74457-36-6; **4**, 74457-37-7; **6**, 23990-17-2; **8**, 891-22-5; **9**, 77764-69-3; **9**·Na, 84066-52-4; **10**, 77764-71-7; **11**, 36597-09-8; **12**, 76620-32-1; **12**·Na, 84066-53-5; **13**, 76620-31-0; **14**, 77764-70-6; **14**·Na, 76620-26-3; **15**, 76633-73-3; **16**, 76620-27-4; **16**·Na, 84066-54-6; **17**, 76620-30-9; **25**, 84066-55-7; **25**·Na, 84066-56-8; **26**, 84066-57-9; **26**·Na, 84066-58-0; **31**, 84066-59-1; **32**, 84066-60-4; *p*-toluenesulfonylhydrazine, 1576-35-8; 1,4-diphenyl-3-buten-1-one, 32363-55-6; *trans*-1,4-diphenyl-4-hydroxy-1-butene, 84107-76-6; phenylpropargyl bromide, 1794-48-5; benzaldehyde, 100-52-7; 1,4-diphenyl-3-butyn-1-ol, 17572-78-0; 1,4-diphenyl-3-butyn-1-one, 17572-79-1; *cis*-1,4-diphenyl-3-buten-1-one, 17572-77-9; phenyldithiane, 5425-44-5; 1-bromo-3-methyl-2-butene, 870-63-3; 1-phenyl-1-(3-methyl-2-butenyl)dithiane, 84066-61-5; crotyl chloride, 591-97-9; (*E*)-1-phenyl-1-(2-butenyl)dithiane, 84066-62-6; *trans*-1-phenyl-3-penten-1-one, 74157-93-0; 1-phenyl-1-(2-propynyl)dithiane, 84066-63-7; 1-phenyl-1-(2-butynyl)dithiane, 84066-64-8; 1-phenyl-3-pentyn-1-one, 76620-28-5; *cis*-1-phenyl-3-penten-1-one, 61752-45-2; cinnamyl bromide, 4392-24-9; anisoin, 30587-18-9; 1,2-di-*p*-anisyl-2-hydroxy-5-phenyl-4-penten-1-one, 84066-65-9; 1,2-di-*p*-anisyl-5-phenyl-4-penten-1,2-diol (isomer 1), 84066-66-0; 1,2-di-*p*-anisyl-5-phenyl-4-penten-1,2-diol (isomer 2), 84066-67-1; (*E*)-1-*p*-anisyl-4-phenyl-3-buten-1-one, 84066-68-2; *p*-nitrobenzaldehyde, 555-16-8; 1,3-propanedithiol, 109-80-8; 1-(*p*-nitrophenyl)-1,1-dithiane, 24588-74-7; 1-(*p*-nitrophenyl)-1-(3-phenyl-2-propenyl)-1,1-dithiane, 84066-69-3; (*E*)-(*p*-nitrophenyl)-4-phenyl-3-buten-1-one, 84066-70-6; diazomethane, 334-88-3; phenyldiazomethane, 766-91-6; *p*-hydroxyphenyldiazomethane, 84066-71-7; formyldiazomethane, 6832-13-9.

Palladium-Catalyzed Acylation of Unsaturated Halides by Anions of Enol Ethers

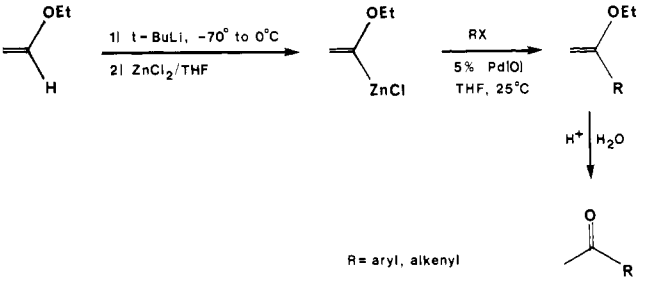
Charles E. Russell and Louis S. Hegedus*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received June 23, 1982*

Abstract: Zinc salts of enol ether anions are coupled to aryl and alkenyl halides by using palladium catalysts, effecting a direct acetylation of aryl and alkenyl halides. Zinc salts of allenic ethers are coupled with aryl and alkenyl halides under similar conditions to give α,β-unsaturated ketones, the allenic ether serving as a source of the acryloyl group. Allenic ethers were γ arylated in a palladium-catalyzed coupling with aryl halides to give β,β-diaryl-α,β-unsaturated aldehydes.

Direct nucleophilic alkylation and acylation of unsaturated organic halides would be a useful procedure in synthesis, but, until recently, such reactions were rare. Recently developed organometallic processes include nickel- and palladium-catalyzed coupling of alkenyl halides with Grignard reagents[1] and the acylation of alkenyl halides by acylnickel carbonylates.[2] A major advance in this area was the result of Negishi's elegant and important work on transmetallation reactions, which resulted in very efficient procedures for the coupling of main-group organometallics to aryl, alkenyl, and allylic halides, using palladium catalysis.[3] Thus, alkenyl alanes have been coupled with aryl[4] and alkenyl[5] halides. Zirconium alkenes have also been coupled with aryl[6] and alkenyl[7] halides, and aluminum and zirconium alkenes have been coupled with alkenyl, alkynyl, and aryl halides by using $ZnCl_2$ as cocatalyst.[8] Alkynyl zincs have been coupled with alkenyl[9] and acyl halides,[10] aryl and benzyl zincs have been coupled with aryl halides,[11] and homoallyl- and homopropargyl zincs have been coupled with alkenyl halides.[12] Finally, alkenyl alanes and various aryl metals (Al, Cd, Mg, Zn, Zr) have been coupled with a variety of allylic substrates.[13]

Scheme I



For a number of synthetic problems, we had the need to directly introduce acyl and α,β-unsaturated acyl groups into aryl and alkenyl halides. From the work of Negishi cited above, it appeared that palladium-catalyzed reactions of these substrates with carbanions of enol and allenic ethers should perform the desired transformation.[14] Herein we report the results of our studies.

Results and Discussion

Acylation of Aryl and Alkenyl Halides with Enol Ether Anions. Initial studies centered on the simple acetylation of aryl and alkenyl halides. The enol ether of acetaldehyde was lithiated with *tert*-

(1) (a) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, S. Knoshi, K. Yamamoto, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **53**, 1138 (1983); (b) T. Hayashi, M. Knoishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika, and M. Kumada, *J. Am. Chem. Soc.*, **104**, 180 (1982); (c) K. Tamao and M. Kumada in "Organometallic Reactions and Syntheses", E. I. Becker and M. Tsutsui, Eds., Plenum, New York, in press.

(2) E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91**, 4926 (1969).

(3) E-i Negishi, *Pure Appl. Chem.*, **53**, 2333 (1981).

(4) E-i Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, 596 (1976).

(5) S. Baba and E-i Negishi, *J. Am. Chem. Soc.*, **98**, 6729 (1976).

(6) E-i Negishi and D. E. VanHorn, *J. Am. Chem. Soc.*, **99**, 3168 (1977).

(7) N. Okukado, D. E. VanHorn, W. L. Klima, and E-i Negishi, *Tetrahedron Lett.*, 1027 (1978).

(8) E-i Negishi, N. Okukado, A. O. King, D. E. VanHorn, and B. I. Spiegal, *J. Am. Chem. Soc.*, **100**, 2254 (1978).

(9) A. O. King, N. Okukado, and E-i Negishi, *J. Chem. Soc., Chem. Commun.*, 683 (1977).

(10) A. O. King and E-i Negishi, *J. Org. Chem.*, **43**, 358 (1978).

(11) E-i Negishi, A. O. King, and N. Okukado, *J. Org. Chem.*, **42**, 1821 (1977).

(12) E-i Negishi, L. F. Valente, and M. Kogayashi, *J. Am. Chem. Soc.*, **102**, 3298 (1980).

