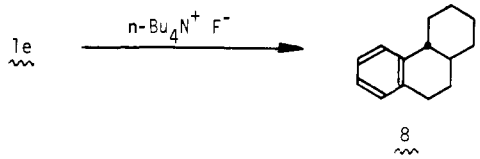
readily derived via alkylation of the silyl-stabilized anion of *o*-(trimethylsilylmethyl)benzyldimethylamine (**6**)[7] and the subsequent quaternalization with methyl halides.

Reaction of *o*-(α-trimethylsilylpentyl)benzyltrimethylammonium iodide (**1c**) with methyl acrylate was similarly caused by tetrabutylammonium fluoride to afford 1,2,3,4-tetrahydro-*cis*-1-butyl-2-carbomethoxynaphthalene (**3**-v)[10] as a major product in 88% yield. Some examples of cycloadditions of *o*-xylylene intermediates with olefins and acetylenes are summarized in Table I.

The present method for generation of *o*-xylylenes and their trappings with olefins can be extended to intramolecular cycloaddition of *o*-xylylenes leading to polycycles. When a solution of 145 mg (0.55 mmol) of tetrabutylammonium fluoride in 10 mL of acetonitrile was added dropwise over 1 h to a refluxing solution of 225 mg (0.44 mmol) of *o*-(1-trimethylsilylhept-6-enyl)benzyltrimethylammonium iodide (**1e**)[11] in 5 mL of acetonitrile, *trans*-octahydrophenanthrene (**8**)[12] was



produced in 70% yield together with an 8% yield of the corresponding spiro[di-*o*-xylylene] derivative (**9**).[13] We plan to report further studies on this reaction and its application to the synthesis of steroidal structure in the near future.

Acknowledgment. We thank Dr. T. Suzuki of Kyoto University for the ^{13}C NMR measurement. We are grateful to Professor K. P. C. Vollhardt for providing us with ^{13}C NMR and 360-MHz NMR spectra of *trans*-octahydrophenanthrene.

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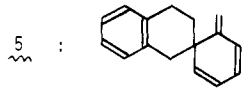
(4) It is known that fluoride anion promotes β elimination of halosilane leading to strained alkene and benzyne: Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153. (b) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936.
(5) **1a**-Cl: IR (KBr disk) 1492, 1247, 1152, 1104, 850 cm^{-1}; NMR (CD_3CN with Me_4Si as an external standard) δ −0.32 (s, 9 H), 2.07 (s, 2 H), 2.85 (s, 9 H), 4.36 (br s, 2 H), 6.6–7.3 (m, 4 H).
(6) Compound **5** was identified as the spiro[di-*o*-xylylene] **5** by comparison of its NMR and IR spectra with those reported by Errede.[2]



(7) **6** was prepared in 85% overall yield via Sommelet rearrangement of benzyltrimethylammonium iodide[8] and silylation[9] of the resulting *o*-methylbenzyldimethylamine. **6**: IR (neat) 1249, 840 cm^{-1}; NMR (CCl_4 with Me_4Si as an external standard) δ 0.00 (s, 9 H), 2.06 (s, 6 H), 2.12 (s, 2 H), 3.13 (s, 2 H), 6.6–7.1 (m, 4 H).
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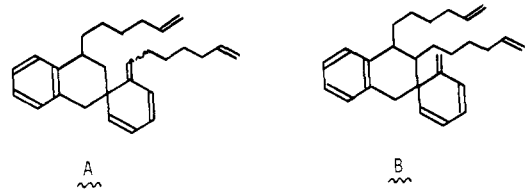
(10) **3**-v: IR (neat) 1738, 1150, 1200, 768 cm^{-1}; NMR (100 MHz) (CCl_4 with Me_4Si) δ 0.8–1.2 (m, 3 H), 1.2–1.8 (m, 6 H), 2.1 (quasi q, 2 H), 2.6–3.3 (m, 4 H), 3.77 (s, 3 H), 7.10 (s, 4 H). Cis configuration of **3**-v was established by decoupling technique which revealed a sharp doublet ($J_{H_1-H_2}$ = 4.5 Hz) at δ 3.15 ascribed to a hydrogen on C_1.
(11) **1e**: IR (KBr disk) 1641, 1246, 990, 910, 842 cm^{-1}; NMR (CD_3CN with Me_4Si as an external standard) δ −0.36 (s, 9 H), 1.2–2.1 (m, 8 H), 2.30 (t, 1 H), 2.76 (s, 9 H), 4.18 (dd, 2 H), 4.3–5.8 (m, 3 H), 6.6–7.3 (m, 4 H).
(12) **8**: ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 26.31, 27.00, 29.92, 30.68, 30.97, 34.40, 40.62, 43.81, 125.36 (2 C), 125.43, 128.94, 137.00, 140.54 ppm. Trans stereochemistry of **8** was convincingly confirmed by comparison of its ^{13}C NMR spectrum with that of *trans*-octahydrophenanthrene, which was provided by Professor Vollhardt.
(13) Structure A was assigned to compound **9** on the basis of its IR and NMR spectra: IR (neat) 1640, 995, 909, 755 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.0–3.0 (m, 21 H), 4.6–6.5 (m, 11 H), 6.9–7.2 (m, 4 H). A possibility of the regioisomeric structure (B) for **9** was excluded by lack of IR absorption band at 890 cm^{-1} characteric of the *exo*-methylene structure.



