80663-70-3; **49**, 80663-71-4; **50**, 80663-72-5; **51**, 38313-10-9; **52**, 80663-73-6; **53**, 80663-74-7; **59**, 122-57-6; **60**, 17488-65-2; **61**, 80663-75-8; **62**, 80663-76-9; **63**, 495-41-0; **64**, 78-94-4; **65**, 53977-97-2; **66**, 107-86-8; **67**, 32064-74-7; **68**, 80663-77-0; **69**, 56312-55-1; **70**, 73587-69-6; **71**, 73587-71-0; **72**, 22844-34-4; (+)-**73**, 15466-88-3; (−)-**73**, 54307-74-3; **74**, 80734-37-8; **75**, 6553-64-6; **76**, 80663-78-1; **77**, 1073-13-8; **78**, 6610-21-5; **79**, 3718-56-7; **80**, 80663-79-2; **81**, 80663-80-5; **82**, 5515-76-4; **83**, 930-30-3; **84**, 20826-91-9; **85**, 80663-81-6; **86**, 75308-19-9; **88**, 937-07-5; **89**, 80663-82-7; (+)-5-methylcyclohex-2-en-1-one 2,4-DNP derivative, 80663-83-8.

Palladium-Catalyzed Reactions of Vinylic Bromides with Allylic Alcohol and Amine Derivatives

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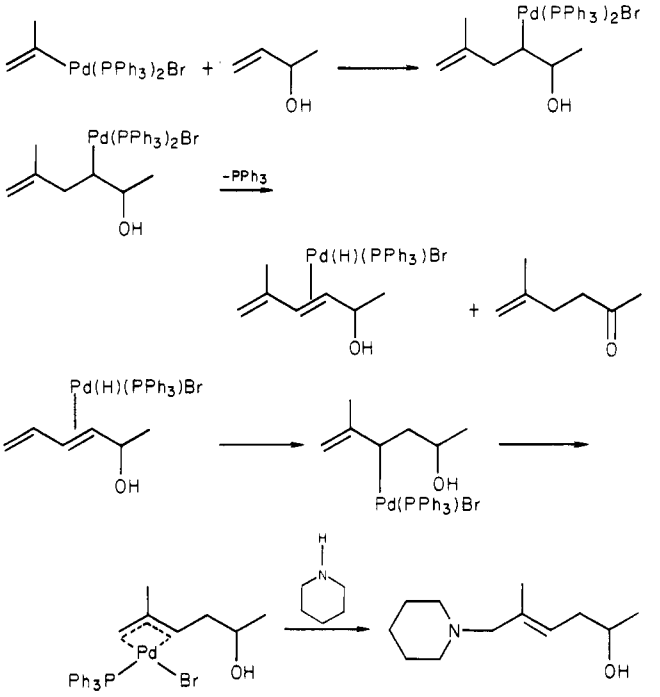
Allylic alcohols, amines, tetrahydropyranyl ethers, *N*-allylphthalimide, and tetraallyl silicate have been reacted with various vinylic bromides and, in some cases, bromobenzene by using a palladium catalyst with an amine as an acid acceptor. Of the allylic alcohols, methallyl alcohol was the most useful synthetically. It produced 4-enals in modest yields in many examples without formation of the regioisomers which are a problem in other cases. Secondary allylic alcohols reacted regioselectively to form mixtures of 4-enals and amino alcohols. Some nonallylic alcohols gave good yields of amino alcohols, also. Allylic tertiary amines reacted more selectively in some instances than allylic alcohols, producing 4-enals after hydrolysis of the enamine products. The allylic tetrahydropyranyl ethers, in general, formed mixtures of dienyl ethers and amino alkenyl ethers. The *N*-allylphthalimide–vinylic bromide reactions were the most selective we found. The products were *N*-(2,4-dienyl) phthalimides, formed in fair to good yields. The reactions of tetraallyl silicate were of limited value. The reaction was selective with bromobenzene, forming after hydrolysis only cinnamyl alcohol, but it was not selective with vinylic halides, and conversions were always low due to facile reduction and inactivation of the catalyst under the reaction conditions.

The palladium-catalyzed reaction of vinylic bromides or iodides with alkenes and an amine has been shown to be a useful method for the synthesis of conjugated dienes[1] and/or allylic amines.[2] The tolerance of the reaction for a variety of functional groups makes it of value for preparing polyfunctional compounds often without the need of employing "protecting groups".[3] We now report applications of the reaction to allylic alcohol and amine derivatives as further examples of its usefulness in the preparation of polyfunctional molecules with relative ease.

Results and Discussion

In the initial experiment, it was observed that 2-bromopropene and 3-buten-2-ol failed to react under conditions where bromobenzene reacted easily.[2] Since the palladium remained in solution, it appeared that a stable organopalladium complex had been formed. Several attempts to isolate this complex from the reaction mixture were unsuccessful. However, we observed that the use of piperidine instead of triethylamine as the acid acceptor caused a rapid catalytic reaction to occur, with, however, formation of the desired ketone 5-methyl-5-hexen-2-one and also 5-methyl-6-piperidino-4-hexen-2-ol. The last product was likely formed by nucleophilic attack of the piperidine upon an intermediate π-allylic complex. It had previously been reported, in one case, that a secondary amine reacted with a π-allylic palladium chloride complex to form an allylic amine,[4] and we had already suspected that π-allylic palladium complexes were intermediates in the reactions of vinylic halides with, at least, some alkenes.[1] Larock more recently isolated π-allylic complexes from related stoichiometric reactions.[5] Therefore, in retrospect, the formation of the relatively stable π-allylic complexes in the allylic alcohol reactions with vinylic halides could have been expected. It appears that the vinylic halide reactions follow the mechanism shown in Scheme I.

Scheme I. Mechanism of the 2-Propenylation of 3-Buten-2-ol



We have now looked at reactions of vinylic bromides with a variety of other allylic alcohols, allylic amines, allylic

(1) H. A. Dieck and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).
(2) B. A. Patel and R. F. Heck, *J. Org. Chem.*, **43**, 3898 (1978).
(3) R. F. Heck, "Proceedings of the PRC-Japan-USA Seminar on Organometallic Chemistry", Van Nostrand-Reinhold, in press.
(4) B. Akermark and K. Zetterberg, *Tetrahedron Lett.*, 3733 (1975).
(5) R. C. Larock and M. A. Mitchell, *J. Am. Chem. Soc.*, **98**, 6718 (1976).

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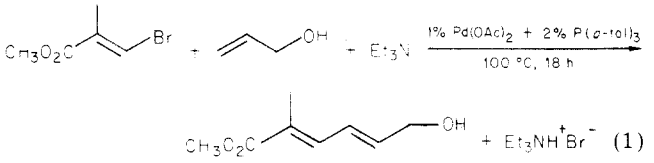
tetrahydropyranyl ethers, *N*-allylphthalimide, and allylic silicate esters in the search for synthetically useful applications for the reactions.

Allylic Alcohols. Table I gives the results obtained in the reactions of several vinylic halides with various allylic alcohols. In these experiments and others described in this report conditions were chosen which were the best combination of reasonable yields, reasonable rates, and selectivity. Yields and selectivity were, in fact, rather insensitive to temperatures and catalyst concentrations. The products reported are stable under the reaction conditions. The structures of the products have been determined by NMR spectroscopy at 250 MHz with decoupling as necessary. The assignment of stereochemistry when its not clear from the NMR spectrum is made by analogy with related reactions; e.g.: the *E* isomers are always preferred when there is a choice; attack of amines upon π-allylic complexes yields *E* isomers; the stereochemistry of the vinylic halide is largely or completely retained when it is added to an alkene via the palladium derivative if π-allylic intermediates are not involved.

Table I shows that, with one exception, allyl alcohol is not a very useful reactant with vinylic bromides and amines since isomeric mixtures of amino alcohols and/or enals and/or dienols are obtained in all cases studied. The exception is the reaction with (*E*)-methyl 3-bromo-2-methylacrylate which gives the (*E,E*)-dienol in 45% yield as the only volatile product (eq 1). Triethylamine is a

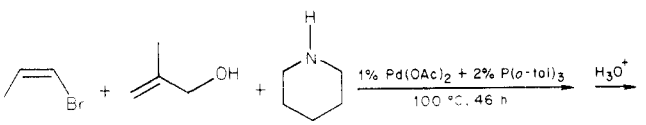


(1)

useful acid acceptor in this example because there is an ester group conjugated with the diene system in the product. In the absence of the conjugating substituent the triethylamine reactions are generally very slow, and serious side reactions may be observed. The low product recovery in these and other examples reported herein is due to the formation of high-boiling and dark nonvolatile side products.

The reaction of allyl alcohol with 2-bromopropene and triethylamine occurred slowly even with 3 times the normal amount of catalyst and produced mainly 4-methyl-4-pentenal. However, it largely underwent the Aldol condensation under the reaction conditions. It is interesting that the 2-bromopropene reaction with 1-hexene and piperidine does *not* give a mixture of regioisomers[2] while the same reaction with allyl alcohol does.

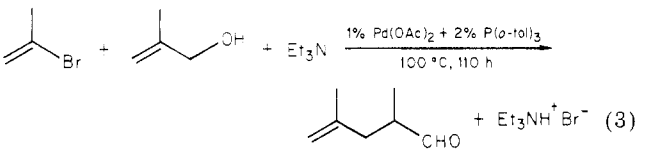
2-Methallyl alcohol reacted more selectively than allyl alcohol did. The steric effect of the 2-methyl group prevents the formation of significant amounts of 2-vinylated products. 1-Bromo-1-propene and 2-bromopropene gave mixtures of 1,4-dienamines and amino alcohols. The crude reaction mixtures could be steam distilled from excess aqueous 5% oxalic acid to give 4-enals. (*Z*)-1-Bromo-1-propene, for example, gave exclusively (*Z*)-2-methyl-4-hexenal from the reaction in 24% yield (eq 2). The related



(2)

24%

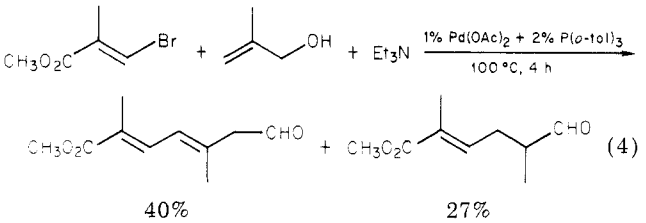
reaction with triethylamine as the base and with 2-bromopropene as the halide gave 68% of the aldehyde directly (eq 3). The Aldol condensation does not occur



(3)

68%

with the α-substituted aldehyde. Other reactions with triethylamine as the base were not as successful. The 2-methyl-1-bromo-1-propene reaction gave mixtures of two aldehydes and two dienols which differed in the position of the double bonds. (*E*)-Methyl 3-bromo-2-methylacrylate reacted with triethylamine as base to form 40% dienol and 27% 4-enal (eq 4). These products are stable under the reaction conditions.