(13) (a) E-i Negishi, S. Catterjee, and H. Matsushita, *Tetrahedron Lett.*, 3737 (1981); (b) S. Matsushita and E-i Negishi, *J. Am. Chem. Soc.*, **103**, 2882 (1981); (c) H. Matsushita and E-i Negishi, *J. Chem. Soc., Chem. Commun.*, 160 (1982).

(14) A general study of heteroatom-containing anions is underway: E-i Negishi, private communication.

0002-7863/83/1505-0943$01.50/0

Scheme II

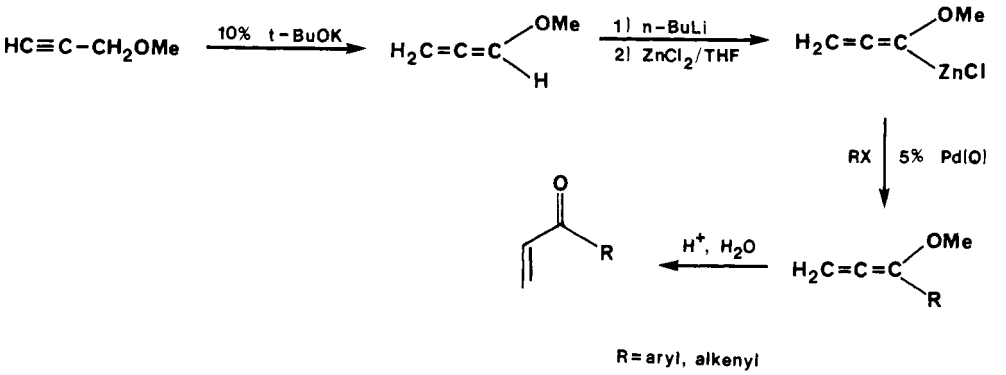
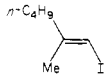
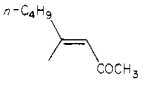
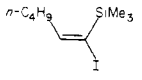
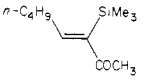
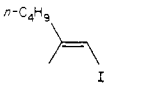
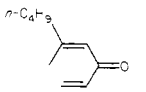
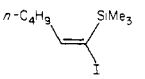
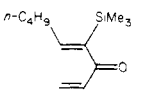


Table I. Acetylation of Halides by Enol Ether Anions (Scheme I)

RX	catalyst[a]	time, h	product	yield,[b] %
PhI	A	14	$PhCOCH_3$	76
PhI	B	7	$PhCOCH_3$	68
PhI	C	7	$PhCOCH_3$	45
o-MePhI	A	6	*o*-$MePhCOCH_3$	72
m-MePhI	A	6	*m*-$MePhCOCH_3$	82
p-MePhI	A	6	*p*-$MePhCOCH_3$	71
m-MeOPhI	A	6	*m*-$MeOPhCOCH_3$	60
m-MeOPhI	D	6	*m*-$MeOPhCOCH_3$	58
o-H_2NPhI	A	6	*o*-$H_2NPhCOCH_3$	41
o-MeO_2CPhBr	A	18[c]	*o*-$MeO_2CPhCOCH_3$	50
o-MeO_2CPhI	A	3	*o*-$MeO_2CPhCOCH_3$	77
o-O_2NPhI	A	6	*o*-$O_2NPhCOCH_3$	72
trans-PhCH=CHBr	A	3.5	*trans*-$PhCH=CHCOCH_3$	84
cis-PhCH=CHBr	B	6	*cis*-$PhCH=CHCOCH_3$	68
trans-n-$C_4H_9CH=CHI$	A	2	*trans-n*-$C_4H_9CH=CHCOCH_3$	33
	A	4		39
	A	6		50

[a] Catalyst A = $PdCl_2(PPh_3)_2$ + 2(*i*-Bu)$_2$AlH; catalyst B = $Pd(dba)_2$ + 2 Ph_3P, catalyst C = $Pd(dba)_2$ + 4Ph_3P; catalyst D = Pd(dba) + 1 diphos. [b] Yields are for isolated, purified products, base on starting halide. [c] This reaction was run at 50 °C.

Table II. Acylation of Halides by Allenic Ether Anions (Scheme II)

RX	product	yield,[a] %
o-MePhI	*o*-$MePhCOCH=CH_2$	52
m-MePhI	*m*-$MePhCOCH=CH_2$	84
p-MePhI	*p*-$MePhCOCH=CH_2$	66
$PhCH_2Br$	$PhCH_2COCH=CH_2$	38
trans-PhCH=CHBr	*trans*-$PhCH=CHCOCH=CH_2$	27
trans-n-$C_4H_9CH=CHI$	*trans-n*-$C_4H_9CH=CHCOCH=CH_2$	40
		59
		75

[a] Yields are for isolated, purified products, based on starting halide.

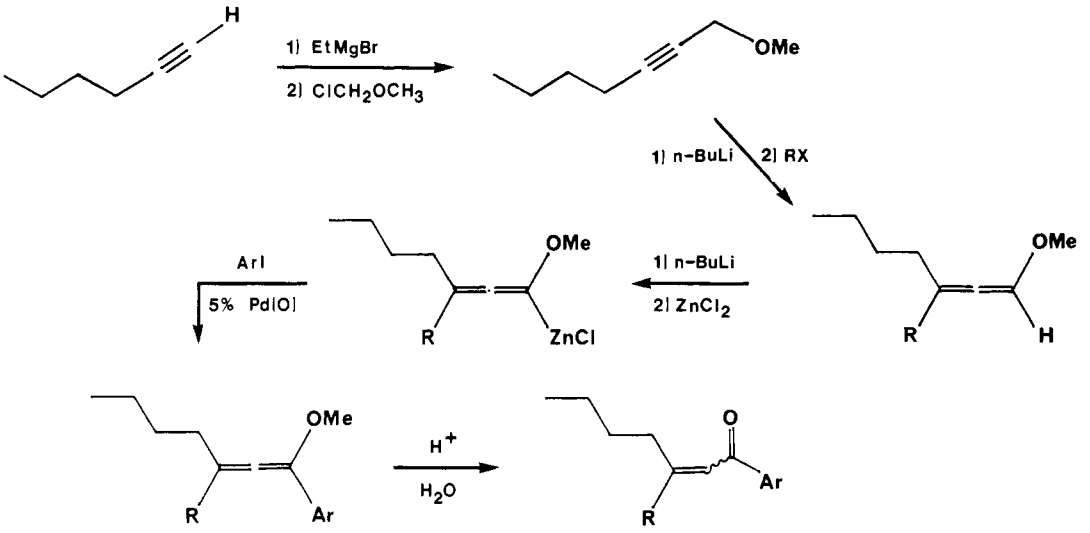
butyllithium[15] and then transmetallated to zinc chloride. Addition of a palladium(0) catalyst, followed by the halide substrate, resulted in acetylation (Scheme I). The results are summarized in Table I. The reaction was relatively insensitive to the nature of the palladium catalyst used. Thus, in situ generation of the palladium(0) catalyst by reduction of $PdCl_2(PPh_3)_2$ with diisobutylaluminum hydride (catalyst A), by reaction of $Pd(dba)_2$[16] (dba is dibenzylideneacetone) with 2 equiv of triphenylphosphine (catalyst B), or by reaction of $Pd(dba)_2$ with 1 equiv of bis(diphenylphosphino)ethane (catalyst D) all resulted in comparable yields of acylation product. The use of 4 equiv of triphenylphosphine per palladium (catalyst C) led to reduced yields, as has been previously observed in related systems.[3] Although most of our work was done using catalyst A, reactions based on $Pd(dba)_2$ are significantly more convenient to carry out, and catalysts B or D are probably the reagents of choice (nickel(0) catalysts failed altogether). As in most of Negishi's work, transmetallation from lithium to zinc was required. In the absence of zinc chloride, only traces of the desired product were obtained. In most cases, optimum reaction times were between 2 and 6 h. Allowing the reaction to proceed for extended periods of time (>24 h) led to a decrease in yield. A 5-fold excess of enol ether carbanion was used. With only 2 equiv, 30% yields were realized. This probably reflects an inefficiency in the generation of the initial anion and not in the subsequent steps, since with the more easily deprotonated allenic ethers a 2-fold excess of anion sufficed.

