hexanes) gave 1.53 g (68% yield) of **42** as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.5–2.6 (m, 17 H), 2.17 (s, 3 H), 3.04 (two t, total 2 H, J = 6 Hz), and 4.14 (broad t, 2 H); ir (tf) λ_{max} 3.40, 3.49, and 5.83 μ.

Preparation of Diketone 27. A mixture of the hemithioketals **42** (1.53 g, 5.7 mmol), $HgCl_2$ (3.39 g, 12.5 mmol), and $CaCO_3$ (1.43 g, 14.3 mmol) in 52 ml of CH_3CN and 13 ml of distilled water was stirred at room temperature under argon for 10 min. The reaction mixture was filtered through Celite with the aid of ether, extracted with ice-cooled NH_4OAc solution, ice–water, and saturated NaCl solution, and then dried over $MgSO_4$, filtered, and concentrated to afford 1.17 g (99% yield) of **27** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.4–2.5 (m, 17 H) and 2.12 (s, 3 H); ir (tf) λ_{max} 3.40, 3.49, and 5.84 μ; an exact mass determination gave m/e 208.1459 (calcd for $C_{13}H_{20}O_2$, 208.1463).

Acknowledgment. This work was assisted financially by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—**4**, 100-52-7; **6**, 124-13-0; **8**, 108-94-1; **10**, 120-92-3; **14**, 1124-96-5; **15**, 57132-07-7; **16**, 1123-26-8; **17**, 2890-62-2; **20**, 42393-59-9; **21**, 35730-87-1; *cis*-**22**, 35730-88-2; *trans*-**22**, 35730-89-3; **25**, 57132-08-8; **26a**, 57132-09-9; **27**, 57132-10-2; *cis*-**28**, 57132-11-3; **29**, 2568-20-9; **30** isomer a, 57132-12-4; **30** isomer b, 57132-13-5; **30** isomer c, 57527-69-2; **30** isomer d, 57527-70-5; **31**, 1072-21-5; **33**, 110-13-4; **35**, 1489-28-7; **36** isomer a, 57132-14-6; **36** isomer b, 57173-49-6; **37**, 12312-06-0; **39**, 35730-86-0; **40** isomer a, 57132-15-7; **40** isomer b, 57173-50-9; **41** isomer a, 57132-16-8; **41** isomer b, 57173-51-0; **42** isomer a, 57132-17-9; **42** isomer b, 57173-52-1; acetone, 67-64-1; cycloheptanone, 502-42-1; acetaldehyde, 75-07-0; methanesulfonyl chloride, 124-63-0; 2-mercaptoethanol, 60-24-2; diisoamylborane, 6838-83-1; mercuric chloride, 7487-94-7; magnesium, 7439-95-4; cyclopentadienyltitanium trichloride, 1270-98-0; lithium aluminum hydride, 16853-85-3; boron trifluoride etherate, 109-63-7; titanium tetrachloride, 7550-45-0.

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A Palladium-Catalyzed Arylation of Allylic Alcohols with Aryl Halides

John B. Melpolder and Richard F. Heck*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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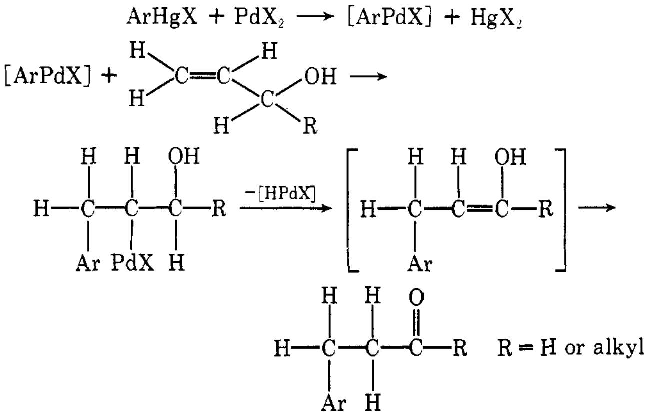
A convenient reaction for preparing 3-arylaldehydes and ketones from allylic alcohols and aryl halides is described. In some instances 3-arylallylic alcohols may also be obtained in varying yields depending upon the aryl halide used and the catalyst employed. The effects of substituents in both reactants on the reaction course are discussed. Homoallylic alcohols react similarly, giving substantial amounts of aryl ketones or aldehydes.

The previously reported allylic alcohol arylation with organopalladium compounds[1] was shown to be useful for the synthesis of 3-arylaldehydes and ketones when primary or secondary allylic alcohols, respectively, were allowed to react. The reaction required a molar amount of an organomercury compound to prepare, in situ, the organopalladium reagent with either an equivalent amount of a palladium(II) salt or a catalytic amount of this salt plus an equivalent amount of cupric chloride to regenerate the palladium after each reaction cycle. The addition of a hindered tertiary amine to the reaction mixtures also proved beneficial. Even under the most favorable conditions found, however, yields were never over 53% and were often considerably lower.

