Organometallics 1988, *7*, 2435–2439

Since thermochemical data were available for this reaction, additional kinetic studies were indicated. Determination of the activation energy for reaction 28 would allow comparison of kinetic and thermodynamic bond strength estimates. An additional aspect of interest was the role of the M⋯H–C agostic bond in this process. Standard kinetic studies confirmed the mechanism outlined by eq 9. The kinetic isotope effect $k_H/k_D = 1.2$, showed that the reaction must involve interaction of the tungsten center with the cyclohexyl group of the phosphine. The activation parameters, when coupled with the thermochemical data, give some suggestion as to the mechanism of this reaction.

The reaction profile in Figure 4 combines the thermochemical data in Figure 1 with the enthalpy of activation of 24 kcal/mol for $\Delta H^{\ddagger}_1 + [\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}]$ with an estimate of 2.0 kcal/mol for $[\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}]$ based on the value of 0.06 for k_2/k_{-1}. It should be noted that the kinetic selectivity ($k_{-1}/k_2 = 17$) of the reactive intermediate $(PCy_3)_2W(CO)_3$ is high and that it favors the thermodynamically less stable pyridine complex. The selectivities of most such reaction intermediates have been shown to be small ($k_{-1}/k_2 = 1.0$).[9] The high kinetic selectivity in this system may reflect the fact that the intermediate is a stable complex. Since pyridine has a smaller cone angle[20] than $P(OMe)_3$, it is preferred kinetically despite a smaller heat of binding.

The major question regarding the mechanism of this substitution is whether replacement of coordinated pyridine is a concerted process. That is, is it an intramolecular associative reaction with the W⋯H–C ligand rotating into position and displacing the pyridine, or does the pyridine ligand dissociate followed by formation of the agostic bond. The activation energy is only about 3 kcal/mol larger than the ground-state energy difference as shown in Figure 4. If the agostic interaction does have a value on the order of 10 kcal/mol, then it must be at least partially formed during the expulsion of pyridine. The alternative interpretation is that the W⋯H–C interaction is very weak. In view of the thermochemical experiments that show a close correspondence between relative heats of substitution in this and related systems, it seems more likely that the mechanism is a concerted one.

Conclusion

Thermochemical data reported for addition of ligands to $W(CO)_3(PCy_3)_2$ showed binding of molecular hydrogen and nitrogen to be relatively weak, in keeping with the "reversible" nature of this addition. The value for addition of H_2 was in agreement with theoretical calculations done earlier.[4] For the ligands $NCCH_3$, py, $P(OMe)_3$, and CO, there was close correspondence of stability between the $W(CO)_3(PCy_3)_2(L)$ system and the $L_3W(CO)_3$ complexes. This was most likely due to the fact tht the ligands used were not bulky enough to induce large steric repulsions.[22] The enthalpy of addition of CO to $W(CO)_3(PCy_3)$ was unusually low, probably due to the fact that addition reactions involve cleaving the W⋯H–C agostic bond.

Kinetics of substitution for the complex $W(CO)_3(PCy_3)_2(py)$ also showed the importance of the agostic bond in these compounds. A kinetic isotope effect, $k_H/k_D = 1.2$, was observed when $W(CO)_3(P(C_6D_{11})_3)_2(py)$ was used in place of $W(CO)_3(P(C_6H_{11})_3)_2(py)$. The activation energy for dissociation of pyridine from this complex is 22 ± 3 kcal/mol, only 3 kcal/mol higher than the thermodynamic value for this dissociation. Since the agostic bond is estimated to be on the order of 10 kcal/mol, it is proposed that the reaction mechanism involves concerted displacement of the W–pyridine bond by the cyclohexyl group on the phosphine ligand. Additional kinetic and thermodynamic studies on these and related complexes are in progress.