This acylation reaction tolerated a variety of functional groups on the aromatic ring. Thus, methyl-, methoxy-, and nitro-containing aryl halides underwent acetylation in fair to excellent yields. *o*-Iodoaniline and methyl *o*-bromobenzoate reacted in somewhat lower yields, and more slowly, because oxidative-addition reactions of electron-rich aryl iodides and of aryl bromides are slow relative to electron-poor aryl iodides. With alkenyl halides, the stereochemistry of the double bond was maintained. With *cis*-β-bromostyrene, routine hydrolysis (HCl) led to *trans*-benzalacetone by rearrangement of the cis enol ether during hydrolysis. Isolation of the enol ether itself by hydrolysis with 20% aqueous ammonium chloride, followed by hydrolysis of the enol ether with magnesium sulfate in ether, led to the pure *cis*-benzalacetone in fair yield. This acylation of alkenyl halides was relatively insensitive to steric hindrance on the halide, as evidenced by the vinyltrimethylsilane.

Acylation of Aryl and Alkenyl Halides with Allenic Ethers—Introduction of α,β-Unsaturated Carbonyl Groups. The above procedure allows the efficient direct "nucleophilic" acetylation of unsaturated halides. By using allenic ether anions (available from the base-catalyzed rearrangement of propargyl ethers to allenic ethers followed by α lithiation),[17] the direct "nucleophilic" introduction of the acryloyl group (α,β-unsaturated-carbonyl group) into these substrates is possible (Scheme II).[18] The results are summarized in Table II. With allenic ether anions, a 2-fold

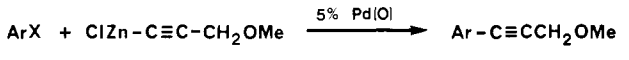
(15) J. E. Baldwin, G. A. Höfle, and O. W. Lever, Jr., *J. Am. Chem. Soc.*, **96**, 7125 (1974).
(16) Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *J. Chem. Soc. D*, 1065 (1970).
(17) S. Hoff, L. Brandsma, and J. T. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 916 (1968).
(18) Simple allenyl anions were arylated by aryl halides in the presence of palladium(0) catalysts: K. Ruitenberg, H. Kleijn, J. Meijer, E. A. Ostveen, and P. Vermeer, *J. Organomet. Chem.*, **224**, 399 (1982).

Scheme III



R = TMS, Ar = m-MePh 74%
R = Me, Ar = m-MePh 60%
R = n-Bu, Ar = m-MePh 50%

Scheme IV



ArX = PhI, 75%; o-MePhI, 87%; m-MePhI, 84%; p-MePhI, 80%; m-MeOPhI, 64%; p-MeOPhBr, 0%

excess of anion was sufficient to ensure reasonable conversion. The reactions were all run at room temperature for from 3 to 8 h, with a catalyst (5 mol %) prepared by the reduction of $PdCl_2(PPh_3)_2$ with diisobutylaluminum hydride. The lower yields of products obtained in this reaction were, in part, due to the reactivity of the dienone products, which caused losses of material during isolation and purification. Use of aqueous ammonium chloride rather than hydrochloric acid permitted the isolation of the allenic ether itself. However, these compounds decomposed on standing, and direct hydrolysis to the enone was the preferred isolation procedure.

γ-Monosubstituted allenic ethers were prepared by deprotonation of the corresponding propargyl ethers with *n*-butyllithium to give a mixture of propargyl and allenic anions.[19] Although protonation of this mixture of anions gave mixtures of propargyl and allenic ethers, transmetallation to zinc followed by hydrolysis with aqueous ammonium chloride gave exclusively the allenic ether. However, attempts to generate exclusively the α anion have not been successful. Rather, mixtures of α and γ anions were obtained upon lithiation with *n*-butyllithium. Efforts continue in this area.

γ,γ-Disubstituted allenic ethers were prepared in two ways. Reaction of 1-hexyne with ethylmagnesium bromide followed by chloromethyl methyl ether gave the propargyl ether in good yield.[20] Lithiation with butyllithium followed by alkylation with an alkyl halide resulted in exclusive production of the allenic ether (exclusive γ alkylation). This could be isolated if desired. However, it proved more convenient to α lithiate this allenic ether without isolation, transmetalate to zinc, and then couple to aryl halides with the palladium-catalyzed process discussed above. This process, summarized in Scheme III, led to fair yields of β,β-dialkyl-α,β-unsaturated aryl ketones in a one-pot procedure from the propargyl ether.

γ-Aryl allenic ethers were prepared by the palladium(0)-catalyzed coupling of aryl halides with alkynyl zinc reagents[10] to give the propargyl ether, (Scheme IV) followed by lithiation and alkylation at the γ-position with methyl iodide.[19a] This allenic ether could be isolated if desired. However, in situ lithiation, transmetallation to zinc, and palladium(0)-catalyzed coupling to aryl or alkenyl halides was the most efficient method to produce β-aryl-β-alkyl-α,β-unsaturated aryl ketones (Scheme V). When the γ-aryl group was *o*- or *p*-tolyl, the coupling process proceeded as expected. However, with a *m*-tolyl group or an unsubstituted phenyl group at the γ-position, coupling did not occur. Control experiments showed that lithiation and transmetallation to zinc had occurred, but apparently transmetallation to palladium had not. Stabilization of the α anion by the aryl group is the likely explanation for these observations. (These anions also were very slow in their reactions with methyl iodide.) The electron-donating ability of an *o*- or *p*-methyl group on the aromatic ring was sufficient to permit the coupling reaction to procede with these anions.

An alternative approach to species containing these unreactive allenic ether anion precursors was devised and consisted of using the allenic ether as the *halide* member of the coupling reaction. Thus, the allenic ether was lithiated and iodinated by reaction with iodine. Reaction of this species with an organozinc reagent and a palladium(0) catalyst led to coupling in modest yield (Scheme VI). Although this process has not been optimized, it does demonstrate that both approaches are viable. Finally, preliminary attempts to couple the γ anions of allenic ethers with aryl iodides succeeded (Scheme VII).

Summary

The chemistry reported above permits the direct introduction of the carbonyl functional groups CH_3CO, $CH_2{=}CHCO$, $R_2C{=}CHCO$, and $RC{=}CHCHO$ into aryl and alkenyl halides. The reactions proceed under mild conditions and in fair to good yield in the presence of small amounts of palladium catalysts. The reactions are regiospecific, and, with alkenyl halides, the stereochemistry of the olefin is maintained.

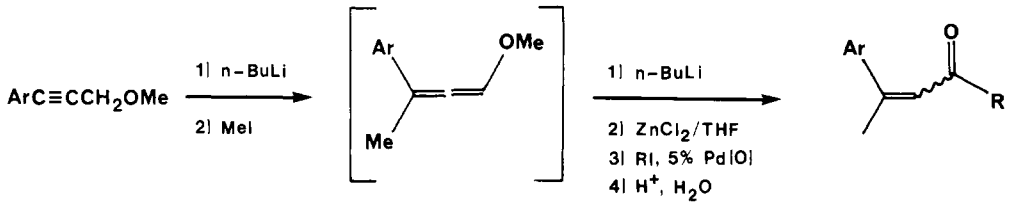
Experimental Section

General Procedures. Tetrahydrofuran (THF) was dried over and distilled from sodium/benzophenone ketyl and was stored under argon. A stock solution of $ZnCl_2$ was prepared by melting the solid under vacuum, crystallizing from dry THF, and dissolving in THF. The solution

(19) (a) R. Mantione and Y. Leroux, *Tetrahedron Lett.*, 593 (1971); (b) R. Mantione and Y. Leroux, *J. Organomet. Chem.*, **31**, 5 (1971); (c) E. J. Corey and S. Terashima, *Tetrahedron Lett.*, 1815 (1972); (d) Y. Leroux and C. Roman, *ibid.*, 2585 (1973); (e) Y. Leroux and R. Mantione, *ibid.*, 591 (1971); (f) Y. Leroux and R. Mantione, *J. Organomet. Chem.*, **30**, 295 (1971).

