Regioselective Palladium-Catalyzed Alkylation of Allylic Halides with Benzylic Grignard Reagents. Two-Step Synthesis of Abietane Terpenes and Tetracyclic Polyprenoid Compounds

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A highly regioselective palladium-catalyzed α-alkylation of allylic bromides **1a**,**c**−**e** and chloride **1b** with substituted and unsubstituted benzylic Grignard reagents is reported. The resulting all-trans polyenehomobenzene derivatives were obtained in excellent yields and regioselectivity. These products were easily converted to abietane-type diterpenes (**10**−**12**) and tetracyclic polyprenoid compounds (**13**, **14**) through a Lewis acid-promoted cascade polyene cyclization reaction.

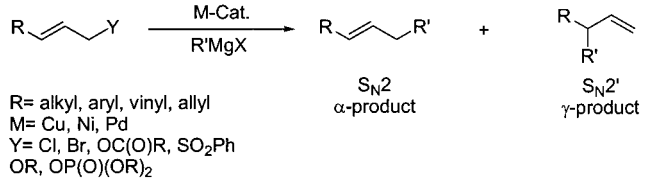
Introduction

Because of the frequently unsatisfactory success of carbon−carbon bond formation involving Grignard reagents as nucleophiles in substitution reactions, a major field of research has grown aiming at the "catalysis" of such reactions by the addition of transition metal complexes.[1] Among the transition metal complexes used for the regioselective alkylation of allylic compounds, copper reagents,[2] nickel,[3a−b] zinc,[3c] and palladium[4] complexes have proved to be the most effective.

During this transformation, the leaving group (Y, Scheme 1) can be displaced either in an α (S_N2) or γ (S_N2') fashion by the organometallic reagent (M-catalyst). The development of chiral catalysts for the asymmetric formation of the γ-product (S_N2' process) has emerged as an important branch of research endeavors.[5] On the other hand, the α-allylation (S_N2 process) has not received the same degree of attention presumably due to the lack of generality, difficulties in preparing the catalyst or generating the Grignard reagent, and scarce applications of the resulting products.

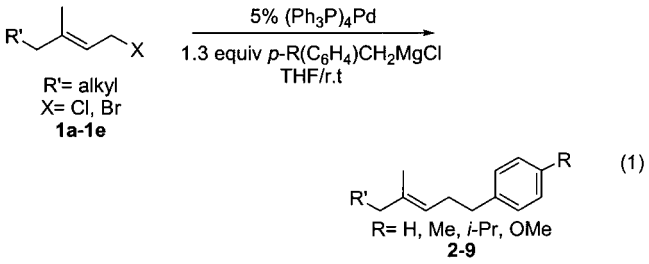
In the course of developing methodologies designed for the easy preparation of polycyclic compounds,[6] we wish to report a practical, scalable, and atom economical synthetic method for the regioselective α-allylation of a variety of benzylic Grignard reagents to generate polyenehomobenzene derivatives. Although these polyenehomobenzene products are important by themselves,[7] they were further converted to diterpenes and polyprenoid compounds by using the well precedented Lewis acid-catalyzed polyene cascade cyclization reaction.[8]

Scheme 1



Results and Discussion

A. Regioselective Alkylations. Allylic bromides were obtained from the corresponding allylic alcohols in good yields following a literature procedure.[9] The allylic alkylation of substrates **1a**−**e** (eq 1) was studied employing catalytic amounts (5 mol %) of a palladium catalyst



(1)

[$(Ph_3P)_4Pd$] in THF.[10] The reaction was first explored by using commercially available benzylmagnesium chloride

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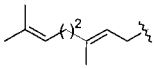
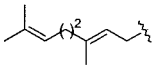
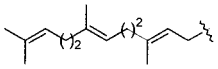
Table 1[a]

Entry	Substrate[b]	X	R[c]	R'	Product	Yield(%)[d]
1	**1a**	Br	H	H	**2**	78
2	**1b**	Cl	H		**3**	82
3	**1c**	Br	H		**3**	94 (60)[f]
4	**1c**	Br	Me		**4**	79
5	**1c**	Br	*i*-Pr		**5**	70
6	**1c**	Br	OMe		**6**	70 (40)[e]
7	**1d**	Br	H		**7**	49
8	**1d**	Br	Me		**8**	63
9	**1e**	Br	H		**9**	78

