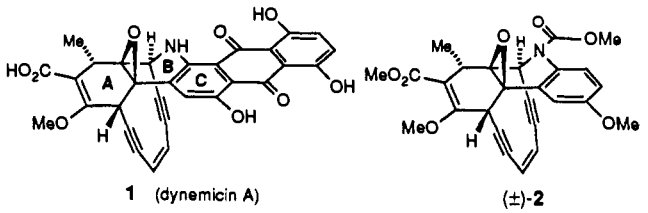

1 (dynemicin A) (±)-2

Figure 1.

to simultaneously reposition the C(3)–C(4) olefin and set the C(4) methyl stereochemistry of **4** by applying an oxidation/reduction protocol [ceric ammonium nitrate (CAN), then $EtAlCl_2/Et_3SiH$] produced a product (**9**) possessing a transposed olefin, but incorrect methyl stereochemistry (Scheme I).[3] In our more recent investigations, we reasoned that increasing the convex/concave nature of the ring system might alter the stereochemical outcome of the Et_3SiH reduction. Hence, **4** was epimerized to *cis*-lactone **5**[6] (DBU, 25 °C, 14 h, 92% yield), which underwent benzylic oxidation with CAN to furnish alcohol **6**[6] as a single regioisomer (97% yield).[7] Surprisingly, **6** underwent $EtAlCl_2/Et_3SiH$-mediated reduction (−78 °C) to regenerate lactone **5** as the only isolable product. Thus, instead of altering the stereoselectivity of nucleophilic addition, epimerization to the *cis*-lactone results in an increased preference for attack at the benzylic position.

Although the increased propensity for nucleophilic addition to C(11) thwarted attempts at direct substitution by hydride at C(4), it suggested the possibility of utilizing an allylic diazene rearrangement as an alternative reduction strategy. After considerable experimentation, it was found that ionization of **6** ($MeAlCl_2$, CH_2Cl_2, −78 → −35 °C) and trapping of the presumed intermediate carbonium ion with mesitylenesulfonohydrazide[8] provided the desired isomer **8**[6] in 92% yield. A likely mechanism for this transformation involves a stereospecific [1,5] sigmatropic rearrangement of diazene **7**. The structure of **8** was secured by single-crystal X-ray analysis of **10**,[6] which resulted from epoxidation with *m*-CPBA (CH_2Cl_2, pH 7 buffer, 75% yield).

Having simultaneously established the methyl stereochemistry and correct positioning of the olefin for eventual epoxidation, we next focused our attention on developing an efficient protocol for conversion of the butyrolactone moiety in **8** to the vinylogous carbonate found in **1**. Toward this end, α-hydroxylation of **8** to **11**[6] (KHMDS, MoOPH, 72% yield) followed by lithium borohydride reduction delivered triol **12**,[6] which was selectively converted to the 1,2-cyclic carbonate **13**[6] (triphosgene, Et_3N, CH_2Cl_2, −78 °C).[9] Oxidation at C(6) and oxidative excision of C(8) were then performed via a five-step sequence without isolation of intermediates. Thus, sequential oxidation of **13** with the Dess–Martin periodinane and then aqueous sodium chlorite[10,11] furnished, after base/acid workup, the crude acid/carbonate which was, in turn, saponified (LiOH), esterified (CH_2N_2), and subjected to glycol cleavage ($NaIO_4$) to afford **14**[6] in 20% yield for the five steps.[12] Finally, etherification of **14** with CH_2N_2 in MeOH provided cyclohexadiene **15**,[6] which underwent selective epoxidation (*m*-CPBA, CH_2Cl_2, K_2HPO_4/KH_2PO_4 pH 7 buffer) to provide (±)-**2** (Scheme II).[6]

In summary, the combination of a transannular Diels–Alder polycyclization and an allylic diazene rearrangement provides a synthetic intermediate that can be efficiently elaborated to the enediyne-bridged tricyclic core of dynemicin A. Studies directed toward completion of the total synthesis are currently underway.