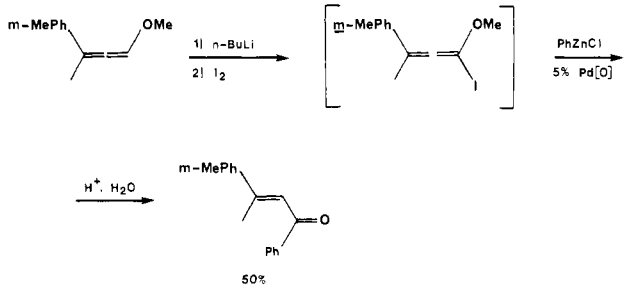
(20) G. F. Hennion and F. P. Bell, *J. Am. Chem. Soc.*, **65**, 1847 (1943).

Scheme V

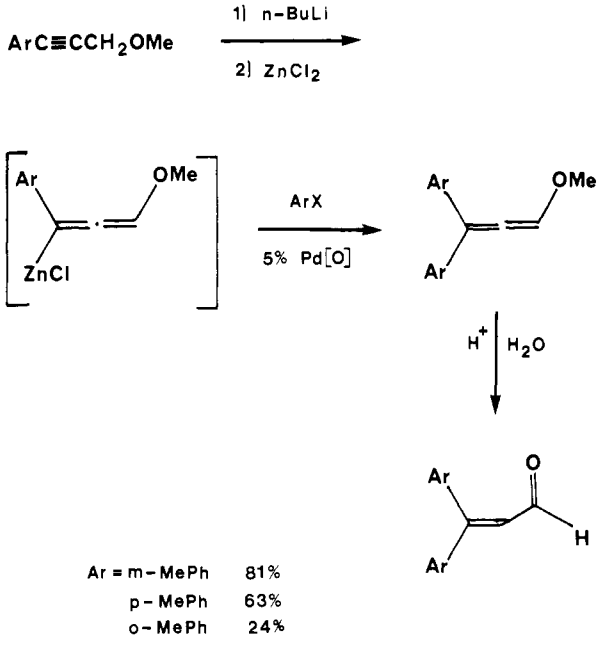


Ar = p-MePh	R = o-MePh	59%
Ar = p-MePh	R = n-C_4H_9	44%
Ar = R = o-MePh		43%

Scheme VI



Scheme VII



Ar = m-MePh	81%
p-MePh	63%
o-MePh	24%

thus obtained was stored over Linde type 4A molecular sieves under argon. $PdCl_2(PPh_3)_2$[10] and $Pd(dba)_2$[16] were prepared by published procedures. Pure *trans*-β-bromostyrene was obtained from a mixture of the cis and trans isomers.[21] Pure *cis*-β-bromostyrene was prepared by a published procedure.[22] 2-Iodoaniline was purified by acid–base extraction. Methyl 2-bromo- and methyl 2-iodobenzoate were prepared by esterification of the acids. (*E*)-1-Iodo-1-hexene,[23] (*E*)-1-iodo-2-methyl-1-hexene,[24] and (*E*)-1-iodo-1-trimethylsilyl-1-hexene[25] were prepared by published procedures, as were 1-methoxy-1,2-propadiene,[17] 1-methoxy-2-heptyne,[26] and 1-methoxy-4,4-dimethyl-2-propyne.[27] Other starting materials were commercially available and used without further purification. All reaction flasks and syringes were oven-dried and cooled under argon, and all coupling reactions were carried out under an argon atmosphere.

NMR spectra were recorded on either a Varian EM-360 60-MHz spectrometer in CCl_4 or a Nicolet 360-MHz instrument in $CDCl_3$, in both cases with tetramethylsilane as internal standard, and are reported in δ. IR spectra were recorded on a Beckman Acculab 3 spectrometer and are reported in cm^{-1}. Products were purified by medium-pressure liquid chromatography (MPLC) on silica gel.

Preparation of Pd(0)-Catalyst Solutions. The Pd(0) catalyst was prepared in THF as described below and added to the reaction flask by using a cannula. In some cases, catalyst was prepared for more than one reaction in the same flask, in which case a degassed syringe was used to divide the solution among reactions.

A. $PdCl_2(PPh_3)_2$ + 2(*i*-Bu)$_2$AlH. $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) was placed in a flask that was then degassed and filled with argon. THF (~10 mL) was added to give a suspension, and 0.1 mL (0.1 mmol) of an $(i\text{-Bu})_2AlH$ solution (1 M in hexane) was added. The mixture was stirred for 10–15 min to give a dark brown homogeneous solution before it was added to the reaction.

B. $Pd(dba)_2$ + 2PPh_3. A mixture of 29 mg (0.05 mmol) of $Pd(dba)_2$ and 26 mg (0.1 mmol) of PPh_3 was dissolved in ~10 mL in THF to give a homogeneous brown-green solution after being stirred for 10 min.

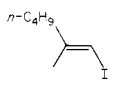
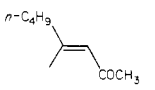
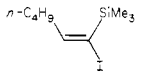
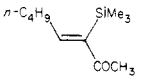
C. $Pd(dba)_2$ + 4PPh_3. The catalyst solution was prepared as described above (B) with 52 mg (0.2 mmol) of PPh_3.

D. $Pd(dba)_2$ + $Ph_2PCH_2CH_2PPh_2$. The catalyst solution was prepared as described above (B) with 20 mg (0.05 mmol) of diphos.

General Coupling Procedure—Enol Ethers. A solution of 0.5 mL of ethyl vinyl ether (5 mmol) in THF (30 mL) was cooled to −70 °C, and *n*-butyllithium (5 mmol, in hexane solution) was added dropwise to give a bright yellow solution. After being stirred at −70 °C for 5–10 min, it was placed in a bath at 0 °C and stirred for 30–45 min, the yellow slowly fading. A solution of $ZnCl_2$ (5–6 mmol) in THF was added to give a clear, colorless solution. After 5–10 min at 0 °C, the bath was removed and the solution stirred at room temperature for 30 min. The Pd catalyst (0.05 mmol, in 10–20 mL of THF) was then added, followed by the substrate (1 mmol). After several hours of stirring, the reaction mixture was shaken with 5% HCl, extracted with ether, washed with saturated NaCl, dried over magnesium sulfate and filtered, and the solvent was removed. The brown oil thus obtained was triturated with hexane and

