A Novel Palladium- or Platinum-Catalyzed Cyclocarbonylation Reaction of Cinnamyl Compounds for Synthesis of 1-Naphthol Derivatives[1]

Hiroyuki Matsuzaka, Yoshitaka Hiroe, Masakazu Iwasaki, Youichi Ishii, Yukio Koyasu, and Masanobu Hidai*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Received March 29, 1988

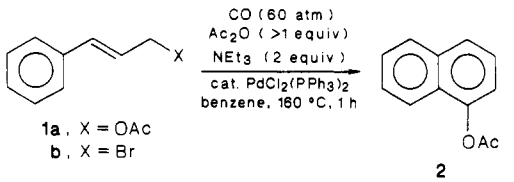
Cinnamyl compounds undergo smooth cyclocarbonylation to afford 1-naphthol derivatives at 160 °C under 60 atm of CO in the presence of Ac_2O, NEt_3, and a catalytic amount of palladium- or platinum-phosphine complexes. Similar cyclocarbonylation of 3-(2′-naphthyl)allyl acetate selectively proceeds to give 4-phenanthryl acetate. The mechanistic investigation reveals that cyclocarbonylation of cinnamyl compounds proceeds through the intramolecular attack on the aromatic ring by the acyl moiety of the intermediary (*Z*)-4-aryl-2- or -3-butenoyl-palladium complex, which is formed by oxidative addition of cinnamyl compounds to a Pd(0) species followed by CO insertion into the Pd-C bond of the δ-allyl intermediate and carbon-carbon double-bond migration.

Introduction

Transition-metal-catalyzed carbonylation reactions have proved to be very useful and versatile in organic syntheses. A variety of reagents have been employed to attack intermediary acyl complexes to yield aldehydes, carboxylic acids, esters, amides, and ketones.[2] However, aromatic systems have received little attention in carbonylation reactions as reagents to attack intermediary acyl complexes. We have been interested in such reactions because intramolecular reactions of that type (cyclocarbonylation) are expected to offer a novel synthetic method for polycyclic systems, which have attracted much attention in organic and bioorganic chemistry. Several examples of the cyclocarbonylation of aromatic compounds have been reported, including the syntheses of anthraquinone from benzophenone with $PdCl_2$,[3] indanones from benzene and polyfunctional halides with $AlCl_3$,[4] an indanone from tetraphenylbutatriene with $Co_2(CO)_8$,[5] indenones from benzene and diphenylacetylene with $Rh_4(CO)_{12}$,[6] and 2-phenylindan-1-one from diphenylacetylene with $Co_2(CO)_8$ and PPh_3.[7] During the course of our studies on transition-metal-catalyzed carbonylation reactions,[8] we have recently discovered a novel cyclocarbonylation of cinnamyl compounds to form 1-naphthol derivatives, which includes an intramolecular carbonylation of the aromatic ring. This was briefly reported in a previous paper.[9] Here we present the scope and limitation of this reaction as well as the results of mechanistic investigations.

Results and Discussion

Cyclocarbonylation of Cinnamyl Acetate. Cinnamyl compounds such as cinnamyl acetate (**1a**) and cinnamyl bromide (**1b**) were smoothly cyclocarbonylated to form 1-naphthyl acetate (**2**) in 74% and 41% yield, respectively, when heated at 160 °C under 60 atm of CO (initial pressure at room temperature) in the presence of Ac_2O (>1 equiv), NEt_3 (2 equiv), and a catalytic amount of $PdCl_2(PPh_3)_2$ (0.7 mol %) (eq 1).



(1)

Addition of both NEt_3 and Ac_2O is essential for this reaction. Thus, only a low yield of **2** was formed from **1a** in the absence of NEt_3, while the reaction without Ac_2O resulted in some unfavorable side reactions, giving an unidentified complex mixture, and no **2** was obtained. NEt_3 is added to suppress the acid HX in the reaction media which is generated during the catalysis, and Ac_2O is employed to convert 1-naphthol, the first-stage product of the cyclocarbonylation, into its acetate. Free 1-naphthol would inhibit the catalytic cyclocarbonylation because of the reaction with intermediary palladium(0) or acyl-palladium species. The reaction was slightly accelerated by an increase in the amount of Ac_2O. This rate enhancement effect by Ac_2O is more apparent, especially in the case of β-methylcinnamyl acetate (vide infra). Reaction temperature also has a profound effect on the yield of **2**. The reaction proceeded smoothly at 160 °C to give **2** in good yield; however, lower reaction temperature resulted in a drastic decrease in the yield of **2** and formation of un-

Table I. Influence of Catalysts on Cyclocarbonyaltion of Cinnamyl Acetate (1a)[a]

catalyst	% conversn[b]	% yield of 2[b]
$PdCl_2(PPh_3)_2$	92	74 (46)[c]
$Pd(CO)(PPh_3)_3$	88	88
$Pd(PPh_3)_4$	73	70
$PdCl_2(PPh_3)_2$[d]	25	15
$PdCl_2(PMePh_2)_2$[d]	53	39
$PdCl_2(PMe_2Ph)_2$[d]	47	43
$PdCl_2(PMe_3)_2$[d]	48	36
$PdCl_2(PCy_3)_2$[d]	78	42
$PtCl_2(PPh_3)_2$	66	44
$NiBr_2(PPh_3)_2$	14	14
$Ru_3(CO)_{12}$	9	9
$Co_2(CO)_8$	7	5
$RhCl(CO)(PPh_3)_2$	2	2

[a] See Experimental Section. [b] Determined by GLC. [c] Isolated yield in parentheses. [d] Catalyst, 0.2 mol %.

(1) Construction of Polycyclic Systems by Cyclocarbonylation. 3. For 2, see ref 16.

(2) (a) Collman, J. P.; Hegedus, L. S. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Books/Cole: Montery, CA, 1985. (c) Stille, J. K. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1985. (d) Pearson, A. J. *Metallo-organic Chemistry*; Wiley: Chichester, 1985.

(3) Bruson, H. A.; Plant, H. L. *J. Org. Chem.* **1967**, *32*, 3356.

(4) Arzoumanidis, G. G.; Rauch, F. C. *J. Mol. Catal.* **1980**, *9*, 335.

(5) Kim, P. J.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2022.

(6) Hong, P.; Cho, B.; Yamazaki, H. *Chem. Lett.* **1979**, 339.

(7) Doyama, K.; Joh, T.; Maeshita, K. *Proceedings of the 34th Symposium on Organometallic Chemistry*; Kyoto, Japan, **1986**, P208.

(8) (a) Hidai, M.; Orisaku, M.; Ue, M.; Koyasu, Y.; Kodama, T.; Uchida, Y. *Organometallics* **1983**, *2*, 292. (b) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Mol. Catal.* **1986**, *35*, 29. (c) Hidai, M.; Koyasu, Y.; Chikanari, K.; Uchida, Y. *Ibid.* **1987**, *40*, 243.

(9) Koyasu, Y.; Matsuzaka, H.; Hiroe, Y.; Uchida, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1987**, 575.

