 42 % and 56% yields, shown in table 1. Interestingly the product distribution was time-dependent. At the early stage of reaction (ca 2h), isomer  $5c^9$  was observed in addition to 6c and 7c. Once isolated 5c was treated under the same reaction conditions, 5c rapidly converted into 6c and 7c (ca 4h). Therefore isomer 5c may be the precursor of 6c. On the other hand, no cyclization was observed in 1b, which isomerized to 5b. Even if the isomer 5b was subjected to similar reaction conditions, no cyclization product was yielded but the corresponding allene 7b.<sup>10</sup>



80°C, 4h

61

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32

47

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46

According to scheme 4, the zwitter ionic  $\eta^3$ -thioallyl complexes (9) nicely accommodates our experimental observations. The isomerization of 1 to 5 was promoted by  $\alpha$ -anion stabilization effect of trimethylsilyl group in  $\eta^1$ -thioallyl complex. The cyclization product 6 was yielded via  $\eta^3$ -thioallyl complex 9 which was isomerized from 8. From our results, the rate of isomerization from 8 to 5 may be faster than one from 8 to 6 via 9. Of particular note is the dependence of cyclization of 5b and 5c on the nature of substituent, presumably in the case of 5b, the steric interactions between two phenyl groups and dimethylsilyl group prevent the formation of the intermediate 9 from 8; therefore, no reaction between 5b and Pd(PPh\_3)<sub>4</sub> is observed under the same reaction condition used for 5c. But 5c has a fluorenyl group which is fixed on a plane, since the steric interaction between a fluorenyl group and dimethylallyl group is smaller than 5b, 5c was able to afford 6 via  $\eta^3$ -thioallyl complex 9. Reductive elimination of 10 then generated the observed product 6c, but not yielded 11 and 12 as likely alternatives. The desulfurization of allene episulfides to form allenes 7a, 7b is due to the presence of PPh<sub>3</sub> removing from Pd(PPh\_3)<sub>4</sub>. We reported earlier that a Lewis acid promoted cyclization of 1b and 1c to provide cyclopentenethione via thioallyl cation intermediate.<sup>11</sup> Although, we don't have any good reason about strikingly different product profile, it makes such a zwitter ionic  $\eta^3$ -thioallyl intermediate likely in the present case.

In the view of a formation sulfur containing medium ring compounds, the Pd(0)-promoted reaction of allene episulfides with acetylene or olefin will provide a facile synthetic utility as well as mechanistic interest.