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A Kinetic Investigation of Some Electronic Factors and Ligand Effects in the Heck Reaction with Allylic Alcohols

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The effect of several factors (salt, ligand, base, temperature, aryl iodide) on the initial reaction rate of the palladium-catalyzed arylation of pent-1-en-3-ol and but-3-en-2-ol was kinetically studied, and the activation parameters were calculated for the latter. It was shown that a tertiary amine not only neutralizes the hydrogen iodide formed in the reaction but also acts as a ligand of the palladium atom. The resulting catalytic species was very efficient, allowing the reaction to be carried out at low temperatures in good yields. A linear Hammett relationship ($\rho = -1.6$) was established with a series of para-substituted aryl iodides. All these results suggest that the rate-limiting step of the reaction is the oxidative addition of the halogenated compound to the palladium.

Introduction

The palladium-catalyzed arylation of double bonds[1] known as the Heck reaction[2] is generally applied to electron-deficient olefins.[3] With allylic alcohols, arylated ketones are obtained, but the reaction is rather sluggish.[4] There have been a number of studies aimed at both improving this reaction and determining its mechanism.[3]

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[1] (a) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Soc. Chem. Jpn.* **1971**, *4*, 581. (b) Heck, R. F.; Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320.

[2] Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8; p 799.

[3] (a) Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

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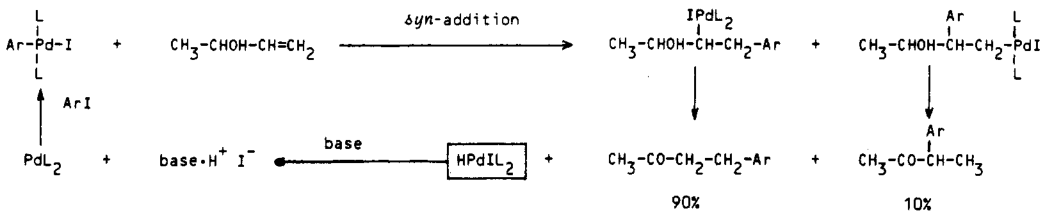
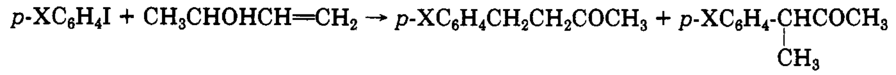
Scheme I



Scheme II



$$p\text{-}XC_6H_4I + CH_3CHOHCH{=}CH_2 \rightarrow p\text{-}XC_6H_4CH_2CH_2COCH_3 + p\text{-}XC_6H_4\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCH_3$$

X = OMe	**1a**	**6**	**1b**	**1c**
X = Me	**2a**		**2b**	**2c**
X = H	**3a**		**3b**	**3c**
X = F	**4a**		**4b**	**4c**
X = Cl	**5a**		**5b**	**5c**

The latter is now well established[3,5] and illustrated in Scheme I for the formation of the major product of arylation of but-3-en-2-ol.

The reaction has been shown to proceed in a multistage process: formation of an active arylpalladium halide by the oxidative addition of the organic halide to Pd^0; syn addition of the arylpalladium to the double bond leading to an organopalladium intermediate, which decomposes to the arylated ketone;[5] regeneration of Pd^0 at the end of the catalytic cycle by reaction of $HPdL_2I$ with a base.

Since the kinetics of the Heck reaction has hitherto received virtually no attention, we believed it would be instructive to investigate the reaction from this vantage point in order to gain some additional insight into its scope and limitations. An important goal of this study was the development of a more efficient procedure for the synthetic utilization of the Heck reaction based on a clearer understanding of the influence of several factors (salt, ligand, base, temperature, aryl iodide) on reaction rate.

Arylation of but-3-en-2-ol was chosen as the model reaction which was carried out under various conditions with a series of para-substituted aryl iodides (**1a**–**5a**) (Scheme II).

Results and Discussion

In the studied reaction, the required catalyst is a Pd^0 complex which is generally formed in situ by reduction of a readily available Pd^{II} salt such as $PdCl_2$. It has been suggested that the olefin itself serves as a reducing agent in a Wacker-type reaction.[3b] Another possibility would be the oxidation of the allylic alcohol to an enone:

