and *erythro*-**2a**. The data for *threo*-**2a** are identical with those described above. The data for *erythro*-**2a** follow: NMR ($CDCl_3$) δ 3.4–3.7 (m, 4), 3.45 (dq, 1, J = 9.2, 7.1 Hz), 3.3 (br, 1, OH), 1.9 (m, 1), 1.20 (t, 3, J = 7 Hz), 1.16 (d, 3, J = 6.5 Hz), 0.88 (d, 3, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 77.2 (C-3), 64.8 (C-1), 63.7 (OCH_2CH_3), 39.4 (C-2), 15.2, 15.1, and 11.5 (C-2 CH_3); IR (CCl_4) 3630, 3510, 2970, 1120 cm^{-1}; $\epsilon_{3510}/\epsilon_{3630}$ = 2.5; GC (A, 100 °C) t_R 26.3 min.

***threo*-3-[(Trimethylsilyl)oxy]-2-methyl-1-butanol (*threo*-2e; Run 6).** Trimethylsilyl propenyl ether (106 mg, 0.81 mmol), paraformaldehyde (494 mg, 1.6 mmol), and Me_3Al (1.1 mL of 1.48 M solution in heptane, 1.6 mmol) in 3 mL of CH_2Cl_2 for 15 min at 0 °C reacted to give 120.3 mg (84%) of *threo*-**2e** containing <10% of the erythro isomer: NMR (CCl_4) δ 3.74 (dq, 1, J = 6, 6 Hz), 3.49 (m, 2), 1.58 (m, 1), 1.3 (br, 1, OH), 1.16 (d, 3, J = 6 Hz), 0.90 (d, 3, J = 6 Hz), 0.13 (s, 9); ^{13}C NMR ($CDCl_3$) δ 72.4, 65.4, 42.0, 21.2, 13.4, –0.1; IR (CCl_4) 3640, 3530, 2960, 1250, 1070, 1050, 850 cm^{-1}.

If precautions were not taken to keep the workup alkaline, the adduct **2e** slowly decomposed to *threo*-2-methyl-1,3-butanediol, which was characterized as the bis(*p*-nitrobenzoate): mp 127–128 °C (lit.[25] mp 128 °C for threo isomer and 113 °C for erythro isomer); NMR ($CDCl_3$) δ 8.28 (d, 4, J = 9 Hz), 8.16 (d, 4, J = 9 Hz), 5.30 (dq, 1, J = 6,6 Hz), 4.49 (dd, 1, J = 5,11 Hz), 4.32 (dd, 1, J = 6, 11 Hz), 2.41 (m, 1), 1.44 (d, 3, J = 6 Hz), 1.17 (d, 3, J = 7 Hz).

***threo*-3-Methoxy-2-methyl-1-butanol (*threo*-2f; Run 7).** Methyl propenyl ether (148 mg, 2.0 mmol), paraformaldehyde (124 mg, 4.1 mmol), and Me_3Al (2.7 mL of 1.48 M solution in heptane, 4.0 mmol) in 6 mL of CH_2Cl_2 at 0 °C for 30 min reacted to give 80 mg (33%) of a 16:1 mixture of *threo*-**2f** and *erythro*-**2f**: NMR ($CDCl_3$) δ 3.57 (d, 2, J = 6 Hz), 3.36 (s, 3), 3.30 (dq, 1, J = 6, 6 Hz), 3.0 (br, 1, OH), 1.73 (dtq, 1, J = 6, 6, 6 Hz), 1.17 (d, 3, J = 6 Hz), 0.90 (d, 3, J = 6 Hz); NMR (C_6D_6) δ 3.51 (d, 2, J = 6 Hz), 3.09 (s, 3), 2.9–3.2 (m, 1), 2.8 (br, 1, OH), 1.69 (m, 1), 0.96 (d, 3, J = 6 Hz), 0.79 (d, 3, J = 7 Hz) (this spectrum is different than that reported for the erythro isomer in the same solvent[26]); ^{13}C NMR ($CDCl_3$) δ 81.8, 66.7, 56.1, 40.6, 16.2, 13.3; the erythro isomer absorbed at δ 79.2, 64.8, and 38.8; IR (CCl_4) 3640, 3530, 2980, 2960, 1100 cm^{-1}; GC (A, 100 °C) t_R 28.3 (threo) and 30.3 min (erythro).

2-Ethoxy-3-methylcyclobutanemethanols (7a and 7b). $Al(i\text{-}Bu)_3$ (17 mL of 0.87 M in hexane, 15 mmol) was placed in a flame-dried flask under nitrogen equipped with a condenser. A 64:36 mixture of dihydropyrans **6b** and **6a** (1.04 g, 7.3 mmol) was added and the solution heated at 67 °C for 22 h. Normal workup gave 898 mg (85%) of a 54:46 mixture of **7a** and **7b**. Evaporative distillation of 770 mg (66 °C, 1.85 torr) gave 690 mg (76%) of pure product. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.38; H, 11.22. Pure samples of **7a** and **7b** were obtained by preparative GC.