[a] Unless stated otherwise the reactions were carried out according to the procedure in the Experimental Section. [b] Substrates **1b**/**1c** were >95% (*E*)-; **1d** > 94% (*E*,*E*)-; and **1e** > 93% (*E*,*E*,*E*)-isomer. [c] For RH, Grignard reagents were prepared according to ref 16. [d] Isolated yield. [e] Reaction was run without Pd-catalyst: 20% of γ-product was obtained. [f] Reaction was run without Pd-catalyst: 25% of 1,2-diphenylethane and 10% of γ-product were obtained.

(1.1−1.3 equiv), which gave complete conversion usually within 1 h at room temperature, to afford the α-benzylated allylic compounds **2**, **3**, **7**, and **9** in excellent yields as major products (Table 1). The corresponding γ-benzylated products were observed only by GC analysis, which indicated the formation of these regioisomers in less than 5%. The corresponding (*Z*)-isomers were not detected. Unexpectedly, a more important side reaction was the formation of the homocoupling product diphenylethane. According to our GC analysis, this side reaction consumed about 10% of the Grignard reagent. To circumvent this problem, the amount of benzylmagnesium chloride was increased from 1.1 to 1.3 equiv.[11] The effect of the substituent on the substrate leaving group was also examined. It was found that geranyl chloride **1b** gave a lower yield of **3** (82%, Table 1, entry 2) than the corresponding bromide **1c** (94% yield, Table 1, entry 3). The allylic alkylation employing substituted benzylic Grignard reagents was also studied (Table 1, entries 4−6 and 8). However, the formation of these substituted benzylic Grignard reagents was not straightforward. As previously reported,[12] benzylic halides are considered almost unreactive for the synthesis of Grignard reagents, leading to low yields and/or incomplete conversion. Several synthetic methods to prepare benzylic Grignard reagents were employed. First, sonication of commercial unactivated magnesium turnings at room temperature showed no formation of reagent either in ether or THF solutions.[13] Second, magnesium anthracene provided a viable method to generate the desired benzylic Grignard reagents.[14] Disadvantageously, the enormous amount of anthracene formed in this procedure made the purification process of the resulting product extremely tedious and inefficient.[15] After these attempts, the indicated substituted benzylic Grignard reagents were successfully prepared by mechanical activation of commercial magnesium turnings according to a previous report.[16] As indicated in Table 1, dienes **4**, **5**, and **6** and triene **8** (entries 4, 5, 6, and 8, respectively) were prepared in yields of 63−79%.[17] Regioisomeric γ-products or (*Z*)-olefinic isomers were not detected by ^{1}H NMR analysis of the crude reaction mixtures. Again, the main impurity (<10%) was the corresponding homocoupled byproduct. Some of these reactions were scaled up to 20 g without affecting the yield or regioselectivity. The background reaction (reaction run without palladium catalyst) was also investigated (Table 1, entries 3 and 6).[18] As shown with these examples, the absence of palladium catalyst significantly lowered the product yields by 30−34% and the regioselectivity of these processes (γ-product: 10−20% yield).[19]

B. Application. Although cyclization via 2-(2-arylethyl)-1,3,3-trimethylcyclohexyl carbocations has been widely employed to construct the B-ring of podocarpa-8,11,13-triene diterpenoids,[20] there have been only a few reports on successive cyclizations of homogeranylbenzene derivatives to diterpenoid compounds.[21] There are even fewer reports on polyene cyclizations of homofarnesylbenzene to afford tetracyclic polyprenoids.[22] Herein, we report an important application of our α-benzylated allylic products for an overall two-step preparation of the known diterpenoids **10**,[23] **11**,[24] and **12**[25] (eq 2) and the first syntheses of the unnatural polyprenoids **13** and **14** (eq 3) through cationic polyene cyclization employing $SnCl_4$ (1 equiv, THF) as a Lewis acid.[26] The ^{13}C NMR data of **13** and **14** showed an almost perfect match with

(11) The excess amount of BnMgCl was optimized with substrate **1b**. The use of 1.1 equiv of BnMgCl gave a 70% yield of **3**. On the other hand, the use of 1.3 equiv of BnMgCl gave a 94% yield of **3**.