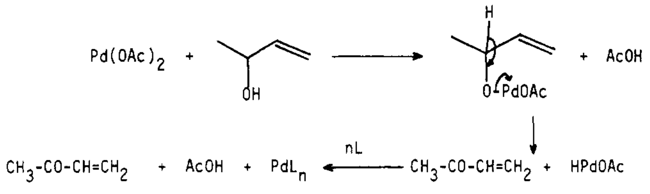


Table I. Initial Pseudo-First-Order Rate Constants for the Formation of Ketones: Influence of the Catalyst[a]

entry	t (°C)	cat. (10^{-2} molar equiv)	10^5k_i (s^{-1})	other ligand (molar equiv)
1	74	$PdCl_2$ (1)	2.20	
2[b]	74	$PdCl_2$ (1)	38.7	Et_3N (1)
3[b]	74	$PdCl_2$ (1)	70.0	n-Bu_3N (1)
4	50	$PdCl_2$ (1)	0.06	Et_2NH (0.2)
5	54	$PdCl_2$ (1)	0.06	pyridine (0.2)
6	74	$PdCl_2$ (1)	0.05	$[(CH_3)_2NCH_2]_2$ (0.1)
7	74	$Pd(dba)_2$ (5)	3.9	
8	74	$PdCl_2$ (4)	0.13	$(Ph)_3P$ (0.1)
9	74	$Pd[(Ph)_3P]_4$ (1)	0.26	

[a] [But-3-en-2-ol] = [PhI] = [AcONa] = 1 M in DMF. [b] Without AcONa.

Table II. Initial Pseudo-First-Order Rate Constants Using Sodium Acetate or Tertiary Amines: Influence of the Base[a]

entry	t (°C)	R	base (molar equiv)	10^5k_2 (s^{-1})
1	74	Me	AcONa (1)	2.2
2	104	Me	AcONa (1)	27.7[b]
3	120	Me	AcONa (1)	39.7[b]
4	74	Et	AcONa (1)	2.4
5	74	Me	Et_3N (1)	38.7
6	74	Me	Bu_3N (1)	70.0
7	74	Et	Et_3N (1)	30.6
8	74	Me	AcONa (1) + Et_3N (0.2)	70.3
9	74	Et	AcONa (1) + Et_3N (0.2)	66.7
10	74	Me	AcONa (1) + Bu_3N (0.2)	94.4

[a] $[RCHOHCH{=}CH_2] = [PhI] = 10^2(PdCl_2) = 1$ M in DMF. [b] An estimated amount of 10–14% biphenyl was detected during the reaction.

In order to verify the origin of Pd^0, **6** was treated with a stoichiometric amount of palladium chloride under the conditions used for the kinetic study (vide infra) *without* aryl iodide. But-3-enone was formed (GLC) and isolated in 80% yield (see Experimental Section). Such an oxidation of secondary alcohols by palladium salts was already mentioned in the literature.[6]

Since the determination of the rate law of a complex reaction is usually difficult, a convenient way of evaluating the reaction rate is the measurement of the initial rate constants for the formation of the arylated ketones. Preliminary experiments showed that the initial rate was nearly proportional to the initial aryl iodide concentration but independent of the alcohol concentration. Thus, it seemed pertinent to us to evaluate the formation rate of the ketones as a pseudo-first-order rate constant vs aryl iodide concentration. The concentration of ketones was monitored by GLC in the presence of an internal standard at a number of different initial concentrations of the several reactants. Table I shows the results obtained with

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(4) (a) Melpolder, J. B.; Heck, R. F. *J. Org. Chem.* **1976**, *41*, 265. (b) Chalk, A. J.; Magennis, S. A. *J. Org. Chem.* **1976**, *41*, 273.

(5) Smadja, W.; Czernecki, S.; Ville, G.; Georgoulis, C. *Organometallics* **1987**, *6*, 166.

(6) (a) Lloyd, W. G. *J. Org. Chem.* **1967**, *32*, 2816. (b) Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977**, 157.

