Tetrahedron Vol. 43, No. 13, pp. 2901 to 2908, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

CLEAVAGE OF (3-CHLORO-2-METHYLENECYCLOALKYL)PALLADIUM CHLORIDE DIMERS: FORMATION OF OLEFINS AND α-METHOXYOLEFINS†

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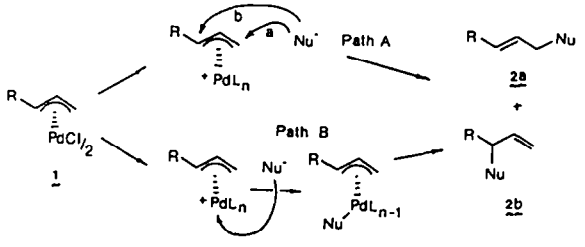
(*Received in USA 27 February* 1987)

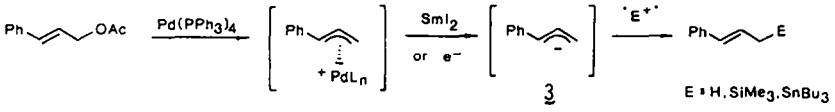
SUMMARY: The cleavage of the title compounds (7) in methanolic potassium hydroxide gives mixtures of olefins and α-methoxyolefins in good yields. The ratio of the products is dependent on the size of the carbocyclic ring. The mechanism proposed involves cleavage of 7 to the corresponding allylic chloride (8). Solvolysis of the chloride gives the α-methoxyolefin. Alternatively, oxidative addition of 8 to Pd(0) generates a new π-allyl complex which affords the olefin product upon subsequent cleavage.

The catalytic and stoichiometric utilization of π-allyl palladium complexes (1) in organic synthesis has become important due to the great chemo-, regio- and stereoselectivity which these reagents provide.[1] Complexes 1 react as electrophiles in the presence of a wide variety of nucleophiles (and excess phosphine ligand) to afford allylically substituted products 2 (Scheme 1). Two mechanisms have been proposed for nucleophilic attack: either direct attack on the allyl ligand at the face opposite palladium (Path A); or, attack at palladium followed by reductive elimination (Path B). A number of elegant experimental schemes have established that "soft" nucleophiles react by the former mechanism, while "hard" nucleophiles react by the latter mechanism.[2] The structure of the reactive electrophilic Pd-allyl species has been probed by spectroscopic and conductivity methods.[3]



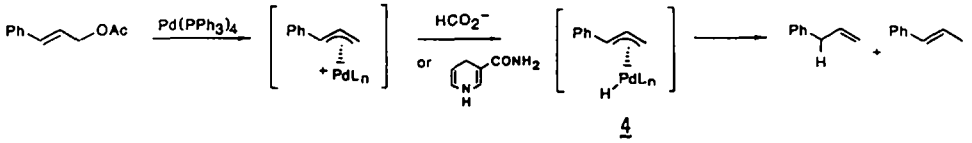
Scheme 1.

Inversion of the reactivity of Pd-allyl complexes to act as nucleophilic species has recently been effected by electrolysis[4a] and by the use of samarium iodide[4b] (eqn. 1). These reactions are suggested to proceed via the formation of the allyl anion (3), which is trapped by an electrophile present in solution (H^+ or Me_3SiCl). Formation of the more substituted olefinic product is observed, as expected for the proposed intermediate.



(1)

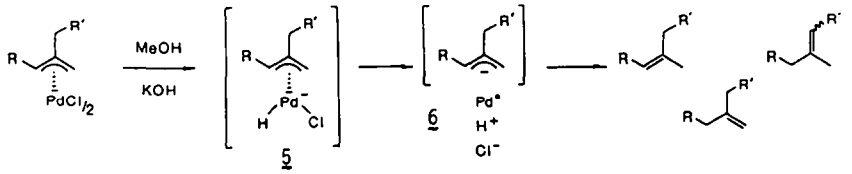
A similar chemical transformation may be accomplished by the use of ammonium formate[5] or NAD(P)H model compounds,[6] in the presence of Pd(0) catalysts (eqn. 2). In the former case, the reaction is believed to proceed via formation of an (allyl)(hydride)palladium species (4).[7] The intermediate 4 undergoes reductive elimination at the more substituted allylic terminus to predominantly afford the less substituted olefinic isomer.



