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The Oxyphenylation of Cyclic Olefins Conjugated to the Benzene Ring by Means of Palladium Chloride[1)]

Hiroshi Horino, Mannosuke Arai, and Naoto Inoue
College of General Education, Tohoku University, Kawauchi, Sendai 980

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The reaction of 1,2-dihydronaphthalene, indene, and acenaphthylene with phenylpalladium chloride prepared *in situ* from phenylmercuric chloride and lithium chloropalladate in aqueous acetone afforded 2-phenyltetrarol, 2-phenylindanol, and 2-phenylacenaphthenol respectively, accompanying by the corresponding phenylated olefins. Acetoxyphenylation products were also obtained in the reactions in acetic acid. The configurations of these oxyphenylated compounds were determined to be *trans*.

Recently, extensive studies of the arylation of olefins using palladium complexes have been reported.[2-5)] Heck reported that the reaction of olefins with the reactive organopalladium compounds prepared *in situ* from organomercurials and palladium salts gave the substituted olefins.[3)] The Heck reaction is a representative example of the addition of a reactive carbon-palladium-σ-complex to olefins. In addition, the reaction has the valuable characteristic that the arylation takes place at the carbon atom bonded to the mercury of the organomercurials. When this reaction was applied to the cyclic olefin conjugated to the benzene ring in a protic solvent, a new reaction was found in which an aryl group and an anion part of the solvents were added simultaneously to the olefins.[1)]

In spite of many studies of the Heck reaction,[3,4)] no report describing such a kind of product has appeared. In this paper, we will report the oxyphenylation of 1,2-dihydronaphthalene, indene, and acenaphthylene in various protic solvents.

Results and Discussion

The reaction of 1,2-dihydronaphthalene (I) with phenylmercuric chloride and lithium chloropalladate in aqueous acetone (1: 1) at room temperature gave an unexpected oxygenated compound, $C_{16}H_{16}O$ (IIIa) (mp 76—77 °C), in a 60% yield, accompanied by 2-phenyl-3,4-dihydronaphthalene (II).[6)] The IR spectrum of IIIa showed an absorption band at 3300 cm^{-1} (OH) and 1020 cm^{-1} (C–O), with a characteristic signal of a doublet (1H, J=9 Hz) at 4.65 ppm in its NMR spectrum. The structure of IIIa was confirmed to be *trans*-2-phenyltetrarol by a mixed-melting-point test with an authentic sample.[7)] The experiment in a mixture of dioxane and water (1: 1) gave also IIIa in a 52% yield.

In the reaction of I with phenylpalladium chloride in methanol or ethanol, methyl (IIIb) or ethyl ether (IIIc) of 2-phenyltetrarol was obtained in a 45 to 50% yield. However, the yield of isopropyl ether

Table 1. Results of oxyphenylation in various solvents

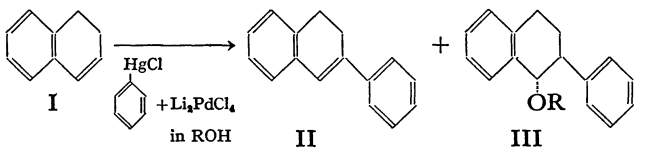
Olefin	Organomercurial	Solvent	Product (% to Pd)
I	PhHgCl	Acetone–H_2O (1:1)	II (13) IIIa (60)
I	PhHgCl	Dioxane–H_2O (1:1)	II (14) IIIa (52)
I	PhHgCl	Methanol	II (12) IIIa (45)
I	PhHgCl	Ethanol	II (10) IIIc (49)
I	PhHgCl	Isopropanol	II (23) IIId (27)
I	PhHgCl	*t*-Butanol	II (57)
I	PhHgCl	Acetic acid	II (40) IIIe (14)
I	PhHgCl	Acetic acid (sodium acetate 4 mol. eq.)	II (28) IIIe (47)
I	PhHgCl	Acetone (Phenol 10 mol. eq.)	II (67)
I	*p*-Cumylmercuric chloride	Acetone–H_2O (1: 1)	IV (9) V (43)
I	β-Naphthylmercuric chloride	Acetone–H_2O (1: 1)	VI (21) VII (53)
VIII	PhHgCl	Acetone–H_2O (1: 1)	IX (16) Xa (53)
VIII	PhHgCl	Dioxane–H_2O (1: 1)	IX (26) Xa (50)
VIII	PhHgCl	Acetic acid–H_2O (1: 1)	IX (19) Xa (36) Xb (17)
VIII	PhHgCl	Acetic acid	IX (72) Xb (4)
VIII	PhHgCl	Acetic acid (Sodium acetate 4 mol.eq.)	IX (25) Xb (35)
VIII	PhHgCl	Acetone–H_2O (1: 1) (Sodium acetate 4 mol.eq.)	IX (17) Xa (62)
XI	PhHgCl	Acetone–H_2O (1: 1)	XII (—) XIIIa (48)
XI	PhHgCl	Acetic acid (Sodium acetate 4 mol.eq.)	XII (28) XIIIb (13)

