and naphthalene 0.14 g, 0.0011 g). The mixture was stirred for about 2 h, at which time no sodium was visible. The mixture was stirred for an extra 2 h to ensure complete consumption of the sodium. To the brownish colored reaction mixture, (2-bromo-ethyl)benzene (1.47 mL 0.011 mol) was added slowly by syringe at room temperature with stirring. The mixture warmed slightly after addition. After being stirred for 30 min at room temperature, the mixture changed color to a light orange. The mixture was stirred for an extra 30 min, and then an aliquot was removed, stripped of solvent, added to CCl₄, filtered, and analyzed by NMR spectroscopy. Integration of the methylene protons of the starting halide and methylene protons of the product indicated 80% conversion. The reaction mixture was filtered and the filtrate stripped of solvent. The oily, orange residue was chromatographed on silica gel, first with hexane and then with benzene. An orange band was eluted with benzene and stripped of solvent. The orange liquid which remained was analyzed by NMR (CCl₄): δ 7.2 (s, C_6H_5), 3.2–3.0 (broadened t, CH_2CH_2); no signals attributable to starting material or naphthalene were observed. Analysis by GC/MS (in hexane): 368 ($(C_6H_5CH_2CH_2)_2Se_2$), 291 (loss of C_6H_5), 263 ($C_6H_5CH_2CH_2Se$), 115 ($C_6H_5CH_2CH_2$). Yield, 2.97 g or 75%. Subsequent reactions were analyzed by comparison of NMR integrated ratios of methylene protons of diselenide and methylene protons of the starting (2-bromoethyl)benzene.

V. Synthesis of Di-2-octyl Diselenide. In a clean, dry, three-neck, round-bottom flask equipped with condenser and nitrogen inlet were placed selenium powder (1.25 g, 0.016 mol), THF (25 mL), lithium wire (0.11 g, 0.016 mol), and naphthalene (0.20 g, 0.0016 mol). The reaction flask was partially submerged in a fan-cooled bath sonicator and sonicated. After 9 h, no lithium was visible in the flask. The flask was sonicated for an extra 5 h to ensure complete consumption of the lithium. Into the flask was syringed 2-bromooctane (2.5 mL, approximately 0.016 mol) without interruption of sonication. Within 1 h after halide addition, the reaction mixture turned from brown to orange. An aliquot of the solution was removed, and observed to have undergone 87% conversion by NMR integration. The orange solution was stripped of solvent and the oily orange residue dissolved in hexane. The hexane solution was filtered and stripped of solvent. The orange oil which remained was chromatographed on silica gel with hexane. A greenish band was eluted through the column in 5-mL increments. Analysis of the second aliquot by capillary GC indicated only naphthalene (comparison with authentic standard) and product. The aliquot was sublimed at room temperature to remove naphthalene, leaving a greenish liquid. Anal. Calcd for $C_{16}H_{34}Se_2$: C, 49.98; H, 8.93. Found: C, 49.66; H, 8.73. NMR (C_6D_6): δ 2.7–3.2 (m, SeCH). Subsequent runs were analyzed by NMR comparison of SeCH with BrCH of starting 2-octylbromide as well as comparison of SeCH vs all aliphatic protons.

Table I. Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in DMF in the Presence of Lithium Halides (LiX)[a]

LiX added	β/α	cis/trans	yield, %[b]
none	1.5	0.5	82
LiCl	13	0.6	68
LiBr	14	0.9	74
LiI	5.2	1.4	23

[a] The triflate (5 mmol), butyl vinyl ether (10 mmol), triethylamine (6 mmol), lithium halide (10 mmol), and palladium acetate (0.05 mmol) were heated at 95 °C in 12 mL of DMF for 18 h. [b] GLC yields; not optimized. 4,4′-Dinitrobiphenyl and minor amounts of 4-nitrophenol and bis(4-nitrophenyl) ether accounted for remaining material.

substitution at either the α-[2] or β-olefinic[3] carbon are desirable.

In a recent report we presented results from a systematic study of factors governing the regiochemistry of arylation reactions of enol ethers with halobenzenes.[4] It was established that the halide exerts a considerable influence on regiochemistry. In that study, 4-nitrobromobenzene and 4-nitroiodobenzene were important reagents since (i) assessment of the influence of halide on regioselectivity, both in the presence and absence of phosphine ligand, was possible,[5] and (ii) formation of stable products allowed accurate determination of isomeric distributions.[6]

Aryl triflates[7] and, particularly, vinyl triflates[8] have been proven to serve as useful precursors to organopalladium intermediates. Stille and co-workers reported that aryl[7a] or vinyl[9] triflates undergo palladium-catalyzed coupling reactions with organotin reagents, provided lithium chloride is present in the medium. It was proposed that a vinylpalladium chloride complex is the species which undergoes transmetalation with the organotin reagent.