(2)

†*Dedicated to Professor Max Tishler on the occasion of his 80th birthday.*

The base mediated cleavage of Pd-allyl complexes is perhaps the oldest reported reaction in which these complexes act as nucleophilic species (Scheme 2).[8] Although this reaction has been known for more than 20 years, the mechanism has been a matter of some controversy.[9]



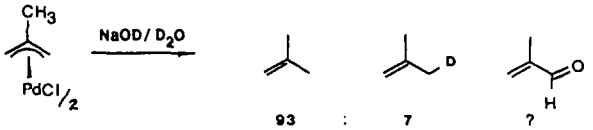
Scheme 2.

Hüttel has proposed that the reaction, *in methanol*, proceeds via hydride attack at the metal to afford an (allyl)(hydride)palladium complex (5). The intermediate 5 decomposes to form the allyl anion 6 and Pd(0). The allyl anion undergoes protonation, or rearrangement followed by protonation. The proposed mechanism was based on evidence from deuterium labelling experiments (i.e., CH_3OD vs. CD_3OH vs. CD_3OD, Scheme 3).[8c]

Scheme 3.

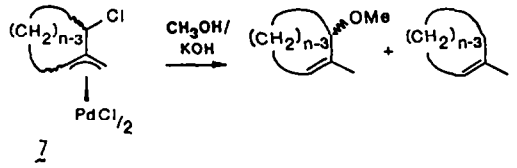
conditions	^1H integration (γ:β)
H_2O / CH_3OH / NaOH	2 : 3.05
D_2O / CD_3OD / NaOD	2 : 1.9
H_2O / CD_3OH / NaOH	2 : 2.8
D_2O / CH_3OD / NaOD	2 : 2.2

Shortly thereafter, Schenach and Caserio reported that the decomposition of Pd-allyls, *in aqueous base*, proceeds with only slight deuterium incorporation (63% chemical yield, <8% D incorporation in D_2O based on MS analysis, eqn. 3). They alternatively proposed that cleavage proceeds via disproportionation of two π-allyls, and that the "dehydrogenated" allyl adds water and/or molecular oxygen to yield an oxidized by-product.[10]



(3)

As part of our program directed at the development of a ring homologation-functionalization methodology, we had the opportunity to study the cleavage of (3-chloro-2-methylenecycloalkyl) palladium chloride dimers (7). Treatment of these complexes with 1M methanolic potassium hydroxide affords cyclic olefins and α-methoxy cyclic olefins (eqn. 4).[11] We herein report our results on the mechanism for the formation of these products.



(4)

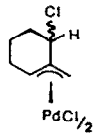
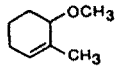
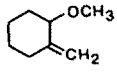
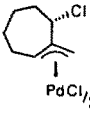
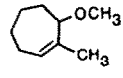
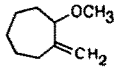
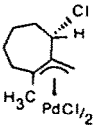
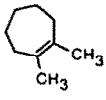
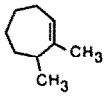
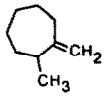
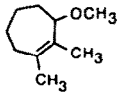
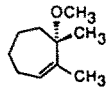
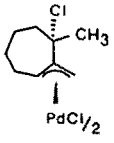
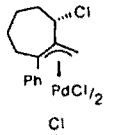
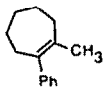
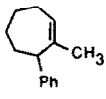
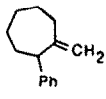
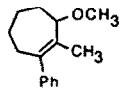
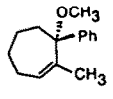
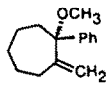
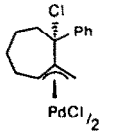
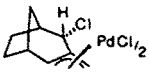
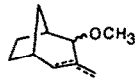
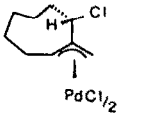
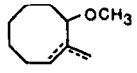
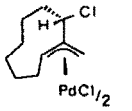
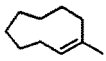
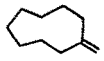
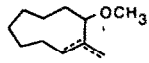
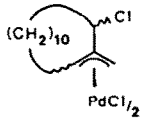
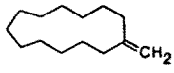
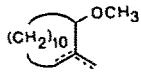
7