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(17) Magnesium activation was easily achieved by stirring the turnings for at least 4 days under an argon atmosphere. Freshly distilled THF was subsequently added followed by the commercially available substituted benzyl chloride.

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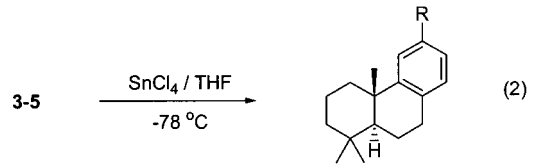
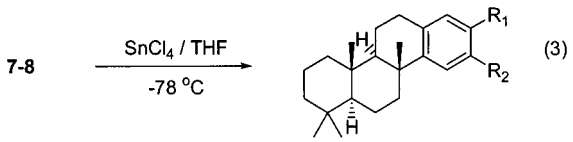
the data for the natural polyprenoid **15**,[27] hence concluding that minor substituent changes in the aromatic portion of the products do not influence the gross chemical shifts.



10 R= H (45%)
11 R=Me (35%)
12 R= *i*-Pr (30%)



13 R_1= H; R_2= H (15%)
14 R_1= H; R_2= Me (20%)
15 R_1= Me; R_2= H

Conclusions

In this report, we describe a practical, scalable, and atom economical regioselective allylation of substituted and unsubstituted benzylic Grignard reagents employing catalytic amounts of $[(Ph_3P)_4Pd]$ in THF at room temperature. The reaction can be performed in a multigram scale (up to 20 g) to obtain the desired α-benzylated substrates (polyenehomobenzenes) in excellent yields. The usefulness of this methodology has been illustrated by preparing podocarpa-type diterpenes as well as tetracyclic polyprenoid compounds via cationic cyclization, allowing ready access to these important products in two steps only from commercially available starting materials.

Experimental Section

General. All manipulations of compounds and solvents were carried out using standard airless techniques. All glassware was flame-dried and purged with argon prior to use. Tetrahydrofuran was distilled under sodium/benzophenone prior to use as a solvent. Melting points are uncorrected. Infrared Spectra (IR) were measured as KBr pellets. Spectroscopic measurements were recorded for $CDCl_3$ solutions with the following instruments: a DRX-500 (500 MHz for ^{1}H, 125.8 MHz for ^{13}C), an AM-400 (400 MHz for ^{1}H, 100.6 MHz for ^{13}C), or an ARX-250 (250 MHz for ^{1}H, 62.9 MHz for ^{13}C). Chemical shifts are reported in δ units (parts per million) assigning the residual $CHCl_3$ resonance in ^{1}H spectra at 7.24 ppm and $CDCl_3$ resonance in ^{13}C spectra at 77.0 ppm. All coupling constants, J, are reported in Hertz. High-resolution mass spectrometry (HRMS) was recorded at 70 eV ionization energy. Column chromatography was performed on a silica gel 60 (0.063−0.20 or 0.04−0.063 mm). All reactions were monitored by TLC on silica gel 60 F_{254} precoated aluminum plates and were developed with UV light followed by spraying with acidic vanillin solution. High-performance liquid chromatography (HPLC) was performed on a gradient system coupled with a differential refractometer and a computer system (column: 7-C-18, 250 × 21 mm, 100% methanol). Elemental analysis was done in Mülheim an der Ruhr.

General Procedure for Palladium-Catalyzed Alkylation with Grignard Reagents. Palladium catalyst $[(Ph_3P)_4Pd]$ (0.7 mmol, 5 mol %) was dissolved in THF (10 mL) at room temperature under an argon atmosphere. The allylic halide (0.014 mol) was then added via syringe. The initially yellow mixture gradually became clear within 5 min. The reaction mixture was cooled to 0 °C, and the Grignard reagent (0.018 mol) was then added via syringe. The reaction was stirred at room temperature until judged to be complete according to TLC. The reaction was quenched by addition of water (10 mL). The organic phase was collected, and the water phase was extracted with ether (2 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The resulting crude products were purified by column chromatography. In most cases, a simple filtration through silica gel (washing with pentane) was enough to obtain the product with >95% purity.