0022-3263/88/1953-3832$01.50/0 © 1988 American Chemical Society

Table II. Cyclocarbonylation of Substituted Cinnamyl Acetates 3 or 5[a]

reactant	R	R′	% conversn[b]	product	% yield[b]	ratio of 6 to 7[b]
3a	H	Me	69	4a	59	
3a[c]	H	Me	76	**4a**	76 (44)[d]	
3b	2-Me	H	81	**4b**	58	
3c	4-Me	H	90	**4c**	76	
3d[e]	4-Me	Me	93	**4d**	(67)[d]	
5a	3-Me	H	83	**6a** and **7a**	69	58:42
5b	3-OMe	H	77	**6b** and **7b**	77	78:22
5c	3-Cl	H	91	**6c** and **7c**	88	74:26

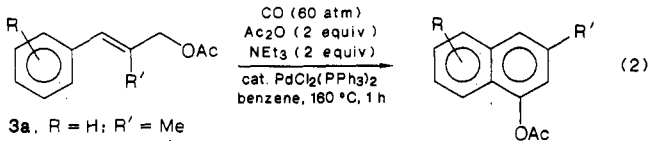
[a] See Experimental Section. [b] Determined by GLC. [c] Ac_2O, 1 equiv; reaction time, 4 h. [d] Isolated yield in parentheses. [e] Reaction time, 3 h.

identified high boiling compounds.[10]

As shown in Table I, a variety of palladium–monodentate tertiary phosphine complexes are excellent catalysts for cyclocarbonylation of **1a**. Zero-valent palladium–phosphine complexes such as $Pd(PPh_3)_4$ and $Pd(CO)(PPh_3)_3$ were the most effective catalysts. For comparison of the catalytic activities of a series of complexes of the type $PdCl_2(PR_3)_2$, the conversion and yield were compared at 160 °C by using a smaller amount of the catalyst (0.2 mol %) than the standard conditions (Table I). **2** was obtained in moderate yield in these reactions. Complexes such as $PdCl_2(PMePh_2)_2$, $PdCl_2(PMe_2Ph)_2$, and $PdCl_2(PMe_3)_2$ showed similar catalytic activity, whereas $PdCl_2(PPh_3)_2$ was inactivated at an earlier stage of the reaction with the concomitant precipitation of palladium metal. Reaction using $PdCl_2(PCy_3)_2$ (Cy = cyclohexyl) also gave **2** in moderate yield; however, the selectivity of **2** decreased and some unidentified high boiling products were formed. This may be because steric hindrance around the metal center suppresses the desirable intramolecular reaction. In contrast, $PdCl_2$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) did not show catalytic activity. Complexes without monodentate tertiary phosphine ligands such as $PdCl_2(AsPh_3)_2$ and $Pd(OAc)_2$ were also inactive. Not only palladium complexes but also $PtCl_2(PPh_3)_2$ was an effective catalyst for the cyclocarbonylation of **1a**. **2** was also formed by the catalysis of $NiBr_2(PPh_3)_2$, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $RhCl(CO)(PPh_3)_2$; however yields were quite low.

These findings lead to the conclusion that smooth cyclocarbonylation of **1a** to give **2** requires a reaction temperature of about 160 °C and the presence of Ac_2O (2 equiv), NEt_3 (2 equiv), and a catalytic amount of palladium– or platinum–monodentate tertiary phosphine complexes.

Cyclocarbonylation of Substituted Cinnamyl Acetates. Cyclocarbonylation of a series of substituted cinnamyl acetates was examined (eq 2 and 3). Results are shown in Table II.



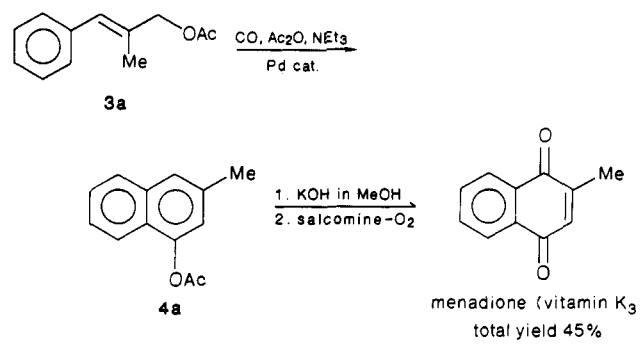
(2)

3a, R = H; R′ = Me
b, R = 2-Me; R′ = H
c, R = 4-Me; R′ = H
d, R = 4-Me; R′ = Me

4a, R = H; R′ = Me
b, R = 5-Me; R′ = H
c, R = 7-Me; R′ = H
d, R = 7-Me; R′ = Me

Although the expected product, 3-methyl-1-naphthyl acetate (**4a**) was obtained from β-methylcinnamyl acetate (**3a**) (eq 2) in good yield, reactivity of **3a** was lower than

Scheme I

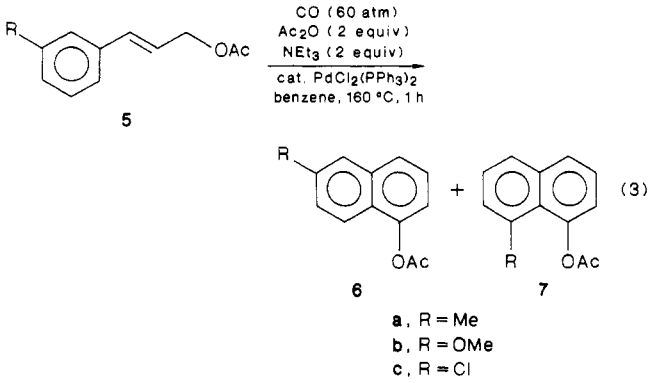


that of **1a**. It took 4 h to convert **3a** to **4a** in 76% yield when the reaction was carried out in the presence of 1 equiv of Ac_2O, while the reaction of **1a** under similar conditions was completed within 1 h. Effective rate enhancement by Ac_2O was observed in this reaction. When the reaction of **3a** was carried out in the presence of 2 equiv of Ac_2O, **3a** was readily cyclocarbonylated to form **4a** in 59% yield within 1 h. The mechanism of this rate enhancement by Ac_2O is still under investigation. **4a** was transformed into 2-methyl-1,4-naphthoquinone (menadione) in 59% yield by saponification and oxidation with O_2 in the presence of bis(salicylidene)ethylenediiminocobalt(II) (salcomine) (Scheme I).[11] This synthetic naphthoquinone derivative which shows antihemorrhagic activity of vitamin K has previously been prepared by carefully controlled oxidation of β-methylnaphthalene with chromic oxide.[12] On the other hand, neither α- nor γ-methylcinnamyl acetate was cyclocarbonylated under our reaction conditions. Effect of substituents in the aromatic ring on cyclocarbonylation of cinnamyl acetate was also examined. Cyclocarbonylation of *o*- and *p*-methylcinnamyl acetates (**3b** and **3c**) gave the expected products, 5- and 7-methyl-1-naphthyl acetates (**4b** and **4c**), in 58% and 76% yield, respectively. Reactivities of **3b** and **3c** were similar to that of **1a** when reactions were carried out in the presence of 2 equiv of Ac_2O. Disubstituted cinnamyl acetate, *p*-methyl-β-methylcinnamyl acetate (**3d**), was also smoothly cyclocarbonylated to afford 3,7-dimethyl-1-naphthyl acetate (**4d**). It should have potential utility for the preparation of 2,6-dimethylnaphthalene, which is an industrial precursor of naphthalene-2,6-dicarboxylic acid, a monomer of a new class of functionalized polymer.[13]

Meta-substituted cinnamyl acetates **5a–c** were cyclocarbonylated to yield a mixture of 6- and 8-substituted 1-naphthyl acetates, **6a–c** and **7a–c** in similar yields (eq

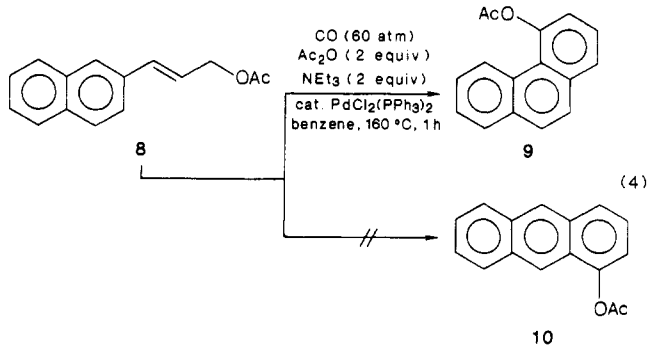
(10) These high boiling products were not detected under our GLC conditions. TLC analysis indicated that a complex mixture was formed in this reaction.