(IIId) was relatively low and no alkoxy derivative was found in the reaction in *t*-butanol, while the yeild of the substitution product, II, increased with the size of the alkoxy group. The major product of the reaction in acetic acid was II, and the oxyphenylation product, IIIe, was obtained in only a 14% yield.

When the reaction was carried out in the presence of 4 molar equivalents of sodium acetate to palladium chloride, the formation of IIIe was the main reaction.

The structures of these oxyphenylated products were determined by their elemental analyses and by means of their IR and NMR spectra.

These results are shown in Table 1.



a; $R=H$
b; $R=CH_3$
c; $R=CH_2CH_3$
d; $R=CH(CH_3)_2$
e; $R=COCH_3$

trans-2-Phenyltetrarol and its acetate, synthesized according to the method of Hanaya,[7] were identical with the oxyphenylation products, IIIa and IIIe respectively. The treatment of IIIa with sodium hydride and subsequently with methyl iodide afforded IIIb.

The NMR data of the oxyphenylated products are shown in Table 2.

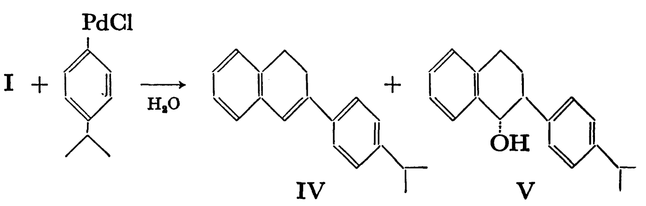
The coupling constants of hydrogen attached to carbinol carbon in the NMR spectra are found in the range of 7 to 9 Hz: this shows that the *trans* configuration is between the phenyl group and the hydroxy one.

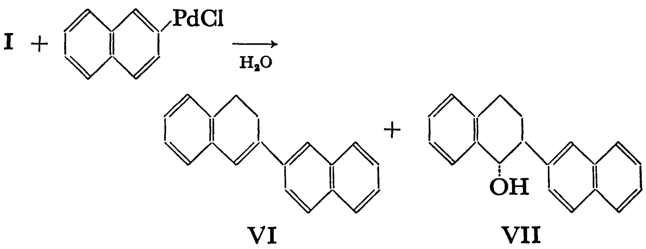
In the reaction of I with *p*-cumyl- and *β*-naphthylmercuric chloride in aqueous acetone, the respective corresponding alcohols (V) and (VII) were obtained, accompanied by the arylated olefins, (IV) and (VI).

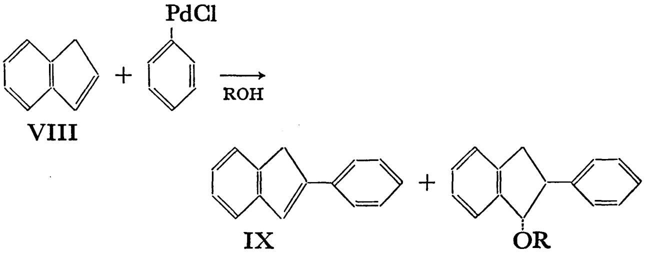
Table 2. IR and NMR data of oxyphenylation products

