

Table I. Absorption Properties of Azulene Retinoids and the Corresponding Analogues

analogue	λ_{\max} , nm				OS, ^c cm ⁻¹
	RCHO ^a	SB ^b	PSB ^b	BR	
1, trans	446	430	541	644	2960
1, 13-cis	444	426	542	631	2600
2, trans	416	401	489	520	1220
3, trans	473	450	590	694	2540
4, trans	444	421	532	601	2160
4, 13-cis	442	418	510	596	2830
5, 13-cis	506	388	545	830	6300
6, trans	490	460	640	795	3050
6, 13-cis	465	450	638	795	3100
7, trans ^d				475	1170

^a In hexane. ^b In ethanol. ^c Opsin shift; see footnote 10 for discussion. ^d Data from ref 7.

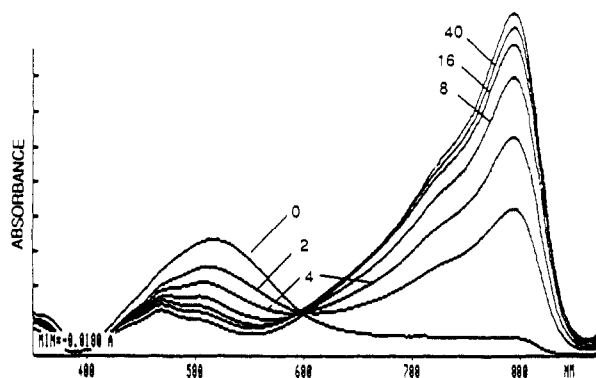


Figure 1. Formation of the 795-nm BR analogue from interaction of retinal analogue 6 with BO. Spectra were recorded immediately after mixing (0 min) and 2, 4, 8, 16, and 40 min and 18 h thereafter. The λ_{\max} of the longest wavelength band is at 795 nm.

groups in guaiazulene pigments should stabilize the tropylium ion, making 3 more red-shifted than 1, and 4 more than 2 (more so than those in the free molecules). Electron-withdrawing substituents on the polyene chain (13-CF₃ and 14-F) should increase the electron density of the side chain, thus stabilizing the enamino structure giving the unusual red-shifts of 5 and 6. However, a substituent at C-9 (CF₃) introduces ring-chain steric interaction. The resultant conformational distortion would favor the imino structure, leading to the blue-shifted spectra of 2 and 4. The absence of a resonance structure containing the stable tropylium ion in 7 and 8 probably accounts for their blue-shifted spectra.

Furthermore, the relatively narrow long-wavelength band of these pigments is reminiscent of those in the cyanine dye analogues.⁴ The increased planarity of the chromophore associated with the proposed resonance hybrid is expected to lead to a less diffused spectrum.

In summary, we believe that the current investigation has defined a new direction for preparing red-shifted BR and rhodopsin pigments. In progress are quantitative studies on the nature of the red shift of these and related pigments.¹⁰

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Supplementary Material Available: ¹H NMR data of azulene retinoids (1 page). Ordering information is given on any current masthead page.

(10) At the suggestion of a referee, we have included opsin shift data in Table I. The unusual entries from our compounds (2 and 5) are believed to be due to a different conformation of the free chromophore versus that in the protein. A twisted *S*-cis conformation is suspected for the CF₃-substituted compounds. This point is under active investigation. Results will be communicated separately.

Cine Substitution in Vinylstannane Cross-Coupling Reactions

Gilbert Stork* and Richard C. A. Isaacs[†]

Department of Chemistry, Columbia University
New York, New York, 10027

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We report the first examples of palladium(0)-catalyzed coupling of vinylstannanes with aryl halides¹ in which attachment of the aryl group occurs exclusively² adjacent to the trialkyltin-bearing carbon (cine substitution) instead of at the carbon that originally bore the tin substituent (ipso substitution).

