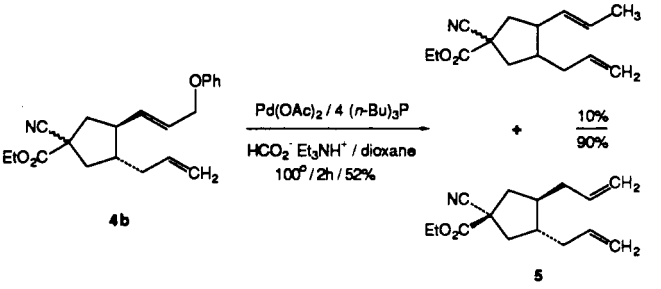
With respect to the stereochemistry of cyclization, the reaction of tetraene **2** with benzyl alcohol or phenol afforded as the major products a 1:1 mixture of stereoisomeric cyclopentanes **4**. Only minor amounts of other diastereomers were detected. As expected, the diastereomeric cyclopentanes **4** were stereoisomeric at the resident quaternary stereocenter. Assignment of the trans relative stereochemistry to the side chains is based upon reduction of the stereoisomeric mixture of allyl phenyl ethers **4b** by the method of Tsuji[14] to give predominantly the (*d,l*)-*trans*-diene **5** rather than the corresponding cis-diastereomers.[15] In the five-membered ring carbocyclizations investigated to date, the level of trans/cis simple diastereoselectivity varied from 5:1 (entry 11) to >20:1 (entries 3, 8, 9, 12), as determined by capillary gas chromatography, HPLC, and/or high-field $^1H/^{13}C$ NMR analysis. The origin of the stereoselectivity is at this point unclear. Certain literature data, obtained for the telomerizations of isoprene[5a] and piperylene,[16] suggest that the oxidative cyclization of the tetraene substrate to the intermediate fused-bicyclic palladacycle (the stereochemical-determining step in the proposed mechanism) should be reversible under the cyclization conditions. Consequently, the relative stabilities of the diastereomeric trans/cis metallacycles[17] and/or their relative rates of trapping by H–X may determine the diastereoselectivity of the cyclization. We find that the trans/cis ratio of cyclized products is sensitive to the nature of the tetraene substrate (e.g. **1** vs **6** entries 2, 8), the nature of the trapping reagent (e.g. PhOH vs $PhCH_2OH$, entries 1, 2, or PhOH vs AcOH, entries 10, 11), and also the reaction temperature. Palladium-catalyzed cyclization of tetraene **1** with benzyl alcohol at 65 °C gave a 3:1 trans/cis ratio as compared to the 7:1 ratio observed when the reaction was carried out at ambient temperature.



This catalytic palladium-mediated tetraene carbocyclization method provides a versatile new strategy for the stereoselective preparation of functionalized ring systems. The observed bond construction complements the palladium-catalyzed cyclization-via-isomerizations,[10] palladium–ene cyclizations,[11] and other palladium-mediated carbocyclizations[12] and under development elsewhere. The requisite tetraene substrates are easily prepared, and such substrates have been previously employed for other cyclization reactions, including Ni(0)-catalyzed [4 + 4]-cycloaddition[9a–c] and acid-catalyzed [4 + 2]-cycloaddition[18] reactions. Further studies on the stereoselectivities of other trapping reagents and on the application of this methodology to the stereo- and regioselective construction of other ring systems are in progress.

Acknowledgment. Financial support of this work by the University of Nebraska-Lincoln and the National Institutes of Health (Grant GM34927) is gratefully acknowledged. High-resolution mass spectral analyses were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. 8620177).

(14) Tsuji, J.; Shimizu, I.; Minami, I. *Chem. Lett.* **1984**, 1017–9.

(15) The trans stereochemical assignment of the other vicinally substituted five-membered ring compounds was made by analogy to **4b** and is consistent with the close correlation of ^{13}C NMR ($CDCl_3$) chemical shifts observed for the two methine carbons (δ 48.0 ± 0.5 and 44.5 ± 0.5 ppm) in each cyclized product reported in Table I. In cases where the cis diastereomers could be detected by ^{13}C NMR, the corresponding methine carbon resonances were at approximately δ 44.9 ± 0.3 and 42.4 ± 0.3 ppm.

(16) (a) Beger, J.; Duschek, C.; Reichel, H. *J. Prakt. Chem.* **1973**, *315*, 1077. (b) Hata, G.; Takahashi, K.; Miyake, A. *J. Org. Chem.* **1971**, *36*, 2116.

