This alternation is as expected of $d\pi$–$p\pi$ back-bonding.

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Registry No. 5, 85957-15-9; 6, 85957-16-0; 7, 85957-10-4; 8, 85957-12-6; 9, 85957-14-8; FpCOT, 55672-79-2.

Exceedingly Mild, Selective and Stereospecific Phase-Transfer-Catalyzed Hydrogenation of Arenes

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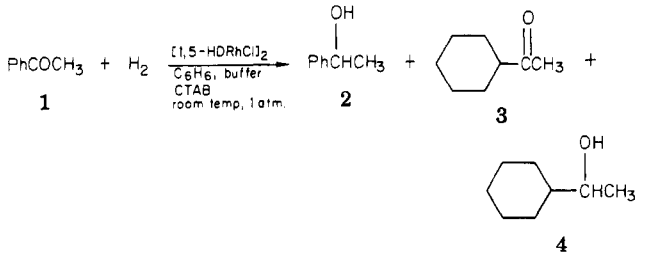
Summary: Arenes and heterocyclic compounds react with hydrogen, a catalytic amount of the dimer of chloro(1,5-hexadiene)rhodium (100:1 ratio of substrate/catalyst), benzene or hexane as the organic phase, a buffer solution, and a quaternary ammonium salt as the phase-transfer catalyst, to give reduced products in good to excellent yields. This very mild process (room temperature, 1 atm) is applicable to a variety of functionalized arenes, and the stereospecificity of the reaction was demonstrated with naphthalene and *p*-methylanisole.

Phase-transfer catalysis is a valuable method for effecting metal-catalyzed reactions under very gentle conditions.[1] Examples include the cobalt carbonyl catalyzed regiospecific acylation of dienes and trienes[2] and the palladium(0)-catalyzed carbonylation of vinylic dibromides to diacids, monoacids, or diynes.[3]

There has been considerable interest in asymmetric synthesis, under phase-transfer catalysis, using optically active quaternary ammonium salts. However, a number of claims in this area have been found to be incorrect.[4] Besides ammonium salts, bovine serum albumin (BSA) has been used in the two-phase asymmetric oxidation of dithioacetals with aqueous sodium metaperiodate.[5]

We reasoned that BSA might coordinate to a metal atom giving a complex capable of catalyzing reactions so as to give products in good optical, as well as chemical, yields. The metal-catalyzed and phase-transfer-catalyzed hydrogenation of acetophenone to 1-phenylethanol, in the presence of the protein, was chosen as a model reaction for this investigation. The homogeneous hydrogenation of acetophenone has been reported to occur in up to 51% optical yield using the dimer of chloro(1,5-hexadiene)-rhodium [1,5-HDRhCl]$_2$ as the catalyst with added optically active phosphine.[6]

Treatment of acetophenone (1) with hydrogen, [1,5-HDRhCl]$_2$ (100:1 ratio of 1/Rh complex), buffer of pH 9.2, benzene, BSA, and cetyltrimethylammonium bromide (CTAB) as the phase-transfer agent afforded racemic 1-phenylethanol (2) in 21% yield. However, the major and unexpected pathway was reduction of the benzene ring of 1, giving methyl cyclohexyl ketone (3) in 28% yield and 1-cyclohexylethanol (4) in 3% yield. Since 2 was optically



inactive, it seemed conceivable that BSA was not participating in the reaction. The mixture of BSA and the buffer of pH 9.2 gave a solution of pH 7.6. Therefore, the hydrogenation reaction was repeated by using a buffer of pH 7.6, but no BSA. In this case, the yield of methyl cyclohexyl ketone (3) improved significantly (to 53%—Table I). Use of hexane as the organic phase gave 3 and 4, products of reduction of the arene ring, in a total yield of 90%.

Application of the reaction to other aromatic ketones (phenylacetone, benzylacetone) gave saturated ketones in good yields. The selectivity of the arene reduction reaction was further demonstrated with benzamide, methyl benzoate, and phenyl acetate, all of which experienced reduction of only the benzene ring. Even phenol can be hydrogenated to form either cyclohexanol or cyclohexanone as the predominant product, depending on the reaction conditions.

Simple aromatic compounds are also hydrogenated. Naphthalene can be partially reduced to tetralin or completely and stereospecifically converted to *cis*-decalin. *cis*-4-Methylcyclohexyl methyl ether was obtained as the only product, in 92% yield, from *p*-methylanisole. Reasonable quantities of hydrogenated products were also formed from *n*-butylbenzene from *o*-xylene.

