since the cerium excited states involve 5d character, the luminescence data are a sensitive test of covalent bonding character and the involvement of 5d orbitals in this bonding.[2] The results are consistent with the expectation that these figure more prominently than do 4f orbitals in covalent bonding, since the shifts in emission maxima (relative to the aquo ion) are much greater for organocerium compounds than for any other series of organolanthanide compounds studied thus far. Therefore, while the chemical properties of these compounds do indicate predominant ionic character, our data are indicative of a significant degree of covalency (up to ca. 20–25%) that increases in the rough order halides < alkyls, aryls < cyclopentadienyls < COT, C_5Me_5. It is clear that the luminescent cerium(III) center represents a sensitive probe of environmental effects, and we intend to build a wider luminescence data base for making predictions and assignments.

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Hydrozirconation of Aromatic Olefins

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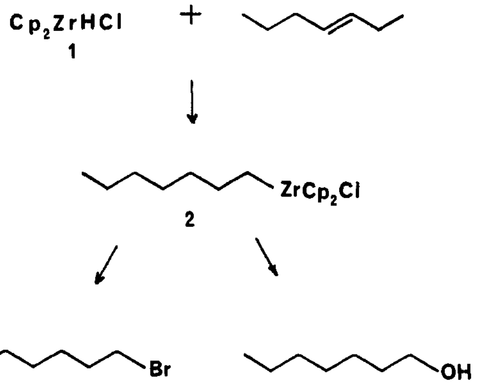
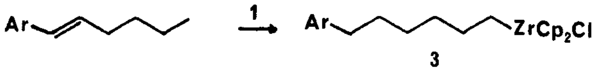
The hydrozirconation of aromatic olefins was found to give mixtures of benzylic and terminally substituted alkyl zirconiums. In contrast to the behavior of simple acyclic olefins, movement of the zirconium to the end of the chain is sluggish and incomplete. At moderate temperatures, the benzylic product predominates almost exlusively, and this was exploited to determine the stereochemistry of oxidation of secondary alkyl zirconiums by *tert*-butyl hydroperoxide and oxygen.

Introduction

The hydrozirconation reaction was discovered by Wailes, Weigold, and Bell[1] and later developed by Schwartz.[2] The zirconium hydride 1, known as Schwartz's reagent, reacts with an isolated olefinic bond to generate an alkyl zirconium species. Reversal of the addition occurs at moderate temperatures and can lead to the original olefin or to a new olefin in which the double bond has moved to an adjacent position.[3] In simple linear alkenes, the zirconium rapidly migrates to the most stable position at the end of the chain, to give 2, and thus a method is provided for the synthesis of simple terminally substituted alkyl compounds, by reaction of 2 with various electrophiles. We have previously applied the process to the synthesis of long-chain compounds, in which symmetrical disubstituted olefins are converted to the terminal alcohols or halides.[3]





Hydrozirconation has not been used extensively in synthesis because the reagent reduces a wide range of functional groups, including carbonyl and halogen. The oxazoline group is stable to the reagent and has been used to protect the carboxylic acid group during hydrozirconation.[4] However, mixtures of products are formed resulting from interaction of the oxazolyl group with the zirconium. Oleyl oxazoline, for example, has been reported to give products of substitution in the 3- and 18-positions.[4] In this paper, we report an investigation into the use of an aromatic ring as a source of latent functionality at one chain terminus, with the idea that hydrozirconation would generate terminally substituted intermediate 3, which with proper manipulation would provide access to a variety of α,ω-disubstituted compounds. During the course of this work, we have found that a mixture of benzylic and terminal zirconium compounds is formed and that it is not possible to drive the zirconium entirely to the terminal position. This reduces the utility of the process in the originally intended sense; however, the formation of the benzylic zirconiums does provide access to secondary alkyl

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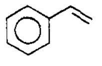
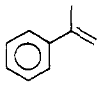
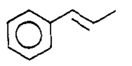
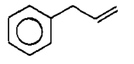
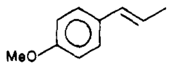
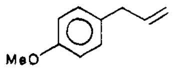
(1) Wailes, P. C.; Weigold, H.; Bell, A. P.; *J. Organomet. Chem.* **1972**, *43*, C72.

