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Palladium-Catalyzed Vinyl Substitution Reactions. II. Synthesis of Aryl Substituted Allylic Alcohols, Aldehydes, and Ketones from Aryl Halides and Unsaturated Alcohols

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A variety of substituted bromo- and iodobenzenes reacted with 2-methyl, 1-methyl, and 1-1-dimethyl allyl alcohols to give aryl substituted aldehydes, ketones, and allyl alcohols, respectively. Bromo- and iodobenzene reacted in a similar manner with some nonallylic unsaturated alcohols. In these cases, the double bond migrated along the carbon chain until captured by the alcohol function to give a carbonyl product. Formation of the intermediate phenyl substituted unsaturated alcohols was minimal unless a quaternary carbon separated the double bond and alcohol functions.

Phenyl substituted carbonyl compounds can be prepared by the palladium-catalyzed reaction of iodobenzene and bromobenzene with allylic alcohols.[1] Heck and co-worker have described a related reaction in which considerable amounts of phenyl substituted unsaturated alcohols were also formed, particularly from the bromo compounds.[2] The reaction was shown to apply to homoallylic alcohols, but again a mixture of products was formed.

In the present paper our work is extended to the reaction of a variety of substituted aryl halides with allylic alcohols and to the reaction of bromobenzene and iodobenzene with some nonallylic unsaturated alcohols. Since the major products were carbonyl compounds even when aryl bromides were used, the reaction has considerable synthetic utility.

Results

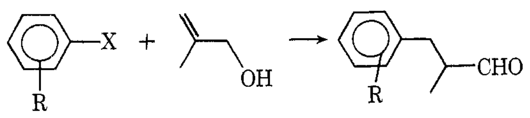
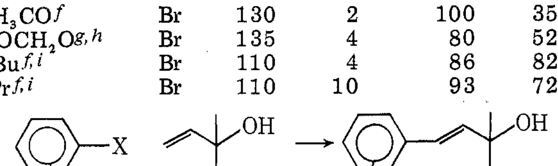
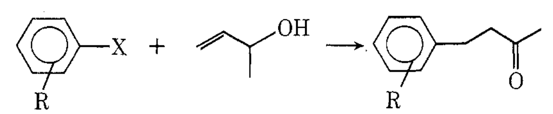
Reaction of Substituted Aryl Halides with Allylic Alcohols. The reactions summarized in Table I, parts i and iii, gave predominantly carbonyl compounds as products. Variations in the catalyst and solvent have no special significance, but special conditions were used in some cases to achieve better yields. Where a GC yield is quoted, the product was also isolated and identified in earlier experiments.

Although a wide variety of substituents were tolerated, there were side reactions which appeared to relate to the electron-donating character of the substituent. Thus, the reaction of the 4-nitroiodobenzene gave a 20% yield (isolated) of 4,4′-dinitrobiphenyl which is a fourfold increase over the amount of biphenyl produced from iodobenzene under corresponding conditions.

With electron-donating substituents (OH, OMe, OCH_2O) another side reaction developed, namely reduction of the aryl halide. This occurred in reactions with 1-buten-3-ol, and to a lesser extent with 2-methyl-2-propen-1-ol. This reduction was more significant with the bromide than the iodide and was more pronounced when a tertiary amine was used as base in place of sodium bicarbonate. Thus, in the reaction of 4-iodophenol and 1-buten-3-ol the yields of 4-(4′-hydroxyphenyl)-2-butanone and phenol were 36 and 44%, respectively, when triethylamine was used as base. However, when sodium bicarbonate was used as base with only a catalytic amount of triethylamine, these yields changed to 77 and 2%. In the reaction of 3,4-methylenedioxybromobenzene with methallyl alcohol, methylenedioxybenzene was the sole product when tripropylamine was used as base. However, the use of sodium bicarbonate with or without a catalytic amount of tripropylamine gave yields of approximately 50% of the expected aldehyde.