Table I
Arylation of Allylic Alcohols

					Products[a]								
					3-Arylation			2-Arylation					
Registry no.	Alcohol	Aryl halide (registry no.)	Catalyst	Reaction time, hr	Alcohol, %	Carbonyl compd, %	Alcohol/carbonyl	Alcohol, %	Carbonyl compd, %	Alcohol/carbonyl	Other products (yield)	Total yield, %	% 3-aryl addition
107-18-6	$CH_2{=}CHCH_2OH$	C_6H_5I (591-50-4)	$Pd(OAc)_2$	0.5^{b}		84			16			71	84
	$CH_2{=}CHCH_2OH$	C_6H_5I	$Pd(OAc)_2(PPh_3)_2$	5.5^{c}		76			24			74	76
	$CH_2{=}CHCH_2OH$	C_6H_5I	$PdBr(Ph)(PPh_3)_2$	$26^{c,d}$		78			22			72	78
6117-91-5	$CH_3CH{=}CHCH_2OH$	C_6H_5I	$Pd(OAc)_2$	12^{b}		74			26			84	74
556-82-1	$(CH_3)_2C{=}CHCH_2OH$	C_6H_5I	$Pd(OAc)_2$	12^{c}		51		34	2	17	$C_6H_5C_6H_5$ (6.5) Unknown (6.5)	25	59
	$(CH_3)_2C{=}CHCH_2OH$	C_6H_5I	$Pd(OAc)_2$	96^{c}		62		19	3	6.3	$C_6H_5C_6H_5$ (7) Unknown (9)	51	74
	$(CH_3)_2C{=}CHCH_2OH$	C_6H_5I	$Pd(OAc)_2$	12^{b}		16		29	7	4.1	$C_6H_5C_6H_5$ (48)	44	31
	$(CH_3)_2C{=}CHCH_2OH$	C_6H_5HgOAc (62-38-4)	$Pd(OAc)_2$	7^{g}		24		76				42	24
513-42-8	$CH_2{=}C(CH_3)CH_2OH$	C_6H_5I	$Pd(OAc)_2$	8^{b}		96			4			95	96
598-32-3	$CH_2{=}CHCHOHCH_3$	C_6H_5I	$Pd(OAc)_2$	5^{b}	Trace	90			10			95	90
	$CH_2{=}CHCHOHCH_3$	C_6H_5I	$Pd(OAc)_2(PPh_3)_2$	6^{c}	14	76	0.18	4	6	0.67		96	90
	$CH_2{=}CHCHOHCH_3$	C_6H_5I	$Pd(OAc)_2$ + $18PPh_3$	$14^{c,e}$	10	77	0.13	6	7	0.86		71	87
	$CH_2{=}CHCHOHCH_3$	C_6H_5I	$Pd(OAc)_2(PPh_3)_2$	$62^{c,f}$	7	85	0.08	2	6	0.33		97	92
	$CH_2{=}CHCHOHCH_3$	4-$CH_3OC_6H_4I$ (696-62-8)	$Pd(OAc)_2$	12^{b}		87			12		4-$CH_3OC_6H_4CH{=}CHCH{=}CH_2$ (1)	96	88
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br (108-86-1)	$Pd(OAc)_2(PPh_3)_2$	35^{c}	40	50	0.8	8	2	4.0		95	90
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br	$Pd(OAc)_2$ + $4PPh_3$	50^{c}	47	39	1.2	12	2	6		94	86
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br	$Pd(OAc)_2$ + $18PPh_3$	$144^{c,f}$	58	26	2.2	14	2	7		74	84
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br	$PdCl_2(PPh_3)_2$	30^{c}	38	51	0.75	9	2	4.5		92	89
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br	$PdBr_2(PPh_3)_2$	35^{c}	36	50	0.72	9	2	4.5	$C_6H_5CH{=}CHCH{=}CH_2$ (3)	93	89
	$CH_2{=}CHCHOHCH_3$	C_6H_5Br	$PdI_2(PPh_3)_2$	40^{c}	40	48	0.83	9	3	3.0		90	88
	$CH_2{=}CHCHOHCH_3$	4-$CF_3C_6H_4Br$ (402-43-7)	$Pd(OAc)_2(PPh_3)_2$	44^{c}	25	69	0.36	5	1	5.0		93	94
	$CH_2{=}CHCHOHCH_3$	4-$CH_3C_6H_4Br$ (106-38-7)	$Pd(OAc)_2$ + $3PPh_3$	48^{c}	53	36	1.5	11				75	89
	$CH_2{=}CHCHOHCH_3$	2-$CH_3C_6H_4Br$ (95-46-5)	$Pd(OAc)_2$ + $3PPh_3$	2 weeks^{c}	71^{h}	17	4.2	10			2-$CH_3C_6H_4CH{=}CHCOCH_3$ (2)	88	90
115-18-4	$CH_2{=}CHCOH(CH_3)_2$	C_6H_5I	$Pd(OAc)_2$	5^{b}	8			1			$C_6H_5CH{=}CHC(CH_3){=}CH_2$ (91)	99	99
	$CH_2{=}CHCOH(CH_3)_2$	C_6H_5I	$Pd(OAc)_2(PPh_3)_2$	4^{c}	98			1			$C_6H_5CH{=}CHC(CH_3){=}CH_2$ (1)	98	99

[a] Product yields were determined by GLC and were based on the aryl halide used. All reactions were carried out in capped glass tubes under argon at 100° except where noted. [b] Reaction solution consisted of 25 mmol of allylic alcohol, 20 mmol of aryl halide, 0.06 mmol of palladium complex, 25 mmol of triethylamine, and 6.5 ml of acetonitrile. [c] Reaction solution consisted of 25 mmol of allylic alcohol, 20 mmol of aryl halide, 0.06 mmol of palladium complex, and 10 ml of triethylamine. [d] Carried out at 60°. [e] Carried out at 50°. [f] Used 0.20 mmol of the palladium complex, instead of 0.06 mmol, and 1.0 g of PPh_3. [g] Reaction mixture consisted of 2 ml of allylic alcohol, 10 ml of acetonitrile, 50 mmol of phenylmercuric acetate, and 55 mmol of palladium acetate at 0–25° as described in ref 1. [h] 69% *E* isomer and 2% *Z* isomer.

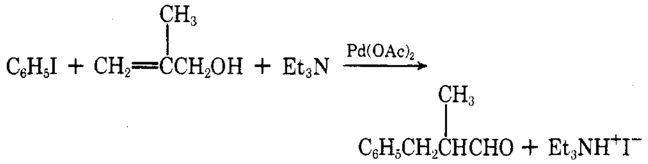


$$ArHgX + PdX_2 \longrightarrow [ArPdX] + HgX_2$$
$$[ArPdX] + H_2C{=}CH{-}CH(OH)R \longrightarrow$$
$$ArCH_2{-}CH(PdX){-}CH(OH)R \xrightarrow{-[HPdX]} [ArCH_2{-}CH{=}C(OH){-}R] \longrightarrow ArCH_2CH_2C(=O){-}R \quad R = H \text{ or alkyl}$$

Recently we have found that organopalladium compounds can be made more practically from aryl halides and that a combination of an aryl halide, a catalytic amount of a palladium salt, and a tertiary amine will arylate alkenes.[2] It seemed likely that this reaction could also be applied to the arylation of allylic alcohols. We report herein the results of a study of this reaction.

Results and Discussion

Preliminary studies of the reaction of 2-methyl-2-propen-1-ol with iodobenzene under the usual olefin arylation conditions[2,3] revealed that the major product formed was the expected 2-methyl-3-phenylpropanal. Further exploration of the reaction, however, showed that differences existed from the reactions previously investigated. Since the reaction appeared to be of potential synthetic utility, a thorough investigation of reaction variables with several different allylic alcohols and two homoallylic alcohols was undertaken.

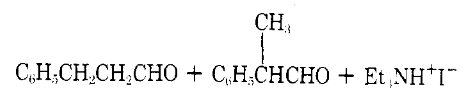


$$C_6H_5I + CH_2{=}C(CH_3)CH_2OH + Et_3N \xrightarrow{Pd(OAc)_2} C_6H_5CH_2CH(CH_3)CHO + Et_3NH^+I^-$$

Allylic Alcohol Reactions. The allylic alcohols studied and the results obtained are summarized in Table I. We chose to look at reactions of allyl alcohol, *trans*-crotyl alcohol, 2-methyl-2-propen-1-ol, 3-buten-2-ol, 2-methyl-3-buten-2-ol, 3-methyl-2-buten-1-ol, and 2-methyl-3-buten-2-ol. Generally, the reactions were carried out at 100° in capped bottles under argon where the time required for disappearance of the aryl halide reactant varied from less than 1 to more than 50 hr depending upon the reactants and reaction conditions. In some examples, long reaction times decreased the yields of products obtained. As we had observed with simple olefins,[2] aryl iodides underwent the reaction with palladium acetate as catalyst while aryl bromides required triphenylphosphine to be present, also. The iodide reactions often gave significantly different product mixtures when triphenylphosphine was present. It appeared to make no difference in which of several possible forms the catalyst was added. The dihalobisphosphinepalladium derivative behaved essentially the same as the diacetatobisphosphine or the halobisphosphine(phenyl) complexes.