(2) Schwartz, J.; Labinger, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.

(3) Gibson, T.; Tulich, L. *J. Org. Chem.* **1981**, *46*, 1821. Gibson, T. *Tetrahedron Lett.* **1982**, 157. During the course of the work described in this reference, we found that variable amounts of olefin were always recovered from the hydrozirconation of very long-chain olefins. Oxidation of this recovered olefin by $KMnO_4/NaIO_4$, followed by esterification with diazomethane, gave a mixture of esters. GC analysis showed this to be a mixture of approximately equal amounts of esters with chain lengths from about 4 to 20, showing that the olefin was completely randomized along the chain.

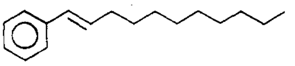
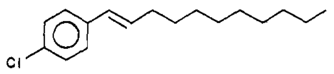
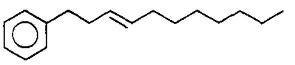
(4) Alvhall, J.; Gronowitz, S.; Hallberg, Svenson, R. *Chem. Scr.* **1984**, *24*, 170.

Table I. Hydrozirconation of Simple Aromatic Olefins

compd	temp,[a] °C	time,[a] h	oxidant[b]	yield,[c] %	compositn,[d] % α-OH	ω-OH	α-keto
	25	4	A	52	19	65	13
	25	4	B	60	7	93	
	25	4	A	49		93	
	25	4	B	73		100	
	25	4	A	68	75	5	13
	25	4	B	61	82	5	e
	40	4	A	78	44	36	12
	25	24	A	74	57	23	12
	40	48	A	58	6	87	1
	40	48	B	56	15	78	e
	25	4	A	75	6	90	3
	25	4	A	81	44	4	11[f]
	25	24	A	56	34	16	10[f]
	40	24	A	39	10	46	f, g
	25	4	B	80	45	5	f
	25	4	A	75	5	80	

[a] For the hydrozirconation step. [b] A = O_2; B = *t*-BuOOH. [c] For distilled product, as the alcohol. [d] Determined gas chromatographically, see Experimental Section. [e] 6–7% of 3-phenylpropyl formate formed. [f] Remainder is starting olefin. [g] 25% 1-(4-methoxyphenyl)propane formed.

Table II. Hydrozirconation of Long-Chain Aromatic Olefins

compd	temp,[a] °C	time,[a] h	oxidant[b]	α-OH[c]	ω-OH[c]	olefin[c]
	25	4	A	50		50
	40	72	A	19	24	59
	40	96	B	25	26	49
	40	72	B	26	14	56[d]
	40	96	B	11	31	56[e]

[a] For hydrozirconation step. [b] A = O_2; B = *t*-BuOOH. [c] Yields (%) of materials isolated by flash chromatography. [d] Each fraction is a mixture of chloro and dechloro in about 1:1 ratio. [e] 1:3 ratio of *trans*-1-phenyl-1-undecene and 1-phenylundecane.

zirconiums, from which useful information concerning the stereochemistry of their reactions can be obtained.

Results and Discussion

The results of reactions between 1 and simple aromatic olefins are shown in Table I. These reactions were carried out by the in situ generation method described in previous publications,[3] under the conditions shown in Table I. It quickly became apparent that significant differences exist between the reactions of these aromatic olefins and those of simple aliphatic olefins. Styrene gives moderate yields of mixtures of alcohols with either oxygen or *tert*-butyl hydroperoxide,[5] in which the terminal alcohol predominates.[6] Acetophenone is formed in substantial amount when the oxidation is performed with oxygen, along with the unexpected benzylic alcohol. α-Methylstyrene gives the primary alcohol very cleanly, but 1-phenylpropene gives predominantly the benzylic alcohol under these conditions. Small amounts of the terminal alcohol are observed, with no evidence for the formation of the 2-isomer. Again, some of the benzylic ketone is formed in the oxygen reactions, but *tert*-butyl hydroperoxide gives a new minor product, identified as the formate ester of the terminal alcohol.