RESULTS AND DISCUSSION

Cleavage of the (3-chloro-2-methylenecycloalkyl)palladium chloride dimers 7a-7k were carried out in 1M methanolic potassium hydroxide, first at 25°C for 1h and then at 50°C for 4-24h. After cooling and removal of the palladium metal biproduct, dilution with water followed by extraction and removal of the solvent led to isolation of a mixture of products, which could be analyzed by ^1H NMR spectroscopy and gas chromatography. Formation of mixtures containing different ratios of the products from isomeric starting π-allyls (eg. 7c and 7d, or 7e and 7f) indicates that in most cases, the products do not isomerize under the reaction conditions.[12] Thus the composition of the product mixture reflects the relative rates of formation of the constituents.

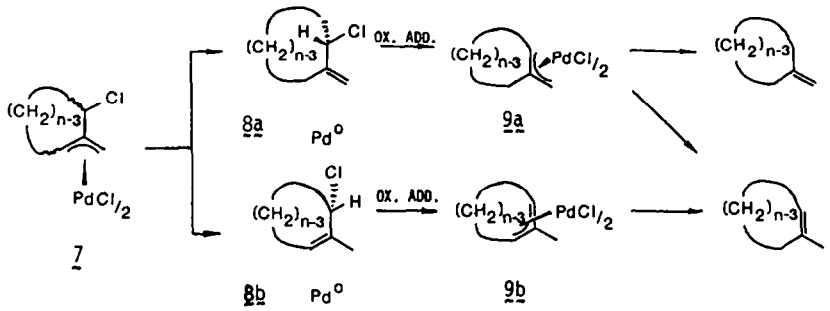
It should be noted that, in all cases, the major product is the cyclic olefin(s). This product is the result of π-allyl cleavage as well as a formal reduction of the C3-Cl bond. This occurs by cleavage of the π-allyl 7 to afford the allylic halides 8a and 8b, and finely divided Pd(0)(Scheme 4). Oxidative addition of metallic palladium(0) to the allylic halides[13]

TABLE I. Cleavage of (3-Chloro-2-methylenecycloalkyl)palladium Chloride Dimers.

Entry	π-Allyl Complex	Time	Products [Reg. #] olefins			α-methoxy olefins		Combined Yield
7a*		4h	 [108-87-2] 15%	 [108-88-3] 38%	 [38445-61-3] 38%	 [10300-04-6] 9%		72%
7b		4h	 64% [1453-25-4]	 8% [2505-03-5]	 24%	 4%		93%
7c**		4h	27%  [20053-89-8]	33%  [81505-07-9]	10%  [76802-29-4]	16% 	14% 	45%†
7d		16h	25%	44%	8%	8%	11%	61%
7e		4h	35% 	45% 	10% 	5% 	5% 	0% 	93%
7f		4h	25%	25%	7%	16%	19%	7%	94%
7g		4h	 66% [4877-38-7]	 33% [4877-39-8]		 1%		91%
7h		4h	 98% [15840-64-9]			 2%		43%†
7i		4h	 71% [13151-62-7]	 28% [56133-38-1]		 1%		78%
7j***		18h	 97%	 [88015-61-6] 2%		 1%		89%
7k		24h	85%	15%				98%

*This compound is an inseparable mixture of diastereomers, see ref. 22. **This material contains 20% 7d, see ref. 22. ***This compound is a mixture of three diastereomers, see ref. 22. †Low yield may be due to volatility of products.

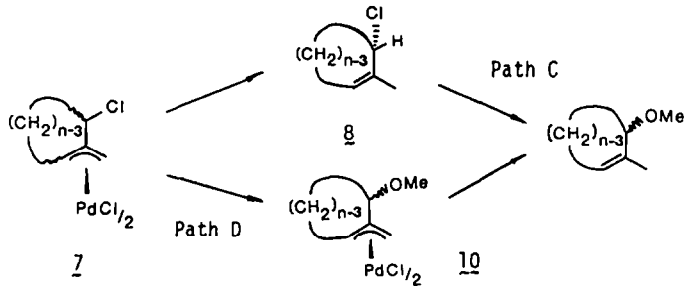
affords the exo- and endocyclic π-allyls 9a and 9b. Subsequent cleavage of the endocyclic π-allyl 9b can only afford the endocyclic olefin, while cleavage of the exocyclic π-allyl 9a should, in principle, give both endo- and exocyclic olefin products.[14]



Scheme 4.

