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Reactivity of (3-chloro-2-methylenecycloalkyl)palladium chloride dimers: coupling with phenyl nucleophiles

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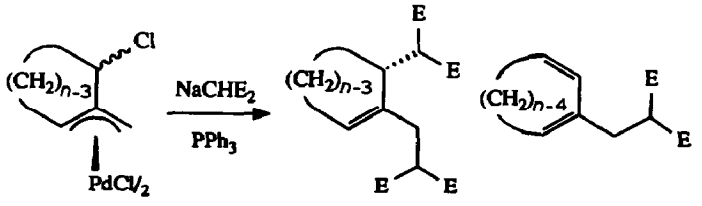
Abstract

Reaction of the (3-chloro-2-methylenecycloalkyl)palladium complexes (**1**) with sodium tetraphenylborate proceeds via coupling at either the exocyclic or endocyclic terminus to afford phenyl substituted π-allyl complexes **5** and/or **11**. The regioselectivity of this coupling reaction is somewhat dependent on ring size. The new π-allyl complexes **5/11** can further undergo cleavage reaction or nucleophilic addition.

The alkylation of stabilized carbon nucleophilies with π-allyl Pd complexes is well known [1]. While perhaps less common, the reaction of π-allyl Pd complexes with "unstabilized" nucleophiles has also been reported [2]. A number of researchers have demonstrated that the latter reaction proceeds via attack at palladium followed by reductive elimination [3]. We have investigated the reaction of (3-chloro-2-methylenecycloalkyl)palladium complexes, **1**, [4**] with either two or one equivalents of stabilized carbon nucleophiles, to give products **2** and/or **3** [5]. We herein report on the reaction of complexes **1** with phenyl nucleophiles.



(1) E = CO_2R *(2)* and/or *(3)*

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** Reference number with asterisk indicates a note in the list of references.

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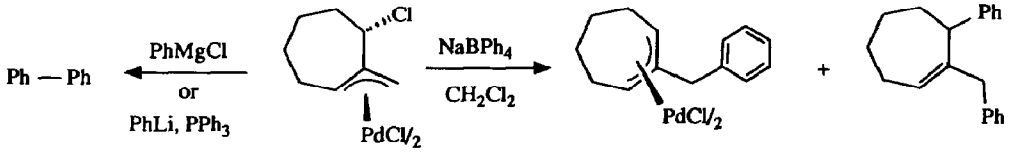
Results and discussion

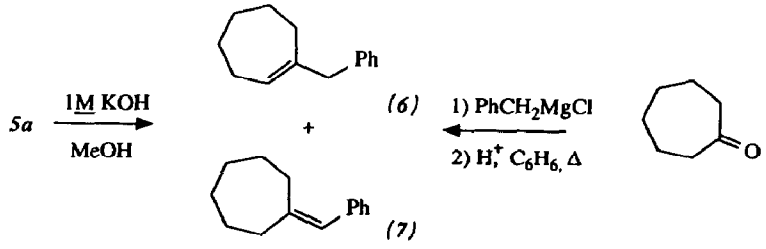
The reaction of **1a** with phenyllithium (7 equiv.) in the presence of triphenylphosphine [2a], or phenylmagnesium chloride (10 equiv.) [2b] gave biphenyl as the only isolable product, as identified by mp, ^{1}H NMR, and mass spectrometry. In contrast, the reaction of **1a** with sodium tetraphenylborate (2 equiv.) [2c] in CH_2Cl_2 at room temperature gave 1-benzyl-7-phenylcycloheptene (**4**) and biphenyl along with a new π-allyl Pd complex **5a** (39%). The yield of this new π-allyl complex is dependent upon the amount of $NaBPh_4$ used; some unreacted **1a** is recovered when 1 equiv. $NaBPh_4$ is used, while the optimum yield of **5a** (68%) is obtained when 1.5 equiv. of $NaBPh_4$ is used. It should be noted that addition of PPh_3 to the reaction mixture results in a slower rate of reaction.



