Palladium-Catalyzed Inter- and Intramolecular Cross-Coupling Reactions of *B*-Alkyl-9-borabicyclo[3.3.1]nonane Derivatives with 1-Halo-1-alkenes or Haloarenes. Syntheses of Functionalized Alkenes, Arenes, and Cycloalkenes via a Hydroboration–Coupling Sequence[1]

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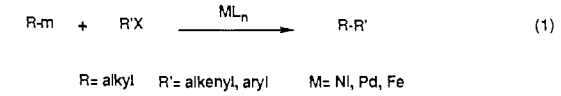
Abstract: The cross-coupling reaction of *B*-alkyl-9-borabicyclo[3.3.1]nonanes (*B*-R-9-BBN), readily obtainable from alkenes by hydroboration, with 1-halo-1-alkenes or haloarenes in the presence of a catalytic amount of $PdCl_2$(dppf) and bases, such as sodium hydroxide, potassium carbonate, and phosphate, gave the corresponding alkenes or arenes. Because the reaction is tolerant of a variety of functionalities on either coupling partner, stereochemically pure functionalized alkenes and arenes can be obtained under mild conditions. The utility of the reaction was demonstrated by the stereoselective synthesis of 1,5-alkadienes (**7** and **8**) and the extension of a side chain in a steroid (**11**). The hydroboration of haloalkadienes (**12**), followed by the intramolecular cross-coupling, gave a short-step procedure for synthesis of cycloalkenes, benzo-fused cycloalkenes, and exocyclic alkenes (**14** and **16**).

The cross-coupling reaction[2] of organic electrophiles with organometallic reagents in the presence of transition metals is a very mild and most straightforward method of forming carbon–carbon bonds. Although organometallic reagents with alkyl, 1-alkenyl, 1-alkynyl, and aryl groups have been successfully used for the coupling reactions, those with alkyl groups having sp^3 carbons containing β hydrogens have been severely limited due to the competive side reactions.



In 1971–1972, Kochi,[3] Kumada,[4] and Corriu[5] reported independently that the reaction of alkyl Grignard reagents with alkenyl or aryl halides could be markedly catalyzed by Fe(III) or Ni(II) complexes. Recent studies by Negishi[6] demonstrated the synthetic utility of alkylzincs by use of palladium catalyst. Alkyllithium,[7] -tin,[8] and-aluminum[9] reagents were also used for the cross-coupling reactions. Among these studies dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) [$NiCl_2$(dppp)][4c] and dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) [$PdCl_2$(dppf)],[4g] reported by Kumada, Tamao, and Hayashi, are recognized as the most selective catalysts, which suppress the unavoidable side reactions, e.g., the isomerization of alkyl groups and the reduction of halides, caused by hydridopalladium species generated by β-hydride elimination from alkylpalladium complexes. The alkyl–aryl or alkyl–alkenyl coupling involving secondary or even tertiary alkylmagnesium halides proceeds selectively. The recent discovery by Castle and Widdowson[10] that even alkyl iodides undergo the coupling reaction with Grignard reagents in the presence of $PdCl_2$(dppf) should be a great success of this catalyst in the field of the cross-coupling reaction.

We have previously reported the palladium-catalyzed cross-coupling reaction of 1-alkenyl-[11] and arylboron[12] compounds with

Table I. Reaction Conditions: Cross-Coupling of *B*-Octyl-9-BBN with Iodobenzene (Eq 2)[a]

entry	catalyst	base (equiv)	solvent	temp, °C	% yield[b]
1	$PdCl_2$(dppf)	NaOH (3)	THF–H_2O (5:1)	65	99
2	$PdCl_2$(dppf)	TlOH (1.5)	THF–H_2O (5:1)	20	79
3	$PdCl_2$(dppf)	NaOMe (1.5)	THF	65	98
4	$PdCl_2$(dppf)	NaOMe (1.5)	THF–MeOH (5:1)	65	18
5	$PdCl_2$(dppf)	K_2CO_3 (2)	DMF	50	98
6	$PdCl_2$(dppf)	K_3PO_4	DMF	50	94
7	$Pd(PPh_3)_4$	NaOH (3)	THF–H_2O (5:1)	65	84
8	$Pd(PPh_3)_4$	NaOH (3)	benzene–H_2O	80	97

[a] Reactions were carried out in 5 mL of solvent for 16 h with 3 mol % of palladium catalyst, bases, iodobenzene (1 mmol), and *B*-octyl-9-BBN (1.1 mmol). [b] GLC yields are based on the iodobenzene employed.

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organic halides. The reaction proceeds readily and stereo- and regioselectively to give conjugated alkadienes or alkenynes in high yields. The configuration of both the haloalkenes and 1-alkenylboranes are retained during the reaction, thus providing versatile and reliable procedures for the syntheses of stereodefined conjugated (*E,E*)-, (*E,Z*)-, (*Z,E*)-, and (*Z,Z*)-alkadienes and enynes under mild conditions.[11] However, organoboranes with alkyl groups have not been used successfully for the coupling reaction. Alkylboranes are readily prepared by hydroboration[13] of alkenes, which is essentially quantitative, proceeds through a cis-Markovnikov addition from the less hindered side of double bond, and can tolerate various functional groups. Since alkylboranes thus obtained are also quite inert toward many functional groups, the couplings can be carried out without protecting these groups. Herein, we report on the scope and limitations of the palladium-catalyzed coupling reaction of such alkylboranes with haloalkenes or haloarenes, as well as its synthetic application.

Results and Discussion

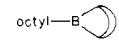
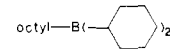
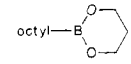
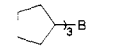
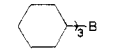
Reaction Conditions. A series of reactions was examined with iodobenzene and *B*-octyl-9-borabicyclo[3.3.1]nonane (*B*-octyl-9-BBN] as partners to establish the reaction conditions (eq 2 and Table I). As reported previously,[1] iodobenzene coupled in high

(2)

yields with *B*-octyl-9-BBN in the presence of 1–3 mol % of $PdCl_2$(dppf) and 3 equiv of sodium hydroxide in refluxing THF–water (5:1) to give octylbenzene. The base is essential for the success of the reaction. The reaction did not proceed at a detectable rate in the absence of a base, and the reaction also failed when weak bases such as sodium acetate were used. Thallium(I) hydroxide, successfully utilized by Kishi[14] for the cross-coupling reaction of 1-alkenylboronic acids, also accelerated the reaction even at room temperature. When there are no functionalities sensitive to bases on either the alkylboranes or the organic halides, a combination of $PdCl_2$(dppf) and sodium hydroxide in THF–H_2O worked nicely in most cases. For the functionalized alkylboranes and halides, aprotic conditions were desirable. Although it was found that powdered sodium methoxide suspended in THF accelerated the reaction with iodobenzene, such conditions were less effective with vinylic halides, as shown later. A more promising coupling was achieved by using powdered potassium carbonate or phosphate suspended in DMF at 50 °C (Table I, entries 5 and 6). Under these conditions, a wide variety of functional groups, such as ester, cyano, and carbonyl groups, can be tolerated on either coupling partner as shown in Tables III and IV. Although $PdCl_2$(dppf) was used in most of the present work, $Pd(PPh_3)_4$ is perhaps more commonly used for such a coupling reaction. The reaction in the presence of 3 mol% of $Pd(PPh_3)_4$ and sodium hydroxide in benzene gave octylbenzene in a yield of 97% (entry 8 in Table I).

A comparison of various *B*-octylylboron compounds in the reaction with iodobenzene demonstrated that the representative hydroborating reagents, such as 9-BBN, disiamylborane, dicyclohexylborane, and borane, can be used for the present reaction (entries 1–4 in Table II). One of three alkyl groups in tri-

Table II. Coupling Reaction of Iodobenzene with Various *B*-Alkylboron Compounds[a]

entry	borane	% yield[b]
1		99
2	octyl-B(Sia)$_2$	82
3		93
4	(octyl)$_3$B	98
5		1
6	(2-butyl)$_3$B	40[c]
7		65[c]
8		55[c]

[a] Reactions were conducted in THF at refluxing temperature with 3 mol % of $PdCl_2$(dppf), 3 M NaOH in H_2O (1 mL), iodobenzene (1 mmol), and *B*-alkylboron compounds (1.1 mmol), unless otherwise noted. [b] GLC yields are based on the iodobenzene employed. [c] 3 M KOH in H_2O (1 mL) was used as a base. Biphenyl (10–30%) was also obtained.

octylborane participated in the coupling (entry 4), and the leaving ability of the primary alkyl on the boron atom was shown to be higher than that of a secondary alkyl group. Under all the reaction conditions examined, none of the coupling products with secondary alkyls were detected in the crude reaction mixture (entries 1–3). 2-Octyl-1,3-dioxaborinane was almost inactive under the conditions indicated (entry 5). Entries 6–8 demonstrate that the coupling between secondary alkylboron compounds and iodobenzene can occur in moderate yields by using 3 M KOH in water as a base. Lower yields in the coupling of secondary alkyls may not be due to β-elimination, but rather to the slow rate of transmetalation of secondary alkylboranes to PhPdI. Indeed, the yields of *n*-butylbenzene and benzene derived from β-elimination were less than 1% in the coupling of tri-2-butylborane (entry 6), whereas 10–30% biphenyl, arising from homo-coupling, was obtained (entries 6–8).