The predominance of the benzylic alcohol in reactions of this compound led us to explore the effects of time and temperature on the process, the results of which are included in Table I. It turned out not to be possible to drive the zirconium completely to the end of the chain, even after 2 days at 40 °C. The terminal olefin, 3-phenylpropene, gives small amounts of the benzylic alcohol in a reaction performed at 25 °C for 4 h. Even more sluggish movement is observed with the para methoxy derivitive. In this case, about 40–50% of the product is recovered olefin, as a mixture of cis and trans isomers, with no evidence for the terminal isomer. When the reaction is carried out at 40 °C, a substantial amount of the reduced hydrocarbon is formed.

Similar results are obtained with the longer chain olefin 1-phenyl-1-undecene (Table II). Clean conversion to the benzylic alcohol is observed at 25 °C, and about 1:1 mixtures of benzylic and terminal alcohols are obtained at higher temperature. In all cases, the olefin recovered is a mixture of the cis and trans isomers of the conjugated compound, with no evidence for the other isomers. The para chloro derivative gives similar results, complicated by reduction of the chloride to the hydrocarbon in sub-

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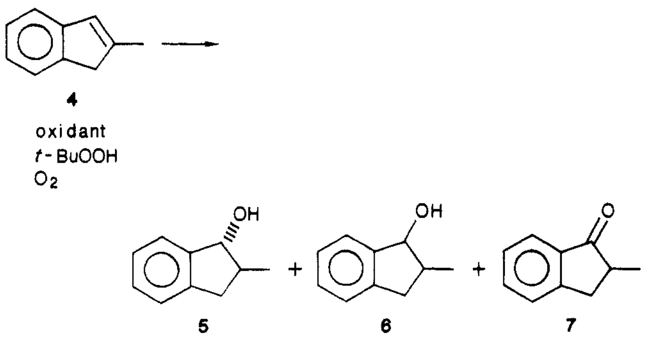
[5] Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041.

[6] Negishi, E.; Miller, J. *Tetrahedron Lett.* **1984**, 3407. These authors carrier out the hydrozirconation of styrene with bis(cyclopentadienyl)zirconium dichloride and *tert*-butylmagnesium bromide, followed by treatment with iodine, which afforded a 9:1 mixture of (2-iodoethyl)- and (1-iodoethyl)benzene in 55% yield. Treatment of styrene with 1 followed by iodine gave (2-iodoethyl)benzene in 68% yield, with no evidence for the 1-isomer in the GC or NMR analysis.

Scheme I

$$R^{*}Zr + O_2 \longrightarrow R^{*}ZrOO$$
$$R^{*}ZrOO \longrightarrow R\cdot + ZrOO\cdot$$
$$R\cdot + ZrOO\cdot \longrightarrow ROOZr$$
$$ROOZr + R^{*}Zr \longrightarrow ROZr + R^{*}OZr$$