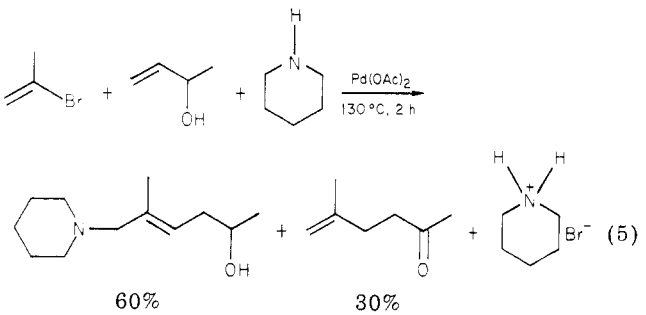


(4)

40% 27%

(*E*)-Crotyl alcohol gives mixtures of regioisomers and low yields in all of the vinylic halide reactions we tried, and, therefore, this reactant is not of general synthetic value.

The secondary allylic alcohol reactions, on the other hand, generally give mixtures of a ketone and an amino alcohol and are of synthetic value. The reaction of vinyl bromide with 3-buten-2-ol gave a low yield of a mixture of regioisomeric amino alcohols; however, 2-bromopropene produced only ketone and amino alcohol in good yield. The relative yields of the products is very dependent upon the phosphine, if any, that is used with the palladium acetate catalyst. Without a phosphine, a 60:30 mixture of amino alcohol and ketone is produced (eq 5), while with

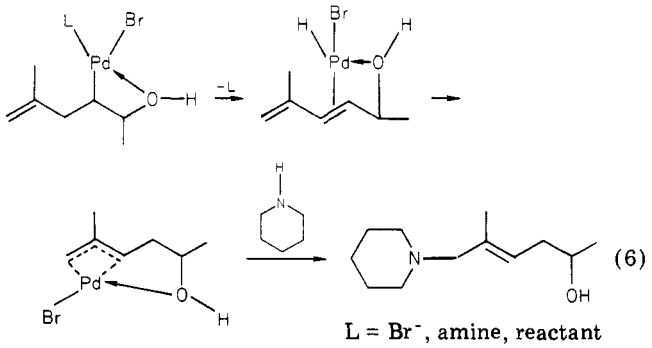


(5)

60% 30%

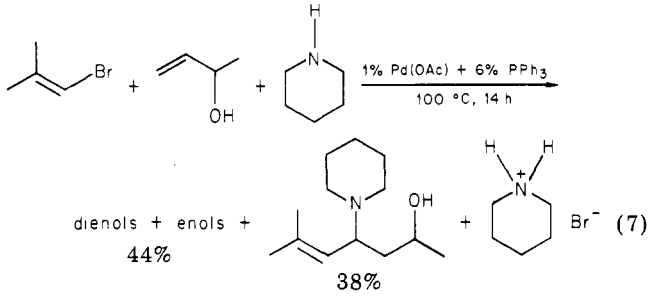
2 mol of triphenylphosphine/mol of palladium acetate a 33:63 mixture is formed in a much faster reaction. A possible explanation for this effect is that in the absence of phosphine, hydroxyl coordination to the palladium occurs in the initial adduct, and this directs elimination exocyclically to the dienol π complex which ultimately forms the π-allylic palladium intermediate and amino alcohol (eq 6). In the presence of a phosphine, the hydroxyl may *not* coordinate in preference to the phosphine.

1-Bromo-2-methyl-1-propene and 3-buten-2-ol with piperidine as the base and a 6:1 ratio of triphenylphosphine to palladium acetate as the catalyst produced a mixture of regioisomeric enols and dienols, but only one amino alcohol, 6-methyl-4-piperidino-5-hepten-2-ol, in 38% yield (eq 7). The presence of the hydroxyl group in this reaction



(6)

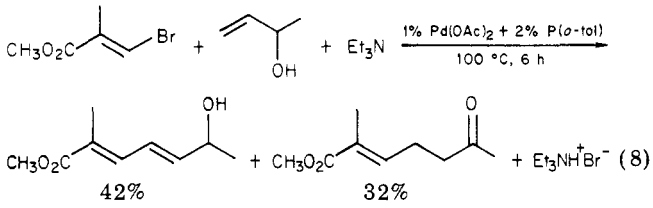
L = Br^-, amine, reactant



(7)

has influenced the position of attack of the amine on the π-allylic intermediate. The related reaction (without the hydroxyl group) of 1-hexene with 1-bromo-2-methyl-1-propene gave only the N-tertiary alkyl amine product rather than the N-secondary one formed when the hydroxyl was present.[2] A possible explanation for the effect is that the hydroxyl group hydrogen bonds with the amine and directs the nucleophilic attack to the closer, secondary π-allylic position. The transition state would involve a six-membered ring if this occurred.

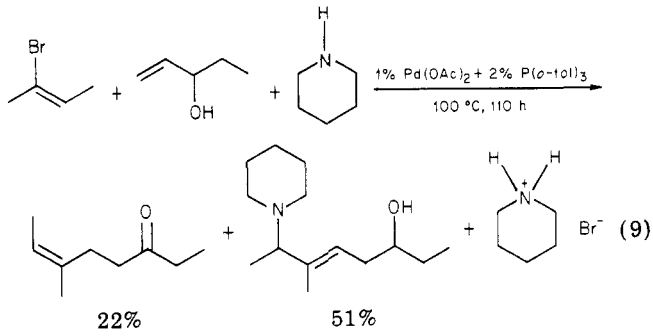
(*E*)-Methyl 3-bromo-2-methylacrylate and 3-buten-2-ol with triethylamine as the base form two products, 42% dienol and 32% enone (eq 8).



(8)

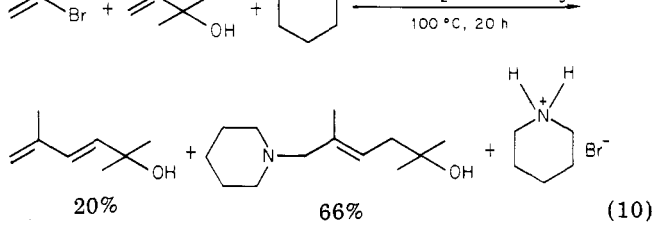
1-Penten-3-ol has been reacted with 2-bromo-1-butene and piperidine with a variety of catalysts to explore the influence of the phosphine upon the products formed. In the absence of phosphine the enone to amino alcohol product ratio is 1.20 with a total yield of 90%. The addition of 2 mol of triphenylphosphine/mol of palladium acetate increased the reaction rate by a factor of 10 but only changed the product ratio to 0.89. Triphenylphosphine (6 mol) gave a product ratio of 1.62. The effect is similar to that observed in the related reactions of 3-buten-1-ol. Bis(diphenylphosphino)ethane, triethylphosphine, and tris[*p*-(dimethylamino)phenyl]phosphine showed only minor effects. Tris(2,5-diisopropylphenyl)-phosphine (2 equiv) in a very slow reaction gave a product ratio of 0.46 with a total yield of 82%. Six equivalents of this phosphine, surprisingly, gave a product ratio of 1.05. While we do not understand the phosphine substituent effects, it is clear that the products can be varied substantially by changing the phosphines in the catalyst and the phosphine concentration.

1-Penten-3-ol also was reacted with (*Z*)-2-bromo-2-butene and piperidine. With 2 mol of tri-*o*-tolylphosphine/mol of palladium acetate as catalyst, a mixture of 23% enone (we believe the *Z* isomer on the basis that retention of the stereochemistry of the carbon skeleton is usually observed in closely related reactions[3]) and 51% amino alcohol (probably the *E* isomer because of equilibration of the π-allylic intermediate) was obtained (eq 9).



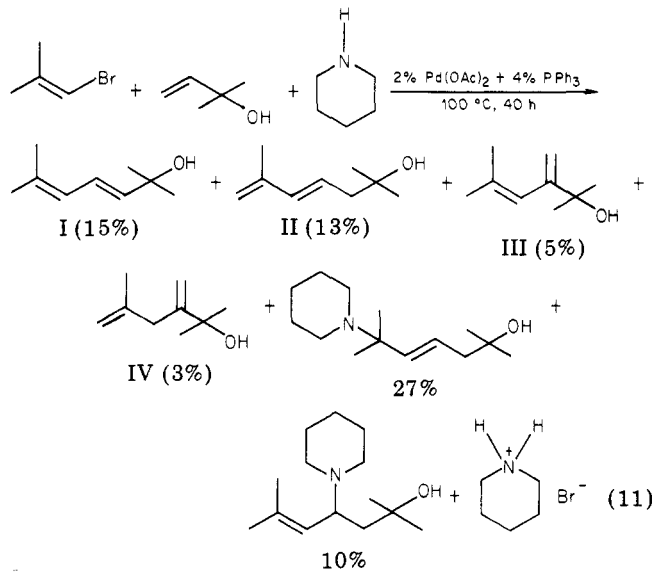
(9)

The tertiary allylic alcohol, 2-methyl-3-buten-2-ol, was reacted with three vinylic bromides. 2-Bromopropene formed a mixture of dienol (20%) and amino alcohol (66%) (eq 10). The reaction of 1-bromo-2-methyl-1-propene, the



(10)

tertiary alcohol with piperidine, and a triphenylphosphine–palladium acetate catalyst produced a mixture of four isomeric nonadienols and two allylic amino alcohol isomers (eq 11). The nonadienols arose from the two



(11)

possible regioisomeric adducts each of which, in turn, gave two isomeric conjugated dienes. At least, the terminal conjugated dienes must be forming via a palladium hydride elimination and readdition in the reverse direction. The allylic amino alcohols are both formed from the terminal π-allylic intermediate, but both possible allylic amines were produced. The yields of the various products vary with the phosphine in the catalyst. The use of tris(2,5-diisopropylphenyl)phosphine instead of triphenylphosphine caused the yield of amino alcohols to increase 10% at the

Table I. Reactions of Vinylic Bromides with Amines and Unsaturated Alcohols[a]