This finding suggested that various arylpalladium halide intermediates would be accessible from aryl triflates and the appropriate halide salts. Hence, we decided to examine the potential of this approach with respect to regiocontrolled Heck arylation of electron-rich olefins.

Here, we report that the presence of lithium or tetrabutylammonium halides strongly affects the regiochemical outcome as well as the reaction rate in palladium-catalyzed reactions of 4-nitrophenyl triflate with butylvinyl ether.

Results and Discussion

The arylation reactions were performed at 95–100 °C under standard Heck arylation conditions, using 1% palladium acetate as catalyst precursor and triethylamine as base. The results obtained from addition of lithium

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Regioselective Palladium-Catalyzed Arylation of Vinyl Ethers with 4-Nitrophenyl Triflate. Control by Addition of Halide Ions

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For effective use of enol ethers in palladium-mediated vinylic substitution reactions,[1] procedures for selective

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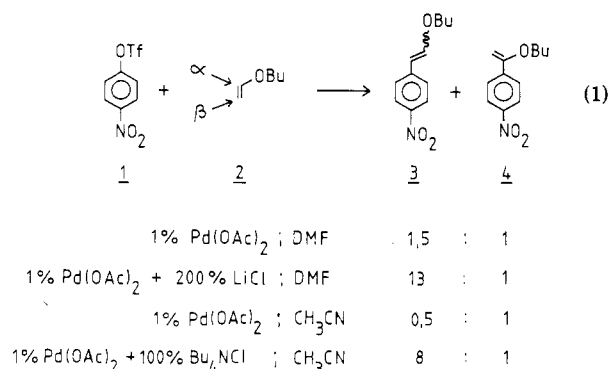
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Table II. Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in Acetonitrile in the Presence of Tetrabutylammonium Halides[a]

Bu₄NX, X	reactn time, h	β/α	cis/trans	yield, %[b]
no salt added	4			<2
	20	0.5	0.7	4
Cl	4	7.2	0.7	30
	20	8.0	0.9	57
Br	4	6.0	1.1	50
	20	5.8	1.2	62
I	4	2.9	1.9	19
	20	3.3	1.7	37

[a] The triflate (1 mmol), butyl vinyl ether (2 mmol), triethylamine (1.2 mmol), tetrabutylammonium halide (1 mmol), and palladium acetate (0.01 mmol) were heated at 100 °C in 3 mL of acetonitrile. [b] GLC yields; not optimized. Unreacted triflate, 4,4'-dinitrobiphenyl, and minor amounts of bis(4-nitrophenyl) ether and nitrobenzene accounted for remaining material.

halides to reactions run in DMF are presented in Table I. In all cases, the 4-nitrophenyl triflate (1) had been consumed, furnishing α- and β-arylated vinyl ethers 3 and 4 and biaryl (eq 1). While the reaction of 1 without

$$1\% \; Pd(OAc)_2 \; ; \; DMF \qquad 1.5 \; : \; 1$$
$$1\% \; Pd(OAc)_2 + 200\% \; LiCl \; ; \; DMF \qquad 13 \; : \; 1$$
$$1\% \; Pd(OAc)_2 \; ; \; CH_3CN \qquad 0.5 \; : \; 1$$
$$1\% \; Pd(OAc)_2 + 100\% \; Bu_4NCl \; ; \; CH_3CN \qquad 8 \; : \; 1$$

lithium salt exhibited little regioselectivity (β/α = 1.5), addition of lithium chloride or bromide to the medium strongly promoted β-arylation (β/α = 13 and 14, respectively). Presence of lithium iodide resulted in predominant formation of 4,4'-dinitrobiphenyl but also in a moderate selectivity for β-substitution.

The same qualitative trend was found with tetrabutylammonium halides in acetonitrile (Table II, eq 1), although the overall β/α ratios were somewhat lower in this solvent.[10] The β/α ratios observed with added iodide (3.3), bromide (5.8), and chloride (8.0) accord with those reported previously, starting from bis(triphenylphosphine)(4-nitrophenyl)palladium halides.[4] The principal byproduct was again the biaryl, although nitrobenzene was also observed, and again, the amount of byproducts increased in going from chloride to iodide. The conversion, however, appeared to be independent of which halide was added (vide infra). A reaction run in the presence of tetrabutylammonium hydrosulfate gave a product mixture similar to that obtained in the absence of salt.