Several classes of heterocycles were also easily reduced, including 2-ethylfuran, 2-methylpyridine, and quinoline, the latter undergoing hydrogenation of the heterocyclic ring only. Surprisingly, isoquinoline was inert under identical reaction conditions.

Qualitatively, electron-donating substituents activate the arene ring toward hydrogenation while the presence of electron-withdrawing groups ($CONH_2$, $COOCH_3$) slows down or inhibits [NO_2] reduction.

The constituents which make up the buffer are not important. It is the pH of the buffer that is critical—i.e., pH 7.4–7.6. As noted in Table I, $C_6H_{11}CH_2CH_2COCH_3$ was isolated in 97% yield from the reaction of benzyl acetone with hydrogen, tetrabutylammonium hydrogen sulfate (THS) as the phase-transfer catalyst, hexane, and the buffer solution of pH 7.6 (prepared from boric acid, citric acid, and sodium phosphate).[7] Substitution of a pH 7.4 buffer, prepared from KH_2PO_4 and NaOH, in the latter reaction gave the saturated ketone in 100% yield. Likewise, $C_6H_{11}CH_2CH_2COCH$ was formed in 96% yield using a buffer of the same pH (7.4) but prepared by using tris(hydroxymethyl)aminomethane and HCl.

Several other points are noteworthy. First, the rhodium(III) catalyst, hydrated rhodium chloride ($RhCl_3 \cdot 3H_2O$), is inert under these conditions, as is rhodium acetate and chlorodicarbonylrhodium(I) dimer. Second, the reaction is an authentic phase-transfer process, since produce yields in the absence of the quaternary ammonium salt are much

(1) Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183.
(2) Alper, H.; Currie, J. K. *Tetrahedron Lett.* **1979**, 2665.
(3) Galamb, V.; Gopal, M.; Alper, H. *Organometallics* **1983**, *2*, 801.
(4) Dehmlow, E. V.; Singh, P.; Heider, J. *J. Chem. Res., Synop.* **1981**, 292.
(5) Ogura, K.; Fujita, M.; Iida, H. *Tetrahedron Lett.* **1980**, *22*, 2233.
(6) Heil, B.; Toros, S.; Vastag, S.; Marko, L. *J. Organomet. Chem.* **1975**, *94*, C47.
(7) Carmody, W. R., *J. Chem. Educ.* **1961**, *38*, 559.

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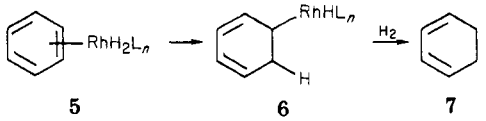
Table I. Hydrogenation of Arenes by H_2 and $[1,5\text{-HDRhCl}]_2$ at Room Temperature and 1 Atm