Our interest in these coupling reactions arose because of our need for a general method for the synthesis of 6-arylnorbornenes 2, a task for which palladium cross-coupling chemistry seemed particularly well suited. We therefore examined vinyl derivatives (cf. 1) that would be expected to couple with aryl nucleophiles according to the protocol of Stille² (Scheme I). For this purpose, enol triflate 1, X = OTf, was converted to vinylstannane 1, X = SnMe₃, (Sn₂Me₆, LiCl, 2 mol % Pd(Ph₃P)₄, refluxing THF; 82%),^{1c} which was then coupled with 1-bromonaphthalene (2 mol % Pd(Ph₃P)₄, catalytic 2,6-di-*tert* butyl-4-methylphenol, refluxing toluene)^{1d} to give, in 83% yield, a product that showed a ¹H NMR spectrum [CDCl₃; δ 6.19 (d, 1 H, *J* = 2.8 Hz), 3.66 (s, 3 H), 1.52 (s, 3 H)] compatible with that expected for the desired product 2, Ar = 1-naphthyl, but which later work showed (vide infra) actually to be the product of cine substitution 3, Ar = 1-naphthyl.

Recent reports³ that enol triflates undergo facile coupling with arylzinc reagents led us to examine this procedure as well. Indeed, treatment of enol triflate 1, X = OTf, with 1-naphthylzinc chloride in the presence of 2 mol % Pd(Ph₃P)₄ (THF, room temperature, 1 h) led to a smooth coupling reaction. To our surprise, however, the product, isolated in 94% yield [¹H NMR (CDCl₃): δ 6.37 (d, 1 H, *J* = 3.0 Hz), 2.78 (s, 3 H), 1.44 (s, 3 H)], was different from the isomeric (mass spectrum) product we had obtained from the tin coupling sequence. The similarities in the ¹H NMR spectra suggested that the two products were regioisomeric at C-5 and C-6. Our suspicion was confirmed by examination of the ¹H NMR spectra of the iodolactones obtained from these isomers.⁴ This established that, in contrast to the zinc reaction which gave the expected coupling product 2, Ar = 1-naphthyl, the tin coupling sequence had led to the unexpected C-5 isomer 3, Ar = 1-naphthyl.

We have now shown by the following experiments (Scheme II) that the unexpected cine substitution leading to 3 takes place during the vinylstannane-aryl bromide coupling reaction. The enol triflate of *d*-camphor 4 gave a vinylstannane 5 with a vinyl doublet [δ 6.14 (d, *J* = 2.9 Hz)] in its ¹H NMR spectrum. Coupling of this stannane with bromobenzene gave a 91:9 mixture of isomers. The ¹H NMR spectrum of the major isomer 7 had a vinyl singlet at δ 6.02. In contrast, phenylzinc chloride coupling with 4 gave a *single* product 6, which had a vinyl doublet [δ 6.00

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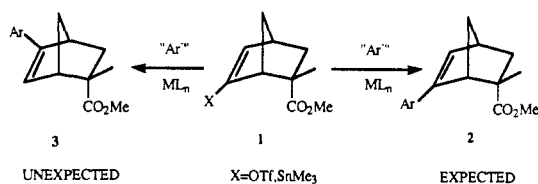
(1) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (c) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (d) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422.

(2) During the preparation of this manuscript there appeared a report (Ennis, D. S.; Gilchrist, T. L. *Tetrahedron Lett.* **1989**, *30*, 3735) that palladium-catalyzed coupling of (1-bromovinyl)trimethylsilane with organozinc bromides gives mixtures of 1- and 2-substituted vinylsilanes. The possibility of directive influence of the trimethylsilyl group may, however, make this a special case.

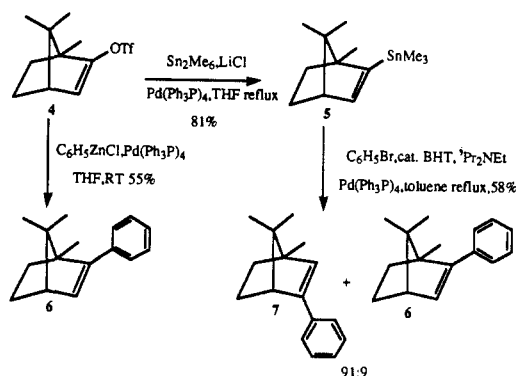
(3) (a) McCague, R. *Tetrahedron Lett.* **1987**, *28*, 701. (b) Keenan, R. M.; Kruse, L. I. *Synth. Commun.* **1989**, *19*, 793.