(11) (a) Kamikawa, T.; Kubo, I. *Synthesis* **1986**, 431. (b) Hibino, S.; Weibreb, S. M. *J. Org. Chem.* **1977**, *42*, 232.
(12) Fieser, L. F. *J. Biol. Chem.* **1940**, *133*, 391.
(13) Ouchi, I.; Aoki, H.; Shimotsuma, S.; Asai, T.; Hosoi, H. *Proceedings of the 17th Japan Congress on Materials Research–Non Metallic Materials*, Kyoto, Japan, 1974, P217.



3, Table II). In each case, the more sterically favorable compound **6** was the major product. The ratio of **6** to **7** varied with the starting compounds from 58:42 to 78:22. Relative reactivities of **1a**, **5b**, and **5c** were compared in competitive reactions using a mixture of **5b** and **1a** or **5c**. As shown in Table III, **1a**, **5b**, and **5c** had almost similar reactivities and the expected products **6** and **7** were obtained in similar yields. Therefore, methoxy and chloro groups in the aromatic ring do not have distinct activating and deactivating effects on the cyclocarbonylation reaction, although such an effect is generally observed in electrophilic aromatic substitution. On the other hand, the reaction was greatly prohibited when a nitro group was introduced into the aromatic ring in **1a** and a complex mixture of unidentified high boiling compounds was obtained. It seems plausible that the formation of isocyanates under the reaction conditions induced unfavorable side reactions.[14]

Cyclocarbonylation of Other Compounds. This cyclocarbonylation reaction is also effective for constructing tricyclic systems. 3-(2′-Naphthyl)allyl acetate (**8**) was smoothly cyclocarbonylated under similar reaction conditions to those for **1a**. Interestingly, the more sterically unfavorable α-position of the naphthalene ring was selectively attacked to yield 4-phenanthryl acetate (**9**) in 80% yield and no 1-anthryl acetate (**10**) was detected by GLC (eq 4). Details of the cyclocarbonylation of bicyclic compounds will be reported elsewhere.[15]



Mechanistic Investigation. Much interest is focused on the following two steps in the catalytic cyclocarbonylation reaction. One is the formation of the intermediary (*Z*)-acyl complex and the other is intramolecular cyclization of this.

In order to shed light on the catalytic intermediates and elucidate the reaction mechanism, reaction of $Pd(CO)(PPh_3)_3$ with *trans*- or *cis*-cinnamyl bromide was investigated in detail.[16] The reaction of $Pd(CO)(PPh_3)_3$ with

(14) Tietz, H.; Unverferth, K.; Schwetlick, K. *Z. Chem.* **1980**, *20*, 411.
(15) Iwasaki, M.; Matsuzaka, H.; Hiroe, Y.; Ishii, Y.; Koyasu, Y.; Hidai, M. *Chem. Lett.*, in press.

Table III. Competitive Cyclocarbonylation of 1a, 5b, and 5c[a]

reactant	% conversn[b]	product	% yield[c]
1a	64	2	64
5b	74	6b and 7b	50[c]
5b	74	6b and 7b	48[c]
5c	74	6c and 7c	57[c]

[a] See Experimental Section. [b] Determined by GLC. [c] Total yield.

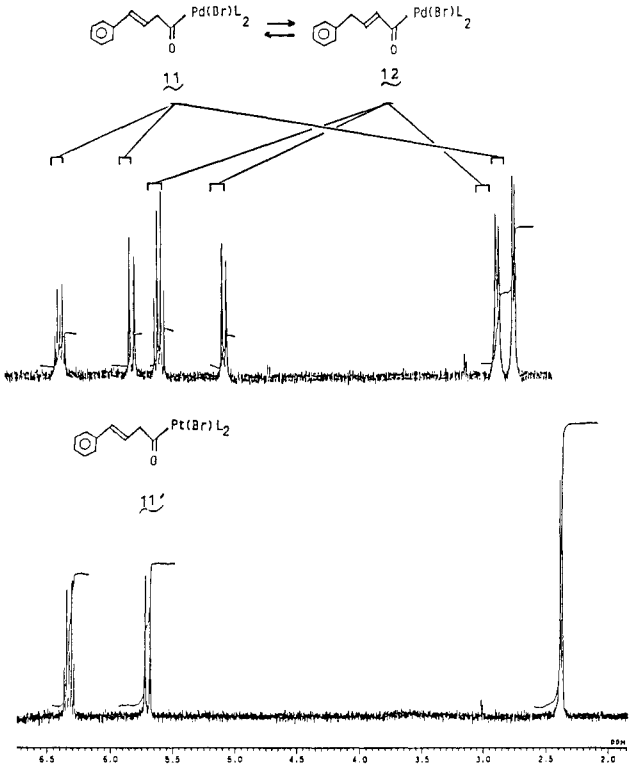
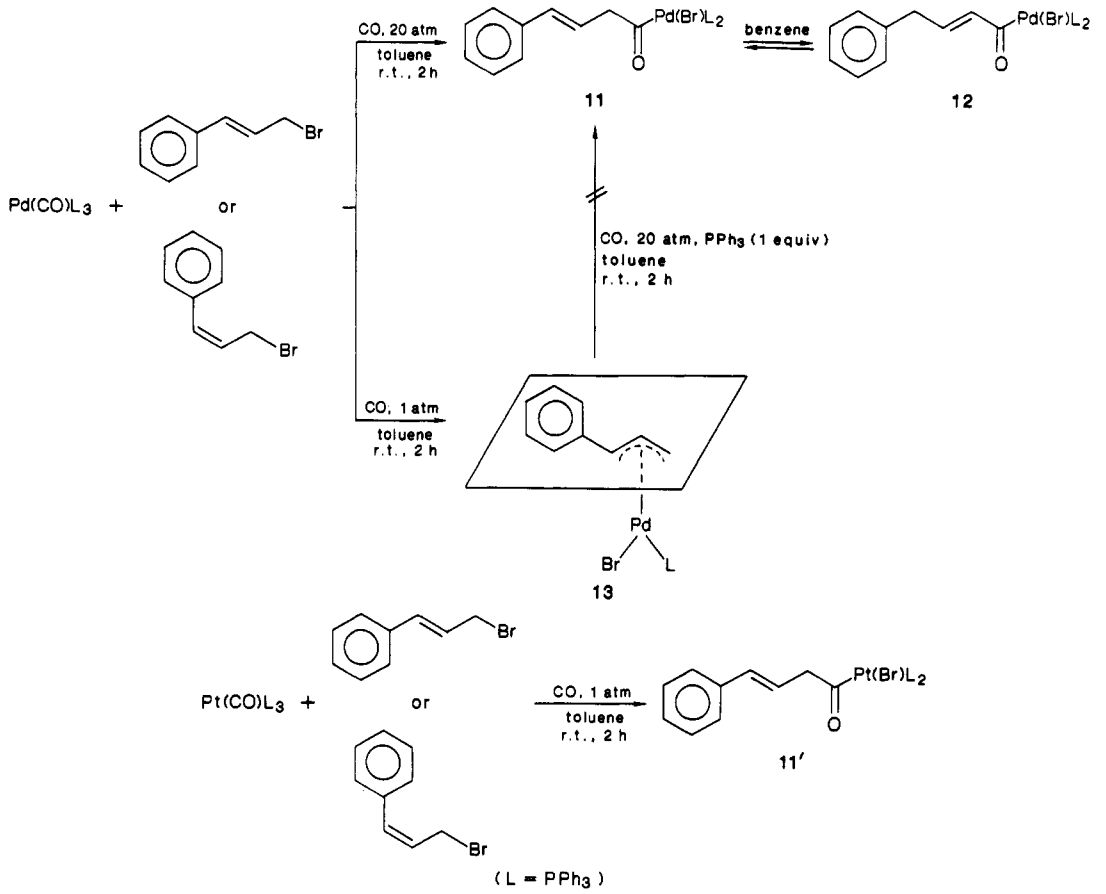