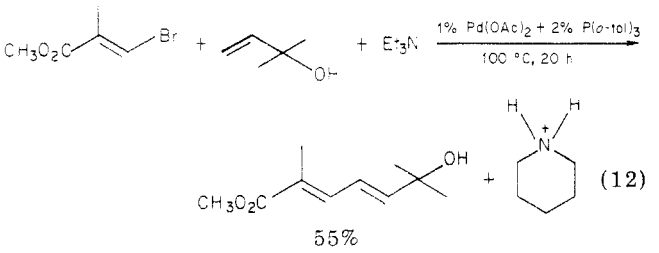
unsaturated alcohol	vinylic bromide	amine[b]	catalyst mol % $P(o\text{-tol})_3$/ mol % $Pd(OAc)_2$ ratio	reaction time, h (at 100 °C)	products (% yield)
$CH_2=CHCH_2OH$	(*Z*)-$CH_3CH=CHBr$	P*H	2	1.5	(*E*)-P*$CH(CH_3)CH=CH(CH_2)_2OH$ (28), (*E*)-P*$CH(CH_3)CH=C(CH_3)CH_2OH$ (11), (*E*)-$CH_3CH=CHCH(P^*)(CH_2)_2OH$ (7)
		MH	2	1.5	(*E*)-M$CH(CH_3)CH=CH(CH_2)_2OH$ (22), (*E*)-M$CH(CH_3)CH=C(CH_3)CH_2OH$ (10), (*E*)-$CH_3CH=CHCH(M)(CH_2)_2OH$ (9)
	$CH_3C(Br)=CH_2$	P*H	2	5	$CH_2=C(CH_3)(CH_2)_2CHO$ (17),[c] $CH_2=C(CH_3)CH(CH_3)CHO$ (7), (*E*)-P*$CH_2C(CH_3)=CH(CH_2)_2OH$ (28), (*E*)-P*$CH_2C(CH_3)=C(CH_3)CH_2OH$ (12)
		Et_3N	6/3	56	$CH_2=C(CH_3)(CH_2)_2CHO$ (5), $CH_2=C(CH_3)CH=CHCH_2OH$ (5), $CH_2=C(CH_3)(CH_2)_2CH=C(CHO)(CH_2)_2C(CH_3)CH_2$ (60)
	$(CH_3)_2C=CHBr$	P*H	2	13	$(CH_3)_2C=CHC(=CH_2)CH_2OH$ (2), (*E*)-$CH_2=C(CH_3)CH=CH(CH_2)_2OH$ (6), $(CH_3)_2C=CHCH=CHCH_2OH$ (18, *E*/*Z* ratio 6.4), $(CH_3)_2C=CHCH(P^*)(CH_2)_2OH$ (37)
	(*E*)-$CH_3O_2CC(CH_3)=CHBr$	Et_3N	2	18	(*E*,*E*)-$CH_3O_2CC(CH_3)=CHCH=CHCH_2OH$ (45)
$CH_2=C(CH_3)CH_2OH$	(*Z*)-$CH_3CH=CHBr$	MH	2	155	(*Z*)-$CH_3CH=CHCH_2C(CH_3)=CHM$ (16), (*E*)-M$CH(CH_3)CH=CHCH(CH_3)CH_2OH$ (35)
		P*H	2	46	(*Z*)-$CH_3CH=CHCH_2C(CH_3)=CHP^*$ (18), (*E*)-P*$CH(CH_3)CH=CHCH(CH_3)CH_2OH$ (32)
	$CH_2=C(CH_3)Br$	P*H	2	18	$CH_2=C(CH_3)CH_2C(CH_3)=CHP^*$ (42), several minor unknowns
		P*H	$Pd(OAc)_2$ used	7	$CH_2=C(CH_3)CH_2C(CH_3)=CHP^*$ (49), several minor unknowns
		Et_3N	2	110	$CH_2=C(CH_3)CH_2CH(CH_3)CHO$ (50)
	$(CH_3)_2C=CHBr$	P*H	2	52	$(CH_3)_2C=CHCH_2C(CH_3)=CHP^*$ (47), $P^*C(CH_3)_2CH=CHCH(CH_3)CH_2OH$ (40)
		Et_3N	2	17	$(CH_3)_2C=CHCH_2CH(CH_3)CHO$ (15), $(CH_3)_2CHCH_2CH=C(CH_3)CHO$ (3), $(CH_3)_2C=CHCH=C(CH_3)CH_2OH$ (42), $(CH_3)_2C=CHCH_2C(CH_2OH)=CH_2$ (10)
		Et_3N	2	4	$CH_3O_2CC(CH_3)=CHCH_2CH(CH_3)CHO$ (27), $CH_3O_2CC(CH_3)=CHCH=C(CH_3)CH_2OH$ (40)
$CH_2=C(CH_3)CH_2OH$	(*Z*)-$C_2H_5CH=C(I)C_2H_5$	P*H	2	40	(*Z*,*E*)-$C_2H_5CH=C(C_2H_5)CH_2C(CH_3)=CHP^*$ (48)
(*E*)-$CH_3CH=CHCH_2OH$	$CH_2=CHBr$	MH	2	35	$MCH_2CH=C(CH_3)(CH_2)_2OH$ (11), $MCH_2CH=C(C_2H_5)CH_2OH$ (7)
	$CH_2=C(Br)CH_3$	MH	2	48	$MCH_2C(CH_3)=C(CH_3)(CH_2)_2OH$ (18), $MCH_2C(CH_3)=C(C_2H_5)CH_2OH$ (12), $CH_2=C(CH_3)CH(CH_3)CH=CHM$ (11)
		P*H	2	18	$P^*CH_2C(CH_3)=C(CH_3)(CH_2)_2OH$ (19), $P^*CH_2C(CH_3)=C(C_2H_5)CH_2OH$ (13), $CH_2=C(CH_3)CH(CH_3)CH=CHP^*$ (23)
	$(CH_3)_2C=CHBr$	P*H	2	20	$(CH_3)_2C=CHC(C_2H_5)=CHP^*$ (12), $(CH_3)_2C=CHCH(CH_3)CH=CHP^*$ (31)
	(*E*)-$CH_3O_2CC(CH_3)=CHBr$	Et_3N	2	4	(*E*)-$CH_3O_2CC(CH_3)=CHCH(CH_3)CH_2CHO$ (47), dienols (11)
$CH_2=CHCH(OH)CH_3$	$CH_2=CHBr$	P*H	2	1	$P^*CH_2CH=CHCH_2CH(OH)CH_3$ (31), $P^*CH_2CH=C(CH_3)CH(OH)CH_3$ (8)
	$CH_2=C(Br)CH_3$	P*H	$Pd(OAc)_2$[d] used	2[e]	$CH_2=C(CH_3)(CH_2)_2COCH_3$ (30), (*Z*)-P*$CH_2C(CH_3)=CHCH_2CH(OH)CH_3$ (60)
	$CH_2=C(Br)CH_3$	P*H	2[f]	1.5	$CH_2=C(CH_3)(CH_2)_2COCH_3$ (63), (*Z*)-P*$CH_2C(CH_3)=CHCH_2CH(OH)CH_3$ (33)
		MH	2[f]	2	$CH_2=C(CH_3)(CH_2)_2COCH_3$ (63), (*Z*)-M$CH_2C(CH_3)=CHCH_2CH(OH)CH_3$ (33)
		MH	2	6	$CH_2=C(CH_3)(CH_2)_2COCH_3$ (34), (*Z*)-M$CH_2C(CH_3)=CHCH_2CH(OH)CH_3$ (40)

	$(CH_3)_2C{=}CHBr$	P*H	6[g]	14	dienols and enone (44), $(CH_3)_2C{=}CHCH(P^*)CH_2CH(OH)CH_3$ (38)
	(*E*)-$CH_3O_2CC(CH_3){=}CHBr$	Et_3N	2	6	$CH_3O_2CC(CH_3){=}CHCH{=}CHCH(OH)CH_3$ (42), $CH_3O_2CC(CH_3){=}CH(CH_2)_2COCH_3$ (32)
$CH_2{=}CHCH(OH)C_2H_5$	$C_2H_5C(Br){=}CH_2$	P*H	$Pd(OAc)_2$ used	24	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (49), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (41)
			2[g]	2	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (41), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (46)
			6[g]	5.5	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (60), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (37)
			1[h]	9	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (45), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (40)
	$C_2H_5C(Br){=}CH_2$	P*H	2[i]	90	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (32), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (44)
		P*H	2	42	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (51), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (36)
		P*H	2[j]	22	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (60), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (38)
		P*H	2[k]	90	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (33), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (52)
		P*H	6[k]	42	$CH_2{=}C(C_2H_5)(CH_2)_2COC_2H_5$ (41), $C_2H_5C(CH_2P^*){=}CHCH_2CH(OH)C_2H_5$ (39)
	(*Z*)-$CH_3C(Br){=}CHCH_3$	P*H	2	110	(*Z*)-$CH_3CH{=}C(CH_3)(CH_2)_2COC_2H_5$ (23) (*E*)-$CH_3CH(P^*)C(CH_3){=}CHCH_2CH(OH)C_2H_5$ (51)
$CH_2{=}CHC(CH_3)_2OH$	$CH_2{=}C(Br)CH_3$	P*H	2	20	$CH_2{=}C(CH_3)CH{=}CHC(CH_3)_2OH$ (20), $P^*CH_2C(CH_3){=}C(CH_3)C(CH_3)_2OH$ (66)
	$(CH_3)_2C{=}CHBr$	P*H	2[f]	40	nonadienols (36; 15% I, 13% II, 5% III, 3% IV)[l]
	$(CH_3)_2C{=}CHBr$	P*H	2[g]	40	nonadienols (61; 25% I, 22% II, 8% III, 5% IV), $P^*C(CH_3)_2CH{=}CHCH_2C(CH_3)_2OH$ (27), $(CH_3)_2C{=}CHCH(P^*)CH_2C(CH_3)_2OH$ (10)
		P*H	2[k]	24	nonadienols (51; 32% I, 8% II, 8% III, 4% IV), $P^*C(CH_3)_2CH{=}CHCH_2C(CH_3)_2OH$ (39), $(CH_3)_2C{=}CHCH(P^*)CH_2C(CH_3)_2OH$ (8)
		Et_3N	2[g]	72	nonadienols (59; 30% I, 5% II, 17% III, 7% IV)
		Et_3N	2	72	nonadienols (63; 40% I, 4% II, 14% III, 3% IV)
		Et_3N	6	72	nonadienols (73; 46% I, 4% II, 18% III, 4% IV)
		Et_3N	2[m]	72	nonadienols (65; 44% I, 7% II, 10% III, 4% IV)
		Et_3N	2[n]	72	nonadienols (81; 66% I, 4% II, 10% III, 2% IV)
$CH_2{=}CHC(CH_3)_2OH$	(*E*)-$CH_3O_2CC(CH_3){=}CHBr$	Et_3N	2	20	(*E,E*)-$CH_3O_2CC(CH_3){=}CHCH{=}CHC(CH_3)_2OH$ (55)
$CH_2{=}CH(CH_2)_2OH$	(*Z*)-$CH_3CH{=}CHBr$	P*H	2	3	(*E*)-$CH_3CHP^*CH{=}CH(CH_2)_3OH$ (32), $CH_3CH{=}CHCHP^*(CH_2)_3OH$ (10), $CH_3CHP^*CH{=}C(CH_3)(CH_2)_2OH$ (10)
$CH_2{=}CH(CH_2)_3OH$	(*Z*)-$CH_3CH{=}CHBr$	MH	2	25	(*E*)-$CH_3CHMCH{=}CH(CH_2)_4OH$ (32), $CH_3CH{=}CHCHM(CH_2)_4OH$ (12), $CH_3CHMCH{=}C(CH_3)(CH_2)_3OH$ (12)
	(*Z*)-$CH_3CH{=}CHBr$	P*H	2	6	(*E,Z*)-$CH_3CH{=}CHCH{=}CH(CH_2)_3OH$ (20), (*E,Z*)-$CH_3CH{=}CHCH_2CH{=}CH(CH_2)_2OH$ (2), (*Z*)-$CH_3CH{=}CHC(=CH_2)(CH_2)_3OH$ (5), $P^*CH(CH_3)CH{=}CH(CH_2)_4OH$ (23), (*E*)-$CH_3CH{=}CHCH(P^*)(CH_2)_4OH$ (11), (*E*)-$CH_3CH(P^*)CH{=}C(CH_3)(CH_2)_3OH$ (11)
$CH_2{=}C(CH_3)(CH_2)_2OH$	$(CH_3)_2C{=}CHBr$	Et_3N	2	14[e]	$(CH_3)_2C{=}CHCH{=}C(CH_3)(CH_2)_2OH$ (64, *E/Z* ratio ≈ 2)
$CH_2{=}CH(CH_2)_8OH$[n]	$CH_2{=}CHBr$	MH	2	7	(*E*)-$MCH_2CH{=}CH(CH_2)_3OH$ (82)
$CH_2{=}CHC(CH_3)_2OH$	(*E*)-$CH_3O_2CC(CH_3){=}CHBr$	Et_3N	2	20	(*E,E*)-$CH_3O_2CC(CH_3){=}CHCH{=}CHC(CH_3)_2OH$ (55)