reactant	$R_4N^+X^-$	buffer pH	BSA	organic phase	products, % yield
1	CTAB	9.2	yes	C_6H_6	2, 21; 3, 28; 4, 3
	CTAB	7.6		C_6H_6	2, 31; 3, 53; 4, 9
	CTAB	7.6		C_6H_{14}	2, 10; 3, 39; 4, 51
	THS	7.6		C_6H_{14}	3, 23; 4, 77
	CTAB	9.2		CH_3OH/C_6H_6 (10/3)	2, 84; 3, 8; 4, 8
$PhCH_2COCH_3$	CTAB	7.6		C_6H_6	$C_6H_{11}CH_2COCH_3$, 54 $C_6H_{11}CH_2CH(OH)CH_3$, 14
	THS	7.6		C_6H_{14}	$C_6H_{11}CH_2COCH_3$, 100
		7.6		C_6H_{14}	$C_6H_{11}CH_2COCH_3$, 29 $C_6H_{11}CH_2CH(OH)CH_3$, 8 $PhCH_2CH(OH)CH_3$, 19
$PhCH_2CH_2COCH_3$	THS	7.6		C_6H_{14}	$C_6H_{11}CH_2CH_2COCH_3$, 97
	DTAC	7.6		C_6H_{14}	$C_6H_{11}CH_2CH_2COCH_3$, 80
	CTAB	7.6		C_6H_{14}	$C_6H_{11}CH_2CH_2COCH_3$, 82 $C_6H_{11}CH_2CH_2CH(OH)CH_3$, 10
	CTAB	7.6		C_6H_6	$C_6H_{11}CH_2CH_2COCH_3$, 30
	CTAB	9.2		C_6H_6	$C_6H_{11}CH_2CH_2COCH_3$, 12
	CTAB	9.2	yes	C_6H_6	$C_6H_{11}CH_2CH_2COCH_3$, 39
	CTAB	H_2O		C_6H_6	$C_6H_{11}CH_2CH_2COCH_3$, 4
	CTAB	6 N NaOH		C_6H_{14}	$PhCH_2CH_2CH(OH)CH_3$, 80 $C_6H_{11}CH_2CH_2CH(OH)CH_3$, 20
p-methylanisole	THS	7.6		C_6H_{14}	*cis*-4-methylcyclohexyl methyl ether, 92
PhC_4H_9	THS	7.6		C_6H_{14}	*n*-butylcyclohexane, 100
$PhCOOCH_3$	THS	7.6		C_6H_{14}	$C_6H_{11}COOCH_3$, 69
$PhCONH_2$	THS	7.6		C_6H_{14}	$C_6H_{11}CONH_2$, 79
CH_3COOPh	THS	7.6		C_6H_{14}	$CH_3COOC_6H_{11}$, 31
C_6H_6	THS	7.6		$C_{10}H_{22}$	cyclohexane, 100
naphthalene	CTAB	7.6		C_6H_6	tetralin, 73 decalin, trace
	CTAB	7.6		C_6H_{14}	tetralin, 20 *cis*-decalin, 80
	CTAB	9.2	yes	C_6H_6	tetralin, 54 *cis*-decalin, 7
2-methylpyridine	THS	7.6		C_6H_{14}	2-methylpiperidine, 39
quinoline	THS	7.6		C_6H_{14}	1,2,3,4-tetrahydroquinoline, 100[a]
isoquinoline	THS	7.6		C_6H_{14}	*b*
2-ethylfuran	THS	7.6		C_6H_{14}	2-ethyltetrahydrofuran, 51
phenol	THS	7.6		C_6H_6	cyclohexanone, 73 cyclohexanol, 27
	THS	7.6		C_6H_{14}	cyclohexanol, 71[c] cyclohexanone, 29

[a] Yield for reaction effected at 75 °C. At room temperature 15% product was formed. [b] No product at room temperature or at 75 °C. [c] Reaction effected at 75 °C.

lower (e.g., compare entries 7 and 8 of Table I).

The results obtained from the following experiments are *suggestive* of a stepwise mechanism for the hydrogenation of arenes. The ease of reduction of cyclohexene, 1,3-cyclohexadiene, and benzene to cyclohexane were compared and found to be in the order cyclohexene > cyclohexadiene > benzene. After a reaction time of 2 h using 1,3-cyclohexadiene as the substrate, the ratio of diene to cyclohexene was approximately 1:1, with small amounts of cyclohexane and benzene formed as well. In addition, the reduction of 1,3-cyclohexadiene to cyclohexene is faster than the corresponding reduction using 1,4-cyclohexadiene. No benzene was detected during the latter process, indicating that 1,4-cyclohexadiene does not isomerize to 1,3-cyclohexadiene prior to reduction since the reactivity pattern is different. These results imply a stepwise reduction of benzene to cyclohexane and clearly not a direct reduction of the diene to the saturated hydrocarbon. η^2 complexation of an arene to a rhodium hydride species would give **5**, which on hydrogen transfer to **6**, and reductive elimination would afford **7** and regenerate the catalyst. Repetition of this process would eventually lead to cyclohexene and cyclohexane.



5 **6** **7**

How does the phase-transfer process compare with the use of other methods for the hydrogenation of arenes? Very favorably, indeed! For example the allylcobalt(I) complex $\eta^3\text{-}C_9H_5[P(OCH_3)_3]_3$ can serve as a catalyst precursor for the hydrogenation of arenes at room temperature and 1–3 atm pressure. However, hydrogenolysis of the η^3-allyl ligand results in a reduced catalyst lifetime and low conversions in many instances. In addition, hydrogenation does not occur in the case of phenol, and ethyl cyclohex-1-enecarboxylate is the major product (13% conversion) obtained from ethyl benzoate.[8] It is claimed that $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]^+$ and $[Ru(H)(Cl)(PPh_3)(\eta^6\text{-}C_6Me_6)]$ can catalyze the hydrogenation of arenes, but under drastic conditions (50 atm, 50 °C).[9] The same conditions have been employed by using (pentamethylcyclopentadienyl)rhodium dichloride dimer as the catalyst.[10] Furthermore, none of these catalysts are as easily prepared from commercial materials as is the dimer of chloro(1,5-hexadiene)rhodium.