Figure 1. The 400-MHz ^1H NMR spectra of palladium and platinum acyl complexes in C_6D_6 at 25 °C. (a) Complex **11**. This complex rapidly isomerized to form a equilibrium mixture of **11** and **12** under this conditions. (b) Complex **11′**.

trans-cinnamyl bromide (**1b**) in toluene at room temperature under 20 atm of CO gave an acyl complex, *trans*-[(*E*)-PhCH=$CHCH_2CO$)$PdBr(PPh_3)_2$] (**11**), in 74% yield (Scheme II). The platinum analogue, *trans*-[((*E*)-PhCH=$CHCH_2CO$)$PtBr(PPh_3)_2$] (**11′**), was obtained in 78% yield by similar treatment of $Pt(CO)(PPh_3)_3$ under 1 atm of CO. As shown in Figure 1, the ^1H NMR spectrum of **11** in C_6D_6 indicates that **11** rapidly isomerizes in solution to form an equilibrium mixture of **11** and *trans*-[((*E*)-$PhCH_2CH$=$CHCO$)$PdBr(PPh_3)_2$] (**12**) in a ratio of 1:1 at room temperature. Complex **12** seems to be formed by carbon–carbon double-bond migration in **11**; however, such migration was not observed for complex **11′** in its ^1H NMR spectrum under similar conditions. On the other hand, when $Pd(CO)(PPh_3)_3$ was treated with **1b** under 1 atm of CO, a π-allyl complex (η^3-1-Ph-allyl)$PdBr(PPh_3)$ (**13**) precipitated during the reaction, which was not converted to **11** at room temperature under 20 atm of CO in the presence of 1 equiv of PPh_3 (Scheme II).[17] These results indicate that, in the reaction of $Pd(CO)(PPh_3)_3$ with **1b** at room temperature under high CO pressure, migratory

(16) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *Chem. Lett.* **1988**, 377.
(17) This shows sharp contrast to the fact that reaction of $Pd(CO)(PPh_3)_3$ with allyl bromide results in the formation of a mixture of 2- and 3-butenoyl complexes. Kudo, M.; Sato, M.; Hidai, M.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2820.

Scheme II



insertion of CO into the palladium–carbon bond of the first formed σ-allyl complex proceeds smoothly before the σ–π equilibrium is attained. It is of great interest that **11** was isolated in 70% yield instead of the expected acyl complex *trans*-[((*Z*)-PhCH=CHCH$_2$CO)PdBr(PPh$_3$)$_2$] (**14**) when Pd(CO)(PPh$_3$)$_3$ was treated with *cis*-cinnamyl bromide under 20 atm of CO. Even when the reaction was carried out at −78 °C, only **11** was isolated. Complex **11** is supposed to be formed by carbon–carbon double-bond migration in **14** as shown in Scheme III, because the first formed σ-allyl complex should be smoothly carbonylated under high CO pressure at room temperature before σ–π equilibrium is attained as mentioned above. The equilibrium among acyl complexes **11**, **12**, **14**, and **15** (Scheme III) lies considerably to **11** and **12** which have more sterically favorable structures.

Reactivities of **11** and **11′** under catalytic cyclocarbonylation conditions were examined. Treatment of **11** and **11′** with excess Ac$_2$O and NEt$_3$ under 60 atm of CO at 160 °C gave **2** in 54% and 40% yield, respectively. Furthermore, complex **11** showed similar catalytic activity to PdCl$_2$(PPh$_3$)$_2$ in the cyclocarbonylation of **1b**. The reaction of **11** is thought to proceed through (*Z*)-acyl complexes **14** and/or **15**, which are formed by carbon–carbon double-bond migration in **11**. It should be noted that carbonylation of the (*Z*)-σ-allyl complex arising from syn–anti and σ–π isomerization of **13** is also a possible path to form **14** under the catalytic conditions; however, results described here strongly suggest that the prior formation of **11** rather than **13** is a more favorable process.