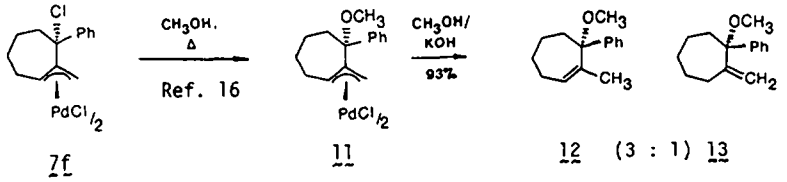
The isolation of >75% olefin products in certain cases indicates that this reaction does not proceed via the disproportionation mechanism of Schenach and Caserio. In addition, the preferential formation of the more substituted cyclic olefin may be taken as evidence against a mechanism which involves reductive elimination of an (allyl)(hydride)palladium species.

The minor α-methoxyolefin products might arise from either *i*) solvolysis[15] of the intermediate allylic halides 8 (Scheme 5, Path C) and/or *ii*) initial solvolysis of the C3 chloride to produce the methoxy substituted complex 10, followed by cleavage of 10 (Scheme 5, Path D). In order to determine the pathway for the formation of the α-methoxyolefin products, it is necessary to compare the cleavage products from 7f with the cleavage products from 11.



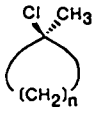
Scheme 5.

We have previously shown that the solvolysis of (3-chloro-2-methylene-3-phenylcycloheptyl)-palladium chloride (7f) gives only (3-methoxy-2-methylene-3-phenylcycloheptyl)palladium chloride (11).[16] This solvolysis is believed to occur via ionization of the axial chloride followed by rapid, irreversible trapping by methanol. Subjecting 11 to the standard cleavage conditions affords 3-methoxy-2-methyl-3-phenylcycloheptene (12) and 2-methoxy-2-phenylmethyl-enecycloheptane (13) (eqn. 5). In comparison, the cleavage of 7f gives a mixture of olefins and α-methoxyolefins comprised of 12, 13 and 3-methoxy-2-methyl-1-phenylcycloheptene (14) (Table I). The presence of 14 in this mixture clearly cannot be accommodated for by the solvolysis-cleavage mechanism (Path D, Scheme 5). The most plausible explanation for the formation of this product is cleavage of 7f to the corresponding allylic chloride followed by solvolysis with rearrangement.[17]



(5)

Since the cyclic olefin and α-methoxyolefin products do not interconvert under the reaction conditions, the relative ratios of the two products reflect the relative rates of oxidative addition versus solvolysis for the allylic chlorides 8. It should be noted that a marked decrease in the percent of α-methoxyolefin products is observed for the cleavage of π-allyl complexes 7 with ring size ≥8 carbons. The rate of solvolysis of chlorocycloalkanes



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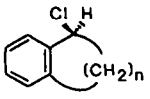

16

(15) is known to be dependent on ring size.[18] This has been attributed to *I*-strain, the change in internal strain in a ring caused by a change in coordination number (hybridization) of the ring atom undergoing reaction. In addition, the rate of solvolysis of a series of benzocycloalkenylchlorides (16) is known to decrease with increasing ring size.[19] This trend is explained on the basis of increasing difficulty for aligning the C-Cl bond perpendicular to the aromatic ring, since, in this geometry the incipient p-orbital formed on ionization of chlorine has the optimum overlap with aromatic π-system. Thus a decrease in the rate of methanolysis of cyclic allylic chlorides 8b with increasing ring size is expected. What is the effect of ring size on the rate of oxidative addition of Pd(0) to allylic halides 8b?