Although we have not studied the reaction mechanism in detail, the synthetic study described above has been carried out on the assumption that the desired coupling reaction of alkylboranes may proceed by a pathway similar to that of palladium-catalyzed cross-coupling reactions of organometallics[2-10] which involves (a) oxidative addition, (b) transmetalation, and (c) reductive elimination (eq 3). Due to the low nucleophilicity of alkylboranes, the transmetalation may be the rate-determining step[15] among these three steps. It has been reported that the addition of sodium hydroxide exerts a remarkable effect on the reaction of alkylboranes with mercuric,[16] silver,[17] auric,[17b] and platinic[17b] halides. It is also known that some of the M–OR reagents, such as $Hg(OAc)_2$,[16] $Hg(OR)_2$,[16d,e] and AgO,[17] undergo the transmetalation reaction with alkylboranes in the absence of bases. Our preliminary experiments indicated that trioctylborane (1 equiv) reacts with $Pd(OAc)_2$ in refluxing benzene by forming metallic palladium to give octane (59%) and octene (3%), whereas no reactions were observed with $PdCl_2$, $PdCl_2(PPh_3)_2$, and $PhPd(PPh_3)_2I$ under such neutral conditions. The results suggested that the rate of transmetalation is highly dependent on the ligands on the palladium (II) complexes, as observed in our previous study[11a] on the cross-coupling reaction of 1-alkenylboron compounds. On the other hand, lithium tetraalkylborates, which led to unsatisfactory results in the case of 1-alkenyltrialkylborates,[11a,15] brought about a clean coupling reaction. For instance, the reaction of the ate

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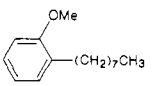
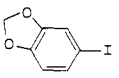
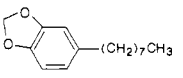
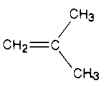
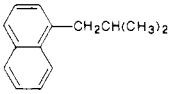
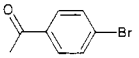
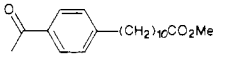
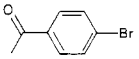
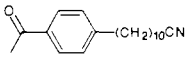
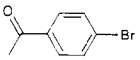
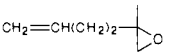
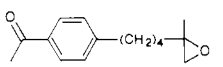
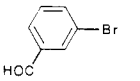
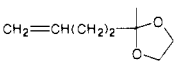
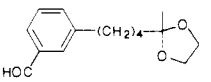
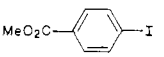
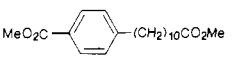
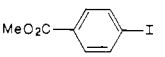
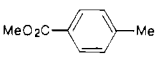
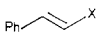
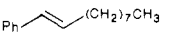
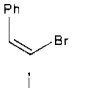
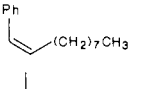
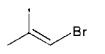
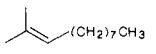
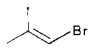
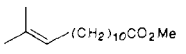
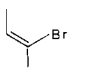
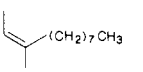
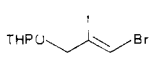
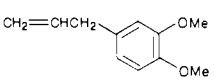
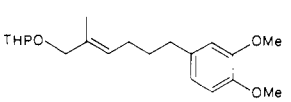
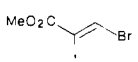
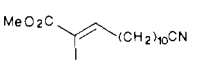
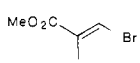
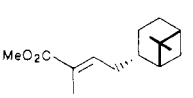
Table III. Cross-Coupling Reaction of 9-Alkyl-9-BBN with Haloarenes (Eq 6)

entry	haloarene	alkene	product	% yield[a] procedure A[b]	B[b]	C[b]
1		1-octene		90	71	
2		1-octene			(78)	
3				(88)	(71)	
4		CH_2=$CH(CH_2)_8CO_2Me$				(88)
5		CH_2=$CH(CH_2)_8CN$				98
6						(52)[c]
7						(77)
8		CH_2=$CH(CH_2)_8CO_2Me$			82	84
9					(77)	(49)

[a] GLC yields are based on the haloalkenes employed, and the isolated yields are in parentheses. [b] 9-Alkyl-9-BBN was prepared by the usual method from alkene (1.1 equiv) and 9-BBN (1.1 equiv). The coupling reaction with haloarene (1 equiv) was conducted under the following conditions. Procedure A: $PdCl_2$(dppf) (3 mol %) and NaOH (3 equiv) in THF at 65 °C. Procedure B: $PdCl_2$(dppf) (3 mol %), NaOMe (1.5 equiv) in THF at 65 °C. Procedure C: $PdCl_2$(dppf) (3 mol%) and K_2CO_3 (2 equiv) in DMF–THF at 50 °C. [c] A 30% yield of 7-(4-acetylphenyl)-2-methylheptane-1,2-diol was also obtained.

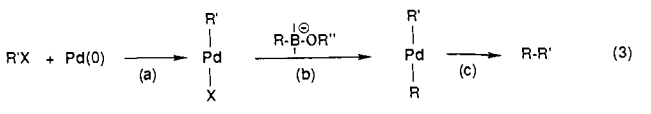
Table IV. Cross-Coupling Reaction of 9-Alkyl-9-BBN with 1-Halo-1-alkenes (Eq 7)

entry	haloalkene	alkene	product	% yield[a] procedure A[b]	C[b]	D[b]
1		1-octene		85 (X = Br),[c] 70 (X = I)[c]	82[c]	
2		1-octene		90[d]		
3		1-octene		94		
4		CH_2=$CH(CH_2)_8CO_2Me$			69	92
5		1-octene		98		
6				(80)		
7		CH_2=$CH(CH_2)_8CN$			(80)	
8					(73)	(79)
9					85	
10		CH_2=$CH(CH_2)_8CN$			(81)	(72)

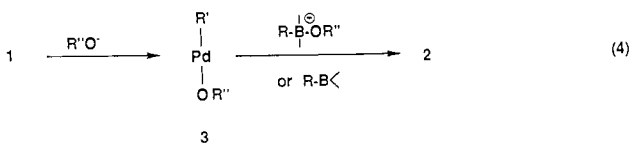
[a] GLC yields are based on the haloalkenes employed, and the isolated yields are in parentheses. [b] The 9-alkyl-9-BBN obtained by hydroboration of alkene (1.1 equiv) with 9-BBN (1.1 equiv) was directly used for the next coupling reaction with 1-halo-1-alkene (1 equiv). Procedure A: $PdCl_2$(dppf) (3 mol %) and NaOH (3 equiv) in THF at 65 °C. Procedure C: $PdCl_2$(dppf) (3 mol %) and K_2CO_3 (2 equiv) in DMF–THF at 50 °C. Procedure D: $PdCl_2$(dppf) (3 mol %) and K_3PO_4 (1 equiv) in DMF–THF at 50 °C. [c] β-Halostyrene (E/Z = 99/1) gave decenylbenzene (E/Z = 99/1). [d] β-Bromostyrene (E/Z = 1/99) gave decenylbenzene (E/Z = 3/97).

complex, obtained from *B*-octyl-9-BBN and 1 equiv of BuLi, with iodobenzene in refluxing THF in the presence of 3 mol % of $PdCl_2$(dppf) was complete in 5 h to give octylbenzene (50%) and butylbenzene (30%).