The data for **7a** follow: NMR ($CDCl_3$) δ 3.7–3.5 (m, 2), 3.48 (q, 2, J = 7 Hz), 3.5–3.2 (m, 1), 2.5–2.1 (m, 3), 1.6 (m, 2), 1.18 (t, 3, J = 7 Hz), 1.10 (d, 3, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) (determined from mixture) δ 81.8, 63.6, 63.4, 42.8, 34.9, 23.0, 14.8, 14.6; IR (CCl_4) 3640, 2980, 2960, 2880, 1130 cm^{-1}; GC (B, 150 °C) t_R 11.7 min.

The data for **7b** follow: NMR ($CDCl_3$) δ 3.8–3.5 (m, 1), 3.66 (br d, 2, J = 6 Hz), 3.40 (q, 2, J = 7 Hz), 2.7–2.3 (m, 1), 1.6–1.3 (m, 4), 1.18 (t, 3, J = 7Hz), 1.09 (d, 3, J = 7 Hz); ^{13}C NMR ($CDCl_3$; determined from mixture) δ 75.0, 63.6, 63.4, 42.2, 30.7, 19.0, 14.8, 13.8; IR (CCl_4) 3640, 2980, 2940, 2880, 1140 cm^{-1}; GC (B, 150 °C) t_R 12.8 min.

Reaction of pure *cis*-**6b** gave a 30:70 mixture of **7a** and **7b** as determined by GC analysis. Reaction of pure *trans*-**6a** gave a 90:10 mixture of **7a** and **7b** as determined by GC analysis.

***trans,trans*-2-Ethoxy-4-methylcyclobutanemethanol (9).** Reaction of a 60:40 mixture of pyrans **8a** and **8b** (66 mg, 0.47 mmol) and $Al(i\text{-}Bu)_3$ (1.1 mL of 0.87 M in hexane, 1.3 mmol) as described above gave 64 mg (94%) of crude **9**. Evaporative distillation (70 °C, 2.9 torr) gave 57 mg (84%) of pure **9**: NMR (CCl_4) δ 3.56 (d, 2, J = 6 Hz), 3.38 (q, 2, J = 6 Hz), 3.6–3.0 (m, 2), 2.30 (ddd, 1, J = 10, 6, 6 Hz), 2.0–1.2 (m, 3), 1.17 (t, 3, J = 6 Hz), 1.13 (d, 3, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 72.2, 63.3, 63.1, 53.4, 35.0, 23.6, 20.5, 15.0; IR (CCl_4) 3640, 2980, 2940, 2880, 1150 cm^{-1}; GC (A, 150 °C) t_R 13.9 min. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 64.08; H, 11.08.

Acknowledgment. We thank the National Institutes of Health for financial support. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Registry No. **2a** (isomer 1), 86335-63-9; **2a** (isomer 2), 86335-64-0; *threo*-**2b**, 86335-65-1; **2d** (isomer 1), 86335-66-2; **2d** (isomer 2), 86335-67-3; *threo*-**2e**, 86335-68-4; **2f** (isomer 1), 86335-69-5; **2f** (isomer 2), 86335-70-8; **2g**, 82655-81-0; **2h**, 86335-71-9; **3a**, 39781-72-1; **3b**, 86335-72-0; **3c**, 86335-73-1; **4**, 86335-74-2; **6a**, 60582-03-8; **6b**, 60582-02-7; **7a**, 86335-75-3; **7b**, 86363-10-2; **8a**, 17322-76-8; **8b**, 17322-77-9; **9**, 86335-76-4; CH_2O, 50-00-0; Me_3Al, 75-24-1; Et_3Al, 97-93-8; Et_2AlCN, 5804-85-3; $Me_2AlC{\equiv}CC_6H_{13}$, 68113-74-6; $EtClAlC{\equiv}CC_6H_{13}$, 86335-77-5; $Al(i\text{-}Bu)_3$, 100-99-2; ethyl (*E*)-propenyl ether, 4696-26-8; ethyl (*Z*)-propenyl ether, 4696-25-7; trimethylsilyl propenyl ether, 19879-97-1; methyl propenyl ether, 7319-16-6; ethyl vinyl ether, 109-92-2; trimethylsilyl isobutenyl ether, 6651-34-9; methyl 1-cyclohexenyl ether, 931-57-7; trimethylsilyl 1-cyclohexenyl ether, 6651-36-1; *tert*-butyldimethylsilyl 1-cyclohexenyl ether, 62791-22-4; (*Z*)-3-[(trimethylsilyl)oxy]-2-pentene, 51425-54-8; *threo*-2-methyl-1,3-butanediol bis(*p*-nitrobenzoate), 19903-09-4; acrolein, 107-02-8; crotonaldehyde, 4170-30-3; 3-ethoxy-2-methylbutanal (isomer 1), 80060-41-9; 3-ethoxy-2-methylbutanal (isomer 2), 80060-40-8.