Compound No	IR (cm^{-1}) ν(OH)	IR (cm^{-1}) ν(C=O)	IR (cm^{-1}) ν(C–O)	NMR H_1 (ppm)[a]	NMR $J_{1,2}$ (Hz)[b]
IIIa	3300		1020	4.65	9
IIIb[c]			1040	4.58	8
IIIc[c]			1070	4.50	8
IIId[c]			1025	4.48	7
IIIe		1735	1235, 1030	6.20	8
V	3260		1030	4.72	8
VII	3390		1030	4.70	9
Xa	3200		1055	5.00	6
Xb[c]		1735	1230, 1020	6.25	5
XIIIa	3400		1030	5.24	3
XIIIb[c]		1745	1230, 1030	6.52	3

a) The chemical shift of H_1.
b) The coupling constant between H_1 and H_2.
c) neat.

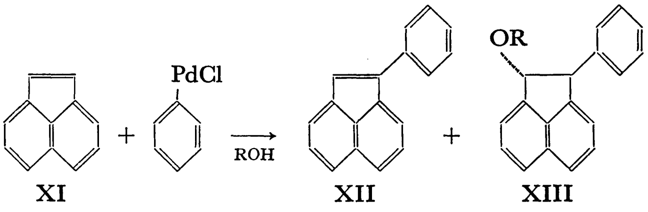






X

a; $R=H$
b; $R=COCH_3$



a; $R=H$
b; $R=COCH_3$

These structures were proved by their elemental analyses and by the spectral data shown in Table 2.

trans-2-Phenylindanol (Xa) and *trans*-2-phenylacenaphthenol (XIIIa) were obtained by the reaction of indene (VIII) and acenaphthylene (XI) respectively, with phenylpalladium chloride in aqueous acetone. The oxyphenylation products of VIII or XI in an acetic acid solution of sodium acetate were found to be *trans*-2-phenylindanol acetate (Xb) and *trans*-2-phenylacenaphthenol acetate (XIIIb). These structures were confirmed by the following experiments.

The application of hydroboration to 2-phenylindene (IX)[8] and 1-phenylacenaphthylene (XII)[9] gave the corresponding *trans* alcohols, which were identical with the oxyphenylation products, Xa and XIIIa.

These substances were then acetylated to Xb and XIIIb with acetic anhydride and pyridine.

According to the reaction mechanism proposed by Heck,[3] hydrochloric acid and mercuric chloride are produced in the reaction of olefins with phenylmercuric chloride and lithium chloropalladate.

Thus, the catalytic action of these acids might bring about an addition reaction of water to the arylated olefins.

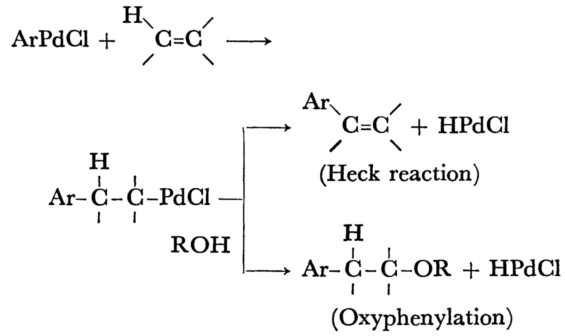
The treatment of II (or IX) with hydrochloric acid (two molar equivalents of II) or mercuric chloride (equimolecular) in an aqueous acetone mixture (1: 1) resulted in the recovery of II (or IX).

The same results were observed in the case of methanol.

The presence of sodium acetate in the reaction mixture of I or VIII with phenylpalladium chloride caused an increase in the acetoxy- and hydroxyphenylation products at the expense of the arylated olefin, as is shown in Table 1. Therefore, it is clear that the oxyphenylation products were not derived from the arylated olefins.

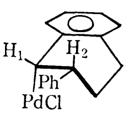
The function of sodium acetate is probably not only to neutralize hydrochloric acid, but also to raise the nucleophilic attack of acetic acid on the reactive intermediate. Taking into account the fact mentioned above, the same reaction intermediate as that of the Heck reaction may be assumed to give the oxyphenylation product as well as the arylated olefin:

$$\mathrm{ArHgCl} + \mathrm{PdCl_2} \longrightarrow \mathrm{ArPdCl} + \mathrm{HgCl_2}$$

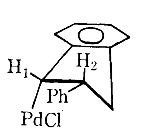


Heck suggested a step-by-step and stereospecific reaction mechanism including a *cis*-elimination of the hydridopalladium species.[3]

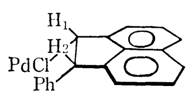
When this reaction mechanism is applied to the cyclic olefins, I, VIII, and XI, the organopalladium intermediates may be represented by the following formulae, (XIVa), (XIVb), and (XIVc) respectively.