On the basis of these results, the role of bases can be attributed to the increase in the nucleophilicity of alkylboranes by their coordination with the boron atoms, thereby facilitating the transfer of the alkyl group from boron to palladium to make complexes **2** (eq 3 and 4). Although it is not clear at present whether the



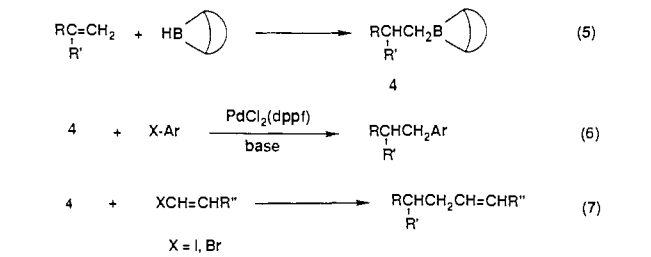
(3)



(4)

halogen ligand on **1** is displaced by base to give the more reactive Pd–OR complex **3** prior to the subsequent transmetalation reaction (eq 4), such a complex should be an intermediate in some of the reactions herein described because alkoxo- or hydroxopalladium (II) complexes have been postulated as reaction intermediates[18b-d] or isolated[18a] from the reaction of **1** with sodium hydroxide or methoxide.

Intermolecular Cross-Coupling. In Tables III and IV, the representative results of reaction of a variety of aryl halides or 1-halo-1-alkenes with 9-alkyl-9-BBN in the presence of $PdCl_2$-(dppf) and bases are summarized (eq 6 and 7). From these results



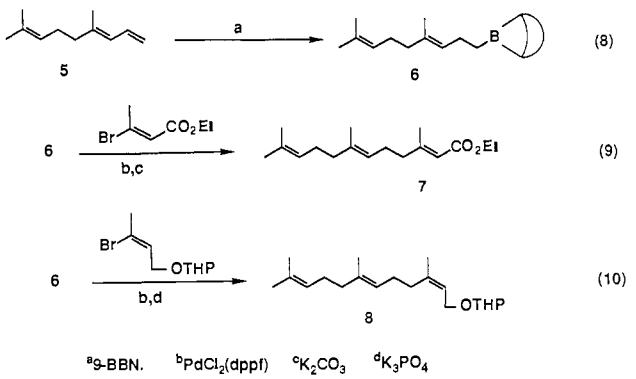
(5)

(6)

(7)

it is shown that this coupling reaction is applicable to aryl iodides and bromides substituted with various functional groups (Table III). Good yields of geometrically pure alkenes are also afforded from reactions with haloalkenes (Table IV). Although such coupling products were obtained in high yields when aqueous NaOH was used as a base (procedure A), the reaction can be carried out successfully under milder conditions with K_2CO_3 or K_3PO_4 in DMF (procedures C and D). The hydroboration is tolerant of various functional groups, and the organoboranes thus obtained are quite inert toward many functional groups. With use of K_2CO_3 or K_3PO_4 in DMF at 50 °C, the coupling between such functionalized alkylboranes and halides can proceed without protecting these groups. For example, the coupling between 1-bromo-2-methylpropene and *B*-(10-carbomethoxydecyl)-9-BBN in DMF at 50 °C in the presence of $PdCl_2$(dppf) and K_2CO_3 provided the expected ester in a yield of 69% after 8 h (entry 4 in Table IV). The same reaction gave the ester in 66% and 64% yields after 5 and 16 h, respectively. According to these results, the coupling was likely complete within 5–8 h, and the saponification of the ester group was not observed even for such a prolonged reaction. The synthesis of several other functionalized arenes and alkenes having cyano, acetyl, formyl, and carbomethoxy groups was demonstrated. In the case of the coupling reaction with *B*-alkyl-9-BBN having an epoxy group (entry 6 in Table III), the expected coupling product was obtained in only 52% yield, contaminated with a 30% yield of 7-(4-acetylphenyl)-2-methylheptane-1,2-diol, which was formed as a result of the epoxide ring opening with K_2CO_3.

The usefulness of the present method was demonstrated by the synthesis of 1,5-alkadienes and the extension of a side chain in a steroid (eq 8–11). Although the coupling reaction of two



(8)

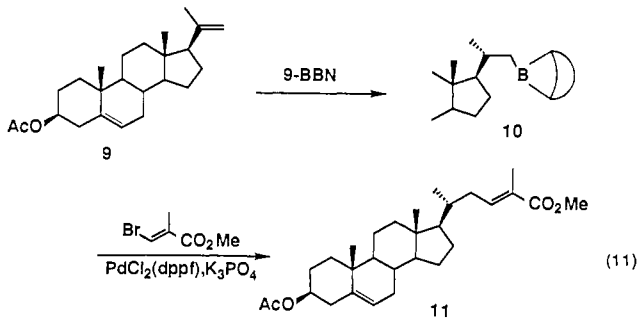
(9)

(10)

[a]9-BBN. [b]$PdCl_2$(dppf) [c]K_2CO_3 [d]K_3PO_4

different allylic units has been studied for the synthesis of 1,5-alkadienes,[19] the procedure does not afford good results due to extensive homo-coupling, allylic transposition, and loss of geometrical integrity of trisubstituted double bonds. A promising route would entail the cross-coupling between homoallylic metals[6] and vinylic halides. The selective hydroboration of a terminal double bond in the triene **5**, followed by the coupling with ethyl (*E*)-2-bromocrotonate in DMF using $PdCl_2$(dppf) and K_3PO_4, afforded the trienic ester[20] in 60% yield (eq 9). The reaction of **6** with (*Z*)-3-bromo-2-butanol tetrahydropyranyl ether gave a 67% yield of farnesol tetrahydropyranyl ether (**8**) (eq 10).

It has been reported that the hydroboration of 20(21)-methylene steroid **9**, prepared from pregrenolone acetate by Wittig reaction, with 9-BBN produces predominantly (20*R*)-21-boryl steroid **10**,[21] which has the natural configuration at C-20. The boronyl steroid thus obtained was subjected to cross-coupling with ethyl (*E*)-β-bromomethacrylate to give **11** in 75% yield (eq 11). The present



(11)

hydroboration-coupling approach for the construction of carbon skeletons affords several advantages. The stereoselectivity of hydroboration provides a stereodefined alkyl center on boron. The hydroboration occurs chemoselectively at the less hindered C19–C20 double bond even in the presence of a 5(6) double bond and acetyl group. In addition, the alkyl group thus constructed can be readily cross-coupled with alkenyl halides and probably aryl halides under mild conditions.

Intramolecular Cross-Coupling. A combination of hydroboration and the cross-coupling reaction may provide a versatile method

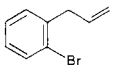
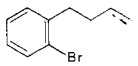
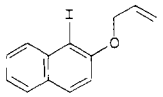
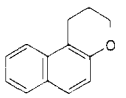
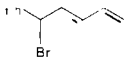
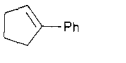
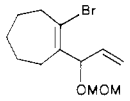
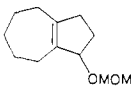
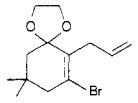
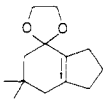
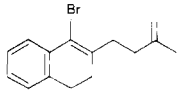
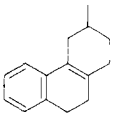
(18) (a) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (b) Anderson, C. B.; Burreson, B. J.; Michalowski, T. J. *J. Org. Chem.* **1976**, *41*, 1990. (c) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157. (d) Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619.

(19) (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595. (b) Godschalx, J.; Stille, J. K. *Ibid.* **1980**, *21*, 2599. (c) Goliaszewski, A.; Schwartz, J. *Tetrahedron* **1984**, *40*, 5779 and references therein.

(20) For a review on the synthesis of juvenile hormones, see: Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980; p 58.

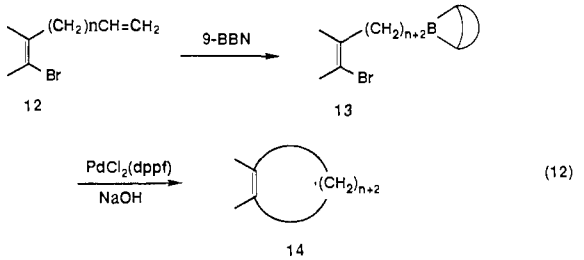
(21) (a) Bottin, J.; Fetizon, M. *J. Chem. Soc., Chem. Commun.* **1971**, 1087. (b) Midland, M. M.; Kwon, Y. C. *J. Org. Chem.* **1981**, *46*, 229.