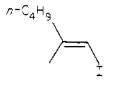
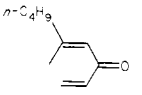
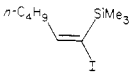
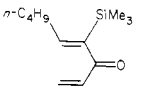
(21) L. J. Dolby, C. Wilkins, and J. A. Frey, *J. Org. Chem.*, **31**, 1110 (1966).
(22) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).
(23) A. Zweifel and C. A. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1976). IR (neat): 1610 (C=C), 950 (C=C); NMR 0.7–2.3 (m, 9 H, alkyl H), 5.9 (d, J = 14 Hz, 1 H, C=C*H*I), 6.45 (d of t's, J_d = 14 Hz, J_t = 6 Hz, *H*C=CI).
(24) E. Negishi, D. E. VanHorn, A. O. King, N. Okukado, *Synthesis*, 501 (1979). The product was purified by distillation (bp 50 °C (1.8 mm)).
(25) A. Zweifel and W. Lewis, *J. Org. Chem.*, **43**, 2739 (1978).
(26) See ref 20. NMR: 1.2 (s, CMe_3), 3.2 (s, OMe), 3.9 (s, ≡CH_2—O).
(27) See ref 20. For NMR see R. Gelin, S. Gelin, and M. Albrand, *Bull. Soc. Chim. Fr.*, 4146 (1971). The crude product was used without distillation.
(28) Aldrich: NMR, **6**, 6A; IR, 746H.
(29) Aldrich: NMR, **6**, 20B; IR, 749E.
(30) Aldrich: NMR, **6**, 20C; IR, 750G.
(31) (a) Aldrich: IR, 750H; (b) Beilstein: **7**, 307.
(32) Aldrich: NMR, **6**, 27D; IR, 758H.
(33) Aldrich: NMR, **6**, 38C; IR, 767A.
(34) E. E. Smissman, J. P. Li, and Z. H. Israili, *J. Org. Chem.*, **33**, 4231 (1968).
(35) Aldrich: NMR, 41B; IR, 769A.
(36) Aldrich: NMR, **6**, 42A; IR, 745G.
(37) F. Rocquet and A. Sevin, *Bull. Soc. Chim. Fr.*, 881 (1974).
(38) Identical by IR and NMR with material prepared by the method of Ansell and Mahmood from *trans*-2-heptenoic acid: M. F. Ansell and S. A. Mahmood, *J. Chem. Soc., Perkins Trans. 1*, 2789 (1973); G. Zweifel and R. B. Steel, *J. Am. Chem. Soc.*, **89**, 2754 (1967).
(39) W. TenHoeve and H. Wynberg, *J. Org. Chem.*, **45**, 2754 (1980).

Table III. Scale, Purification, and Characterization of Acetylation Reactions of Halides by Enol Ether Anions (Table I)

RX	mg	mL	mmol	product	mg	MPLC purification, hexane/Et_2O	TLC, R_f	character-ization[a]
PhI		0.11	1.0	$PhCOCH_3$	91	4:1	0.21	A[28]
PhI		0.11	1.0	$PhCOCH_3$	82	4:1	0.21	A[28]
PhI		0.11	1.0	$PhCOCH_3$	55	4:1	0.21	A[28]
o-MePhI		0.13	1.0	*o*-$MePhCOCH_3$	96	4:1	0.35	A[29]
m-MePhI		0.13	1.0	*m*-$MePhCOCH_3$	109	4:1	0.25	A[30]
p-MePhI	218		1.0	*p*-$MePhCOCH_3$	95	4:1	0.28	A[31]
m-MeOPhI	117		0.5[b]	*m*-$MeOPhCOCH_3$	43	10:1	0.12	A[32]
m-MeOPhI	117		0.5[b]	*m*-$MeOPhCOCH_3$	43	10:1	0.12	A[32]
o-NH_2PhI	218		1.0	*o*-$NH_2PhCOCH_3$	55[c]			A[33]
o-MeO_2CPhBr	218		1.0	*o*-$MeO_2CPhCOCH_3$	90	4:1	0.11	A[34]
o-MeO_2CPhI	262		1.0	*o*-$MeO_2CPhCOCH_3$	137	4:1	0.11	A[34]
o-NO_2PhI	250		1.0	*o*-$NO_2PhCOCH_3$	117	4:1	0.08	A[35]
trans-PhCH=CHBr		0.13	1.0	*trans*-PhCH=$CHCOCH_3$	123	4:1	0.18	A[36]
cis-PhCH=CHBr	184		1.0	*cis*-PhCH=$CHCOCH_3$	99[c]	4:1	0.26	A[37]
trans-*n*-C_4H_9CH=CHI	210		1.0	*trans*-*n*-C_4H_9CH=$CHCOCH_3$	42	4:1	0.25	B[38]
	112		0.5[b]		27	8:1	0.26	B[39]
	141		0.50		54	20:1	0.25	C

[a] A, infrared and NMR spectra identical with that reported for pure, authentic material; B, identical with material prepared by an alternate procedure; C, compounds gave suitable IR and NMR spectra and elemental analysis. [b] Reaction run on half normal scale but with 10% Pd catalyst. [c] See Experimental Section for modified isolation procedure.

Table IV. Scale, Purification, and Characterization of Acylation of Halides by Allenic Ether Anions (Table II)

RX	mg	mL	mmol	time, h	cata-lyst[a]	product	mg	MPLC purifi-cation, hexane/Et_2O	TLC, R_f	charac-teriza-tion[b]
o-MePhI		0.13	1.0	3	B	*o*-$MePhCOCH=CH_2$	77	10:1	0.33	A[43]
m-MePhI		0.13	1.0	3	B	*m*-$MePhCOCH=CH_2$	123	10:1	0.30	A[43]
p-MePhI	218		1.0	3	B	*p*-$MePhCOCH=CH_2$	96	10:1	0.28	A[43]
$PhCH_2Br$		0.12	1.0	6	A	$PhCH_2COCH=CH_2$	56	10:1	0.19	A[44]
trans-PhCH=CHBr		0.13	1.0	10	B	*trans*-PhCH=$CHCOCH=CH_2$	33	6:1	0.26	B[45]
trans-*n*-C_4H_9CH=CHI	210		1.0	6	B	*trans*-*n*-C_4H_9CH=$CHCOCH=CH_2$	51	8:1	0.19	B
	224		1.0		B		49	8:1	0.29	B
	270		1.0	7	A		149	8:1	0.38	B

[a] See Table I. [b] A, infrared and NMR spectra identical with those reported for authentic material; B, satisfactory infrared and NMR spectra and elemental analysis.

filtered and the solvent again removed. The crude product was then purified by MPLC using hexane/ether mixtures as the solvent system (Table III).

***p*-Methylacetophenone.** ^1H NMR δ 2.40–2.45 (2 s, total 6 H, $ArCH_3$, $COCH_3$), 7.15 (d, J = 16 Hz, 2 H, Ar H), 7.75 (d, J = 16 Hz, 2 H, Ar H).

***o*-Aminoacetophenone.** The standard isolation procedure was modified as follows. After quenching with 5% HCl, the reaction was extracted with ether, the ether extracts were discarded, and the aqueous layer was then neutralized with saturated Na_2CO_3 and extracted with ether, and the ether extracts treated as described above. Removal of solvent gave 55 mg of product (41%), which was pure (by NMR and IR spectra). Purification by MPLC of the crude product from a separate reaction gave a 25% yield of product identical in all respects with the above material.

***cis*-4-Phenyl-3-buten-2-one.** After 6 h of stirring, the reaction was quenched with ~50 mL of 20% NH_4Cl and extracted with Et_2O. The ether extracts were washed with saturated NaCl, and the solvent was evaporated. The oil thus obtained was triturated with hexane and filtered and the solvent again removed. ^1H NMR analysis of the crude product showed the presence of the cis enol ether [δ 1.15 (t, J = 7 Hz, OCH_2CH_3), 3.65 (q, J = 7 Hz, OCH_2CH_3), 4.1 (br s, $=CH_2$), 5.85 (d, J = 13 Hz, =CH), 6.4 (d, J = 13 Hz, =CH), 7.1–7.5, m, ArH)] with no trace of the cis or trans ketone or the trans enol ether.[40] Without purification, the crude enol ether was taken up in ~50 mL of Et_2O and stirred over $MgSO_4$ for 2 h. Filtration and removal of solvent gave the crude cis ketone,[41] which was purified as above (see Table III).

(*E*)-3-Octen-2-one. IR (neat) cm^{-1} 1705, 1680 (C=O), 1630 (C=C), 980 (C=C); ^1H NMR δ 0.7–1.7 (m, 7 H, alkyl H), 1.9–2.3 (m, $=CHCH_2$), 2.1 (s, $COCH_3$, total 5 H), 5.85 (d of t, J = 16, 1 Hz, 1 H, H_α), 6.6 (d of t, J = 16, 6 Hz, 1 H, H_β).

