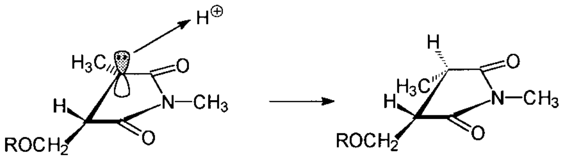

Scheme 5. Model for stereochemical control of the protonation step.

In addition to the intermolecular additions to electron-poor alkenes described here, intramolecular cyclization of α-silyl ethers having electron-poor double bonds also seems promising.

Experimental Section

General conditions for PET reactions: A jacketed Schlenk tube was charged with a solution of the α-silyl ethers **1**–**5** in acetonitrile/methanol (2/1) containing ADC (4 mol%) and BP (10 mol%). The electron-poor alkenes **6** and **7**, each dissolved in 3 mL of CH_3CN, were added before irradiation, solutions of **8**–**10** were added dropwise during irradiation. A 450 W xenon-arc lamp with a wavelength filter ($\lambda > 345$ nm) was used as a light source. The solutions were degassed with argon prior to and during irradiation and thermostated by water-cooling.

11: (analogous for **12**–**15** and **20**): A mixture of **1** (350 mg, 2.9 mmol), **6** (543 mg, 4.3 mmol), BP (45 mg), and ADC (7 mg) was dissolved in 20 mL of acetonitrile and 10 mL of methanol. During subsequent irradiation for 11 h two 10-mg portions of ADC were added every 3–4 h (27 mg total). Evaporation of the solvent followed by flash chromatography on silica gel (first separation: ethyl acetate/*n*-heptane 1/5; $R_f = 0.31$), (second separation: petroleum ether/dichloromethane 2/1; $R_f = 0.1$)) provided 228.5 mg (46%) of a light yellow oil. The signal doubling observed in the ^{1}H and ^{13}C NMR spectra indicates the formation of diastereomers. The data for the diastereomers are separated by slashes. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.98/1.05 (d, $J = 6.8$ Hz, 3 H), 2.45–2.6 (m, 1 H), 3.18–3.22 (1 H), 3.25/3.3 (s, 3 H), 3.31–3.4 (m, 1 H), 3.51/3.9 (d, $J = 4.2$ Hz, 1 H), 3.73/3.75 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 12.9/14.9$, 34.6/35.1, 40.2/41.3, 53.1/53.3, 58.9/59.0, 74.0, 114.8/115.4, 166.2/166.6; MS (EI, 70 eV): *m/z* (%): 171 (1) [M^+], 140 (7), 109 (7), 72 (58), 45 (100); HRMS (EI, 70 eV): calcd for $C_8H_{13}NO_3$: 171.0895; found 171.0890; CHN analysis calcd for $C_8H_{13}NO_3$: C 56.13, H 7.65, N 8.18; found C 56.40, H 7.83, N 7.64.

18: (analogous for **16**, **17**, and **19**): A mixture of **4** (348 mg, 1.6 mmol), ADC (21.8 mg, 0.09 mmol), and BP (24.6 mg, 0.16 mmol) were dissolved in 20 mL of acetonitrile and 10 mL of methanol. A solution of **9** (300 mg, 2.4 mmol) in 3 mL of CH_3CN was added dropwise to the reaction mixture, which was irradiated for 18 h. Evaporation of the solvent and subsequent flash chromatography on silica gel (cyclohexane/ethyl acetate 10/1; $R_f = 0.05$) provided 115 mg (18%) of a light yellow oil. The data refer to the *cis* product. The relative configuration was determined by NOE experiments. ^{1}H NMR (500 MHz, C_6D_6): $\delta = -0.11$ (s, 3 H), -0.09 (s, 3 H), 0.70 (s, 9 H), 1.26 (d, $J = 6.9$ Hz, 3 H), 2.76–2.85 (m, 2 H), 2.88 (s, 3 H), 3.42–3.45 (dd, $J = 10.0$ Hz, $J = 2.0$ Hz, 1 H), 3.86–3.89 (dd, $J = 10.0$ Hz, $J = 3.2$ Hz, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 181.1$, 179.0, 60.4, 47.1, 37.6, 26.0, 25.1, 18.3, 9.7, -5.2, -5.3; MS (EI, 70 eV): *m/z* (%): 270 (1) [$M^+ - H$], 256 (41), 214 (100), 156 (4), 129 (4), 75 (14); HRMS (EI, 70 eV): calcd. for $C_{13}H_{25}NO_3Si$: 271.1603; found: 256.1371 [$M^+ - 15$]; CHN analysis calcd for $C_{13}H_{25}NO_3Si \cdot 1/6\,H_2O$: C 57.53, H 9.28, N 5.16; found: C 56.99, H 9.26, N 5.27.