It is well established that *phosphine-ligated* Pd(0) oxidatively adds to 3-chlorocyclohexene, benzylic halides, and cinnamyl acetates with inversion of configuration at carbon,[20] thus implying an S_N2-like mechanism. In contrast, vapor deposited palladium *atoms* have been suggested to oxidatively add to saturated and unsaturated alkyl halides via a "caged" radical species.[21] The radical mechanism must proceed via an electron transfer followed by rapid collapse of the "caged" species. It is unlikely that ring size would have an appreciable effect on the rate of the initial electron transfer step, since a change in geometry during this step is not anticipated. Thus, we propose that while the rate of methanolysis of 8b decreases with increasing ring size, the rate of oxidative addition of Pd(0) to 8b remains essentially unchanged with ring size. The results, decreasing percent of α-methoxyolefin product with increasing ring size, are consistent with this proposal.

SUMMARY

The cleavage of (3-chloro-2-methylenecycloalkyl)palladium chloride dimers 7 in methanolic potassium hydroxide gives cyclic olefins and α-methoxyolefins. These products result by the cleavage of 7 to afford the corresponding cyclic allylic chloride. Solvolysis of the allylic chloride (via an ionic mechanism) affords the α-methoxyolefin, while oxidative addition of Pd(0) to the allylic chloride (via initial electron transfer) results in the formation of a new π-allyl. Subsequent cleavage of this new π-allyl affords the cyclic olefin product.

EXPERIMENTAL SECTION

General Data. All IR spectra were recorded on a Perkin Elmer 700 or 337 spectrometer and were calibrated against the 1601 cm^{-1} peak of polystyrene. All 60 MHz ^1H NMR spectra and 15 MHz $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian EM360L or a JEOL FX60Q spectrometer; chemical shifts are reported in ppm downfield of TMS and couplings are reported in hertz. Gas chromatographic analyses of certain product mixtures were carried out on a Packard 7400 instrument (1.9m x 2mm, 3% SP-2100 on Supelcoport 100/120, isothermal, FID, 17 mL/min He). Integration was determined by triangulation.

All reactions were run under an atmosphere of nitrogen. Spectrograde solvents were used without further purification except for ether and THF, which were distilled from sodium- and potassium-benzophenone ketyl respectively. The π-allyl palladium complexes 7a-7k and 11 were prepared by literature prodedures.[16,22] All organic compounds prepared as standards were shown to be >97% pure by GC analysis.

Methylenecycloheptane (17) was prepared from cycloheptane and methylenetriphenylphosphonium bromide in a fashion similar to the literature preparation of methylenecyclohexane[23]: 53%; bp 130° C (kugelrohr).

(2-methylenecycloheptyl)palladium chloride dimer (18) was prepared from 17 and palladium chloride according to the general procedure of Trost, *et. al.*[24] and was identified by comparison with literature ^{1}H NMR spectral data[8b]: 60%; 15 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.56, 83.19, 61.60, 35.14, 31.90, 30.35, 28.89, 27.19.

3-Methoxy-2-methylcycloheptene (19). A solution of 2-methyl-2-cycloheptenone[25], (0.22 g, 1.77 mmoles) in dry ether (12 mL) was added dropwise to lithium aluminum hydride (0.10 g, 2.60 mmoles) in dry ether (15 mL). The reaction mixture was stirred for 45 min and worked up in the usual manner,[26] to afford 2-methyl-2-cycloheptenol (0.18 g, 1.42 mmoles, 81%).[27] A solution of the crude alcohol in dry THF (14 mL) was added dropwise, via syringe, to a suspension of excess sodium hydride in dry THF (7 mL). Iodomethane (1.0 mL, 1.6 mmoles) was added and the solution stirred for 24 h. Cautious addition of H_2O (10 mL), extraction with ether (2 x 20 mL), drying over $MgSO_4$ and removal of the solvent under reduced pressure afforded 19 as a pale oil: 0.16 g, 1.14 mmoles, 80%; IR (neat, cm^{-1}) 2970s, 1460m, 1100s; ^{1}H NMR ($CDCl_3$) δ 5.61 (br t, J = 6.7, 1H, alkene *H*), 3.76 (m, 1H, C*H*OCH$_3$), 3.31 (s, 3H, OC*H*$_3$), 2.2-0.8 (m), 1.72 (br s, allylic C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 140.90, 127.10, 82.70, 56.89, 30.52, 27.03, 26.78, 26.54, 22.40.

