purified by preparative scale gas chromatography. The product had a carbonyl absorption in carbon tetrachloride solution at 1720 cm^{-1}. The compound gave an orange 2,4-dinitrophenylhydrazone, mp 170.0–170.5° after recrystallization from chloroform–ethanol.

In the absence of dicyclohexylethylamine but with an equal volume of acetonitrile in its place, this reaction produced a solution that was only 0.20 *M* in 3-phenylcyclohexanone under the same reaction conditions.

1-(3-Carbomethoxyphenyl)-3-pentanone. was prepared by the same procedure used above to prepare 1-phenyl-3-pentanone, with 3-carbomethoxyphenylmercuric chloride used in place of phenylmercuric chloride. There was obtained as product, 2.43 g of an orange liquid, bp 142–150° (2 mm), which was about 60% 1-(3-carbomethoxyphenyl)-3-pentanone. A pure sample was separated by preparative scale gas chromatography.

1-(3,4-Dichloro-5-nitrophenyl)-3-pentanone. A mixture of 10 mmol of 5-chloromercuri-3-nitro-1,2-dichlorobenzene, 10 mmol of cupric chloride, 10 mmol of lithium chloride, 12 ml of 1.0 *M* 1-penten-3-ol, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The reaction mixture was concentrated at room temperature under reduced pressure and the product was extracted from the residue with boiling hexane. After concentrating and cooling, the hexane solution gave a sticky solid. Three recrystallizations from aqueous methanol gave nearly colorless needles, mp 56.0–56.5°.

In another experiment like the above the entire crude hot hexane-soluble product was converted into the 2,4-dinitrophenylhydrazone. There was obtained 0.715 g of yellow-orange crystals, mp 158–159°, after recrystallizing from chloroform–methanol.

2-Methyl-4-phenyl-3-buten-2-ol. A mixture of 0.10 mol of phenylmercuric acetate, 50 mmol of mercuric acetate, 100 ml of acetonitrile, 20 ml of 2-methyl-3-buten-2-ol, and 10 mmol of palladium acetate was stirred at room temperature overnight with initial cooling to keep temperature at about room temperature. Gas chromatographic analyses showed the solution to be 0.69 *M* in 2-methyl-4-phenyl-3-buten-2-ol. The product was isolated by adding water and extracting with pentane. After being washed with water and aqueous sodium bicarbonate, the extracts were dried with anhydrous magnesium sulfate and distilled under reduced pressure. There was obtained 8 g of product, bp 100–107° (2 mm). Recrystallization from pentane at −5° gave 6.4 g of colorless needles, mp 38.5–39.0°. In isooctane solution, the product had bands at 292 mμ (ε 900), (1270) and at 250 (18,000). The infrared spectrum of the compound in carbon tetrachloride solution had bands at 3580, 3350, and 1580 cm^{-1}. The nmr spectrum in carbon tetrachloride solution had bands at −718 ppm (singlet, five protons), −6.36 ppm (AB quarter, two protons), −3.27 ppm (singlet, one proton), and at −1.35 ppm (singlet, six protons).

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Allylation of Aromatic Compounds with Organopalladium Salts

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Abstract: Arylpalladium salts, prepared *in situ* from arylmercuric salts and palladium(II) compounds, react with allylic halides at room temperature to produce allylaromatic derivatives. Moderate yields were obtained with a wide variety of aromatic compounds; even nitro, ester, and aldehyde groups could be present in the arylmercury compounds.

Allyl derivatives of aromatic compounds are readily obtained by the reaction of aromatic Grignard reagents or lithium compounds with allylic halides. The reaction is limited, however, because substituents which react with the Grignard reagents or lithium compounds cannot be present. A method of allylating aromatic compounds which does not have this limitation is reported in this paper.