(14) **3**-i: NMR (100 MHz) ($CDCl_3$ with Me_4Si) δ 1.28 (t, 6 H), 3.01 (br t, 2 H), 3.17 (br d, 4 H), 4.21 (t, 4 H), 7.05 (s, 4 H).
(15) Dehydrogenation of **3**-iv by palladium on charcoal gave 1-methyl-2-cyanonaphthalene. **3**-iv: NMR ($CDCl_3$ with Me_4Si) δ 1.45 (d, 3 H), 1.8–2.3 (m, 2 H), 2.6–3.3 (m, 4 H), 7.05 (br s, 4 H).
(16) **4**-ii: NMR (100 MHz) ($CDCl_3$ with Me_4Si) δ 0.7–1.1 (m, 3 H), 1.1–1.2 (m, 10 H), 2.9–3.7 (m, 2 H), 3.52–3.82 (4s, 6 H), 7.0–7.4 (m, 4 H), 7.56 and 7.61 (2s, 1 H, olefinic proton).

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Palladium(II) Chloride Catalyzed Cope Rearrangements of Acyclic 1,5-Dienes[1]

Sir:

The Cope rearrangement of 1,5-dienes typically requires elevated temperatures.[2] Catalytic methods for effecting this carbon-carbon-bond-forming transformation enhance its synthetic utility, and in recent years impressive accomplishments have been recorded in catalyzing Cope rearrangements of functionalized 1,5-dienes.[3] The development of more general methods for catalyzing the rearrangement of simple 1,5-dienes remains, however, a challenging problem.[4] In 1966 Jonassen and co-workers[7a] reported that treatment of excess *cis,trans*-1,5-cyclodecadiene at room temperature with bis(benzonitrile)palladium(II) chloride gave the crystalline palladium(II) dichloride complex of *cis*-1,2-divinylcyclohexane in 82% yield.[7,8] The similar rearrangement of *cis*-1,2-divinylcyclobutanes to give palladium(II) dichloride complexes of 1,5-cyclooctadienes has been extensively studied by Heimbach and co-workers.[9] These studies,[7-9] while clearly demonstrating that stoichiometric amounts of palladium(II) chloride can promote the Cope rearrangement of strained cyclic 1,5-dienes, leave unanswered questions of the generality or potential catalytic nature of this reaction. In this communication we report for the first time that palladium(II) promoted Cope rearrangements can be conducted in a *catalytic* fashion to produce the rearranged diene, rather than the diene-palladium(II) dichloride complex. We moreover report *that Cope rearrangements of many unstrained, conformationally flexible, acyclic 1,5-dienes are dramatically catalyzed by palladium(II) chloride salts and occur readily at room temperature.*

Treatment of 2-methyl-3-phenyl-1,5-hexadiene (**1**)[10] with 0.06 equiv of $PdCl_2(PhCN)_2$ in tetrahydrofuran (THF) at room temperature for 24 h produced dienes **2**[11,12a] and **3**[11] in a 93:7 ratio (87% yield after bulb-to-bulb distillation). In contrast, thermal Cope rearrangement of diene **1** required elevated temperatures (half-life, 13 h; 177 °C; C_6D_6 solvent) and proceeded less stereoselectively, to yield **2** and **3** in a kinetically controlled[13] 3:1 ratio. Although the ^1H NMR, IR, and mass spectra for stereoisomers **2** and **3** are nearly identical, stereochemical assignments follow unambiguously from ^{13}C

