Regioselective Reduction of the Homoisoflavone System with Dialkylboranes in the Presence of Palladium Catalysts

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(*E*)-3-Benzylidene-4-chromanones were regioselectively reduced to 3-benzyl-4-chromanones through the 1,4-addition of dialkylboranes, especially 9-borabicyclo[3.3.1]nonane, in excellent yields. The reaction was efficiently promoted by some palladium catalysts. Among them, dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) was most effective, followed by palladium(II) chloride. Furthermore, the reaction was characteristic of the structurally rigid exo-cyclic α,β-unsaturated ketones, such as (*E*)-3-benzylidene-4-chromanone, while no reaction occurred in the case of 3-benzyl-4*H*-chromen-4-one, which is an endo-cyclic one. 2-Benzylidene-3,4-dihydro-1(2*H*)-naphthalenone and 2-benzylideneindanone were similarly reduced at an olefin moiety only as the result of a 1,4-reduction.

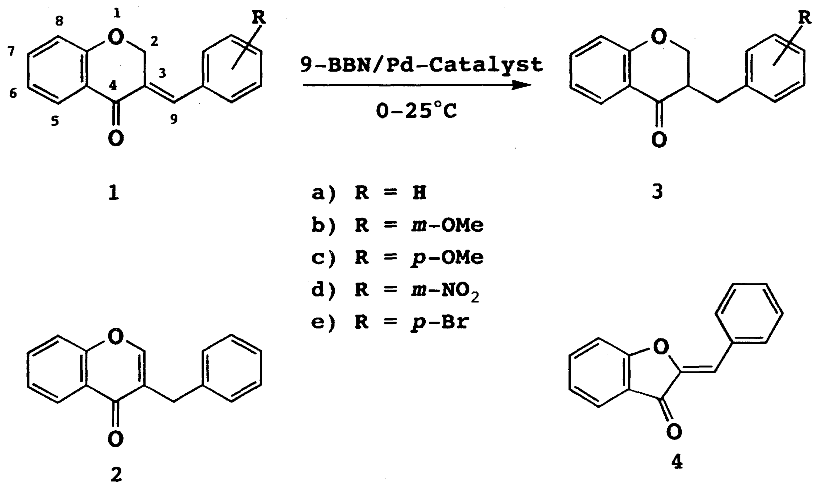
In a previous article, we reported that the double-bond migration in the homoisoflavone system occurred effectively at 200 °C in hexamethylphosphoric triamide through the promotion of some palladium catalysts.[1] Namely, (*E*)-3-benzylidene-4-chromanones (**1**) isomerized efficiently to 3-benzyl-4*H*-chromen-4-ones (**2**) in the presence of Pd-catalysts, such as tetrakis(triphenylphosphine)palladium(0) [$\mathrm{Pd(PPh_3)_4}$]. The reaction was often encountered along with contamination of the unreacted substrate. In this case, complete separation of the substrate and the desired product was impossible because of a small difference between the R_f-values in a TLC analysis and the solubilities of both materials. This problem encouraged us to establish a chemical approach for its solution.

It has been known that a carbonyl group of 4-pyrone is comparatively inert, and does not react with the general carbonyl reagents in the usual manner. On the other hand, a 4*H*-chromen-4-one shows a α,β-unsaturated ketonic property to a certain extent, and reacts with such reagents as Grignard reagents,[2] except for phenylhydrazine.[3] Although **1** do not have a 4-pyrone ring, they are also α,β-unsaturated ketones in a structural sense. However, there is a great difference in the structure between **1** and **2**. Namely, the former has an *exo*-cyclic double bond which is a *cis*-form against the carbonyl group, and the latter has an *endo*-cyclic one, which is a *trans*-form. These aspects prompted us to examine a transformation of the carbonyl groups in both materials to other functional groups for the above-mentioned purpose.