Supplementary Material Available: Experimental data for runs 2, 3, 5 and 8–13 in Table I (4 pages). Ordering information is given on any current masthead page.

(25) Fremnaux, B.; Davidson, M.; Hellios, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1967**, 4243.

(26) Maskens, K.; Polgar, N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1117.

Palladium-Catalyzed Cyclizations of Bromo Dienes

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Received November 15, 1982

1-Bromo 1,5-dienes, 2-bromo 1,6-dienes, and 2-bromo 1,7-dienes have been found to undergo palladium–triarylphosphine catalyzed cyclizations in the presence of piperidine to form five- or six-membered ring products in good yields. The major or only cyclic products formed are piperidino- or (piperidinomethyl)cyclopentenes and -cyclohexenes. The five-membered ring products are preferred over the six when there is a choice.

Palladium-catalyzed ring closures involving formation of carbon–nitrogen or carbon–oxygen bonds are well-known. Ring closures by forming carbon–carbon bonds have received much less attention. Palladium enolates obtained by exchange of palladium acetate with trimethylsilyl ethers will cyclize if a double bond is present

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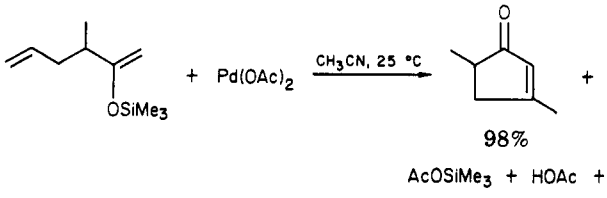
Table I. Palladium-Catalyzed Cyclizations of Bromo Dienes with Piperidine

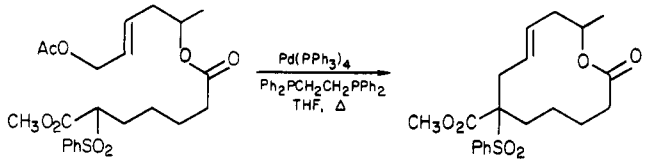
bromo diene	conditions	products (% yield)[a]
(*Z*)-1-bromo-1,5 hexadiene	no solvent, 100 °C, 7 h	I (41), II (13)
	CH_3CN solvent,[b] 100 °C, 2 h	I (68), II (9)
	C_6H_6 solvent,[b] 100 °C, 22 h	I (50), II (29)
2-bromo-1,6-heptadiene	no solvent, 100 °C, 66 h	III (71)[c]
2-bromo-1,7-octadiene	no solvent, 100 °C, 68 h	IV (33), V (16), VI (28), VII (5)
	CH_3CN solvent,[b] 100 °C, 68 h	IV (10), V (8), VI (72), VII (6)
(*E*)-2-bromo-1,6-octadiene	no solvent, 100 °C, 168 h	VII (40) (35)[c]
2-bromo-1,8-nonadiene	CH_3CN solvent,[b] 125 °C, 12 h[d]	VIII (8), IX (4), one unknown
	CH_3CN solvent,[e] 125 °C, 72 h[d]	VIII (10), IX (5), one unknown
(*Z*)-6-bromo-1,5-heptadiene	no solvent, 100 °C, 60 h	X (30) (27)[c]

[a] Yield obtained by GLC unless otherwise noted. [b] One milliliter of solvent was used per millimole of bromo diene. [c] Isolated yields. [d] Three percent $Pd(OAc)_2$ and 6% P(*o*-tol)$_3$ were used. [e] Two milliliters of solvent was employed per millimole of bromo diene.