In the reactions of aryl iodides where phosphines were not added, reactions were carried out with acetonitrile as solvent. Without this solvent or with only excess triethylamine as solvent, the product triethylammonium iodide crystallized out during the reactions. In these cases the crystals apparently removed the palladium metal catalyst as they precipitated and consequently these reactions did not go to completion. Acetonitrile dissolves the salts. When triphenylphosphine was present the palladium apparently remained in solution until the reactions were essentially complete even if amine salt crystallized out.

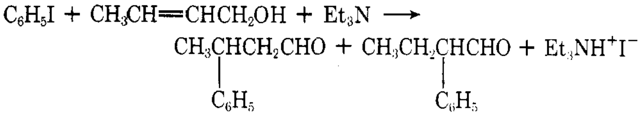
The reaction of iodobenzene with allyl alcohol gave a maximum yield of products (71%) after only 30 min at 100°. The reaction was quite exothermic and became uncontrollable if more than about 0.3 mol % of catalyst based upon the aryl halide present, was used. The products formed were 84% 3-phenyl- (3-arylation) and 15% 2-phenylpropionaldehyde (2-arylation). Apparently, the phenylpalladium group added in both possible directions to the double bond and both adducts eliminated metal hydride to ultimately form aldehydes. The 2-phenylpropionaldehyde formation may require two intermediate steps, the initial elimination, a readdition of the hydride in the reverse direction, and then another elimination of metal hydride toward the hydroxyl bearing carbon. These steps apparently occur with ease with the palladium acetate catalyst, since neither of the possible intermediate phenylallyl alcohols (3-phenyl-2-propen-1-ol and 2-phenyl-2-propen-1-ol) were observed as products.



$$C_6H_5I + CH_2{=}CHCH_2OH + Et_3N \xrightarrow[30\ \text{min},\ 100°]{Pd(OAc)_2} C_6H_5CH_2CH_2CHO + C_6H_5CH(CH_3)CHO + Et_3NH^+I^-$$

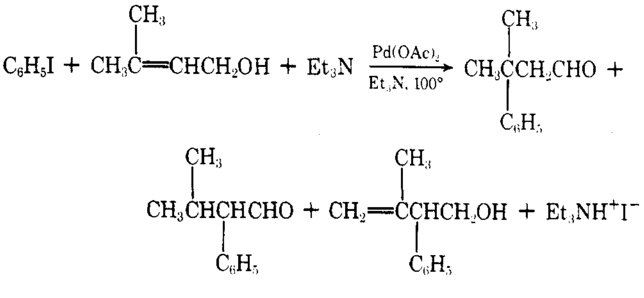
There is no advantage to adding triphenylphosphine to this reaction, since it only slows it down and slightly decreases the yield of 3-arylaldehyde relative to the 2-aryl derivative. Bromobenzene reacts poorly with allyl alcohol because it reacts considerably slower than the iodide does and the 3-phenylpropionaldehyde product suffers decomposition during the reaction, presumably by undergoing the aldol condensation.

trans-Crotyl alcohol and iodobenzene with a palladium acetate catalyst react in 12 hr at 100° to give an 84% yield of a mixture containing 74% 3-phenylbutyraldehyde and 26% of the 2-phenyl isomer. The addition of the terminal methyl group to allyl alcohol in this case considerably slowed down the rate of the reaction and increased the amount of 2-arylation from 16 to 26%.



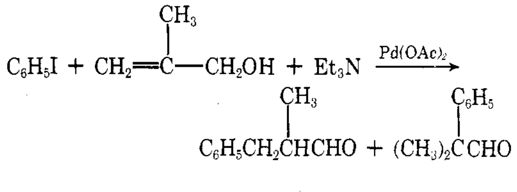
$$C_6H_5I + CH_3CH{=}CHCH_2OH + Et_3N \longrightarrow CH_3CH(C_6H_5)CH_2CHO + CH_3CH_2CH(C_6H_5)CHO + Et_3NH^+I^-$$

Even the presence of two terminal methyl groups in 3-methyl-2-buten-1-ol is not enough to cause phenylation to occur exclusively at the 2 carbon of the alcohol. This reaction, with iodobenzene and palladium acetate as catalyst at 100°, gave a mixture of an allylic alcohol and two isomeric aldehydes. Because the allylic alcohol formed, 3-methyl-2-phenyl-3-buten-1-ol, contained a more reactive double bond than the starting alcohol, it disappeared during the reaction. At about 25% reaction, approximately 40% of the products were formed by 2-arylation and 60% by 3-arylation.



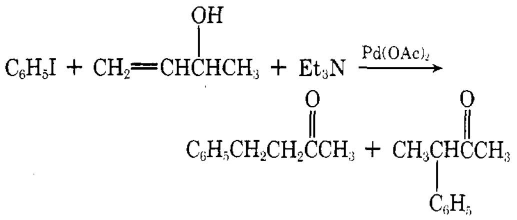
$$C_6H_5I + CH_3C(CH_3){=}CHCH_2OH + Et_3N \xrightarrow[Et_3N,\ 100°]{Pd(OAc)_2} CH_3C(CH_3)(C_6H_5)CH_2CHO + CH_3CH(CH_3)CH(C_6H_5)CHO + CH_2{=}C(CH_3)CH(C_6H_5)CH_2OH + Et_3NH^+I^-$$

The addition of a methyl group to the second carbon of allyl alcohol to form 2-methyl-2-propen-1-ol produced a more significant product change than the addition of the 3-methyl did. In the reaction with iodobenzene and palladium acetate, 2-methyl-2-propen-1-ol produced, in 95% yield, a mixture containing 96% of the 3-phenylaldehyde and only 4% of the 2-phenylaldehyde. This reaction also occurred slightly more rapidly than did the corresponding reaction of *trans*-crotyl alcohol.



$$C_6H_5I + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2OH + Et_3N \xrightarrow{Pd(OAc)_2} C_6H_5CH_2\overset{CH_3}{\overset{|}{C}}HCHO + (CH_3)_2\overset{C_6H_5}{\overset{|}{C}}CHO + Et_3NH^+I^-$$

We also looked at reactions of the 1-methylated allyl alcohol, 3-buten-2-ol. With iodobenzene and a palladium acetate catalyst we obtained, in 95.4% yield, a mixture composed of 90% of the terminal 3-phenyl ketone and 10% of the 2-phenyl ketone. This alcohol was a little more reactive than 2-methyl-2-propen-1-ol but less reactive than allyl alcohol. Thus, the 1-methyl group exerted a small effect raising the percent of terminal 3-phenyl product formed from 84 to 90%.



$$C_6H_5I + CH_2{=}CH\overset{OH}{\overset{|}{C}}HCH_3 + Et_3N \xrightarrow{Pd(OAc)_2} C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 + CH_3\underset{\underset{C_6H_5}{|}}{C}H\overset{O}{\overset{\|}{C}}CH_3 + Et_3NH^+I^-$$