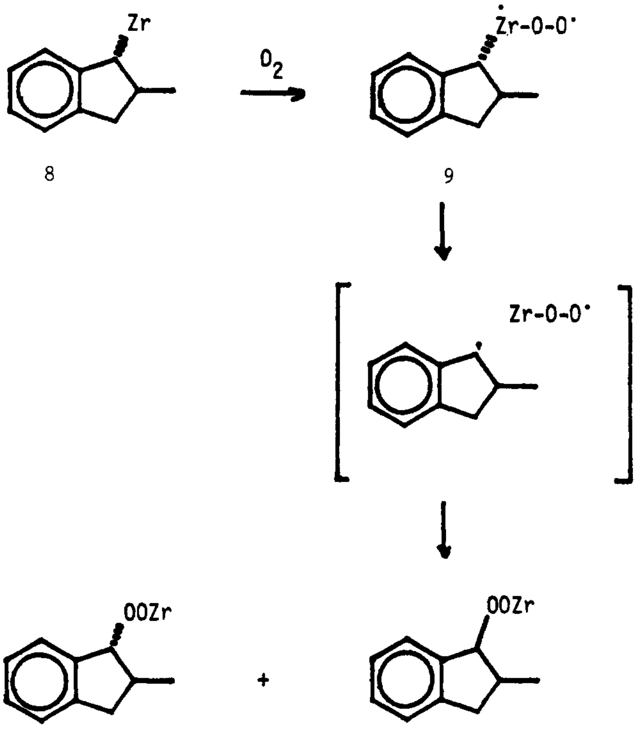
Scheme II



4 5 6 7

oxidant	5	6	7
	yields		
t-BuOOH	18	0	0
O_2	9	3	16

Scheme III



8 9 11 10

stantial amounts. Movement of the double bond out of conjugation with the aromatic ring, e.g. 1-phenylundec-3-ene, again gives substantial amounts of the benzylic product, although the ratio of terminal to benzylic alcohols is higher. The recovered olefin is again almost entirely a mixture of the cis and trans conjugated isomers, and a substantial amount of undecylbenzene is also formed.

It is possible that compounds with double bonds further from the ring, or those in which access to the benzylic position is blocked by chain branching, could be cleanly converted to terminal products, but these have not been investigated. However, the accessibility of the benzylic zirconium intermediate suggests that some useful information should be available concerning the stereochemistry of its oxidation reactions. Previous work on this point had to deal with the restriction that only primary alkyl zirconiums were available, and Schwartz derived some useful stereochemical information from the study of some deuterium-labeled compounds.[7] He proposed a mechanism for the reaction with oxygen as shown in Scheme I, in which oxygen slowly converts the alkyl zirconium to a peroxy radical which dissociates, allowing racemization. Recombination gives an alkylperoxy zirconium, which rapidly converts unreacted alkyl zirconium with retention to the final product mixture. Our observation of the formation of benzylic zirconiums provides access for the first time to secondary alkyl zirconiums, whose oxidation should provide useful stereochemical information complementary to Schwartz's. A likely candidate for this work appeared to be 2-methyl-1*H*-indene (4), which, if it could be induced to undergo hydrozirconation, could potentially form either cis or trans alcohols 5 and 6.

On hydrozirconation, 4 undergoes low conversion to the products shown in Scheme II. Oxidation with *tert*-butyl hydroperoxide gave exclusively the trans alcohol 5,[8] with no evidence for the presence of the cis product 6. Oxidation with oxygen gave a 75:25 mixture of 5 and 6 and some of the ketone 7 as well. Both of these results are in good agreement with the conclusions reached by Schwartz, as outlined in Scheme III. Addition of 1 to 4 should proceed in a cis fashion to give 8, which is oxidized by peroxide stereospecifically with retention of configuration to give the trans alcohol 5. With oxygen, slow reaction of 50% of 8 present, followed by recombination of radicals to give 10 and 11 in equal amounts, would result in a 75:25 ratio of final products 5 and 6, assuming that 10 and 11 would react rapidly in a stereospecific fashion with remaining 8. The result obtained provides clear confirmation of Schwartz's earlier conclusions for acyclic systems. Perhaps the most interesting result is that the diradical does appear to recombine to give equal amounts of 10 and 11, even though some preference for 11 might be expected on steric grounds. The NMR and HPLC methods used to determine the isomer ratio are in excellent agreement with each other and should easily detect a preference for one isomer in excess of about 10%.

This initial study has shown that aromatic olefins react with 1 quite differently than do their aliphatic counterparts. Synthetically, hydrozirconation of simple systems in which the double bond is conjugated with the aromatic ring could provide a useful route to benzylic alcohols, in those instances where acid-catalyzed hydration is prohibited. The formation of significant amounts of isomerized olefins appears to be without precedent for this reagent, except for our own unreported study,[3] and should be useful for obtaining information about the mechanism of movement of the zirconium along the chain.

Experimental Section

General Data. All reactions were run under an argon atmosphere. THF was dried with benzophenone ketyl. Styrene, indene, α-methylstyrene, propenyl benzene, allylbenzene, estragole, and anethole were obtained from commercial sources and distilled before use. Infrared spectra were obtained with a Perkin-Elmer Model 298 spectrometer, ^{1}H NMR spectra were obtained with Varian Model EM 360A spectrometer, ^{13}C NMR spectra were obtained with either a Varian CFT 20 or JEOL FX 270 spectrometer at 20 or 67.8 MHz, respectively, and gas chromatographic data were obtained with a Hewlett-Packard Model 5840A instrument using helium as carrier gas and thermal conductivity detectors. Analyses were performed on 6 ft by $^1/_8$ in. 3% OV-17

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[7] Labinger, J. A.; Hart, D. W.; Seibert, W. E., III; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851.