Spectral data for 4-methyl-1-phenyl-3-pentene (**2**),[28] (3*E*)-4,8-dimethyl-1-phenyl-3,7-nonadiene (**3**),[29] and (3*E*)-4,8-dimethyl-1-(4-methoxyphenyl)-3,7-nonadiene (**6**)[30] were consistent with data reported in the literature.

(3*E*)-4,8-Dimethyl-1-(4-methylphenyl)-3,7-nonadiene (4). Isolated as a colorless oil. IR (KBr): 2966, 1515 cm^{-1}. ^{1}H NMR: δ 7.08 (s, 4H), 5.19 (t, J = 5.9 Hz, 1H), 5.09 (t, J = 5.3 Hz, 1H), 2.60 (dd, J = 15.7, 7.5 Hz, 2H), 2.31 (s, 3H), 2.30−2.26 (m, 2H), 2.07−2.04 (m, 2H), 1.99−1.97 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.57 (s, 3H). ^{13}C NMR: δ 139.4, 135.6, 135.0, 131.3, 128.9, 128.3, 124.4, 123.8, 39.7, 35.7, 30.1, 26.7, 25.7, 20.9, 17.7, 15.9. HRMS (EI) *m/z*: calcd for $C_{18}H_{26}$, 243.2113; found, 243.2112. Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.08; H, 10.90.

(3*E*)-4,8-Dimethyl-1-(4-isopropylphenyl)-3,7-nonadiene (5). Isolated as a colorless oil. IR (KBr): 2925, 1514 cm^{-1}. ^{1}H NMR: δ 7.19 (d, J = 1.6 Hz, 4H), 5.27 (dt, J = 7.1, 1.0 Hz, 1H), 5.17 (tt, J = 6.7, 1.3 Hz, 1H), 2.94 (sep, J = 6.9 Hz, 1H), 2.68 (m, 2H), 2.37 (ddd, J = 7.9, 7.5, 7.3 Hz, 2H), 2.11 (m, 4H), 1.76 (s, 3H), 1.68 (s, 3H), 1.64 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H). ^{13}C NMR: δ 146.1, 139.7, 135.5, 131.2, 128.3, 126.2, 124.4, 123.8, 39.7, 35.7, 33.7, 29.9, 26.7, 25.7, 24.1, 17.6, 15.9. HRMS (EI) *m/z*: calcd for $C_{20}H_{30}$, 270.2347; found, 270.2346. Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.73; H, 10.81.

(3*E*,7*E*)-4,8,12-Trimethyl-1-phenyl-3,7,11-tridecatriene (7). Isolated as a colorless oil. IR (KBr): 2966, 1496 cm^{-1}. ^{1}H NMR: δ 7.28−7.24 (m, 2H), 7.18−7.16 (m, 3H), 5.17 (dt, J = 0.9, 7.0 Hz, 1H), 5.11−5.08 (m, 2H), 2.63 (dd, J = 15.7, 7.4 Hz, 2H), 2.32−2.26 (m, 2H), 2.07−2.03 (m, 4H), 1.99−1.96 (m, 4H), 1.67 (s, 3H), 1.59 (s, 6H), 1.55 (s, 3H). ^{13}C NMR: δ 142.4, 135.8, 134.9, 131.2, 128.4, 128.2, 125.6, 124.4, 124.2, 123.6, 39.7, 39.7, 36.1, 29.9, 26.8, 26.6, 25.7, 17.7, 15.9, 15.9. HRMS (EI) *m/z*: calcd for $C_{22}H_{32}$, 297.2582; found, 297.2583. Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.84; H, 10.79.

(3*E*,7*E*)-4,8,12-Trimethyl-1-(4-methylphenyl)-3,7,11-tridecatriene (8). Isolated as a colorless oil. IR (KBr): 2966, 1515 cm^{-1}. ^{1}H NMR: δ 7.07 (s, 4H), 5.17 (t, J = 7.0 Hz, 1H), 5.11−5.07 (m, 2H), 2.58 (dd, J = 15.8, 7.5 Hz, 2H), 2.31 (s, 3H), 2.30−2.28 (m, 2H), 2.06−1.96 (m, 8H), 1.67 (s, 3H), 1.59 (s, 6H), 1.55 (s, 3H). ^{13}C NMR: δ 139.3, 135.6, 135.0, 134.9, 131.2, 128.9, 128.9, 128.3, 124.4, 124.2, 123.7, 39.7, 39.7, 35.7, 30.1, 26.8, 26.6, 25.7, 20.9, 17.7, 16.0. HRMS (EI) *m/z*: calcd for $C_{23}H_{34}$ 310.2661, found 310.2660. Anal. Calcd for $C_{23}H_{34}$: C, 88.96; H, 11.04. Found: C, 89.10; H, 10.95.