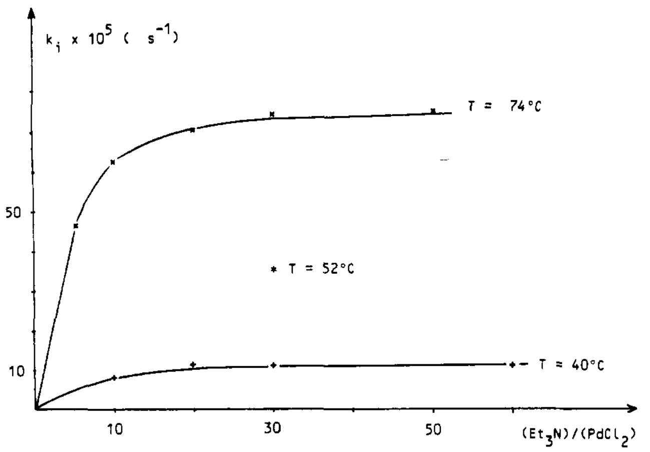

Figure 1. Plot of k_i against (Et_3N) for the phenylation of but-3-en-2-ol in the presence of an excess of sodium acetate: (AcONa)/($PdCl_2$) = 100.

various combinations of catalysts, bases, and complexing agents.

A secondary amine (entry 4), pyridine (entry 5), and a bis(tertiary amine) (entry 6) were shown to block the reaction, an observation cited occasionally by other authors.[4,5] Triphenylphosphine as a ligand (entries 8 and 9) slows the reaction considerably, although a stabilizing effect of Pd^0 by this ligand is generally accepted. The use of a Pd^0 complex such as $Pd(dba)_2$ (entry 7) did not show any remarkable increase of k_i. Reasonable reaction rates were obtained only in the presence of AcONa or a tertiary amine and with $PdCl_2$ as the catalyst. Therefore these systems were further investigated, and the results are summarized in Table II.

For the reaction with AcONa, k_i was measured for temperatures in the range 74–120 °C. Plotting log k_i against $1/T$ gives a linear relationship from which the classical thermodynamic values of activation can be calculated: $\Delta G^* = 73$ kJ mol^{-1}, $\Delta H^* = 71$ kJ mol^{-1}, and $\Delta S^* = -53$ J mol^{-1} K^{-1}.

With the two allylic alcohols employed in this study, the initial rate constants k_i were considerably higher with R_3N (R = Me or Bu) than with AcONa (compare entries 1 and 4 to entries 5, 6, and 7). This observation strongly suggests that R_3N not only neutralizes the HX formed in the reaction[3] but also acts as a ligand of the palladium atom to form a very reactive species in the oxidative addition step that could be the rate-determining step:

$$Pd^0L_n + PhI \rightarrow PhPdIL_{n-2} + 2L$$

In order to test these hypotheses, a study was carried out by using increasing amounts of Et_3N *in the presence* of AcONa at various temperatures (Figure 1).

Our results clearly demonstrate the role of the amine as a ligand of the palladium catalyst. A ratio of (Et_3N)/($PdCl_2$) = 20 is necessary to ensure the complete formation of the active catalytic species, resulting in maximum rate constants.

The same phenomenon was observed with pent-1-en-3-ol (7) (entries 7 and 9 of Table II).

Our observation is, therefore, not in accord with claims that tertiary amines are not good ligands for palladium,[7] but it is in agreement with the ortho-palladation effect of benzylic tertiary amines, which allows the isolation of stable ortho-palladated aromatic compounds.[8a] This effect also exercises a remarkable regiochemical control over the Heck reaction[2] and also improves both the yield and regioselectivity of the Wacker reaction.[8b]

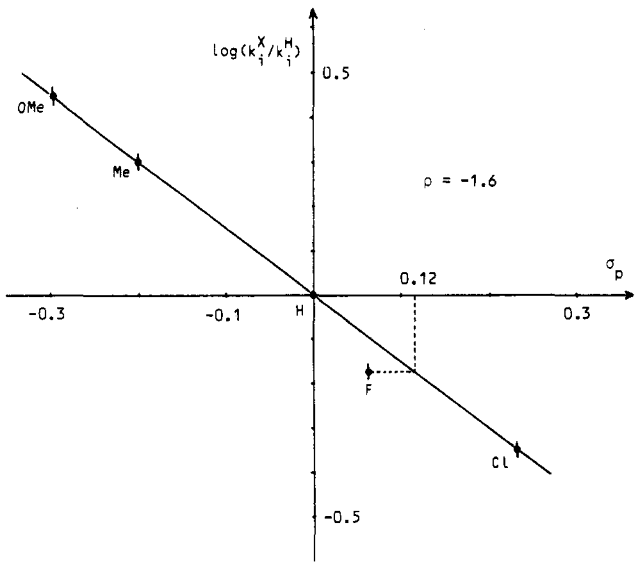

Figure 2. Plot of log (k_i^X/k_i^H) against σ_p.