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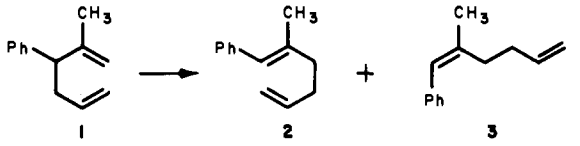
Table I. Bis(benzonitrile)palladium(II) Chloride Catalyzed Cope Rearrangements of Methyl-Substituted 3-Phenyl-1,5-hexadienes (**4**)[a]

$$R^1CH{=}CR^2\overset{Ph}{\underset{|}{C}}R^3CH_2CR^5{=}CHR^6\ (\mathbf{4}) \longrightarrow Ph\text{-}CR^3{=}CR^2CHR^1CHR^6CR^5{=}CH_2\ (\mathbf{5})$$

entry	starting substituted **4**	reaction time, h	yield, % recovery[c]	product composition[b] % Cope product **5**[d]	product composition[b] Cope stereoselectivity, %
1	unsubstituted[e]	24	93	nd[f]	
2	1-methyl	24	88	nd[f]	
3	2-methyl[g]	30	92	99	93 *E*
4	5-methyl[g]	5	96	100	97 *E*
5	6-methyl	24	91	nd[f]	
6	1,2-dimethyl[g]	48	89	81	>90 *E*
7	(*E*)-2,6-dimethyl[g]	48	91	59	>90 *E*
8	(*E*)-3,6-dimethyl[e]	24	89	nd[f]	
9	2,5-dimethyl	24	90	nd[f]	
10	(*E*)-2,3,6-trimethyl[g]	18	88	100	71 *E*

[a] A 0.1 M THF solution of the starting diene (>98% pure) was treated with 0.10 equiv of $PdCl_2(PhCN)_2$ at room temperature with stirring. Reactions were allowed to proceed until isomer ratios became constant or for 24 h if no conversion was observed. [b] By GLC analysis. [c] Combined yield of **4** and **5** isolated after concentration and bulb-to-bulb distillation to remove the catalyst. [d] The remainder of the material was the starting diene **4**. In no case were significant products other than **5** detected (estimated detection limits, 2–4%). For entries 3 and 7 reversibility was confirmed by treatment of the Cope product with $PdCl_2(PhCN)_2$. [e] A suspension was formed upon catalyst addition. [f] None detected by GLC. [g] The values reported represent the mean of three experiments. Isomer ratios were reproducible within ±2%.

NMR spectra which show characteristic[15] absorptions for the *E* isomer **2** at 17.9 (CH_3) and 40.2 ppm (C-3), and for the *Z* isomer **3** at 24.0 (CH_3) and 32.1 ppm (C-3). The catalyzed rearrangement of **1** was remarkably free of competing side reactions, e.g., carbon-carbon double-bond isomerizations,[16] and GC-MS analysis showed that $C_{13}H_{16}$ isomers other than **1–3** comprised <1% of the crude reaction product. We have examined a number of potential catalysts and reaction conditions for the transformation of eq 1. The $PdCl_2(PhCN)_2$

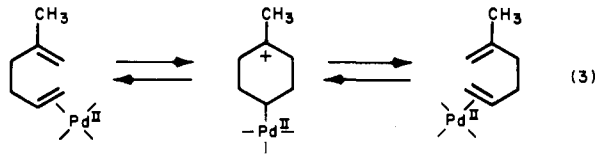


1 2 3 (1)

catalyzed rearrangement showed significant solvent effects and was considerably faster in the benzene than in THF or CH_2Cl_2. In benzene the Cope rearrangement of **1** was *complete within 1 h at room temperature* [0.10 equiv of $PdCl_2(PhCN)_2$], and a catalytic rate acceleration of 10^{10} (1 M catalyst) can be estimated for this transformation.[17] Interestingly, $Pd(OAc)_2$, $Pd(Ph_3P)_4$, and $Hg(OCOCF_3)_2$[19] were ineffective catalysts.[20] In all of the solvents that we examined, the $PdCl_2(PhCN)_2$ catalyzed rearrangement of **1** left 0.5–2% of **1** unchanged at long reaction times. That this reflected the equilibrium conversion at 25 °C was confirmed by treatment of the pure *E* diene **2** with $PdCl_2(PhCN)_2$ (0.10 equiv, THF, 25 °C) to give after 36 h a mixture of **1** (0.6%), **2** (92%), and **3** (7.4%).