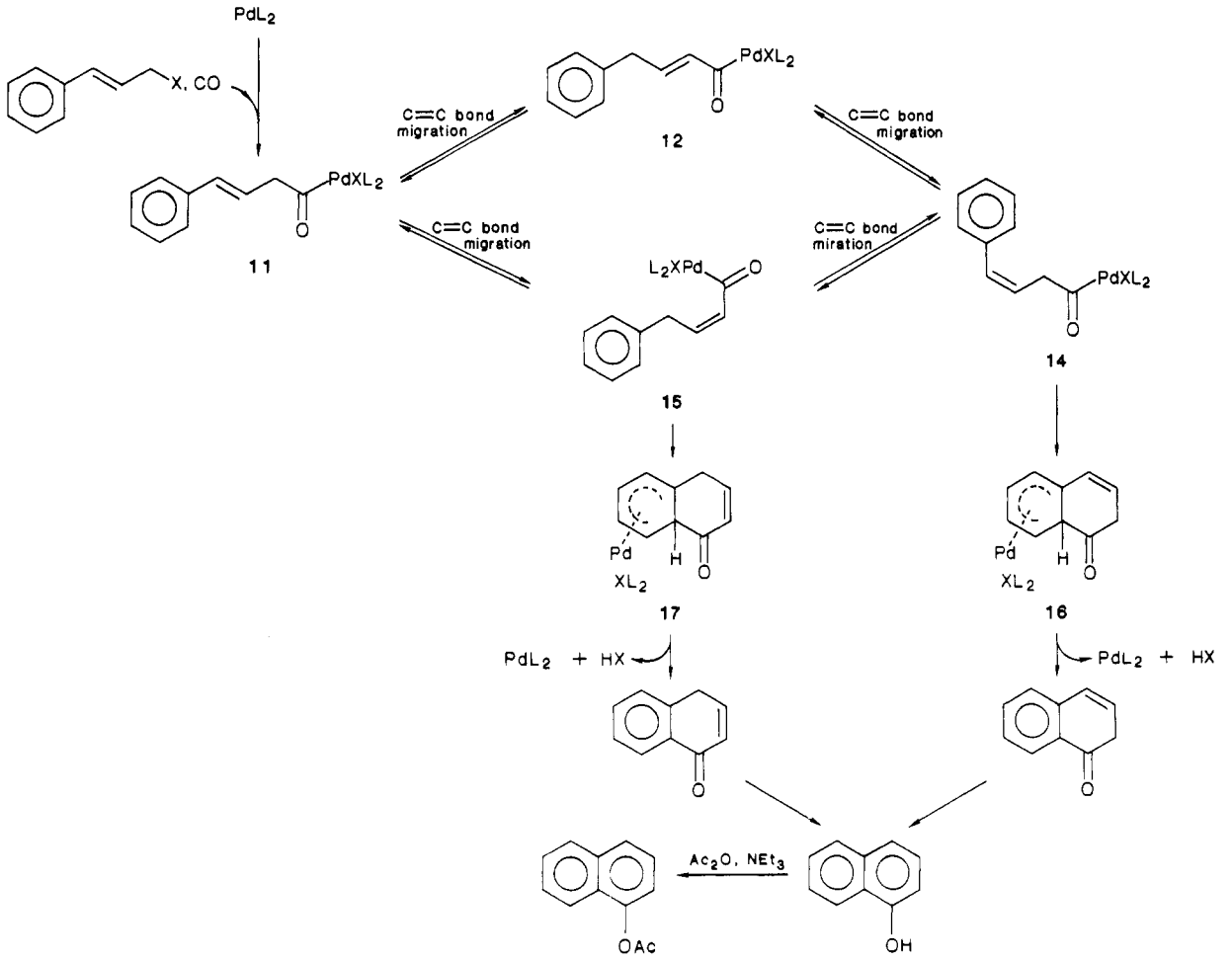
As for the intramolecular cyclization of **14** and/or **15**, details of the mechanism are still ambiguous. The selective formation of **9** but not **10** from **8** indicates that palladation is not included in the cyclization step, because palladation of the naphthalene system is known to occur at the β-position.[18] Probably electrophilic attack of the acyl moiety to the aromatic ring in **14** and/or **15** leads to cyclized palladium complexes **16** and/or **17**, which yield 2*H*- and/or 4*H*-naphthalenone, tautomers of 1-naphthol, by hydrogen elimination. The α-selectivity in the cyclocarbonylation of **8** is reasonable because it is in good accordance with the orientation of electrophilic substitution in the naphthalene ring.

Since the oxidative addition of **1b** to a Pd(0) complex and consecutive CO insertion to give **11** proceeds smoothly even at room temperature, the rate-determining step of the cyclocarbonylation should be carbon–carbon double-bond migration in **11** to give the (*Z*)-acyl complexes or the intramolecular cyclization of these complexes. The fact that the substituent effect on the reactivity was not observed in the cyclocarbonylation of **1a**, **5b**, and **5c** suggests that carbon–carbon double-bond migration in **11** giving (*Z*)-acyl complexes **14** and/or **15** is probably the rate-determining step.

In summary, the palladium-catalyzed cyclocarbonylation of cinnamyl compounds proceeds in the following way. The first step of the reaction is the oxidative addition of cinnamyl compounds to a palladium(0) species to afford a σ-allyl complex, which is readily carbonylated to form the (*E*)-acyl complex **11**. Carbon–carbon double-bond migration in **11** produces the (*Z*)-acyl complexes **14** and/or **15**. Intramolecular attack of the acyl moiety in **14** and/or **15** to the aromatic ring gives naphthalen-1(2*H*)-one and/or -1(4*H*)-one concurrent with the regeneration of the palladium(0) species (Scheme III). The naphthalenone(s) readily isomerizes to 1-naphthol which is acetylated by Ac$_2$O and NEt$_3$ to afford 1-naphthyl acetate.

(18) Fujiwara, Y.; Asano, R.; Moritani, S.; Teranishi, S. *Chem. Lett.* **1975**, 1061.

Scheme III



Conclusion

We have designed a new type of palladium- or platinum-catalyzed carbonylation reaction using an aromatic ring as a reagent to attack intermediary acyl complexes and illustrated that it provides an effective synthetic method for polycyclic compounds such as 1-naphthol derivatives and 4-phenanthryl acetate. The present reaction offers a versatile tool for the synthesis of a wide variety of polycyclic systems, including heteropolycyclic systems which will be reported in due course.[19] On the other hand, intermolecular carbonylation of this type is expected to present a novel synthetic route for aromatic ketones. This is now under investigation.

Experimental Section

The 90- and 400-MHz ^1H NMR spectra were recorded on a Hitachi R-40 and a JEOL GX-400 spectrometer, respectively. Chemical shifts were expressed in parts per million downfield from the internal reference tetramethylsilane. The ^{31}P NMR spectra were determined as solutions in C_6D_6 on a JEOL GX-400 spectrometer operating at 161.8 MHz. Chemical shifts were expressed in parts per million downfield from the external reference 85% H_3PO_4. Couplings (J) are in hertz. The IR spectra were obtained on a Shimazu IR-408 spectrometer. The GLC analysis was carried out on a Shimazu GC-9A spectrometer equipped with a flame ionization detector and a 25-m capillary column of HiCap-CBP1 (200 °C, He 40 mL/min). Column chromatography was carried out with Wakogel C-200 (Wako Pure Chemical Industries). Melting points were measured in open capillary tubes and uncorrected.

Complexes $PdCl_2(PR_3)_2$ (PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, and PCy_3),[20] $PdCl_2$(dppe),[20] and $PtCl_2(PPh_3)_2$[21] were prepared according to the published procedures. Compounds **1a** and **1b** were obtained commercially. **3a** was prepared by $LiAlH_4$ reduction and acetylation (Ac_2O–pyridine) of α-methylcinnamaldehyde. **3b**, **3c**, **5a**, and **5b** were prepared by $LiAlH_4$ reduction and Ac_2O–pyridine acetylation of the corresponding substituted ethyl cinnamates which were obtained by condensation of ethyl acetate and substituted benzaldehydes. **3d** and **8** were prepared analogously as described above. **5c** was prepared by $LiAlH_4$ reduction and Ac_2O–pyridine acetylation of methyl 3-chlorocinnamates, which was obtained by condensation of 3-chlorobenzaldehyde and malonic acid followed by esterification. 3-Nitrocinnamyl acetate was prepared by $NaBH_4$ reduction and acetylation (Ac_2O–pyridine) of 3-nitrocinnamaldehyde obtained by aldol condensation of 3-nitrobenzaldehyde and acetaldehyde. *cis*-Cinnamyl bromide was prepared by hydrogenation (5% Pd, $BaSO_4$)[22] and bromination (Ph_3P/Br_2)[23] of 3-phenyl-2-propyn-1-ol obtained by condensation of formaldehyde and 2-phenylethynyl magnesium bromide and purified by column chromatography. This compound quite easily isomerizes to the trans form **1b** and must be protected from light. All the chemicals except *cis*-cinnamyl bromide were distilled and stored under nitrogen.

Preparation of complexes **11** and **11′** was carried out under a dry carbon monoxide atmosphere by using standard Schlenk tube techniques.