When the above reaction was carried out with diacetatobis(triphenylphosphine)palladium(II) as catalyst substantial amounts of two unsaturated alcohols were obtained in addition to the same two carbonyl products. The presence of the triphenylphosphine apparently stopped or at least reduced the tendency for the palladium hydride to readd to the unsaturated alcohol intermediates. Larger amounts of triphenylphosphine than two per palladium had little further effect, other than slowing the reaction and decreasing the total yield of products. The decreased yield is due to the palladium(II)-catalyzed reaction of the excess phosphine with some of the iodobenzene forming tetraphenylphosphonium iodide. Lowering the reaction temperature from 100 to 60° decreased the reaction rate considerably, but it did not alter the ratio of the 2- to 3-arylation products formed. There were small but significant changes in the alcohol to carbonyl ratios observed, however. At 100° the ratio of 3-aryl alcohol to 3-aryl ketone was 0.18 while at 60° the ratio was 0.086. The corresponding ratios for the 2-aryl alcohol to the 2-aryl ketone were 0.61 and 0.32, respectively. Thus, lowering the temperature decreased substantially the amounts of unsaturated alcohols and increased the amounts of saturated ketones produced.

p-Iodoanisole was also treated with 3-buten-2-ol with a palladium acetate catalyst. The *p*-methoxyl group had very little effect upon the distribution of reaction products. The ratio of 3- to 2-aryl additions was only slightly lower than in the reaction of iodobenzene. This contrasts with the results obtained previously in the reaction of phenyl- and *p*-anisylmercuric acetates with palladium acetate and propylene at 0° where the methoxyl group caused about 17% more addition of the aryl group to the more substituted carbon of the double bond.[4]

The reaction of bromobenzene with 3-buten-2-ol with the diacetatobis(triphenylphosphine)palladium catalyst proceeded in high yield in 35 hr at 100° in contrast to the corresponding reactions with primary allylic alcohols, where the products were not completely stable under the reaction conditions. The 3-buten-2-ol reaction with bromobenzene produced in 95% overall yield a mixture of alcohols and ketones with about 90% of the products arising from addition of the aryl group to the third carbon and 10% from addition to the second carbon. The total 2 and 3 isomer yields were the same as obtained with iodobenzene. The 3-aryl products consisted of 50% 4-phenyl-2-butanone and 40% 4-phenyl-3-buten-2-ol. The 2-aryl products were 2% 3-phenyl-2-butanone and 8% 3-phenyl-3-buten-2-ol. The addition of more than 2 equiv of triphenylphosphine per palladium as catalyst in this reaction slowed it down and caused a significant change in the product distribution. The maximum effect was caused with an 18:1 ratio of phosphine to palladium. However, as noted above, the excess phosphine also lowered the total yield by an amount approximately equivalent to the excess phosphine (to 71%) indicating that some bromobenzene was being converted into tetraphenylphosphonium bromide under the reaction conditions. The yields of 3-aryl alcohol are increased from 40 to 58% by the excess phosphine compared with the reaction containing only two phosphines per palladium while the 3-aryl ketone yield is reduced from 50 to 26%. A similar change occurred with the 2-phenyl products; the 2-phenyl alcohol yield increased from 8 to 14% while the 2-phenyl ketone yield remained about the same, 2%. The total amount of addition to the 3 carbon was now 84% compared to 90% with only 2 mol of phosphine.

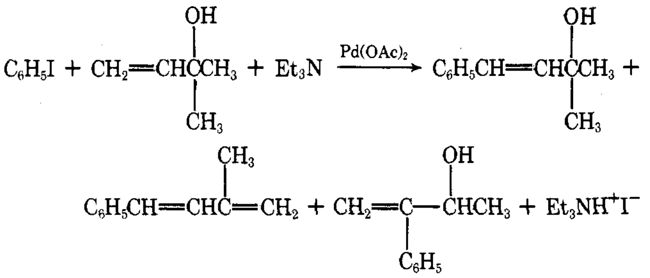
We have also noted in the reaction of bromobenzene with 3-buten-2-ol that it made essentially no difference whether acetate, chloride, bromide, or iodide ions were present as the anions in the catalyst.

The reaction of *p*-trifluoromethylbromobenzene with 3-buten-2-ol was investigated in order to observe the effect of an electron-withdrawing group on the product distribution. The reaction was a little slower than with bromobenzene. The total yield of products was 93% of which 94% was from aryl addition to the third carbon. Thus, 3-aryl addition was increased about 4% by the trifluoromethyl group compared with phenyl. The trend is explicable on the basis of electronic effects[4] and is consistent with the reverse effect found above in the *p*-iodoanisole reaction and with the arylmercuric acetate reactions studied previously.[4] The effect is less, however, than the previous example, probably mainly because of the higher reaction temperature used. The trifluoromethyl group also changed the alcohol to ketone ratio obtained. The ratio of the 3-phenyl alcohol to 3-ketone went from 0.79 to 0.34 with the CF_3 group and from 4.4 to 4.25 for the 2-aryl products, respectively. These results suggest that the more hydridic hydrogen tends to be eliminated but the effect is minor.

The addition of *o*-bromotoluene to 3-buten-2-ol was investigated to assess the importance of steric effects in the arylating group. For comparison purposes the *p*-bromotoluene reaction with 3-buten-2-ol was also carried out. As expected from the related reactions in Table I, the yields of products from the *p*-bromotoluene reaction were quite similar to those formed in the bromobenzene reaction except that they were *p*-methyl derivatives. Thus, the *p*-bromotoluene reaction produced 53% 4-*p*-tolyl-3-buten-2-ol (3-alcohol), 30% *p*-tolyl-2-butanone (3-carbonyl), 11% 3-*p*-tolyl-3-buten-2-ol (2-alcohol), and no 3-*p*-tolyl-2-butanone (2-carbonyl). In contrast, the products obtained from a similar reaction carried out with *o*-bromotoluene consisted of 71% 4-*o*-tolyl-3-buten-2-ol (3-alcohol), 17% 4-*o*-tolyl-2-butanone (3-carbonyl), 10% 3-*o*-tolyl-3-buten-2-ol (2-alcohol), and no 3-*o*-tolyl-2-butanone (2-carbonyl). Thus, the *o*-