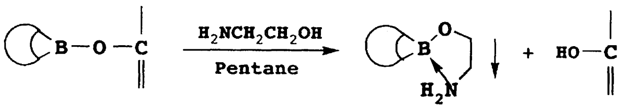
A variety of articles concerning the reduction of α,β-unsaturated aldehydes and ketones have hitherto been reported. In those cases, various metal hydrides were employed as reducing agents.[4] It has also been recognized that these reductions proceed through the 1,2- and/or 1,4-addition and the priority is dependent on the hydride used. For example, sodium borohydride gives saturated alcohols predominantly[5] (1,4-addition), but aluminium hydride[6] and diisopropylaluminium hydride[7] yield allylic alcohols primarily (1,2-addition), while lithium alminium hydride affords a mixture of both alcohols.[8] On the other hand, Brown and his co-worker[9] have already indicated that simple α,β-unsaturated aldehydes and ketones, such as crotonaldehyde and 2-cyclohexenone, were selectively and cleanly reduced with 9-borabicyclo[3.3.1]nonane (9-BBN) to the corresponding allylic alcohols in THF at 0 °C. Thus, as a first step we tried to reduce the carbonyl groups of **1** and **2** according to a procedure given in the above-cited literature. In the course of this investigation we found that some dialkylboranes, especially 9-BBN, reduced **1** not to the corresponding allylic alcohols (3-benzylidene-4-chromanol, 1,2- addition), but to the saturated ketones (**3**, 3-benzyl-4-chromanones, 1,4-addition), while no reaction occurred in the case of **2**. Furthermore, the reaction was found to be effectively promoted by some palladium catalysts. The results of this study are reported in the present paper (Scheme 1).

Results and Discussion

Reductions of 1a and 2 with 9-BBN. According to a procedure by Brown et al.,[9] the reductions of **1a** and **2** with 9-BBN were examined, and the following results were obtained: (1) **1a** gave the corresponding saturated ketone (**3a**) in 52% yield; (2) **2** afforded only a trace of **3a**, and almost all of the substrate was recovered. To remove the 9-BBN moiety from the product resulting from hydroboration, two methods are possible. One is oxidation by the addition of alkaline hydrogen peroxide; another is precipitation of the 9-BBN moiety as an adduct with 2-aminoethanol in pentane under neutral conditions (Eq. 1[9]).



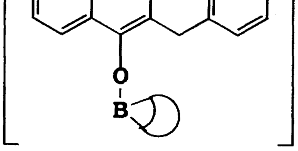
Scheme 1.



(1)

In the present case, the latter was adopted because of an instability of the chromanone and/or chromenone ring under basic conditions.[10] Matsumoto and Hayashi[11] have already reported that a chalcone is reduced to a β-phenylpropiophenone by 9-BBN or 1,3,2-benzodioxaborole (catecholborane (CB)) in a quantitative yield. A double bond and a carbonyl group in the chalcone seem to be favored over those of **1a** and **2** for 1,4-hydroboration from the view point of structure. In the case of **2**, furthermore, it is reasonable to consider that when 9-BBN attacks the carbonyl group, a stable chromenylium cation attributed to the construction of a six π-electrons system is formed to give a trace of **3a** (Scheme 2). On the other hand, **1a** may be thought to react with 9-BBN in an almost similar manner to that of chalcone, resulting in the formation of **3a** in a moderate yield.

Effect of Palladium Catalysts. One is frequently encountered by reactions accelerated by some transition metal catalysts, especially by palladium complexes, where organoboranes participate.[12] Thus, this hydroboration was carried out in the presence of some palladium and other transition metal catalysts. While no reaction occurred in the case of **2**, as well as in the absence of catalysts, the obtained results in the case of **1a** are summarized in Table 1 comprising those mentioned in the foregoing paragraph. Among several Pd-catalysts, dichloro[1,1′-bis(diphenylphosphino)-ferrocene]palladium(II) [$PdCl_2(dppf)$][13] (Run 5) showed the greatest promoting effect upon this reaction, followed by palladium(II) chloride (Run 2). The following observations and interpretations may be possible: (1) Among Pd-catalysts, those possessing chlorine atoms as the ligands, functioned more powerfully in this reaction than did the others, except for dichlorobis(acetonitrile)palladium(II) [$PdCl_2(CH_3CN)_2$] (Run 6). Miyaura et al.[12,14] have reported that the catalytic hydroboration proceeds smoothly through an oxidative addition of the H–B bond to Pd(0)-, or Pd(II)-catalysts, followed by the reductive elimination of alkyl-, or alkenylboranes, regenerating Pd-catalysts. Although the mechanism of the present reaction is still not clear in detail, the reaction should be considered to occur in a similar manner to that proposed in the above-cited literature. Thus, the chlorine ligand on palladium(II) might exert certain positive effects to an induction period, where an active species is formed, during the