A further complication was found with 4-alkylbromobenzenes. Although the corresponding iodides reacted satisfactorily, the bromides reacted slowly and palladium metal formed early in the reaction, which stopped at only a partial conversion. A variety of different solvents, bases, and phosphines were tried with 4-*tert*-butylbromobenzene but the best yields were obtained when sodium iodide was used in place of triphenylphosphine. Sodium iodide was used in the hope that halogen exchange might occur to give the 4-*tert*-butyliodobenzene. No evidence for this exchange was found, but the desired product was formed under mild conditions (110 °C) in the absence of phosphine. The reaction rate, conversion, and yield all increased with an increasing amount of the solvent (hexamethylphosphoramide, HMP).

Table I. Reactions of Aryl Halides with Allylic Alcohols[a]

R	X	Temp, °C	Time, h	Conversion,[b] %	Yield,[c] %
(i)  (1)					
2-CH_3	I	140	0.7	100	77
4-OCH_3	I	125	16.5	100	61
4-OH	I	130	2.5	100	42
4-NO_2	I	130	5.5	100	50
4-*t*-Bu	I	130	6	100	95[d]
4-COOEt[e,f]	Br	130	0.7	100	82
4-CHO	Br	130	7	100	57
4-CN	Br	130	4	79	52
4-CH_3CO[f]	Br	130	2	100	35
3,4-OCH_2O[g,h]	Br	135	4	80	52[d]
4-*t*-Bu[f,i]	Br	110	4	86	82
4-*i*-Pr[f,i]	Br	110	10	93	72
(ii)  (2)					
4-OCH_3[e,f,j]	Br	130	3.5	100	59
4-CH_3CO[f,k]	Br	110	2.5	100	67
4-CH_3[f,h,l]	Br	120	3	100	80
(iii)  (3)					
4-OH[f,m]	I	120	3.5	87	77[d]
4-CH_3CO[f]	Br	130	2	100	35

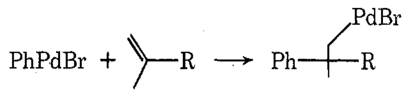
[a] 50 mmol of aryl halide, 75 mmol of allylic alcohol, 60 mmol of $NaHCO_3$, 0.45 mmol of $PdCl_2$ with 0.9 mmol of PPh_3 if X = Br, 20 ml of *N*-methylpyrrolidinone (unless otherwise specified). [b] Conversion of aryl halide by GC. [c] Isolated yield based on 100% conversion except as noted. [d] Yield by GC (internal standard). [e] Hexamethylphosphoramide used as solvent. [f] $PdOAc_2$ used in place of $PdCl_2$. [g] 1 mmol of tripropylamine added. [h] Dimethylformamide as solvent. [i] 60 ml of hexamethylphosphoramide as solvent and PPh_3 replaced by 16.5 mmol of NaI. [j] 8 mmol of diisopropylethylamine added. [k] 2.5 mmol of trilaurylamine added. [l] 2.3 mmol of trioctylamine added. [m] 1 mmol of triethylamine added, dimethylacetamide as solvent.

Thus, when the volume of solvent was increased from the usual 20 ml to 40 ml and then to 60 ml, the conversion and yield increased dramatically (conversions, 19, 76, and 86%; yields 14, 60, and 76%, respectively).

An interesting by-product, 3-phenyl-2-methylpropanal, was formed in the reaction of 4-*tert*-butylbromobenzene and methallyl alcohol. The amount of this side product was proportional to the amount of triphenylphosphine used in the reaction and was completely absent when triphenylphosphine was omitted. It therefore appears that a phenylpalladium intermediate was formed via the scission of a P–C_6H_5 bond. A similar reaction has been reported between triphenylphosphine and styrene to give stilbene.[3] The reaction was confirmed by the formation of 3-(methoxyphenyl)-2-methylpropanal when triphenylphosphine was replaced by tris(4-methoxyphenyl)phosphine.

The reaction between substituted aryl halides and 3-methyl-1-buten-3-ol gave good yields of the expected products providing the precautions used in preparing the unsubstituted analogue were followed.[1]

Nonallylic Alcohols. Table II shows that iodobenzene and bromobenzene may be treated with a variety of unsaturated alcohols to produce the corresponding phenyl substituted carbonyl compounds. Surprisingly, bromobenzene reacted faster than iodobenzene and it was noticed that palladium metal was formed more easily in the latter case. Similar small amounts of phenyl substituted unsaturated alcohols were formed in both cases.