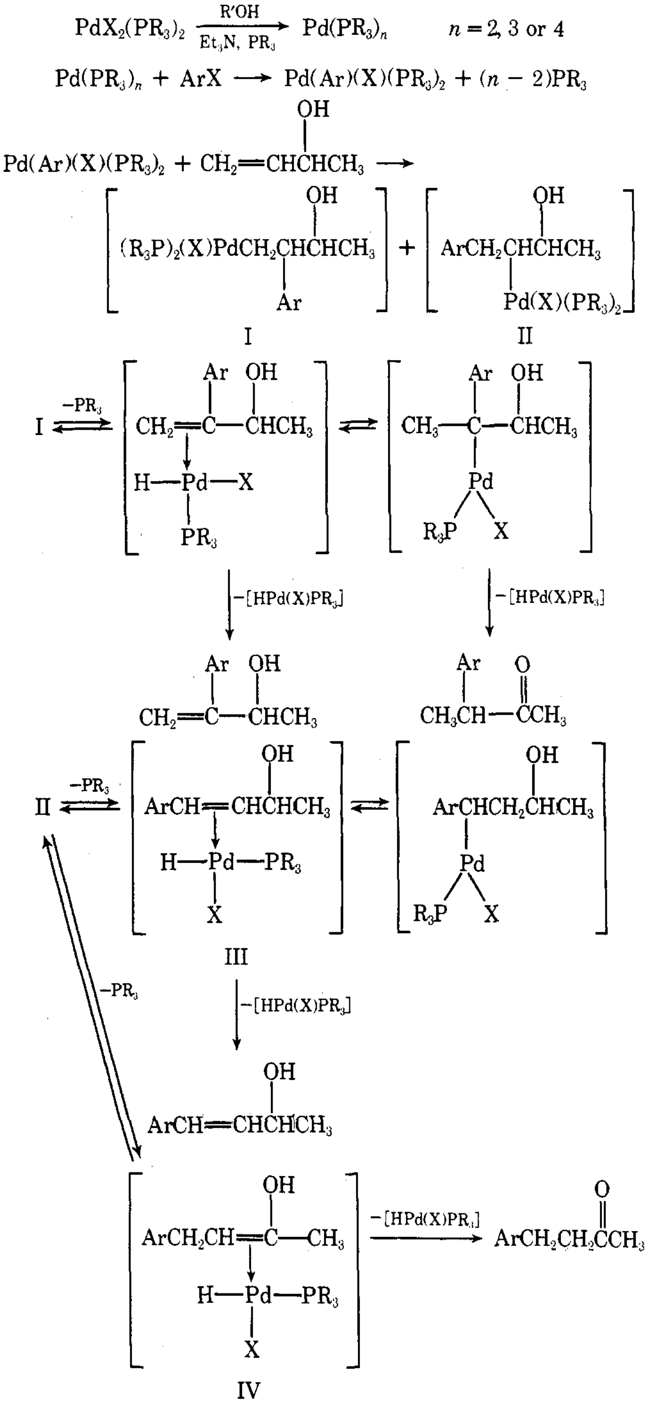
methyl group caused a significant increase in the 3-alcohol to 3-carbonyl product ratio (1.5 to 4.2).

The effect of the presence of two α methyl groups in allyl alcohol upon the reaction products with iodobenzene is now predictable. The large steric effect of the tertiary alcohol group would be expected to substantially increase the amount of addition of phenyl to the third carbon. This proved to be the case. The reaction proceeded to completion in 4 hr at 100°, giving in 98% yield a mixture consisting of 99% of 3-phenylated products, 97% 2-methyl-phenyl-3-buten-2-ol, 1% 1-phenyl-3-methyl-1,3-butadiene, and 1% of the 2-aryl product, 2-methyl-3-phenyl-3-buten-2-ol.



$$C_6H_5I + CH_2{=}CH\overset{OH}{\underset{CH_3}{C}}CH_3 + Et_3N \xrightarrow{Pd(OAc)_2} C_6H_5CH{=}CH\overset{OH}{\underset{CH_3}{C}}CH_3 + C_6H_5CH{=}CH\overset{CH_3}{C}{=}CH_2 + CH_2{=}\underset{C_6H_5}{C}-\overset{OH}{C}HCH_3 + Et_3NH^+I^-$$

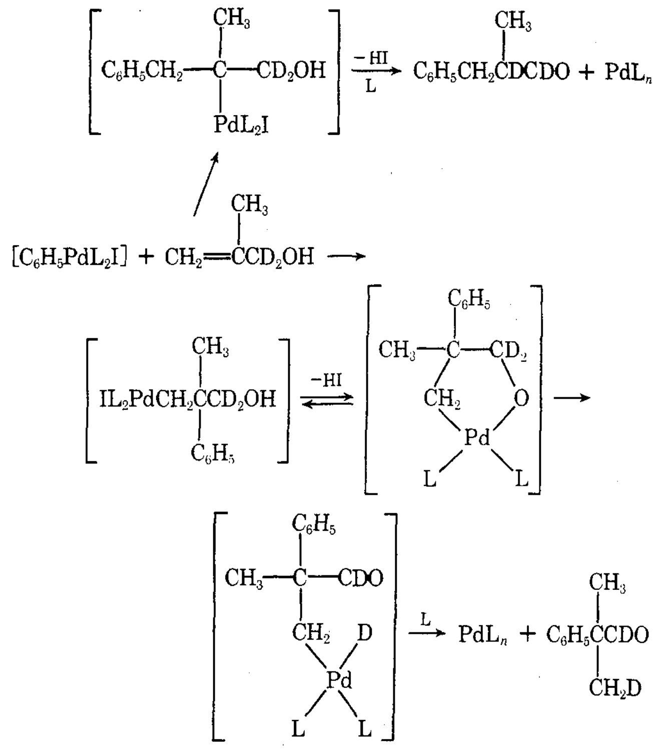
Scheme I
Mechanism of Arylation 3-Buten-2-ol



Mechanism of Reaction. The products obtained in the allylic alcohol arylations can be accounted for by the reactions shown in Scheme I, exemplified with 3-buten-2-ol. The scheme is similar to the one proposed for the related olefin arylation reaction.[2] Initially, the palladium(II) catalyst is believed to be reduced by the allylic alcohol to the true catalyst, a palladium(0)–triphenylphosphine complex or in the palladium(II) acetate reactions simply to finely divided palladium metal. In the latter reactions the precipitation of the metal can be seen when the reactants are mixed together. The palladium(0) species then oxidatively adds the aryl halide to form an arylpalladium complex. The last complex then adds to the allylic double bond in both possible directions to give adducts I and II. These adducts next undergo elimination of a hydridopalladium group to form olefin π complexes with the hydride. Dissociation at this stage produces the 2-aryl alcohol from I and either 3-aryl alcohol or the 3-aryl carbonyl product (in the enol form) from II. The presence of triphenylphosphine increases the rate of dissociation presumably by displacing the olefinic group from the metal in a second-order reaction. If dissociation does not occur then readdition and elimination reactions of the hydride group occur, leading ultimately to the carbonyl derivative, at which point the reaction becomes essentially irreversible. The dissociated, free hydride apparently rapidly decomposes, since once formed the unsaturated alcohols are generally stable in the reaction mixtures.