To explore the scope of the $PdCl_2$ catalyzed Cope rearrangement, a series of methyl-substituted 3-phenyl-1,5-hexadienes[10,11] were treated identically (Table I) with 0.10 equiv of $PdCl_2(PhCN)_2$ at room temperature in THF. With half of the substituted dienes examined (Table I), rearrangement occurred readily under these mild conditions to give the corresponding Cope products[11] in high yields. As was observed with **1**, the catalyzed Cope rearrangements were extremely clean, and only traces of other products were detected. The successful rearrangement of (*E*)-2,6-dimethyl-3-phenyl-1,5-hexadiene to give (*E*)- and (*Z*)-2,4-dimethyl-1-phenyl-1,5-hexadiene (eq 2) is particularly significant, since it demonstrates that a [3,3] shift is involved in the catalyzed rearrangement. There are significant structural limitations to the $PdCl_2(PhCN)_2$ catalyzed Cope rearrangement under these conditions, since five of the substituted 1,5-hexadienes examined gave no trace of Cope products. In the case of entries 1 and 8 this failure may be due to precipitation of the catalyst as an insoluble diene-palladium(II) dichloride complex, since cloudy suspensions were formed in these cases upon addition of the catalyst. The methyl substituent effects observed are dramatic. It would appear that, at least under these experimental conditions, the $PdCl_2(PhCN)_2$ catalyzed Cope rearrangement of acyclic 1,5-dienes requires a substituent at either C-2 or C-5. Interestingly, if both these positions are substituted (entry 9), no rearrangement occurs. Although we feel a detailed discussion of the mechanism of the $PdCl_2$ catalyzed rearrangement is premature at this point, we note that the critical role indicated for substituents at carbons 2 and 5 of the acyclic 1,5-diene may be rationalized by a "cyclization-induced rearrangement" mechanism.[19a] In such a process (eq 3),

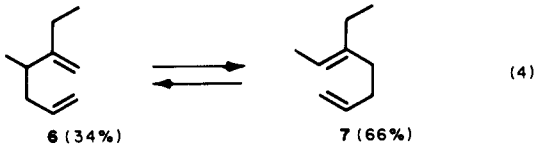
(2)



(3)

preferential Pd(II) complexation with the least substituted double bond[21] would be followed by cyclization to a cyclohexyl cation,[22] if a donor substituent was present at C-2. A substituent at C-5 should hinder this transformation by disfavoring[21] initial π complexation.

To confirm that the 3-phenyl substituent did not play a significant role (other than providing a thermodynamic driving force) in the catalyzed rearrangements reported here, we examined 2-ethyl-3-methyl-1,5-hexadiene (**6**) under similar conditions. When **6** was treated at room temperature for 8 h with 0.10 equiv of $PdCl_2(PhCN)_2$, it was readily equilibrated[23]



6 (34%) **7** (66%) (4)

in high yield with its Cope isomer **7** (eq 4). Diene **7** is believed to be primarily the *E* stereoisomer,[24] since it was homogeneous

by GLC and showed only a single vinyl methyl absorption at δ 1.57 in the 90-MHz ^{1}H NMR spectrum.

The ability to conduct the Cope rearrangement of acyclic 1,5-dienes in a catalytic fashion at room temperature should have significant implications in synthesis. We are continuing to explore the scope, mechanism, and synthetic applications of this mild carbon-carbon-bond-forming reaction.