(17) Preliminary molecular modeling studies of the postulated cis- and trans-fused bicyclic palladacyclic intermediates suggest that five-membered ring carbocyclizations leading to a trans diastereomer should be particularly facile. Modeling studies were performed using MODEL (v 2.93), PCMODEL (v 1.1), and Gilbert and Gajewski's MMXss minimization program. The metallcyclic intermediates were constructed starting from the crystal coordinates reported for the related palladacycle described in ref 4b. The atoms directly bonded to palladium were restricted to the crystal positions during all minimizations.

(18) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085.

High Stereoselectivity in the 1,2-Nucleophilic Additions to a Hindered 2-Alkylidenecyclohexanone: An Example of Predominant Axial Attack by Sterically Demanding Nucleophiles

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Summary: 1,2-Additions of various nucleophiles including sterically demanding carbanions have been shown to take place preferentially from an axial direction to a highly hindered 2-alkylidenecyclohexanone, thus providing an interesting example where the continuous orbital overlap between a newly forming bond and the C=C π-system appears to play a significaant role in controlling the stereochemical outcome in these 1,2-additions.

Sir: The stereochemistry of nucleophilic addition to cyclohexanones[1] and conjugated cyclohexenones has been the subject of increasing attention.[2] The enhanced axial selectivity for 1,2-addition to cyclohexenones over their corresponding saturated ketones is now amply documented for sterically undemanding[2] as well as moderately bulky nucleophiles.[2d,3] A number of theories have been advanced that attempt to rationalize the origin of this enhanced preference for axial addition.[4] The most recent computational model for the transition state by Wu, Houk, and Trost[4c] postulates the thesis that the torsional strain can be employed as the principal determinant to account for the observed selectivity. Here we report a remarkable

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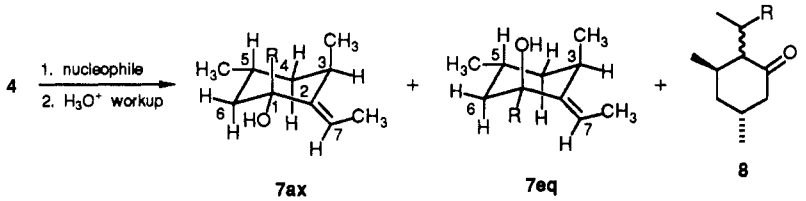
Table I. Addition Reactions of Various Nucleophiles onto Enone 4



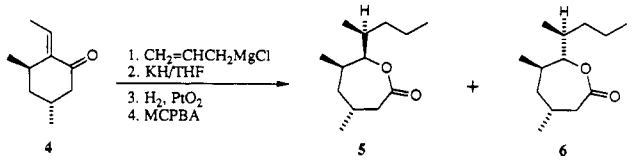
entry	nucleophile	R	7ax + 7eq, % yield	7ax/7eq	% yield of 8	recovered 4, %
1	$NaBH_4$, $CeCl_3$/MeOH	H	97	>100/1		
2	$LiAlH_4$/THF	H	96	80/1		
3	$NaBH_4$/MeOH	H	95	40/1		
4	DIBAL/THF	H	43	21/1	29	4
5	DIBAL/benzene or toluene	H	50	5/1	22	8
6	CH_2=$CHCH_2MgCl$/THF, −20 °C	allyl	95	>50/1		
7	PhLi/Ether, THF, cyclohexane, −20 °C	Ph	38	>37/1	28	13
8	MeLi/Ether, THF, −20 °C	Me	47	>25/1	14	25
9[a]	MeMgBr/THF, toluene, −20 °C	Me	21	>25/1	10	7
10	*n*-BuLi/hexanes, THF, −20 °C	*n*-Bu	16	5/1	44	22
11[a]	*i*-PrMgCl/ether, THF, −20 °C	*i*-Pr	0		<9	5

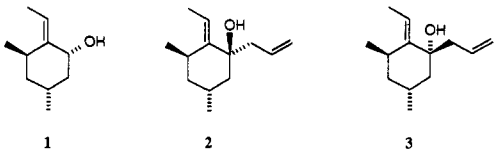
[a] The enolates generated by the 1,4-additions by the reagents reacted, upon aqueous workup, faster with air oxygen than water and considerable amounts of α-oxo hydroperoxides were isolated (e.g., 79% yield with *i*-PrMgCl) (details to be published separately).

example where preferential axial addition is observed by sterically demanding nucleophiles upon their 1,2-addition to a highly hindered 2-alkylidenecyclohexanone.