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[1] J. E. Saavedra in *Umpoled Synthons* (Ed.: T. A. Hase), Wiley, New York, **1987**.

[2] P. Sommerfeld, D. Hoppe, *Synlett* **1992**, 764; W. Guarnieri, M. Grehl, D. Hoppe, *Angew. Chem.* **1994**, *106*, 1815; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1734.

[3] K. D. Ginzel, E. Steckhan, D. Degner, *Tetrahedron* **1987**, *43*, 5797; T. Shono, Y. Matsumura, O. Onomura, Y. Yamada, *Synthesis* **1987**, 1099.

[4] J. Yoshida, T. Maekawa, T. Murata, S. Matsunaga, S. Isoe, *J. Am. Chem. Soc.* **1990**, *112*, 1962; J. Yoshida, *Top. Curr. Chem.* **1994**, *170*, 39.

[5] E. Meggers, E. Steckhan, S. Blechert, *Angew. Chem.* **1995**, *107*, 2317; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2137.

[6] M. A. Brumfield, S. L. Quillen, U. C. Yoon, P. S. Mariano, *J. Am. Chem. Soc.* **1984**, *106*, 6855.

[7] Y. M. Tsai, K.-H. Tang, W.-T. Jiaang, *Tetrahedron Lett.* **1996**, *37*, 7767; D. P. Curran, W.-T. Jiaang, M. Palovich, Y.-M. Tsai, *Synlett* **1993**, 403.

[8] J. M. Harris, I. MacInnes, J. C. Walton, B. Maillard, *J. Organomet. Chem.* **1991**, *403*, C25.

[9] Reduction potentials of the most important sensitizers: H. D. Roth, *Top. Curr. Chem.* **1992**, *163*, 131; S. L. Murov, J. Carmichael, G. L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, New York, **1993**.

[10] G. Gutenberger, *Diploma Thesis*, Universität Bonn **1996**; see also ref. [4].

[11] S. Tazuke, N. Kitamura, *J. Chem. Soc. Chem. Commun.* **1977**, 515; T. Majima, C. Pac, A. Nakasone, H. Sakurai, *J. Am.Chem. Soc.* **1981**, *103*, 4499.

[12] J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P.Todd, S. L. Mattes, *J. Am. Chem. Soc.* **1989**, *111*, 8973.

Heck Reactions without Salt Formation: Aromatic Carboxylic Anhydrides as Arylating Agents[**]

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The Friedel-Crafts reaction is still the most commonly used method for the attachment of a carbon fragment to an aromatic ring. From an industrial point of view the reaction is less desirable because of the highly corrosive conditions and the concomitant formation of a large amount of waste. Recently the Heck reaction has come into the spotlight as a means of arylating double bonds.[1] Though the reaction has a wide scope, the arylating agent is limited to aryl bromides, iodides, or triflates, aroyl halides, arylsulfonyl halides, and aryldiazonium salts. In all cases a stoichiometric amount of base is required to neutralize the acid that is formed during the reaction. In addition, an equivalent amount of halide salt is formed as waste.

The development of a stable palladium catalyst, based upon a palladacycle, has allowed the conversion of activated aryl chlorides with high turnover numbers and has brought the Heck reaction into the industrial realm.[2] But also in this reaction a stoichiometric amount of chloride salt is formed as waste product. There clearly is a need for a cheap aryl source that does not lead to the formation of halide salts in the Heck reaction.