[8] Marshall, P. A.; Prager, R. H. *Aust. J. Chem.* **1979**, *32*, 1251.

on 80/100 Supelcoport columns, supplied by Supelco. HPLC analyses were performed on a hybrid instrument using Whatman PXS Partisil PAC columns.

1-Phenyl-1-undecene. A mixture of triphenyldecylphosphonium bromide (42.3 g), benzaldehyde (8.5 g), and potassium carbonate (16.5 g) in 98 mL of dioxane and 2 mL of water was heated to reflux for 2 days.[9] The reaction mixture was cooled and filtered, and hexane was added to precipitate triphenylphosphine oxide. Filtration followed by repetition of the process two times and finally distillation in a Kugelrohr apparatus gave 11.7 g (60%) of product: bp 80–130 °C (0.1 mm); IR 1600, 966 (w) cm^{-1}; ${}^{13}C$ NMR (67.8 MHz) δ 137.8, 133.1, 131.0, 129.8, 128.7, 128.4, 128.1, 126.7, 126.4, 125.9, 33.1, 32.0, 30.0, 29.6, 29.4, 28.7, 22.8, 14.1; ^{1}HMR δ 6.95 (5 H, m), 6.07 (m), 5.50 (t, J = 14 Hz), 5.30 (t, J = 14 Hz), 2.07 (t), 1.18 (14 H), 0.83 (3 H, t); MS m/e 230.2025 (calcd for $C_{17}H_{26}$ m/e 230.2035). Gas chromatographic analysis indicated this to be a 73:27 mixture of isomers, identified as *cis*- and *trans*-1-phenyl-1-undecene, respectively, on the basis of the above data and the following information. Hydrogenation over Pt in EtOH gave a single product in 95% yield, which showed data in excellent accord with that expected for 1-phenylundecane.[10] Isomerization of 638 mg of the mixture with 59 mg of *p*-toluenesulfinic acid in refluxing dioxane[11] gave 551 mg of *trans*-1-phenyl-1-undecene. This substance showed a GC retention time identical with that of the minor isomer in the mixture: IR 1595, 962 (s) cm^{-1}; ${}^{1}H$ NMR δ 7.00 (5 H, m), 6.07 (2 H, m), 2.03 (2 H, m), 1.22 (14 H), 0.88 (3 H, t).

1-(4-Chlorophenyl)-1-undecene. Application of the same reaction to 4-chlorobenzaldehyde gave the desired product in 87% yield as a 64:36 mixture of cis and trans isomers. This mixture showed the following spectral properties: IR 1593, 957 (m) cm^{-1}; ${}^{1}H$ NMR δ 6.87 (4 H, s), 5.92 (m), 5.43 (t), 5.23 (t), 2.03 (2 H), 1.17 (14 H), 0.85 (3 H, t); ${}^{13}C$ NMR (67.8 MHz) δ 136.4, 136.2, 133.9, 132.3, 132.1, 131.9, 130.0, 128.5, 128.2, 127.5, 127.1, 33.1, 31.9, 29.9, 29.6, 29.3, 28.6, 22.7, 14.1; MS, m/e 264.1616 (calcd for $C_{17}H_{25}Cl$ m/e 264.1645).