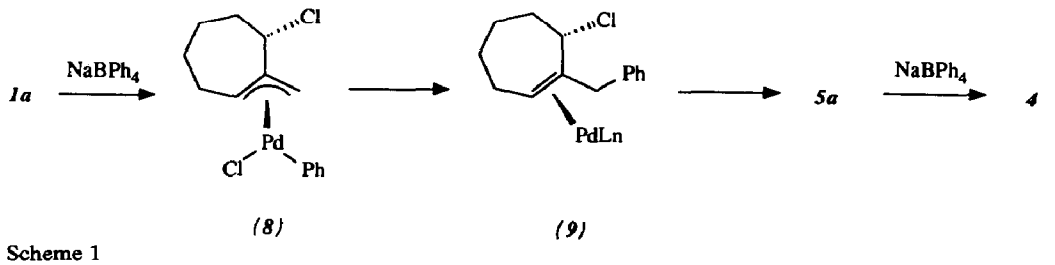
(1a) *(5a)* *(4)*

+ Ph—Ph

The structural assignment for **5a** is based upon its NMR spectral data. The ^{1}H NMR spectrum exhibits a single broad signal at δ 4.70 ppm corresponding to the terminal allylic protons [6]. In addition, the ^{13}C NMR spectrum contains signals at δ 117.2 and 83.1 ppm indicating the presence of a symmetrical cyclic π-allyl complex [7]. Because the compound **5a** is symmetrical, the ^{13}C NMR spectrum exhibits only three other non-aromatic carbon signals (δ 46.3, 33.4, 26.8). The structure of **5a** is further indicated by cleavage of the ligand in methanolic potassium hydroxide. The cleavage of Pd-allyl complexes is known to give a mixture of olefins [8]. Treatment of compound **5a** in methanolic KOH gave 1-benzylcycloheptene (**6**) and benzylidenecycloheptane (**7**). Olefins **6** and **7** were identified by comparison with the literature data [9] and by independent synthesis.



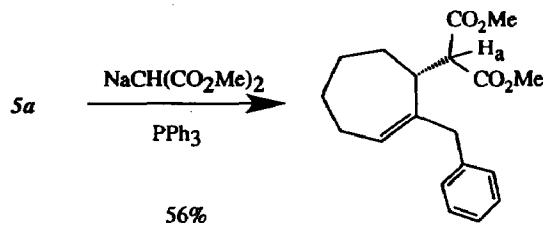
The reaction of compound **5a** with $NaBPh_4$ gave a mixture of **4** and biphenyl. We propose the following mechanism to explain the experimental results (Scheme 1). Reaction of $NaBPh_4$ with **1a** proceeds via transmetallation to yield a phenyl-Pd-allyl species **8**. *Cis*-reductive elimination affords a Pd^0 olefin complex **9** [10*]. Oxidative addition of the allylic halide gives the new π-allyl **5a**. Further reaction of **5a** with $NaBPh_4$ gives the product **4**. We have proposed the intermediacy of a



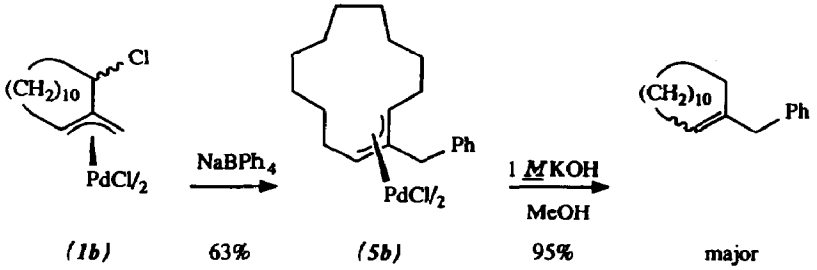
Scheme 1

π-allyl similar to **5a** in the reaction of **1a** with two equivalents of malonate anion in the presence of PPh_3, however unequivocal proof for the involvement of such a new π-allyl complex could not be obtained [5]. Thus isolation of **5a** provides substantial new evidence for our proposal that the reaction of **1a** with two equivalents of nucleophile proceeds via an intermediate of this type.

