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Diolefin Reactions Catalyzed by Transition Metal–Schiff Base Complexes

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It has been found that certain Schiff bases when coordinated to Fe(acac)$_3$ or Ni(acac)$_2$ reduced with an aluminum alkyl results in active catalysts for the cyclo-oligomerization of isoprene and butadiene. With the iron–Schiff base catalysts cyclodimerization of isoprene and butadiene occurs whereas cyclotrimerization of butadiene takes place with the nickel–Schiff base catalysts. The Schiff base ligands studied have aromatic and nonaromatic nitrogen donor atoms, which differ from most other ligands used for the catalytic enhancement of metals in nonaqueous systems. In such cases, aromatic α-diamines such as 2,2′-dipyridyl have been used. Variations in the Schiff base structure has a pronounced effect on reaction rate, suggesting that electronic and geometric factors play an important role for the promotion of metal catalysis.

INTRODUCTION

It has been recognized for some time that a ligand coordinated to a metal can have pronounced effects on the catalytic conversion of a substrate. Phosphorous compounds coordinated to metals have resulted in catalysts for several different catalytic reactions in organic media (*1*). Phosphorus compounds are known for their ability to stabilize lower valence states of transition metals, which is an important requirement for homogeneous catalyst systems. Nitrogen compounds coordinated to transition metals have also resulted in active catalysts systems in both organic (*2–6*) and aqueous systems (*7–10*). In most cases, aromatic amine ligands have been found to be much more effective than aliphatic amines in increasing catalysis rates when coordinated to metals. Compared to phosphorus ligands, nitrogen compounds have been used to a lesser extent in nonpolar systems. The work of Misono and coworkers (*3–4*) on the use of 2,2′-dipyridyl coordinated to iron as the catalyst for the oligomerization of isoprene is one of the few examples using a nitrogen ligand for activating a metal in an organic medium.

Recently, we reported (*11*) that adding 2-cyanopyridine to iron acetylacetonate [Fe(acac)$_3$] and triethylaluminum (TEA) results in a very active catalyst system for the polymerization of isoprene or butadiene. In this work it was shown that the nature of the ligand is very important. For example, the use of 3- and 4-cyanopyridine resulted in no polymerization.

This paper reports an investigation of the use of Schiff bases derived from pyridine-2-carboxaldehyde and 2-pyridyl phenyl ketone as ligands for isoprene and butadiene oligomerization reactions. These Schiff bases result from slight structural modifications of the ligands previously studied and provide a structural link between aliphatic α-diamines and aromatic α-diamines.

EXPERIMENTAL

The metal acetylacetonates and the other metal compounds used in this study were obtained from the K & K Laboratories, Inc.

Before use, the solid compounds were dried in vacuum at 50–60°C for 16 hr, then stored in a nitrogen atmosphere.

The nitrogen compounds, other than the Schiff bases, were obtained from the Aldrich Chemical Company. The 2-cyanopyridine was vacuum distilled and stored under nitrogen. The other compounds were dried in vacuum at room temperature for 16 hr and stored under nitrogen.

Isoprene (Eastman and J. T. Baker) was distilled under nitrogen and stored in a nitrogen atmosphere. Butadiene (Matheson C. P. Grade) was dried by passing it through dried-activated molecular sieves. Benzene (B&A) and toluene (Fisher) were distilled under nitrogen and stored over molecular sieves in a nitrogen atmosphere. Triethylaluminum (TEA) (Texas alkyls) and the other aluminum alkyls were used as received.

The Schiff bases were not commercially available, so they had to be prepared. For example, N-(2-pyridylidene)-aniline (NPA) was prepared by condensing pyridine-2-carboxaldehyde (PA) and aniline. The reaction mixture was distilled under vacuum to give a thick yellow oil, bp 114–116°/2 mm Hg. Evacuation of the thick oil in a vacuum desiccator to remove traces of the unreacted material resulted in the crystallization of NPA in 95.6% yield. The melting point of the material was 37–38°C which agrees with the reported value of 38.5°C (*11*). The C, H, and N analyses also agreed. Calculated C, H, and N percentages based on $C_{12}H_{10}N_2$ are: 79.12, 5.50, and 15.39% compared to experimental values of 78.81, 5.61, and 14.97%.