***cis*-1-Phenyl-3-undecene.** A mixture of 5.2 g of sodium hydride (50% in mineral oil) in 100 mL of Me_2SO was heated for 16 h at 50 °C. The resulting solution was cooled to ambient temperature, and a solution of triphenyloctylphosphonium bromide (47.3 g, ca. 90% pure) in 200 mL of Me_2SO was added. To the resulting dark red solution was added 10.6 g of 3-phenylpropanal in 10 mL of Me_2SO. The solution was heated for 23 h at 50 °C, cooled, diluted with water, and extracted with hexane (3×) and the hexane extract washed (4×) with water. After drying, filtration, and removal of solvent, distillation gave 7.7 g (38%) of pure cis olefin. This substance showed a single peak on GC analysis and the following spectral properties: IR 1600 cm^{-1}; ${}^{1}H$ NMR δ 6.92 (5 H, s), 5.12 (2 H, t, J = 9 Hz), 2.35 (4 H, m), 1.82 (2 H, m), 1.18 (10 H, s), 0.85 (3 H, t); ${}^{13}C$ NMR (67.8 MHz) δ 142.1, 130.7, 128.5, 128.4, 125.7, 36.1, 31.9, 29.6, 29.2, 27.2, 22.7, 14.1; MS, m/e 230.2012 (calcd for $C_{17}H_{26}$ m/e 230.2035). Hydrogenation gave only 1-phenylundecane, identical with that obtained from 1-phenyl-1-undecene.

2-Methyl-1*H*-indene. To a solution of 9.2 g of 2-indanone in 50 mL of ether was added 50 mL of 3.2 N MeMgCl in THF. After 3 h at ambient temperature, the mixture was decomposed with saturated NH_4Cl solution, diluted with ether, and extracted with NH_4Cl and saturated Na_2SO_4 solutions. Drying with Na_2SO_4, filtration, and removal of solvent gave 10.2 g of a 85:15 mixture of alcohol and starting ketone. This was added to 250 g of a 10% solution of oxalic acid in water and heated to reflux for 2 h. Distillation, followed by ether extraction, gave 7.1 g of a mixture of 2-methyl-1*H*-indene and 2-indanone, which was subjected to flash chromatography. Elution with hexane, followed by distillation, gave 5.5 g of pure 2-methyl-1*H*-indene, bp 68–96 °C, which gave NMR data in complete agreement with published data.[12]

General Procedure for Hydrozirconation.[3] To a solution of 4.38 g (15 mmol) of Cp_2ZrCl_2 and 10 mmol of the olefin in 45 mL of THF at ambient temperature was added 2.16 g (7.5 mmol) of a 70% solution of Red-Al in toluene. After maintainance for the time and at the temperature shown in Table I, the mixture was cooled to room temperature. Oxidation with oxygen was carried out by introduction of a flow of dry oxygen gas through a side arm for about 1 h, followed by stirring at ambient temperature overnight. Oxidation with *tert*-butyl hydroperoxide was performed by addition of 4.3 mL of a 3.7 M solution in toluene,[13] followed by stirring at ambient temperature for about 1 h. The reaction was then quenched with about 2 mL of water, diluted with hexane, and stirred for a few minutes, during which time the zirconium containing products precipitated from solution. After filtration, the solution was extracted two or three times with water, dried, and stripped. Products were further purified by distillation or chromatography as described in Tables I and II. Identification was performed by comparison of spectroscopic and chromatographic data with published information or with actual compounds, except as noted below.

1-Phenyl-1-undecene. Flash chromatography of the 4-h reaction (cf. Table II) gave nearly pure 1-phenyl-1-undecanol. Further purification by preparative HPLC, followed by Kugelhohr distillation, gave pure material: bp 130–140 °C (0.7 mm); IR 3350, 1604 cm^{-1}; ${}^{13}C$ NMR (67.8 MHz) δ 145.0, 128.2, 127.2, 125.8, 74.5, 39.0, 31.9, 29.5, 29.3, 25.7, 22.6, 14.1; ${}^{1}H$ NMR δ 6.98 (5 H, s), 4.32 (1 H, t, J = 6 Hz), 2.22 (1 H, s, OH), 1.17 (16 H), 0.85 (3 H, t). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.64; H, 11.56. This substance has been described only once previously;[14] mp 19 °C. Chromatography of the 72-h reaction gave 11-phenyl-1-undecanol, purified as above; mp 35–36 °C (lit.[15] mp 23 °C). This substance showed the following spectral properties: IR 3360 cm^{-1}; ${}^{13}C$ NMR (67.8 MHz) δ 142.8, 128.3, 128.1, 125.4, 62..8, 35.9, 32.7, 31.4, 29.5, 25.7; ${}^{1}H$ NMr δ 6.90 (5 H, s), 3.37 (2 H, t, J = 6 Hz), 2.40 (2 H, t, J = 7 Hz), 1.72 (1 H, s, OH), 1.18 (16 H); MS, m/e 248.2140 (calcd for $C_{17}H_{28}O$ m/e 248.2140).