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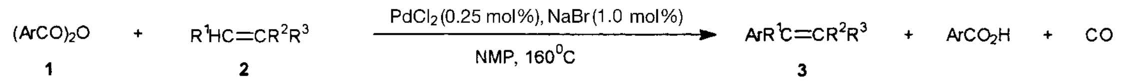

Scheme 1. Heck reaction of olefins **2** with aromatic carboxylic anhydrides **1**. For Ar, R^1, R^2, and R^3, see Table 1.

The solution to this problem lies in the use of aromatic carboxylic anhydrides as the arylating source.[3] Thus, heating benzoic anhydride (**1**, Ar = Ph) and *n*-butyl acrylate (**2**; R^1, R^2 = H, $R^3 = CO_2Bu$) in an *N*-methylpyrrolidinone (NMP) solution containing $PdCl_2$ (0.25 mol%) and NaBr (1.0 mol%) at 160°C for 90 min led to complete conversion of benzoic anhydride and formation of (*E*)-*n*-butyl cinnamate with 90% selectivity (Scheme 1). The product was isolated in 77% yield by evaporation of solvent, followed by extraction of the benzoic acid in hot water and purification of the residue by distillation (Table 1, entry 1). Side products in the reaction are benzoic acid and carbon monoxide. The latter can be easily burnt to carbon dioxide. Benzoic acid can be recycled into its anhydride.

A number of different palladium catalyst precursors can be used, such as $PdCl_2$, Na_2PdCl_4 and Na_2PdCl_6; however, they all require a catalytic amount of chloride or bromide for optimal activity (iodide was much less active).[4] Figure 1 shows the dependence of the yield *y* of **3** in the reaction between benzoic anhydride and *n*-butyl acrylate at 155°C after 1 h on the amount of sodium halide used. Alkali metal halides can be used as well as tetraalkylammonium halides or tetraalkylphosphonium halides. Initially we were not sure about the role of the tetraalkylammonium halide, as it has been shown that tetraalkylammonium salts can induce the formation of giant palladium clusters, known catalysts in the Heck reaction.[5, 6] However, use of non-halide tetraalkylammonium salts led to much slower reactions. These results seem to support a mechanism based upon halide-ligated palladium(0) catalyst[7, 8] as suggested by Jeffery.[4] This seems quite reasonable as Yamamoto et al. have shown that benzoic anhydride oxidatively adds to zerovalent $[(PMe_3)_2(C_6H_5CH{=}CH_2)Pd]$ and can be homogeneously hydrogenated to benzaldehyde and benzoic acid with this catalyst.[9] However, using electrospray mass spectrometry we have so far been unable to detect any halide-ligated Pd^0 complexes, leaving open the possibility that the reaction proceeds by a Pd^{II}/Pd^{IV} mechanism.[10]

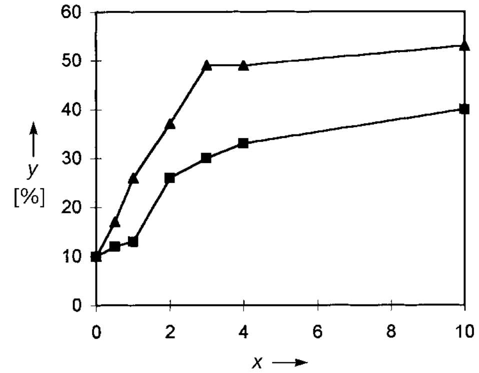

Figure 1. Dependence of yield *y* of **3** at 155°C after 1 h on halide: palladium ratio *x* for the reaction of benzoic acid with *n*-butyl acrylate at 155°C after 1 h. ■ NaCl, ▲ NaBr.

Phosphane ligands are not required in this reaction, which is thus more attractive as an industrially viable method. In fact, use of $[PdCl_2(PPh_3)_2]$ or $[Pd(PPh_3)_4]$, even in the presence of added halide, resulted in inferior conversions and selectivities. $[(PhCN)_2PdCl_2]$ also gave good results in conjunction with halides.