[a] Reaction conditions: 10 mmol of vinylic bromide, 12.5 mmol of unsaturated alcohol, 30 mmol of amine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 mmol of triarylphosphine (if used) were heated at 100 °C until all of the vinylic halide had disappeared as determined by GLC analyses. [b] P*H = piperidine and MH = morphine. Yields are based upon the vinylic halide employed. [c] Products obtained after acidic hydrolysis. [d] 2.5% $Pd(OAc)_2$ used. [e] Carried out at 130 °C. [f] 0.20 mmol of $Pd(OAc)_2$ and 0.40 mmol of triphenylphosphine were employed. [g] Triphenylphosphine was used. [h] 1,2-Bis(diphenylphosphino)ethane was used. [i] Triethylphosphine was used. [j] Tris[*p*-(dimethylamino)-phenyl]-phosphine was used. [k] Tris(2,5-diisopropylphenyl)phosphine was used. [l] I = $(CH_3)_2C{=}CHCH{=}CHC(CH_3)_2OH$; II = $CH_2{=}C(CH_3)CH{=}CHCH_2C(CH_3)_2OH$; III = $(CH_3)_2C{=}CHC(=CH_2)C(CH_3)_2OH$; IV = $CH_2{=}C(CH_3)CH{=}C(CH_3)C(CH_3)_2OH$. [m] Tris(*o*-ethylphenyl)phosphine was used. [n] 30 mmol of alcohol used with 10 mmol of $CH_2{=}CHBr$.

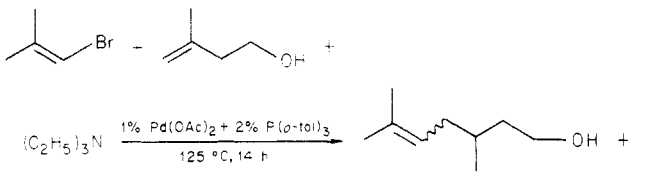
expense of the nonadienols, and the isomer ratios change moderately. The effect can be seen more clearly in the series of reactions carried out with triethylamine and various phosphines where nonadienols are the only volatile products. A significant steric effect of the phosphine can be seen in the series triphenyl-, tri-*o*-tolyl-, tri-*o*-ethylphenyl-, and tris(2,5-diisopropylphenyl)phosphine. The total yield of nonadienols increased from 59% to 81%, and the percentage of the major isomer, 2,6-dimethyl-3,5-heptadien-2-ol, increased also from 50% to 81% through the series. The larger phosphines apparently orient the coordinated unsaturated alcohol in the intermediate so that migration of the 1-isobutenyl group to the terminal double bond carbon is more favorable.

The third vinylic bromide reacted with the tertiary allylic alcohol was (*E*)-methyl 3-bromo-2-methylacrylate. This reaction with triethylamine as the base gave a single product, the conjugated dienol, in 55% yield (eq 12).



55% (12)

Four unsaturated alcohols which were not allylic were also reacted with vinylic bromides. The reaction products of 3-buten-1-ol and 4-penten-1-ol with (*Z*)-1-bromo-1-propene and piperidine or morpholine are predictable on the basis of formation of both regioisomeric adducts and then either elimination of metal hydride to form dienol or elimination and readdition to form π-allylic complexes which form allylic amines. The reactions are not preparatively useful since isomeric mixtures are obtained. The methyl branch in 3-methyl-3-buten-1-ol causes a much more selective reaction. Even with 1-bromo-2-methyl-1-propene only one product is formed, 3,6-dimethyl-3,5-heptadien-1-ol in a 64% yield as a 2:1 mixture of *E* and *Z* isomers (eq 13).



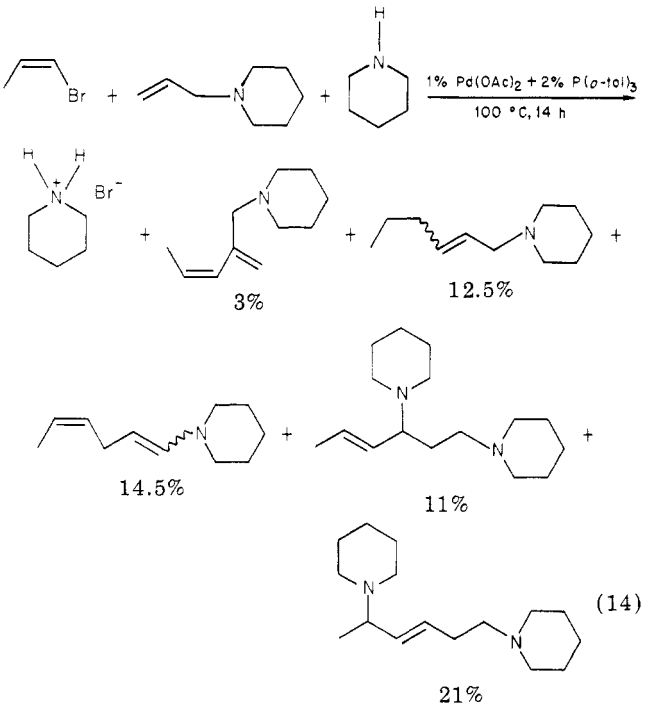
64% (*E*/*Z* ratio = 2)

$(C_2H_5)_3NH^+Br^-$ (13)

The fourth nonallylic alcohol studied, 9-nonen-1-ol, was reacted with vinyl bromide and morpholine to form 12-morpholino-10-dodecen-1-ol in 82% yield. This yield was obtained by use of 3 mol of the alcohol/mol of vinyl bromide. A 15% lower yield is obtained when only a 25% excess of the alcohol is present because of competitive decomposition of the vinyl bromide.[2] The amine product is of value since when submitted to the Hofmann elimination, it forms the pheromone of the red bollworm moth, 9,11-dodecadien-1-ol, in 83% yield with an *E*/*Z* ratio = 2.6, close to the ratio produced by the insect.

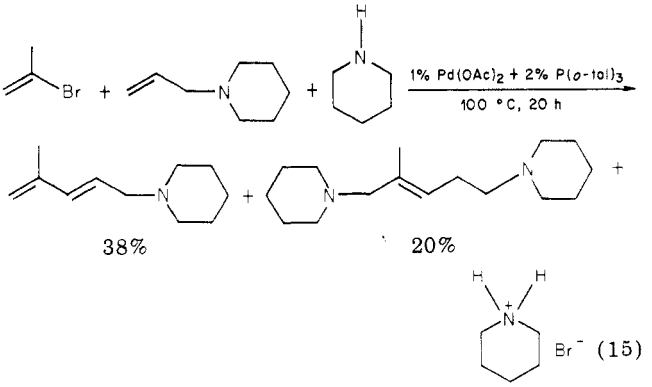
Allylic Amines. Since enamines generally are products of the palladium-catalyzed reaction of primary allylic alcohols with vinylic halides and secondary amines, it could be possible to prepare them directly by reacting tertiary allylic amines with vinylic halides and a palladium catalyst. We studied several examples of the reaction, and the results are shown in Table II. Because of the problem of the palladium-catalyzed interchange of allylic amine groups with secondary amines,[6] it was necessary to have the same two groups on the secondary amines as were in the tertiary allylic amine. Some significant differences from the allylic alcohol reactions were seen.

(*Z*)-1-Bromo-1-propene and *N*-allylpiperidine with piperidine as the base react in the presence of the usual catalyst to form a mixture of five products: two regioisomeric allylic amines, two regioisomeric diamines, and the piperidine enamine of (*Z*)-4-hexenal (eq 14). (*Z*)-4-Hexenal was not seen in the corresponding allyl alcohol reaction. Pure (*Z*)-4-hexenal can be obtained easily in good yield on the basis of the enamine present from the crude reaction mixture by treatment with aqueous acid followed by extraction or steam distillation of the aldehyde.



(14)

The 2-bromopropene–*N*-allylpiperidine reaction gave only two products: the enamine of 4-methyl-4-pentenal and 1,5-dipiperidino-2-methyl-2-pentene (eq 15). The regioisomers observed in the related allyl alcohol reaction were not found in this reaction.