Scheme 2.

Table 1. Reduction of 3-Benzylidene-4-chromanone (**1a**) with 9-BBN in the Presence of Transition Metal Catalysts[a)]

Run	Catalyst[b)]	Yield of **3a**[c)] / %
1	—	52
2	$PdCl_2$ (0.1)	72
3	$Pd(OAc)_2$ (0.1)	48
4	$Pd(PPh_3)_4$ (0.03)	42
5	$PdCl_2(dppf)$ (0.03)	88
6	$PdCl_2(CH_3CN)_2$ (0.1)	47
7	$PdCl_2$ (0.1)+PPh_3 (0.03)	62
8	$Pd(PPh_3)_4$ (0.03)+PPh_3 (0.03)	46
9	$PdCl_2(dppf)$ (0.03)+PPh_3 (0.03)	47
10	$RhCl_3\cdot 3H_2O$ (0.1)	64
11	$ZrCl_4$ (0.1)	28
12	$FeCl_3\cdot 6H_2O$ (0.1)	41
13	Fe(acac)$_3$[d)] (0.1)	68
14	Ni(acac)$_2$ (0.1)	58

a) All the reactions were carried out under a nitrogen atmosphere at 0—25 °C, using 1 mmol of **1a**. b) Figures in parenthese indicate the added amount in a mmol-unit. c) GLC yields based on the substrate. d) acac: acetylacetonate.

course of the reaction. (2) When a triphenylphosphine was added as an additive, a remarkable decrease in the yield of **3a** was observed in the case using [$PdCl_2$(dppf)] (Run 9). This was also the case for the run using $PdCl_2$ (Run 7). This phosphine itself seems to have little influence on the substrate and 9-BBN, since **3a** was obtained in 55% yield by the reaction being added in the absence of [$PdCl_2$(dppf)]. Accordingly, it should be recognized that this reagent interacts retardingly with Pd-catalysts in the present reaction. This may be one of the causes for the low yield of **3a** in a reaction employing [$Pd(PPh_3)_4$] (Run 4). (3) Several transition metal compounds other than palladium were also examined in the reaction, but all of them afforded yields of **3a** less than that obtained by [$PdCl_2$(dppf)] or $PdCl_2$ (Runs 10—14).

The unreactivity of **2** for the present reduction should be recognized as being due to a steric reason. Although both olefin moieties of **1a** and **2** are trebly substituted, the former is a structurally rigid *cis*-form and the latter is a *trans*-one, against the carbonyl group. It is easily predictable from a steric sense that the *cis*-form is more favorable than the *trans*-one for the 1,4-reduction of α,β-unsaturated ketones. In the case of chalcone, which is structurally non-rigid,[11] accordingly, the substrate would presumably react with 9-BBN in the *cis*-form.