The preparation of Schiff bases derived from 2-pyridyl phenyl ketone has not been reported in the literature. In a few instances transition metal complexes were prepared directly from a metal salt, 2-pyridyl phenyl ketone, and substituted anilines (*13*). We found that these Schiff bases can be prepared in near quantitative yield by condensing 2-pyridyl phenyl ketone and substituted anilines. For example, 2-(2-pyridyl)-benzylideneaniline (PBA) was prepared by reacting 2-pyridyl phenyl ketone (5 g) and aniline (2.5 g) to give approximately 90% yield. A detailed description of the procedure used will be reported later. The reaction mixture was distilled at 160–170°C/1 mm Hg with PBA solidifying in the receiver. Analyses for C, H, and N found: 83.22, 5.38, and 10.55%, respectively. These values compare quite favorably with the calculated values of 83.75, 5.40, and 10.85%, respectively.

Similarly, 2-(2-pyridyl)-benzylidene-*p*-toluidine (PBT) was prepared by condensing phenyl 2-pyridyl ketone (PPK) with *p*-toluidine. PBAn 2-(2-pyridyl)-benzylidene-*p*-anisidine) was prepared by condensing PPK with *p*-anisidine. PMA (α-(2-pyridyl)-methyleneaniline) was prepared by condensing 2-acetylpyridine and aniline. PEA (α-(2-pyridyl)ethyleneaniline) was prepared by condensing ethyl 2-pyridyl ketone with aniline. 2,6-NPX (N-2-pyridylidene-2,6-xylidine) was prepared by condensing PA with 2,6-xylidine. 2,4-NPX (N-2-pyridylidene-2,4-xylidine) was prepared by condensing PPK with 2,4-xylidine. NPAn (N-(2-pyridylidene)-*p*-anisidine) was prepared by condensing 2-pyridinealdehyde (PA) with *p*-anisidine. NPT (N-2-pyridylidene-*p*-toluidine) was prepared by condensing PA with *p*-toluidine. The high purity of the Schiff bases is demonstrated by the analytical data given in Table 1.

Isoprene dimerization experiments were carried out in 200-ml beverage bottles. The procedure for a typical dimerization run is as follows:

To a beverage bottle was added 1 mmole of $Fe(acac)_3$, 0.5 mmole of PBA, 50 ml of benzene and 1000 mmoles of isoprene. This was done in a dry nitrogen atmosphere. The bottle was sealed with a two-hole beverage cap over a Buna-N gasket. A solution of 3 mmoles of TEA in 2 ml of benzene was added with a hypodermic syringe. This mixture was stirred at a high rate with a magnetic stirrer at ambient temperature.

Products were analyzed by glc using a Varian-Aerograph 200 series chromatograph. The column was 5 ft × ¼ in. stainless steel packed with 20% SE-30 on 60/80 mesh chromosorb W. The column temperature was programmed at a rate of 20°C/min from 50 to 200°C. Positive identifica-

TABLE 1
ANALYSIS OF SCHIFF BASE LIGANDS

Schiff Base	% Carbon		% Hydrogen		% Nitrogen	
	Found	Calc.	Found	Calc.	Found	Calc.
NPA	78.81	79.12	5.61	5.50	14.97	15.39
NPT	79.36	79.59	6.17	6.12	14.55	14.28
NPAn	72.83	73.58	5.63	5.66	12.80	13.21
2,4-NPX	79.71	80.00	6.61	6.67	13.42	13.33
2,6-NPX	79.59	80.00	6.69	6.67	13.08	13.33
PMA	79.35	79.59	6.32	6.12	14.10	14.29
PEA	79.77	80.00	6.59	6.67	13.26	13.33
PBA	83.22	83.75	5.38	5.40	10.55	10.85
PBT	83.81	83.82	5.93	5.88	10.13	10.30
PBAn	78.88	79.17	5.47	5.56	9.67	9.72

tion of the products was made by ir, NMR, and mass spectroscopy.