Table V. Cyclization of Bromoalkenes via Intramolecular Cross-Coupling Reaction[a]

entry	haloalkene	product	% yield[b]
1			86
2			66
3			70
4			67
5			(68)
6			84 (71)
7			77 (68)

[a] Hydroboration of bromoalkenes with 9-BBN was carried out in THF at 0 °C–room temperature for 4 h, and then the boranes thus obtained were cross-coupled intramolecularly in the presence of $PdCl_2$(dppf) (1.5 mol %) and NaOH (3 equiv). [b] GLC yields are based on the bromoalkenes employed, and the isolated yields are in parentheses.

for the synthesis of cycloalkenes and benzo-fused cycloalkanes (eq 12). It has been found that five- and six-membered rings

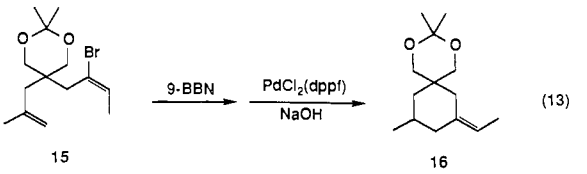


(12)

(**14**) can be obtained in good yields by hydroboration of haloalkenes (**12**) with 9-BBN, followed by treatment with 1.5 mol % of $PdCl_2$(dppf) and 3 equiv of aqueous sodium hydroxide (Table V). The addition of boron to double bonds occurs at the terminal position exclusively. Thus the size of rings can be varied depending on the chain length of the ω-alkenyl groups. Although the intramolecular cyclization proceeded especially smoothly when the cyclization resulted in the formation of either a five- or a six-membered ring, the synthesis of a four- or a seven-membered ring was unsuccessful. For example, 2-bromostyrene led to styrene (45%) and some minor unidentified products formed by β-elimination of the hydridopalladium(II) from the palladacyclopentane intermediate. No volatile compounds were obtained from 1-bromo-2-(4-pentenyl)benzene, presumably due to intermolecular coupling.

Several routes are available for syntheses of the starting haloalkenes: (a) a palladium-catalyzed addition[22] of allylic halides to alkynes (entry 4), (b) a allylmetalation[23] of alkynes, followed by halogenolysis, (c) a modified Vilsmeier reaction[24] with ketones using triphenylphosphine diboromide in DMF to give α-bromo-α,β-unsaturated aldehydes, which is especially useful for the synthesis of cyclic bromoalkenes (entries 5 and 7), (d) Corey's reductive halogenation[25] of ethynyl carbinols, and (e) the haloboration[26] or addition of hydrogen bromide[27] to terminal alkynes. The cyclization methods that are available include hydroalumination–halogenolysis–cyclization process[23] and radical cyclization.[28] The present procedure, however, affords an alternative and simple method for cyclization of such haloalkenes.

The potential versatility of this reaction is indicated in eq 13. The hydroboration of dienic bromide **15** and subsequent intramolecular coupling gave **16** in 75% yield without any difficulty. As illustrated in eq 13, the stereodefined exocyclic alkenes[29] can be readily synthesized by the present procedure. Further studies of the cyclization process to other five- or six-membered exocyclic alkenes are in progress.



15 16 (13)

Experimental Section

All the experiments were carried out under a nitrogen atmosphere. THF was purified by distillation from benzophenone ketyl under a nitrogen atmosphere before use. DMF was distilled from calcium hydride. The IR spectra were recorded on a Hitachi Perkin-Elmer Model 125 spectrometer. The ^1H NMR spectra were measured with a Hitachi R-90H (90 MHz) or a Brucker MSL-400 (400 MHz) spectrometer (solvent, $CDCl_3$; TMS as an internal reference). Mass spectra were recorded on a JEOL JMS-D 300 for the high-resolution analysis and a Finnigan ITD 800. GLC analyses were performed with a Hitachi 023 gas chromatograph using a fused silica capillary column (OV-101, 25 m).

Boranes. Diborane in THF and 9-borabicyclo[3.3.1]nonane (9-BBN) in THF from Aldrich Chemical Co. were used directly. Trioctylborane, octyldisiamylborane, and octyldicyclohexylborane were prepared by hydroboration[13a] of octene. 9-Methyl-9-BBN[30] and 2-octyl-1,3,2-dioxaborinane[31] were prepared according to the literature procedures.

Haloarenes and Alkenes. 4-Bromoacetophenone, 3-bromobenzaldehyde, 1-bromonaphthalene, 2-iodoanisole, methyl 4-iodobenzoate, and (*E*)-β-bromostyrene were commercial products. (*Z*)-β-Bromostyrene,[32] 1-bromo-2-methyl-1-propene,[33] (*Z*)-2-bromo-2-butene,[34] methyl (*E*)-β-bromomethacrylate,[35] 3-bromo-5,5-dimethyl-2-cyclohexenone,[36] and 3,4-(methylenedioxy)-1-iodobenzene[37] were prepared by using the reported procedures. A mixture of (*E*)- and (*Z*)-β-bromocrotonates (4:6)[38] was prepared by the reaction of hydrogen bromide with ethyl propynoate, which was purified by chromatography over silica gel with hexane–CH_2Cl_2 (2:1).

Haloalkenes used for the intramolecular cross-coupling reaction are as follows.

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(Z)-1-Bromo-1-phenyl-1,4-pentadiene.[22] The reaction of allyl bromide with phenylethyne in the presence of $PdCl_2(PhCN)_2$ gave the compound in a yield of 90%.

1-Bromo-2-[1-(methoxymethoxy)-2-propenyl]-1-cycloheptene. To a solution of triphenylphosphine (80 mmol) in benzene (100 mL) was added slowly bromine (80 mmol) at 0 °C, and then the mixture was stirred for 15 min at room temperature. Then, DMF (20 mL) was introduced and the mixture was stirred for an additional hour. A solution of cycloheptanone (35 mmol) in benzene (15 mL) was added and stirred for 1 h at room temperature and then for 3 h at refluxing temperature. The reaction mixture was poured into ice water (100 mL) and made alkaline by careful addition of sodium carbonate. The product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Distillation gave 1-bromo-2-formyl-1-cycloheptene, bp 68 °C (0.1 mmHg), in 45% yield.

To a solution of 1-bromo-2-formyl-1-cycloheptene (10 mmol) in 10 mL of THF was added 10 mL (1.2 M, 12 mmol) of vinylmagnesium bromide in THF at 0 °C. The mixture was stirred for 2 h at room temperature. To this was added chloromethyl methyl ether (12 mmol), and then the mixture was refluxed for 2 h. The resulting solution was poured into aqueous NH_4Cl, and then the organic phase was washed with brine and aqueous Na_2CO_3 and dried over $MgSO_4$. The compound was isolated by distillation, bp 85–90 °C (0.1 mmHg) (oven temperature of the Kugelrohr apparatus), in 80% yield: IR (film) 1650, 1155, 1040, 924 cm^{-1}; ^1H NMR δ 1.25–1.90 (m, 6 H), 2.1–2.2 (m, 2 H), 2.65–2.85 (m, 2 H), 3.38 (s, 3 H), 4.59 (s, 2 H), 5.0–5.9 (m, 4 H); MS (ITD), *m/e* 133 (100), 163 (16), 195 (9), 213, 215 (42 and 32), 274 (3) and 276 (3); exact mass calcd for $C_{12}H_{19}O_2Br$ 274.056 02 and 276.051 50, found 274.056 10 and 276.051 80.

2-Allyl-3-bromo-5,5-dimethyl-2-cyclohexenone and Its Ethylene Acetal. 2-Allyl-5,5-dimethyl-1,3-cyclohexanedione (19 mmol) was treated with triphenylphosphine dibromide according to the peported procedure.[36] The bromo enone (3.3 g) thus obtained was converted into its ethylene acetal by using an excess of ethylene glycol (38 mmol), trimethyl orthoformate (0.11 mol), and TsOH (0.3 g) in ether (15 mL) for 4 days at room temperature. Chromatography over silica gel with benzene–ethyl acetate (20:1) gave the compound (61%): n_D 1.5160; IR (film) 1653, 1640, 1307, 1103, 1025, 980, 950, 910, 850, 798 cm^{-1}; ^1H NMR δ 1.02 (s, 6 H), 1.68 (s, 2 H), 2.43 (s, 2 H), 2.98 (d, 2 H, J = 7.0 Hz), 3.97 (s, 4 H), 4.90–5.25 (m, 2 H), 5.6–6.1 (m, 1 H); MS (ITD), *m/e* 87 (28), 151 (100), 207 (91), 230 (29), 232 (28), 245 (20), 271 (8), 273 (7), 286, and 288 (52 and 34); exact mass calcd for $C_{13}H_{19}O_2Br$ 286.055 36 and 288.053 26, found 286.055 50 and 288.053 40.