1-(4-Chlorophenyl)-1-undecene. Hydrozirconation/oxidation gave a complex mixture, separated by flash chromatography into olefin, secondary alcohol, and primary alcohol fractions. The olefin fraction consisted of four compounds, in 29:25:33:13 ratio, corresponding in GC retention time to *cis*-1-phenyl-1-undecene, *trans*-1-phenyl-1-undecene, *cis*-1-(4-chlorophenyl)-1-undecene, and *trans*-1-(4-chlorophenyl)-1-undecene, respectively. The secondary alcohol fraction consisted of two compounds in 43:57 ratio on GC. The minor constituent corresponded in retention time to 1-phenyl-1-undecanol, and the ${}^{1}H$ NMR spectrum of the mixture was consistent with the identification of 1-(4-chlorophenyl)-1-undecanol as the major constituent. The primary alcohol fraction also showed two components on GC in 57:43 ratio, with the major constituent corresponding to 11-phenyl-1-undecanol, and the mixture showed ${}^{1}H$ NMR data consistent with 11-(4-chlorophenyl)-1-undecanol as the minor constituent. No attempts were made to obtain pure samples of these compounds.

1-Phenyl-3-undecene. Chromatography of the product gave a hydrocarbon fraction composed of two major components in a 1:3 ratio, identified by GC, IR, and ${}^{1}H$ NMR as *trans*-1-phenyl-1-undecene and 1-phenylundecane, respectively. The only alcohols formed were 1-phenyl-1-undecanol and 11-phenyl-1-undecanol, as noted in Table II.

2-Methyl-1*H*-indene. a. Oxidation with *t*-BuOOH. The olefin was subjected to hydrozirconation at 25 °C for 24 h, followed by oxidation. Flash chromatography gave recovered olefin (81%) and *trans*-2-methyl-2,3-dihydro-1*H*-inden-1-ol: mp 87–88 °C; 18% yield. This compound proved to be identical with a sample prepared by hydroboration of 2-methyl-1*H*-indene[8] and showed ${}^{13}C$ NMR (20 MHz) signals at δ 144.9, 127.9, 126.5, 124.6, 123.8, 82.7, 45.2, 37.8, and 17.7.

b. Oxidation with Oxygen. Hydrozirconation for 24 h at 27 °C was followed by treatment with oxygen. Flash chromatography gave recovered olefin (46%), 2-methyl-2,3-dihydro-1*H*-inden-1-one (**7**; 16%), identified by comparision with material from oxidation of the hydroboration product,[8] and a mixture of two alcohols in 12% yield. Analysis by ${}^{1}H$ NMR showed this to be a 71:29 mixture of trans and cis alcohols **5** and **6**, respectively, by integration of the signals at 4.93 and 4.67 ppm.[8] Previous

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(11) Gibson, T. W.; Strassburger, P. *J. Org. Chem.* **1976**, *41*, 791.

(12) Edland, U. *Org. Magn. Reson.* **1978**, *11*, 516.

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references to these compounds state that they are inseparable by GC, but we found that they are partially resolved on HPLC, showing a 3:1 trans:cis ratio. The ^{13}C NMR spectrum of the mixture showed, in addition to major signals corresponding to the trans alcohol, minor signals (20–30%) at 77.5 and 13.5 ppm, due to C1 and the methyl group of the cis isomer, shifted upfield as expected from the corresponding signals in the trans isomer at 82.7 and 17.7 ppm. A reaction carried out at 40 °C for 24 h gave the alcohols in 19% yield and the same isomer ratio.