The arylation of olefins with arylpalladium salts has been described previously.[1] We have now found that, if this reaction is carried out with an allylic halide as the olefin, an allyl group is added to the aromatic system and little or none of the arylallylic halide is formed.

$$[ArPdX] + CH_2{=}CHCH_2X \longrightarrow ArCH_2CH{=}CH_2 + PdX_2$$

Results

Arylpalladium salts were prepared, *in situ*, as before, by the exchange reaction between aryltin, -lead, or particularly -mercury compounds, and palladium salts, generally lithium palladium chloride.[1] The reaction is catalytic with respect to the palladium salt. However, some side reactions occur and about 10–30 mol % of the palladium salt or 10–30 mol % of a reoxidant (cupric chloride) and a catalytic amount of the palladium salt generally must be used to obtain optimum yields. Acetonitrile, methanol, acetone, and acetic acid were used as solvents. The reaction was complete within a few hours at room temperature, producing allylated aromatics in 31–87% yields. Isomerization of the initially formed allylaromatic compound into a propenyl derivative usually occurred only if there was insufficient catalyst or reoxidant present or if the allylic halide concentration was below *ca.* 0.1 *M*. Isomerization generally did not occur unless a precipitate of palladium metal appeared in the reaction mixture. Palladium generally did not precipitate in acetonitrile solution when 10–30 mol % of cupric chloride based upon the mercurial used was present as a reoxidant and the allylic halide concentration was above 0.1 *M*. Typical examples of the aromatic allylation reaction are given in Table I. The properties of the products are given in Table II.

Discussion of Results

The allylation reaction is a quite general reaction, but rearrangements can produce unexpected products. Aside from the product isomerization to the propenyl structure mentioned above, allylic rearrangements of

(1) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

Table I. Preparation of Allylaromatic Compounds

Product	Prepared from: Mercurial	Prepared from: Allylic halide	Catalyst	Solvent	Yield,[a] %
$C_6H_5CH_2CH{=}CH_2$	C_6H_5HgCl	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$	CH_3CN	61
$C_6H_5CH_2CH{=}CH_2$	C_6H_5HgOAc	$CH_2{=}CHCH_2Br$	$Pd(OAc)_2$–$CuBr_2$	CH_3CN	33
$C_6H_5CH_2CH{=}CH_2$	C_6H_5HgOAc	$CH{=}CHCH_2Cl$	$Pd(OAc)_2$–$Hg(OAc)_2$	CH_3CN	30 (62)[b]
$C_6H_5CH_2CH{=}CH_2$	C_6H_5HgCl	$CH_2{=}CHCH_2Cl$	Li_2PdCl_4–$CuCl_2$	CH_3OH	6 (31)[b]
$C_6H_5CH_2CH{=}CH_2$	C_6H_5HgCl	$CH_2{=}CHCH_2Cl$	Li_2PdCl_4–$CuCl_2$	CH_3COCH_3	17 (36)[b]
$C_6H_5CH_2CH{=}CHCH_3$	C_6H_5HgCl	$CH_3CH{=}CHCH_2Cl$	$LiPdCl_3$	CH_3CN	15 (78)[c]
$C_6H_5CH_2CH{=}CHCH_3$	C_6H_5HgCl	$CH_2{=}CHCHClCH_3$	$LiPdCl_3$	CH_3CN	50
$C_6H_5CH_2C(CH_3){=}CH_2$	C_6H_5HgCl	$CH_2{=}CCH_2Cl$, Cl → CH_3	$LiPdCl_3$	CH_3CN	74
$C_6H_5CH_2C(Cl){=}CH_2$	C_6H_5HgCl	$CH_2{=}CCH_2Cl$	$LiPdCl_3$	CH_3CN	68[d]
4-$CH_3OC_6H_4CH_2CH{=}CH_2$	4-$CH_3OC_6H_4HgCl$	$CH_2{=}CHCH_2Cl$, CH_3 → Cl	$LiPdCl_3$–$CuCl_2$	CH_3CN	47
4-$CH_3OC_6H_4CH_2C(CH_3){=}CH_2$	4-$CH_3OC_6H_4HgCl$	$CH_2{=}CCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	35[d]
4-$(C_2H_5)_2NC_6H_4CH_2CH{=}CH_2$	4-$(C_2H_5)_2NC_6H_4HgCl$	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	33[d]
4-$CH_3OCOC_6H_4CH_2CH{=}CH_2$	4-$CH_3OCOC_6H_4HgCl$	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	31[d]
3-$NO_2C_6H_4CH_2C(Cl){=}CH_2$	3-$NO_2C_6H_4HgCl$	$CH_2{=}CCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	87 (51)[d]
3,4-$Cl_2C_6H_3CH_2CH{=}CH_2$	3,4-$Cl_2C_6H_3HgCl$	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	28[d]
3-$OCHC_6H_4CH_2CH{=}CH_2$	3-$OCHC_6H_4HgCl$	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	43[d]
2-$C_4H_3SCH_2CH{=}CH_2$	2-C_4H_3SHgCl	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	12[d]
1,3,5-$(CH_3)_3C_6H(CH_2CH{=}CH_2)_2$	1,3,5-$(CH_3)_3C_6H(HgOCOCH_3)_2$	$CH_2{=}CHCH_2Cl$	$LiPdCl_3$–$CuCl_2$	CH_3CN	49[d]