Acknowledgment. Support for this work was provided by the NIGMS (GM-40883 awarded to S.L.S.) and the NCI (CA-24487 awarded to J.C.). We also gratefully acknowledge the support of the American Cancer Society (PF-03636) and the NSF for postdoctoral and graduate fellowships to J.L.W. and J.T., respectively. Mass spectra were obtained by Dr. A. Tyler and Ms. Laura Romo at the Harvard University Mass Spectrometry Facility. NMR data were obtained on a Bruker AM-500 for which we acknowledge the NIH (1-S10-RR04870-01) and the NSF (CHE88-14019).

Supplementary Material Available: Complete spectral data for compounds **2**, **5**, **6**, **8**, and **10–15** and crystallographic data for compound **10** (10 pages). Ordering information is given on any current masthead page.

(5) (a) Although the Yamaguchi macrolactonization protocol[5b] had been employed in preliminary studies,[3] improved yields were observed when the reaction was effected with PyBroP.[5c,d] The experimental simplicity and improved efficiency has currently led to routine use of PyBroP in large-scale cyclizations (e.g., 5 g of **3** were converted to 2.6 g of **5**). (b) Inanaga, J.; Hirata, K.; Saeki, H.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1989. (c) Coste, J.; Frērot, E.; Jouin, P.; Castro, B. *Tetrahedron Lett.* **1991**, *32*, 1967. (d) Available from Novabiochem (cat. no. 01-62-0017), P.O. Box 12087, San Diego, CA 92112-4180.

(6) The structure assigned to each new compound is in accord with its infrared and high-field ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra, as well as appropriate parent ion identification by high-resolution mass spectrometry.

(7) Previous experiments in the *trans*-lactone series provided a mixture of the C(4)OH:C(11)OH regioisomers (1:3, respectively, 85% yield).

(8) Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeikar, B. *Tetrahedron* **1976**, *32*, 2157.

(9) Eckert, H.; Forster, B. *Angew. Chem.* **1987**, *99*, 922.

(10) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. This reaction is attended with a small amount of a byproduct (ca. 10%) which appears to be the C(3)-C(11) epoxide. However, this structure has yet to be fully delineated.

(11) (a) Dalcanale, E.; Montanari, F. *J. Org. Chem.* **1986**, *51*, 567. The use of DMSO as solvent and NaH_2PO_4 adjusted to pH 2 with concentrated HCl were required to minimize the formation of a byproduct, likely the C(3)–C(11) epoxide, which presumably derives from the presence of the $HOCl/Cl^-$ redox pair. (b) For the alternate use of 2-methyl-2-butene as an HOCl scavenger, see: Kraus, G. A.; Taschner, M. J. *J. Org. Chem.* **1980**, *45*, 1175 and references cited therein.

(12) For a similar opening and esterification of a butyrolactone, see: Marshall, J. A.; Andrews, R. C.; Lebioda, L. *J. Org. Chem.* **1987**, *52*, 2378.

Asymmetric α-Amination of Ketone Enolates by Chiral α-Chloro-α-nitroso Reagents: A New Approach to Optically Pure *erythro*-β-Amino Alcohols

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We have recently reported highly diastereoface selective C,N-bond formations in the reactions of 1-chloro-1-nitrosocyclohexane with chiral enolates.[1] More ambitiously, we envisaged the development of chiral α-chloro-α-nitroso reagents **V** capable of "aminating" prochiral ketone enolates **I** with high enantiofacial differentiation. Acid hydrolysis of the resulting nitrones **II** would provide optically pure β-keto *N*-hydroxylammonium salts **III** together with chiral ketone **IV**, which could be recycled to reagent **V** (Scheme I).

Oximation of known sulfonamides **1**[2] followed by chlorination furnished, after crystallization, pure blue chloro nitroso compounds **2a** (78% from **1a**) and **2b** (70% from **1b**, Scheme II). The structure of **2b**, as determined by X-ray diffraction,[3] is similar to that of (+)-10-bromo-2-chloro-2-nitrosocamphane.[4] Thus, the

(1) Oppolzer, W.; Tamura, O. *Tetrahedron Lett.* **1990**, *31*, 991–994.
(2) Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5885–5888.
(3) Bernardinelli, G.; Oppolzer, W.; Sundarababu, G. *Acta Crystallogr.*, in press.