A wide variety of olefins can be arylated under similar conditions at temperatures ranging between 140–190°C. Olefins with electron withdrawing groups generally give high yields of the *β*-arylated products.[11] Even butyl methacrylate was arylated in good yield, though double-bond isomerization of the product resulted in a mixture of isomers.[12] Terminal olefins are good substrates, but in this case double-bond isomerization is very rapid, causing formation of a mixture of isomeric olefins. Unfortunately, at the relatively high reaction temperature arylation also took place at the internal positions. This was proven by hydrogenating the product mixture of the

Table 1. Palladium-catalyzed arylation of olefins **2** with aromatic carboxylic anhydrides **1**.[a]

Entry	Ar	R^1	R^2	R^3	Time (min)	Conversion of **1** (%)	Yield of **3** (%) (GC yield %)
1.	Ph	H	H	CO_2Bu	90	100	77 (90)
2.	Ph	H	H	nC_8H_{17}	90	85	60 (95)
3.	Ph	H	H	Ph	120	90	76 (85)[g]
4.	Ph	$-(CH_2)_6-$		H	120	100	54 (85)
5.	Ph	$Oc\text{-}C_6H_{11}$	H	H	120	80	*α* (25)
6.[b]	Ph	H	H	CN	180	90	60 (*E*/*Z* = 75/20)
7.	Ph	H	Me	CO_2Bu	90	100	62[h]
8.[c, d]	Ph	CO_2Bu	CO_2Bu	H	180	100	73 (*E*/*Z* = 7/2) (90)
9.	Ph	$N(CH_2)_3CO$	H	H	90	100	25 (*α*/*β*-*E* = 20/5)[j]
10.[c]	[e]	H	H	CO_2Bu	60	100	75 (80)
11.	[f]	H	H	CO_2Bu	90	100	77 (85)

[a] Conditions: see Experimental Section; *T* = 160°C, unless otherwise noted. [b] Reaction at 140°C. [c] Reaction at 190°C. [d] Maleate. [e] *p*-$MeOC_6H_4$. [f] 2-Furyl. [g] 1,1′-Diphenylethene (11%) also formed. [h] *n*-Butyl *α*-benzylacrylate (10%) also formed. [j] *N*-Benzoyl-2-pyrrolidinone was also isolated in 58% yield.

phenylation of 1-decene (H_2, Pd/C), which gave a mixture of all five possible phenyldecane isomers. Cyclooctene gave a mixture of phenylcyclooctenes in addition to some diphenylcyclooctene.

Arylations with olefins carrying electron-donating substituents were less successful. Vinyl esters invariably reacted by cleavage of the carbon–oxygen bond leading to the formation of styrene and stilbene. Reaction of cyclohexyl vinyl ether gave some Heck product (25% yield) in which phenylation had exclusively taken place in the α position.[11] *N*-vinyl-2-pyrrolidinone was arylated to give a mixture of isomeric *N*-styrylpyrrolidinones (α:β = 4:1) in 25% yield of the isolated product. A major side product was *N*-benzoyl-2-pyrrolidinone (58%).

Other aromatic carboxylic anhydrides reacted similarly. *p*-Methoxybenzoic anhydride required a slightly higher temperature (190°C) for the reaction with *n*-butyl acrylate to go to completion. Furanoic anhydride was successfully used to furylate *n*-butyl acrylate.

In conclusion, we have discovered an environmentally benign method to arylate olefins. The products of these reactions can be hydrogenated to arylalkanes or oxidized as in the Wacker reaction to aryl alkyl ketones, thus providing a clean alternative to the Friedel–Crafts reaction.

Experimental Section[13]

A 300 mL Schlenk-tube, fitted with a rubber septum inlet and equipped with magnetic stirring, is charged with $(PhCO)_2O$ (23 g, 100 mmol), $PdCl_2$ (45 mg, 0.25 mmol), and NaBr (103 mg, 1 mmol). After repeated degassing under vacuum and purging with argon, $n\mathrm{Hex_2O}$ (10 mmol) as internal standard, dibutyl maleate (28.0 mL, 120 mmol) and NMP (100 mL) are successively injected. The Schlenk tube is heated at 190°C for 3 h. The course of the reaction is monitored by gas chromatography (CP-Sil 8 CB column). A mixture of dibutyl phenylfumarate and dibutyl phenylmaleate (7:2) is obtained by fractional distillation (170°C/3 Torr) of the crude reaction mixture in 73% yield.