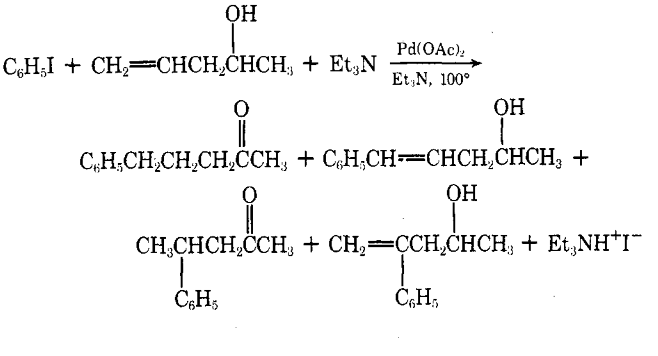
In the reaction of *o*-bromotoluene with 3-buten-2-ol the formation of less 3-aryl carbonyl and more 3-alcohol product than from *p*-bromotoluene is very probably the result of the sterically accelerated decomposition of complex III in Scheme I caused by the *o*-methyl group. Thus, more dissociation of III to alcohol occurs; consequently, less rearrangement to the carbonyl product can take place. If this explanation is correct it also indicated that elimination of the hydridopalladium group in II occurs initially mainly to π complex III rather than to IV, at least in the bromotoluene reactions.

The hydride addition–elimination sequence, however, is clearly not the only mechanism to be considered by which allylic alcohols are converted into carbonyl compounds. A direct metal assisted one–three hydrogen shift through a chelated alkoxide intermediate is another possibility. The formation of some 2-methyl-2-phenylpropionaldehyde (4%) in the phenylation of 2-methyl-2-propen-1-ol must have occurred by an alternative route, since the hydride 1:2 addition–elimination mechanism is not possible in this case. In order to gain more information about the origin of this alcohol we carried out the reaction of 2,2-dideuterio-2-methyl-2-propen-1-ol with iodobenzene and determined the fate of the deuterium. The major product, the 2-methyl-3-phenylpropanal, was found by NMR to contain essentially only one deuterium, on the aldehyde group, indicating that the 1,2-hydride addition–elimination mechanism was operating, since the other deuterium would have ended up on the carbon α to the aldehyde group and would have been lost by exchange in the aqueous isolation procedure employed. The minor product, the 2-methyl-2-phenylpropanal, contained two deuteriums, one in the aldehyde group and the other at least partly if not exclusively on a methyl group. The answer is not more definite because analyses were performed by mass spectroscopy and there was an appreciable amount of deuterium in the phenyl$^+$ and the $C_6H_7^+$ peaks. This was probably due to rearrangements but we did not establish this with model compounds. In any case the deuterium shift in the compound is exclusively intramolecular. It may occur by a direct 1:3 shift or more probably it occurs, at least partially, through an alkoxide intermediate as shown below.



In order to assess the importance of the cyclic alkoxide mechanism in the arylation of another allylic alcohol, we studied the reaction of iodobenzene with 2-deuterio-3-buten-2-ol. No deuterium was found in the terminal methyl group of the 3-phenyl-2-butanone produced and less than 10% of the benzylic position was deuterated. Deuterium was no doubt lost from this position by exchange during the isolation of the products. Thus, it appears that the 1,2-metal hydride addition–elimination mechanism for hydrogen shift is much preferred over the direct 1,3 shift.

Homoallylic Alcohol Reactions. Two homoallylic alcohols were treated with iodobenzene to determine how much carbonyl product would be formed in these cases. The results appear in Table II. 4-Penten-2-ol with a $Pd(OAc)_2$ catalyst gave a mixture of 44% 5-phenyl-2-pentanone, 38% *trans*- and 1.5% *cis*-5-phenyl-4-penten-2-ol, 9% 4-phenyl-2-pentanone, and 7% 4-phenyl-penten-2-ol. Thus, 44% of the aryl carbonyl product was formed. It is noteworthy that no more than ca. 1% of the possible intermediate 5-phenyl-3-penten-2-ol was detected. Presumably, the intermediate metal hydride π complex of this alcohol does not dissociate to an appreciable extent during the reaction. The total per-



$$C_6H_5I + CH_2{=}CHCH_2CH(OH)CH_3 + Et_3N \xrightarrow[Et_3N,\ 100°]{Pd(OAc)_2} C_6H_5CH_2CH_2CH_2C(O)CH_3 + C_6H_5CH{=}CHCH_2CH(OH)CH_3 + CH_3CH(C_6H_5)CH_2C(O)CH_3 + CH_2{=}C(C_6H_5)CH_2CH(OH)CH_3 + Et_3NH^+I^-$$

Table II
Arylation of Homoallylic Alcohols

Registry no.	Alcohol	Aryl halide	Reaction time, hr	4-Arylation: Alcohol, %, *E/Z*	4-Arylation: Carbonyl compd, %	4-Arylation: Alcohol/carbonyl	3-Arylation: Alco-hol, %	3-Arylation: Carbonyl compd, %	3-Arylation: Alcohol/carbonyl	Other products (yield)	Total yield, %	% 4-aryl addition
627-27-0	$CH_2{=}CHCH_2CH_2OH$	C_6H_5I	1[a]	30/0	49	0.6	4	17	4		70	79
625-31-0	$CH_2{=}CHCH_2CHOHCH_3$	C_6H_5I	6.5[a]	38/2	44	0.9	7	9	0.8	Unknown[b] (trace)	96	84
	$CH_2{=}CHCH_2CHOHCH_3$	C_6H_5Br[c]	24	63/9	7	10	16	1	16	Unknown[b] (4)	81	83

[a] Reaction solution consisted of 25 mmol of homoallylic alcohol, 20 mmol of aryl halide, 0.06 mmol of palladium acetate, 25 mmol of triethylamine, and 6.5 ml of acetonitrile at 100° in capped tubes under argon. [b] Unknown, believed to be 5-phenyl-3-penten-2-ol. [c] Catalyst was $Pd(OAc)_2(PPh_3)_2$.

cent terminal phenyl addition in this case (84%) is the same as found in the similar reaction carried out with allyl alcohol.

As expected from our previous results, the use of bromobenzene in this reaction with diacetatobis(triphenylphosphine)palladium(II) as catalyst gave about the same percent terminal phenyl addition but the 4-phenyl alcohol to 4-phenyl carbonyl ratio was much higher, 10.4 vs. 0.90 in the iodobenzene–palladium acetate reaction.

The second homoallylic alcohol allowed to react with iodobenzene was 3-buten-1-ol. The reaction proceeded about six times faster than the reaction with 4-penten-2-ol. The reaction products consisted of 49% 4-phenylbutanal, 30% 4-phenyl-3-buten-1-ol, 17% 3-phenylbutanal, and 4% 3-phenyl-3-buten-1-ol. Again, little of the possible intermediate 4-phenyl-2-buten-1-ol was formed. The percent terminal addition was 79% in this case. The fact that this value is 5% lower than found for allyl alcohol and 4-penten-2-ol suggests that some of the 4-phenylbutanal decomposed by aldol condensation during the reaction. Even using the experimental value, however, it is clear that somewhat more rearrangement to the carbonyl product occurred with the primary homoallylic alcohol than with the secondary one (49% vs. 44%). The fact that 17% of 3-phenyl carbonyl product was formed along with only 4% of the 3-phenyl alcohol from the phenylation of 3-buten-1-ol indicates that the palladium group is able to move over three carbons under these conditions easily.