1-Bromo-2-(3-methyl-3-butenyl)-3,4-dihydronaphthalene. The procedure used for the synthesis of 1-bromo-2-formyl-1-cycloheptene gave 1-bromo-2-formyl-3,4-dihydronaphthalene from 5.1 g (35 mmol) of α-tetralone, bp 115 °C (0.1 mmHg), in 73% yield. Reduction of the formyl group with diisobutylaluminum hydride (28 mmol) in ether (50 mL) at 0 °C gave the allylic alcohol, which was treated with PBr_3 (13 mmol) in ether (30 mL) at 0 °C for 5 h to give 1-bromo-2-(bromomethyl)-3,4-dihydronaphthalene (64%), bp 139 °C (0.1 mmHg).

To a solution of the above allylic bromide (13 mmol) and copper(I) iodide (2 mmol) in THF was added (2-methyl-2-propenyl)magnesium bromide (20 mmol) in THF at −50 °C. The mixture was stirred for 1 h, gradually warmed up to room temperature, and then stirred overnight. The mixture was quenched with 1 N HCl and then extracted with hexane. The product was isolated by chromatography over silica gel with hexane, 58%: n_D 1.5880; IR (film) 1650, 1620, 1480, 940, 885, 803, 755 cm^{-1}; ^1H NMR δ 1.89 (s, 3 H), 2.0–2.9 (m, 8 H), 4.73 (s, 2 H), 7.0–7.7 (m, 4 H); MS (ITD), *m/e* 115 (10), 141 (44), 197 (100), 221 (59), 223 (64), 276 (39), 278 (39); exact mass calcd for $C_{15}H_{17}Br$ 276.049 87 and 278.049 08, found 276.050 00 and 278.049 10.

Alkenes. 1-Octene, 2-methyl-1-propene, β-pinene, camphene, and methyl 10-undecenoate were commerical products. (3*E*)-4,8-Dimethyl-1,3,7-nonatriene,[39] 10-cyano-1-decene,[40] and 6-methyl-6,7-epoxy-1-pentene[41] were prepared by using the reported procedures. 3β-Acetoxy-20-methylenepregn-5-ene was prepared from pregnenolone acetate by the Sondheimer's method[42] in 65% yield.

Palladium Catalyst. Palladium(II) acetate and dichlorobis(triphenylphosphine)palladium(II) were commerical products. Tetrakis(triphenylphosphine)palladium(0),[43] dichlorobis[1,1′-bis(diphenylphosphino)ferrocene]palladium(II),[48] *trans*-iodophenylbis(triphenylphosphine)palladium(II),[15] and dichlorobis(benzonitrile)palladium(II)[44] were prepared by using the literature procedures.

Reaction Conditions (Tables I and II). The best conditions for the formation of octylbenzene were determined by employing the following general procedure. The palladium catalyst (3 mol %) was placed in a 25-mL flask containing a septum inlet, a reflux condenser, and a oil bubbler. The flask was flushed with nitrogen and then charged with 5 mL of solvent. One millimole of iodobenzene, octylboranes, or boronate in THF (1.1 mmol) and a base were added by means of a hypodermic syringe through the septum inlet. Then, the mixture was stirred for 16 h at the temperature indicated in the tables. After the reaction was over, the mixture was cooled to room temperature and the residual borane was oxidized with an aqueous solution of NaOH (3 M, 0.5 ml)–H_2O_2 (30%, 0.5 mL) for 1 h. Octylbenzene was extracted with hexane, washed with water four times to remove cyclooctane-1,5-diol or DMF, and dried over $MgSO_4$. GLC yields are summarized in Tables I and II.

Stoichiometric Reaction of Trioctylborane with Palladium(II) Complexes. To 90 mg (0.4 mmol) of $Pd(OAc)_2$ in 4 mL of benzene was added 0.5 mL (0.8 M, 0.4 mmol) of trioctylborane in THF. The mixture was refluxed for 30 min. When the reaction mixture was heated, it immediately turned into a dark solution, and palladium black was precipitated. GLC analysis of the reaction mixture using cyclooctane as an internal standard indicated that octane (59%), octene (3%, a mixture of several isomers), and hexadecane (<1%) were formed.

In the same way, the reaction of trioctylborane (0.4 mmol) with $PdCl_2$ (0.4 mmol), $PdCl_2(PPh_3)_2$ (0.4 mmol), or $PhPd(PPh_3)_2I$ (0.4 mmol) in benzene (4 mL) was conducted at refluxing temperature for 1 h. No precipitate of palladium black or change of color of the palladium(II) complexes was observed. GLC analysis indicated that yields of octane, octene, or octylbenzene were less than 1%.

Reaction of Iodobenzene with the Ate Complex Obtained from *B*-Octyl-9-BBN and Butyllithium. To a solution of *B*-octyl-9-BBN (1.1 mmol) in 5 mL of THF was added a solution of BuLi (1.4 M, 1.1 mmol) in hexane at −60 °C. The reaction mixture was warmed up slowly and stirred for 30 min at room temperature. Iodobenzene (1 mmol) and $PdCl_2(dppf)$ (22 mg) were added, and then the mixture was refluxed for 5 h. The residual borane was oxidized by addition of aqueous 3 M NaOH (1 mL) and 30% H_2O_2 (1 mL) at room temperature for 1 h. GLC analysis using tetradecane as an internal standard indicated that butylbenzene (30%) and octylbenzene (50%), which were identified by coinjection with authentic samples and their mass spectra, were formed.

General Procedure for Intermolecular Cross-Coupling (Tables III and IV). A dry 50-mL flask equipped with a magnetic stirring bar, a septum inlet, an oil bubbler, and a reflux condenser was flushed with nitrogen. To the flask were added an alkene (5.5 mmol) and dry THF (2.5 mL) and then a solution of 9-BBN (0.5 M solution in THF, 5.5 mmol) at 0 °C. The mixture was warmed up slowly to room temperature and then stirred for 4–6 h to give a solution of *B*-alkyl-9-BBN.

Procedure A. To the above solution were added $PdCl_2(dppf)$ (0.15 mmol), haloarene or 1-halo-1-alkene (5 mmol), additional THF (12 mL), and aqueous NaOH (5 mL of 3 M solution) at room temperature. The mixture was refluxed overnight (ca. 14–16 h). After the reaction was completed, the reaction mixture was diluted with hexane or benzene (20 mL), and the residual borane was oxidized by addition of H_2O_2 (30%, 2 mL) at room temperature. The product was extracted, washed with brine, and dried over $MgSO_4$. When a product was sensitive to the alkaline hydrogen peroxide oxidation, the extracts were directly subjected to column chromatography without oxidation.

Procedure B. To a solution of 9-alkyl-9-BBN in THF were added an additional 12 mL of THF, $PdCl_2(dppf)$ (0.15 mmol), haloarene (5 mmol), and powdered NaOMe (7.5 mmol). After heating at the reflux temperature for 16 h, the reaction mixture was treated by the usual manner as shown in procedure A.

Procedure C and D. To the above borane solution were added DMF (25 mL), $PdCl_2(dppf)$ (0.15 mmol), haloalkene or haloarene (5 mmol), and powdered K_2CO_3 (10 mmol) (procedure C) or K_3PO_4 (6 mmol) (procedure D). The mixture was stirred for 8 h at 50 °C and then poured into water. The product was extracted with benzene, washed with water four times, and dried over $MgSO_4$.

The compounds prepared by the above procedures are as follows.

2-Methoxy-1-octylbenzene: n_D 1.4925; IR (film) 1605, 1595, 1498, 1242, 750 cm^{-1}; ^1H NMR δ 0.88 (t, 3 H, J = 6 Hz), 1.0–1.8 (m, 12 H), 2.60 (t, 2 H, J = 7.2 Hz), 3.81 (s, 3 H); MS (ITD), *m/e* 65 (6), 91 (33), 121 (100), 220 (50); exact mass calcd for $C_{15}H_{24}O$ 220.181 93, found 220.182 00.

3,4-(Methylenedioxy)-1-octylbenzene: n_D 1.5028; IR (film) 1247, 1050, 946, 805 cm^{-1}; ^1H NMR δ 0.88 (t, 3 H, J = 6 Hz), 1.1–1.7 (m, 12 H), 2.52 (t, 2 H, J = 7.0 Hz), 5.90 (s, 2 H), 6.5–6.9 (m, 3 H); MS (ITD), *m/e* 135 (89), 136 (30), 234 (100); exact mass calcd for $C_{15}H_{22}O_2$ 234.161 79, found 234.161 80.