(4) The iodolactone, mp 232-235 °C, corresponding to 3, Ar = 1-naphthyl [originating from methyl (2*S*)-(-)-2-*exo*-methyl-6-*oxo*-2-*endo*-bicyclo-[2.2.1]heptanecarboxylate, mp 48.5-49.5 °C, [α]_D²⁰ -20.8 ° (c 3.2, EtOH)], showed an absorption in its ¹H NMR spectrum at δ 5.35 (d, *J*_{1,6 α} = 6.0 Hz), ascribed to the C6 *exo* hydrogen adjacent to the lactone oxygen. The iodolactone, mp 155-157 °C, derived from coupling product, 2, Ar = 1-naphthyl [originating from the (\pm)-oxobicycloheptanecarboxylic ester above, mp 62-63 °C], instead showed an absorption at δ 4.82 (d, *J*_{5n,7n} = 2.6 Hz) ascribed to the C5 *endo* hydrogen α to the iodine. See: Ramey, K. C.; Lini, D. C.; Moriarty, R. M.; Gopal, H.; Welsh, H. G. *J. Am. Chem. Soc.* **1967**, *89*, 2401.

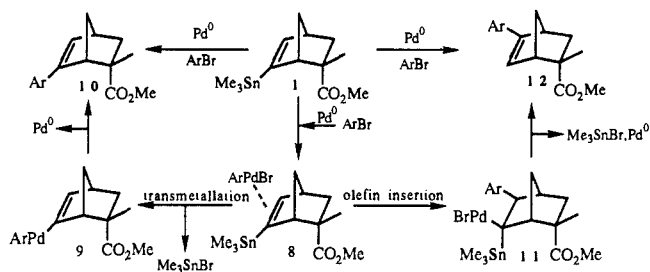
Scheme I



Scheme II



Scheme III



(d, $J = 3.4$ Hz)] and which was identical with the *minor* isomer we had obtained in the coupling of vinylstannane **5** with bromobenzene.⁵

Mechanistically, the initial steps of the reaction of compound **1**, X = SnMe₃, are probably oxidative insertion of the catalyst into the aryl bromide to give an Ar-Pd^{II}-Br species followed by coordination of this species to the vinylstannane (Scheme III). For the "normal" ipso substitution to occur, transmetalation to a vinylpalladium species **9** would have to be the next step but is inhibited here by what we believe to be steric factors.^{6,7} An alternative pathway could be Heck-type olefin insertion. The resulting intermediate **11** might then undergo the somewhat unusual trans β -hydride elimination which has been invoked to rationalize some Heck coupling products.⁸ It might also conceivably proceed to **12** via 1,1-elimination to a carbene.

Whatever the precise factors that cause cine substitution of certain vinylstannanes, it is clear that cine substitution can

sometimes entirely supplant the ipso substitution that is normally expected.

Acknowledgment. We thank Dr. Viresh Rawal for the details of the syntheses of the enol triflate and vinylstannane **1** we used in the synthesis of **2** and **3** and the National Science Foundation and the National Institutes of Health for their support of this work.

Hydrothermal Synthesis of Metal Polychalcogenides. Structural Characterization of [Mo₁₂Se₅₆]¹²⁻. A Cluster of Clusters

Ju-Hsiou Liao and Mercuri G. Kanatzidis*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University
East Lansing, Michigan 48824

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Recently, we have been exploring the chemistry of metal polychalcogenides with various synthetic methods such as traditional room temperature solution and unusual molten salt techniques with considerable success.¹ In order to expand the synthetic repertoire in this area, we have been experimenting with hydrothermal conditions to assess their potential as variable synthetic routes to novel metal polychalcogenides. Hydrothermal synthesis of chalcogenides is very little studied, despite its demonstrated usefulness in the synthesis of a variety of other important, and often inaccessible by other techniques, materials such as quartz and zeolites.² Hydro(methano)thermal conditions have been used to prepare some very interesting metal monochalcogenide compounds by using alkali carbonates as mineralizers.³ Using Se_x²⁻ as mineralizers, we have uncovered a new route to novel polychalcogenides. We report here the first hydrothermal synthesis of a metal polychalcogenide complex, the remarkable [Mo₁₂Se₅₆]¹²⁻ (**1**), possessing an extraordinary structure.^{4,5}