In connection with our study directed toward the synthesis of propionate-derived polymethylated natural products, access to allylic alcohols **1** and **2** was required. Reduction of exo-cyclic enone **4**[5] under Luche conditions[6] ($NaBH_4$, $CeCl_3$/MeOH, 0 °C) cleanly afforded the desired equatorial allylic alcohol **1** in 97% yield. It was originally envisioned that, in view of the presence of the quasi-axially oriented allylic methyl group, nucleophilic addition to the carbonyl carbon of the enone functionality in **4** would provide **2** through equatorial addition of the nucleophile from the opposite face of this methyl group, thus avoiding the severe 1,3-diaxial interaction between the methyl and the incoming nucleophile. Treatment of enone **4** with allylmagnesium chloride resulted in the highly stereoselective (>50:1) formation of the allyl adduct at the carbonyl carbon. The anionic oxy-Cope rearrangement of this adduct with KH,[7] followed by catalytic hydrogenation of the terminal olefin and Baeyer–Villiger oxidation, gave rise to two stereoisomeric lactones **5** and **6** in 31% and 26% overall yields, respectively, from **4** (Scheme I). Surprisingly, X-ray analysis[8] of these lactones revealed that the stereochemistry of the methyl-bearing side chain center is as shown in structures **5** and **6**, thus necessitating the assignment of the axial adduct structure **3** to the allyl 1,2-addition product of **4**. This unexpected observation prompted us to query if this strong propensity of the allyl Grignard for axial addition to the carbonyl carbon of enone **4** holds with other nucleophiles. The results summarized in Table I clearly point to the notion that highly hindered

Scheme I





(1) (a) Dauben, W. G.; Fonken, G. S.; Noyce, G. S. *J. Am. Chem. Soc.* **1956**, *78*, 2579. (b) Brown, H. C.; Deck, H. R. *Ibid.* **1956**, *78*, 5620. (c) Just, G.; Nagarajan, R. *Experientia* **1962**, *18*, 402. (d) Kamernitzky, A. V.; Akhrem, A. A. *Tetrahedron* **1962**, *18*, 705. (e) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701. (f) Cherest, M.; Felkin, H. *Tetrahedron Lett.* **1968**, 2205. (g) Cherest, M.; Felkin, H.; Prudent, N. *Ibid.* **1968**, 2199. (h) Klein, J.; Lichtemberg, D. *J. Org. Chem.* **1970**, *35*, 2654. (i) Lemmle, J.; Ashby, E. C.; Rolling, P. V. *Ibid.* **1973**, *38*, 2526. (j) Klein, J. *Tetrahedron Lett.* **1973**, 4307. (k) *Tetrahedron* **1974**, *30*, 3349. (l) Rei, M.-H. *Ibid.* **1979**, *44*, 2760. (m) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145. (n) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540. (o) Heathcock, C. H. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, p 177. (p) Wu, Y.-D.; Houk, K. N. *J. Am. Soc.* **1987**, *109*, 908.

(2) (a) Kienzle, F.; Mayer, M. *Helv. Chim. Acta* **1978**, *61*, 2609. (b) Stork, G.; Stryker, J. M. *Tetrahedron Lett.* **1983**, *24*, 4887. (c) Trost, B. M.; Florez, J.; Jebaratnam, D. J. *J. Am. Soc.* **1987**, *109*, 613. (d) Idrissi, M. E.; Santelli, M. *J. Org. Chem.* **1988**, *53*, 1010.

(3) Trost, B. M.; Florez, J.; Haller, K. J. *J. Org. Chem.* **1988**, *53*, 2396.

(4) (a) Toromanoff, E. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Interscience: New York, 1967; Vol. 2, p 157. (b) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 738. (c) Wu, Y.-D.; Houk, K. N.; Trost, B. M. *J. Am. Chem. Soc.* **1987**, *109*, 5560.