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1-(2-Methylpropyl)naphthalene: n_D 1.5749; IR (film) 1600, 1510, 1395, 1385, 1365, 1165, 790, 775 cm^{-1}; ^1H NMR δ 0.97 (d, 6 H, J = 6.6 Hz), 2.07 (qqt, 1 H, J = 6.6, 6.6, and 7.0 Hz), 2.93 (d, 2 H, J = 7.0 Hz), 7.15–8.10 (m, 7 H); MS (ITD), m/e 115 (7), 141 (70), 142 (25), 183 (21), 184 (100); exact mass calcd for $C_{14}H_{16}$ 184.125 09, found 184.125 10.

4-(10-Carbomethoxydecanyl)acetophenone: mp 48 °C; IR (Nujol) 1741, 1685, 1610 cm^{-1}; ^1H NMR δ 1.2–1.4 (m, 12 H), 1.4–1.8 (m, 4 H), 2.30 (t, 2 H, J = 7.0 Hz), 2.58 (s, 3 H), 2.66 (t, 2 H, J = 7.0 Hz), 3.66 (s, 3 H), 7.25 (d, 2 H, J = 8.5 Hz), 7.87 (d, 2 H, J = 8.5 Hz); MS, m/e 43 (100), 105 (33), 147 (50), 244 (16), 286 (33), 318 (25); exact mass calcd for $C_{20}H_{30}O_3$ 318.219 13, found 318.219 10.

4-(10-Cyanodecanyl)acetophenone: n_D 1.5120; IR (film) 2250, 1683, 1610, 1360, 1267, 1182, 960 cm^{-1}; ^1H NMR δ 1.2–2.0 (m, 16 H), 2.32 (t, 2 H, J = 6.9 Hz), 2.58 (s, 3 H), 2.67 (t, 2 H, J = 6.8 Hz), 7.21 (d, 2 H, J = 8.2 Hz), 7.88 (d, 2 H, J = 8.2 Hz); MS, m/e 147 (98), 270 (100), 271 (22), 285 (33); exact mass calcd for $C_{19}H_{27}NO$ 285.210 03, found 285.209 96.

4-(6,7-Epoxy-6-methylhexyl)acetophenone: n_D 1.5209; IR (film) 1685, 1615, 1360, 1275, 1190, 963, 904 cm^{-1}; ^1H NMR δ 1.29 (s, 3 H), 1.35–1.80 (m, 6 H), 2.58 (s, 5 H), 2.68 (t, 2 H, J = 7.4 Hz), 7.25 (d, 2 H, J = 8.3 Hz), 7.88 (d, 2 H, J = 8.3 Hz); MS, m/e 147 (47), 204 (29), 217 (22), 232 (25); exact mass calcd for $C_{15}H_{20}O_2$ 232.145 66, found 232.145 71.

3-[5,5-(Ethylenedioxy)hexyl]benzaldehyde: low melting solid; IR (Nujol) 1700, 1607, 1590 cm^{-1}; ^1H NMR δ 1.30 (s, 3 H), 1.4–1.8 (m, 6 H), 2.69 (t, 2 H, J = 6.8 Hz), 3.92 (s, 4 H), 7.2–8.0 (m, 4 H); MS, m/e 43 (30), 87 (100), 119 (7), 147 (3), 186 (5), 233 (8, M^+ – Me), 249 (1, M^+ + 1); exact mass calcd for $C_{14}H_{17}O_3$ (M^+ – Me) 233.117 74, found 233.117 73.

Methyl 4-(10-carbomethoxydecanyl)benzoate: mp 40 °C; IR (Nujol) 1740, 1725, 1620, 1280, 1170, 1115 cm^{-1}; ^1H NMR δ 1.2–1.4 (m, 12 H), 1.45–1.80 (m, 4 H), 2.30 (t, 2 H, J = 7.0 Hz), 2.66 (t, 2 H, J = 7.0 Hz), 3.66 (s, 3 H), 3.89 (s, 3 H), 7.20 (d, 2 H, J = 8.1 Hz), 7.90 (d, 2 H, J = 8.1 Hz); MS, m/e 131 (69), 149 (32), 302 (100), 334 (1); exact mass calcd for $C_{20}H_{30}O_4$ 334.212 09, found 334.212 29.

Methyl 4-Methylbenzoate, (*E*)-1-Phenyl-1-decene, (*Z*)-1-Phenyl-1-decene, and 2-Methyl-2-undecene. The products were directly compared with the corresponding authentic samples.

(*Z*)-3-Methyl-2-undecene: n_D 1.4378; IR (film) 1120, 810, 720 cm^{-1}; ^1H NMR δ 0.88 (t, 3 H, J = 6.0 Hz), 1.1–1.4 (m, 12 H), 1.56 (d, 3 H, J = 7.0 Hz), 1.66 (t, 3 H, J = 1.3 Hz), 5.16 (q, 1 H, J = 7.0 Hz); MS, m/e 55 (38), 70 (100), 83 (20), 139 (4), 168 (12); exact mass calcd for $C_{12}H_{24}$ 168.187 30, found 168.187 34.

(*E*)-2-Methyl-6-(3,4-dimethoxyphenyl)-2-hexenol tetrahydropyranyl ether: n_D 1.5230; IR (film) 1610, 1595, 1260, 1235, 1030 cm^{-1}; ^1H NMR δ 1.4–1.85 (m, 11 H), 1.85–2.25 (m, 2 H), 2.57 (t, 2 H, J = 7.2 Hz), 3.85 (s, 3 H), 3.87 (s, 3 H), 3.3–4.2 (m, 4 H), 4.60 (br s, 1 H), 5.46 (t, 1 H, J = 7.2 Hz), 6.6–6.9 (m, 3 H); MS, m/e 85 (100), 151 (76), 164 (38), 177 (17), 191 (14), 232 (15), 233 (16), 334 (20); exact mass calcd for $C_{20}H_{30}O_4$ 334.213 44, found 334.213 52.

Methyl 13-Methyl-12-tetradecenoate: n_D 1.4523; IR (film) 1753, 1200, 1180 cm^{-1}; ^1H NMR δ 1.15–1.4 (m, 16 H), 1.59 (s, 3 H), 1.68 (s, 3 H), 1.8–2.1 (m, 2 H), 2.30 (t, 2 H, J = 7.1 Hz), 3.66 (s, 3 H), 5.10 (t, 1 H, J = 7.1 Hz); MS, m/e 69 (100), 167 (11), 199 (10), 222 (10), 254 (5); exact mass calcd for $C_{16}H_{30}O_2$ 254.224 88, found 254.224 85.

Methyl (*E*)-13-cyano-2-methyl-2-tridecenoate: n_D 1.4681; IR (film) 2260, 1720, 1660 cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 16 H), 1.83 (s, 3 H), 2.0–2.5 (m, 4 H), 3.73 (s, 3 H), 6.77 (t, 1 H, J = 6.0 Hz); MS, m/e 95 (100), 233 (30), 265 (1); exact mass calcd for $C_{16}H_{27}NO_2$ 265.205 48, found 265.205 36.

Methyl (*E*)-2-methyl-3-(pinan-10-yl)-2-propenoate: n_D 1.960; IR (film) 1720, 1650, 1285, 1200, 1155, 1120, 1090, 740 cm^{-1}; ^1H NMR δ 1.06 (s, 3 H), 1.19 (s, 3 H), 1.3–2.5 (m, 11 H), 1.83 (s, 3 H), 3.73 (s, 3 H), 6.75 (t, 1 H, J = 7.0 Hz); MS, m/e 69 (100), 81 (58), 114 (37), 123 (80), 149 (11), 161 (7), 177 (8), 193 (4), 205 (6), 236 (4); exact mass calcd for $C_{15}H_{24}O_2$ 236.177 47, found 236.178 40.

Methyl (*E*)-2-methyl-4-(2,2-dimethylnorborn-3-yl)-2-butenoate: n_D 1.4945; IR (film) 1720, 1655, 1280, 1255, 1120, 1105, 1090, 743 cm^{-1}; ^1H NMR δ 0.84 (s, 3 H), 0.95 (s, 3 H), 0.9–1.8 (m, 9 H), 1.84 (s, 3 H), 2.12 (dd, 2 H, J = 6.9 and 7.4 Hz), 3.72 (s, 1 H), 6.71 (t, 1 H, J = 7.4 Hz); MS, m/e 67 (78), 81 (57), 93 (39), 123 (100), 136 (56), 148 (9), 205 (9), 236 (11); exact mass calcd for $C_{15}H_{24}O_2$ 236.177 47, found 236.177 48.