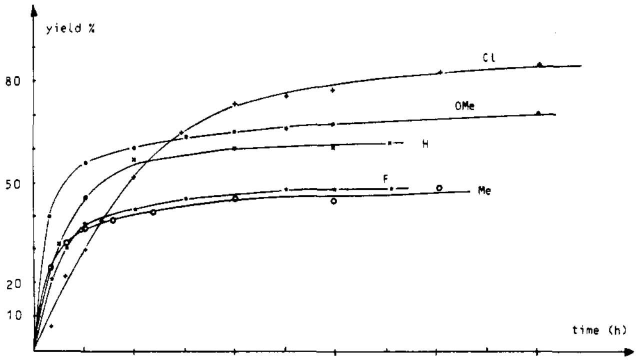

Figure 3. Yield of reaction versus time with various p-XC_6H_4I.

The occurrence of a strong synergistic effect has been observed. The initial rate constant of the reaction is greater when a small amount of R_3N (0.2 molar equiv) is used *in the presence* of AcONa than when a tertiary amine is employed alone with $PdCl_2$ (compare entry 8 to 5, entry 9 to 7, and entry 10 to 6 in Table II).

In order to get some information on the origin of that synergistic effect, the reaction was carried out with $Pd(OAc)_2$ instead of $PdCl_2$, *in the presence* of 1.2 equiv of Et_3N but *without* AcONa. Under these conditions the reaction rate was very similar (72.0×10^{-5} s^{-1}) to that measured with the AcONa/Et_3N/$PdCl_2$ system (70.3×10^{-5} s^{-1}). Such a result can be explained in terms of ligand exchange on the palladium, where Cl^- is replaced by AcO^- leading to the rapid formation of $Pd(OAc)_2$, which is known to be a very reactive catalyst in the Heck reaction.[2]

Variation of the temperature allowed the determination of the thermodynamic values in the range 40–74 °C for this new system: $\Delta G^* = 46$ kJ mol^{-1}, $\Delta H^* = 43$ kJ mol^{-1}, and $\Delta S^* = -75$ J mol^{-1} K^{-1}. With either AcONa alone or the AcONa–Et_3N system, the activation values are in the range of the values usually reported for the oxidative additions with various transition metals.[9] The large negative ΔS^* values are generally interpreted in terms of the increased solvation of a transition state with a greater dipole moment than the ground state.[10]

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[7] Spencer, A. *J. Organomet. Chem.* **1983**, *258*, 101.

[8] (a) Bridson, B. J.; Nair, P.; Dyke, S. F. *Tetrahedron* **1981**, *37*, 173. (b) Bregeault, J. M., Université P. et M. Curie, personal communication.

[9] Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

Table III. Initial Pseudo-First-Order Rate Constants for Formation of the Ketones: Influence of the Aryl Iodide[a]

entry	X	$10^6 k_i$ (s^{-1})	log (k_i^X/k_i^H)	σ_p^{10}
1	OMe	131	0.45	−0.27
2	Me	94	0.30	−0.17
3	H	47	0	0
4	F	32	−0.17	0.06
5	Cl	21	−0.35	0.23

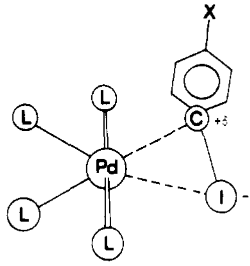
[a] [But-3-en-2-ol] = [p-XC_6H_4I] = [AcONa] = 10^2[$PdCl_2$] = 3.3-[Et_3N] = 1 M in DMF at 52 °C.

If oxidative addition is the rate-determining step, then a change in the nature of the aryl iodide should provide additional insight into the nature of the transition step. The study was therefore extended to include a series of para-substituted aryl iodides. The results are summarized in Table III and Figures 2 and 3.