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[1] a) R. F. Heck, *Org. React.* **1982**, *27–390*, 345; b) R. F. Heck in *Comprehensive Organic Synthesis, Vol.4*, (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, 833–863; c) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411; d) W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2–7; e) J. Tsuji, *Palladium Reagents and Catalysts-Innovations in Organic Synthesis*, Wiley, Chichester, UK, **1995**.

[2] a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989-1992; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1847; b) W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357–1364.

[3] The rhodium-catalyzed benzoylation of styrene with benzoic anhydride has been reported: K. Kokubo, M. Miura, M. Nomura, *Organometallics* **1995**, *14*, 4521–4524.

[4] T. Jeffery, *Tetrahedron* **1996**, *52*, 10113–10130, and references herein.

[5] Halides are not a prerequisite for the formation of clusters aided by tetraalkylammonium salts: M. T. Reetz, S. A. Quaiser, *Angew. Chem.* **1995**, *107*, 2461–2463; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2240–2241.

[6] a) M. Beller, H. Fischer, K. Kühlein, C.-P. Reisinger, W. A. Herrmann, *J. Organomet. Chem.* **1996,** *520*, 257–259; b) M. T. Reetz, R. Breinbauer, K. Wanninger, *Tetrahedron Lett.* **1996**, *37*, 4499–4502.

[7] The role of chloride-ligated palladium phosphane complexes in oxidative addition reactions has been discussed: a) C. Amatore, M. Azzabi, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 8375–8384; b) C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.* **1993**, *115*, 9531–9541.

[8] We have observed the reduction of $PdCl_2$ to Pd black in NMP solutions at room temperature. This might be due to amine impurities in the solvent.

[9] K. Nagayama, F. Kawataka, M. Sakamoto, I. Shimizu , A. Yamamoto, *Chem. Lett.* **1995**, 367–368.

[10] On taking samples from the reaction mixture at 160°C and directly injecting these in the mass spectrometer (Finnigan Navigator) we found evidence for the following anionic complexes: $[PdCl_3]^-$ (or more likely the bridged dimer $[Pd_2Cl_6]^{2-}$), an adduct of $[PdCl_3]^-$ and benzoic acid, and $[Cl_3Pd(CO)]^-$).

[11] For a discussion on the factors influencing the stereochemical and regiochemical outcome of Heck reactions, see refs. [1b, 1c] and a) A. Spencer, *J. Organomet. Chem.* **1982**, *240*, 209–216; b) C.-M. Andersson, A. Hallberg, *J. Org. Chem.* **1988**, *53*, 235–239.

[12] M. Beller, T. H. Riermeier, *Tetrahedron Lett.* **1996**, *37*, 6535–6538.

[13] Use of only 0.1 mol% of $PdCl_2$ and 0.4 mol% halide is also possible without reducing the yield; reaction times increase to 3–5 h.

Synthesis of Microporous Transition Metal Oxide Molecular Sieves with Bifunctional Templating Molecules**

Tao Sun and Jackie Y. Ying*

Porous inorganic materials have been widely studied, and the mechanism by which their structures form remains an area of great interest. When synthesized with high surface area and narrow pore size distribution, these structures are highly useful as active and/or selective catalytic materials.[1] Inorganic and organic cations have been frequently used to construct microporous zeolitic frameworks, but our understanding of their function in the process remains rather limited and disparate.[2] In contrast, a more generalized approach for formation of mesoporous structures has been developed in the last five years with the discovery of M41S silicates by Mobil scientists.[3] Through charge matching between the hydrophilic head groups of surfactant molecules and inorganic precursors, silicates and surfactants can be self-assembled into supramolecular aggregates with long-range order of packing.[4] Upon removal of surfactants through

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