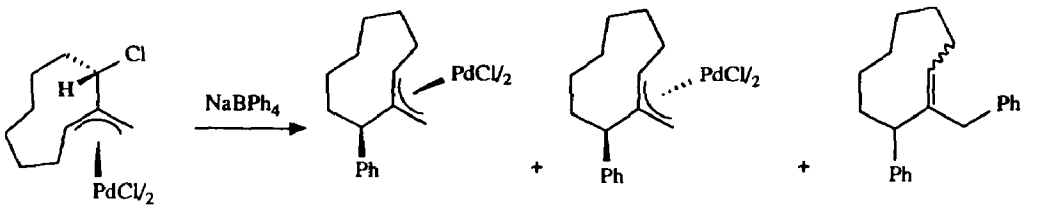
The reaction of **5a** with sodio dimethylmalonate in the presence of PPh_3 gave **10**. The structural assignment for **10** is based upon its spectral data. The signal for H_a appears as a doublet at δ 4.06 ($J = 12$ Hz) clearly indicating that the malonate functionality is attached to a methine carbon. A single olefinic signal (δ 5.63, t) and the appearance of the methyl esters as two distinct singlets (δ 3.63, 3.60) suggests the presence of a cyclic olefin containing a single asymmetric center. We have previously indicated that complexes **1** may act as a "trimethylenemethane dication" synthon [5]. The successful preparation of **10** indicates that it is possible to deliver two uniquely different nucleophiles to the two different electrophilic sites of this synthon in a controlled fashion.



The reaction of (3-chloro-2-methylenecyclotridecyl)palladium chloride dimer (**1b**) [4] with $NaBPh_4$ gave the π-allyl complex **5b**. The structural assignment for **5b** as the *syn,anti*-isomer is based upon its NMR spectra data. In comparison to **5a**, the ^1H NMR spectrum of **5b** contains two terminal allylic proton signals (δ 4.28 and 3.95), and the ^{13}C NMR spectrum of **5b** contains three allylic carbon signals (δ 121.7, 80.7, 78.8). This evidence clearly indicates a non-symmetrical structure. The cleavage of **5b** gives predominantly 1-benzylcyclotridecene.

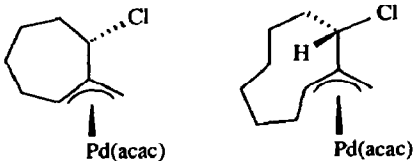


The reaction of **1c** with $NaBPh_4$ gave a mixture of π-allyl complexes **11a** and **11b** (ca. 2:1) in poor yield. Attempts to improve the yield of **11a,b** by varying the solvent, reaction time and equivalents of $NaBPh_4$ were unsuccessful. The major product in these reactions is a mixture of 1-benzyl-9-phenylcyclononene and biphenyl. The structural assignments for **11a** and **11b** are based upon comparison of their NMR spectral data with those obtained for **1c** and its isomer [4].