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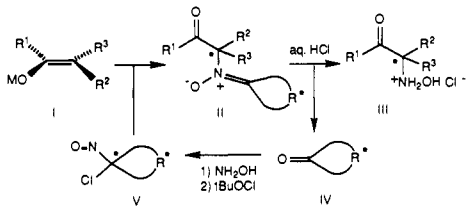
Table I. Transformation of Ethyl Ketones into Optically Pure *erythro*-β-Aminols: **3** + **2a** → **6** → **9**[5]

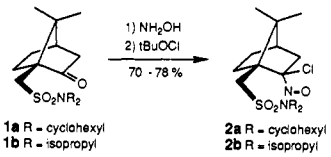
entry	R	enolate formation[a]	metal M	nitrone ratio **5**:**6**[b]	aminol **9**[c] yield (%) from **3**	aminol **9**[c] ratio *erythro*:*threo*	aminol **9**[c] ee (%)
a	C_6H_5	A	Zn	<1:>99	68 (43)	95:5 (>99.9:0.1)	96 (>99)
b	2,5-$(OMe)_2C_6H_3$	B	Na	<1:>99	57 (39)	90:10 (>98:<2)	(>99)
c	*t*-C_4H_9	C	Zn	5:95	54	>99.9:<0.1	>99.9
d	*i*-C_3H_7	C	Zn	5:95	65 (59)	98:2 (99.8:0.2)	(>99.9)
e	C_2H_5	C	Zn	5:95	65 (42)	90:10 (>99.9:<0.1)	98.2 (>99.9)

[a] A: (1) $LiN(TMS)_2$, (2) $ZnCl_2$; B: $NaN(TMS)_2$; C: (1) $LiN(SiMe_2Ph)_2$, (2) $ZnCl_2$. [b] **5**:**6** ratios determined by ^1H NMR (entries a, b) or HPLC (entries c–e) of crude reaction mixtures after workup at pH 7. [c] Values in parentheses after crystallization of free base **9d** or of hydrogen maleates of **9a**, **9b**, and **9e**; *erythro*:*threo* ratios and ee values determined by GC analysis of the *N*,*O*-bistrifluoroacetyl derivatives of **9** using a chiral capillary column: Lipodex-D (**9a**) or Chirasil-Val (**9c–e**). **9b**: *erythro*:*threo* ratio by ^1H NMR, ee by $[\alpha]_D$.[5]

Scheme I



Scheme II

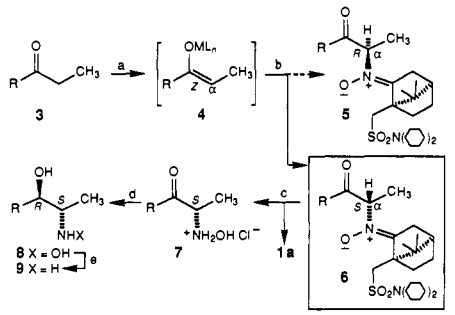


nitroso group is trans to the CMe_2 bridge and the O-atom adopts a syn-periplanar orientation to the Cl-atom, as shown by the torsional angle Cl—C—N—O = −14.7°. It appears that the bulky sulfonamide group selectively shields the "front" face of the N=O group and thereby dictates the topicity of enolate attack. Our results, as summarized in Scheme III and Table I, are consistent with this hypothesis.

Deprotonation of propiophenone (**3a**) with $LiN(SiMe_3)_2$, transmetalation of the lithium enolate with $ZnCl_2$, and reaction of this zinc enolate **4a** with nitroso reagent **2a** gave exclusively nitrone **6a** within the limits of detection.[8]

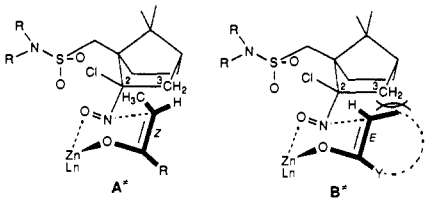
The C(α)-(*S*)-configuration of nitrone **6a** was assigned by its conversion to (−)-norephedrine. After hydrolysis of crude **6a** with aqueous HCl, ketone **1a** was recovered by extraction (Et_2O) of the acidic medium (82% after crystallization). Evaporation of the aqueous phase, *erythro*-selective reduction of the residual β-keto *N*-hydroxylamine hydrochloride **7a** with $NaBH_4$ in MeOH[9]

Scheme III[a]



[a] (a) $MN(SiMe_2R)_2$ (1.1 equiv), THF; $ZnCl_2$ (1.5–2 equiv, entries a, c–e); (b) **2a** (1 equiv); (c) 1 N aqueous HCl, extraction of **1a**, evaporation; (d) $NaBH_4$ (2 mol equiv), MeOH (entries a, b) or EtOH (entries c–e); (e) zinc powder (10 equiv), 1 N aqueous HCl/AcOH (2:1).