2-Methylmethylenecycloheptane (20) was prepared from 2-methylcycloheptanone and methyltriphenylphosphonium bromide in a fashion similar to the preparation of 17: 45%; bp 130-135° C; IR (neat, cm^{-1}) 3130w, 2960s, 1700m, 1670m, 1450m, 890m; ^{1}H NMR ($CDCl_3$) δ 4.70 (s, 2H, C=C*H*$_2$), 2.5-1.0 (m, 11H), 1.05 (d, J = 6.0, 3H, C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.80, 109.73, 40.09, 36.28, 33.84, 30.60, 30.03, 26.86, 22.72.

3-Methoxy-1,2-dimethylcycloheptene (21) was prepared from 2,3-dimethylcycloheptenone[28] in a fashion similar to the preparation of 19: 54%; bp 95-100° C/19 mm Hg (kugelrohr); IR (neat, cm^{-1}) 2960s, 1680w, 1440m, 1390m, 1100s; ^{1}H NMR ($CDCl_3$) δ 3.80 (m, 1H, C*H*OCH$_3$), 3.25 (s, 3H, OC*H*$_3$), 2.3-0.9 (m, 8H), 1.7 (br s, 6H, allylic C*H*$_3$).

3-Methoxy-2,3-dimethylcycloheptene (22). To a solution of 2-methyl-2-cycloheptenone (0.51 g, 4.10 mmoles) in ether (40 mL) was added, via syringe, methyl lithium (5.0 mL, 1.4 M in ether, 7.0 mmoles) at 0°C. The reaction was stirred for 1 h and then cautiously quenched with H_2O (15 mL). The ethereal layer was separated, dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The crude alcohol was methylated with NaH/CH_3I (in a fashion similar to the preparation of 19) to afford the product as a clear oil: 0.19 g, 1.23 mmoles, 30%; bp 95-100° C/19 mm Hg (kugelrohr); IR (neat, cm^{-1}) 2960s, 1460m, 1080s; ^{1}H NMR ($CDCl_3$) δ 5.6 (br t, J = 6, 1H, alkene *H*), 3.05 (s, 3H, OC*H*$_3$), 2.1-0.9 (m, 14H).

1-Methyl-2-phenylcycloheptene (23). A solution of phenyllithium (4.5 mL, 1.8M in cyclohexane-ether, 8.1 mmoles) was added, via syringe, to a solution of 2-methylcycloheptanone (1.00 g, 7.93 mmoles) in dry ether (25 mL) at 0°C. The mixture was stirred for 45 min, quenched with H_2O (5 mL), and the layers separated. The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was taken up in benzene (30 mL) and treated with I_2 (1 crystal). The mixture was heated at reflux under a dean-stark trap for 16h. The benzene solution was washed twice with saturated aqueous Na_2SO_3. The combined aqueous washes were extracted once with petroleum ether. The combined organic phases were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Distillation under high vacuum gave the product as a pale yellow oil[30]: 0.69 g, 3.70 mmoles, 47%; bp 54-57° C/0.08 mm Hg (kugelrohr); IR (neat, cm^{-1}) 3100w, 2960s, 1720w, 1690w, 1450m, 760s, 690; ^{1}H NMR ($CDCl_3$) δ 7.3-7.0 (m, 5H, C$_6$*H*$_5$), 2.6-2.1 (m, allylic C*H*$_2$), 1.8-1.4 (br s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 145.93, 137.98, 135.70, 128.07, 127.83, 125.55, 36.03, 35.87, 32.63, 27.27, 26.05, 22.81.