3-(10-Cyanodecanyl)-5,5-dimethyl-2-cyclohexenone: n_D 1.4858; IR (film) 2250, 1670, 1630, 1370, 1300, 1280, 1245, 903 cm^{-1}; ^1H NMR δ 1.03 (s, 6 H), 1.2–1.8 (m, 16 H), 2.17 (s, 2 H), 2.17 (t, 2 H, J = 7.1 Hz), 2.20 (s, 2 H), 2.33 (t, 2 H, J = 6.7 Hz), 5.87 (s, 1 H); MS, m/e 82 (100), 95 (33), 138 (39), 151 (85), 274 (49), 289 (18); exact mass calcd for $C_{19}H_{31}NO$ 289.238 94, found 289.239 08.

Ethyl (2*E*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrienoate (7). To a solution of (3*E*)-4,8-dimethyl-1,3,7-nonatriene (1.4 mmol) in THF (1 mL) was added a solution of 9-BBN in THF (0.5M, 1.4 mmol) at 0 °C over 10 min. The mixture was stirred for 1 h at 0 °C and then for 4 h at room temperature. DMF (7 mL), ethyl (*E*)-β-bromocrotonate (1.4 mmol), $PdCl_2$(dppf) (22mg), and K_3PO_4 (0.32 g) were added. After heating at 50 °C for 8 h, the mixture was poured into water. The product was extracted with benzene, washed with water four times, and dried over $MgSO_4$. Chromatography over silica gel with benzene–ethyl acetate (40:1) gave a oil, 0.21 g (60%). **7**: n_D 1.4859; IR (film) 1710, 1645, 1215, 1127, 1055, 1035, 860 cm^{-1}; ^1H NMR δ 1.27 (t, 3 H, J = 7.0 Hz), 1.60 (s, 6 H), 1.67 (s, 3 H), 1.9–2.4 (m, 8 H), 2.16 (d, 3 H, J = 1.3 Hz), 4.14 (q, 2 H, J = 7.0 Hz), 5.07 (br s, 2 H), 5.63 (q, 1 H, J = 1.3 Hz); exact mass calcd for $C_{17}H_{28}O_2$ 264.207 61, found 264.207 72.

(2*Z*,6*E*)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol Tetrahydropyranyl Ether (8). The hydroboration of triene **5** was conducted under the same procedure as for the synthesis of trienic ester **7**. $PdCl_2$(dppf) (20 mg), (*Z*)-β-bromocrotyl alcohol tetrahydropyranyl ether (1.4 mmol), and aqueous 3 M NaOH (1.4 mL) were added. After refluxing for 8 h, the product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Chromatography over silica gel with CH_2Cl_2 gave an oil, 0.288 g (67%). The ^1H NMR spectrum and the retention time on GLC were in good agreement with those of authentic samples obtained from commercial (*E*,*E*)- and (*E*,*Z*)-farnesol.

Steroid 11. To a solution of 3β-acetoxy-20-methylenepregn-5-ene (0.356 g, 1 mmol) in THF (1 mL) was added a solution of 9-BBN (0.5M, 1 mmol) at 0 °C; the mixture gradually warmed up to room temperature and was then stirred overnight. DMF (7 mL), $PdCl_2$(dppf) (22 mg), K_3PO_4 (1 mmol), and methyl (*E*)-β-bromomethacrylate (1.1 mmol) were added to the mixture. After stirring for 8 h at 50 °C, the mixture was worked up in the usual way. Chromatography over silica gel with benzene–ethyl acetate (20:1) gave a white solid which was recrystallized from methanol, 0.343 g (75%). **11**: mp 122 °C; IR (Nujol) 1740, 1727, 1660, 1245, 1140, 1040, 740 cm^{-1}; ^1H NMR δ 0.67 (s, 3 H), 0.94 (d, 3 H, J = 6.4 Hz), 1.02 (s, 3 H), 2.02 (s, 3 H), 0.9–2.4 (m, 23 H), 3.73 (s, 3 H), 4.4–4.8 (m, 1 H), 5.35 (d, 1 H, J = 4.1 Hz), 6.8 (t, 1 H, J = 6.9 Hz); MS, m/e 81(59), 145 (36), 283 (26), 381 (11), 396 (100, M^+ – AcOH), 425, (22, M^+ – OMe); exact mass calcd for $C_{27}H_{40}O_2$ (M^+ – AcOH) 396.300 82, found 396.300 99.

General Procedure for Intramolecular Cross-Coupling (Table V). The following procedure for the preparation of 8-(methoxymethoxy)bicyclo-[5.3.0]dec-1(7)-ene is representative. To a solution of 1-bromo-2-(1-(methoxymethoxy)-2-propenyl)cycloheptene (1.72 mmol) in THF (3 mL) was added 9-BBN (0.5 M solution in THF, 1.8 mmol) at 0 °C. Then, the mixture was stirred for 5 h at room temperature, and $PdCl_2$(dppf) (22 mg) and aqueous 3 M NaOH (1.7 mL) were added. After refluxing for 14 h, the unreacted borane was oxidized with 30% hydrogen peroxide (0.5 mL) for 1 h. After the usual workup, the product was isolated by chromatography over silica gel with hexane–ether (20:1), 0.213 g (68%); n_D 1.4845; IR (film) 1140, 1095, 1030, 910 cm^{-1}; ^1H NMR δ 1.4–1.9 (m, 8 H), 1.9–2.5 (m, 6 H), 3.39 (s, 3 H), 4.35–4.7 (m, 1 H), 4.60 (d, 1 H, J = 6.5 Hz), 4.72 (d, 1 H, J = 6.5 Hz); MS (ITD), m/e 135 (100), 165 (2), 195 (4), 268 (0.6); exact mass calcd for $C_{12}H_{20}O_2$ 196.143 77, found 196.144 00.

The following compounds were prepared by the above procedure.

Indan, Tetralin, and Phenylcyclopentene. These were compared directly with authentic samples.

3,4-Dihydro-2*H*-1-oxaphenanthrene: mp 35 °C; IR (Nujol) 3075, 1630, 1605, 1243, 1100, 1075, 820 cm^{-1}; ^1H NMR δ 2.12 (tt, 2 H, J = 5.3 and 6.6 Hz), 3.05 (t, 2 H, J = 6.6 Hz), 4.24 (t, 2 H, J = 5.3 Hz), 6.9–7.8 (m, 6 H); MS, m/e 102 (2), 115 (3), 128 (8), 141 (3), 155 (4), 169 (3), 184 (100); exact mass calcd for $C_{13}H_{12}O$ 184.088 54, found 184.088 56.

2,3-Trimethylene-5,5-dimethyl-2-cyclohexenone ethylene acetal: mp 36 °C; IR (nujol) 1680 cm^{-1}; ^1H NMR δ 0.99 (s, 6 H), 1.67 (s, 2 H), 1.7–2.0 (m, 4 H), 2.1–2.5 (m, 4 H), 3.94 (s, 4 H); MS (ITD), m/e 152 (100), 207 (31), 208 (82); exact mass calcd for $C_{13}H_{20}O_2$ 208.147 41, found 208.147 31.

3-Methyl-1,2,3,4,9,10-hexahydrophenanthrene: n_D 1.5783; IR (film) 1650, 1600, 935, 750, 725 cm^{-1}; ^1H NMR δ 1.07 (d, 3 H, J = 6.2 Hz), 1.2–2.9 (m, 11 H), 7.0–7.2 (m, 4 H); MS (ITD), m/e 141 (3), 155 (1), 169 (1), 183 (0.7), 198 (100); exact mass calcd for $C_{15}H_{18}$ 198.139 57, found 198.139 68.

8-[(*Z*)-Ethylidene]-3,3,10-trimethyl-1,5-dioxaspiro[5.5]undecane (16): n_D 1.4770; IR (film) 1385, 1370, 1205, 1093, 1035, 865, 842, 825 cm^{-1}; ^1H NMR (400 MHz) δ 0.79 (dd, 1 H, J = 12.9 and 12.9 Hz), 0.94 (d, 3 H, J = 6.4 Hz), 1.26 (dd, 1 H, J = 12.1 and 12.1 Hz), 1.41 (s, 6 H), 1.4–1.5 (m, 1 H), 1.59 (dt, 3 H, J = 1.6 and 6.7 Hz), 1.70 (d, 1 H, J = 13.2 Hz), 1.79 (dt, 1 H, J = 1.6 and 13.3 Hz), 2.33 (d, 1 H, J = 13.1 Hz), 2.59 (dt, 1 H, J = 1.8 and 13.1 Hz), 3.4–3.6 (four lines, 4 H), 5.22

(q, 1 H, J = 6.7 Hz); MS, m/e 93 (58), 107 (100), 149 (51), 166 (33), 209 (29), 224 (15); exact mass calcd for $C_{14}H_{24}O_2$ 224.178 26, found 224.178 20.