Reactions Using Other Boranes. A comparison of various boron compounds in the reactions with **1a** demonstrated that, as well as 9-BBN, the representative hydroborating reagents, such as dicyclohexylborane and 1,1,2-trimethylpropylborane (thexylborane) can be used for the present reaction (Runs 5 and 6 in Table 2), while catecholborane and bis(1,2-dimethylpropyl)borane (disiamylborane) are moderately usuable (Runs 2 and 4 in Table 2). These results are consistent with the fact that the regioselectivities of hydroboration with catecholborane appear to approach those of disiamylborane, although the former is still far less reactive than dialkylboranes.[15] On the other hand, diborane (Run 3 in Table 2), which gives a complex reaction mixture was shown to be too reactive for this reaction. In general, mono- and dialkylboranes tend to be slightly more selective than borane, itself, arising from electronic and steric effects together with a decrease in the reaction possibilities through the availability of only one or two B–H bonds.[16] Thus, a compression in the yield of **3a** should be recognized as being partly the result of further reductions of products by diborane in the case of Run 3.

Substituent Effect. For four derivatives (**1b**—**1e**) which introduced some substituents on the side-chain phenyl group in **1a**, the reductions were carried out under the same conditions in order to examine a substituent effect on this reaction (Table 3). Although the catalytic effect of [$PdCl_2$(dppf)] was shown more or less in every case, a remarkable substituent one was not observed irrespective of its electronic property, except for the *p*-Br-derivative (**1e**, Entry 4 in Table 3). This suggests, at least, that the driving force of the reaction is not the 1,4-addition of 9-BBN, since the C_9-position, to which the hydride anion transfers, is a benzyl one against the substituents on the side-chain phenyl group. The lowest yield of *m*-NO_2-derivative (**1d**, Entry 3 in Table 3), which was treated with the addition of benzene, seems to be due to low solubility in THF. It is worth noting that there is a tendency to diminish the yields of **3** by introducing substituents. This propensity may be interpreted as being the result of a twisting of the side-chain phenyl group toward a chromanone skeleton by introducing a substituent on it, to interfere with the approach of an adduct of a Pd-catalyst and 9-BBN to the reaction center.

Reductions of Related Compounds. 2-Benzylidene-3,4-dihydro-1(2*H*)-naphthalenone and 2-benzylideneindanone, whose structures are analogous to those of **1**, except that they don't have a hetero-ring, and that the latter have a five-membered ring, were also tested under the optimum conditions with and without several Pd-catalysts. The obtained results are summarized in Table 4. In both cases, [$PdCl_2$(dppf)] exerted its effect more powerfully than in that of **1**. Brown et al.(loc. cit.) have reported that 2-cyclopentenone, which has been known for its susceptibility to undergo conjugate reduction, and 2-cyclohexenone were converted to the corresponding allylic alcohols by 9-BBN in essentially quan-

Table 2. Reduction of 3-Benzylidene-4-chromanone (**1a**) with Several Organoboranes in the Presence of [$PdCl_2$(dppf)][a]

Run	Organoborane[b]	Yield of (**3a**)[c] %
1	9-BBN	88
2	Catecholborane	66
3	Diborane	34
4	Disiamylborane	63
5	Dicyclohexylborane	83
6	Thexylborane	82

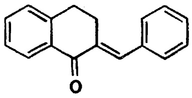
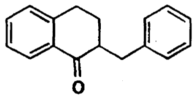
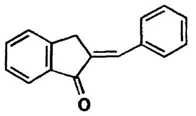
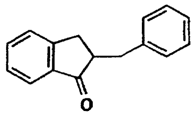
a) All the reactions were carried out under a nitrogen atmosphere at 0—25 °C in the presence of 0.03 mmol of [$PdCl_2$(dppf)], using a 1 mmol of **1a**. b) A 1.3 mmol of borane was employed. c) GLC yields based on the substrate.

Table 3. Reduction of Substituted 3-Benzylidene-4-chromanones (**1b**—**1e**) with 9-BBN in the Absence and Presence of [$PdCl_2$(dppf)][a]

Entry	R	Pd-Catalyst[b]	Yield of **3**[c] %
1	*m*-OMe	—	45 (**3b**)
		[$PdCl_2$(dppf)]	77 (**3b**)
2	*p*-OMe	—	51 (**3c**)
		[$PdCl_2$(dppf)]	71 (**3c**)
3	*m*-NO_2	—	20 (**3d**)
		[$PdCl_2$(dppf)]	31 (**3d**)
4	*p*-Br	—	69 (**3e**)
		[$PdCl_2$(dppf)]	71 (**3e**)

a) All the reactions were carried out under a nitrogen atmosphere at 0—25 °C, using 1 mmol of substrate and 1.3 mmol of 9-BBN. b) A 0.03 mmol of catalyst was added against the substrate. c) GLC yields based on the substrate.