(15)

The reaction of 1-bromo-2-methyl-1-propene with *N*-allylpiperidine is similar to the reaction with allyl alcohol. The products were mixtures of two regioisomeric diamines.

(6) K. E. Atkins, W. E. Walker, and R. W. Manyik, *Tetrahedron Lett.*, 3821 (1970).

Table II. Reactions of Vinylic Bromides with Tertiary Allylic Amines[a]

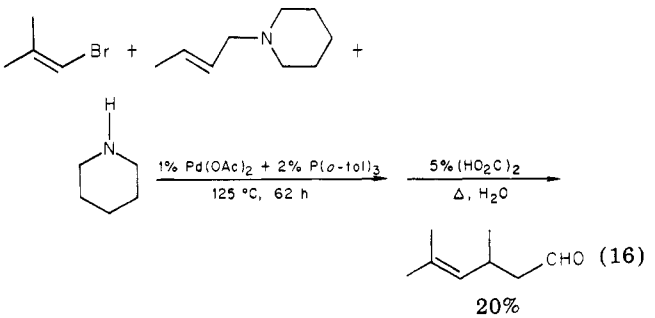
allylic amine[b]	vinylic bromide	reaction time, h (at 100 °C)	products (% yield)
CH_2=$CHCH_2$P*	(Z)-CH_3CH=CHBr	14 h	CH_3CH=$CHC(CH_3)$=CHP* and CH_3CH=$CHC(CH_2P*)$=CH_2 (3), CH_3CH=$CHCH$=$CHCH_2$P* (12.5), CH_3CH=$CHCH_2CH$=CHP* (14.5), CH_3CH=$CHCH(P*)(CH_2)_2$P* and $CH_3CH(P*)CH$=$C(CH_3)CH_2$P* (11), $CH_3CH(P*)CH$=$CH(CH_2)_2$P* (21)
	CH_2=$C(CH_3)$Br	20 h	CH_2=$C(CH_3)CH_2CH$=CHP* (38), P*$CH_2C(CH_3)$=$CH(CH_2)_2$P* (20)
	$(CH_3)_2$C=CHBr	18 h	$(CH_3)_2C$=$CHC(CH_2P*)$=CH_2 (8.5), $(CH_3)_2C$=$CHCH$=$CHCH_2$P* (45), $(CH_3)_2C(P*)CH$=$CH(CH_2)_2$P* (3), $(CH_3)_2C$=$CHCH(P*)(CH_2)_2$P* (3), CH_2=$C(CH_3)CH$=$C(CH_3)CH_2$P* (1.5)
CH_2=$CHCH_2N(CH_3)_2$[c]	CH_2=$C(CH_3)$Br	44 h	CH_2=$C(CH_3)CH_2CH$=$CHN(CH_3)_2$ and $(CH_3)_2NCH_2C(CH_3)$=$CH(CH_2)_2N(CH_3)_2$ (~1:1)
CH_2=$C(CH_3)CH_2$P*	(Z)-CH_3CH=CHBr	282 h	CH_2CH=$CHCH_2C(CH_3)$=CHP* (7), CH_3CH=$CHCH$=$C(CH_3)CH_2$P* (5), $CH_3CH(P*)CH$=$CHCH(CH_3)CH_2$P* (26)
	CH_2=$C(CH_3)$Br	90 h (at 125 °C)	CH_2=$C(CH_3)CH_2C(CH_3)$=CHP* (15), P*$CH_2C(CH_3)$=$CHCH(CH_3)CH_2$P* (12)
	$(CH_3)_2$C=CHBr	10 days (at 125 °C)	$(CH_3)_2C$=$CHCH$=$C(CH_3)CH_2$P* (36), $(CH_3)_2C$=$CHCH_2C(CH_3)$=CHP* (6), CH_2=$C(CH_3)CH$=$CHCH(CH_3)CH_2$P* (4), $(CH_3)_2C(P*)CH$=$CHCH(CH_3)CH_2$P* (12)
(E)-CH_3CH=$CHCH_2$P*	$(CH_3)_2$C=CHBr	62 h (at 125 °C)	$(CH_3)_2C$=$CHCH(CH_3)CH_2CHO$[d] (20), $(CH_3)_2C$=$CHCH(CH_3)CH$=CHP* (22), CH_2=$CHCH[CH$=$C(CH_3)_2]CH_2$P* (6), $(CH_3)_2C$=$CHCH$=$CHCH[CH$=$C(CH_3)_2]CH_2$P* (2), 2 unknowns (~10)

[a] Reaction conditions: 10 mmol of vinylic bromide, 12.5 mmol of allylic amine, 30 mmol of piperidine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 mmol of tri-o-tolylphosphine were heated at 100 °C until the vinylic halide had disappeared as determined by GLC analyses. [b] P*H = piperidine. [c] The base was dimethylamine. [d] Product obtained after hydrolysis of the reaction mixture with aqueous acid.

We briefly investigated the effect of changing the amine substituents upon the allylic amine–vinylic halide reaction. The use of allyldimethylamine with dimethylamine as the base in the reaction with 2-bromopropene led to the formation of enamine and diamine in about a 1:1 ratio at a rate about half that observed for the corresponding piperidine reaction. Therefore, there did not appear to be any advantage to changing amine substituents although yields were not obtained in the dimethylamine reaction.

The *N*-methallylpiperidine–vinylic bromide reactions, in general, were slower than the related methallyl alcohol reactions, and the yields of products were lower. The products were usually mixtures of enamines, dienylamines, and diamines. The *N*-methallylpiperidine was not as useful as methallyl alcohol for forming aldehydes (enamines).

N-(*Z*)-Crotylpiperidine was reacted with only one vinylic bromide, 1-bromo-2-methyl-1-propene. The reaction produced mainly enamine, and acid hydrolysis and steam distillation of the reaction mixture produced pure 3,5-dimethyl-4-hexenal in 20% yield (eq 16). This reaction



(16)

20%

is superior to the related crotyl alcohol reaction because only one regioisomeric aldehyde is obtained although the yield of this isomer is lower from the amine.

The allylic amines offer an advantage over the related allylic alcohol reactions in some cases where enamines are the desired products since the allylic amine reactions are less likely to form mixtures of regioisomers. The yield of any one product is usually low, but the reactants are often readily available, and the reaction may be the most convenient way to prepare certain 4-enals and diamines.

Allylic Tetrahydropyranyl Ethers. Table III reports the reactions of several allylic tetrahydropyranyl ethers with vinylic bromides under the usual catalytic conditions. It is immediately clear from the data in the table that the total yields of products from the allylic tetrahydropyranyl ethers are significantly higher than those obtained from related reactions with either the allylic alcohols or amines. It is also notable that mixtures of regioisomeric products are *not* obtained in any of the examples. Even 1-bromo-2-methyl-1-propene and allyl tetrahydropyranyl ether only gave products with the 2-methylpropenyl group added to the terminal carbon of the ether.

2-Bromopropene and allyl tetrahydropyranyl ether with piperidine as the base produced 28% enol ether (*E*/*Z* ratio = 0.87), 17% dienol ether, and 51% amino ether (eq 17). This reaction, therefore, is useful for preparing the amino alcohol since it can be obtained by hydrolysis of the ether, and the ether is produced in higher yield than from allyl alcohol and is free of the regioisomer.

Similarly, the 1-bromo-2-methyl-1-propene–allyl tetrahydropyranyl ether reaction (eq 18) would be more useful than the ally alcohol reaction for preparing an amino alcohol (ether) also because the yield is higher from the allyl ether and because only one of the two possible allylic amine isomers is formed.

Table III. Reactions of Vinylic Bromides with Allylic Tetrahydropyranyl Ethers and Amines[a]

allylic tetrahydropyranyl ether[b]	vinylic bromide	amine[c]	catalyst $P(o\text{-tol})_3$/$Pd(OAc)_2$ ratio	reaction time, h (at 100 °C)	products (% yield)
CH_2=$CHCH_2OTHP$	CH_2=$C(CH_3)Br$	P*H	2	19	(*Z*)-CH_2=$C(CH_3)CH_2CH$=$CHOTHP$ (15), (*E*)-CH_2=$C(CH_3)CH_2CH$=$CHOTHP$ (13), CH_2=$C(CH_3)CH$=$CHCH_2OTHP$ (17), P*$CH_2C(CH_3)$=$CH(CH_2)_2OTHP$ (51)
	$(CH_3)_2C$=$CHBr$	P*H	2	19	CH_2=$C(CH_3)CH$=$CH(CH_2)_2OTHP$ (14), $(CH_3)_2C$=$CHCH$=$CHCH_2OTHP$ (23), $(CH_3)_2C$(P*)CH=$CH(CH_2)_2OTHP$ (35)
CH_2=$CHCH(CH_3)OTHP$	CH_2=$C(CH_3)Br$	P*H	2[d]	44	CH_2=$C(CH_3)CH$=$CHCH(CH_3)OTHP$ (63), P*$CH_2C(CH_3)$=$CHCH_2CH(CH_3)OTHP$ (28)
		P*H	2[e]	37	(*E*)-CH_2=$C(CH_3)CH$=$CHCH(CH_3)OTHP$ (63), P*$CH_2C(CH_3)$=$CHCH_2CH(CH_3)OTHP$ (28)
		MH	2	65	CH_2=$C(CH_3)CH$=$CHCH(CH_3)OTHP$ (33), MC$H_2C(CH_3)$=$CHCH_2CH(CH_3)OTHP$ (46)
CH_2=$C(CH_3)CH_2OTHP$	CH_2=$C(CH_3)Br$	P*H	2	44 (at 125 °C)	CH_2=$C(CH_3)CH_2C(CH_3)$=$CHOTHP$ (26, *E*/*Z* ratio = 1), CH_2=$C(CH_3)CH_2C(=CH_2)CH_2OTHP$ (11), P*$CH_2C(CH_3)$=$CHCH(CH_3)CH_2OTHP$ (30)

[a] Reaction conditions: 10 mmol of vinylic bromide, 12.5 mmol of allylic ether, 30 mmol of amine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 mmol of tri-*o*-tolylphosphine were heated at 100 °C until the vinylic bromide had disappeared as determined by GLC analysis. Yields are based upon the vinylic halide employed. [b] THP = tetrahydropyranyl. [c] P*H = piperidine; MH = morpholine. [d] Triphenylphosphine was used. [e] Tris(2,5-diisopropylphenyl)phosphine was used.