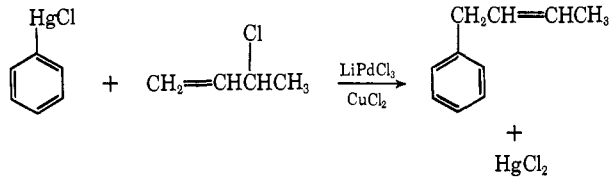
[a] Yields determined by gas chromatography unless otherwise noted. [b] Yield of allylbenzene and propylbenzene. [c] Total yield of isomeric mixture of phenylbutenes. [d] Yields of isolated product.

Table II. Properties and Analyses of Allylaromatic Compounds

Compound	Bp, °C (mm)	Found, % C	Found, % H	Found, % Other	Calcd, % C	Calcd, % H	Calcd, % Other	Nmr spectrum,[b] ppm (no. of protons)
$C_6H_5CH_2C(Cl){=}CH_2$	89–90 (15)	70.68	6.37	...	70.82	5.94	...	−7.14, single (5) −5.02, doublet (2) −3.47, single (2)
4-$CH_3OC_6H_4CH_2C(CH_3){=}CH_2$	108–115 (15)	81.44	8.50	...	81.44	8.70	...	−1.60, single (3) −3.17, singlet (2) −3.62, singlet (3)
4-$(C_2H_5)_2NC_6H_4CH_2CH{=}CH_2$	98–100 (2)	82.46	9.88	7.89 (N)	82.48	10.12	7.40 (N)	−6.70, quartet (4) −6.00, multiplet (1) −4.95, multiplets (2) −3.25, multiplets (6)
4-$CH_3OCOC_6H_4CH_2CH{=}CH_2$	90–92 (2.5)	75.03	6.51	...	74.97	6.87	...	−7.90, doublet (2) −7.14, doublet (2) −4.8 to −6.2, multiplet (3) −3.83, singlet (3) −3.33, doublet (2)
3-$NO_2C_6H_4CH_2C(Cl){=}CH_2$	107–112 (2)	54.16	4.36	7.26 (N)	54.70	4.08	7.09 (N)	−8.00 multiplet (2) −7.50 multiplet (2) −5.28 singlet (2) −3.72, singlet (2)
3,4-$Cl_2C_6H_3CH_2CH{=}CH_2$	73–79 (2)	57.93	4.47	38.1 (Cl)	57.78	4.31	37.9 (Cl)	−6.8 to −7.3, multiplet (3) −5.5 to −6.2, multiplet (1) −4.8 to −5.1, 3 peaks (2) −3.22, doublet (2)
3-$HOC_6H_4CH_2CH{=}CH_2$[a]	77–83 (3)	81.30	7.30	...	82.16	6.90	...	−9.90, singlet (1) −7.50, complex multiplet (4) −5.9 and −5.1, vinyl multiplet (3) −3.46, doublet (2)
2-$C_4H_3SCH_2CH{=}CH_2$	155–190	68.25	6.25	...	67.69	6.49	...	−6.90, multiplet (3) −4.8 to −6.1, multiplet (3) −3.41, doublet (2)
1,3,5-$(CH_3)_3C_6H(CH_2CH{=}CH_2)_2$	...	89.22	9.71	...	89.94	10.06	...	−6.71, singlet (1) −5.8 and −4.8, vinyl multiplet (3) −3.28, 2 overlapping multiplets (4) −2.15, singlet (9)