(4)

For those alcohols having an isopropenyl group, one carbonyl product predominated. This was expected since the alternative mode of addition of phenylpalladium halide to the double bond (reaction 4) yields an intermediate which cannot eliminate palladium hydride to form an olefin. In the case of methallyl alcohol, however, reaction 4 does lead to 5% of a product (2-methyl-2-phenylpropanal) which must be explained by a special mechanism.[1,2] Similar products were found in about 1% yield for three of the four alcohols which had an isopropenyl group listed in Table II. In each case a small GC peak occurring immediately before the main product (on both SE-30 and 20M columns) was identified by mass spectrometry. The molecular ion was

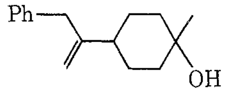
Table II. Reactions of Unsaturated Alcohols with Bromo- and Iodobenzene[a]

					Product yields,[b] %			
Alcohol	Halogen	Temp, °C	Time, h	Conversion, %	Linear carbonyl	Branched carbonyl	Biphenyl	Unsaturated alcohols[c]
3-Buten-1-ol	I	130	2	100	44[d]	13[d]	4	3, 5
4-Penten-1-ol	I	130	2	98	30[d]	12[d]	Trace	Traces
3-Methyl-3-buten-1-ol	I	130	4	100	39[e]	~1	10	3, 4
3-Methyl-3-buten-1-ol	Br	130	3	100	58	~1	4	4, 5
5-Methyl-5-hexen-2-ol	I	130	22.5	100	40	~1	15	Trace, 9,[f] 16[g]
5-Methyl-5-hexen-2-ol	Br	120	7.5	100	49	~1	7	3, 9,[f] 11[g]
4-Methyl-4-penten-2-ol	I	130	24	86	48	~1	14	3,[h] 3,[i] 9[j]
4-Methyl-4-penten-2-ol	Br	120	17	100	56	~1	Trace	3,[h] 8,[i] 16[j]
4-Methyl-4-penten-1-ol	I	120	13	100	16		13	2, 4,[k] 2,[l] 4[m]
4-Methyl-4-penten-1-ol	Br	100	14	100	27		0	0, 4,[k] 6,[l] 8[m]

[a] 50 mmol of halobenzene, 75 mmol of alcohol, 60 mmol of $NaHCO_3$, 0.45 mmol of $PdCl_2$ or $PdOAc_2$, and in the case of C_6H_5Br, 2 mol of PPh_3 per mole of palladium in 20 ml of *N*-methylpyrrolidinone. [b] From GC using internal standards unless otherwise specified (based on 100% conversion). [c] Approximate yields based on GC using internal standard. Identification below by NMR. [d] Isolated yields. [e] In a second example, a 70% conversion (45% isolated yield) was obtained after 7 h at 110 °C. [f] Mixture of (*E*)- or (*Z*)-5-methyl-6-phenyl-5-hexen-2-ol, 5-methyl-6-phenyl-4-hexen-2-ol, and 5-benzyl-5-hexen-2-ol (~1:3:1). [g] (*Z*)- or (*E*)-5-methyl-6-phenyl-5-hexen-2-ol. [h] 4-Benzyl-4-penten-2-ol. [i] Mixture of 4-methyl-5-phenyl-4-penten-2-ol and 4-methyl-5-phenyl-3-penten-2-ol (~7:3). [j] (*E*)- or (*Z*)-4-methyl-5-phenyl-4-penten-2-ol. [k] 4-Benzyl-4-penten-1-ol. [l] (*E*)- or (*Z*)-5-phenyl-4-methyl-4-penten-1-ol. [m] (*Z*)- or (*E*)-5-phenyl-4-methyl-4-penten-1-ol.

found together with a large *m/e* 119 peak corresponding to the dimethylbenzyl group. In one case (3-methyl-3-phenyl-1-butanal), the mass spectral pattern fitted that obtained from an authentic sample, while in another case, sufficient material was isolated to identify it by NMR as the expected 4-methyl-4-phenyl-2-pentanone.