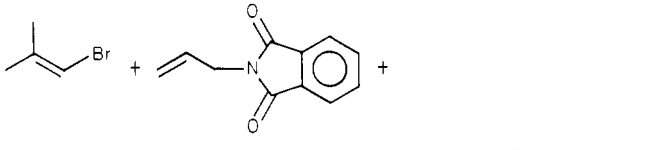
The methallyl tetrahydropyranyl ether–2-bromopropene reaction also is most useful for preparing the amino alcohol (ether). In a slow reaction, these reactants form a mixture of enol ether, dienyl ether, and amino ether.

Reactions of 3-buten-2-yl tetrahydropyranyl ether with 2-bromopropene, on the other hand, are useful for the preparation of dienyl ethers or dienols since dienols were not seen in the related allylic alcohol (3-buten-2-ol) reaction. Under the most favorable conditions with triphenylphosphine in the catalyst, the dienyl ether was obtained in 63% yield along with 28% amino ether (eq 19).

The use of tris(2,4-diisopropylphenyl)phosphine in place of triphenylphosphine gave a higher yield of amino ether (39%) and less of the dienyl ether (54%). Morpholine with tri-*o*-tolylphosphine in the catalyst produced 46% amino ether and 33% dienyl ether in the same reaction. The acid hydrolysis of the dienyl pyranyl ethers does not occur cleanly. The dienol is best obtained by pyrolysis of the ether.

The allylic ethers, therefore, complement the allylic alcohol and amine reactions, in some instances producing products not obtained in the other reactions.

***N*-Allylphthalimide.** Previous results indicate that *N*-allylphthalimide will alkenylate to form the allylic rather than vinylic imide products since the more hydridic hydrogen is usually eliminated. Three vinylic bromides and bromobenzene were reacted with the *N*-allylphthalimide and triethylamine. In all cases only allylic elimination was observed. It is surprising in view of the difficulties observe in other cases (see above) that triethylamine performed well as the base, giving 58–85% yields of the allylic imides as the only identifiable products. Tri-*o*-tolylphosphine (6%) was used in two reactions to prevent precipitation of palladium during the reaction. The results are summarized in Table IV. For example, 1-bromo-2-methyl-1-propene gave 70% of the dienylimide (eq 20). Attempts

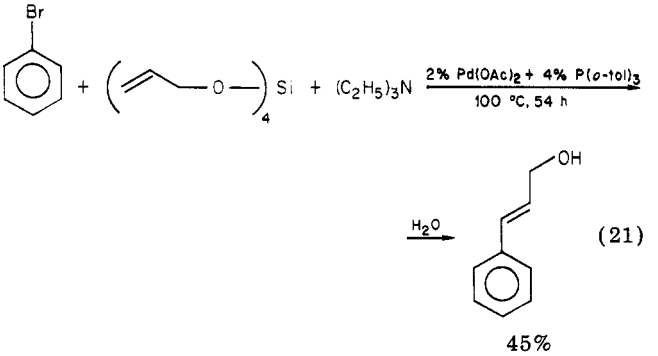


70%

$(C_2H_5)_3NH^+Br^-$ (20)

to isomerize the allylic double bond in the above product to form the vinylic imide with potassium *tert*-butoxide in benzene were unsuccessful. Only the starting material was recovered from the reaction. The reaction provides a convenient route to 2,4-dienyl amines and cinnamylamines obtained by conventional hydrolysis of the imide products.

Allylic Silyl Ethers. We briefly studied the palladium-catalyzed 1-bromo-2-methyl-1-propene and bromobenzene reactions with tetraallyl silicate in the hope of finding selective reactions. The results are summarized in Table V. The reactions were rather slow with triethylamine as the base, and there was a serious problem with incomplete reactions. In all of the examples studied, reactions stopped because of precipitation of palladium after only about 50% reaction. Changing reactant ratios, phosphine concentration, reaction temperature, solvent, etc. failed to cause the reactions to go to completion. Products were analyzed after basic aqueous hydrolysis since mixtures of silicate esters were the direct products. When 4:2 mol % ratios (relative to the halide) of tri-*o*-tolylphosphine to palladium acetate were used as catalyst, yields of products were high based upon the bromide reacted. The vinylic bromide gave mixtures of regioisomeric products, unfortunately, while bromobenzene gave only cinnamyl alcohol after hydrolysis (eq 21). The phenylation



(21)

45%

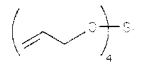
of tetraallyl silicate is much more selective than the phenylation of allyl alcohol, and the product is cinnamyl al-

Table IV. Reactions of Vinylic Bromides with *N*-Allylphthalimide and Amines[a]

vinylic bromide	catalyst $P(o\text{-tol})_3$/$Pd(OAc)_2$ ratio	reaction time, h (at 100 °C)	products (% yield)
CH_2=$CHCH_2$PHTH[b]	CH_2=$C(CH_3)$Br	6	98 (at 125 °C)	(*E*)-CH_2=$C(CH_3)$$CH$=$CHCH_2$PHTH (58)
	$(CH_3)_2C$=CHBr	6	44	(*E*)-$(CH_3)_2C$=$CHCH$=$CHCH_2$PHTH (70)
	(*E*)-$CH_3O_2CC(CH_3)$=CHBr	2	12	(*E,E*)-$CH_3O_2CC(CH_3)$=$CHCH$=$CHCH_2$PHTH (85)[c]
	C_6H_5Br	2	20	(*E*)-C_6H_5CH=$CHCH_2$PHTH (73)

[a] The amine was Et_3N in all cases. Reaction conditions: 11 mmol of vinylic bromide, 10 mmol of *N*-allylphthalimide, 30 mmol of amine, 0.10 mmol of $Pd(OAc)_2$, and 0.20 or 0.60 mmol of tri-*o*-tolylphosphine were heated at 100 or 125 °C as indicated. Yields are based upon the organic halide employed. [b] PHTH = phthalimidyl group. [c] Experiment carried out by Dr. K. T. Mak.

Table V. Palladium-Catalyzed Reactions of Tetraallyl Silicate with Halides and Amines

silicon compd	halide[a]	catalyst mol % $P(o\text{-tol})_3$/ mol % $Pd(OAc)_2$ ratio[d]	reaction time, h (100 °C)	product (% yield after hydrolysis)
		2/1	7 (125 °C)	$(CH_3)_2C{=}CHCH{=}CHCH_2OH$ (25),[b] $(CH_3)_2CHCH{=}C(CH_3)CHO$ (4)[b]
	[c]	4/2	24 + 24 (125 °C)	$(CH_3)_2C{=}CHCH{=}CHCH_2OH$ (40), $(CH_3)_2C{=}CHC(=CH_2)CH_2OH$ (10)
	PhBr	2/1	24	$PhCH{=}CHCH_2OH$ (20)[b]
	[c]	4/2	54	$PhCH{=}CHCH_2OH$ (45)
		2/1	24 (50 °C)	$PhCH{=}CHCH_2OH$ (16)

[a] Conditions were 20% excess halide. [b] Yields are based upon the silicate ester employed. [c] Ratio of halide to silicate = 2. Yields are based upon the organic bromide. [d] The amine was NEt_3 in all cases.

cohol rather than a mixture of 2- and 3-phenylpropanals.[7] The low conversions limit the value of the reaction, however. A reaction of the trimethylsilyl ether of 3-methyl-1-buten-3-ol with 1-bromo-2-methyl-1-propene and triethylamine was very slow and produced products containing methyl groups from the trimethylsilyl group rather than allylic ether derivatives.

Conclusions

Five classes of allylic derivatives have been reacted with vinylic bromides (and in some cases bromobenzene) and a palladium catalyst with an amine to determine the synthetic value of the reactions. In the allylic alcohol group we found that methallyl alcohol is useful for the synthesis of 2-methyl-4-pentenal derivatives, and the secondary allylic alcohols 3-buten-2-ol and 1-penten-3-ol give good yields of easily separable mixtures of 4-enones and amino alcohols. The nonallylic, unsaturated alcohols 3-methyl-3-buten-1-ol and 9-decen-1-ol also reacted selectively with vinylic bromides. The second class of derivatives reacted was allylic amines. In some instances, the allylic amines showed higher selectivity in forming 4-enals after hydrolysis of the product enamines than the allylic alcohols did because there was generally less tendency for the allylic amines to undergo vinylation at the internal double bond carbon and form regioisomers. The allylic tetrahydropyranyl ethers generally reacted with vinylic bromides to give high yields of products. Mixtures of dienyl ethers and aminoalkenyl ethers were obtained. These reactions complement the allylic alcohol reactions since substantial amounts of dienyl ethers are obtained while little dienol is fomed in most of the allylic alcohol reactions. *N*-Alkylphthalimide was the most useful reactant in terms of product selectivity. In the four examples studied, all gave a single product, *N*-(2,4-dienyl) phthalimides, in fair to good yields. The last group of the five studied is the allylic silyl ethers. Their reactions with vinylic bromides showed high selectivity with aryl but not with vinylic brmoides; however, low conversions were generally encountered, limiting the value of the reactions.

Experimental Section

Materials. Vinylic Bromides. Vinyl bromide (Aldrich), 2-bromopropene (Aldrich), (*E* + *Z*)-1-bromo-1-propene (Columbia), 2-bromo-1-butene (Columbia), and (*E* + *Z*)-2-bromo-2-butene (Columbia) were used as received from commerical sources. The isomeric mixtures were separated by fractional distillation. 1-bromo-2-methyl-1-propene,[8] (*E*)-methyl 3-bromo-2-methylacrylate,[9] and (*Z*)-3-iodo-3-hexene[10] were prepared by literature methods. **Unsaturated Alcohols.** Allyl alcohol (Eastman), methallyl alcohol (Aldrich), crotyl alcohol (Aldrich), 3-buten-2-ol (Aldrich), 1-penten-3-ol (Chemical Samples), 2-methyl-3-buten-2-ol (Aldrich), 3-buten-1-ol (Aldrich), 4-penten-1-ol (Aldrich), 9-decen-1-ol (Aldrich), and 3-methyl-3-buten-1-ol (Aldrich) were obtained from commercial sources and used without further purification. **Allylic Amines.** *N*,*N*-dimethylallylamine was obtained from Eastman Organic Chemicals while *N*-allylpiperidine [bp 46 °C (14 mm)], *N*-methallylpiperidine [bp 57 °C (9 mm)], and *N*-crotylpiperidine [bp 94 °C (38 mm)] were obtained from the reaction of excess piperidine with the appropriate allylic chloride follwed by aqueous base treatment and distillation. **Allylic Tetrahydropyranyl Ethers.** The allyl [bp 65 °C (20 mm)], methallyl [bp 50 °C (10 mm)], and 3-buten-2-yl [bp 52 °C (10 mm)] ethers were all obtained by treatment of the alcohol and dihydropyran with a concentrated hydrochloric acid catalyst.[11] ***N*-Allylphthalimide.** This compound was prepared from potassium phthalimide and allyl chloride in ethanol: 90% yield; mp 63–64 °C.[12] **Tetraallyl Silicate.** The preparation of this compound [bp 79–81 °C (34 mm)] was carried out according to the procedure of Peppard et al.[13] **3-Methyl-1-buten-3-yl Trimethylsilyl Ether.** 3-Methyl-1-buten-3-ol, trimethylsilyl chloride, and pyridine formed the ether: 70% yield; bp 38–39 °C (38 mm). **Miscellaneous.** Palladium acetate, tri-*o*-tolylphosphine, tris(2,5-diisopropylphenyl)phosphine, and tris(*o*-ethylphenyl)phosphine were obtained as previously described.[2,14] Triphenylphosphine (Aldrich), triethylphosphine (Aldrich), and 1,2-bis(diphenylphosphino)ethane (Strem) were commercial samples and were used as received. Dimethylamine (Union Carbide), piperidine (Aldrich), triethylamine (Aldrich), and morpholine (Aldrich) were also commercial samples which were used after being dried with molecular sieves.