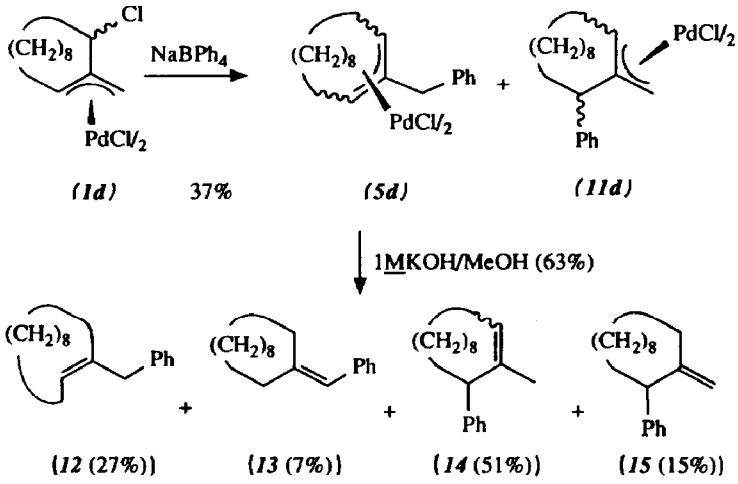
(1c) *(11a)* *(11b)* + Ph—Ph

The reductive elimination of the π-allyl-σ-aryl complex is believed to occur in a *cis* fashion [11], thus the regioselectivity of coupling of "hard" nucleophiles with π-allyl palladium complexes depends upon the coordination of the aryl substitutent relative to the π-allyl. Since a σ-aryl ligand has a greater trans influence than μ-Cl [12], the phenyl group should be preferentially coordinated *trans* to the Pd-allyl terminus with the longer Pd–C bond length (ie. *cis* to the shorter Pd–C bond). While care should be exercised in the extrapolation of crystal structure data to the solution phase, one possible explanation for the different regioselectivity observed for the coupling of **1a** and **1c** with $NaBPh_4$ might be the difference in bonding observed in the X-ray structures for their acetylacetonato derivatives [13]. For compound **A** the bond distance from Pd to the unsubstituted allylic terminus is shorter than the distance from Pd to the substituted allylic terminus ($\Delta r = 0.037$ Å). In contrast, for structure **C** the distance from the substituted allylic terminus to Pd is shorter than the distance from the unsubstituted allylic terminus to Pd ($\Delta r = 0.030$ Å).



(A) *(C)*

The reaction of (3-chloro-2-methylenecycloundecyl)palladium chloride dimer (**1d**) with $NaBPh_4$ gave a complex mixture of π-allyl complexes. The ^1H and ^{13}C NMR spectra of this inseparable mixture could not be interpreted unambigously. However, cleavage of this mixture of π-allyls gave a mixture of five $C_{18}H_{26}$ isomers. Two of these isomers could be identified as *trans*-1-benzylcycloundecene (**12b**, 27%) and benzylidenecycloundecane (**13**, 7%) by GC coinjection with authentic samples prepared by independent synthesis. The remaining three components most likely



correspond to *cis*- and *trans*-1-methyl-11-phenylcycloundecene and 1-methylene-2-phenylcycloundecane (**14** and **15**; 51% and 15% respectively). Notably the MS fragmentation patterns of *cis*- and *trans*-**14** are nearly identical. Compounds **12b** and **13** may arise from the π-allyl **5d**, while **14** and **15** must arise from cleavage of the π-allyl **11d**.

In summary, the reagent $NaBPh_4$ is air stable, easily handled and readily available, and serves as a complementary reagent to phenyl lithium and phenyl Grignards for coupling with π-allyl palladium complexes. In comparison to stabilized carbon nucleophiles, the reaction of $NaBPh_4$ with compound **1** may be stopped at the intermediate π-allyl complex.

Experimental section

General data. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. Spectrograde solvents were used without further purification with the exception of diethylether and tetrahydrofuran which were distilled from the sodium and potassium benzophenone ketals, DMSO which was refluxed over CaH_2 before distillation, and methylenechloride which was distilled from phosphorus pentoxide. The π-allyl Pd complexes **1a**,**1b**,**1c** and **1d** were prepared by literature procedures [4]. Sodium tetraphenylborate was purchased from Aldrich Chemical Co., Milwaukee, WI, and used without further purification.