[a] Mixture of isomers, ~85% *meta*. nmr data is for major component. [b] 60 Mc with TMS as internal standard in CCl_4 solution.

the starting halides can occur, and, of course, unexpected products may be formed in unsymmetrical systems. Unfortunately, cupric and palladium halides are catalysts for the allylic rearrangement, and we have not been able to avoid this rearrangement completely. 3-Chloro-1-butene and phenylmercuric chloride, with lithium palladium chloride and cupric chloride as catalyst, produce the expected 1-phenyl-2-butene in 50% yield with little of the isomeric phenylbutenes being formed. Under the same conditions, however,



trans-crotyl chloride and phenylmercuric chloride form a mixture of at least seven products including 34% 2-phenyl-2-butene, 29% 1-phenyl-1-butene, and 15% 1-phenyl-2-butene. In control experiments, both chlorides were converted into the equilibrium mixture under the reaction conditions at rates comparable with the rate of reaction of crotyl chloride with "phenylpalladium chloride" but slower than the rate of reaction of 3-chloro-1-butene with "phenylpalladium chloride." These results suggest that the mechanism of the allylation reaction involves the addition of the "arylpalladium chloride" to the allylic double bond, forming a 1-aryl-3-chloro-2-propylpalladium chloride. This material then probably decomposes by eliminating palladium chloride, producing the allylated aromatic compound. Conceivably, 1-aryl-3-halo-1-propenes

$$ArHgX + PdX_2 \rightleftharpoons [ArPdX] + HgX_2$$

$$[ArPdX] + CH_2{=}CHCH_2X \rightleftharpoons [ArCH_2\underset{\displaystyle PdX}{\underset{|}{C}}HCH_2X]$$

$$ArCH_2\underset{\displaystyle PdX}{\underset{|}{C}}HCH_2X \longrightarrow ArCH_2CH{=}CH_2 + PdX_2$$

could also be produced in this reaction by eliminating a hydride group rather than the halide, but such products have not been observed.

Experimental Section

Mercurials. The arylmercuric salts used in this work were obtained as described previously.[1]

Allylbenzene. 1. A mixture of 1.0 mmol of phenylmercuric chloride, 1 ml of allyl chloride, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. Gas chromatographic analyses on a 6-ft Carbowax 20M column at 125° indicated that the solution was 0.072 *M* in allylbenzene with no propenylbenzene detected.

2. A similar reaction employing 1 ml of 2 *M* allyl chloride in place of 1 ml of pure allyl chloride led to the formation of a mixture of allyl- and propenylbenzene. The reaction mixture was found to be 0.024 *M* in allylbenzene and 0.0078 *M* in *trans*-propenylbenzene.

3. In another similar experiment, 10 mmol of phenylmercuric chloride, 10 mmol of $CuCl_2$, 1 ml of allyl chloride, and 9 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile under the same conditions produced a solution of 0.235 *M* in allylbenzene and 0.025 *M* in *trans*-propenylbenzene.

4. Finally, carrying out expt 3 with 4 ml of allyl chloride instead of 1 ml, other reagents remaining the same, led to the exclusive formation of allylbenzene, 0.472 *M*.