(3*E*,7*E*,11*E*)-4,8,12,16-Tetramethyl-1-phenyl-3,7,11,15-heptadecatetraene (9). Isolated as a colorless oil after

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purification by HPLC. IR (KBr): 2925, 1452, 1376 cm^{-1}. ^1H NMR: δ 7.27−7.24 (m, 2H), 7.18−7.16 (m, 3H), 5.17 (dd, J = 1.4, 7.3 Hz, 1H), 5.12−5.07 (m, 3H), 2.62 (dd, J = 7.3, 15.6 Hz, 2H), 2.31−2.27 (m, 2H), 2.07−2.03 (m, 6H), 1.98−1.95 (m, 6H), 1.67 (s, 3H), 1.59 (s, 9H), 1.54 (s, 3H). ^{13}C NMR: δ 142.4, 135.8, 134.9, 134.9, 131.2, 128.4, 128.2, 125.6, 124.4, 124.3, 124.2, 123.6, 39.7 (2C), 36.1, 29.9, 29.7, 26.8, 26.7, 26.6, 25.7, 17.7, 16.0, 15.9 (2C). HRMS (EI) *m*/*z*: calcd for $C_{27}H_{40}$, 364.3130; found, 364.3130. Anal. Calcd for $C_{27}H_{40}$: C, 88.94; H, 11.06. Found: C, 88.76; H, 11.01.

1,1,4a,10b-Tetramethyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydrochrysene (13). Isolated as a waxy solid. Mp: 75−77 °C. IR (KBr): 2925, 2865, 1454 cm^{-1}. ^1H NMR: δ 7.25 (dd, J = 2.8, 7.8 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.06−7.01 (m, 2H), 2.92 (dd, J = 16.9, 6.4 Hz, 1H), 2.86−2.79 (m, 1H), 2.38 (dd, J = 9.6, 3.2 Hz, 1H), 1.87−1.80 (m, 2H), 1.73−1.39 (m, 8H), 1.29−1.12 (m, 3H), 1.21 (s, 3H), 0.94 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H). ^{13}C NMR: δ 150.4, 135.1, 128.7, 125.6, 125.1, 124.5, 56.3, 55.2, 42.1, 40.6, 39.9, 38.2, 37.7, 33.3, 33.3, 30.8, 26.1, 21.5, 19.1, 18.6, 17.9, 16.3. HRMS (EI) *m*/*z*: calcd for $C_{22}H_{32}$, 296.2504; found, 296.2505. Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 89.20; H, 10.96.

1,1,4a,9,10b-Pentamethyl-1,2,3,4,4a,4b,5,6,10b,11,12,-12a-dodecahydrochrysene (14). Mp: 96−98 °C. IR (KBr): 2925, 1488. ^1H NMR: δ 7.05 (s, 1H), 6.92−6.87 (m, 2H), 2.88 (dd, J = 5.9, 17 Hz, 1H), 2.81−2.77 (m, 1H), 2.39 (dd, J = 2.9, 9.2 Hz, 1H), 2.29 (s, 3H), 1.83−1.79 (m, 2H), 1.71−1.37 (m, 8H), 1.28−1.15 (m, 3H), 1.19 (s, 3H), 0.93 (s, 3H), 0.87 (s, 3H), 0.86 (s, 3H). ^{13}C NMR: δ 150.3, 134.8, 131.9, 128.7, 125.9, 125.1, 56.3, 55.3, 42.1, 40.7, 39.9, 38.1, 37.7, 33.32, 33.29, 30.5, 26.1, 21.5, 21.3, 19.1, 18.6, 18.0, 16.3. HRMS (EI) *m*/*z*: calcd for $C_{23}H_{34}$, 310.2660; found, 310.2659. Anal. Calcd for $C_{23}H_{34}$: C, 88.96; H, 11.04. Found: C, 89.11; H, 11.14.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **2**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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