XIVa



XIVb



XIVc

The *trans*-configurations of benzylic hydrogen, H_2, and the palladium atom in XIVa, XIVb, and XIVc make the *cis*-elimination of hydridopalladium chloride difficult. Thus, the reaction intermediates with long lives are subjected to nucleophilic replacement by protic solvents. The *trans*-configuration between the phenyl group and the acetoxy, alkoxy, or hydroxy group means that the solvent anion attacks the carbon atom bearing a palladium atom from the back side of the metal. The reaction mechanism proposed above is consistent with the results of the acetoxypalladation studies of cyclohexene by Henry,[10] in which the nucleophilic attack of the acetate ion on palladium occurred from outside the co-ordination sphere in an S_N2 fashion.

In conclusion, the oxyphenylation has presented an useful method for synthesizing *trans*-2-phenylcycloalkanols from benzocycloalkenes. The extension of the reaction to acyclic olefins, *e.g.*, methylstyrenes, is now under investigation.

Experimental

All the melting points are uncorrected. The IR and NMR spectra were measured with a Hitachi 215 grating infrared spectrometer by the KBr disk method, and with Varian A-60D (60 MHz) in carbon tetrachloride, using TMS as the internal standard.

Materials. The following compounds were synthesized by the method described in the literature: phenylmercuric chloride,[11] *p*-cumylmercuric chloride,[3] *β*-naphthylmercuric chloride,[12] and 1,2-dihydronaphthalene.[13] Indene and acenaphthylene of a commercial grade were used.

Reaction of I with Phenylmercuric Chloride and Lithium Chloropalladate in a Mixture of Acetone and Water (1: 1). To a solution of palladium chloride (356 mg, 2 mmol) and lithium chloride (168 mg, 4 mmol) in a mixture of acetone and water (1: 1) (20 ml), I (290 mg, 2.2 mmol) and then phenylmercuric chloride (626 mg, 2 mmol) were added, after which the mixture was stirred for 6 hr at room temperature. The mixture was then added to 100 ml of a saturated solution of sodium chloride, and the resulting oil was extracted with benzene.

The benzene layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to give a yellow oily residue (430 mg). The residue was chromatographed on silica gel. Elution with *n*-hexane and a mixture of benzene and *n*-hexane (1: 1) gave colorless crystals (II) (51 mg, 13%, mp 58—60 °C) and a yellow oil (IIIa) (269 mg, 60%) respectively. The latter was crystallized from *n*-hexane; mp 76—77 °C. Neither showed any depression in a mixed-melting-point test with 2-phenyl-3,4-dihydronaphthalene[6] and *trans*-2-phenyltetrarol.[7]

In a similar way, the following experiments in various solvents were carried out. The yields and spectrographic data of the oxyphenylation products are shown in Table 1 and Table 2.

In Methanol; *trans*-2-Phenyltetrarol methyl ether IIIb; colorless oil; bp 133—136 °C/1 mmHg.

Found: C, 85.86; H, 7.50%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

In Ethanol; *trans*-2-Phenyltetrarol ethyl ether IIIc; colorless oil; bp 142—144 °C/3 mmHg.

Found: C, 85.16; H, 8.38%. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99%.

In 2-Propanol; *trans*-2-Phenyltetrarol isopropyl ether IIId; colorless crystals; mp 59—60 °C; recrystallized from *n*-hexane.

Found: C, 84.94; H, 8.46%. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 7.99%.

In an Acetic Acid Solution of Sodium Acetate; To an acetic acid solution of palladium chloride (356 mg, 2 mmol) and lithium chloride (168 mg, 4 mmol), I (290 mg, 2.2 mmol), sodium acetate (656 mg, 8 mmol), and phenylmercuric chloride (626 mg, 2 mmol) were added successively. The mixture was then stirred for 7 hr at room temperature, and the reaction mixture was treated as has been described above.

trans-2-Phenyltetrarol acetate IIIe: colorless crystals; recrystallized from ethanol; mp 113—114 °C.