3-Methoxy-2-methyl-3-phenylcycloheptene (12). To a solution of 2-methyl-2-cycloheptenone (0.39 g, 3.14 mmoles) in dry ether (25 mL) was added dropwise a solution of phenyllithium (3.0 mL, 1.8 M in cyclohexane-ether, 4.9 mmoles). The reaction was stirred for 45 min and quenched with H_2O (8 mL). The layers were separated, the organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (17 x 1 cm), elution with hexanes (40 mL) followed by elution with ether (50 mL). The ether fraction, upon evaporation, gave the alcohol as a pale yellow oil (0.41 g, 2.03 mmoles, 65%). Methylation of the crude alcohol with NaH/CH_3I (in a fashion similar to the preparation of 19) gave 12 as a clear oil: 0.26 g, 1.20 mmoles, 60%; bp 63°C/0.05 mm Hg (kugelrohr); IR (neat, cm^{-1}) 3080w, 2960s, 1440m, 1080m, 1060m, 750m, 690m; ^{1}H NMR ($CDCl_3$) δ 7.5-7.1 (m, 5H, C$_6$*H*$_5$), 6.05, (br t, J = 6, 1H, vinyl *H*), 3.27 (s, 3H, OC*H*$_3$), 2.2-1.0 (br m, 11H).

General Procedure for the Cleavage of Allyl Palladium Complexes. To the solid π-allyl complex (0.2-5.0 mmoles) was added a freshly prepared 1M methanolic potassium hydroxide solution (50 mL). The reaction mixture was stirred at ambient temperature for 1 h, and then heated to 50°C for 4-24 h. Finely divided palladium metal begins to deposit about 15 min after heating is begun. After cooling, the reaction mixture is filtered into H_2O (100 mL). The cloudy aqueous solution is extracted with methylenechloride (2 x 30 mL) and the combined organic extracts are dried over $MgSO_4$, filtered, and the solvent carefully removed under reduced pressure to afford the product mixture. Mixtures were analysed by ^{1}H NMR spectroscopy and, in certain cases, gas chromatography.

Cleavage of 7a. Reaction of 7a (0.10 g, 0.37 mmoles) gave a mixture of products (30 mg). Analysis of the mixture by NMR spectroscopy indicated the results in Table I. The products 3-methoxy-2-methylcyclohexene and 2-methoxymethylenecyclohexane were indentified by comparison to literature NMR data.[31]

Cleavage of 18. Reaction of 18 (0.04 g, 1.59 mmoles) gave a mixture of 1-methylcycloheptene (24) and methylenecycloheptane (17) (7 : 3 ratio, 0.15 g, 1.36 mmoles, 86%). The products were identified by comparison to a reference spectrum.[32]

Cleavage of 7b. Reaction of 7b (0.32 g, 1.12 mmoles) gave a mixture of products (0.13 g). Analysis of the mixture by NMR spectroscopy indicated the results which appear in Table I. The products 17, 19, and 24 were identified by comparison to authentic spectra (vide supra), signals at δ 3.25 (s) and 4.90 (br s) were assigned to the product 2-methoxymethylenecycloheptane. Analysis by GC gave approximately the same ratios (oven temp. 65°C; retention times: 17 and 24 [1.7 min], 2-methoxymethylenecycloheptane [4.7 min], 19 [5.15 min]).

Cleavage of 7c. Reaction of 7c (0.25 g, 0.83 mmoles) gave a mixture of products (50 mg). Analysis of the mixture by NMR spectroscopy indicated the results which appear in Table I. Products 1,2-dimethylcycloheptene (25) and 2,3-dimethylcycloheptene (26) were identified by comparison to literature NMR data,[33] 20, 21, 22 were identified by comparison to NMR data of independently synthesized samples (vide supra). Analysis by GC gave the same ratios (oven temp. 80°C; retention times: 20 [1.7 min], 25 and 26 [1.9 min], 22 [5.2 min], 21 [5.6 min]).

Cleavage of 7d. Reaction of 7d (0.32 g, 1.07 mmoles) gave a mixture of products (80 mg). Analysis of the mixture by NMR spectroscopy indicated the results which appear in Table I.

Cleavage of 11. Reaction of 11 (0.20 g, 0.55 mmoles) gave a mixture of 12 and 13 (3 : 1 ratio, 0.11 g, 0.51 mmoles, 93%). Product 12 was identified by comparison to spectral data (vide supra). 13: ^{1}H NMR ($CDCl_3$) δ 7.5-7.1 (C_6H_5), 5.00 (s, C=CH_2), 3.00 (s, OCH_3), 2.5-1.2 (m, CH_2). Analysis by GC (oven temp. 145°C; retention times: 13 [5.8 min], 12 [6.2 min]) gave approximately the same ratio.