When a quaternary carbon atom separated the double bond and the alcohol function, phenyl substitution occurred to give unsaturated alcohols. Thus, 1-methyl-3-cyclohexene-1-methanol reacted with iodobenzene (18 h, 130 °C, in HMP) to give a 12% yield of phenyl substituted products. Eighty percent of the mixture was identified as 1-methyl-5-phenyl-3-cyclohexene-1-methanol and 20% as the isomer having either a 3- or 4-phenyl. Similarly β-terpineol (30 h, 130 °C in HMP) gave a 23% yield of a mixture of 9-phenyl substituted menthen-1-ols (8% **1**, 11% **2**, 27% **3**, and 54% **4**). In these cases, sodium bicarbonate was used as base with a catalytic amount of diisopropylethylamine. When the amine was used in stoichiometric amount in place of sodium bicarbonate, the products from β-terpineol suffered dehydration. Thus after 6.5 h at 130 °C, a 19% yield of phenyl substituted diolefins was obtained whose NMR spectrum was consistent with a mixture in which **5** and **6** predominated.



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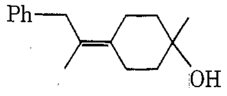

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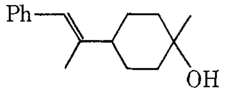

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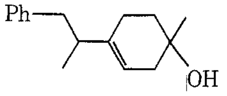

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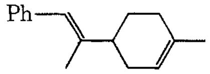

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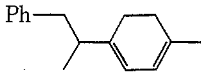

6

Biphenyl (29%) was also formed in this reaction which was not atypical.

For NMR data see paragraph at end of paper regarding supplementary material.

Discussion

The reaction of aryl halides with allylic alcohols was shown to be applicable to a wide variety of substituted iodides and bromides. Owing to competing side reactions, aryl bromides gave better results than iodides when the substituents were electron withdrawing while iodides gave the better results when the substituents were electron donating.

In the former case, the competing side reaction was biaryl formation which must result from the decomposition of the arylpalladium halide formed in reaction 5.[4]

$$ArX + Pd^0 \rightleftharpoons ArPdX \qquad (5)$$

Reaction 5 is expected to be an equilibrium which is displaced to the right by electron-withdrawing substituents or by replacing X = Br by X = I. It is therefore also significant that in general biphenyl is a more important by-product of reaction 1 (R = H) when X = I than when X = Br.[1]

When the aryl substituent was electron donating, a competing side reaction caused reduction of the aryl halide. The principal hydrogen source was the alcohol since 1-buten-3-one was obtained from 1-buten-3-ol. Dimethylformamide may also be a hydrogen source since it appeared to promote the reduction more than other solvents. The reduction was most actively promoted by the amine hydrohalide which suggests reaction 6.

$$H^+ + ArPdX \longrightarrow ArH + PdX^+ \qquad (6)$$

Reduction of PdX^+ to Pd^0 by the alcohol, followed by reaction 5, would complete the catalytic cycle for reduction.

The reaction mechanism previously discussed[1] suggests that the synthesis should be generally applicable to unsaturated alcohols. Providing the intermediate phenyl substituted olefins are not displaced from the coordination sphere of palladium, the double bond should shift along any carbon chain until "captured" by a hydroxyl function with the formation of a carbonyl group. This occurred under the experimental conditions used with certain unsaturated alcohols having as many as four carbon atoms separating the hydroxyl function from the double bond. Some unsaturated alcohols were formed, and the distribution of isomers was different for bromobenzene and iodobenzene. However, the total yield of unsaturated alcohols was similar in both cases. As previously noted with certain allylic alcohols, biphenyl formation was more pronounced for iodobenzene than bromobenzene.

In order to see how far the double bond would migrate along a carbon chain, we also examined the reaction of iodobenzene with 1-decen-10-ol. The crude reaction product contained aldehydes but these could not easily be separated from the complex mixture of alcohols which was also present.

For most of the examples given in Table II, a single carbonyl product predominated and was obtained in good yield. These results should not be generally extrapolated, however, since four of the alcohols used in Table II have the same structure about the double bond, a structure which favors terminal addition to the double bond. Further, using different experimental conditions, Heck and coworker have noted that aryl bromides can give rise to a higher ratio of unsaturated alcohols to carbonyl compounds than aryl iodides.[2] The possibility of changing reaction conditions to produce solely unsaturated alcohols is presently under study.