(5) Prepared from 5-methyl-2-cyclohexen-1-one in three steps (1. Me_2CuLi, 2. CH_3CHO, 3. H^+) in 60% overall yield. A small amount of the *Z* isomer of **4** (10%) was also obtained. Undoubtedly, the huge $A^{1,3}$-CH_3-CH_3 interaction makes the conformation drawn in Figure 1 to be the most stable conformer of **4** (see: Castello, A.; Jaime, C.; Marquet, J.; Moreno-Manas, C. *Tetrahedron* **1985**, *41*, 3791). For **4**: bp 60–63 °C (0.70 mmHg); ^1H NMR (360 MHz, $CDCl_3$) δ 1.005 (d, 3 H, *J* = 6.5 Hz, 5-CH_3), 1.042 (d, 3 H, *J* = 7.3 Hz, 3-CH_3), 1.526 (ddd, 1 H, *J* = 5.1, 12.3, 13.4 Hz, 4ax-H), 1.702 (dddd, 1 H, *J* = 2.1, 2.5, 3.1, 13.4 Hz, 4eq-H), 1.759 (d, 3 H, *J* = 7.3 Hz, 7-CH_3), 1.907 (dd, 1 H, *J* = 12.5, 16.6 Hz, 6ax-H), 2.183 (ddqdd, 1 H, *J* = 3.1, 4.3, 6.5, 12.3, 12.5 Hz, 5-H), 2.539 (ddd, 1 H, *J* = 2.5, 4.3, 16.6 Hz, 6eq-H), 3.124 (dddq, 1 H, *J* = 1.2, 2.1, 5.1, 7.3 Hz, 3-H), and 6.568 ppm (dq, 1 H, *J* = 1.2, 7.3 Hz, 7-H); ^{13}C NMR (90.56 MHz, $CDCl_3$) δ 13.15 (q, 7-CH_3), 20.46 (q), 22.30 (q), 25.32 (d, 5-C), 29.94 (d, 3-C), 39.31 (t, 4-C), 48.96 (t, 6-C), 132.91 (d, 7-C), 142.07 (s, 2-C), and 201.32 ppm (s, 1-C). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.72; H, 10.40.

(6) (a) Luche, J.-L.; R-Hahn, L.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601. (b) Gamal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

(7) Two stereoisomers produced upon KH treatment of the allyl adduct were readily separable and each of these was also subjected to the subsequent reaction conditions (steps 3 and 4 in Scheme I), providing pure lactone **5** or **6**.

(8) Performed by Dr. William M. Butler of this department, details to be published.

enone 4 has the structural characteristics that inherently favor axial 1,2-addition.

The stereochemistry of the 1,2-addition products of 4 was ascertained by 300-MHz ^{1}H NMR spectroscopy. Extensive proton–proton decoupling experiments unequivocally established the conformation of all 1,2-addition products as being in the chair from **7ax** or **7eq** where the 3-methyl group is disposed as quasi-axial. The stereochemistry at C-1 of the carbanion addition products was assigned on the basis of Eu(fod)$_3$-induced shift study of ^{1}H NMR spectra of **7ax** (R = CH_3 and Ph) and two *n*-butyl adducts **7ax** and **7eq** (R = *n*-Bu).[9] In each of ^{1}H NMR spectra of the major adducts **7ax** (R = *n*-Bu, CH_3, and Ph), a large lanthanide-induced shift (LIS) was observed for the vinylic 7-H and two hydrogens at C-6, whereas the extent of the shift of the olefinic proton was quite small in the ^{1}H NMR spectrum of the minor *n*-butyl adduct **7eq** (R = *n*-Bu). A large LIS of the latter was noted for the 5-H and 6eq-H. Interestingly, the ^{1}H NMR peak of the 3-CH_3 of the major phenyl adduct **7ax** (R = Ph) appears at δ 0.466 ppm (in $CDCl_3$), about 0.6 ppm high-field shifted as compared with the other axial adducts **7ax** (R = H, allyl, CH_3, and *n*-Bu), thus supporting the conformation where the methyl group juxtaposes on top of the phenyl ring.

Reduction of enone 4 with $NaBH_4$ or $LiAlH_4$ afforded exclusively allylic alcohol 1 through virtually complete axial 1,2-hydride addition (entries 1–3, Table I). In contrast, the use of the larger hydride reagent DIBAL for the same reduction resulted in the formation of substantial amounts of 1,4-hydride addition products (entries 4 and 5). It is of interest to note that the preference for the axial 1,2-hydride addition by the DIBAL was found to be more pronounced in THF than in benzene or toluene. This may be interpreted as a manifestation of the difference in the relative importance of the coordination of the DIBAL reagent with the enone oxygen of 4 versus the solvent molecule in two types of solvent system. The DIBAL reagent is likely to coordinate more tightly with the enone oxygen in benzene or toluene than in THF. This should result in decrease in the ratio of axial/equatorial 1,2-hydride addition products in the former solvent system compared with the latter.