Table 4. Reduction of 2-Benzylidene-3,4-dihydro-1(2*H*)-naphthalenone and 2-Benzylideneindanone with 9-BBN in the Absence and Presence of Pd-Catalysts[a)]

Substrate[b)]	Pd-Catalyst[c)]	Product	Yield[d)] %
	—		53
	$[Pd(PPh_3)_4]$		65
	$PdCl_2$		67
	$[PdCl_2(dppf)]$		95
	—		0
	$[Pd(PPh_3)_4]$		21
	$PdCl_2$		36
	$[PdCl_2(dppf)]$		83

a) All the reactions were carried out under a nitrogen atmosphere at 0—25 °C, using 1.3 mmol of 9-BBN. b) A 1.0 mmol was employed. c) A 0.03 mmol of catalyst was added against the substrate. d) GLC yields based on the substrate.

titative yields. In contrast, the *exo*-cyclic enones shown in the table were smoothly subjected to a conjugate reduction to give the corresponding saturated ketones, though greatly promoted by $[PdCl_2(dppf)]$. Antus et al.[17)] have reported that 2-(*p*-methoxybenzylidene)-3,4-dihydro-1(2*H*)-naphthalenone and 2-(*p*-methoxybenzylidene)indanone were reduced to the corresponding saturated ketone (71% yield) and allylic alcohol (42% yield), respectively, by the use of diisobutylalminium hydride (DIBAH) as a reductant. DIBAH is a stronger reductant than 9-BBN, and seems to be very susceptible to minor structural changes. Conversely, 9-BBN and some other alkylboranes are more mild, tolerant, and regioselective reducing agents than DIBAH and the other conventional ones (e.g., $LiBH_4$, $NaBH_4$, $LiAlH_4$, etc.) for this type of reduction. It should be additionally mentioned that 2-benzylidene-3(2*H*)-benzofuranone (aurone) (**4**), which is a member of flavonoid and an oxygen analogue of the corresponding indanone, afforded only a complex mixture in this reaction, and no isolable product was obtained. In this case, certain side-reactions, i.e., a ring-opening by fission of ether linkage and so on, may concertedly occur. Antus et al.[17)] (loc. cit.) have reported that 6-methoxyaurone is reduced with DIBAH to the corresponding allylic alcohol in 65% yield. Thus, the olefin moiety in aurones may be inert for this type of reduction.

Conclusion

Although its reaction mechanism is still not clear in detail, the palladium-catalyzed conjugate reduction of 3-benzylidene-4-chromanones, 2-benzylidene-3,4-dihydro-1(2*H*)-naphthalenone and 2-benzylideneindanone with 9-borabicyclo[3.3.1]nonane and a few mono-, or dialkylboranes has been demonstrated to proceed smoothly and regio-, and chemoselectively to give the corresponding saturated ketones, while no reaction has occurred in the case of 3-benzyl-4*H*-chromen-4-one with recovering almost all of the substrate. Since the resulting 3-benzyl-4-chromanones are easily separated from 3-benzyl-4*H*-chromen-4-ones by a normal chromatographic procedure, our initial purpose, mentioned in an introductory section, has been achieved.

Experimental

All of the experiments were carried out under a nitrogen atmosphere. All of the melting points are uncorrected. The IR spectra were recorded on a JASCO-IRA-1 spectrometer by means of a KBr pellet or neat. ^{1}H NMR spectra were obtained with a JEOL-EX270 Fourier Transform NMR spectrometer (270 MHz), and are reported in δ units using tetramethylsilane as an internal standard. Mass spectra were taken on a JEOL-JMS-D300. GLC analyses were performed on a Hitachi-263-30 instrument with Silicone SE-30 (2 m) on Uniport B using pentadecane as an internal standard. THF was purified by distillation from diphenylketyl under a nitrogen atmosphere before use. All of the other solvents employed were dried and stored over sodium under a nitrogen atmosphere after distillation.