We also briefly examined the effect of steric requirement in the vinyl ether. As expected, reactions between 1 and butyl (Z)-1-propenyl ether were much more sluggish and proceeded only to the extent of about 20% under the conditions given in Table I. A similar, but less pronounced, directive effect of halide ion was still established. Thus, a shift in the β/α ratio from 2/3 to 5/3 was observed upon the addition of 2 equiv of LiCl to the medium. In an experiment employing 3,4-dihydro-2H-pyran as the olefin,

extensive formation of 4,4'-dinitrobiphenyl occurred, and only a trace of arylated product was obtained.

Interestingly, in both media, the observed variation in regioselectivity correlates with an influence on the ratio of cis and trans β-product (Tables I and II). Thus, absence of halide ion gave about a 1/2 ratio of cis- and trans-3, whereas addition of chloride, bromide and iodide ion favored the formation of the cis isomer, in that order. The overall β-selectivity was lower in acetonitrile, as compared to DMF, and this is accompanied by a slightly higher cis/trans ratio in this solvent (compare Tables I and II).

In addition to the control of product distribution, a significant enhancement of the reaction rate was achieved upon addition of halide ion. In the absence of halide the reaction proceeded to the extent of only 4% in 20 h in acetonitrile,[11] whereas virtually all of the starting material was consumed during the same time in the cases where salt was added (Table II). The rate enhancement resulting from addition of halide to the medium was also evident in reactions of phenyl triflate (5) with 2 in DMF at conditions similar to those above (eq 2). A much slower
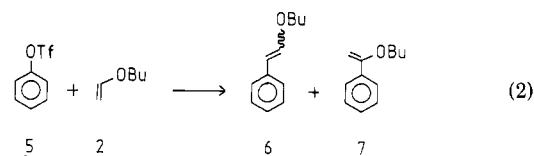
reaction was encountered in this case, and in the absence of lithium salt, no products derived from arylation could be detected. The presence of 1 molar equiv of lithium chloride gave a 16% yield of the expected 6 and 7 (β/α = 2.3), with 84% of starting material remaining unchanged.

In conclusion, we have described here an example of the transformation of an activated phenol, via its triflate, into the corresponding arylacetaldehyde enol ether (eq 3). We

$$Ar-OH \longrightarrow Ar-CH=CH-OBu \; (\rightarrow Ar-CH_2-CHO) \qquad (3)$$
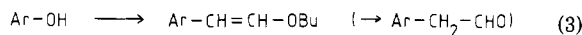
believe that this reaction is general for activated aryl triflates and possibly the more reactive vinyl triflates. These reagents, in combination with halide ions, should serve as good starting materials in selective β-arylation/vinylation of electron-rich olefins. To our knowledge, this is the first example of a Heck reaction in which the regiochemical outcome has been controlled through addition of external halides.

Experimental Section

General. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatograph–mass spectrometer, operating at 70 eV. Gas chromatographic analyses were performed with a Varian 3300 instrument equipped with a 2.5-m glass column of 5% OV 17 on Chromosorb W. Peak areas were determined by means of a Varian 4270 electronic integrator.

Chemicals were obtained from commercial sources and used as received with the exception of tetrabutylammonium chloride, which was prepared from the hydrosulfate with alkaline sodium chloride. Solvents were dried over molecular sieves, and triethylamine was distilled from potassium hydroxide prior to use. The products discussed have been fully characterized previously.[4]

Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in DMF (Table I). A catalyst solution was prepared by dissolving palladium acetate (11.2 mg, 0.05 mmol) and, if present, the lithium halide (10 mmol) in 10 mL of DMF in a thin-necked Pyrex tube, fitted with a Teflon-lined screw cap. To the homogeneous solution, a mixture of 4-nitrophenyl triflate[12] (1.36 g, 5

(10) This is in agreement with previous results; see ref 4.

(11) More forced conditions led to higher yields of the same regio- and stereoisomeric mixture.

(12) The preparation of triflates has been reviewed recently: Staug, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85–126.

mmol), triethylamine (0.6 g, 6 mmol), and butyl vinyl ether (1.0 g, 10 mmol) in 2 mL of DMF was added. The tube was closed and heated for 18 h at 95 °C in an oil bath. After cooling, 75 mL of diethyl ether (containing naphthalene as internal standard) and 25 mL of water were added. The organic layer was then subjected to GLC-MS analysis.