5. Experiment 3, with methanol as solvent instead of acetonitrile (also Li_2PdCl_4 instead of $LiPdCl_3$), led to a reaction mixture 0.25 *M* in *trans*-propenylbenzene and 0.050 *M* in allylbenzene.

6. Experiment 3 employing acetone as solvent instead of acetonitrile (also Li_2PdCl_4 instead of $LiPdCl_3$) led to a reaction mixture 0.175 *M* in *trans*-propenylbenzene and 0.156 *M* in allylbenzene.

7. A reaction mixture containing 10 mmol of phenylmercuric acetate, 5 mmol of mercuric acetate as a reoxidant for the palladium catalyst, 10 ml of acetonitrile, 1 ml of allyl chloride, and 1 mmol of palladium acetate, after stirring at room temperature overnight, yielded a solution 0.288 *M* in *trans*-propenylbenzene, 0.267 *M* in allylbenzene, and 0.043 *M* in cinnamyl acetate. The latter compound is probably formed by arylation of allyl acetate produced by exchange between mercuric acetate and allyl chloride.[1]

8. A reaction mixtures containing 10 mmol of phenylmercuric acetate, 10 mmol of LiBr, 10 mmol $CuBr_2$, 1 ml of allyl bromide, 10 ml of acetonitrile, and 1 mmol of palladium acetate, after being stirred at room temperature overnight, yielded a solution which was 0.18 *M* in allylbenzene, 0.10 *M* in *trans*-propenylbenzene, and 0.30 *M* in bromobenzene.

1-Phenyl-2-butene. A mixture of 1 mmol of phenylmercuric chloride, 1 ml of crotyl chloride (95% crotyl chloride and 5% 3-chloro-1-butene), and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight and analyzed by gas chromatography. The solution was 0.01 *M* in *trans*-1-phenyl-2-butene. A major product was unidentified, but it probably was 3-phenyl-1-butene. A similar experiment employing 3-chloro-1-butene instead of crotyl chloride yielded a reaction mixture which was 0.05 *M* in *trans*-1-phenyl-2-butene with other, unknown, products also present. The remaining allylic chlorides in both of these experiments were found to be mixtures containing 74% of crotyl chloride and 26% of 1-chloro-3-butene.

In a larger scale experiment, a reaction mixture containing 50 mmol (15.65 g) of phenylmercuric chloride, 10 mmol (1.34 g) of $CuCl_2$, 10 ml of crotyl chloride, 25 ml of acetonitrile, and 5 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The products were isolated by adding 25 ml of water and 100 ml of pentane. Insoluble material was removed by filtration and the solids were extracted several times with fresh pentane. The pentane layer was separated and the water layer was extracted four more times with pentane. The combined pentane extracts were washed twice with water, dried over anhydrous magnesium sulfate and distilled under reduced pressure. There was obtained 1.9 g of colorless liquid product, bp 95–125° (47 mm). At least seven compounds were detected by gas chromatography in the product. By comparing retention times, three of the products were tentatively identified as 2-phenyl-2-butene (~34%), 1-phenyl-1-butene (~29%), and 1-phenyl-2-butene (15%).

Methallylbenzene. A reaction mixture containing 1 mmol of phenylmercuric chloride, 1 ml of methallyl chloride and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. Analysis by gas chromatography indicated that the reaction mixture was 0.067 *M* in methallylbenzene. No 1-phenyl-2-methyl-1-propene was detected.

1-Phenyl-2-chloro-2-propene. A mixture containing 50 mmol (15.65 g) of phenylmercuric chloride, 20 ml of 2,3-dichloro-1-propene, 80 ml of acetonitrile, and 20 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The product was isolated as described in the phenylbutene experiment above. Distillation under reduced pressure gave 5.21 g of colorless product, bp 89–90° (15 mm), which was about 95% pure by gas chromatography. An analytically pure sample was obtained by preparative scale gas chromatography.