Cleavage of 7e. Reaction of 7e (0.24 g, 0.66 mmoles) gave a mixture of products (0.12 g). Gas chromatographic analysis (oven temp. 145°C) of the mixture indicated the presence of 12 and 23 as well as three other components. Peaks eluting at 2.9 and 3.2 min were assigned to 2-methyl-3-phenylcycloheptene (27) and 2-phenylmethylenecycloheptene (28) respectively. A peak which eluted at 5.3 min was identified as 3-methoxy-2-methyl-1-phenylcycloheptene (14) (vide infra). Signals in the ^{1}H NMR spectrum at δ 4.85 and 4.65 (br s) were tentatively assigned to 28 (C=CH_2), and a signal at 5.8 (m) was assigned to 27 (alkene *H*).

Cleavage of 7f. Reaction of 7f (70 mg, 0.19 mmoles) gave a mixture of products (35 mg). Analysis of the mixture by ^{1}H NMR spectroscopy indicated the presence of 12 and 13. A third methoxy singlet at δ 3.25 was assigned to 14. Gas chromatographic analysis (oven temp. 145°C) of the mixture gave the results which appear in Table I.

Cleavage of 7g. Reaction of 7g (0.36 g, 1.23 mmoles) gave a mixture of products (0.14 g). Analysis of the mixture by NMR spectroscopy indicated the results which appear in Table I. The two olefin products were identified by comparison to literature NMR spectral data.[34]

Cleavage of 7h. Reaction of 7h (0.28 g, 0.93 mmoles) gave a mixture of products (50 mg), which contained predominantly 1-methylcyclooctene, identified by comparison to literature spectral data.[35]

Cleavage of 7i. Reaction of 7i (0.32 g, 1.02 mmoles) gave a mixture of products (0.11 g). Analysis by NMR spectrosopy indicated that this was largely a mixture of *cis*-1-methylcyclononene and methylenecyclononane as identified by comparison to literature NMR spectral data.[36]

Cleavage of 7j. Reaction of 7j (1.78 g, 4.80 mmoles) gave a pale oil (0.82 g). NMR spectroscopy indicated the results which appear in Table I. Distillation under high vacuum gave a mixture of *cis*- and *trans*-1-methylcyclotridecene: 0.80 g, 4.11 mmoles, 89%; bp 68-70°C/0.45 mm Hg; IR (neat, cm^{-1}) 910s, 740s; ^{1}H NMR ($CDCl_3$) δ 5.5-5.0 (m, 1H, alkene *H*), 2.2-1.8 (m, 3H), 1.57 and 1.35 (singlets, allylic CH_3), 1.27 (br s).

Cleavage of 7k. Reaction of 7k (0.14 g, 0.54 mmoles) gave a colorless oil (82 mg). Analysis by NMR spectroscopy indicated that this is a mixture of 1-methylcyclohexadecene (29) and methylenecyclohexadecane (30): ^{1}H NMR ($CDCl_3$) δ 5.4-5.0 (m, alkene *H*), 4.70 (s, C=CH_2), 2.2-1.9 (m), 1.7 and 1.6 (singlets, allylic CH_3), 1.3 (br s, HW = 4 Hz). Analysis by GC (oven temp 165°C, retention times: 29 [5.0 min], 30 [5.9 min]) gave the same ratio of products.

ACKNOWLEDGMENT. The author would like to thank the Petroleum Research Fund, administered by the American Chemical Society, and Marquette University for financial support of this research. Acknowledgment is due Johnson-Matthey, Inc. for generous donations of palladium chloride. The author is grateful to Barbara Taylor for the cleavage of π-allyls 7g and 7h and to Michael Finley for the preparation of 20 and 2-methyl-2-cycloheptenone.

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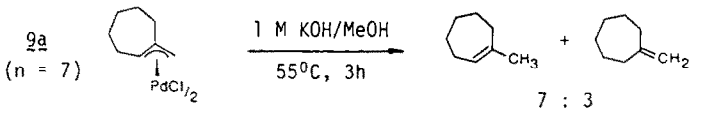

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