(*E*)-4-Methyl-3-octen-2-one. IR (neat) cm^{-1} 1695 (C=O), 1625 (C=C); ^1H NMR δ 0.8–1.6 (m, 7 H, alkyl H), 1.9–2.2 (m, 2 H, $=CHCH_2$), 2.05 (br s, $=CCH_3$, $COCH_3$, $=CH_2C=$, total 8 H), 5.85 (m, 1 H, =CH).[42]

(40) The trans isomer of the enol ether, prepared in the same manner, starting from bromide, had a similar NMR [δ 1.35 (t, J = 6 Hz, OCH_2CH_3), 3.75 (q, J = 6 Hz, OCH_2CH_3), 4.1 (br s, $=CH_2$), 6.35 (d, J = 16 Hz, C=CH), 6.7–7.8 (m, Ar H, C=CH)].

(41) HCl hydrolysis of the cis enol ether or $MgSO_4$ hydrolysis before trituration with hexane gave a mixture of the cis and trans ketones.

(42) NMR at 360 MHz in $CDCl_3$ showed the singlet at δ 2.05 as a singlet at 2.10 ($COCH_3$) and doublet (J = 2 Hz) at 2.15 ($CH_3C=$).

(43) R. Visser and E. A. M. F. Dahmen, *Anal. Chim. Acta*, **100**, 271 (1978).

(44) G. Dana, S. L. T. Thuan, and J. Gharbi-Benaras, *Bull. Soc. Chim. Fr.*, 2089 (1974).

Table V. Conditions for Coupling of γ-Substituted Allenic Ethers (Scheme III)

R X	mL	mmol	time, h	catalyst[a]	product	mg	MPLC purification, hexane/Et_2P	TLC, R_f
MeI	0.9	2.0	3	A	*m*-MePhCOCH=C(Me)-*n*-Bu (*E* + *Z*)	28	20:1	0.40
						67	20:1	0.32
Me_3SiCl[c]	0.13	1.0	3	A[b]	*m*-MePhCOCH=C$SiMe_3$-*n*-Bu (*E* + *Z*)	70	20:1	0.49
						32		0.43
n-BuBr	0.11	1.0	6	A	*m*-MePhCOCH=C(*n*-Bu)$_2$	116	40:1	0.30

[a] See Table I. [b] 10% used. [c] At room temperature, only 5 min.

Table VI. Preparation and Purification of Arylpropargyl Ethers (Scheme IV)

ArX	g	mL	mmol	time, h	product	g	MPLC purification, hexane/Et_2O	TLC, R_f
PhI		1.3	10	6	PhC≡CCH_2OCH_3	1.0	4:1	0.52
o-MePhI		2.4	18.9[a]	13	*o*-MePhC≡CCH_2OCH_3	2.6	8:1	0.33
m-MePhI		1.3	10	19	*m*-MePhC≡CCH_2OCH_3	1.3	8:1	0.33
p-MePhI	4.36		20[a]	25	*p*-MePhC≡CCH_2OCH_3	2.6	7:1	0.42
m-MeOPhI	2.24		9.6	12	*m*-MeOPhC≡CCH_2OCH_3	1.1	10:1	

[a] Run on twice the normal scale but with 2.5% catalyst.

(*Z*)-3-(Trimethylsilyl)-3-octen-2-one. IR (CCl_4) cm^{-1} 1665 (C=O), 1595 (C=C); ^1H NMR δ 0.15 (s, 9 H, $SiMe_3$), 0.8–1.6 (m, 7 H, alkyl H), 2.05–2.4 (m, =CCH_2), 2.15 (s, $COCH_3$, total 5 H), 6.75 (t, *J* = 7 Hz, 1 H, =CH). Anal. ($C_{11}H_{22}OSi$): C, H.

General Coupling Procedure—Unsubstituted Allenic Ethers. A solution of 140 mg (2.0 mmol) of 1-methoxy-1,2-propadiene in 20 mL of THF was cooled to −40 °C, and 2.0 mmol of *n*-BuLi were added dropwise. After 30 min of stirring (between −40 and −30 °C), 3 mL (~3.0 mmol) of $ZnCl_2$ in THF was added. After 5 min, the bath was removed, and the reaction was stirred for 30 min. The Pd-catalyst solution (0.05 mmol, prepared as described above) was added, followed by the substrate (added neat). After several hours (see Table IV) of stirring, the product was isolated and purified as described above.

1-(2-Methylphenyl)-2-propen-1-one: IR (neat) cm^{-1} 1680 (C=O), 1660, 1610; ^1H NMR δ 2.35 (s, 3 H, $ArCH_3$), 5.8 (d of d's, *J* = 10, 2 Hz, trans CH=CCO), 6.0 (d of d's, *J* = 17, 2 Hz, 1 H, cis CH=CCO), 6.7 (d of d's, *J* = 10, 17 Hz, 1 H, =CHCO), 6.9–7.45 (m, 4 H, Ar H).

1-(3-Methylphenyl)-2-propen-1-one: IR (neat) cm^{-1} 1685 (C=O), 1625, 1600; ^1H NMR δ 2.35 (s, 3 H, $ArCH_3$), 5.7 (d of d's, *J* = 9, 2 Hz, 1 H, trans CH=CCO), 6.25 (d of d's, *J* = 17, 2 Hz, 1 H, cis CH=CCO), 6.8–7.7 (m, 5 H, Ar H, =CHCO).

1-(4-Methylphenyl)-2-propen-1-one: IR (neat) cm^{-1} 1670 (C=O); ^1H NMR δ 2.35 (s, 3 H, $ArCH_3$), 5.7 (d of d's, *J* = 10, 2 Hz, 1 H, trans CH=CCO), 6.2 (d of d's, *J* = 17, 2 Hz, 1 H, cis CH=CCO), 7.0 (d of d's, *J* = 17, 10 Hz, 1 H, =CHCO), 7.1 (d, *J* = 8 Hz, 2 H, Ar H), 7.65 (d, *J* = 8 Hz, 2 H, Ar H).

(*E*)-1-Phenyl-1,4-pentadien-3-one: IR (CCl_4) cm^{-1} 1680 (C=O); ^1H NMR (360 MHz) δ 5.88 (d of d's, *J* = 11,2 Hz, 1 H, *E* HC*H*=CHCO), 6.38 (d of d's, *J* = 15, 2 Hz, 1 H, *Z* *H*CH=CHCO), 6.70 (d of d's, *J* = 11, 15 Hz, 1 H, H_2C=C*H*CO), 7.06 (d, *J* = 16 Hz, 1 H, *E* PhCH=C*H*CO), 7.35–7.45 (m, 3 H, Ar H), 7.55–7.60 (m, 2 H, Ar H), 7.67 (d, *J* = 16 Hz, 1 H, *E* PhC*H*=CHCO). Anal. ($C_{11}H_{10}O$): C, H.

(*E*)-1,4-Nonadien-3-one: IR (neat) cm^{-1} 1675 (C=O); ^1H NMR (360 MHz) δ 0.9 (t, *J* = 10 Hz, 3 H, CH_3), 1.2–1.5 (m, 4 H, CH_2CH_2), 2.25 (m, 2 H, CH_2C=C), 5.79 (d of d's, *J* = 11, 2 Hz, *E* HC*H*=CHCO), 6.27 (d of d's, *J* = 18, 2 Hz, 1 H, *Z* HC*H*=CHCO), 6.33 (d of t's, J_d = 16 Hz, J_t = 1 Hz, 1 H, *E* CH_2CH=C*H*CO), 6.57 (d of d's, *J* = 11, 18 Hz, 1 H, H_2C=C*H*CO), 6.93 (d of d's, J_d = 16 Hz, J_t = 7 Hz, 1 H, CH_2CH=CHCO). Anal. ($C_{11}H_{14}O$): C, H.