Figure 2 shows a linear correlation between log (k_i^X/k_i^H) and σ_p (r = 0.993) except for the fluoro derivative which is well outside the range of experimental error. Similar discrepancies were also reported by other authors[12,13] in the case of oxidative addition reactions in aprotic solvents.

Since the fluorine atom is a strong hydrogen-bond acceptor, such irregularities were also observed when the σ_p(F) value, measured in water, was used to correlate pK_A values in aprotic solvents.[14] Thus, the discrepancies mentioned above could have their origin in solvation effects. Reexamination of all these results lead us to calculate a more appropriate value of σ_p(F) = 0.12 which provides an excellent fit for seven Hammett correlations described in the literature.[12,13] This new value for fluorine gives a still better correlation (r = 0.998) for the reaction we studied.

The small negative ρ value (−1.6) shows that an electron-donating substituent enhances reactivity and is in agreement with a three-center reaction model already proposed by several authors.[12,15] They suggested that in oxidative additions a small positive charge is developed at the carbon bearing the iodine, the dispersal of which is facilitated by electron-donating substituents on the benzene ring:



However, comparison with other results published in the literature for similar reactions shows that the influence of electron-directing substituents is not always clearly understood. In particular, Fauvarque et al.[16a] found that the rate of the reaction of para-substituted aryl iodides with $Pd[(Ph)_3P]_4$ had the reverse reactivity order and a positive activation entropy (ΔS^* = 135 J mol^{-1} K^{-1}) which is unusual for this kind of reaction.[13,17,18]

Table IV. Yield Limit in the Phenylation of But-3-en-2-ol[a]

entry	PhI (molar equiv)	base (molar equiv)	t (°C)	yield after 3 h (%)
1	1	Et_3N (0.1)	74	68
2	1	Et_3N (0.2)	74	70
3	1	Et_3N (0.5)	74	84
4	1	Et_3N^b (1.2)	74	80
5	1.5	Et_3N (0.2)	74	80
6	1.5	Et_3N (0.2)	100	89
7	2	Et_3N (0.2)	74	97
8	1	Et_3N (0.2)	40	48
9	1	Et_3N (0.2)	100	82
10	1	Et_3N (0.2)	120	70[c]
11	1	Bu_3N (0.2)	74	92
12	1	Bu_3N^b (1.2)	74	98
13	1	Bu_3N (0.2)	25	96[d]

[a] [But-3-en-2-ol] = [AcONa] = 10^2[$PdCl_2$] = 1 M in DMF. [b] Without AcONa. [c] The yield decreased from 87% after 30 min to 70% after 2 h. [d] After 24 h.

Our results also show an apparent discrepancy with the reactivity order proposed by Fitton and Rick[16b] for the reaction studied by Fauvarque. These authors did not carry out a kinetic study but assessed the reactivity by measuring the reaction yield after 16 h. But, as can be seen from Figure 3, the kinetic curves show that for the Heck reaction the yield reaches a limit that is influenced by the nature of the substituent on the aromatic ring. However, there is no obvious correlation between this limit and the electronic effects of the substituents. The order of reactivity is completely different when comparing k_i (p-OMe > p-Me > p-H > p-F > p-Cl) with the yield after 3 h (p-Cl > p-H > p-OMe > p-F > p-Me) which may suggest an explanation to the apparent discrepancy mentioned above.

In order to determine the factors influencing the yield limit, the reaction was carried out under various reaction conditions (reagents ratio, temperature, ligand). The results are summarized in Table IV.

Variation of Et_3N (entries 1 to 4) or PhI concentrations (entries 2, 5, and 7) showed a noticeable effect on the yield limit, suggesting that the irreversible decomposition of the catalyst to Pd metal (precipitation) is slowed either by stabilization with a ligand or in the presence of a sufficient concentration of aromatic iodide to favor further oxidative addition.

The effect of varying the temperature (entries 3, 10, 11, and 12) gave best results in the range 74–100 °C for short reaction times. At higher temperature the yield decreased with the time, probably by decomposition of the formed ketones, unless the reaction was stopped after 30–45 min (87% yield).

Finally, an almost quantitative yield was obtained with $AcONa/Bu_3N/PdCl_2$ after 24 h at room temperature (entry 13 of Table IV).