Boranes. Diborane in THF, 9-borabicyclo[3.3.1]nonane in THF, and 1,3,2-benzodioxaborole (catecholborane) in THF from Aldrich Chemical Co. were used directly. Other mono-, and dialkylboranes were prepared via the hydroboration of appropriate alkenes with diborane, and were transferred to the main reaction flask ajusted at 0 °C with double-ended needles under a nitrogen atmosphere.

Transition Metal Catalysts. Tetrakis(triphenylphosphine)palladium(0)[18)] and dichloro[1,1′-bis(diphenylphosphino)-ferrocene]palladium(II)[13)] were prepared according to the reported procedures. Rhodium(III) chloride trihydrate, zirconium(IV) chloride, iron(III) chloride hexahydrate, iron(III) acetylacetonate, and nickel acetylacetonate were all commercially available grades, and were used without further purification.

Materials. 3-Benzylidene-4-chromanones (**1a**—**1e**) were prepared by a known procedure;[19)] the physical data were reported in our previous work,[1)] as well as 3-benzyl-4*H*-chromen-4-one (**2**). 2-Benzylidene-3,4-dihydro-1(2*H*)-naphthalenone[20)] and 2-benzylideneindanone[21)] were also obtained in a similar manner[19)] and were identified based on values given in the literature. The main products of the present reductions were isolated from the residual solutions after GLC analyses by silica-gel column chromatography using a mixture of benzene–ether (4 : 1) as an eluent, recrystallized from hexane and a small amount of benzene. These physical data are as follows.

3-Benzyl-4-chromanone (3a): Mp 62.2–63.5 °C; IR (KBr) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.72$ (dd, $J_{gem} = 13.9$ Hz, $J_{syn} = 10.2$ Hz, 1H, C_9–H_a), 2.89—2.97 (m, 1H, C_3–H), 3.30 (dd, $J_{gem} = 13.9$ Hz, $J_{anti} = 4.3$ Hz, 1H, C_9–H_b), 4.18 (dd, $J_{gem} = 11.5$ Hz, $J_{ax\cdot ax} = 8.3$ Hz, 1H, C_2–H_a), 4.38 (dd, $J_{gem} = 11.5$ Hz, $J_{ax\cdot eq} = 4.5$ Hz, 1H, C_2–H_b), 6.96—7.51 (m, 8H, aromatic), and 7.94 (dd, $J_{ortho} = 7.9$ Hz, $J_{meta} = 1.7$ Hz, 1H, C_5–H). MS Found: *m/z* 238.0996. Calcd for $C_{16}H_{14}O_2$: M, 238.0994.

3-(*m*-Methoxybenzyl)-4-chromanone (3b): Mp 57.2—58.5 °C; IR (KBr) 1695 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.68$ (dd, $J_{gem} = 13.9$ Hz, $J_{syn} = 10.5$ Hz, 1H, C_9–H_a), 2.89—2.99 (m, 1H, C_3–H), 3.28 (dd, $J_{gem} = 13.9$ Hz, $J_{anti} = 4.3$ Hz, 1H, C_9–H_b), 3.81 (s, 3H, OCH3), 4.18 (dd, $J_{gem} = 11.5$ Hz, $J_{ax\cdot ax} = 8.6$ Hz, 1H, C_2–H_a), 4.38 (dd, $J_{gem} = 11.5$ Hz, $J_{ax\cdot eq} = 4.3$ Hz, 1H, C_2–H_b), 6.78—7.52

(m, 7H, aromatic), and 7.93 (dd, $J_{\text{ortho}} = 7.9$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, C_5–H). MS Found: *m*/*z* 268.1107. Calcd for $C_{17}H_{16}O_3$: M, 268.1100.