General Procedure for the Cyclocarbonylation of Cinnamyl Compounds. A cinnamyl compound (10 mmol), Ac_2O (20 mmol), NEt_3 (20 mmol), a catalyst (0.07 mmol), and benzene

(19) Iwasaki, M.; Matsuzaka, H.; Kobayashi, Y.; Hiroe, Y.; Ishii, Y.; Koyasu, Y.; Hidai, M., in preparation.

(20) Kharasch, M. R.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.
(21) Jensen, K. A. *Z. Anorg. Allg. Chem.* **1936**, *229*, 225.
(22) Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1956**, *78*, 2518.
(23) Schaefer, J. P.; Weinberg, D. S. *J. Org. Chem.* **1965**, *30*, 2635.

as solvent (8 mL) were charged in a 100-mL Hastelloy autoclave under a nitrogen atmosphere. The reactor was closed, pressurized to 60 atm with CO at room temperature, heated up to 160 °C within 20 min, and kept at this temperature for 1 h with magnetic stirring. The reactor was then cooled to room temperature and the gas purged. Naphthalene (120 mg) as an internal standard was added to the reaction mixture and liquid products were immediately analyzed by GLC. After the GLC analysis, the reaction mixture was washed with 1 N HCl, aqueous $NaHCO_3$, and water, and the resulting solution was evaporated to give a residual oil. The oil was purified by silica gel column chromatography followed by bulb-to-bulb distillation or recrystallization to give a 1-naphthol derivative.

Competitive Reaction. The reactor was charged with a mixture of cinnamyl compounds **5b** (5 mmol) and **1a** (5 mmol) or **5c** (5 mmol), $PdCl_2(PPh_3)_2$ (0.7 mmol), Ac_2O (10 mmol), NEt_3 (20 mmol), benzene (8 mL), and CO (60 atm at room temperature) as described above. The reactor was heated to 160 °C within 20 min and kept at this temperature with magnetic stirring. After 20 min the reactor was rapidly cooled to stop the reaction and the pressure was carefully released. Naphthalene (120 mg) as an internal standard was added to the reaction mixture and liquid products were immediately analyzed by GLC.

Saponification of 3-Methyl-1-naphthyl Acetate (4a). All manipulations handling free 3-methyl-1-naphthol were carried out under a nitrogen atmosphere in the dark, because of its sensitivity to O_2 and light.

To a methanol solution (10 mL) of **4a** (2.01 g, 10.1 mmol) was added dropwise a methanol solution of KOH (2.0 g) at room temperature. After being stirred for 1 h, the solution was acidified with concentrated HCl and water was added. The mixture was extracted with benzene three times and dried over $MgSO_4$. Evaporation of benzene gave crude product as a white solid, which was recrystallized from hot hexane to afford pure 3-methyl-1-naphthol as white needles (1.37 g, 92%).

Oxidation of 3-Methyl-1-naphthol. A mixture of 3-methyl-1-naphthol (0.300 g, 1.90 mmol) and salcomine (60 mg) was dissolved in DMF (15 mL) in the dark and O_2 was passed through it for 3 h. Water (50 mL) was added and the mixture was extracted with benzene three times. The combined organic layer was washed with water, dried over $MgSO_4$, and evaporated. The resulting brown solid was chromatographed on silica gel to give menadione (0.210 g, 64%) as yellow crystals.

Compound 4a: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.46 (s, 3 H), 2.51 (d, 3 H, J = 0.6 Hz), 7.09 (d, 1 H, J = 1.2 Hz), 7.44 (td, 1 H, J = 9.8 Hz, 1.5 Hz), 7.46 (td, 1 H, J = 10.0 Hz, 1.8 Hz), 7.52 (s, 1 H), 7.77 (dd, J = 7.6 Hz, 1.8 Hz), 7.79 (dd, 1 H, J = 7.6 Hz, 1.8 Hz). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.97; H, 6.05. Found: C, 78.06; H, 6.16.

Compound 4b: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.40 (s, 3 H), 2.70 (s, 3 H), 7.24 (d, 1 H, J = 7.6 Hz), 7.34 (d, 1 H, J = 7.3 Hz), 7.41 (t, 1 H, J = 7.6 Hz), 7.50 (t, 1 H, J = 7.9 Hz), 7.73 (d, 1 H, J = 8.2 Hz), 7.90 (dd, 1 H, J = 8.5 Hz, 0.6 Hz). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.97; H, 6.05. Found: C, 78.01; H, 6.22.

Compound 4c: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.52 (s, 3 H), 7.20 (dd, 1 H, J = 7.3 Hz, 0.9 Hz), 7.34 (dd, 1 H, J = 8.5 Hz, 1.8 Hz), 7.39 (t, 1 H, J = 7.8 Hz), 7.60 (s, 1 H), 7.69 (d, 1 H, J = 8.2 Hz), 7.77 (d, 1 H, J = 8.6 Hz).

Compound 4d: ^1H NMR (90 MHz, $CDCl_3$, δ) 2.36 (s, 3 H), 2.42 (s, 3 H), 2.43 (s, 3 H), 6.96 (d, 1 H, J = 1 Hz), 7.16 (dd, 1 H, J = 9 Hz, 2 Hz), 7.35 (br s, 1 H), 7.47 (br s, 1 H), 7.56 (d, 1 H, J = 9 Hz).

Compound 6a: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.41 (s, 3 H), 2.78 (s, 3 H), 7.16 (dd, 1 H, J = 7.3 Hz, 0.9 Hz), 7.35 (dd, 1 H, J = 8.5 Hz, 1.5 Hz), 7.42 (t, 1 H, J = 7.9 Hz), 7.64 (s, 1 H), 7.65 (d, 1 H, J = 8.2 Hz), 7.75 (d, 1 H, J = 7.9 Hz).

Compound 6b: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.44 (s, 3 H), 3.92 (s, 3 H), 7.01 (dd, 1 H, J = 7.6 Hz, 0.9 Hz), 7.16 (s, 1 H), 7.17 (dd, 1 H, J = 11.7 Hz, 2.4 Hz), 7.42 (dd, 1 H, J = 8.2 Hz, 7.3 Hz), 7.62 (d, 1 H, J = 7.3 Hz), 7.76 (dd, 1 H, J = 8.9 Hz, 0.9 Hz).

Compound 6c: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.46 (s, 3 H), 7.25 (dd, 1 H, J = 7.5 Hz, 1.1 Hz), 7.45 (dd, 1 H, J = 8.9 Hz, 2.1 Hz), 7.49 (t, 1 H, J = 7.9 Hz), 7.65 (d, 1 H, J = 8.2 Hz), 7.81 (d, 1 H, J = 8.9 Hz), 7.86 (d, 1 H, J = 2.1 Hz).

Compound 7a: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.46 (s, 3 H), 2.51 (s, 3 H), 7.12 (dd, 1 H, J = 7.3 Hz, 1.2 Hz), 7.26 (d, 1 H, J = 7.0 Hz), 7.35 (t, 1 H, J = 7.6 Hz), 7.42 (t, 1 H, J = 7.8 Hz), 7.71 (d, 1 H, J = 9.2 Hz), 7.74 (d, 1 H, J = 8.2 Hz).