Preparative Reactions. The reactions listed in Table I have all been carried out in capped tubes or bottles. Since this is not convenient for larger scale preparations, we investigated some of the reactions at reflux temperatures at atmospheric pressure. This was found to be a very useful procedure. While the reactions proceeded more slowly, since reflux temperatures were usually below 100°, the progress of the reactions could be observed simply by noting the temperature of the boiling reaction mixtures. It usually rose by 5° or more as reactants were used up. When the boiling point stopped increasing, the aryl halide usually had all reacted. The products then were easily isolated from the cooled reaction mixtures by adding ether and water and then separating, washing, and distilling the ether extracts. The yields were good to excellent. Some reactions with methyl acrylate and acrylonitrile were also successfully carried out by this procedure. The results of the preparative scale experiments are summarized in Table III.

The physical properties of all of the products prepared in this investigation are given in Table IV, which will only appear in the microfilm edition of this journal. (See paragraph at end of paper regarding supplementary material.)

Experimental Section

Reagents. Alcohols. Allyl and crotyl alcohol were distilled before use and stored over Linde 4A molecular sieves. 3-Methyl-2-buten-1-ol was prepared by the lithium aluminum hydride reduction of 3-methyl-2-butenoic acid. 3-Buten-1-ol was used as received from the Aldrich Chemical Co. All other alcohols were commercial products that were dried over molecular sieves before use.

Other Materials. The triethylamine was distilled and dried over molecular sieves before use. Iodobenzene and 4-bromobenzotrifluoride were only dried before use but the other liquid aromatic halides were distilled before drying. The solid, 4-iodoanisole, was used as received from Aldrich. Acetonitrile was used as received from Baker while 2-butanol was dried over 4A molecular sieves before use. Palladium acetate was prepared by the procedure of Wilkinson,[5] as was its complex with triphenylphosphine.[5] The triphenylphosphine was recrystallized from methanol. Other palladium complexes were prepared as noted previously.[6]

General Procedure for Small-Scale Allylic Alcohol Arylations. Reactions were carried out in 20-ml heavy-walled Pyrex tubes. The palladium catalyst, internal standard (naphthalene, 1-

Table III
Preparative Scale Reactions

Olefinic reactant (mol)	Aryl halide (mol)	Catalyst (mmol)	Amine (mol)	Solvent	Bp change, °C (reaction time, hr)	Isolated products (% yield)	% purity by GC
2-Methyl-3-butene-2-ol (0.25)	C_6H_5I (0.20)	$Pd(OAc)_2(PPh_3)_2$ (0.60)	Et_3N (0.52)	None	96–105 (6)	4-Phenyl-2-methyl-3-buten-2-ol (88)	98
2-Methyl-2-propen-1-ol (0.25)	C_6H_5I (0.20)	$Pd(OAc)_2$ (0.60)	Et_3N (0.25)	2-Methyl-1-propanol (65 ml)	107–113 (14)	3-Phenyl-2-methylpropanal (60)	98
3-Buten-2-ol (0.25)	C_6H_5I (0.20)	$Pd(OAc)_2$ (0.60)	Et_3N (0.25)	Acetonitrile (65 ml)	80–88 (10)	4-Phenyl-2-butanone (85)	>99
(*E*)-Methyl 2-butenoate (0.25)	C_6H_5Br (0.20)	$Pd(OAc)_2(PPh_3)_2$ (2.0)	Et_3N (0.25)	None	105–115 (72)	(*E*)-Methyl 3-phenyl-2-butenoate (54)[a]	99
Acrylonitrile (0.19)	C_6H_5I (0.15)	$Pd(OAc)_2(PPh_3)_2$ (1.5)	Et_3N (0.19)	None	81–100 (4)	*cis*-Phenylacrylonitrile (29) *trans*-Phenylacrylonitrile (59)	[b]
Methyl acrylate (0.19)	C_6H_5Br (0.15)	$Pd(OAc)_2(PPh_3)_2$ (1.5)	Et_3N (0.19)	None	87–~97 (68)	Methyl cinnamate (88)	99
Methyl acrylate (0.19)	1-$C_{10}H_7Br$ (0.15)	$Pd(OAc)_2(PPh_3)_2$ (1.5)	Et_3N (0.19)	None	96–~106 (120)	Methyl 3-(1′-naphthyl)-propenoate (62)	99

[a] Also formed in this reaction were 1.5% (*Z*)-methyl 3-phenyl-2-butenoate, 3% methyl 3-phenyl-3-butenoate, 2% (*E*)-methyl 4-phenyl-3-butenoate, and 0.5% (*Z*)-methyl 2-phenyl-2-butenoate. [b] Not determined.

methylnaphthalene, 2,3-dimethylnaphthalene, or benzophenone), and aryl halide were weighed into the tube. The air in the tube was replaced by argon and the tube was capped with a rubber-lined metal cap with two small holes in it for syringe needles. The alcohol, triethylamine, and solvent, if any, were then introduced from syringes. The tube was placed in a thermostated bath or the steam bath for 100°. Samples were removed by microsyringe for GLC analyses periodically. Analyses were carried out generally on 0.25 in. × 6 ft SE-30 or Carbowax 20M on Chromosorb W columns.

Products were isolated by diluting the cooled reaction mixtures with water and ether. The ether phase was separated, washed several times with water, dried over anhydrous magnesium sulfate, and concentrated. Alcohols were separated from carbonyl compounds where necessary by liquid chromatography on silica gel. The concentrated eluates were then separated by GLC using 0.25 in. or 0.5 in. columns.

General Procedure for Preparative Scale Reactions. The olefinic reactant, the aryl halide, solvent, if any, and the triethylamine were combined in a round-bottomed flask and the catalyst was added. The flasks were then connected to a condenser with a mercury bubbler attached at the top and flushed out with nitrogen. The solution was then heated to boiling in an oil bath keeping a slight nitrogen pressure on the flask. The boiling point of the solution was observed by means of a thermometer inserted into one of the necks of the flask. Stirring was not necessary. When the boiling point stopped increasing, the reaction mixture, now containing crystalline amine salt, was cooled and diluted with water and ether. The ether phase was separated, washed five times with water, dried over anhydrous magnesium sulfate, and then distilled under reduced pressure. The reactions carried out are listed in Table III. A detailed example is given below.

Preparation of 4-Phenyl-2-butanone. To a 250-ml three-necked round-bottomed flask equipped with a condenser and a thermometer was added 40.8 g (0.20 mol) of iodobenzene, 18.0 g (0.25 mol) of 3-buten-2-ol, 35 ml (0.25 mol) of triethylamine, 65 ml of acetonitrile, and 0.135 g (0.6 mmol) of palladium acetate. The solution formed was heated to boiling in an oil bath. The boiling point rose slowly from 80 to 88° over a period of 10 hr and then remained constant. The reaction mixture was now cooled and diluted with water and ether and the ether layer was separated. After the ether phase was washed five times with water, it was dried over anhydrous magnesium sulfate, filtered, concentrated, and distilled through a Nester-Faust spinning band distillation column, bp 114–116° (16 mm). There was obtained an 85% yield of greater than 99% pure (GLC) 4-phenyl-2-butanone.