Registry No. 5, 19945-61-0; **7**, 19954-66-6; **8**, 110990-63-1; **9**, 38388-16-8; **11**, 117582-51-1; **15**, 117582-60-2; **16**, 117582-59-9; 9-BBN, 280-64-8; *B*-$CH_3(CH_2)_7$-9-BBN, 30089-00-0; *B*-Me-9-BBN, 23418-81-7; $CH_3(CH_2)_7B(Sia)_2$, 32327-50-7; $CH_3(CH_2)_7B(c\text{-}C_6H_{11})_2$, 38103-67-2; $PdCl_2(dppf)$, 72287-26-4; $Pd(PPh_3)_4$, 14221-01-3; $CH_3(CH_2)_7BOCH_2CH_2CH_2O$, 117582-36-2; *s*-$Bu_3B$, 1113-78-6; $Pd(OAc)_2$, 3375-31-3; $PdCl_2$, 7647-10-1; *o*-$MeOC_6H_4I$, 529-28-2; $CH_2{=}CH(CH_2)_8CN$, 53179-04-7; $CH_2{=}CH(CH_2)_2C(CH_3)OCH_2$, 117582-37-3; $CH_2{=}CH(CH_2)_2C(CH_3)OCH_2CH_2O$, 20449-21-2; (*E*)-PhCH=CHBr, 588-72-7; PhCH=CH•, 23065-05-6; (*Z*)-PhCH=CHBr, 588-73-8; $(CH_3)_2C{=}CHBr$, 3017-69-4; (*Z*)-$CH_3CH{=}CBrCH_3$, 3017-68-3; (*E*)-$THPOCH_2C(CH_3){=}CHBr$, 117582-49-7; (*E*)-$MeO_2CC(CH_3){=}CHBr$, 40053-01-8; *o*-$BrC_6H_4(CH_2)_2CH{=}CH_2$, 71813-50-8; $PdCl_2(PhCN)_2$, 14220-64-5; octylbenzene, 2189-60-8; iodobenzene, 591-50-4; trioctylborane, 3248-78-0; tricyclopentylborane, 23985-40-2; tricyclohexylborane, 1088-01-3; butylbenzene, 104-51-8; 5-iodo-1,3-benzodioxole, 5876-51-7; 1-bromonaphthalene, 90-11-9; 1-(4-bromophenyl)ethanone, 99-90-1; 3-bromobenzaldehyde, 3132-99-8; methyl 4-iodobenzoate, 619-44-3; 1-octene, 111-66-0; 2-methyl-1-propene, 115-11-7; methyl 10-undecenoate, 111-81-9; 2-methoxy-1-octylbenzene, 20056-59-1; 3,4-(methylenedioxy)-1-octylbenzene, 109636-18-2; 1-(2-methylpropyl)naphthalene, 16727-91-6; 4-(10-carbomethoxy)acetophenone, 117582-38-4; 4-(10-cyanodecanyl)-acetophenone, 117582-39-5; 4-(6,7-epoxy-6-methylhexyl)acetophenone, 117582-40-8; 3-[5,5-(ethylenedioxy)hexyl]benzaldehyde, 117582-41-9; methyl 4-(10-carbomethoxydecanyl)benzoate, 109636-19-3; methyl 4-methylbenzoate, 99-75-2; 7-(4-acetylphenyl)-2-methylheptane-1,2-diol, 117582-42-0; (*E*)-1-phenyl-1-decene, 62839-71-8; (*Z*)-1-phenyl-1-decene, 62839-72-9; 2-methyl-2-undecene, 56888-88-1; methyl 13-methyl-12-tetradecenoate, 117582-43-1; (*Z*)-3-methyl-2-undecene, 57024-90-5; (*E*)-2-methyl-6-(3,4-dimethoxyphenyl)-2-hexenol tetrahydropyranyl ether, 117582-44-2; methyl (*E*)-13-cyano-2-methyl-2-tridecenoate, 117582-45-3; methyl (*E*)-2-methyl-4-(pinan-10-yl)-2-butenoate, 117582-46-4; methyl (*E*)-2-methyl-4-(2,2-dimethylnorborn-3-yl)-2-butenoate, 117582-47-5; 3-(10-cyanodecanyl)-5,5-dimethyl-2-cyclohexanone, 117582-48-6; 1,2-dimethoxy-4-(2-propen-1-yl)benzene, 93-15-2; 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane, 127-91-3; 2-methylene-3,3-dimethylbicyclo[2.2.1]heptane, 79-92-5; 3-bromo-5,5-dimethyl-2-cyclohexen-1-one, 13271-49-3; ethyl (*E*)-β-bromocrotonate, 1118-80-5; (*Z*)-β-bromocrotyl alcohol tetrahydropyranyl ether, 117582-50-0; 1-iodo-2-[(2-propen-1-yl)oxy]naphthalene, 117582-52-2; (*Z*)-1-bromo-1-phenyl-1,4-pentadiene, 68091-91-8; 1-bromo-2-[1-(methoxymethoxy)-2-propenyl]-1-cycloheptane, 117582-53-3; 2-allyl-3-bromo-5,5-dimethyl-2-cyclohexenone ethylene acetal, 117582-54-4; 1-bromo-2-(3-methyl-3-butenyl)-3,4-dihydronaphthalene, 117582-55-5; indan, 496-11-7; tetralin, 119-64-2; 3,4-dihydro-2*H*-1-oxaphenanthrene, 3722-88-1; 1-phenylcyclopentene, 825-54-7; 1-(methoxymethoxy)-1,2,3,4,5,6,7,8-octahydroazulene, 117582-56-6; 2,3-trimethylene-5,5-dimethyl-2-cyclohexenone ethylene acetal, 117582-57-7; 3-methyl-1,2,3,4,9,10-hexahydrophenanthrene, 117582-58-8; allyl bromide, 106-95-6; phenylethyne, 536-74-3; 1-bromo-2-formyl-1-cycloheptene, 85236-13-1; cycloheptanone, 502-42-1; vinylmagnesium bromide, 1826-67-1; chloromethyl methyl ether, 107-30-2; 2-allyl-5,5-dimethyl-1,3-cyclohexanedione, 1131-02-8; 2-allyl-3-bromo-5,5-dimethyl-2-cyclohexen-1-one, 117582-61-3; 1-bromo-2-formyl-3,4-dihydronaphthalene, 117582-62-4; α-tetralone, 529-34-0; 1-bromo-2-(bromomethyl)-3,4-dihydronaphthalene, 117582-63-5; (2-methyl-2-propenyl)magnesium bromide, 33324-92-4; 1-bromo-2-allylbenzene, 42918-20-7.

Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold[1]

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Abstract: Long-chain alkanethiols, $HS(CH_2)_nX$, adsorb from solution onto gold surfaces and form ordered, oriented monolayer films. The properties of the interfaces between the films and liquids are largely independent of chain length when $n > 10$; in particular, wetting is not directly influenced by the proximity of the underlying gold substrate. The specific interaction of gold with sulfur and other "soft" nucleophiles and its low reactivity toward most "hard" acids and bases make it possible to vary the structure of the terminal group, X, widely and thus permit the introduction of a great range of functional groups into a surface. Studies of the wettability of these monolayers, and of their composition using X-ray photoelectron spectroscopy (XPS), indicate that the monolayers are oriented with the tail group, X, exposed at the monolayer–air or monolayer–liquid interface. The adsorption of simple *n*-alkanethiols generates hydrophobic surfaces whose free energy (19 mJ/m^2) is the lowest of any hydrocarbon surface studied to date. In contrast, alcohol and carboxylic acid terminated thiols generate hydrophilic surfaces that are wet by water. Measurement of contact angles is a useful tool for studying the structure and chemistry of the outermost few angstroms of a surface. This work used contact angles and optical ellipsometry to study the kinetics of adsorption of monolayer films and to examine the experimental conditions necessary for the formation of high-quality films. Monolayers of thiols on gold appear to be stable indefinitely at room temperature but their constituents desorb when heated to 80 °C in hexadecane. Long-chain thiols form films that are thermally more stable than films formed from short-chain thiols.

This paper describes studies on the preparation and characterization of well-ordered monolayer films formed by the adsorption of long-chain alkanethiols ($HS(CH_2)_nX$) from solution onto the surface of gold. This work is part of a program of physical–organic chemistry intended to explore the relationships between the microscopic structure of organic surfaces and their macroscopic properties (especially wettability). Studies of organic monolayer films have focussed on two distinct methods of preparation: Langmuir–Blodgett techniques,[3,4] involving the transfer

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