The structure of [Mo₁₂Se₅₆]¹²⁻ is shown in Figure 1. It is a discrete molecule which can be viewed as a cluster of four smaller

(1) (a) Kanatzidis, M. G. *Comments Inorg. Chem.* **1990**, *10*, 161-195. (b) Kanatzidis, M. G.; Huang, S.-P. *Angew. Chem.* **1989**, *28*, 1513-1514. (c) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767-3769. (d) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767-3769. (e) Kanatzidis, M. G.; Dhingra, S. *Inorg. Chem.* **1989**, *28*, 2024-2026. (f) Huang, S.-P.; Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1990**, *9*, 1389-1395. (g) Kanatzidis, M. G.; Huang, S.-P. *J. Am. Chem. Soc.* **1989**, *111*, 760-761. (2) Barrer, R. M. In *Hydrothermal Chemistry of Zeolites*; Academic Press: 1982.

(3) (a) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23-30. (b) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 98-104. (c) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105-111.

(4) For other Mo polyselenide complexes, see: (a) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.*, in press. (b) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971-1973. (c) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790-2795. (d) Adel, J.; Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1988**, *347*, 343-348.

(5) (a) A Pyrex tube containing Mo metal (0.048 g, 0.5 mmol), K₂Se₄ (0.394 g, 1.0 mmol), and 0.3 mL of water was sealed off under vacuum, and it was kept at ~140 °C for 60 h. The black chunky crystals that formed are insoluble in water. They were isolated by filtration and subsequently washed with water. The nature of these crystals, which are insoluble in all organic solvents, was established by X-ray diffraction analysis to be K₁₂Mo₁₂Se₅₆.^{5b} (b) Semiquantitative analyses were run on a scanning electron microscope using an energy dispersive (EDS) microprobe technique. The crystals, though sufficiently large, diffract weakly. Thus the data had to be collected by using intense X-rays from a rotating anode source. Crystal data for K₁₂Mo₁₂Se₅₆: orthorhombic *Cmc*2₁, $Z = 4$, $a = 23.73$ (2) Å, $b = 17.70$ (1) Å, $c = 20.434$ (9) Å, $V = 8584$ (9) Å³ at 23 °C. $2\theta_{max}$ (Mo K α) = 51°. The structure was solved by direct methods. Number of unique data: 4153. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 2531. Number of variables: 174. Number of atoms: 80. $\mu = 258$ cm⁻¹. Final $R = 0.080$ and $R_w = 0.051$. In order to ensure product homogeneity, the X-ray powder diffraction diagrams of the product were compared with and found to be identical with that calculated from the single-crystal data.

(5) Due to the volatility of the products **6** and **7**, yields in the couplings of camphor derivatives **4** and **5** were only moderate. We performed a variety of coupling reactions using triflate **1**, stannane **1**, and various aryl halides. All of these were very efficient (80-100%) and regioselective.

(6) When the vinylstannane analogue of **5** derived from (\pm)-epicamphor (4,7,7-trimethylbicyclo[2.2.1]heptan-2-one) was coupled with bromobenzene, the ratio of products **7:6** was 70:30. This suggests that steric crowding about the vinylstannane is in part responsible for steering the aryl group to the cine position. The vinylstannane derived from 4-*tert*-butylcyclohexanone gave the normal ipso-coupled product under these conditions. For an additional example of a cyclic vinylstannane that undergoes ipso coupling, see: Laborde, E.; Lesheski, L. E.; Kiely, J. S. *Tetrahedron Lett.* **1990**, *31*, 1837.

(7) The regiochemical outcome of these reactions is also subject to electronic effects. Stille made the observation^{1d} that the coupling of vinyltributylstannane with aryl halides is accelerated by the presence of electron-withdrawing substituents on the aromatic ring. We found that coupling of vinylstannane **5** with 1-bromo-4-nitrobenzene, under the usual conditions, gave a 55:45 mixture of products corresponding to **7** and **6**, respectively.

(8) We thank a referee for bringing this fact to our attention. Cf.: (a) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712. (b) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.