General Procedure for the Reaction of Vinylic Bromides with Allylic Derivatives. Solutions of 10 mmol of vinylic (or aryl) bromide, 12.5 mmol of allylic derivative (or other amount as noted in the tables), 30 mmol of the amine, 1 mol % of palladium acetate (based upon the vinylic bromide), and 2 mol % of phosphine (or other amounts as indicated in the tables) were prepared in heavy-walled Pyrex tubes. Reaction mixtures with 5–10 times the above quantities were prepared in Pyrex bottles for preparative experiments. The homogeneous reaction mixtures were heated in a steam or oil bath at the appropriate temperature until GLC analyses showed that the vinylic bromide (or bromobenzene) had all reacted. Products were isolated by adding dilute

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aqueous sodium hydroxide to the cooled reaction mixtures and extracting the products with ether. Generally the combined extracts were dried with $MgSO_4$ and distilled under reduced pressure.

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Registry No. (*E*)-P*CH(CH$_3$)CH=CH(CH$_2$)$_2$OH, 80719-73-9; (*E*)-P*CH(CH$_3$)CH=C(CH$_3$)CH$_2$OH, 80719-74-0; (*E*)-CH$_3$CH=CHCH(P*)(CH$_2$)$_2$OH, 80719-75-1; (*E*)-MCH(CH$_3$)CH=CH-(CH$_2$)$_2$OH, 80719-76-2; (*E*)-MCH(CH$_3$)CH=C(CH$_3$)CH$_2$OH, 80719-77-3; (*E*)-CH$_3$CH=CHCH(M)(CH$_2$)$_2$OH, 80719-78-4; CH$_2$=C(CH$_3$)(CH$_2$)$_2$CHO, 3973-43-1; CH$_2$=C(CH$_3$)CH(CH$_3$)CHO, 80719-79-5; (*E*)-P*CH$_2$C(CH$_3$)=CH(CH$_2$)$_2$OH, 80719-80-8; (*E*)-P*CH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$OH, 80719-81-9; CH$_2$=C(CH$_3$)CH=CHCH$_2$OH, 80719-82-0; CH$_2$=C(CH$_3$)(CH$_2$)$_2$CH=C(CHO)CH$_2$C(CH$_3$)=CH$_2$, 3979-63-3; (CH$_3$)$_2$C=CHC(=CH$_2$)CH$_2$OH, 80719-83-1; (*E*)-CH$_2$=C(CH$_3$)-CH=CH(CH$_2$)$_2$OH, 80719-84-2; (*E*)-(CH$_3$)$_2$C=CHCH=CHCH$_2$OH, 60958-55-6; (*Z*)-(CH$_3$)$_2$C=CHCH=CHCH$_2$OH, 80719-85-3; (CH$_3$)$_2$C=CHCH(P*)(CH$_2$)$_2$OH, 80719-86-4; (*E*,*E*)-CH$_3$O$_2$CC(CH$_3$)-=CHCH=CHCH$_2$OH, 80719-87-5; (*Z*,*X*)-CH$_3$CH=CHCH$_2$C-(CH$_3$)=CHM, 80719-88-6; MCH(CH$_3$)CH=CHCH(CH$_3$)CH$_2$OH, 80719-89-7; (*Z*,*X*)-CH$_3$CH=CHCH$_2$C(CH$_3$)=CHP*, 80719-90-0; P*CH(CH$_3$)CH=CHCH(CH$_3$)CH$_2$OH, 80719-91-1; CH$_2$=C(CH$_3$)-CH$_2$C(CH$_3$)=CHP*, 80719-92-2; CH$_2$=C(CH$_3$)CH$_2$CH(CH$_3$)CHO, 5187-72-4; (CH$_3$)$_2$C=CHCH$_2$C(CH$_3$)=CHP*, 80719-93-3; P*C-(CH$_3$)$_2$CH=CHCH(CH$_3$)CH$_2$OH, 80719-94-4; (CH$_3$)$_2$C=CHCH$_2$C-H(CH$_3$)CHO, 870-17-7; (CH$_3$)$_2$CHCH$_2$CH=C(CH$_3$)CHO, 35158-33-9; (CH$_3$)$_2$C=CHCH=C(CH$_3$)CH$_2$OH, 80719-95-5; (CH$_3$)$_2$C=CHCH$_2$C-(CH$_2$OH)=CH$_2$, 80719-96-6; CH$_3$O$_2$CC(CH$_3$)=CHCH$_2$CH(CH$_3$)CH-O, 80719-97-7; CH$_3$O$_2$CC(CH$_3$)=CHCH=C(CH$_3$)CH$_2$OH, 80719-98-8; (*Z*,*E*)-C$_2$H$_5$CH=C(C$_2$H$_5$)CH$_2$C(CH$_3$)=CHP*, 80719-99-9; MCH$_2$CH=C(CH$_3$)(CH$_2$)$_2$OH, 80720-00-9; MCH$_2$CH=C(C$_2$H$_5$)-CH$_2$OH, 80720-01-0; MCH$_2$C(CH$_3$)=C(CH$_3$)(CH$_2$)$_2$OH, 80720-02-1; MCH$_2$C(CH$_3$)=C(C$_2$H$_5$)CH$_2$OH, 80720-03-2; CH$_2$=C(CH$_3$)CH-(CH$_3$)CH=CHM, 80720-04-3; P*CH$_2$C(CH$_3$)=C(CH$_3$)(CH$_2$)$_2$OH, 80720-05-4; P*CH$_2$C(CH$_3$)=C(C$_2$H$_5$)CH$_2$OH, 80720-06-5; CH$_2$=C-(CH$_3$)CH(CH$_3$)CH=CHP*, 80720-07-6; (CH$_3$)$_2$C=CH(C$_2$H$_5$)=CHP*, 80720-08-7; (CH$_3$)$_2$C=CHCH(CH$_3$)CH=CHP*, 80720-09-8; (*E*)-CH$_3$O$_2$CC(CH$_3$)=CHCH(CH$_3$)CH$_2$CHO, 80720-10-1; P*CH$_2$CH=CHCH$_2$CH(OH)CH$_3$, 80720-11-2; P*CH$_2$CH=C(CH$_3$)-CH(OH)CH$_3$, 80720-12-3; CH$_2$=C(CH$_3$)(CH$_2$)$_2$COCH$_3$, 3240-09-3; (*Z*)-P*CH$_2$C(CH$_3$)=CHCH$_2$CH(OH)CH$_3$, 80720-13-4; (*Z*)-MCH$_2$C-(CH$_3$)=CHCH$_2$CH(OH)CH$_3$, 80720-14-5; (CH$_3$)$_2$C=CHCH(P*)-CH$_2$CH(OH)CH$_3$, 80720-15-6; CH$_3$O$_2$CC(CH$_3$)=CHCH=CHCH(O-H)CH$_3$, 80720-16-7; CH$_3$O$_2$CC(CH$_3$)=CH(CH$_2$)$_2$COCH$_3$, 80720-17-8; CH$_2$=C(C$_2$H$_5$)(CH$_2$)$_2$COC$_2$H$_5$, 80720-18-9; C$_2$H$_5$C(CH$_2$P*)=CHCH$_2$CH(OH)C$_2$H$_5$, 80720-19-0; (*Z*)-CH$_3$CH=C(CH$_3$)-CH$_2$)$_2$COC$_2$H$_5$, 80720-20-3; CH$_3$CH(P*)C(CH$_3$)=CHCH$_2$CH-(OH)C$_2$H$_5$, 80720-21-4; CH$_2$=C(CH$_3$)CH=CHC(CH$_3$)$_2$OH, 70254-39-6; P*CH$_2$C(CH$_3$)=C(CH$_3$)C(CH$_3$)$_2$OH, 80720-22-5; P*C-(CH$_3$)$_2$CH=CHCH$_2$C(CH$_3$)$_2$OH, 72908-65-7; (CH$_3$)$_2$C=CHCH(P*)-CH$_2$C(CH$_3$)$_2$OH, 72908-66-8; (*E*,*E*)-CH$_3$O$_2$CC(CH$_3$)=CHCH=CHC-(CH$_3$)$_2$OH, 80720-23-6; (*E*)-CH$_3$CH(P*)CH=CH(CH$_2$)$_3$OH, 80720-24-7; CH$_3$CH=CHCH(P*)(CH$_2$)$_3$OH, 80720-25-8; CH$_3$CH(P*)CH=C(CH$_3$)(CH$_2$)$_2$OH, 80720-26-9; (*E*)-CH$_3$CH(M)CH=CH(CH$_2$)$_4$OH, 80720-27-0; CH$_3$CH=CHCH(M)(CH$_2$)$_4$OH, 80720-28-1; CH$_3$CH-(M)CH=C(CH$_3$)(CH$_2$)$_3$OH, 80720-29-2; (*E*,*Z*)-CH$_3$CH=CHCH=CH(CH$_2$)$_3$OH, 80720-30-5; (*E*,*Z*)-CH$_3$CH=CHCH$_2$CH=CH-(CH$_2$)$_2$OH, 80720-31-6; (*Z*)-CH$_3$CH=CHC(=CH$_2$)(CH$_2$)$_3$OH, 80720-32-7; P*CH(CH$_3$)CH=CH(CH$_2$)$_4$OH, 80720-33-8; (*E*)-CH$_3$CH=CHCH(P*)(CH$_2$)$_4$OH, 80720-34-9; (*E*)-CH$_3$CH(P*)CH=C-(CH$_3$)(CH$_2$)$_3$OH, 