Compound 7b: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.38 (s, 3 H), 3.92 (s, 3 H), 6.84 (dd, 1 H, J = 7.6 Hz, 0.9 Hz), 7.07 (dd, 1 H, J = 7.6 Hz, 0.9 Hz), 7.38 (t, 1 H, J = 7.9 Hz), 7.42 (t, 1 H, J = 8.2 Hz), 7.45 (dd, 1 H, J = 8.2 Hz, 0.9 Hz), 7.69 (dd, 1 H, J = 8.2 Hz, 0.9 Hz).

Compound 7c: ^1H NMR (400 MHz, $CDCl_3$, δ) 2.43 (s, 3 H), 7.19 (dd, 1 H, J = 7.6 Hz, 1.2 Hz), 7.36 (t, 1 H, J = 7.9 Hz), 7.49 (t, 1 H, J = 7.9 Hz), 7.54 (dd, 1 H, J = 7.3 Hz, 1.2 Hz), 7.77 (dd, 1 H, J = 7.6 Hz, 0.9 Hz), 7.78 (dd, 1 H, J = 7.9 Hz, 1.2 Hz).

Compound 9: mp 60.3–61.5 °C; IR (KBr, cm^{-1}) 1757 ($\nu_{C=O}$), 1220 (ν_{C-O}); ^1H NMR (400 MHz, $CDCl_3$, δ) 2.55 (s, 3 H), 7.33 (dd, 1 H, J = 7.6 Hz, 1.2 Hz), 7.56–7.65 (m, 3 H), 7.73 (s, 2 H), 7.81 (dd, 1 H, J = 7.9 Hz, 1.2 Hz), 7.89 (dd, 1 H, J = 6.6 Hz, 2.1 Hz), 9.10 (dd, 1 H, J = 7.3 Hz, 2.1 Hz). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.26; H, 5.10.

Preparation of *trans*-[((*E*)-PhCH=CHCH$_2$CO)PdBr(PPh$_3$)$_2$] (11). A 100-mL stainless steel autoclave was charged with a toluene solution (20 mL) of $Pd(CO)(PPh_3)_3$ (0.29 g, 0.31 mmol) and *trans*-cinnamyl bromide (**1b**) (0.41 g, 2.1 mmol). The reactor was closed, pressurized to 20 atm with CO at room temperature, and stirred magnetically for 2 h. A yellow solid was precipitated by adding hexane to the concentrated yellowish orange reaction mixture, which was washed with hexane several times and recrystallized from toluene (7 mL)–hexane (15 mL) to give **11** as yellow cubic crystals (0.21 g, 74%): IR (KBr, cm^{-1}) 1667 (ν_{CO}), 1640 ($\nu_{C=C}$); ^1H NMR (400 MHz, C_6D_6, δ) 2.77 (d, 2 H, J = 9.0 Hz), 5.83 (d, 1 H, J = 16.2 Hz), 6.40 (dt, 1 H); ^{31}P NMR (C_6D_6, δ) 18.46 (s). Anal. Calcd for $C_{46}H_{39}BrOP_2Pd \cdot {}^1/_2$toluene: C, 65.82; H, 4.92; Br, 9.25. Found: C, 65.27; H, 5.04; Br, 8.84. Complex **11** is stable under a CO atmosphere; however, it gradually decomposes in solution to form **13** under an atmosphere of nitrogen.

Treatment of $Pd(CO)(PPh_3)_3$ with *cis*-cinnamyl bromide was carried out in the dark, because the bromide easily isomerized to the trans form **1b**. Complex **11** was also isolated in 70% yield after recrystallization.

Preparation of *trans*-[((*E*)-PhCH=CHCH$_2$CO)PtBr(PPh$_3$)$_2$] (11′). To a toluene solution (5 mL) of $Pt(CO)(PPh_3)_3$ (0.27 g, 0.27 mmol) was added **1b** (0.45 g, 2.3 mmol), and the solution was stirred under 1 atm of CO for 1 day at room temperature. During the reaction a white solid was precipitated. The solid was filtered, washed with hexane several times, and recrystallized from benzene (15 mL)–hexane (20 mL) to give **11′** as white needle-like crystals (0.23 g, 83%): IR (KBr, cm^{-1}) 1660 (ν_{CO}), 1635 ($\nu_{C=C}$); ^1H NMR (400 MHz, C_6D_6, δ) 2.38 (d, 2 H, J = 7.3 Hz), 5.70 (d, 1 H, J = 15.9 Hz), 6.33 (dt, 1 H); ^{31}P NMR (C_6D_6, δ) 18.45 (s); satellite peaks were also observed ($J_{^{31}P-^{195}Pt}$ = 3486 Hz). Anal. Calcd for $C_{46}H_{39}BrOP_2Pt \cdot {}^1/_2$benzene: C, 59.82; H, 4.31; Br, 8.12. Found: C, 59.98; H, 4.38; Br, 8.06. Complex **11′** is stable in solution even under a nitrogen atmosphere.

Treatment of $Pt(CO)(PPh_3)_3$ with *cis*-cinnamyl bromide was carried out analogously in the dark and complex **11′** was isolated in 73% yield after recrystallization.

Complex 12: ^1H NMR (400 MHz, C_6D_6, δ) 2.89 (d, 2 H, J = 9.2 Hz), 5.09 (d, 1 H, J = 13.7 Hz), 5.55 (dt, 1 H). Complex **12** could not be isolated under our reaction conditions.

Preparation of (η^3-1-Ph-allyl)PdBr(PPh$_3$) (13). To a toluene solution (10 mL) of $Pd(CO)(PPh_3)_3$ (0.31 g, 0.34 mmol) was added **1b** (0.77 g, 3.9 mmol), and the solution was stirred at room temperature for 2 h under 1 atm of CO. During the reaction, a pale yellow solid was precipitated. The solid was filtered, washed with hexane several times, and recrystallized from chloroform (2 mL)–hexane (6 mL) to give **13** as yellow cubic crystals (0.15 g, 81%): ^1H NMR (400 MHz, $CDCl_3$, δ) 5.06 (d, 1 H, J = 7.6 Hz), 5.06 (d, 1 H, J = 22.9 Hz), 5.90 (m, 1 H), 6.72 (dd, 1 H, J = 15.7 Hz, 5.7 Hz). Anal. Calcd for $C_{27}H_{24}BrPd$: C, 57.31; H, 4.28; Br, 14.12. Found: C, 57.85; H, 4.34; Br, 14.50.

Formation of 1-Naphthyl Acetate from Complex 11 or 11′. A 100-mL stainless steel autoclave was charged with a mixture of **11** (0.14 g, 0.15 mmol), Ac_2O (2 mL), NEt_3 (3 mL), benzene (10 mL), and CO (60 atm at room temperature). The reactor was closed, heated to 160 °C within 20 min, and kept at that temperature for 1 h with magnetic stirring. After CO was gradually released, naphthalene (120 mg) as an internal standard was added

to the reaction mixture and liquid products were immediately analyzed by GLC.

Treatment of 11′ under catalytic cyclocarbonylation conditions was carried out analogously.