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(2) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.
(3) Methods typically exploit the acidity or basicity of a heteroatom substituent. Examples include the following. (a) Base catalyzed oxy-Cope rearrangement: Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242. (b) Acid catalyzed rearrangements of 1- or 3-acyl-1,5-dienes: Yates, P.; Eaton, P. *Tetrahedron Lett.* **1960**, *11*, 5. Cookson, R. C.; Hudec, J.; Williams, R. O. *Ibid.* **1960**, *22*, 29. Widner, U., Zsindely, J.; Hansen; H.-J., Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 75. Miller, B. *Acc. Chem. Res.* **1975**, *8*, 245.
(4) To our knowledge the only reports of catalyzed Cope rearrangements of 1,5-diene hydrocarbons are alumina catalysis of the Cope rearrangement of *meso*- and *dl*-3,4-diphenyl-1,5-hexadlene,[5] Ni(II) catalysis of the Cope rearrangement of *cis*-divinylcyclobutane,[6] and the Pd(II) and Pt(II) catalyzed rearrangements summarized in ref 7-10.
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(6) Heimbach, P.; Brenner, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 800.
(7) (a) Trebellas, J. C.; Olechowski, J. R.; Jonassen, H. B. *J. Organomet. Chem.* **1966**, *6*, 412. (b) Heimbach, P.; Molin, M. *Ibid.* **1973**, *49*, 477.
(8) The $PdCl_2$ promoted rearrangement of *trans,trans*-1,5-cyclononadienes has also been reported: Brown, E. D.; Sam, T. W.; Sutherland, J. K.; Torre, A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2326.
(9) Heimbach, P.; Molin, M. *J. Organomet. Chem.* **1973**, *49*, 483.
(10) Diene **1** was prepared from 1-phenyl-2-propanone by successive treatment with (a) KH and allyl bromide, and (b) methylenetriphenylphosphorane. Other dienes utilized in this study were prepared by related procedures.[11]
(11) New compounds were characterized by ^{1}H NMR, ^{13}C NMR (in most cases), IR, and low resolution mass spectra. All yields refer to isolated product of >96% purity as determined by GLC analysis.
(12) Representative spectral data follow. (a) **2**: IR (film) 3080, 3060, 3030, 2980, 2930, 1640, 1600, 1490, 1440, 990, 910 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.2 (m, C_6H_5), 6.28 (br s, $W_{h/2}$ = 5 Hz, PhC*H*=CMeR), 6.0-5.6 (m, C*H*=CH_2), 5.1-4.9 (m, CH=CH_2), 2.2-3.0 (m, CH_2C=), 1.85 (d, J = 1.3 Hz, =CCH_3); ^{13}C NMR ($CDCl_3$) δ 138.9 (*ipso*-Ph), 138.7 (C-5), 129.2 (*m*-Ph), 128.4 (*o*-Ph), 126.2 (*p*-Ph), 125.6 (C-1), 115.0 (C-6), 40.2 (C-3), 32.6 (C-4), 17.9 (CH_3); mass spectrum (rel intensity) (methane CI) *m/z* 173 (21), 131 (100), 91 (75). (b) **7**: IR (film) 3075, 2960, 1640, 990, 818 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.1-5.6 (m, C*H*=CH_2), 5.4-4.9 (m, =CH_2 and CH=C), 1.59 (d, J = 6.8 Hz, =CHCH_3), 0.96 (t, J = 7.6 Hz, CH_2CH_3); mass spectrum (rel intensity) (methane CI) *m/z* 125 (4), 109 (45), 95 (93), 83 (78), 55 (100).
(13) The unusually low stereoselectivity observed in the thermal rearrangement of **1** can be ascribed to destabilizing steric interactions[14] between the quasi-equatorial phenyl and the vinylic methyl in the "chair-transition state"[2] leading to the *E* isomer **2**.
(14) Cf. Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
(15) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757. Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426.
(16) Cf. Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic: New York, 1971; Vol. II, Chapter 3.
(17) A second-order rate constant (k_{cat} = 0.3 M^{-1} s^{-1}) for the catalyzed rearrangement in benzene can be estimated from the observed half-life of 220 s [$PdCl_2(PhCN)_2$, 0.010; **1**, 0.10 M]. The corresponding rate constant for the thermal isomerization of **1** (k = 3.4 × 10^{-11} s^{-1}) was estimated using 3-phenyl-1,5-hexadiene (**8**) as a model and the activation parameters of Dewar and Wade[16] for the Cope rearrangement of **8** in *o*-dichlorobenzene. The measured rate constant for thermal Cope rearrangement of **1** at 177 °C (k = 1.4 × 10^{-5} s^{-1}; benzene solvent) is slightly smaller than that calculated[18] for **8** at this temperature (k = 4.6 × 10^{-5} s^{-1}; *o*-dichlorobenzene solvent).
(18) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417.
(19) A number of mercuric trifluoroacetate catalyzed [3,3]-sigmatropic rearrangements have been reported from our laboratory. Cf.: (a) Overman, L. E.; Campbell, C. B.; Knoll, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 4822. (b) Overman, L. E. *Ibid.* **1976**, *98*, 2901.
(20) No trace of **2** was detected by GLC, and >90% of **1** was recovered when **1** was treated with 0.1 equiv [0.4 equiv in the case of $Hg(OCOCF_3)_2$] of these catalysts for 24 h at room temperature in THF.
(21) Cf.: Hartley, F. R. *Chem. Rev.* **1973**, 163. Akermark, B.; Bäckvall, J.-E. *Tetrahedron Lett.* **1975**, 819. Pregaglia, G. F.; Conti, F.; Minasso, B. *J. Organomet. Chem.* **1973**, *47*, 165.
(22) The cyclization step of a "cyclization-induced rearrangement" mechanism[19a] for the Pd(II) catalyzed Cope rearrangements derives precedent from reported cyclizations of acyclic 1,5-dienes to give cyclohexane products under oxymetalation conditions. Cf.: Julia, M.; Fourneron, J.-D. *J. Chem. Res. (M)* **1978**, 5401 (S466). Renold, W.; Ohloff, G; Norin, T. *Helv. Chim. Acta* **1979**, *62*, 985.
(23) The same mixture of **6** and **7** was obtained when **7** was treated (28 h, THF, 25 °C) with 0.10 equiv of $PdCl_2(PhCN)_2$.
(24) Based on analogy with **2**. Unfortunately we did not obtain enough **7** for ^{13}C NMR analysis.