Experimental Section

Materials were obtained from commercial sources (aryl halides, Aldrich, Eastman; unsaturated alcohols, Chemical Samples). They were used without purification.

Procedures have been previously reported.[1] Products were isolated by distillation or by preparative GC (6 ft × 0.25 in. Carbowax 20M or SE-30) and identified by NMR, MS, and ir. A typical example follows.

3-(4′-Carboethoxyphenyl)-2-methylpropanal. Palladium acetate (0.30 g, 1.35 mmol) and triphenylphosphine (0.72 g, 2.7 mmol) were dissolved in 60 ml of hexamethylphosphoramide and sodium bicarbonate (15 g, 0.18 mol), 2-methyl-2-propen-1-ol (13.1 g, 0.18 mol), and ethyl 4-bromobenzoate (37.8 g, 0.16 mol) added. The mixture was heated to 130 °C under nitrogen. After 42 min the reaction was stopped and the mixture cooled when GC revealed 100% conversion of the aryl halide. The reaction mixture was then poured into 1 l. of water and extracted three times with 150-ml portions of toluene. The combined toluene extracts were then back extracted with 150 ml of water, evaporated to give 34.2 g of product, and distilled using a short-path still to give 25.8 g (71%) of product.

Supplementary Material Available. Full NMR data for the compounds synthesized (5 pages). Ordering information is given on any current masthead page.

Registry No.—2-Methyl-2-propen-1-ol, 513-42-8; 2-methyliodobenzene, 615-37-2; 4-methoxyiodobenzene, 696-62-8; 4-iodophenol, 540-38-5; 4-nitroiodobenzene, 636-98-6; 4-*tert*-butyliodobenzene, 35779-04-5; ethyl 4-bromobenzoate, 5798-75-4; 4-bromobenzaldehyde, 122-91-4; 4-bromobenzonitrile, 623-00-7; 4-bromoacetophenone, 99-90-1; 3,4-methylenedioxybromobenzene, 2635-13-4; 4-*tert*-butylbromobenzene, 3972-65-4; 4-isopropylbromobenzene, 586-61-8; 4-methoxybromobenzene, 104-92-7; 4-methylbromobenzene, 106-38-7; 3-methyl-1-buten-3-ol, 115-18-4; 1-buten-3-ol, 598-32-3; 3-buten-1-ol, 627-27-0; 4-penten-1-ol, 821-09-0; 3-methyl-3-buten-1-ol, 763-32-6; 5-methyl-5-hexen-2-ol, 50551-88-7; 4-methyl-4-penten-2-ol, 2004-67-3; 4-methyl-4-penten-1-ol, 22508-64-1; bromobenzene, 108-86-1; iodobenzene, 591-50-4; β-terpineol, 138-87-4; 1-methyl-3-cyclohexene-1-methanol, 50552-10-8.

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The Chemistry of Carbanions. XXVIII. The Carbon-13 Nuclear Magnetic Resonance Spectra of Metal Enolates[1]

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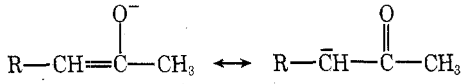
The natural abundance ^{13}C NMR spectra of several metal enolates **5–10** have been measured in various aprotic solvents including Et_2O, THF, and DME. The chemical shifts of the enolate α-carbon atoms are readily measured and have been compared with the chemical shifts of the same carbon atoms in the corresponding enol acetates **17–22** and trimethylsilyl enol ethers **23–26**. The observed chemical shift differences ($\Delta\delta$) between the enolates and the enol acetates appear to be related both to the π-electron density and the reactivity at the enolate α-carbon atom. The following changes increase the magnitude of the chemical shift differences (and presumably the π-electron charge density) in metal enolates: (1) changing the metal cation from Li^+ to Na^+ to K^+; (2) changing the solvent from Et_2O to THF to DME; (3) addition of 4 molar equiv of HMP to a Li^+ enolate; and (4) addition of 1 molar equiv of dicyclohexyl-18-crown-6 polyether to a Na^+ enolate. The magnitudes of the chemical shift differences at the enolate α-carbon atoms are relatively insensitive to the presence or absence of α-alkyl or α-phenyl substituents.