Scheme IV



followed by N,O-hydrogenolysis of the resulting β-hydroxy *N*-hydroxylamine **8a** with Zn/AcOH/HCl, and distillation of the free base afforded (−)-norephedrine[5] (**9a**, *erythro*:*threo* = 95:5, 96% ee) in 68% overall yield from propiophenone.

The potential of this amination/reduction sequence for diastereo- and enantioselective syntheses of biologically interesting β-aminols is illustrated by the analogous conversion of ketone **3b** (via its sodium enolate) into the α-adrenergic agent methoxamine **9b**.[5,6]

Similarly, aliphatic ethyl ketones **3** were converted to their (*Z*)-zinc enolates **4**,[10] which underwent 90% enantioface selective C,N-bond formation on treatment with chloro nitroso reagent **2a** (entries c–e). Flash chromatography furnished diastereomerically pure nitrones **6**, which on hydrolysis/carbonyl reduction/N,O-hydrogenolysis provided aliphatic *erythro*-β-aminols **9** in 80 to >99.9% de and in ≥98.2% ee. Aminols **9d** and **9e**[5] were readily purified by crystallization of the free base and the hydrogen maleate, respectively.

The observed C(α)-*si*-face topicity of C,N-bond formation is consistent with the cyclic "chair" transition state **A**‡ (Scheme IV). Postulated transition state *A*‡ accounts for (1) attack of the N=O

(4) Ferguson, G.; Fritchie, C. J.; Robertson, J. M.; Sim, G. A. *J. Chem. Soc.* **1961**, 1976–1987.

(5) The absolute and relative configuration of aminols **9a**, **9b**, and **9e** were confirmed by the following comparisons: *N*,*O*-diacetyl derivatives of **9a** (^1H NMR, $[\alpha]_D$, mixed mp) with a sample obtained from commercial (−)-norephedrine (Fluka); hydrogen maleate of **9b** (^1H NMR, $[\alpha]_D$, mixed mp) with a sample prepared from (*S*)-alanine;[6c] the ester prepared from the *N*,*N*-dibenzyl derivative of **9e** and (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (^1H NMR) with an authentic sample.[7]

(6) (a) Baltzly, R.; Mehta, N. B. *J. Med. Chem.* **1968**, *11*, 833–844. (b) Gabrielsen, M. V.; Sørensen, A. M. *Acta Chem. Scand.* **1974**, *A28*, 1162–1166. (c) Fujita, M.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 5415–5421.

(7) Reetz, M. T.; Drewes, M. W.; Schmitz, A. *Angew. Chem.* **1987**, *99*, 1186–1188; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1141–1143.

(8) Reaction of the sodium or lithium enolate of **3a** with reagents **2a** or **2b** was less stereoselective, yielding ~5:95 mixtures of C(α)-*R*- and C(α)-(*S*)-nitrones. Nitrone **6a** epimerized with 0.3 M NEt_3 in CH_2Cl_2 (room temperature, 3 h) to give a 1:1 mixture **5a**/**6a**. It follows that the reaction **4a** (M = Zn) + **2a** → **6a** is kinetically controlled.

(9) Kametani, T.; Kigasawa, K.; Hiiragi, M.; Wagatsuma, N.; Kohagizawa, T.; Inoue, H. *Heterocycles* **1980**, *14*, 775–778.

(10) Deprotonation with hindered lithium amides gives mainly (*Z*)-enolates from ketones **3** but mainly (*E*)-enolates from esters of 2,6-dimethylphenol: Heathcock, C. H. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 111–212. Masamune, S.; Ellingboe, J. W.; Choy, W. *J. Am. Chem. Soc.* **1982**, *104*, 5526–5528.

group of **2** by a (*Z*)-enolate **4** opposite to the bulky sulfonamide group[3] and (2) coordination of Zn^{II} with the oxygen atom of the nitroso group trans to the N—C(2) bond.[11]

An analogous transition state **B**‡ involving (*E*)-enolates suffers repulsion between the C(3) of the bornane skeleton and the enolate C(α) substituent. Indeed, (**E**)-zinc enolates derived from cyclic ketones such as α-tetralone, β-tetralone, or cyclohexanone or from the propionate ester of 2,6-dimethylphenol[10] reacted sluggishly with **2a**. Only partial conversion to complex mixtures was observed.