Finally, we are not certain whether the phase-transfer process described herein involves a soluble or insoluble rhodium catalyst. But what is undeniable is the fact that

(8) Stuhl, L. S.; Rakowski Du Bois, M.; Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405 and references cited therein.
(9) Bennett, M. A. *Chem. Tech.* **1980**, *10*, 444.
(10) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301.

this hydrogenation is a remarkably mild, stereospecific, selective, and potentially valuable phase-transfer reaction.

The following general procedure was used. To 28 mg (0.063 mmol) of [1,5-HDRhCl]$_2$ in hexane or benzene (15 mL) was added in sequence: the organic reactant (100/1 ratio of substrate/Rh catalyst), the phase-transfer catalyst (0.3–0.5 mmol), and 5 mL of the buffer solution. Hydrogen gas was bubbled through the stirred solution at room temperature and atmospheric pressure (reaction was followed by NMR spectroscopy). The layers were separated, and the organic phase was dried and distilled.

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Registry No. 1, 98-86-2; [1,5-HDRhCl]$_2$, 32965-49-4; $PhCH_2COCH_3$, 103-79-7; $PhCH_2CH_2COCH_3$, 2550-26-7; PhC_4H_9, 104-51-8; $PhCOOCH_3$, 93-58-3; $PhCONH_2$, 55-21-0; CH_3COOPh, 122-79-2; C_6H_6, 71-43-2; CTAB, 57-09-0; THS, 16873-13-5; *p*-methylanisole, 104-93-8; naphthalene, 91-20-3; 2-methylpyridine, 109-06-8; quinoline, 91-22-5; isoquinoline, 119-65-3; 2-ethylfuran, 3208-16-0; phenol, 108-95-2.

Unexpected Ortho-metalated Products Resulting from Dibenzoyldiazomethane Activation in the Presence of Iridium Phosphine Complexes

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Summary: The reaction of *trans*-[IrCl(N_2)(PPh_3)$_2$] with $N_2C(C(O)Ph)_2$ in refluxing toluene yields [IrCl(HC(C(O)Ph)$_2$)(P(C_6H_4)Ph_2)(PPh_3)] in which one phosphine ligand has undergone ortho-metalation and the hydrogen atom has been transferred to the dibenzoylmethylene moiety yielding a β-diketonate group. In refluxing THF [IrCl(PPh_3)$_3$] and $N_2C(C(O)Ph)_2$ yield [IrCl($C_6H_4C(O)CC(Ph)OPPh_2$)(PPh_3)$_2$] in which an unusual tridentate ligand has been formed by loss of a phenyl group from PPh_3 and condensation of the dibenzoylmethylene moiety with the PPh_2 fragment. In addition, one phenyl group of this ligand has ortho-metalated.

The chemistry of dibenzoyldiazomethane ($N_2C(C(O)Ph)_2$) with metal complexes offers an added dimension over that usually observed for diazoalkane molecules. In addition to the diverse chemistry that might be expected of the diazo moiety,[1] the carbonyl functional groups may also become involved in the coordination and chemical transformations of this molecule. We have recently observed this phenomenon both in chemistry that involves the intact dibenzoyldiazomethane molecule[2] and in chemistry in which N_2 loss has occurred from this group. It is some novel findings in this latter area that we now wish to communicate.