(*E*)-5-Methyl-1,4-nonadien-3-one: IR (CCl_4) cm^{-1} 1680 (C=O), 1660, 1625, 1600; ^1H NMR (360 MHz) δ 0.85 (t, *J* = 9 Hz, CH_3CH_2), 1.20–1.50 (m, 4 H, CH_2CH_2), 2.0–2.2 (m, CH_2C=C), 2.10 (d, *J* = 1 Hz, CH_3C=CHCO, total 5 H), 5.67 (d of d's, *J* = 11, 2 Hz, 1 H, *E* *H*CH=CHCO), 6.14 (d of d's, *J* = 18, 2 Hz, 1 H, *Z* HC*H*=CHCO), 6.20 (q, *J* = 1 Hz, 1 H, CH_3C=C*H*CO), 6.35 (d of d's, *J* = 11, 18 Hz, 1 H, H_2C=C*H*CO). Anal. ($C_{12}H_{16}O$): C, H.

(*Z*)-4-(Trimethylsilyl)-1,4-nonadien-3-one: IR (neat) cm^{-1} 1665 (C=O), 1610; ^1H NMR (360 MHz) δ 0.09 (s, 9 H, $SiMe_3$), 0.85 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.30 (m, 4 H, CH_2CH_2), 2.00 (q, *J* = 7 Hz, 2 H, CH_2C=), 5.95 (d of d's, *J* = 11, 2 Hz, 1 H, *E* HC*H*=CHCO), 6.08 (d of d's, *J* = 18, 2 Hz, 1 H, *Z* HC*H*=CHCO), 6.35 (d of d's, *J* = 11, 18 Hz, 1 H, HCH=C*H*CO), 5.95 (t, *J* = 7 Hz, 1 H, CH_2CH=C). Anal. ($C_{12}H_{22}OSi$): C, H.

General Coupling Procedure—δ-Alkyl-Substituted Allenic Ethers. To a solution of 250 mg (2 mmol) of 1-methoxy-2-heptyne in 30 mL of THF at −40 °C was added 1 equiv of *n*-BuLi. After 15 min of stirring, 1 equiv of electrophile (RX) was added, and the reaction was stirred for an additional 15 min at −40 °C and then for 30 min at room temperature. It was then recooled to −40 °C, and 1 equiv of *n*-BuLi was added. After 15 min, the anion was quenched with ~1.5 equiv of $ZnCl_2$ solution. After 5 min, the bath was removed and the reaction allowed to warm to room temperature (15–20 min), at which time the catalyst solution (prepared as described above) was added, followed by 0.13 mL (1.0 mmol) of 3-iodotoluene (neat). After several hours of stirring, the product was isolated and purified as described above and characterized by IR, NMR, and chemical analysis.

1-(3-Methylphenyl)-3-methyl-2-hepten-1-one. Isomer A: IR (neat) cm^{-1} 1670 (C=O), 1620; ^1H NMR δ 0.7–1.8 (m, 7 H, alkyl H), 1.95 (d, *J* = 1 Hz, 3 H, C=CCH_3), 2.45 (s, 3 H, $ArCH_3$), 2.4–2.8 (m, 2 H, C=CCH_2), 6.5 (m, 1 H, C=CH), 7.1–7.7 (m, 4 H, Ar H). Anal. ($C_{15}H_{20}O$): C, H.

Isomer B: IR (neat) cm^{-1} 1670 (C=O), 1620; ^1H NMR δ 0.7–1.7 (m, 7 H, alkyl H), 2.15 (d, *J* = 1 Hz, C=CCH_3), 2.4 (s, $ArCH_3$), 2.0–2.5 (m, C=CCH_2), 2.55 (m, C=CH), 7.1–7.7 (m, Ar H). Anal. ($C_{15}H_{20}O$): C, H.

1-(3-Methylphenyl)-3-(trimethylsilyl)-2-hepten-1-one. Isomer A: IR (CCl_4) cm^{-1} 1665 (C=O); ^1H NMR δ 0.15 (s, 9 H, $SiMe_3$), 0.8–1.7 (m, 7 H, alkyl H), 2.4 (s, 3 H, $ArCH_3$), 2.2–2.5 (m, 2 H, C=CCH_2), 7.1–7.7 (m, 5 H, Ar H, C=CH). Anal. ($C_{17}H_{26}OSi$): C, H.

Isomer B: IR (CCl_4) cm^{-1} 1675 (C=O); ^1H NMR δ 0.2 (s, 9 H, $SiMe_3$), 0.8–1.7 (m, 7 H, alkyl H), 2.4 (s, 3 H, $ArCH_3$), 2.3–2.6 (m, 2 H, C=CCH_2), 6.85 (m, 1 H, C=CH), 7.1–7.7 (m, 4 H, Ar H). Anal. ($C_{17}H_{26}OSi$): C, H.

1-(3-Methylphenyl)-3-*n*-butyl-2-hepten-1-one: IR (CCl_4) cm^{-1} 1670 (C=O); ^1H NMR δ 0.7–1.8 (m, 14 H, alkyl H), 2.0–2.7 (m, 7 H, including S at 2.4 ($ArCH_3$)), 6.5 (m, 1 H, C=CH), 7.1–7.65 (m, 4 H, Ar H). Anal. ($C_{18}H_{26}O$): C, H.

Preparation of δ-Aryl Propargyl Ethers (ArC≡CCH_2OCH_3). To a solution of 1 mL (12 mmol) of methyl propargyl ether in 30 mL of THF at 0 °C was added 12 mmol of *n*-BuLi dropwise. After 5 min of stirring, 15 mL (~15 mmol) of $ZnCl_2$ in THF was added, and after 5 min more of stirring, the bath was removed and the reaction stirred for 30 min. The catalyst solution (0.5 mmol of catalyst A, prepared at ten times the scale described above) was then added, followed by the substrate (~10 mmol, see Table VI). After several hours of stirring, the product was isolated and purified as described above. These materials were used in subsequent reactions without further purification.

1-Methoxy-3-phenyl-2-propyne: IR (neat) cm^{-1} 2240 (C≡C); ^1H NMR δ 3.3 (s, 3 H, OCH_3), 4.15 (s, 2 H, ≡CH_2O), 7.0–7.5 (m, 5 H, Ar H).

1-Methoxy-3-(2-methylphenyl)-2-propyne: IR (neat) cm^{-1} 2300 (C≡C); ^1H NMR δ 2.4 (s, 3 H, $ArCH_3$), 3.4 (s, 3 H, OCH_3), 4.25 (s, 2 H, ≡CH_2O), 6.85–7.4 (m, 4 H, Ar H).

1-Methoxy-3-(3-methylphenyl)-2-propyne: IR (neat) cm^{-1} 2225 (C≡C); ^1H NMR δ 2.3 (s, 3 H, $ArCH_3$), 3.35 (s, 3 H, OCH_3), 4.15 (s, 2 H, ≡CH_2O), 6.85–7.25 (m, 4 H, Ar H).

(45) N. Boccara and P. Maitte, *Tetrahedron Lett.*, 4031 (1977); *Bull. Soc. Chim. Fr.*, 1448 (1972).

Table VII. Scale and Purification of γ-Arylation Reactions (Scheme VII)

Ar	ArX	mg	mL	mmol	time, h	catalyst[a]	product	mg	MPLC purification, hexane/Et_2O	TLC, R_f	characterization[b]
o MePh	*o*-MePhI		0.13	1.0	6	A	(*o*-MePh)$_2$C=CHCHO	56	4:1	0.30	A
m-MePh	*m*-MePhI		0.13	1.0	12	A	(*m*-MePh)$_2$C=CHCHO	191	4:1	0.32	A
p-MePh	*p*-MePhI	109		0.5[c]	15.5	A	(*p*-MePh)$_2$C=CHCHO	74	8:1	0.21	B[47]

[a] See Table I. [b] A, Compound has satisfactory IR and NMR spectra and elemental analysis; B, infrared and NMR spectra identical with that reported for authentic material. [c] Reaction run on half the normal scale.

1-Methoxy-3-(4-methylphenyl)-2-propyne: IR (neat) cm^{-1} 2260 (C≡C); ^1H NMR δ 2.25 (s, 3 H, $ArCH_3$), 3.25 (s, 3 H, OCH_3), 4.1 (s, 2 H, ≡CH_2O), 6.8–7.2 (m, 4 H, Ar H).