In conclusion, reagents **2a** and **2b**, which are readily accessible in both antipodal forms,[2] represent the first chiral [NH_2^+] equivalents and thus open a new route to diastereo- and enantiomerically pure β-aminols. The synthetic potential of electrophilic nitroso compounds is being further explored in our laboratory.

Acknowledgment. Financial support of this work by the Swiss National Science Foundation, Sandoz Ltd., Basel, and Givaudan SA, Vernier, is gratefully acknowledged. We thank Professor M. T. Reetz for kindly providing reference spectra.

Supplementary Material Available: Preparations and analysis data, including mp, IR, ^{1}H NMR, ^{13}C NMR, MS, and [α] values (11 pages). Ordering information is given on any current masthead page.

(11) An X-ray structure analysis of dichlorobis(4-nitroso-*N*,*N*-dimethylaniline)zinc(II) exhibits torsional angles Zn–O–N–C = −171.5° and 176.7°; Hu, S.; Thompson, D. M.; Ikekwere, P. O.; Barton, R. J.; Johnson, K. E.; Robertson, B. E. *Inorg. Chem.* **1989**, *28*, 4552–4554.

The First Example of Transition-Metal-Catalyzed Addition of Aromatic Thiols to Acetylenes

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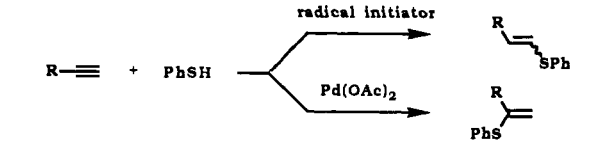
While the properties of the complexes resulting from stoichiometric reactions of thiols with transition-metal complexes have been well-studied,[1] there are few reports of transition-metal-catalyzed synthetic reactions with thiols.[2] For instance, for transition-metal-catalyzed addition of thiols to carbon–carbon unsaturated compounds, there is only one example of addition to a 1,3-diene to the best of our knowledge.[2d] Perhaps widespread prejudice that thiols are catalyst poisons has precluded investigation in this area. In this paper we describe the interesting finding that many transition-metal catalysts indeed catalyze the addition of aromatic thiols to acetylenes to provide vinyl sulfides.[3] Table I summarizes the results of the addition of benzenethiol to 1-octyne (**1a**) in the presence of various transition-metal catalysts. Among

Table I. Effects of Catalysts on the Addition of PhSH to **1a**[a]

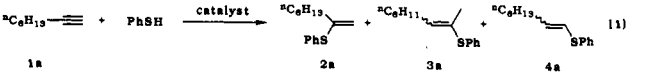
entry	catalyst	condition[b]	yield (%)[c] 2a	3a	4a
1	$Pd(OAc)_2$	A	85[d]	<1	<1
2	$Pd(OAc)_2$	B	62	14	4
3[e]	$Pd(OAc)_2$	C	67	2	<1
4	none	A	0	0	47
5	AcOH	A	0	0	78
6	$Pd(PPh_3)_4$	B	4	10	2
7	$Pd(PPh_3)_4$	C	1	45	4
8	$Pd(PhCN)_2Cl_2$	C	2	73	0
9	$Pt(PPh_3)_4$	C	2	80	18
10	$Ni(PPh_3)_2Cl_2$	C	1	22	2
11	$Rh(PPh_3)_3Cl$	C	14	23	52[f]

[a] **1a** (1.0 mmol), catalyst (0.02 mmol), solvent (0.5 mL), and PhSH (1.0 mmol) for 16 h. [b] A: THF, 40 °C. B: THF, 67 °C. C: PhH, 80 °C. [c] Determined by GLC and ^{1}H NMR spectrometry. [d] Isolated yield. [e] 2,2-Bis(phenylthio)octane (5% based on **1a**) and $(PhS)_2$ (14%) were also produced. [f] *E*/*Z* = 98/2.