Rate data were obtained by withdrawing samples at the desired time and immediately analyzing the amount of isoprene by chromatography. The reaction rates obeyed first-order kinetics with respect to isoprene concentration up to at least two half-times.

The butadiene dimerization reactions were carried out in a 300 ml thick-walled glass reactor equipped with a stirrer, gas inlet and outlet valves, a pressure gauge, and a 100 psig safety rupture-disc. A typical reaction was carried out as follows:

To the reactor was charged 0.5 mmoles of $Fe(acac)_3$, 0.5 mmoles of PBA, 1.5 mmoles of TEA, and 100 ml of toluene. The mixture was cooled to −78°C with a dry ice bath and 500 mmoles of butadiene charged. The reactor was gradually heated to 85°C. A rapid exothermic reaction commenced at this point and the temperature went up to 120°C and the maximum pressure recorded was 72 psig. In less than 10 min the temperature and pressure started to drop. At the end of 1 hr the reaction mixture was cooled to room temperature and the unreacted butadiene was vented through a gas meter. The liquid product was analyzed by gas chromatography, using the same procedure as in the isoprene cyclodimerization using authentic samples for calibration.

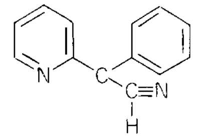
The butadiene trimerization experiments were carried out in the same apparatus as the butadiene dimerization experiments. A typical reaction was carried out as follows:

To the reactor was charged 1.5 mmoles of nickel acetylacetonate $Ni(acac)_2$, 1.5 mmoles of PBA, 3.0 mmoles of TEA in 100 ml of toluene. The mixture was cooled to −78°C and 500 mmoles of butadiene was added. The reactor was slowly heated to 120°C and held at this temperature for 4 hr with vigorous stirring. The reaction mixture was cooled to room temperature and the unreacted butadiene was vented through a gas meter. The liquid product was analyzed by gas chromatography. Authentic samples of the cyclododecatriene isomers were used as references and their identity verified by combinations of ir, NMR, and mass spectroscopy.

RESULTS

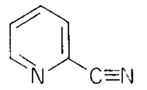
Iron–Schiff Base Catalysts

In a previous paper (*11*), we reported an $Fe(acac)_3$–TEA–nitrogen ligand catalyst which is very active for the polymerization of butadiene and isoprene. With this catalyst the active ligands are in order of decreasing effectiveness; phenyl-2-pyridylacetonitrile, 2-cyanopyridine and 2-pyridine aldoxime. Without ligand there is no reaction. Of these ligands 2-pyridine aldoxime results in the least active catalyst, i.e., lower rate



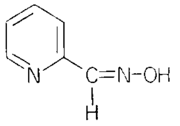
Phenyl-2-pyridylacetonitrile

(I)



2-Cyanopyridine

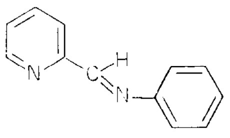
(II)



2-Pyridine aldoxime

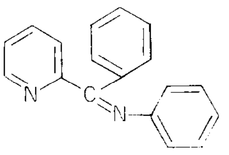
(III)

and overall polymer yield. A further study of this type of ligand has revealed that substituting the hydroxyl group of 2-pyridine aldoxime with a phenyl group to give the Schiff base N-(2-pyridylidene)-aniline (NPA), results in a catalyst which not only gives polymer but also low yields of butadiene and isoprene cyclodimers. Substitution of the hydrogen in NPA with a phenyl group to give PBA results in a catalyst that is very active and selective for the cyclooligomerization of butadiene and isoprene.



N-(2-Pyridylidene)-aniline (NPA)

(IV)



α-(2-Pyridyl)-benzylideneaniline (PBA)

(V)

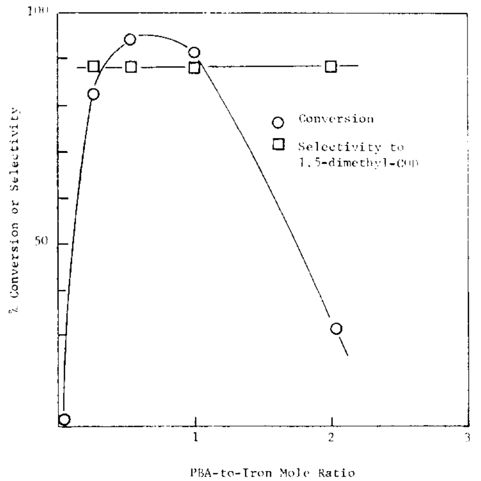


Fig. 1. Isoprene conversion and selectivity as a function of the PBA-to-iron mole ratio.