80720-35-0; (*E*)-(CH$_3$)$_2$C=CHCH=C(CH$_3$)-(CH$_2$)$_2$OH, 80720-36-1; (*Z*)-(CH$_3$)$_2$C=CHCH=C(CH$_3$)(CH$_2$)$_2$OH, 80720-37-2; (*E*)-MCH$_2$CH=CH(CH$_2$)$_9$OH, 80720-38-3; CH$_2$=C(C-H$_3$)CH=CHCH$_2$C(CH$_3$)$_2$OH, 80720-39-4; (CH$_3$)$_2$C=CHC(=CH$_2$)-C(CH$_3$)$_2$OH, 36803-65-3; CH$_2$=C(CH$_3$)CH=C(CH$_3$)C(CH$_3$)$_2$OH, 80720-40-7; (CH$_3$)$_2$C=CHCH=CHC(CH$_3$)$_2$OH, 77411-76-8; CH$_3$CH=CHC(CH$_3$)=CHP*, 10321-86-5; CH$_3$CH=CHC(CH$_2$P*)=CH$_2$, 80720-41-8; CH$_3$CH=CHCH=CHCH$_2$P*, 71739-88-3; CH$_3$CH=CHCH$_2$CH=CHP*, 80720-42-9; CH$_3$CH=CHCH(P*)-(CH$_2$)$_2$P*, 80720-43-0; CH$_3$CH(P*)CH=C(CH$_3$)CH$_2$P*, 80720-44-1; CH$_3$CH(P*)CH=CH(CH$_2$)$_2$P*, 51891-45-3; CH$_2$=C(CH$_3$)CH$_2$CH=CHP*, 80720-45-2; P*CH$_2$C(CH$_3$)=CH(CH$_2$)$_2$P*, 80720-46-3; (CH$_3$)$_2$C=CHC(CH$_2$P*)=CH$_2$, 80720-47-4; (CH$_3$)$_2$C=CHCH=CHCH$_2$P*, 80720-48-5; (CH$_3$)$_2$C(P*)CH=CH(CH$_2$)$_2$P*, 80720-49-6; (CH$_3$)$_2$C=CHCH(P*)(CH$_2$)$_2$P*, 80720-50-9; CH$_2$=C(CH$_3$)CH=C-(CH$_3$)CH$_2$P*, 80720-51-0; CH$_2$=C(CH$_3$)CH$_2$CH=CHN(CH$_3$)$_2$, 80720-52-1; (CH$_3$)$_2$NCH$_2$C(CH$_3$)=CH(CH$_2$)$_2$N(CH$_3$)$_2$, 80720-53-2; CH$_3$CH=CHCH$_2$C(CH$_3$)=CHP*, 80720-54-3; CH$_3$CH=CHCH=C-(CH$_3$)CH$_2$P*, 80720-55-4; CH$_3$CH(P*)CH=CHCH(CH$_3$)CH$_2$P*, 80720-56-5; P*CH$_2$C(CH$_3$)=CHCH(CH$_3$)CH$_2$P*, 80720-57-6; (CH$_3$)$_2$C=CHCH-C(CH$_3$)CH$_2$P*, 80720-58-7; CH$_2$=C(CH$_3$)CH=CHCH(CH$_3$)CH$_2$P*, 80720-59-8; (CH$_3$)$_2$C(P*)CH=CHCH(CH$_3$)-CH$_2$P*, 80720-60-1; (CH$_3$)$_2$C=CHCH(CH$_3$)CH$_2$CHO, 80720-61-2; CH$_2$=CHCH[CH=C(CH$_3$)$_2$]CH$_2$P*, 80720-62-3; (CH$_3$)$_2$C=CHCH=CHCH[CH=C(CH$_3$)$_2$]CH$_2$P*, 80720-63-4; (*Z*)-CH$_2$=C(CH$_3$)-CH$_2$CH=CHOTHP, 80720-64-5; (*E*)-CH$_2$=C(CH$_3$)CH$_2$CH=CHOTHP, 80720-65-6; CH$_2$=C(CH$_3$)CH=CHCH$_2$OTHP, 80720-66-7; P*CH$_2$C(CH$_3$)=CH(CH$_2$)$_2$OTHP, 80720-67-8; CH$_2$=C(CH$_3$)C-H=CH(CH$_2$)$_2$OTHP, 80720-68-9; (CH$_3$)$_2$C=CHCH=CHCH$_2$OTHP, 80720-69-0; (CH$_3$)$_2$C(P*)CH=CH(CH$_2$)$_2$OTHP, 80720-70-3; CH$_2$=C(CH$_3$)CH=CHCH(CH$_3$)OTHP, 72908-64-6; P*CH$_2$C(CH$_3$)=CHCH$_2$CH(CH$_3$)OTHP, 80720-71-4; (*E*)-CH$_2$=C(CH$_3$)CH=CHCH-(CH$_3$)OTHP, 80720-72-5; MCH$_2$C(CH$_3$)=CHCH$_2$CH(CH$_3$)OTHP, 80720-73-6; (*E*)-CH$_2$=C(CH$_3$)CH$_2$C(CH$_3$)=CHOTHP, 80720-74-7; (*Z*)-CH$_2$=C(CH$_3$)CH$_2$C(CH$_3$)=CHOTHP, 80720-75-8; CH$_2$=C(C-H$_3$)CH$_2$C(=CH$_2$)CH$_2$OTHP, 80720-76-9; P*CH$_2$C(CH$_3$)=CHCH-(CH$_3$)CH$_2$OTHP, 80720-77-0; (*E*)-CH$_2$=C(CH$_3$)CH=CHCH$_2$PHTH, 80720-78-1; (*E*)-(CH$_3$)$_2$C=CHCH=CHCH$_2$PHTH, 80720-79-2; (*E*,*E*)-CH$_3$O$_2$CC(CH$_3$)=CHCH=CHCH$_2$PHTH, 80720-80-5; (*E*)-C$_6$H$_5$CH=CHCH$_2$PHTH, 56866-32-1; (CH$_3$)$_2$C=CHCH=CHCH$_2$OH, 79507-91-8; (CH$_3$)$_2$CHCH=C(CH$_3$)CHO, 30567-25-0; PhCH=CHCH$_2$OH, 104-54-1; (*Z*)-CH$_3$CH=CHCH$_2$CH(CH$_3$)CHO, 80720-81-6; CH$_2$=C(CH$_3$)CH$_2$C(CH$_3$)=CHM, 58401-81-3; MCH$_2$C-(CH$_3$)=CHCH(CH$_3$)CH$_2$OH, 80720-82-7; CH$_2$=C(CH$_3$)CH(CH$_3$)C-H$_2$CHO, 58654-03-8; (CH$_3$)$_2$C=CH(CH$_2$)$_2$COCH$_3$, 110-93-0; (CH$_3$)$_2$-C=CHCH=CHCH(CH$_3$)OH, 51500-47-1; (CH$_3$)$_2$C=CHCH(CH$_3$)C-OCH$_3$, 36616-77-0; (CH$_3$)$_2$C=CHC(=CH$_2$)CH(OH)C$_2$H$_5$, 80720-83-8; CH$_2$=C(CH$_3$)CH=CHCH$_2$CH(CH$_3$)OH, 53370-69-7; CH$_3$CH$_2$CH=C(C$_2$H$_5$)CH$_2$CH(CH$_3$)CHO, 80720-84-9; P*CH$_2$CH=CH(CH$_2$)$_2$P*, 51891-41-9; P*CH$_2$CH=C(CH$_3$)CH$_2$P*, 42782-81-0; CH$_2$=CHCH=CHCH$_2$P*, 51180-42-8; CH$_2$=CHCH$_2$OH, 107-18-6; (*Z*)-CH$_3$CH=CHBr, 590-13-6; CH$_3$C(Br)=CH$_2$, 557-93-7; (CH$_3$)$_2$C=CHBr, 3017-69-4; (*E*)-CH$_3$O$_2$CC(CH$_3$)=CHBr, 40053-01-8; CH$_2$=C(CH$_3$)CH$_2$OH, 513-42-8; (*E*)-CH$_3$CH=CHCH$_2$OH, 504-61-0; (*Z*)-C$_2$H$_5$CH=C-(I)C$_2$H$_5$, 16403-13-7; CH$_2$=CHBr, 593-60-2; CH$_2$=CHCH(OH)CH$_3$, 598-32-3; CH$_2$=CHCH(OH)C$_2$H$_5$, 616-25-1; C$_2$H$_5$C(Br)=CH$_2$, 23074-36-4; (*Z*)-CH$_3$C(Br)=CHCH$_3$, 3017-68-3; CH$_2$=CHC(CH$_3$)$_2$O-H, 115-18-4; CH$_2$=CH(CH$_2$)$_2$OH, 627-27-0; CH$_2$=CH(CH$_2$)$_3$OH, 821-09-0; CH$_2$=C(CH$_3$)(CH$_2$)$_2$OH, 763-32-6; CH$_2$=CH(CH$_2$)$_3$OH, 13019-22-2; CH$_2$=CHCH$_2$P*, 14446-67-4; CH$_2$=CHCH$_2$N(CH$_3$)$_2$, 2155-94-4; CH$_2$=C(CH$_3$)CH$_2$P*, 673-33-6; (*Z*)-CH$_3$CH=CHCH$_2$P*, 36807-51-9; CH$_2$=CHCH$_2$OTHP, 4203-49-0; CH$_2$=CHCH(CH$_3$)OT-HP, 72908-63-5; CH$_2$=C(CH$_3$)CH$_2$OTHP, 53250-10-5; CH$_2$=CHC-H$_2$PHTH, 5428-09-1; C$_6$H$_5$Br, 108-86-1; (CH$_2$=CHCH$_2$O)$_4$Si, 1067-43-2; (*E*)-1-bromo-1-propene, 590-15-8; (*E*)-2-bromo-2-butene, 3017-71-8; allyl chloride, 107-05-1; methallyl chloride, 563-47-3; (*Z*)-crotyl chloride, 4628-21-1; piperidine, 110-89-4; 3-methyl-1-buten-3-yl trimethylsilyl ether, 19916-99-5; 3-methyl-1-buten-3-ol, 115-18-4; Pd, 7440-05-3.

Supplementary Material Available: Table VI listing the physical properties, NMR spectra, and molecular weights (high-resolution mass spectrum) for the compounds prepared in this study (20 pages). Ordering information is given on any current masthead page.