A COMPARATIVE STUDY OF TRIPHENYLAMINE, TRIPHENYLPHOSPHINE, TRIPHENYLARSINE, TRIPHENYLANTIMONY AND TRIPHENYLBISMUTH AS LIGANDS IN THE RHODIUM-CATALYZED HYDROFORMYLATION OF 1-DODECENE

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ABSTRACT - Triphenylamine, triphenylphosphine, triphenylarsine, triphenylantimony and triphenylbismuth were evaluated on the basis of olefin to aldehyde conversion, and also on the basis of the normal/iso (n / i) product ratio, as ligands in the rhodiumcatalyzed hydroformylation of 1-dodecene. Two series of reactions were conducted which differed only in total reaction time (120 minutes vs 135 minutes) and in the ligand/rhodium ratio (60:1 vs 300:1). Both reactions series employed 35 grams of 1dodecene, a 176 ppm rhodium charge, 100 psig of 1:1 H₂ / CO, and a reaction temperature of 90°C. In the 60:1 vs 330:1 reaction series, triphenylamine gave olefin conversions and n / i ratios of 2.0%, 2.0 vs 5.8%, 1.8; triphenylphosphine gave 95%, 4.4 vs 86.9%, 8.7; triphenylarsine gave 58%, 3.1 vs 85.8%, 3.5; triphenylantimony gave 13.0%, 6.1 vs 3.5%, 9.1 respectively. Triphenylbismuth failed to promote hydroformylation in both reaction series. These data demonstrate that regiospecificity, as measured by the n / i product ratio, varies inversely to increased ligand basicity.

INTRODUCTION

Triphenylphosphine is generally cited as the ligand of choice in the rhodium-catalyzed hydroformylation of olefins (1,2,3,4,5). However, a search of the literature fails to reveal any study comparing the four other triphenyl Group V compounds with triphenylphosphine in the rhodium-catalyzed hydroformylation of a detergent-range olefin. The fact that hydroformylation represents an industrial process whose products yearly generate hundreds of millions of dollars of corporate revenue mandates such a comparative study.

In this paper we present such a comparison, examining percent olefin to aldehyde conversion and the normal/iso (n / i) aldehyde product ratio when each of the triphenyl Group V family ligands are employed, under similar reaction conditions, in the rhodium-catalyzed hydroformylation of 1-dodecene.

METHODS

In each of these experiments a 1:1 hydrogen/carbon monoxide synthesis gas mixture (Matheson Co.) was used without further purification. I-Dodecene (Humphrey Chemical Co.) was percolated through an 80×2 cm silica gel (Grace) column prior to use. In each reaction 10.4 mg Rh₂O₂ $^{\circ}$ SH₂O, 176 ppm rhodium based on the olefin weight (Strem Chemical Co.), were charged into a stainless steel 250 ml autoclave. This was followed by 35.0g (0.208 mole) of 1-dodecene. In the 330:1 ligand/rhodium experiments 20 mmol of the appropriate triphenyl Group V compound (Alfa Ventron Inc.) was added, whereas in

the 60:1 ligand/rhodium experiments only 3.6 mmol of ligand was added to the reactor. The autoclave was stirred by means of a teflon-coated magnetic bar and the reaction sequence initiated by capping the autoclave, purging the entire system three times to 100 psig with synthesis gas, heating the reation to 90° C in a five minute period, and readjusting the synthesis gas pressure to 100 psig when the reaction temperature was reached.

The autoclave contents were sampled by means of a dip-tube. In the 330:1 ligand/rhodium runs each experiment was sampled every 15 minutes through the 135 minute reaction period while in the 60:1 reactions only one sample was drawn at the end of the 120 minute sequence. Two analyses were performed on each sample. First, the sample was subjected to vapor phase chromatography (VPC) using an instrument containing 10 feet X 1/8 inch O.D. 8% FFAP on 80-100 mesh Varaport 30 (Varian Associates Inc.). The VPC runs were termally programmed from 120° to 250° at 8° /minute. Retention times and thermal response factors were calibrated against known standards (Aldrich Chemical Co.). Secondly each sample was subjected to atomic absorption (AA) analysis to determine if iron was present, and in what quantity, in the reaction mixtures. At the end of each experiment the autoclave was emptied and scrubbed-out with THF until the washings gave no indication of rhodium using AA analysis.

RESULTS

VPC analysis of the autoclave conents at the end

of each experiment consistently indicated that the major products were n-tridecanal and 2methyldodecanal. Only small amounts (less than 2%) of 2-ethylundecanal and 2-propyldecanal were deteced. No alcohol or acetal compounds were found in the final reaction mixtures and greater than 98% of the residual dodecene was present as a mixture of the linear internal-dodecene isomers. No n-dodecane was detected from hydrogenation of the olefin feedstock. AA analyses of all of the samples as well as the percolated olefin feedstock were negative for iron or any of its compounds.