(2-Benzylcycloheptenyl)palladium chloride dimer (5a). To a solution of (3-chloro-2-methylenecycloheptyl)palladium chloride dimer (**1a**, 0.35 g, 1.22 mmol) in CH_2Cl_2 (40 ml) was added solid sodium tetraphenylborate (0.63g, 1.83 mmol) under N_2 at 0 °C. The reaction mixture changed to goldyellow after 10 min, and to black after 4 h. The solvent was evaporated and the residue was chromatographed over SiO_2 (60–200 mesh). Elution first with hexanes (200 ml) gave a fraction containing biphenyl (identified by MS) and 1-benzyl-7-phenylcycloheptene (**4**) (1 : 1, 0.11 g): 60 MHz ^1H NMR ($CDCl_3$, partial) δ 5.77 (t, $J = 6$, 1H), 3.46 (t, $J = 5$, 1H), 3.17 (br s, 2H), 2.4–1.3 (m, 8H); GC/MS: 262 (M^+, 57), 171 (46), 129 (61), 91 (100). Further elution with chloroform gave a yellow fraction which upon evaporation gave **5a** as a

yellow solid: mp 52–56 °C; 0.27 g (68%); 60 MHz ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 4.70 (br s, $\frac{1}{2}W = 7$, 2H), 3.36 (s, 2H), 2.4–1.2 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 139.2, 128.6, 128.4, 126.6, 117.2, 83.1, 46.3, 33.4, 26.8; Anal. Found: C, 51.44; H, 5.26. $[C_{14}H_{17}PdCl]_2$ calcd.: C, 51.40; H, 5.24%.

Cleavage of ***5a.*** To (2-benzylcycloheptenyl)palladium chloride dimer (0.11 g, 0.34 mmol) was added a freshly prepared 1 *M* methanolic potassium hydroxide solution (50 ml). The solution was stirred at room temperature for 1 h, and then stirred at 50 °C for 20 h. After cooling, the reaction mixture was filtered into water (100 ml). The cloudy aqueous solution was extracted with CH_2Cl_2 (2 × 30 ml) and the combined organic extracts were dried ($MgSO_4$), and the solvent was carefully evaporated. The residue was distilled to afford a colorless liquid: 40 °C/0.8 mmHg, 0.03 g (48%). This was identified by ^{1}H NMR and GC/MS as a mixture of **6** and **7** (5.6 : 1).

1-Benzylcycloheptene ***(6)*** *and benzilidenecycloheptene* ***(7)*** were prepared by the literature procedure [8] from the reaction of benzyl Grignard and cycloheptanone followed by dehydration: bp 62–70 °C/0.35 mmHg: GC/MS indicated this to be a mixture of **6** and **7** (4.7 : 1). 60 MHz ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 5H), 6.23 (s, **7**), 5.63 (t, $J = 7$, **6**), 3.27 (s, **6**), 2.6–1.1 (m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, **6**) δ 143.5, 140.4, 129.1, 128.2, 127.2, 125.9, 46.6, 32.6, 32.5, 28.5, 27.4, 26.9; GC/MS: (**6**) 186 (M^+, 62), 129 (34), 104 (39), 95 (100), 91 (72), 67 (43); (**7**) 186 (M^+, 64), 129 (58), 115 (59), 104 (100), 95 (61), 91 (58), 67 (30).

Reaction of ***5a*** *with* $NaBPh_4$. To a solution of **5a** (0.08 g, 0.24 mmol) in CH_2Cl_2 (30 ml) was added solid $NaBPh_4$ (0.13 g, 0.38 mmol) under N_2 at 0 °C. The reaction was stirred for 48 h, the solvent was evaporated and the residue was chromatographed over SiO_2 (60–200 mesh). Elution with hexanes (200 ml) gave a fraction containing biphenyl and 1-benzyl-7-phenylcycloheptene (**4**) (1 : 1, 0.07 g).