Scheme I



the catalysts examined, $Pd(OAc)_2$ exhibited excellent selectivity to afford the adduct **2a** (eq 1) in good yield (entries 1–3).[4,5] In the absence of catalyst or presence of AcOH, **2a** was not obtained at all, and only **4a** was produced (entries 4 and 5).[6] This may indicate that the palladium complex formed in situ also played an important role in suppression of the formation of **4a**.[7] It has been well-established that the free radical additions of thiols to terminal acetylenes provide anti-Markovnikov adducts,[8] while the present $Pd(OAc)_2$-catalyzed addition afforded the Markovnikov adducts successfully. Thus, these methods presented the regiocomplementary approach to give vinyl sulfides (Scheme I).[9] When $Pt(PPh_3)_4$ was employed as a catalyst, **3a** was produced



(1)

(1) For notable examples, see: (a) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Keskinen, A. E.; Senoff, C. V. *J. Organomet. Chem.* **1972**, *37*, 201. (c) Ugo, R.; La Monica, G.; Cenini, S. *J. Chem. Soc. A* **1971**, 522. (d) Nyholm, R. S.; Skinner, J. F.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 38. (e) Chatt, J.; Mann, F. G. *J. Chem. Soc.* **1938**, 1949. (f) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 2807. (g) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1953**, 2363. (h) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc., Dalton Trans.* **1972**, 330. (i) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc. A* **1970**, 3197. (j) Umakoshi, K.; Ichimura, A.; Kinoshita, I.; Ooi, S. *Inorg. Chem.* **1990**, *29*, 4005. (k) Gaylor, J. R.; Senoff, C. V. *Can. J. Chem.* **1972**, *50*, 1868. (l) Osakada, K.; Hayashi, H.; Maeda, M.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1986**, 597. (m) Gaines, T.; Roundhill, D. M. *Inorg. Chem.* **1974**, *13*, 2521. (n) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.

(2) (a) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (b) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147. (c) Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935. (d) Dzhemilev, U. M.; Kunakova, R. V.; Gaisin, R. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *11*, 2655. (e) Talley, J. J.; Colley, A. M. *J. Organomet. Chem.* **1981**, *215*, C38. (f) McKervey, M. A.; Ratananukul, P. *Tetrahedron Lett.* **1982**, *23*, 2509. (g) Holmquist, H. E.; Carnahan, J. E. *J. Org. Chem.* **1960**, *25*, 2240. (h) Iqbal, J.; Pandey, A.; Shukla, A.; Srivastava, R. R.; Tripathi, S. *Tetrahedron* **1990**, *46*, 6423.

(3) For the synthetic utility of vinyl sulfides, see: (a) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (b) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621.

(4) Procedure (entry 1): In a reaction vessel were placed $Pd(OAc)_2$ (0.02 mmol), THF (0.5 mL), **1a** (1.0 mmol), and then PhSH (1.0 mmol). After 16 h at 40 °C, the resulting catalyst was removed by filtration through Celite, and then the solvent was evaporated. The crude oil was subjected to MPLC (silica gel) to obtain **2a** (85%). Also isolated in smaller quantities were 2,2-bis(phenylthio)octane (3% based on **1a**) and diphenyl disulfide (6%).

(5) The additions to **1a** of some other thiols such as nBuSH, C_6F_5SH, $MeOCOCH_2SH$, and 2-pyridinethiol were not catalyzed by $Pd(OAc)_2$ under similar reaction conditions.

(6) The addition proceeded probably via a free radical mechanism by an adventitious amount of oxygen.

(7) It has been reported that $Fe(CO)_5$ inhibited the radical addition of ArSH to phenylacetylene, see: Kandror, I. I.; Petrova, R. G.; Petrovskii, P. V.; Freidlina, R. Kh. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *7*, 1621.

(8) (a) Peach, M. E. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: London, 1974; Vol. 2. (b) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J. L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647. (c) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273.

(9) There are few examples of Markovnikov addition of thiols to acetylenes by nucleophilic attack of thiolate anion, but the relatively longer reaction time or more severe conditions are essential; see: (a) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756. (b) Borisova, A. I.; Filippova, A. K.; Voronov, V. K.; Shostakovski, M. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 2498.

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