Estragole. A mixture of 10 mmol (3.4 g) of *p*-chloromercurianisole, 2 mmol of $CuCl_2$, 4 ml of allyl chloride, and 6 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 3 days. Analysis by gas chromatography showed the presence of 0.47 *M* estragole. There was little or no anethole present.

4-Methallylanisole. In a 500-ml flask, fitted with a stirrer, a thermometer, and a calcium chloride filled drying tube, was placed 34 g (0.1 mol) of *p*-chloromercurianisole, 20 mmol of $CuCl_2$, 40 ml of methallyl chloride, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile. The mixture was stirred at room temperature for 3 hr. Then gas chromatographic analysis showed the solution to be 0.26 *M* in 4-methallylanisole. The product was isolated by dilution with water and pentane, etc., as described in the phenylbutene preparation above. Distillation under reduced pressure gave 5.75 g of colorless liquid, bp 108–120° (15 mm). The product was about 95% pure by gas chromatography. An analytical sample was obtained by preparative scale gas chromatography.

4-Allyl-N,N-diethylaniline. With synthesized by the procedure used for 4-methallylanisole with 0.080 mol of 4-chloromercuri-N,N-diethylaniline, 16 mmol of $CuCl_2$, 32 ml of allyl chloride, 60 ml of

acetonitrile, and 20 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile. Cooling was necessary initially to keep the temperature below 30°. After about 30 min stirring at 25–30° reaction was complete. The mixture was diluted with 12 g of sodium hydroxide in 300 ml of water and 300 ml of ether. The mixture was filtered through Celite; the residue was washed several times with more ether. The aqueous layer was then extracted twice more with ether, and the combined ether extracts were washed with water twice, dried over anhydrous magnesium sulfate, and distilled under reduced pressure. There was obtained 5.3 g of colorless product, 95% pure by gas chromatography, bp 98–100° (2 mm). A pure sample was obtained by preparative scale gas chromatography.

Methyl 4-Allylbenzoate. The apparatus used to synthesize 4-methallylanisole was charged with 0.090 mol (34.4 g) of methyl 4-chloromercuribenzoate, 30 mmol of $CuCl_2$, 20 ml of allyl chloride, 50 ml of acetonitrile and, with stirring, 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile. Cooling with ice water was necessary initially to keep the temperature below 28°. After 3 hr of sirring at room temperature, reaction was complete. The product was isolated by adding 300 ml of hexane and 300 ml of water. The mixture was filtered and the solids were extracted several times with fresh hexane. The hexane layer was separated and the aqueous phase was extracted twice more with hexane and the combined extracts were washed with water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure. There was obtained 4.9 g of colorless product, bp 87–93° (2.5 mm), mainly 90–92° (2.5 mm), which was about 95% methyl 4-allylbenzoate by gas chromatography. A lower boiling fraction of 1–2 g was 75% this product also. A higher boiling fraction of about 2 g solidified, mp 92–94°. It was probably dimethyl 3,3′-diphenyldicarboxylate (lit.[2] mp 104°). A pure sample of methyl 4-allylbenzoate was obtained by preparative scale gas chromatography from the 95% pure fraction above.

1-(3-Nitrophenyl)-2-chloro-1-propene. The procedure used for synthesis of 4-methallylanisole was followed using 0.10 mol (35.8 g) of 3-chloromercurinitrobenzene, 20 mmol of $CuCl_2$, 40 ml of 1,2-dichloro-2-propene, 75 ml of acetonitrile, and 25 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile. After the solution was stirred at room temperature overnight, gas chromatographic analysis showed that it was 0.62 *M* in 1-(3-nitrophenyl)-2-chloro-1-propene. The products were isolated as in the 4-allyl-N,N-diethylaniline preparation. There was obtained 10.0 g of pale yellow liquid, bp 107–112° (2 mm) which was shown by gas chromatography to be about 95% pure. Redistillation, bp 108–110° (2 mm), gave an analytically pure sample $n^{25}D$ 1.5574. The pot residue from the original distillation crystallized on cooling. Recrystallization from benzene–hexane gave 1 g of 3,3′-dinitrodiphenyl, mp 208.0–208.5°.