Conclusion

The results reported in this paper provide additional insight into both the nature of the rate-determining step in the Heck reaction and the effect of a ligand such as a tertiary base on the initial rate and yield. We would like to emphasize that the synergistic effect, observed with a $R_3N/AcONa$ combination, enabled the reaction to be

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(10) Harrod, J. F.; Smith, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2699.

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(15) Mureinik, R. J.; Weitzberg, M.; Blum, J. *Inorg. Chem.* **1979**, *18*(4), 915.

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(18) Burgess, J.; Hacker, M. J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1974**, *72*, 121.

Table V. ^{1}H NMR Data for Arylated Ketones

compd	δ(H-1)	δ(H-3)	δ(H-4)	δ(Ar)	δ(OCH_3)	δ(CH_3Ar)
1b	2.00	2.65 (t) $J_{3,4}$ = 4 Hz		6.6–7.2	3.70	
1c	1.95	3.55 (q) $J_{3,4}$ = 9 Hz	1.20 (d)	6.7–7.2	3.80	
2b	2.00	2.65 (m)		6.85		2.20
2c	1.90	3.55 (q) $J_{3,4}$ = 7 Hz	1.25 (d)	6.90		2.20
4b	1.95	2.60 (m)		6.5–7.0		
4c	1.90	3.55 (q) $J_{3,4}$ = 7 Hz	1.25 (d)	6.5–7.0		
5b	2.13	2.70 (m)		7.1–7.3		
5c	2.05	3.75 (q) $J_{3,4}$ = 4 Hz	1.37 (d)	7.1–7.4		

compd	δ(H-1)	δ(H-2)	δ(H-4)	δ(H-5)	δ(Ar)
7a	2.90 (t) $J_{1,2}$ = 7.8 Hz	2.73 (t)	2.40 (q) $J_{4,5}$ = 7.3 Hz	1.04 (t)	7.17–7.30
7b	1.38 (d) $J_{1,2}$ = 7.0 Hz	3.70 (q)	2.40 (q) $J_{4,5}$ = 7.3 Hz	1.04 (t)	7.20–7.34

carried out with readily available reagents under more convenient conditions than those previously reported.[4,19]

Experimental Section

General Methods. IR spectra (film) were recorded on a Unicam SP3-300 spectrophotometer. ^{1}H NMR spectra were recorded at 90 MHz with a Varian EM-390 instrument, in $CDCl_3$, with tetramethylsilane as the internal standard. Analytical gas chromatography was carried out on a Girdel 75 FD2 instrument equipped with flame ionization detector and fitted with a 2 m × $^1/_8$ in. 6% w/w diethyleneglycol succinate (DEGS) on Chromosorb W AW DMCS column for compounds **1b**, **1c**, 1-phenyl-3-pentanone (**7a**), 2-phenyl-3-pentanone (**7b**), and tetraethyleneglycol dimethyl ether (TAGL) as the internal standard (is.) and for **4b**, **4c**, and triethyleneglycol dimethyl ether (TGL) as is., with a 3 m × $^1/_8$ in. 15% w/w DC 710 on Chromosorb W AW DMCS column for **2b**, **2c**, **5b**, **5c**, and TAGL as is., with a 3 m × $^1/_8$ in. 20% w/w DEGS on Chromosorb W AW DMCS column for **3b**, **3c**, and TGL as is. Preparative gas chromatography was carried out on an Aerograph A700 fitted with a 2.5 m × $^3/_8$ in. 15% DC 710 on Chromosorb W AW DMCS column.

Substituted aryl iodides (Aldrich) **1a**, **2a**, **4a**, and **5a** were used as supplied, and phenyl iodide **3a** was simply distilled.

But-3-en-2-ol (6) and pent-1-en-3-ol (7) (Aldrich) were distilled from CaH_2.

Preparation of arylated ketones was carried out according to a described procedure,[5] and the new compounds **1b**, **1c**, **2b**, **2c**, **4b**, **4c**, **5b**, **5c**, **7a** and **7b** were characterized as follows.

(*p*-Methoxyphenyl)butanones (1b,c). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found for **1b**: C, 74.16; H, 7.86. Found for **1c**: C, 74.33; H, 8.02.