Found: C, 81.15; H, 6.83%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

This substance showed no depression in a mixed-melting-point with an authentic sample.[7]

The following procedure was carried out in the same way as in the reaction of I with phenylmercuric chloride and lithium chloropalladate except for the use of *p*-cumylmercuric chloride and *β*-naphthylmercuric chloride instead of phenylmercuric chloride.

Reaction of I with p*-Cumylmercuric Chloride and Lithium Chloropalladate in a Mixture of Acetone and Water (1: 1).* 2-Isopropylphenyl-3,4-dihydronaphthalene IV; mp 68 °C.

Found: C, 92.26; H, 7.74%. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12%.

trans-2-Isopropylphenyltetrarol V; mp 116 °C.

Found: C, 85.70; H, 8.64%. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33%.

Reaction of I with β-Naphthylmercuric Chloride and Lithium Chloropalladate in a Mixture of Dioxane and Water (1: 1). 2-*β*-Naphthyl-3,4-dihydronaphthalene VI; mp 150—151 °C; recrystallized from ethanol.

Found: C, 93.71; H, 6.29%. Calcd for $C_{20}H_{16}$: C, 93.67; H, 6.34%.

trans-2-*β*-Naphthyltetrarol VII; mp 118—119 °C: recrystallized from *n*-hexane.

Found: C, 87.46; H, 6.73%. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61%.

Analogous procedures were undertaken in the reaction of indene VIII with phenylmercuric chloride and lithium chloropalladate in a mixture of acetone and water (1: 1) and also in an acetic acid solution of sodium acetate.

2-Phenylindene IX;⁹⁾ mp 164—165 °C; recrystallized from benzene.

Found: C, 94.01; H, 6.44%. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29%.

trans-2-Phenylindanol Xa; mp 82—83 °C; recrystallized from *n*-hexane.

Found: C, 85.49; H, 6.55%. Calcd for $C_{15}H_{14}O$: C, 85.68, H, 6.71%.

trans-2-Phenylindanol acetate Xb; bp 163—165 °C/1 mmHg;

Found: C, 80.00; H, 6.31%. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.83%.

Reaction of Acenaphthylene (XI) with Phenylmercuric Chloride and Lithium Chloropalladate in a Mixture of Acetone and Water (1: 1). In a similar manner, the reaction of XI (457 mg 3.3 mmol) with phenylmercuric chloride (940 mg, 3 mmol) in a solution of lithium chloropalladate (130 mg, 3 mmol) was carried out to give yellow crystals (XIIIa) (354 mg, mp 97—98 °C) which were later recrystallized from a mixture of benzene and *n*-hexane. The crystals were found to be identical with the *trans*-2-phenylacenaphthenol synthesized as will be described below by a comparison of their IR spectra and by a mixed-melting-point test.

Synthesis of trans-*2-Phenylacenaphthenol from 1-Phenylacenaphthylene.* 1-Phenylacenaphthylene (684 mg) was dissolved in a solution of sodium borohydride (324 mg) in dried tetrahydrofuran (30 ml).

To the solution boron trifluoride etherate (1.2 ml) was added, drop by drop, at 23 °C for 20 min. After the reaction mixture had then been stirred for 1 hr, water (1 ml) was added to decompose the excess diborane. To the solution was added 3 M sodium hydroxide (1.5 ml) and then 30% hydrogen peroxide (1.5 ml), drop by drop, at 40 °C. After the solution had been stirred for 1 hr, it was poured into water and extracted with ether. The ether extract was concentrated, and the residual paste (820 mg) was chromatographed on a silica gel column. Elution with benzene gave *trans*-2-phenylacenaphthenol as colorless crystals (298 mg); mp 99—100 °C; recrystallized from a mixture of benzene and *n*-hexane.

Found: C, 87.43; H, 5.74%. Calcd for $C_{18}H_{14}O$; C, 87.77; H, 5.73%.

Besides, elution with a mixture of benzene and *n*-hexane (1: 10) gave a recovery of 1-phenylacenaphthylene (XII) (338 mg).

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