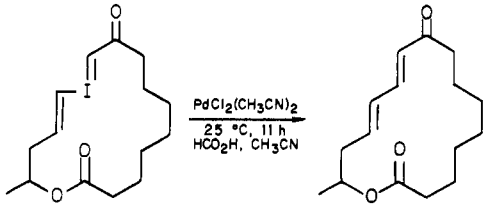
in a position that will yield five- or six-membered ring.[1]



This reaction has been used to form bicyclic ketones as well.[2] The procedure, however, requires stoichiometric quantities of palladium salts. Allylic acetates containing (potential) carbon nucleophiles in the same molecule also have been catalytically cyclized with palladium catalysts. π-Allylic palladium complexes are intermediates. The reaction is useful for the preparation of some medium-size rings as well as the more common ones.[3] The palladium-



catalyzed vinylic substitution reaction also has been applied, in one instance, to the formation of a cyclic product. In this reaction, a 16-membered lactone ring was closed by reaction of a vinylic iodide with an α,β-unsaturated ketone group in the same molecule.[4] The necessity of

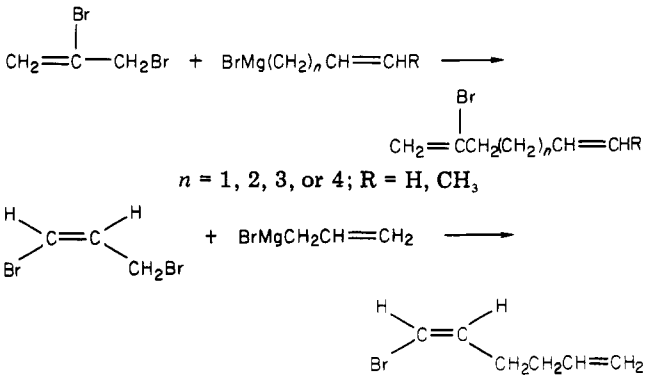


55%

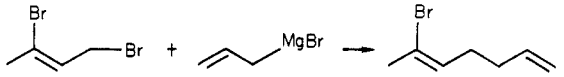
employing high dilution and mild reaction conditions required that the palladium reagent be reduced by formic acid and that a stoichiometric amount be employed. Independently, we became interested in this method of cyclization and have made a more systematic study of it. Herein we report studies on the catalytic cyclization of various bromo dienes.

Results and Discussion

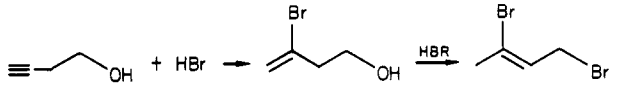
Bromo Dienes. A series of bromo dienes was prepared to determine the scope of the cyclization. All were prepared by a similar method, the coupling of alkenyl Grignard reagents with an alkenyl bromide, either 2,3-dibromopropene or, in one case, (*Z*)-1,3-dibromopropene.



The yields varied from 32% to 90%. We also prepared 6-bromo-1,5-heptadiene in 80% yield (90:10 *Z*:*E*) by this method from (*Z*)-1,3-dibromo-2-butene (90:10 *E*:*Z*) and allylmagnesium bromide. The dibromide was obtained



very conveniently though only in 11% yield by the reaction of concentrated hydrobromic acid with but-3-yn-1-ol. The intermediate 3-bromo-3-buten-1-ol rearranges slowly under the reaction conditions. A small amount of iron powder was added to the reaction mixture to destroy any peroxides present that would catalyze the radical addition of the hydrogen bromide. The product is about 90% *Z* and 10% *E* isomers.



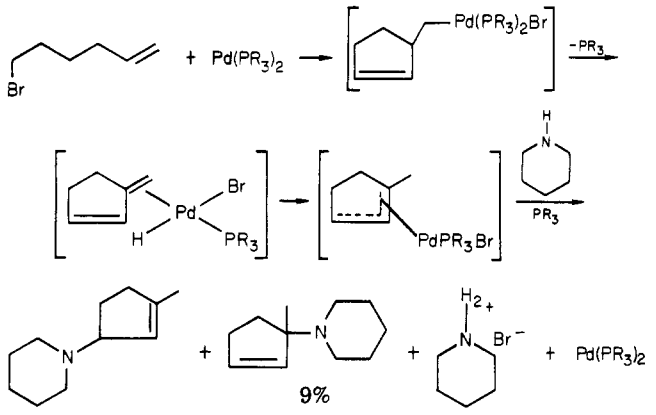
The properites of the bromo dienes are given in Table II (supplementary material).

Cyclizations. Seven bromo dienes with different structural features were submitted to the usual catalytic vinylic substitution reaction conditions with piperidine as the base.[5] This involved heating the bromo dienes with 3 molar equiv of piperidine and 1 mol % (based upon the bromo diene) of palladium acetate and 2 mol % of tri-*o*-tolylphosphine at 100 or 125 °C until analyses by GLC showed that the bromo diene had completely reacted or had stopped reacting. Cycloalkene derivatives were obtained from six of the seven bromo dienes. In some reactions, acetonitrile and, in one example, benzene were employed as solvents. In these cases the solvent improved the yield of the cyclization products. The results obtained are summarized in Table I. As in the intermolecular cases, tertiary amines such as triethylamine instead of piperidine

(1) Ito, Y.; Aoyama, J.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494.
(2) Kende, A. S.; Roth, B.; Sanfilippo, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 1784.
(3) Trost, B. M.; Verhoven, T. R. *J. Am. Chem. Soc.* **1979**, *101*, 1595.
(4) Ziegler, F. E.; Chakraborty, U. R.; Weisenfeld, R. B. *Tetrahedron* **1981**, *37*, 4035.
(5) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898.

as base greatly decreased the reaction rates and yields of identifiable products obtained in these reactions.