(*p*-Methylphenyl)butanones (2b,c). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found for **2b**: C, 81.49; H, 8.82. Found for **2c**: C, 81.39; H, 8.74.

(*p*-Fluorophenyl)butanones (4b,c). Anal. Calcd for $C_{10}H_{11}FO$: C, 72.27; H, 6.67. Found for **4b**: C, 72.29; H, 6.44. Found for **4c**: C, 72.15; H, 6.62.

(*p*-Chlorophenyl)butanones (5b,c). Anal. Calcd for $C_{10}H_{11}ClO$: C, 65.75; H, 6.07. Found for **5b**: C, 65.66; H, 6.12. Found for **5c**: C, 65.65; H, 6.11.

Phenylpentanones (7b,c). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found for **7b**: C, 81.32; H, 8.60. Found for **7c**: C, 81.28; H, 8.64.

General Procedure for Kinetic Studies. The rate study was carried out under pseudo-first-order conditions using a large excess of aryl iodide: (ArI)/($PdCl_2$) = 100. In a 5-mL callibrated flask, a mixture of 5 mmol of but-3-en-2-ol (360 mg), 1 molar equiv of aryl iodide, 1 molar equiv of sodium acetate (393 mg), 10^{-2} molar equiv of palladium chloride (8.5 mg), 0.3 molar equiv of triethylamine (152 mg), and 0.3 molar equiv of internal standard (TGL or TAGL) was dissolved in DMF. The internal standards were chosen for their inertness to the reaction conditions and their GLC retention times. After complete dissolution at room temperature, the solution was transferred into a septum-stopped vial placed in a constant temperature oil-bath and stirred throughout the reaction. Aliquots of the solution were removed by syringe and analyzed by GLC.

Preparative procedure exemplified for the phenylation of but-3-en-2-ol at room temperature (see entry 13 of Table IV). In a round-bottomed flask a mixture of 20 mmol of but-3-en-2-ol (1.44 g), 20 mmol of sodium acetate (1.64 g), 4 mmol of tributylamine (0.74 g), and 20 mmol of iodobenzene (4.08 g) was dissolved in 10 mL of dimethylformamide. The solution was stirred at room temperature for 24 h, then filtered, extracted with ether, washed with water, and dried over anhydrous $MgSO_4$. After filtration the solvent was evaporated in vacuo, yielding 3.256 g of crude product. After filtration on silica 2.656 g of a 1:9 mixture of **3b** and **3c** was isolated (90% yield).

Oxidation of But-3-en-2-ol. In a round-bottomed flask, a mixture of 1.25 mmol of but-3-en-2-ol (102 mg), 0.25 mmol of triethylamine (30 mg), 1.25 mmol of AcONa (123 mg), and 1.25 mmol of $PdCl_2$ (222 mg) was dissolved in 2 mL of DMF and stirred at 74 °C. After 1 h the crude mixture was filtered, extracted with ether, washed with water, and dried over $MgSO_4$. Pure but-3-enone was isolated in 80% yield by preparative GLC (Carbowax 20M) and characterized by comparison of its GLC retention time with that of an authentic sample and by its infrared spectrum ($\nu_{C=O}$ = 1680 cm^{-1}, $\nu_{C=C}$ = 1610 cm^{-1}).

Registry No. **1a**, 696-62-8; **1b**, 104-20-1; **1c**, 7074-12-6; **2a**, 624-31-7; **2b**, 7774-79-0; **2c**, 59115-82-1; **3a**, 591-50-4; **3b**, 2550-26-7; **3c**, 769-59-5; **4a**, 352-34-1; **4b**, 63416-61-5; **4c**, 79341-86-9; **5a**, 637-87-6; **5b**, 3506-75-0; **5c**, 21905-98-6; **6**, 598-32-3; **7a**, 20795-51-1; **7b**, 16819-77-5; pent-1-en-3-ol, 616-25-1; but-3-enone, 78-94-4.

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[19] (a) Tuyêt, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1287. (b) Ziegler, F. E.; Chakraborty, U. R.; Weisenfeld, R. B. *Tetrahedron* **1981**, *37*, 4035.