3-(*p*-Methoxybenzyl)-4-chromanone (3c): Mp 97.0—98.0 °C; IR (KBr) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.69$ (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{syn}} = 10.2$ Hz, 1H, C_9–H_a), 2.81—2.91 (m, 1H, C_3–H), 3.21 (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{anti}} = 4.6$ Hz, 1H, C_9–H_b), 3.80 (s, 3H, OCH_3), 4.18 (dd, $J_{\text{gem}} = 11.5$ Hz, $J_{\text{ax}\cdot\text{ax}} = 7.9$ Hz, 1H, C_2–H_a), 4.38 (dd, $J_{\text{gem}} = 11.5$ Hz, $J_{\text{ax}\cdot\text{eq}} = 4.3$ Hz, 1H, C_2–H_b), 6.84—7.51 (m, 7H, aromatic), and 7.93 (dd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.8$ Hz, 1H, C_5–H). MS Found: *m*/*z* 268.1096. Calcd for $C_{17}H_{16}O_3$: M, 268.1100.

3-(*m*-Nitrobenzyl)-4-chromanone (3d): Mp 105.2—106.9 °C; IR (KBr) 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.87$ (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{syn}} = 9.2$ Hz, 1H, C_9–H_a), 2.98—3.05 (m, 1H, C_3–H), 3.38 (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{anti}} = 4.8$ Hz, 1H, C_9–H_b), 4.19 (dd, $J_{\text{gem}} = 11.5$ Hz, $J_{\text{ax}\cdot\text{ax}} = 8.6$ Hz, 1H, C_2–H_a), 4.43 (dd, $J_{\text{gem}} = 11.5$ Hz, $J_{\text{ax}\cdot\text{eq}} = 4.3$ Hz, 1H, C_2–H_b), 6.97—8.13 (m, 7H, aromatic), and 7.93 (d, $J_{\text{ortho}} = 7.9$ Hz, 1H, C_5–H). MS Found: *m*/*z* 283.0854. Calcd for $C_{16}H_{13}NO_4$: M, 283.0845.

3-(*p*-Bromobenzyl)-4-chromanone (3e): Mp 112.0—113.0 °C; IR (KBr) 1680 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.70$ (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{syn}} = 9.9$ Hz, 1H, C_9–H_a), 2.82—2.96 (m, 1H, C_3–H), 3.22 (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{anti}} = 4.6$ Hz, 1H, C_9–H_b), 4.16 (dd, $J_{\text{gem}} = 11.7$ Hz, $J_{\text{ax}\cdot\text{ax}} = 8.2$ Hz, 1H, C_2–H_a), 4.38 (dd, $J_{\text{gem}} = 11.7$ Hz, $J_{\text{ax}\cdot\text{eq}} = 4.3$ Hz, 1H, C_2–H_b), 6.96—7.64 (m, 7H, aromatic), and 7.92 (dd, $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.8$ Hz, 1H, C_5–H). MS Found: *m*/*z* 316.0098. Calcd for $C_{16}H_{13}BrO_2$: M, 316.0100.

2-Benzyl-3,4-dihydro-1(2*H*)-naphthalenone: IR (neat) 1680 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 1.76$–1.94 (m, 1H, C_3–H_a), 2.07—2.14 (m, 1H, C_2–H), 2.64 (dd, $J_{\text{gem}} = 13.2$ Hz, $J_{\text{syn}} = 7.5$ Hz, 1H, C_9–H_a), 2.74—2.84 (m, 1H, C_3–H_b), 2.94 (t, $J = 5.1$ Hz, 2H, C_4–H), 3.50 (dd, $J_{\text{gem}} = 13.2$ Hz, $J_{\text{anti}} = 3.3$ Hz, 1H, C_9–H_b), 7.20—7.49 (m, 8H, aromatic), and 8.07 (dd, $J_{\text{ortho}} = 7.9$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, C_8–H). MS Found: *m*/*z* 236.1208. Calcd for $C_{17}H_{16}O$: M, 236.1202.