Dibenzoyldiazomethane reacts with both *trans*-[IrCl(N_2)(PPh_3)$_2$] and [IrCl(PPh_3)$_3$]. In the reaction of 215 mg (0.28 mmol) of *trans*-[IrCl(N_2)(PPh_3)$_2$] with 75 mg (0.30 mmol) of $N_2C(C(O)Ph)_2$ in refluxing toluene for 35 min an orange-yellow solution was obtained from which a yellow crystalline material (1) could be isolated in 90% yield. The elemental analysis was consistent with the formulation [IrCl(C(C(O)Ph)$_2$)(PPh_3)$_2$]·$^1/_2C_6H_5CH_3$, and the infrared spectrum showed bands at 1521, 1541, and 1592 cm^{-1} but showed no bands between 1600 and 2800 cm^{-1}; in particular no band was observed that could be clearly attributed to the diazo or carbonyl moieties or to an Ir–H stretch. The $^{31}P\{^1H\}$ NMR spectrum (at 36.4 MHz) showed two doublets at δ −2.9 and −82.5 (J_{PP} = 21 Hz); the latter chemical shift is characteristic of an ortho-metalated triphenylphosphine group[3] and the coupling suggested that the phosphines were mutually cis. In the ^1H NMR spectrum (at 400 MHz), a single peak (1 H) was observed at δ 6.80 in addition to the phenyl and toluene resonances, but no resonance was observed upfield in the region expected for a metal hydride.

When the above reaction was carried out in refluxing THF, an additional product, **2**, was observed as a minor component. This species could be obtained as the major product (ca. 80% yield) in the reaction of 97 mg (0.39 mmol) of $N_2C(C(O)Ph)_2$ with 392 mg (0.39 mmol) of [IrCl(PPh_3)$_3$] in refluxing THF for 40 min. The infrared and ^1H NMR spectra for **2** closely resembled those for **1**, but the $^{31}P\{^1H\}$ NMR spectrum was significantly different, displaying two doublets at δ −11.0 and −69.2 (J_{PP} = 17 Hz), which again suggested that the phosphines were mutually cis with one being ortho-metalated. Complex **2** could be quantitatively converted to **1** by refluxing in toluene for 18 h. Both **1** and **2** are air stable and showed no reactivity toward CO or PPh_3.

Also observed in the preparation of **2** from [IrCl(PPh_3)$_3$] was a minor product, **3**, in about 10% yield (based on $^{31}P\{^1H\}$ NMR). Its $^{31}P\{^1H\}$ NMR spectrum appeared as a doublet (2 P) at δ −15.7 and a triplet (1 P) at δ 83.7 (J_{PP} = 21 Hz). The infrared spectrum showed medium bands at 1636, 1577, and 1546 cm^{-1}, but no absorptions apart from C–H stretches were observed at higher frequency. The ^1H NMR spectrum of **3** showed only phenyl and toluene resonances. Unambiguous characterization of **1** and **3** was achieved by an X-ray crystal structure determination of each.

Both compounds crystallize with one toluene molecule per unit cell; complex **1** crystallizes in the space group $P\bar{1}$ with Z = 2, a = 12.396 (2) Å, b = 19.272 (3) Å, c = 10.742 (1) Å, α = 97.84 (6)°, β = 115.59 (4)°, γ = 78.77 (1)°, and V = 2268.9 Å^3; compound **3** crystallizes in the space group $P1$ with Z = 1, a = 12.1972 (8) Å, b = 10.163 (1) Å, c = 11.761 (1) Å, α = 103.609 (8)°, β = 95.059 (7)°, γ = 96.619 (7)°, and V = 1397.4 Å^3. Data were collected to 2θ = 120° for both structures on an automated Picker FACS-1 diffractometer using Ni-filtered Cu Kα radiation. The structure of compound **1** was solved by standard Patterson and Fourier techniques, whereas that for **3** was solved by difference Fourier techniques after arbitrarily fixing the iridium atom at the origin of the cell.[4] Both data sets were corrected for absorption and the structures refined by

(1) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.
(2) Cowie, M.; Loeb, S. J.; McKeer, I. R., manuscript in preparation.
(3) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Pregosin, P. S.; Kunz, R. H. "The ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag, New York, 1979. (c) In the $^{31}P\{^1H\}$ NMR spectrum of [IrCl(H)($C_6H_4PPh_2$)(PPh_3)$_2$] for example, we observe the following parameters: δ 4.2 (dd), −6.0 (dd), −92.2 (dd), J_{PP}(cis) = 10, 18 Hz, J_{PP}(trans) = 370 Hz (dd = doublet of doublets).
(4) $P1$ is a polar space group. The correct enantiomer was established by changing all coordinates (x, y, z) to ($\bar{x}$, $\bar{y}$, $\bar{z}$) and comparing subsequent refinements. The wrong enantiomer converged at R = 0.039 and R_w = 0.058. In addition, the polar dispersion error gave rise to a significantly larger spread in chemically equivalent bond distances for the wrong enantiomer. A complete description of the structure will appear.

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