(*Z*)-1-Bromo-1,5-hexadiene cyclized easily to a mixture of two allylically isomeric methylpiperidinocyclopentenes. The total yield of cyclized products and the relative amounts of the two isomers varied significantly when solvents were employed. Acetonitrile caused the fastest and the most selective reaction. It gave 68% of the N-secondary and 9% of the N-tertiary alkylamine, compounds I and II, respectively. The two isomeric amines are believed to be formed by attack of piperidine at both ends of the intermediate allylic palladium complex.

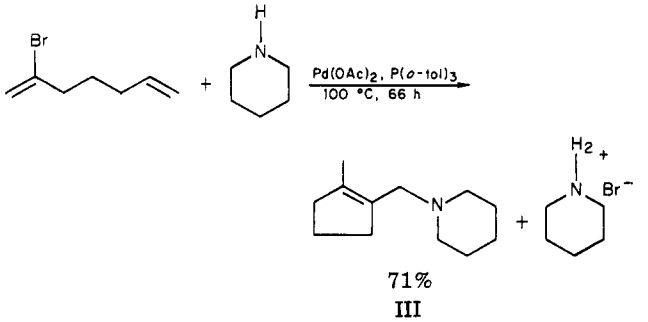


$PR_3 = P(o\text{-tol})_3$

In benzene solution, the yield of the N-tertiary alkylamine was 29% and without a solvent (other than excess piperidine) it was 13%. It is surprising that so much of this rather hindered amine is formed, although we had noted the formation of less hindered N-tertiary alkylamines in similar open-chain reactions previously.[5] Another notable feature of the reaction is the preferred formation of a five- rather than a six-membered ring. In related intermolecular cases, addition of terminal vinylic groups occurs preferentially to the terminal carbon of 1-alkenes rather than to the internal double bond carbon as occurred in the cyclization. Clearly, there is a strong preference for five-membered ring formation over six-membered ring formation.

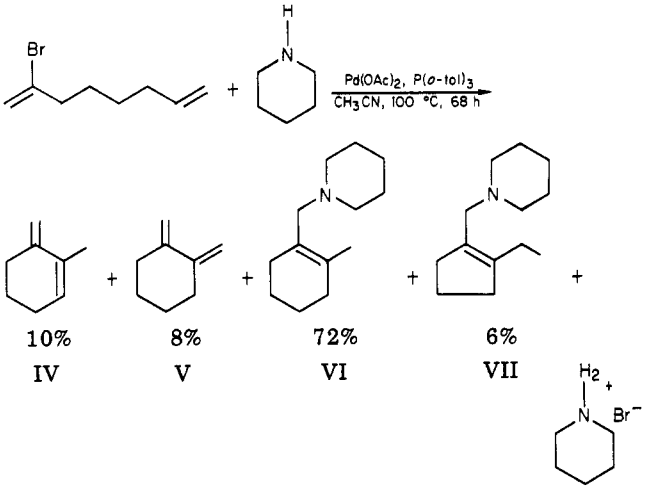
An attempt to form cyclic products from 2-bromo-1,5-hexadiene failed; only polymeric materials were formed. Presumably, a double bond only four carbons removed from the palladium group in the intermediate cannot form a stable internal π-complex, and intermolecular reactions are more favorable.

2-Bromo-1,6-heptadiene, with the double bond five carbons from the palladium, cyclizes in 71% yield to a single, five-membered ring product, III.

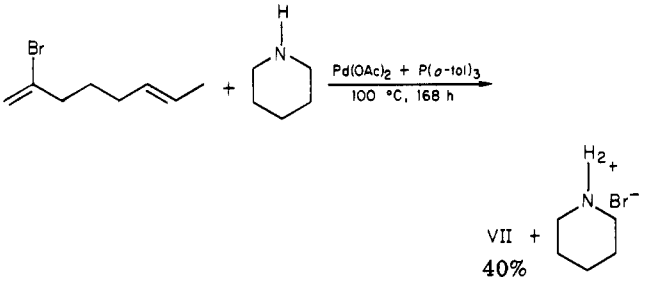


As expected from previous results,[5] the 2-bromo-1,6-diene reacted more slowly than the 1-bromo 1,5-diene isomer in the cyclization. The rate difference seems to be larger in the cyclization reaction than in the intermolecular examples (about 10 compared with about 2, respectively).