Reaction of 4-Nitrophenyl Triflate with Butyl Vinyl Ether in Acetonitrile (Table II). A solution containing 4-nitrophenyl triflate (1.36 g, 5 mmol), butyl vinyl ether (1.0 g, 10 mmol), triethylamine (0.6 g, 6 mmol), palladium acetate (11.2 mg, 0.05 mmol), and naphthalene (internal standard, 0.5 g) in 15 mL of acetonitrile was prepared. Aliquots (3-mL) of this solution were added to Pyrex tubes containing the appropriate tetrabutyl-ammonium salts (1 mmol). The closed tubes were heated in an oil bath at 100 °C. Samples were removed after 4 and 20 h, partitioned between diethyl ether and water, and analyzed by GLC-MS.

Reaction of Phenyl Triflate with Butyl Vinyl Ether. Phenyl triflate[12] (0.45 g, 2 mmol), triethylamine (0.24 g, 2.4 mmol), butyl vinyl ether (0.4 g, 4 mmol), palladium acetate (4.5 mg, 0.02 mmol), and, if present, lithium chloride (85 mg, 2 mmol) were dissolved in 1.5 mL of DMF. After heating at 100 °C for 18 h, the products were quantified as above.

## Novel Synthesis of Dihydrofurans from the Addition of Enolate Dianion Derivatives to (η^4-Diene)Co(CO)$_3$BF$_4$

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Despite the long-standing existence of transition-metal complexes of 1,3-dienes[1] and the commercial importance of metal-catalyzed additions, oligomerizations, and telomerizations of dienes,[2] the reactivity of diene-metal complexes has been surprisingly little studied. Our interest in this subject has been stimulated by recent reports of the contrasting regioselectivity observed in additions of nucleophiles to (η^4-diene)Mo[3] and -Pd[4] species (terminal attack) compared to the -Fe(CO)$_3$ counterparts[5] (internal attack). In our initial studies of nucleophilic reactions of (η^4-butadiene)Co(CO)$_3$BF$_4$ (1) we demonstrated the regiospecific attack at the diene terminus by a variety of carbon and heteroatomic agents,[6] the potential for regioselective 1,4-difunctionalization of dienes via addition

Scheme I
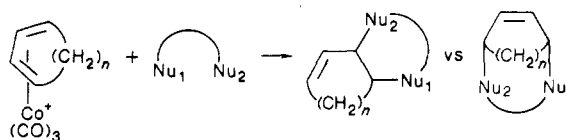
of a second nucleophile to the intermediate allyl complex (eq 1),[6] and we provided a theoretical model to account for the role of the metal fragment in determining regioselectivity.[7]
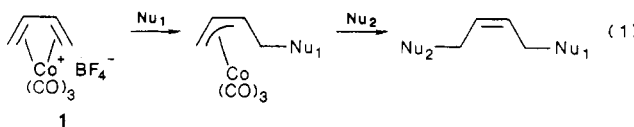
The ability of the (η^4-diene)Co(CO)$_3$$^+$ complexes to serve as olefin dication equivalents has led us to consider annelation schemes based on their reactions with bis nucleophiles (Scheme I). On the basis of the established behavior of dianions of β-dicarbonyl compounds[8] and the related 1,3-bis(siloxy) dienes[9] as 2,4-carbon-centered bis nucleophiles, we anticipated the possibility of forming cyclopentanone (via 1,2-addition to the diene) or cycloheptenone (via 1,4-addition) derivatives. Herein we report the unexpected, but synthetically useful, results of such reactions.

Results and Discussion

When a suspension of complex 1 in THF was treated with 1 equiv of pentanedione dianion 3a at -78 °C, a new complex X formed which persisted at room temperature (IR: 2080 and 1995 cm^{-1}) along with Co(CO)$_4$$^-$. Addition of HMPA to this mixture caused gradual disappearance of X and formation of a single isolable organic product (12% purified yield), which was identified as 2-vinyl-4-acetyl-5-methyl-2,3-dihydrofuran (4a) (eq 2) on the basis of its spectral characteristics, NMR homonuclear decoupling experiments, and comparison with known compounds.
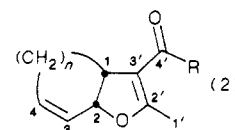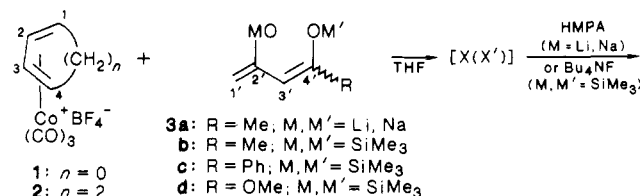
We were pleased to find that such dihydrofuran derivatives could be prepared generally and much more efficiently when 1 was combined at 20 °C with the corre-

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