Dimethyl (1-benzyl-1-cyclohepten-7-yl)propanedioate ***(10).*** To a solution of (2-benzylcycloheptenyl)palladium chloride dimer (0.22g, 0.67 mmol) and triphenylphosphine (0.68 g, 2.6 mmol) in THF (15 ml) was added, in one portion, a freshly prepared solution of sodio dimethylmalonate (1.01 mmol) in THF (15 ml) at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature overnight. The solvent was evaporated and the residue was extracted with ether (3 × 30 ml) via a cannula under N_2. The combined extracts were dried ($MgSO_4$) and the solvent evaporated. The residue was purified by flash column chromatography [13], using ethyl acetate/hexanes (1 : 10) as eluant, to afford **10** as a colorless oil: 0.12 g (56%); IR (CH_2Cl_2, cm^{-1}) 1740s; 60 MHz ^{1}H NMR ($CDCl_3$) δ 7.20 (s, 5H), 5.63 (br t, $J = 6$, 1H), 4.06 (d, $J = 12$, 1H), 3.63, 3.60 (two s, 6H), 3.30 (s, 2H), 3.1–1.0 (m, 9H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 169.0, 143.2, 139.8, 130.4, 129.4, 128.2, 126.0, 52.4, 52.0, 46.4, 42.0, 29.0, 27.5, 27.2, 26.3; GC/MS: *m/z* 316 (M^+, 7), 252 (63), 224 (18), 185 (19), 184 (78), 141 (45), 93 (50), 91 (100); HRMS, *m/z* 316.1676 [calcd for $C_{19}H_{24}O_4$, *m/z* 316.1674]. This compound was determined to be > 95% pure by GC analysis.

(2-Benzylcyclotridecenyl)palladium chloride dimer ***(5b)*** was prepared from the reaction **1b** with $NaBPh_4$ in fashion similar to the preparation of **5a**. The product was purified by column chromatography (elution with hexanes followed by C_6H_6 : $CHCl_3$, 1 : 1) to afford **5b** as a yellow solid: 0.28g (63%); mp 77–79 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m, 5H), 4.28 (m, 1H), 3.95 (m, 1H), 3.69 (s, 2H), 2.22 (m, 2H), 1.95 (m, 2H), 1.9–1.0 (m, 16H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.2,

129.7, 128.5, 128.3, 127.1, 126.9, 121.7, 80.7, 78.8, 38.5, 29.8, 28.6, 27.6, 27.2, 25.5, 24.2, 23.4; Anal. Found: C, 61.63; H, 7.29. $[C_{20}H_{29}PdCl]_2 \cdot C_6H_6$ calcd: C, 61.34; H, 7.16%.

Cleavage of ***5b.*** Reaction of **5b** with 1 *M* KOH/MeOH in a fashion similar to the cleavage of **5a** gave a colorless oil which appeared to be predominantly 1-benzylcyclotridecene: 0.05 g (95%); 60 MHz ^{1}H NMR ($CDCl_3$) δ 7.17 (br s), 5.30 (br t, $J = 7$), 3.36 (s), 2.3–1.0 (m); GC/MS: (major isomer) 270 (M^+, 43), 179 (12), 132 (56), 129 (46), 117 (47), 97 (78), 91 (100), 83 (56), 55 (66).

(2-methylene-3-phenylcyclononyl)palladium chloride dimer ***(11a, 11b)*** was prepared from the reaction of **1c** with $NaBPh_4$ in a fashion similar to the preparation of **5a**. The temperature was maintained at 0–4° C. Elution first with hexanes (200 ml) gave a fraction containing biphenyl (identified by MS) and 1-benzyl-9-phenylcyclononene (1 : 1), 0.21 g: 60 MHz ^{1}H NMR ($CDCl_3$, partial) δ 5.27 (t, $J = 8$, 1H0, 4.1 (m, 1H), 2.97 (br s, 2H), 2.4–1.3 (m, 12H); GC/MS: 290 (M^+, 26), 199 (16), 193 (20), 129 (34), 91 (100). Further elution with chloroform gave a yellow fraction which upon evaporation gave **11a** and **11b** (ca. 2 : 1) as a yellow solid: 0.05g (16%); mp 62–96° C (dec.); 300 MHz ^{1}H NR ($CDCl_3$, partial) **11a**: δ 4.50 (m, H_1), 3.19 (s, H_{anti}), 2.98 (s, H_{anti}), 2.7–2.5 (m); **11b**: δ 4.27 (m, H_1), 3.38 (s, H_{syn}), 3.28 (s, H_{anti}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial) δ 80.4 (C_1), 56.2, 52.8 (methylene C's); Anal. Found: C, 52.28; H, 5.87. $[C_{16}H_{21}PdCl]_2 : 1/2CHCl_3$ calcd: C, 52.33; H, 5.75%.