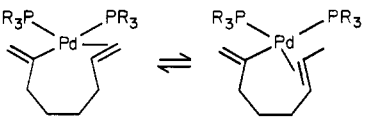
Six-membered ring products were formed when the double bond was six carbons removed from the halogenated carbon. Surprisingly, however, even in this case some five-membered ring isomer was formed. Without added solvent, 2-bromo-1,7-octadiene formed 48% of a mixture of two six-membered ring dienes, IV and V, 28% of the related six-membered ring amine, VI, and 5% of the five-membered ring amine, VII. A considerably more selective reaction occurred in acetonitrile solution where 72% of VI was formed at the expense of the dienes.



The rearranged five-membered ring amine, VII, was obtained as the only volatile product in the cyclization of (*E*)-2-bromo-1,6-octadiene in a slow reaction in 40% yield.



The formation of compound VII from 2-bromo-1,7-octadiene can be rationalized in two ways. Either the starting diene is isomerized to the 1,6-isomer in the reaction mixture or the intermediate dienylpalladium complex rearranges before it cyclizes. We have looked for the presence of the 1,6-diene in partially reacted 1,7-diene reactions and failed to find significant amounts of it. A small amount is present in our 2-bromo-1,7-octadiene as determined by ^{13}C NMR, but its concentration does not increase with time in the cyclization reaction. Therefore, we are included to believe that the intermediate is rearranging. There is a



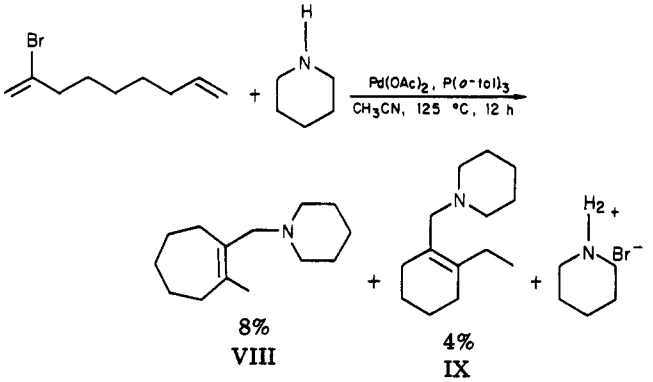
R = *o*-tol

possible precedent for this rearrangement. Dichlorobis(benzonitrile)palladium rearranges 1,3-cyclooctadiene to a mixture of dichlorocycloocta-1,4- and -1,5-dienepalladium complexes.[6] A π-allylic hydride may be involved in a

(6) Tayim, H. A.; Vassilian, A. *J. Chem. Soc., Chem. Commun.* **1970**, 630.

1,3-hydrogen shift in the rearrangement.

An attempt to form larger rings from 2-bromo-1,7-nonadiene was not very successful. In a slow reaction in acetonitrile solution 8% of the seven-membered ring amine, VIII, was formed along with 4% of the rearranged six-membered ring amine, IX. Dilution of the reaction

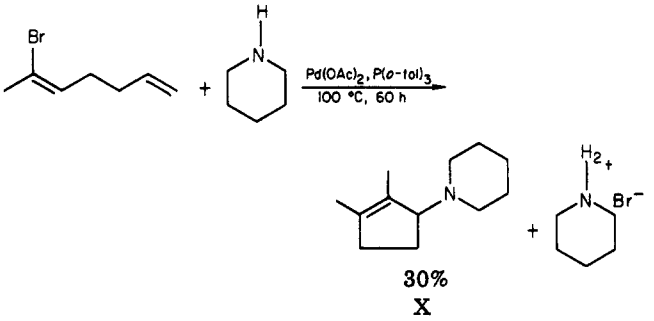


8%
VIII

4%
IX

mixture with twice the volume of acetonitrile employed above gave a slighly higher yield (14%) of the two amines. The low yield and rearrangement indicate that this reaction is not likely to be useful for formation of rings other than those with five or six carbons.

One example of an internal vinylic bromide was studied and it was found to cyclize normally. 6-Bromo-1,5-heptadiene cyclized under the usual conditions to give 30% of 1,2-dimethyl-3-piperidinocyclopentene as the only volatile product.



30%
X

Conclusions

1-Bromo 1,5-dienes or 2-bromo 1,6-dienes cyclize in the presence of piperidine and a $Pd(OAc)_2$ and tri-*o*-tolylphosphine catalyst to produce cyclopentene derivatives. Since the piperidino group introduced in the reaction can easily be removed by reaction with chloroformate esters to form chlorides, this reaction provides a useful method for forming cyclopentene rings with at least one alkyl substituent. Piperidinomethyl six-membered ring products are formed from 2-bromo-1,7-octadiene. However, significant amounts of cyclic dienes and a cyclopentene derivative are also formed. Yields of cyclized amine products decrease sharply with the next homologue, 2-bromo-1,8-nonadiene, even with considerable dilution. From this example it appears that the reaction is not promising as a method for producing medium-size ring compounds.