Figure 1 shows the variation of isoprene conversion and selectivity as a function of the PBA-to-iron mole ratio. Maximum conversion occurs at a PBA-to-iron mole ratio of 0.5 to 1. The selectivity is rather insensitive to the PBA-to-iron mole ratio over the entire range studied. The major products are 1,5- and 2,5-dimethyl-1,5-cyclooctadiene with the minor products being 1-methyl- and 2-methyl-4-isopropenylcyclohexene, 1,4-dimethyl- and 2,4-dimethyl-4-vinylcyclohexene and low molecular weight polyisoprene.

Figure 2 shows the variation of cyclodimer yield with the aluminum-to-iron mole ratio. Keeping the PBA-to-iron ratio at 0.5 and isoprene-to-iron ratio of 500, the maximum yield is obtained at an aluminum-to-iron ratio range of 2–3.

Figure 3 shows the isoprene conversion as a function of the isoprene-to-iron mole ratio. Conversion decreases with increasing isoprene-to-iron ratio for a stated reaction time. Ratios of isoprene-to-iron up to 1500 results in conversions greater than 80%. However, even at a ratio of 3000:1 a high conversion can be obtained if the reaction time is long enough. These results show that the products have no strong inhibiting effect on the activity of the catalyst.

Figure 4 shows the isoprene conversion as a function of temperature. As the tem-

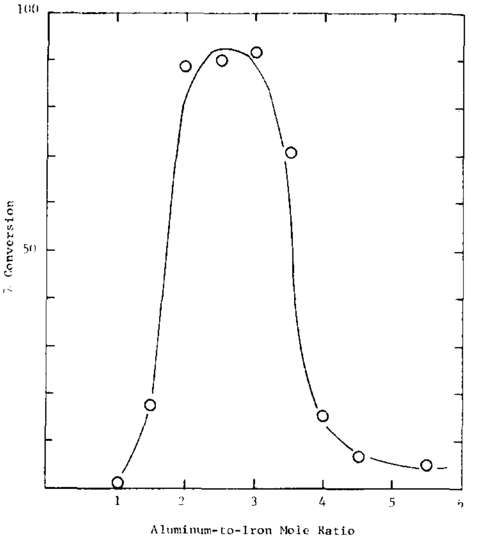


FIG. 2. Isoprene conversion as a function of the aluminum-to-iron mole ratio.

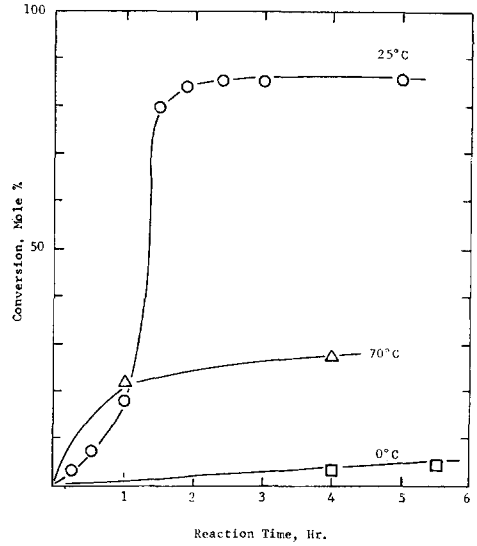


FIG. 4. Isoprene conversion as a function of time and temperature.

perature is increased from 25 to 70°C, there is a sharp drop in conversion, which is probably due to catalyst instability. This is the same trend that was observed with the Fe(acac)$_3$–2-cyanopyridine–TEA polymerization system (*11*). However, the slower reaction at 0°C is not the same behavior as observed with that iron polymerization catalyst, which becomes more active as the temperature is lowered.