2-Benzylindanone: IR (neat) 1715 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.66$ (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{ax}\cdot\text{ax}} = 10.2$ Hz, 1H, C_3–H_a), 2.85 (dd, $J_{\text{gem}} = 16.8$ Hz, $J_{\text{anti}} = 4.0$ Hz, 1H, C_8–H_a), 2.93—3.05 (m, 1H, C_2–H), 3.17 (dd, $J_{\text{gem}} = 16.8$ Hz, $J_{\text{syn}} = 7.6$ Hz, 1H, C_8–H_b), 3.40 (dd, $J_{\text{gem}} = 13.9$ Hz, $J_{\text{ax}\cdot\text{eq}} = 4.1$ Hz, 1H, C_3–H_b), 7.19—7.60 (m, 8H, aromatic), and 7.78 (dd, $J_{\text{ortho}} = 7.6$ Hz, $J_{\text{meta}} = 1.6$ Hz, 1H, C_7–H). MS Found: *m*/*z* 222.1042. Calcd for $C_{16}H_{14}O$: M, 222.1045.

Representative Procedure. In a dry 25 mL two-neck round-bottom flask equipped with a pressure equalizing dropping funnel, septum inlet, and a magnetic stirring bar were charged (*E*)-3-benzylidene-4-chromanone (0.236 g, 1.0 mmol) and [$PdCl_2$(dppf)] (22 mg, 0.03 mmol). The funnel was connected to a nitrogen source and to an aspirator through a three-way stopcock. The flask was flushed with dry nitrogen to displace the air, and cooled to 0 °C with an ice bath. While the flask was filled with 3 mL of THF through the septum inlet by a hypodermic syringe, 2.6 mL (1.3 mmol) of a 0.5 M (1 M = 1 mol dm^{-3}) 9-BBN solution in THF was placed into the dropping funnel with the syringe through a rubber septum set on the top of it. Then, the 9-BBN solution was added dropwise over a period of one hour with vigorous stirring. After 4 h at 0 °C, the ice bath was removed and the reaction solution was stirred at room temperature overnight. Then, 0.5 mL of methanol was added to destroy any excess 9-BBN. THF was removed under reduced pressure by means of the aspirator, and dry pentane (10 mL) was introduced, followed by 80 μL (79 mg, 1.3 mmol) of 2-aminoethanol. Immediately, a white adduct of 9-BBN and 2-aminoethanol started to precipitate. Then, the reaction mixture was filtered and the white adduct on a funnel was washed several times with benzene. The collected filtrate was condensed to ca. 25 mL by an evaporator, followed by a GLC analysis after the addition of 250 μL of pentadecane as an internal standard. 3-Benzyl-4-chromanone was isolated from the residual solution by means of silica-gel column chromatography using a mixture of benzene–ether (4 : 1) as an eluent, and recrystallized from hexane and a small amount of benzene.

Optimum Conditions Concerning Reaction Factors. A series of reactions was examined with 3-benzylidene-4-chromanone (1.0 mmol) and 9-BBN (1.3 mmol) as partners in the presence of [$PdCl_2$(dppf)] to establish the optimum reaction conditions. The obtained results were as follows. The figures in parenthese are the yields of 3-benzyl-4-chromanone. The best one is underlined.

(a) Amounts of Catalyst in mmol Unit: 0 (52%), 0.01 (72%), 0.03 (88%), 0.10 (64%), 0.50 (64%).

(b) Reaction Time in Hour Unit: The dropping time of 9-BBN at 0 °C/the subsequent stirring time at 0 °C = 0.25/0.25 (66%), 1.0/1.0 (70%), 1.0/3.0 (88%), 1.0/5.0 (88%).

(c) Reaction Solvents: 3 mL of solvents was added in all the cases. THF (88%), THP (23%), benzene (72%), Et_2O (69%), hexane (38%), 1,4-dioxane (66%).

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