Comparison of the results on the 1,2-addition of enone 4 by $NaBH_4$ with those of pulegone[6] is revealing. The preference for the 1,2-axial hydride addition of pulegone, 97/3 and 69/31 with $NaBH_4$, $CeCl_3$/MeOH, and $NaBH_4$/MeOH, respectively, is considerably lower than that observed with enone 4. The lower stereoselectivity observed for the 1,2-hydride addition of pulegone may be ascribable to its relatively flexible nature of the cyclohexanone ring system[10] (vide infra).

While the regio- and stereochemical selectivity for the 1,2-axial addition onto 4 by carbanions diminishes with increase in their steric bulk, considerable preference for axial approach among 1,2-adducts still holds even with sterically demanding nucleophiles (entries 6–10). Apparently, the isopropyl nucleophile was too bulky for otherwise favored 1,2-addition onto 4. Importantly, in cases where the 1,2-axial addition onto 4 is sterically costly, the 1,4-, rather than the alternate 1,2-equatorial, addition becomes competitive. The reaction of allylmagnesium chloride with enone 4 was exceptionally high-yielding and completely selective for 1,2-axial addition. It is of interest to note that Idrissi and Santelli[2d] reported that exclusive

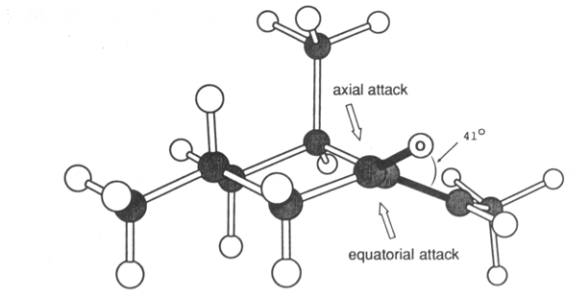


Figure 1.

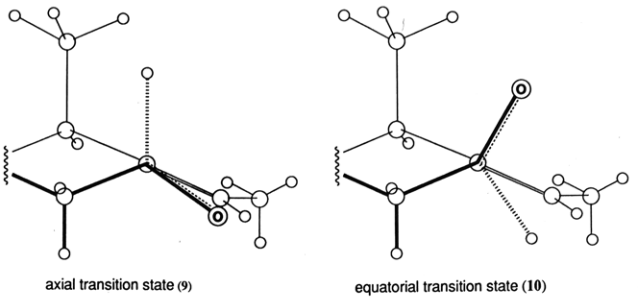


Figure 2.

1,2-axial addition of the allyl group of allylmagnesium chloride to pulegone involves bond formation between the terminal sp^2 carbon of the reagent and the carbonyl carbon of the enone through the "compact approach", which is stabilized by orbital interaction. Futhermore, it is generally believed that an allylmagnesium halide reacts through a six-membered transition state involving coordination of the magnesium to oxygen.[11] This type of "internal-like" delivery of the terminal carbon of the allyl group to the carbonyl carbon is likely to minimize some of the serious 1,3-diaxial interactions, thus further favoring the 1,2-axial addition of the allyl group.

Generally, 2-cyclohexenones have relatively flat ring conformations where the carbonyl and C=C functionalities lie on the same plane.[4c] Therefore, at the early stages of bond formation there is no significant difference in the extent of the orbital overlap of the newly forming bond at C-1 and the C=C π-orbitals between the axial and equatorial 1,2-additions by a nucleophile. As a result the facial selectivity for the 1,2-addition of nonsterically demanding nucleophiles to these enones is primarily controlled by the differernce in torsional strains between the two transition states.[4c] In contrast, 2-alkylidenecyclohexanone 4 adopts a quasi-chair ring conformation with the C=O and C=C groups considerably skewed. Molecular mechanics calculations (Macromodel) as well as its ^{1}H NMR analysis[5] indicate that enone 4 has the rigid chair conformation depicted in Figure 1 and the C=O and C=C units are skewed by 41°. Axial and equatorial attacks by a nucleophile on the carbonyl carbon of 4 should lead to the transition states **9** and **10**, respectively, or those that closely resemble them (Figure 2). While axial attack maintains significant overlap between the forming bond and the C=C π-orbitals in transition state **9**, similar overlap diminishes rapidly during equatorial attack, and in transition state **10** such an overlap is virtually nonexistent. If the pathway involving equatorial attack is to maintain this orbital overlap, the cyclohexane ring needs to be distorted considerably from the stable chair conformation.