Experimental Section

Materials. 2,3-Dibromopropene, allyl bromide, 4-bromo-1-butene, and piperidine were obtained from the Aldrich Chemical Co. The *cis*-1,3-dibromopropene, bp 60 °C (25 mm) was isolated by fractional distillation from a cis–trans mixture supplied by Columbia Organic Chemicals. 5-Bromo-1-pentene[7] and *trans*-5-bromo-2-pentene[8] were prepared by literature methods. Palladium acetate and tri-*o*-tolylphosphine were obtained as described previously.[9]

5-Bromo-1-hexene. To 28 g (0.10 mol) of ice-cooled phosphorus tribromide was added dropwise a mixture of 25 g (0.250 mol) of 5-hexen-1-ol and 5.5 g (0.07 mol) of pyridine with mechanical stirring. After the addition, the mixture was stirred for 1 h and left at room temperature overnight. The reaction mixture was then distilled and the fraction bp 150–165 °C was washed with water, 2 N sodium hydroxide, and water again and dried over calcium chloride. Redistillation gave 32.5 g or 79% of the bromide, bp 150–152 °C.

2,4-Dibromo-2-butene. To 40 g (0.56 mol) of 3-butyn-1-ol (Albany Chemicals) was added a solution of 3.36 g (0.06 mol) of iron powder dissolved in 283 g (1.68 mol) of 48% hydrobromic acid. The mixture was stirred and heated at reflux temperature for 8 h. After cooling, the product was extracted with methylene chloride, and the extracts were washed with aqueous sodium bicarbonate. The extracts were dried with magnesium sulfate and distilled. The fraction bp 88–90 °C (40 mm) was 2,4-dibromo-2-butene. There was obtained 14 g or an 11% yield of a 90:10 *Z*:*E* mixture.

General Procedure for Coupling of 2,3-Dibromo-1-propene with Nonallylic Grignard Reagents. Grignard reagents, ~1.5 M, were prepared in dry THF from magnesium turnings and the alkenyl bromide in the usual manner. To the stirred Grignard solution, 160 mL or 0.24 mol, was added at 0 °C, with stirring, 27 g (0.135 mol) of 2,3-dibromopropene in 300 mL of THF. After the addition, the reaction mixture was stirred at room temperature overnight. The next day saturated aqueous ammonium chloride was added and the organic layer was separated. The aqueous phase was extracted again with ether, and the combined organic phases were dried with magnesium sulfate and distilled. The properties of the products and the yields obtained are given in Table II (supplementary material).

General Procedure for Coupling of 2,3-Dibromo-1-propene or *cis*-1,3-Dibromo-1-propene with Allylic Grignard Reagents. Allylmagnesium bromide in ether solution (120 mL of 1 M) prepared according to the literature[10] was added dropwise to 200 mL of a cooled and stirred solution of 0.065 mol of 2,3-dibromo-1-propene or 2,4-dibromo-2-butene in 200 mL of ether. After the addition, the reaction mixture was stirred at room temperature overnight and the product was isolated as in the preceding procedure. Yields and properties of the bromo dienes prepared are given in Table II (supplementary material).

General Procedure for the Palladium-Catalyzed Cyclization of the Bromo Dienes. A mixture of 40 mmol of the bromo diene, 10.2 g (120 mmol) of piperidine, 0.090 g (0.40 mmol) of palladium acetate, and 0.244 g (0.80 mmol) of tri-*o*-tolylphosphine was prepared in a 200-mL Pyrex pressure bottle. The air in the bottle was flushed out with a stream of nitrogen and the bottle was capped. The mixture was warmed with shaking until it was homogeneous and then heated in a stream or oil bath at the required temperature until the bromo diene had all reacted as determined by GLC analyses of a sample of the reaction mixture. After completion of the reaction, the mixture was cooled and diluted with ether and 20 mL of 6 N hydrochloric acid. The aqueous phase was separated and extracted again with ether. The combined extracts were dried with $MgSO_4$ and distilled to give the dienes that may have been formed in the reaction. The acidic aqueous phase was then made basic with excess 5% sodium carbonate and reextracted twice with ether. After drying with $MgSO_4$, the extracts were distilled to give the amine products. The yield of products and reaction times are given in Table I and the properties of the products, NMR, boiling points, molecular weights or analyses, are given in Table III (supplementary material).

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loaned to us for this study by the Johnson-Matthey Co.