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## **References and Notes**

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- 4. 3;pale yellow oil; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.15(9H,s),3.66(3H,s),3.72(3H,s),5.62(1H,s),and 7.2-7.6(10H,m). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  28.9(q),35.6(s),51.8(d),52.9(q),60.9(q),114.5(d), 121.3(d),126.0(d),126.(d),128.4 (d),129.0(d),130.3(s), 133.4(s), 143.5(s), 146.7(s), 150.6(s), 156.0(s), 164.0(s), 165.5(s). ; MS, m/z 422 (M,15.6%), 365(20.6),333(22.5),190(100).Exact Mass; m/z 422.1468, calcd for C<sub>25</sub>H<sub>26</sub>SO<sub>4</sub> 422.1510.
- 5. 4; pale yellow oil ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.10 (9H,s),3.41(3H,s),3.65 (3H,s),3.73(3H,s),3.79 (3H,s),5.97 (1H,s),7.20-7.56(10H,m).; <sup>13</sup>C-NMR(CDCl<sub>3</sub>) $\delta$ 29.0(q),35.7(s),52.2(s),52.5(sx3), 63.2(d),121.2(d),125.5 (d),125.9(d),126.6(d),128.0(d),128.2(d),129.4(d),131.4(d),133.4(s),135.3(s),143.4(s),147.0(sx3),151.2 (s) ,156.7(s),162.9(s),164.5(s),164.8(s),165.1(s).; MS, m/z 564 (M<sup>+</sup>,100%), 507 (17.5), 475 (34.3), 190 (49.3). Exact Mass; Found m/z 564.1808, calcd for C<sub>31</sub>H<sub>32</sub>SO<sub>8</sub> 564.1813.
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- 7. 6c; pale yellow crystals, mp.139-140°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.05(9H,s),1.17(3H,s),1.52(3H,s), 2.17 (1H,dd,J=2.4,7.7Hz),3.20(1H,dd,J=2.4,11.3Hz),3.54(1H,dd,J=7.7,11.3Hz),7.20-8.08(8H,m).; <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  1.8 (q), 17.4(q), 26.2(q), 33.7(t), 35.9(s), 44.9(s), 45.5(d),119.2(d),123.5(d),124.5 (d),125.8(d),125.95(d),126.02(d),126.6(d),138.2(s),138.6(s). MS, m/z 362(M<sup>+</sup>,45%),73 (100). Anal. Calcd for C<sub>23</sub>H<sub>26</sub>SSi: C,76.19; H, 7.23, Found: C, 76.10; H, 7.25. 8. 7c; white crystals, mp.128.5-129°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.20(9H,s),1.35(6H,s),5.03(1H,dd
- 8. 7c; white crystals, mp.128.5-129°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.20(9H,s),1.35(6H,s),5.03(1H,dd ,J=10.5,1.0Hz),5.12(1H,dd,J=17.0,1.0Hz),6.07(1H,dd,J=10.5,17.0Hz),7.2-7.8(8H,m).; <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  1.4 (q), 29.1(q),43.0 (s),111.5 (t),113.0 (s),115.4 (s),120.0 (d),121.7 (d),126.6 (d), 137.5 (s), 139.1(s),147.4(d),201.1(s).; IR (CCl<sub>4</sub>) v 1910(s) cm<sup>-1</sup>.; Anal. Calcd for C<sub>23</sub>H<sub>26</sub>Si: C, 83.58; H, 7.93. Found: C, 83.11; H, 7.89.
- 9. 5c; pale yellow crystals, mp. 98-99°C ; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.17(9H,s),1.17 (3H,s),1.21(3H,s), 5.08 (1H,d,J=10Hz), 5.10 (1H,d,J=17Hz), 6.09 (1H,dd,J= 10,17Hz), 7.2-7.9 (8H,m).; <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  0.7(q),25.2(q),27.0(q),43.6(s),50.3(s),113.0(t),119.7(d),120.0(d),121.3(dx2),126.4(d),126.7(d),126.9(d) , 127.1 (d),136.8 (s),138.1 (s),138.2 (s),138.9 (s), 145.6 (d). Exact Mass; Found m/z 362.1521, calcd for C<sub>23</sub>H<sub>26</sub>SSi 362.1523. Anal. Calcd for C<sub>23</sub>H<sub>26</sub>SSi : C, 76.19; H, 7.23. Found: C, 76.14; H, 7.22.
- $C_{23}H_{26}SSi \ 362.1523$ . Anal. Calcd for  $C_{23}H_{26}SSi : C, 76.19; H, 7.23$ . Found: C, 76.14; H, 7.22. 10.7b; white crystals, ;<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  0.16 (9H,s),1.29 (6H,s),4.96 (1H,d,J=10.0Hz), 5.02 (1H,d,J=17.0Hz), 6.00 (1H,dd,J=10.0,17.0Hz), 7.2-7.6 (10H,m).; <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  1,24 (q), 28.6 (q),42.0(s),105.9(s),109.3(s),110.8(t),126.3(d),127.8(d),128.4(d),136.3(s),147.8(d),205.8 (s).; IR (CCl<sub>4</sub>) v 1900 (s) cm<sup>-1</sup>.;MS; 332 (M<sup>+</sup>),263,259.;Exact Mass; Found m/z 332.1943, calcd for  $C_{23}H_{28}Si \ 332.1959$ . 11.Tokitoh, N.; Choi, N.; Goto, M.; Ando, W. J. Org. Chem., 1989, 54, 4660.

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