In an early study[2] of the properties and reactions of solutions of metal enolates **1** derived from ketones **2**, comparison of the ^{1}H NMR spectra for a related set of compounds **1–4** (R = Ph) showed that the vinyl H atom signal moved progressively upfield in the order enol acetate **3** (δ 5.80), trimethylsilyl enol ether **4** (δ 5.32), and lithium enolate **1** (δ 5.02 in Et_2O, 4.93 in THF, and 4.83 in DME). Among the various cations and solvents studied with this enolate system, the cation–solvent combinations that resulted in the greatest upfield shift of the vinyl H atom NMR signal were also the combinations that resulted in the greatest proportion of O- to C-acylation of the enolate anions and corresponded qualitatively to conditions that favored most rapid reaction of the enolate anion with alkylating agents. Thus, the location of the ^{1}H NMR signal appeared to offer a useful measure of the reactivity of a metal enolate under various reaction conditions. However, two experimental problems dissuaded us from further study of the ^{1}H NMR spectra of metal enolates. First, the total range of ^{1}H NMR values observed for a particular enolate system was rather small (ca. 0.3 ppm) so that changes in chemical shift arising from nearby anisotropic substituents were likely to be as large as chemical shift differences arising from changes in the degree of association and charge distribution of metal enolates. Even more troubling was the interference from the ^{1}H NMR signals of the various solvents (Et_2O, THF, DME, DMF, etc.) commonly used with metal enolates.

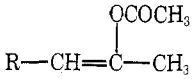


$\mathrm{R{-}CH{=}\overset{O^{-}}{C}{-}CH_3} \longleftrightarrow \mathrm{R{-}\bar{C}H{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$

1a **1b**

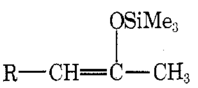
RCH_2COCH_3

2



$\mathrm{R{-}CH{=}\overset{OCOCH_3}{C}{-}CH_3}$

3



$\mathrm{R{-}CH{=}\overset{OSiMe_3}{C}{-}CH_3}$

4

It appeared that both of these problems could be largely alleviated by studying the natural abundance ^{13}C NMR spectra of metal enolate solutions. Because of the much larger range of chemical shift values in ^{13}C NMR and the relatively narrow linewidths obtainable, problems arising from interference between solvent peaks and peaks from the metal enolates would be more easily avoided. Of equal importance is the fact that electron densities at carbon and the atoms bonded to it, but not shielding from neighboring anisotropic substituents, are dominant in determining ^{13}C NMR chemical shift values.[3]

To explore this possibility, a series of metal enolates **5–10** (Scheme I) of ketones **11–16** were prepared. Also included in the study were the corresponding enol acetates **17–22** as well as selected enol silyl ethers **23–26**, one enamine **27**, and the sodium enolate **28** of diethyl malonate.

Although relatively high concentrations (0.5–1.0 M) of metal enolates in solution were required in order to obtain satisfactory natural abundance ^{13}C NMR spectra in a reasonable period of time (1–3 h), we were gratified to find that interference between ^{13}C NMR signals for the metal enolates and the solvents was much less of a problem than had been encountered in measurements of ^{1}H NMR spectra of metal enolates.[2] Consequently, where solubility permitted, satisfactory ^{13}C NMR spectra of various metal enolates could be obtained in most common solvents used in preparative work including Et_2O, THF, DME, DMF, and HMP. The data obtained from these measurements are summarized in Tables I and II. In one case (enolate **5a** in DME, Table I) we demonstrated that the chemical shift values were essentially the same for 1.0 and 0.2 M solutions of the enolate. Because of the time required to obtain satisfactory ^{13}C NMR spectra of dilute solutions, it was not practical to collect data for enolate solutions less concentrated than 0.2 M.

In order to compare the ^{13}C NMR data for various metal enolates, we elected to relate the enolate chemical shift