Registry No. I, 86365-69-7; II, 86365-70-0; III, 86365-71-1; IV, 23611-14-5; V, 2819-48-9; VI, 86365-72-2; VII, 86365-73-3; VIII, 86365-74-4; IX, 86365-75-5; X, 86365-76-6; $Pd(OAc)_2$, 3375-31-3; $P(o\text{-tol})_3$, 6163-58-2; (*Z*)-1-bromo-1,5-hexadiene, 86365-77-7; 2-bromo-1,6-heptadiene, 86365-78-8; 2-bromo-1,7-octadiene, 86365-79-9; (*E*)-2-bromo-1,6-octadiene, 86365-80-2; 2-bromo-1,7-nonadiene, 86365-81-3; (*Z*)-6-bromo-1,5-heptadiene, 86365-82-4; 5-hexen-1-ol, 821-41-0; 3-butyn-1-ol, 927-74-2; (*Z*)-2,4-dibromo-2-butene, 86365-83-5; (*E*)-2,4-dibromo-2-butene, 86365-84-6; (*E*)-6-bromo-1,5-heptadiene, 86365-85-7; 5-bromo-1-hexene, 4558-27-4; piperidine, 110-89-4; allylmagnesium bromide, 1730-25-2.

Supplementary Material Available: Table II containing the boiling points, NMR spectra, and molecular weights determined for the bromo dienes prepared and Table III with the same data for the cyclized products obtained (3 pages). Ordering information is given on any current masthead page.

A New Reducing System: Calcium Metal in Amines. Reduction of Aromatic Hydrocarbons

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A new reducing system consisting of calcium dissolved in a mixture of amines (methylamine–ethylenediamine) is described. Representative aromatic hydrocarbons have been reduced by this new reagent largely to monoalkenes. Hydrocarbons like tetralin, *m*- and *p*-xylene, and indan are reduced in excellent yields by the calcium system to a crude product containing 88% or better of a single alkene. A new technique involving oxymercuration–demercuration is used to purify two of the monoalkene isomer mixtures obtained in these reductions. Unexpectedly, durene is reduced by the calcium reagent to 1,2,4,5-tetramethyl-1,4-cyclohexadiene in excellent yield. Likewise anthracene is reduced in one step to 1,2,3,4,5,6,7,8,9,10-decahydroanthracene. Experiments designed to elucidate why the calcium system does not reduce durene or anthracene to monoalkenes are described. Similarities and differences between the calcium–amine and the lithium–amine reducing systems are discussed.

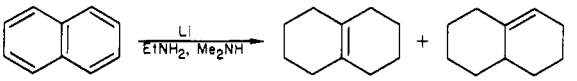
Introduction

Several years ago we disclosed[1] that calcium metal dissolved in a mixture of methylamine and ethylenediamine was capable of reducing simple aromatic hydrocarbons to cyclic alkenes. In this regard, it resembled the lithium–amine reducing system[2] first reported in 1955. As early as 1916, Russian workers[3] reported that calcium dissolved in liquid ammonia or calcium hexaammine $[Ca(NH_3)_6]$ suspended in anhydrous diethyl ether would reduce simple aromatics to monoolefins. The Russian procedures were cumbersome, and, despite claims to the contrary,[4] usually gave products that were highly impure.[5] As a result, calcium reductions never gained wide acceptance[6] and were used only sporadically through the years.

In this paper, we report the reduction of representative aromatic hydrocarbons employing a new calcium–mixed amine reducing system. In several of the examples given, excellent yields of a crude product can be obtained which contain 88% or better of a single cyclic alkene. In these cases, reduction by calcium may develop into the method of choice for obtaining the corresponding cyclic mono- or diene.

Results

Naphthalene–Tetralin. In earlier work,[7] naphthalene was reduced to an 80/20 mixture of Δ^9- and $\Delta^{1(9)}$-octalin by lithium dissolved in a mixture of ethylamine–dimethylamine. Δ^9-Octalin of greater than 99% purity could



80 20

be obtained from this mixture by selective hydroboration of the less sterically hindered $\Delta^{1(9)}$ isomer with disiamylborane.[8] The calcium–amine reduction of both naphthalene and tetralin (Table I, entries 1 and 2) also results in an approximate 80/20 mixture of Δ^9 and $\Delta^{1(9)}$ isomers. A more convenient purification method (see Experimental Section) has been developed involving oxymercuration–demercuration,[9] which permits isolation of the Δ^9 isomer with a minimum purity of 98%.

Durene–Anthracene. Both of these compounds are reduced by the calcium system to unconjugated dienes rather than to the usual monoalkenes. One[10] of the published procedures for preparing 1,2,4,5-tetramethyl-1,4-cyclohexadiene by a Birch reduction of durene reports only an 8% yield of product. This low yield is the result of using a toluene–liquid ammonia mixture to increase[11] the

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