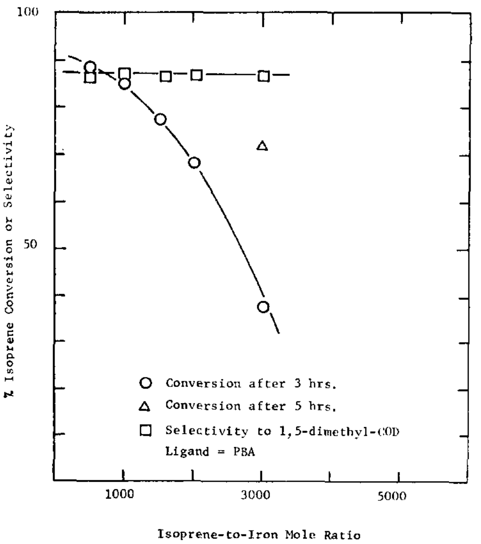


FIG. 3. Isoprene conversion and selectivity as a function of the isoprene-to-iron mole ratio.

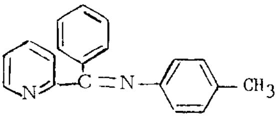
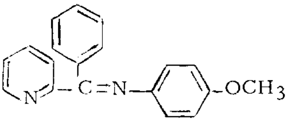
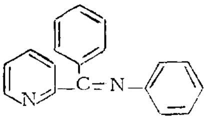
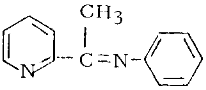
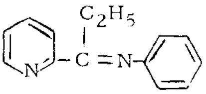
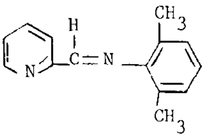
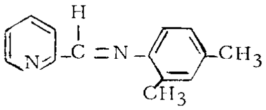
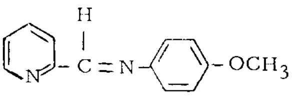
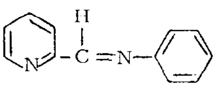
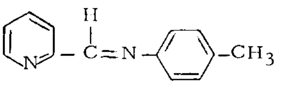
Table 2 gives apparent first-order rate constants and selectivity values for the conversion of isoprene obtained from catalysts containing various Schiff base ligands. These data show that the reaction rate increases approximately an order of magnitude when an alkyl group replaces the hydrogen in the $-\overset{|}{C}{=}N-$ linkage of the ligand and increases almost another order of magnitude when the alkyl group is replaced by an aromatic group. The apparent anomalous behavior of a catalyst made with 2,6-NPX will be discussed later. The data in Table 2 also shows that the most active catalysts for converting isoprene also give the highest selectivity to cyclodimers. These data were obtained using 1 mmoles of Fe(acac)$_3$, 1 mmoles of ligand, 3 mmoles of TEA, 200 moles of isoprene, and 60 ml of toluene at 25°C.

The cyclodimerization of isoprene is only obtained when Fe(acac)$_3$ is used as the iron compound. The $Fe_2(CO)_9$, $(C_5H_5)_2Fe(CO)_2$, $Fe(CO)_5$, and $FeCl_3$ did not give active catalysts when reduced with TEA in the presence of PBA. Triethylaluminum and triisobutylaluminum can be used to give active catalysts with Fe(acac)$_3$ and PBA. Inactive systems result when $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, or $Al_2(C_2H_5)_3Cl_3$ are used.

Table II

RATE CONSTANTS AND SELECTIVITY VALUES USING VARIOUS SCHIFF BASE LIGANDS

THE CYCLODIMERIZATION OF ISOPRENE

Ligand	Structure	First Order Rate Constant	Selectivity
PBT		7.7×10^{-2}	92
PBAn		7.7×10^{-2}	90
PBA		3.0×10^{-2}	92
PMA		9.5×10^{-3}	77
PEA		9.2×10^{-3}	59
2,6-NPX		1.12×10^{-2}	95
2,4-NPX		6.1×10^{-4}	67
NPAn		4.4×10^{-4}	34
NPA		2.6×10^{-4}	10
NPT		2.4×10^{-4}	31

Butadiene reacted differently than isoprene with the Fe(acac)$_3$–TEA–PBA catalyst. There was no reaction of butadiene at room temperature, i.e., approximately 25°C. By heating the reaction mixture to 95°C, an exothermic reaction commenced with about 75% of the butadiene reacting within the first 15 min. The reaction rate then declined with approximately 90% of the butadiene being converted after 1 hr. The major product was 1,5-cyclooctadiene and the minor products were 4-vinylcyclohexene and isomeric methyl-heptatrienes.