Registry No. **4**, 2177-47-1; (±)-**5**, 107298-29-3; (±)-**6**, 73837-42-0; (±)-**7**, 107298-30-6; Cp_2ZrCl_2, 1291-32-3; styrene, 100-42-5; 2-phenylpropene, 300-57-2; 1-phenylpropene, 637-50-3; 3-phenylpropene, 25013-15-4; 1-methoxy-4-(1-propenyl)benzene, 104-46-1; 1-methoxy-4-(methylethenyl)benzene, 1712-69-2; (±)-1-phenylethanol, 13323-81-4; 2-phenylethanol, 60-12-8; acetophenone, 98-86-2; 2-phenylpropanol, 698-87-3; (±)-1-phenylpropanol, 613-86-5; 3-phenylpropanol, 122-97-4; 1-phenyl-1-propanone, 93-55-0; 3-phenylpropyl formate, 104-64-3; (±) 1-(4-methoxyphenyl)propanol, 107298-28-2; 3-(4-methoxyphenyl)-propanol, 5406-18-8; 1-(4-methoxyphenyl)-1-propanone, 121-97-1; 1-methoxy-4-propyl benzene, 104-45-0; *trans*-1-phenyl-1-undecene, 107224-27-1; *trans*-1-(4-chlorophenyl)-1-undecene, 107224-28-2; *cis*-1-phenyl-3-undecene, 107224-29-3; (±)-1-phenyl-1-undecanol, 107224-30-6; 11-phenyl-1-undecanol, 61439-50-7; (±)-1-(4-chlorophenyl)-1-undecanol, 107224-31-7; 11-(4-chlorophenyl)-1-undecanol, 107224-32-8; 1-phenylundecane, 6742-54-7; tripheny decyl phosphonium bromide, 32339-43-8; benzaldehyde, 100-52-7; *cis*-1-phenyl-1-undecene, 107224-33-9; 4-chlorobenzaldehyde, 104-88-1; *cis*-1-(4-chlorophenyl)-1-undecene, 107224-34-0; triphenyl octyl phosphonium bromide, 42036-78-2; 3-phenylpropanal, 104-53-0; 2-indanone, 615-13-4.

Electronic Spectroscopy of Iron and Ruthenium Pentamethylcyclopentadienyl–Trimethylphosphine Complexes

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Electronic spectra have been obtained for a series of complexes (η^5-C_5Me_5)L_2MX (M = Ru, Fe; L = PMe_3, PEt_3, CO; X = hydride, halide, alkoxide, alkyl, aryl). The close similarity of the low-energy regions of the spectra of (η^5-C_5Me_5)$(PMe_3)_2RuCH_3$ and ruthenocene suggests that the electronic transitions in the former molecule are derived from 1e, a → 2e(dσ*). These assignments are consistent with spectra measured on complexes in which systematic substitutions of the metal center, dative ligands, and the σ-bonded ligand have been made. Irradiation of (η^5-C_5Me_5)L_2MX leads to L_nX loss, consistent with a photoactive excited state that involves the population of 2e(dσ*).

Introduction

Little is known about the electronic structures of the excited states of organometallic compounds containing phosphine ligands.[3] The nature of these excited states is particularly significant for those complexes that undergo photoreactions leading to carbon–hydrogen bond activation in hydrocarbons.[4] The primary photochemical process leading to the transient species responsible for C–H activation has been assumed to be either dissociation of a phosphine ligand[5] or, preferentially, photoelimination of H_2,[3a–c] in the case of phosphine–polyhydride complexes.[4a,b,e,f] On the other hand, the previously unprecedented photodissociation of a phosphine ligand rather than H_2 has recently been demonstrated for some polyhydride–phosphine complexes of rhenium, indicating that reductive elimination of dihydrogen[3d,e] is not always the preferred photochemical pathway. Hapticity changes for the metal–cyclopentadienyl bonding mode have also been suggested as an alternative photodissociative process for complexes containing a cyclopentadienyl ligand,[6] e.g. Cp*Ir(CO)$_2$ (Cp* = η^5-C_5Me_5). Many of the known examples of photochemically induced C–H bond activation involve compounds containing at least one, and, in some cases, all three, of the above ligands. At present, our understanding of their electronic structures and primary photochemical processes is insufficient to discern the relative importance of the various dissociative pathways.

We have observed that alkyl complexes of the type Cp*$(PMe_3)_2$RuR thermally activate the C–H bonds of arenes (e.g. eq 1).[7] The mechanism proposed invokes a

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