Reaction of 1,1-Dideuterio-2-methyl-2-buten-1-ol with Iodobenzene. The deuterated alcohol was prepared by reducing methyl methacrylate with $LiAlD_4$ in ether. The NMR spectrum of the deuterated product in $CDCl_3$ was as follows: δ 6.08 (dd) (1 H), $J = 11$ and 18 Hz; 5.45 (d) (1 H), $J = 2$ Hz; 5.1 (m) (1 H), 4.18 (s) (1 H), and 1.23 (s) (3 H).

A mixture of 25 mmol of the deuterated alcohol, 20 mmol of iodobenzene, 25 mmol of triethylamine, 6.5 ml of acetonitrile, and 0.06 mmol of palladium acetate was heated under argon in a capped tube at 100° for 8 hr. The cooled reaction mixture was diluted with ether and water. The ether phase was separated, washed with water, and distilled under reduced pressure. The distillate was then separated into the two carbonyl products by preparative scale GLC. The NMR spectrum of the 2-methyl-3-phenylpropanal showed less than 10% deuterium on the 2 carbon and 100% on the aldehyde carbon. The minor alcohol, 2-methyl-2-phenylpropanal, was analyzed only by mass spectroscopy. The deuterated product showed a molecular ion at m/e 150 and a phenyldimethyl carbon ion at m/e 120 indicating that the aldehyde group contained one deuterium and the rest of the molecule one. The phenyl ion and the protonated benzene ion peaks were also strong as were their monodeuterated derivatives (ca. 1:1 ratios of protonated to monodeuterated ions).

Reaction of 2-Deuterio-3-buten-2-ol with Iodobenzene. The deuterated alcohol was prepared by reduction of 2-buten-3-one with $LiAlD_4$ in ether. The product had the following NMR spectrum in $CDCl_3$: δ 4.93 (m) (1 H), 4.79 (m) (1 H), 4.72 (s) (1 H), and 1.69 (d) (3 H), $J = 1$ Hz. The alcohol was treated with iodobenzene and palladium acetate exactly as in the preceding experiment with about 5 hr reaction time at 100°. Products were isolated as described above also. The 4-phenyl-2-butanone contained less than 10% deuterium and the 3-phenyl-2-butanone contained about 30% deuterium on the 3 carbon and about 15% on the 1 carbon. There was no detectable amount of deuterium on carbon 4 in either product.

Isolation of Tetraphenylphosphonium Iodide from the Phenylation of 3-Buten-2-ol. A reaction mixture consisting of 20 mmol of iodobenzene, 0.2 mmol of palladium acetate, 25 mmol of 3-buten-2-ol, 10 ml of triethylamine, and 3.8 mmol of triphenylphosphine was heated in a capped tube under argon for 10 hr at 100°. After cooling the crystalline solid present was removed by filtration, washed with hexane, and recrystallized from methylene chloride–ethyl acetate. There was obtained 1.1 g (61% based upon the triphenylphosphine) of tetraphenylphosphonium iodide, identified by ir and ^{31}P NMR (−23.2 ppm, authentic material −23.2 ppm, from H_3PO_4).

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Registry No.—(*E*)-Methyl 2-butenoate, 623-43-8; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; 3-phenylpropanal, 104-53-0; 2-phenylpropanal, 93-58-3; 3-phenylbutanal, 16251-77-7; 2-phenylbutanal, 2439-43-2; 3-methyl-3-phenylbutanal, 1009-62-7; 3-methyl-2-phenyl-3-buten-1-ol, 29290-99-1; 3-methyl-2-phenylbutanal, 2439-44-3; biphenyl, 92-52-1; 2-methyl-3-phenylpropanal, 5445-77-2; 2-methyl-2-phenylpropanal, 3805-10-5; (*E*)-4-phenyl-3-buten-2-ol, 36004-04-3; 4-phenyl-2-butanone, 2550-26-7; 1-phenyl-1,3-butadiene, 1515-78-2; 3-phenyl-3-buten-2-ol, 6249-81-6; 3-phenyl-2-butanone, 769-59-5; 4-(4′-methoxyphenyl)-2-butanone, 104-20-1; 1-(4′-methoxyphenyl)-1,3-butadiene, 30448-78-3; 3-4′-methoxyphenyl)-2-butanone, 7074-12-6; (*E*)-4-(4′-trifluoromethylphenyl)-3-buten-2-ol, 57132-18-0; 4-(4′-trifluoromethylphenyl)-2-butanone, 57132-19-1; 3-(4′-trifluoromethylphenyl)-3-buten-2-ol, 57132-20-4; 3-(4′-trifluoromethylphenyl)-2-butanone, 57132-21-5; (*E*)-4-(4′-tolyl)-3-buten-2-ol, 57173-53-2; 4-(4′-tolyl)-2-butanone, 7774-79-0; 3-(4′-tolyl)-3-buten-2-ol, 57132-22-6; (*E*)-4-(2′-tolyl)-3-buten-2-ol, 57132-23-7; (*Z*)-4-(2′-tolyl)-3-buten-2-ol, 57132-24-8; 4-(2′-tolyl)-2-butanone, 57132-25-9; 1-(2′-tolyl)-1,3-butadiene, 57132-26-0; 4-(2′-tolyl)-3-buten-2-one, 16927-82-5; 3-(2′-tolyl)-3-buten-2-ol, 57132-27-1; (*E*)-2-methyl-4-phenyl-3-buten-2-ol, 57132-28-2; 3-methyl-1-phenyl-1,3-butadiene, 21919-51-7; 2-methyl-3-phenyl-3-buten-2-ol, 25982-72-3; (*E*)-4-phenyl-3-buten-1-ol, 770-36-5; phenylbutanal, 18328-11-5; 3-phenyl-3-buten-1-ol, 3174-83-2; (*E*)-5-phenyl-4-penten-2-ol, 54985-34-1; (*Z*)-5-phenyl-4-penten-2-ol, 54985-29-4; 5-phenyl-2-pentanone, 2235-83-8; 4-phenyl-4-penten-2-ol, 57132-29-3; 4-phenyl-2-pentanone, 17913-10-9; (*E*)-methyl 3-phenyl-2-butenoate, 8461-50-5; (*E*)-phenylacrylonitrile, 140-10-3; (*Z*)-phenylacrylonitrile, 102-94-3; (*E*)-methyl cinnamate, 1754-62-7; (*E*)-methyl 3-(1′-naphthyl)propenoate, 22837-81-6; $Pd(OAc)_2$, 3375-31-3; $Pd(OAc)_2(PPh_3)_2$, 14588-08-0; $PdBr(Ph)(PPh_3)_2$, 33381-14-5; $PdCl_2(PPh_3)_2$, 13965-03-2; $PdBr_2(PPh_3)_2$, 23523-33-3; $PdI_2(PPh_3)_2$, 23523-32-2.

Supplementary Material Available. Complete NMR spectra, physical properties, and observed molecular weights for the products prepared in this investigation (10 pp) will appear following these pages in the microfilm edition of this volume of the journal.

References and Notes

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