Anal. Calcd for $C_{12}H_8O_4N_2$: C, 59.02; H, 3.30; N, 11.47. Found: C, 59.57; H, 3.35; N, 11.34.

3,4-Dichloroallylbenzene. In a 500-ml flask equipped with a stirrer, a thermometer, and a drying tube was placed 76.4 g (0.2 mol) of 1,2-dichloro-4-chloromercuribenzene, 40 mmol of $CuCl_2$, 40 ml of allyl chloride, and 120 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile. The mixture was stirred overnight, with initial cooling to keep the temperature at about 25°. The product was isolated by adding water and extracting with pentane as described in the phenylbutene preparation above. Distillation of the product through a short Vigreux column gave three fractions: (1) bp 51–73° (2 mm), 2.9 g which contained about 40% 3,4-dichloroallylbenzene; (2) bp 73–79° (2 mm), 7.8 g which was about 95% 3,4-dichloroallylbenzene, $n^{25}D$ 1.5538; and (3) bp 81–120° (2 mm), 3.62 g which contained about 70% 3,4-dichloroallylbenzene. There was a considerable amount of higher boiling material remaining but it was not investigated further.

3-Allylbenzaldehyde. A mixture containing 0.1 mol of 3-chloromercuribenzaldehyde, 40 mmol of $CuCl_2$, 40 ml of allyl chloride, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was employed as in the above examples. Two fractions were obtained by distillation: (1) bp 77–83° (3 mm), 6.25 g which was about 85% 3-allylbenzaldehyde by gas chromatography and (2) bp 85–120° (3 mm), 0.9 g which contained about 90% of the same product. Samples for nmr and carbon–hydrogen analyses were obtained by preparative-scale chromatography from the crude product. The purified product, $n^{25}D$ 1.5444, appeared homogeneous by gas chromatography, but the nmr spectrum showed it to be a mixture of isomers—about 85% *meta*, and 15% another isomer. A 2,4-dinitrophenylhydrazone was prepared from the crude product and recrystallized from chloroform–methanol, mp 198.0–198.5°.

Anal. Calcd for $C_{16}H_{14}O_4N_4$: C, 58.90; H, 4.32; N, 17.17. Found: C, 58.50; H, 4.40; N, 17.41.

2-Allylthiophene. A reaction mixture containing 0.1 mol of 2-chloromercurithiophene, 0.1 mol of $CuCl_2$, 10 ml of allyl chloride, and 90 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred, with ice cooling, but the temperature rose to 50° initially. After the reaction mixture had been cooled to 25°, stirring was continued for 2 hr at room temperature and then the product was isolated as in the examples above. A flash distillation of the product at atmospheric pressure gave 1.6 g of colorless liquid. Gas chromatographic analyses showed that the distillate was about 95% 2-allylthiophene. A purer sample was isolated by preparative scale gas chromatography.

Diallylmesitylene. A reaction mixture containing 5 mmol (3.18 g) of bis(acetoxymercuri)mesitylene, 10 mmol of LiCl, 4 mmol of $CuCl_2$, 4 ml of allyl chloride, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The reaction mixture was then concentrated at room temperature under reduced pressure. The product was isolated from the residue by extraction with pentane. The pentane was removed by distillation and the residue was flash distilled at 3 mm pressure. There was obtained 0.71 g of colorless liquid which was about 70% diallylmesitylene. No boiling point was obtained because there was too little material. The entire product was purified by preparative scale gas chromatography. A minor component of the crude material was identified as monoallylmesitylene by its nmr spectrum.

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(2) F. Ullmann, *Ann.*, **332**, 72 (1903).