Reaction of ***1d*** *with* $NaBPh_4$. The reaction of (3-chloro-2-methylenecycloundecyl)palladium chloride with $NaBPh_4$ was carried out in a fashion similar to the preparation of **5a**. The product was isolated, after column chromatography, as a yellow solid: 0.10 g (37%). Analysis by ^{1}H and ^{13}C NMR spectroscopy indicated this to be a mixture of π-allyl complexes, probably **5d** and **11d**: ^{1}H NMR ($CDCl_3$, partial) δ 3.60 (br s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial) δ 120.6, 115.2, 83.6, 82.2.

Cis- *and* trans-*1-Benzylcycloundecene* ***(12a,b)*** *and benzylidenecycloundecane* ***(13)*** were prepared from the reaction of benzyl magnesium chloride with cycloundecanone followed by dehydration, in a fashion similar to the preparation of benzylcycloheptene. The crude product was purified by flash chromatography [13] with hexanes : ethyl acetate (60 : 1) as eluent. Evaporation of the solvent from the product fractions gave a colorless liquid: 0.74 g (60%). Analysis by GC revealed this to be a mixture of three isomers in ratio of 7.8 : 4.5 : 1. GC/MS: (**12a**) *m/z* 242 (M^+, 23), 151 (24), 132 (54), 129 (44), 117 (52), 95 (94), 91 (100), 55 (44); (**12b**) *m/z* 242 (M^+, 24), 151 (30), 132 (57), 129 (39), 117 (57), 95 (100), 91 (98), 55 (43); (**13**) *m/z* 242 (M^+, 74), 129 (100), 117 (52), 115 (46), 104 (38), 95 (44), 91 (55), 55 (21); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.20 (s, Ph), 5.51 (t, $J = 7$, **12b**), 5.17 (t, $J = 7$, **12a**), 3.53 (s, **12b**), 3.35 (s, **12a**), 2.4–1.1 (m). Irradiation of the benzylic proton signal at δ 3.35 effected a 11% increase in the intensity of the vinyl triplet at δ 5.16, while irradiation of the benzylic proton signal at δ 3.53 did not effect any change in the intensity of the vinyl signal at δ 5.51.

Cleavage of ***5d*** *and* ***11d.*** Reaction of the mixture of **5d** and **11d** with 1 *M* KOH/MeOH in a fashion similar to the cleavage of **5a** gave a colorless oil which was determined by GC/MS analysis to be a mixture of five $C_{18}H_{26}$ isomers: 0.04g (63%); 60 MHz ^{1}H NMR ($CDCl_3$, partial) δ 7.4–7.0 (br s), 5.8–5.1 (br m), 3.53 (s); GC/MS: (**15**, 15%) *m/z* 242 (M^+, 44), 143 (43), 129 (100), 117 (46), 115 (43), 104 (71), 91 (79); (**14a**, 22%) m/z 242 (M^+, 75), 143 (100), 129 (75), 117 (29), 115 (26),

104 (32), 91 (61); (**14b**, 29%) *m/z* 242 (M^+, 65), 143 (100), 129 (78), 117 (39), 115 (31), 104 (29), 95 (40), 91 (78), 55 (32); (**12b**, 27%) *m/z* 242 (M^+, 25), 151 (30), 132 (53), 129 (40), 117 (56), 95 (100), 91 (96), 81 (43), 55 (43); (**13**, 7%) 242 (M^+, 71), 143 (31), 129 (100), 117 (53), 115 (43), 104 (47), 95 (48), 91 (62). The last two isomers are identical with **12b** and **13**, respectively, by GC retention time and by mass fragmentation pattern. Notably, none of the isomers match **12a**.

Acknowledgment

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