The aldehyde product data are summarized in Table 1.

At 15 minute intervals samples were drawn from the 330:1 ligand/rhodium ractions. The n/i product ratios were calculated from the VPC data derived from these reactions. Graph 1 summarized these n / i ratios plotted against reaction time.

DISCUSSION

In both reaction series, triphenylphosphine promoted the largest olefin to aldehyde conversion followed by triphenylarsine, triphenylantimony and triphenylamine in decreasing order of conversion. No aldehyde product was detected in either of the reactions where triphenylbismuth was used as the ligand.

TABLE 1

ALDEHYDE PRODUCT RESULTS

Triphenyl (Ph ₃) Group V Compound	330:1 Ligand/Rhodium Reactions		60:1 Ligand/Rhodium <u>Reactions</u>	
	% olefin conversion	n/iat <u>135 min</u>	% olefin conversion	n/iat 120 min
(Ph) ₃ N	5.8	1.8	2.0	2.0
(Ph) ₃ P	86.9	8.7	95.0	4.4
(Ph) ₃ As	85.8	3.5	58.0	3.1
(Ph) ₃ Sb	8.5	9. t	13.0	6.1
(Ph) ₃ Bi	0.0		0.0	

GRAPH 1

TIME vs n/i ratio



In both the high and low ligand reaction series, the order of ligands yielding the highest to lowest n / i ratios was the same. Triphenylantimony gave the largest ratio, followed by triphenylphosphine, triphenylarsine, and lastly by triphenylamine.

These n / i data contrast sharply with the findings of Lai and Uccianai (2) who reported that in the rhodium-catalyzed hydroformylation of 3-phenyl-1propene (allylbenzene) the highest n / i ration was obtained using triphenylarsine as the lagand. In our hands triphenylarsine gave the next to lowest n / i ratio of all of the ligands which effected hyroformylation (see Table 1).

With the exception of the triphenylamine experiment, the n / i ratios of all of the 330:1 ligand/rhodium reactions were higher than in the corresponding 60:1 reactions. Conversely, the aldehyde yields of the 330:1 reactions were all lower than in the corresponding 60:1 series. These findings are consistent with reports that high ligand/rhodium ratios increase the n / i ratio whilst decreasing the overall reaction rate (1,6,7).

Pruett and Smith (8,9,10) have examined some phosphine and phosphite ligands on the basis of Strueli's (11) Half-Neutralization Potential (Δ HNP). This derived basicity measurement reflects the difference in the nonaqueous half-neutralization potential between a given ligand and N,N'diphenylguanidine (11,12). The larger the Δ HNP value the weaker the base. Pruett and Smith (9,10,11) reported that triphenylphosphite, a weaker base than triphenylphosphine, gives a higher n / i ratio than triphenylphosphine under similar reaction conditions. They have also shown (9,10,11) that the introduction of a mild electron-withdrawing group, such as chloride, onto the three phenyl para positions of triphenylphosphite further increases the n / i ratio over that observed for the unsubstituted aromatic phosphite.

this theory holds true Apparently when extrapolated to the the triphenyl compounds of other Group V elements. Given the electronegativity of a Group V element (13) the relative basicity of the derived triphenyl compounds can be inferred (14). The least basic of all of the triphenyl Group V compounds is triphenylbismuth, followed in order of increasing basicity by triphenylantimony, triphenylphosphine, triphenylarsine and With the of triphenylamine. exception triphenylbismuth (14), this is the identical order of triphenyl Group V compounds for highest to lowest n / i which we observed in our experiments (see Table 1).

As summarized the Graph I the first sample analyzed during each of the 330:1 ligand/rhodium experiments always had the highest n / i ratio of the entire reaction. The succeeding 15 minute samples established a downward trend in the n / i ratio. VPC analysis of these successive samples in any given reaction indicated that increasingly larger portions of the 1-dodecene had been isomerized to internal dodecene isomers, the hydroformylation of which would necessarily form iso-aldehydes.

AA analysis of these samples, as well as of the percolated olefin charge, showed no presence of iron, the carbonyls of which are know to be olefin isomerization catalysts (1). Thus a rhodium and/or thermal isomerization mechanism must be inferred, both of which have been widely reported (1,5). A second explanation for this n / i ratio decrease is the increasing polarity of the reaction mixture caused by aldehyde formation. There are numerous reports (1,6,7,15,16,17) in which identical hydroformylation reactions run in polar and nonpolar solvents showed lower n / i ratios when polar solvents were employed.

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