1-Methoxy-3-(3-methoxyphenyl)-2-propyne: IR (neat) cm^{-1} 2250 (C≡C); ^1H NMR δ 3.35 (s, 3 H, OCH_3), 3.7 (s, 3 H, $ArOCH_3$), 4.25 (s, 2 H, ≡CH_2O), 6.55–7.3 (m, 4 H, Ar H).

General Coupling Procedure—γ-Aryl Allenic Ethers. To a solution of 320 mg (2.0 mmol) of 3-(4-methylphenyl)-1-methoxy-2-propyne in 20 mL of THF at −70 °C was added 1 equiv of *n*-BuLi. After 15 min of stirring, 0.12 mL (2.0 mmol) of MeI was added dropwise, and after 15 min, the bath was removed and the reaction stirred for 30 min. It was then recooled to −70 °C and 1 equiv more of *n*-BuLi added. After 15 min, ~1.5 equiv of $ZnCl_2$ solution was added, and after ~5 min, the bath was removed and the reaction allowed to warm to room temperature (15–20 min), at which time the catalyst solution (prepared as described above) was added, followed by the substrate (neat). After several hours of stirring, the product was isolated and purified as described above.

2-(4-Methylphenyl)-2,5-decadien-4-one. When the procedure described above was used, 210 mg (1 mmol) of (*E*)-1-iodo-1-hexene was reacted for 6 h. Purification by MPLC using 4:1 hexane/ether gave two isomers of product.

Isomer A: 23 mg (10%) R_f 0.38. IR (CCl_4) cm^{-1} 1690 (C=O); ^1H NMR δ 0.7–1.8 (m, 7 H, alkyl H), 2.2–2.6 (m, including s at 2.3 and d (J = 1 Hz at 2.45 (8 H, CH_2C=C, $ArCH_3$, CH_3C=CH)), 6.3 (m, 1 H, CH_3C=C*H*), 6.8–7.4 (m, 6 H, Ar H and HC=CHCO).

Isomer B: 81 mg (33%) R_f 0.44; IR (CCl_4 cm^{-1} 1660 (C=O); ^1H NMR δ 0.8–1.8 (m, 7 H, alkyl H), 2.0–2.5 (m, including s at 2.35 (CH_3) and d (J = 1 Hz at 2.45 (CH_3, C=CH), alkyl H)), 6.05 (d of m's, J = 16 Hz, 1 H, *Z* CH_2C=C*H*CO), 6.45 (q, J = 1 Hz, 1 H, CH_3C=C*H*), 6.6–7.4 (m, 5 H, Ar H and CH_2CH=CHCO). Anal. (of the combined isomers). ($C_{17}H_{12}O$): C, H.

1,3-Bis(2-methylphenyl)-2-buten-1-one. Following the procedure described above, 0.13 mL (1 mmol) of 2-iodotoluene was reacted for 6 h. Purification by MPLC using 4:1 hexane/Et_2O gave 107 mg of product[46] (43% yield, R_f 0.37).

(*E*)-1-(2-Methylphenyl)-3-(4-methylphenyl)-2-buten-1-one. Following the procedure described above, but on half the normal scale, 0.07 mL (0.5 mmol) of 2-iodotoluene was reacted for 15 h. Purification by MPLC using 8:1 hexane/ether gave 73 mg of product (59%, R_f 0.27): IR (CCl_4) cm^{-1} 1670 (C=O); ^1H NMR δ 2.35 (s, 3 H, $ArCH_3$), 2.45 (s, $ArCH_3$), 2.50 (d, J = 1 Hz, C=CCH_3, total 6 H), 6.75 (q, J = 1 Hz, 1 H, C=CH), 6.8–7.5 (m, 8 H, Ar H). Anal. ($C_{18}H_{18}O$): C, H.

1-Phenyl-3-(3-methylphenyl)-2-buten-1-one. To a solution of 160 mg (1 mmol) of 3-(3-methylphenyl)-1-methoxy-2-propyne in 30 mL of THF at −70 °C was added 1 mmol of *n*-BuLi dropwise. After 15 min of stirring, 0.06 mL (1 mmol) of MeI was added neat, and after 15 min, the bath was removed and the reaction stirred for 30 min. It was then recooled to −70 °C, and a second 1 mmol of *n*-BuLi was added. After 15 min, the septum was removed and 254 mg (1 mmol) of solid I_2 was added. The septum was replaced, and after 15 min, the bath was removed. After stirring, a solution of 1.4 mmol of PhZnCl (prepared by the addition of 1.4 mmol of PhLi in ether to 2.5 mmol of $ZnCl_2$ in 20 mL of THF at −70 °C followed by stirring at room temperature for 1 h) was added, followed by the solution of 0.05 mmol of PdL_2 in THF (prepared as described above).

After 18 h of stirring, the reaction was quenched with 20% aqueous NH_4Cl and extracted with ether. The ether extracts were washed with saturated NaCl, dried over magnesium sulfate, filtered, and concentrated.

The crude product was then taken up in ether, shaken with 5% HCl to hydrolyze the allenic ether, and extracted into ether. The ether extracts were again washed with saturated NaCl, dried over magnesium sulfate, filtered, and concentrated.

The crude ketone was purified by MPLC using 4:1 hexane/ether to give two products.

A: R_f 0.26, 57 mg (24%); IR (CCl_4) cm^{-1} 1665 (C=O); ^1H NMR δ 2.35 (s, 3 H, $ArCH_3$), 2.55 (d, J = 1 Hz, 3 H, C=CCH_3), 6.9–7.9 (m, 10 H, Ar H and C=CH).

B: R_f 0.18, 57 mg (24%); IR (CCl_4) cm^{-1} 1670 (C=O); ^1H NMR δ 2.2 (s, and d (J = 2 Hz), 6 H, $ArCH_3$ and C=CCH_3), 6.45 (q, J = 2 Hz, 1 H, C=CH), 6.7–7.75 (m, 9 H, Ar H). Anal. (of the mixture). ($C_{17}H_{16}O$): C, H.

General Procedure—γ Coupling. To a solution of 320 mg (2.0 mmol) of 3-aryl-1-methoxy-2-propyne in 20 mL of THF at −70 °C was added 2.0 mmol of *n*-BuLi dropwise. The solution turned dark brown. After 15 min of stirring, a solution of 3 mL (~3 mmol) of $ZnCl_2$ in THF was added, the reaction was stirred for 5 min, and the bath was then removed and the reaction allowed to warm to room temperature (15–20 min). The catalyst solution (0.05 mmol, prepared as described above) was added, followed by the substrate. After being stirred for the designated time, the product was isolated and purified as described below (Table VII).

3,3-Bis(2-methylphenyl)-2-propenal: IR (CCl_4) cm^{-1} 1685 (C=O); ^1H NMR δ 2.0 (s, 3 H, $ArCH_3$), 2.25 (s, 3 H, $ArCH_3$), 6.1 (d, J = 8 Hz, 1 H, C=CH), 6.8–7.3 (m, 8 H, Ar H), 9.3 (d, J = 8 Hz, 1 H, CHO). Anal. ($C_{17}H_{16}O$): C, H.

3,3-Bis(3-methylphenyl)-2-propenal: IR (CCl_4) cm^{-1} 1680 (C=O); ^1H NMR δ 2.3 (s, 3 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 6.35 (d, J = 8 Hz, 1 H, C=CH), 6.8–7.3 (m, 8 H, Ar H), 9.35 (d, J = 8 Hz, 1 H, CHO). Anal. ($C_{17}H_{16}O$): C, H.

Acknowledgment. This research was supported by grants CHE 7907832 and CHE 8200522 from the National Science Foundation. High-field NMR spectra were obtained on instruments in the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE 7818581.

(46) L. J. Mazza and A. Guarna, *Synthesis*, 41 (1980).
(47) H. E. Zimmerman, D. Arnesto, M. G. Amezua, T. P. Gannett, and R. P. Johnson, *J. Am. Chem. Soc.*, **101**, 6367 (1979).