Registry No. **1a**, 21040-45-9; **1b**, 26146-77-0; **2**, 830-81-9; **3a**, 65693-16-5; **3b**, 115117-74-3; **3c**, 77134-00-0; **3d**, 115117-75-4; **4a**, 76605-37-3; **4b**, 115117-79-8; **4c**, 62521-66-8; **4d**, 115117-80-1; **5a**, 115117-76-5; **5b**, 115117-77-6; **5c**, 115117-78-7; **6a**, 115117-81-2; **6b**, 115117-83-4; **6c**, 115117-84-5; **7a**, 115117-82-3; **7b**, 82265-46-1; **7c**, 115117-85-6; **8**, 115117-86-7; **9**, 115117-87-8; **11**, 115117-89-0; **11′**, 115117-92-5; **12**, 115117-91-4; **13**, 115117-90-3; $PdCl_2(PPh_3)_2$, 13965-03-2; $Pd(CO)(PPh_3)_3$, 24670-32-4; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2(PMePh_2)_2$, 52611-08-2; $PdCl_2(PMe_2Ph)_2$, 29484-74-0; $PdCl_2(PMe_3)_2$, 25892-38-0; $PdCl_2(PCy_3)_2$, 29934-17-6; $PtCl_2(PPh_3)_3$, 10199-34-5; $NiBr_2(PPh_3)_2$, 14126-37-5; $Ru_3(CO)_{12}$, 15243-33-1; $Pt(CO)(PPh_3)_3$, 15376-99-5; 3-methyl-1-naphthol, 13615-40-2; menadione, 58-27-5; *cis*-cinnamyl bromide, 115117-88-9.

Stereoselectivity Differences in Wittig Reactions of Semistabilized Ylides

Anastasia Mylona,† John Nikokavouras,† and Ioannis M. Takakis*,‡

National Research Center of Physical Sciences "Demokritos", GR-153 10 Aghia Paraskevi Attikis, Greece, and Laboratory of Organic Chemistry, University of Thessaloniki, GR-540 06 Thessaloniki, Greece

Received November 29, 1987

The Wittig reactions of phosphorane **1** with various benzaldehydes **3** (series A) and the phosphoranes **4** with salicylaldehyde **6** (series B) have been studied. The *Z*:*E* stilbene ratio in series B is enhanced relative to that in series A. This difference in the stereochemical outcome between the two series is rationalized in terms of steric factors mainly imposed by the *o*-methoxymethoxy group in ylide **1** and aldehyde **6**, whereas electronic and possibly steric effects due to the para substituents in aldehydes **3** and ylides **4** seem to be relatively unimportant. Oxaphosphetanes that may collapse to olefins or decompose to Li^+-stabilized betaine complexes are postulated as the important intermediates.

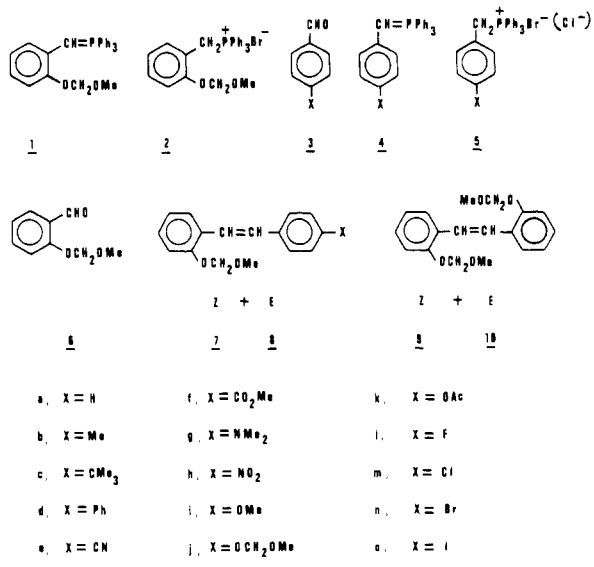
The significance and generality of the Wittig carbonyl olefination process in synthetic organic chemistry have prompted several investigators to consider this reaction from the mechanistic point of view.[1] Efforts have been primarily focused on reactive ylides in salt-free solutions, and relatively little attention has been devoted to semistabilized ylides.[1a,b,g,2] Mechanistically,[1a,b] free betaine,[2a-c] ion-stabilized betaine,[2e,f] and oxaphosphetane[2d,f] intermediates have been entertained.

Herein we report the results of a study concerning the Wittig reactions of [*o*-(methoxymethoxy)benzylidene]triphenylphosphorane (**1**), generated from the corresponding phosphonium salt **2**, with various para-substituted benzaldehydes **3** (series A) on one hand and the para-substituted benzylidenetriphenylphosphoranes **4**, resulting from phosphonium salts **5**, with *O*-(methoxymethyl)salicylaldehyde (**6**) (series B) on the other hand, i.e., interchanging the ylide and the aldehyde substituents. Such a systematic investigation is lacking, particularly in evaluating the effect of steric crowding imposed by a bulky group in the ortho position of the benzylidene group of an ylide,[3] and also in benzaldehyde, from the final *Z*:*E* (7:8) stilbene ratios (Chart I). We have also carried out the Wittig reaction between phosphorane **1** and aldehyde **6** to obtain the isomeric stilbenes **9** and **10**.

The reactions were carried out in benzene, at 25 °C, with *n*-butyllithium as the base as previously described.[4] The lithium salts were not excluded. Product composition was determined by analytical GC with internal standards to correct the GC areas (Table I).

Structural assignments were based on the physical and spectroscopic properties of the products. In the UV spectra (see paragraph at the end of paper about supplementary material) the (*E*)-stilbenes exhibit a bathochromic shift (λ_{max} 311–361 nm) and a hyperchromic effect (ϵ 17 000–37 000) relative to the *Z* (λ_{max} 274–332 nm, ϵ 7000–17 500) in accord with the literature.[4,5a,b] The IR

Chart I



spectra of the (*E*)-stilbenes show an absorption in the region 957–970 (s–m) cm^{-1}, characteristic of *E*-disubsti-

† NRCPS "Demokritos".

‡ University of Thessaloniki.

(1) (a) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1. (b) Gosney, I.; Rowley, A. G. In *Organophosphorous Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic: New York, 1979; pp 17–153. (c) Bestmann, H. J. *Pure Appl. Chem.* **1980**, *52*, 771 and references cited therein. (d) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823 and references cited therein. (e) Olah, G. A.; Krishnamurthy, V. V. *Ibid.* **1982**, *104*, 3987. (f) Schlosser, M.; Schaub, B. *Ibid.* **1982**, *104*, 5821. (g) Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, R. R.; Almond, H. R., Jr.; Whittle, R. R.; Olofson, R. A. *Ibid.* **1986**, *108*, 7664 and references cited therein.

(2) (a) Ketcham, R.; Jambotkar, D.; Martinelli, L. *J. Org. Chem.* **1962**, *27*, 4666. (b) Johnson, A. W.; Kyllingstad, V. L. *Ibid.* **1966**, *31*, 334. (c) Jones, M. E.; Trippett, S. *J Chem. Soc. C* **1966**, 1090. (d) Allen, D. W.; Ward, H. *Tetrahedron Lett.* **1979**, 2707. (e) Allen, D. W. *J. Chem. Res., Synop.* **1980**, 384. (f) Allen, D. W.; Ward, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35b*, 754. (g) Allen, D. W. *Ibid.* **1980**, *35b*, 1455. (h) Vedejs, E.; Fang, H. W. *J. Org. Chem.* **1984**, *49*, 210. (i) Donxia, L.; Dexian, W.; Yaozhong, L.; Huaming, Z. *Tetrahedron* **1986**, *42*, 4161.

0022-3263/88/1953-3838$01.50/0 © 1988 American Chemical Society