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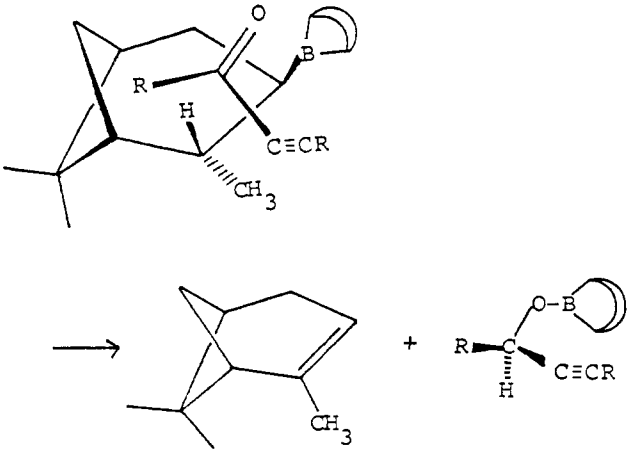
Reduction of α,β-Acetylenic Ketones with *B*-3-Pinanyl-9-borabicyclo[3.3.1]nonane. High Asymmetric Induction in Aliphatic Systems

Sir:

The introduction of asymmetry in a molecule by means of a chiral reagent is a potentially attractive strategy in natural product synthesis. One of the simplest and most useful transformations of this type is the reduction of a prochiral ketone to a carbinol. Several reagents will perform this reduction with high asymmetric induction in simple aryl substrates.[1,2] However, these reagents have been less successful with the aliphatic ketones of interest to most synthetic chemists. Herein we report that the chiral reducing agent prepared from (+)-α-pinene and 9-borabicyclo[3.3.1]nonane (9-BBN) will reduce α,β-acetylenic ketones under mild conditions to secondary propargylic alcohols of exceptionally high enantiomeric purity. Since the products from such reductions are useful intermediates in synthetic organic chemistry,[3] such a reagent may be of enormous practical value.

B-3-Pinanyl-9-BBN has been shown to be highly effective in the reduction of aldehydes to chiral 1-deuterio primary alcohols.[4] The alcohols from these reductions are consistently of the same configuration.[5] Similarly, all of the acetylenic ketones which we have examined are consistently reduced to the propargylic alcohols of the same absolute configuration. Alcohols of the opposite configuration may be obtained with the reagent prepared from (−)-α-pinene. These reactions are thought to proceed through the bimolecular exchange mechanism[6] depicted in Scheme I. The acetylene moiety seems to have the same steric influence as hydrogen in aldehyde reductions.[1a] This is to be contrasted to the $LiAlH_4$-Darvon alcohol or *N*-methylephedrine complexes which, it has been

Scheme I



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