(9) For details, see supplemental material.
(10) Singh, R. D.; Keiderling, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2387.
(11) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.

It should also be noted that equatorial attack on enone 4 suffers from the initial torsional strain due to the near-eclipsing arrangement of the newly forming bond and the axial C-H bond at C-6 and the strain due to the increasing eclipsing between the C=O bond and the equatorial C-H bond at C-6 as the reaction proceeds. Therefore, these torsional effects may be partially responsible for the high axial stereoselectivities observed. In conclusion, the observation delineated above with a highly hindered, conformationally rigid 2-alkylidenecyclohexanone and sterically demanding nucleophiles provides an interesting example where the orbital overlap between the forming bond and the C=C π-system appears to be, at least partially, a significant factor in contributing to the highly selective 1,2-axial additions by a various nucleophiles.

Acknowledgment. We are grateful to the National Institutes of Health (Grant DK-30025) for financial support of this work.

Supplementary Material Available: NMR (^{1}H and ^{13}C) spectroscopic and microanalytical data of **1**, **3**, **7ax** (R = Ph, Me, and *n*-Bu), and **7eq** (R = *n*-Bu) and the LIS data of **7ax** (R = *n*-Bu, Ph, and CH_3) and **7eq** (R = *n*-Bu) (5 pages). Ordering information is given on any current masthead page.

Propargyl and Allyl Grignard and Zinc Reagents. Regioselective Alkylation and Its Application to the Synthesis of PGE_3 and $F_{3\alpha}$ Methyl Ester

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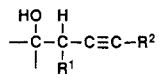
Received May 30, 1989

Summary: Regioselective propargylation and allylation were achieved using acylsilanes as electrophiles, and this methodology was applied to the synthesis of PGE_3 and $F_{3\alpha}$ methyl ester.

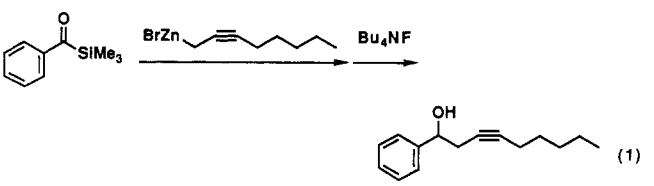
Sir: Methods which have been described previously from our laboratories[1] and others[2] permit the regiospecific synthesis of homopropargyl alcohols of type I, II, and IV from propargylorganometallics, but not of type III. Indeed, the regiocontrolled synthesis of III from the corresponding organometallics has remained an unsolved problem in organic synthesis. The structural features of III, on the other hand, are of great importance in many natural product syntheses. We shall describe a new approach to the synthesis of homopropargyl alcohol of type III which closes this methodological gap[3] using acylsilanes as the electrophiles.



I: $R^1 = R^2 = H$ III: $R^1 = H$; R^2 = Alkyl
II: R^1 = Alkyl; $R^2 = H$ IV: $R^1 = R^2$ = Alkyl

Treatment of the zinc reagent, derived from 2-octynyl bromide and zinc dust in THF, with benzoyltrimethylsilane[4] followed by desilylation afforded only the homopropargylic alcohol without contamination of any regioisomer (eq 1). With benzaldehyde, in contrast, a 35:65 mixture of acetylenic and allenic alcohol was obtained using the same zinc reagent.

The methodology described above was applied to the synthesis of PGs of the 3 series. The syntheses of PGE_3 and $PGF_{3\alpha}$ methyl esters were carried out by starting from



(1)

the readily available aldehyde **1**.[5] Treatment of **1** in THF with the *E* enolate prepared from [(trimethylsilyl)-acetyl]trimethylsilane[6] and lithium diisopropylamide, afforded the *E* α,β-unsaturated acylsilane **2** (68% yield). Acylsilane **2** was converted exclusively (α/γ = >99:1) to the desired $PGF_{3\alpha}$ derivative **3** in 92% yield by means of the zinc reagent derived from 2-pentynyl bromide and zinc dust in THF. Formylation of the C-15 hydroxyl group of **3** with acetic-formic anhydride and 4-(dimethylamino)-pyridine in dichloromethane gave **4**, further transformed into **5** by reaction with tetrabutylammonium fluoride in THF in 67% overall yield.[7] $PGF_{3\alpha}$ derivative **5** was converted to the PGE_3 derivative **8** by a three-step sequence:

(1) (a) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225. (b) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.

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