Nickel–Schiff Base Catalysts

The Ni(acac)$_2$–TEA–Schiff base catalysts convert isoprene to a mixture of six-membered ring isomers. No cyclotrimers were found in the product. Because of the complexity of this system, it is being investigated separately.

The reaction of butadiene proceeded more selectively with the nickel–Schiff base catalysts giving predominantly cyclic trimers. Table 3 gives conversion–selectivity data obtained using different nitrogen ligands with Ni(acac)$_2$. These data show that all the nickel–Schiff base catalysts are very active for the conversion of butadiene to mainly cyclic trimers. The nickel–2-cyanopyridine catalyst was not very active. This ligand was of interest since it resulted in high catalytic activity when complexed with iron. The data obtained from the 1,10-phenanthroline and 2,2′-dipyridylnickel catalysts were obtained for comparative purposes, since data have been reported using these ligand by others (*2*).

The data in Table 3 were obtained using a ligand-to-nickel ratio of 0.5 and alumi-

TABLE 3
CONVERSION AND SELECTIVITY VALUES USING VARIOUS LIGANDS FOR THE CYCLOTRIMERIZATION OF BUTADIENE

Ligand	Conversion: Mole %	Selectivity		
		VCH	COD	CDT
2-Cyanopyridine	8	45	10	45
1,10-Phenanthroline	23.4	25	4	71
2,2′-Dipyridyl	70.8	26	13	61
NPA	70.2	16	5	78
NPT	74.0	12	5	84
PBA	82.5	10	3	87
PBT	87.5	9	3	88
PBAn	94.3	9	3	88

VCH = Vinylcyclohexene
COD = Cyclooctadiene
CDT = Cyclododecatriene

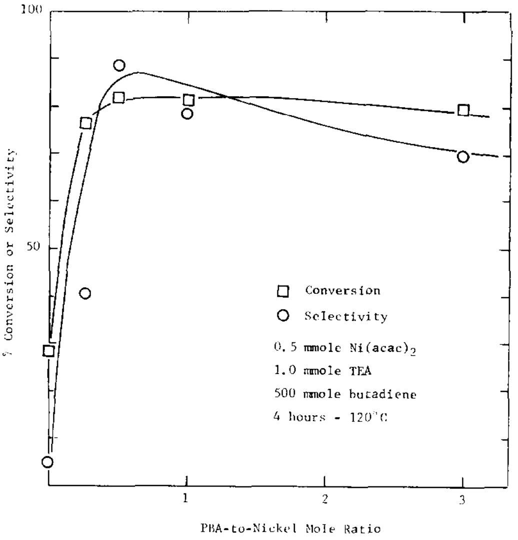


FIG. 5. Cyclotrimerization of butadiene as a function of the PBA-to-nickel mole ratio.

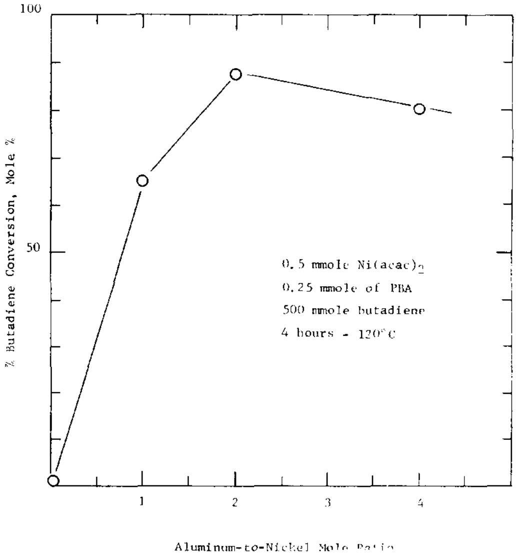
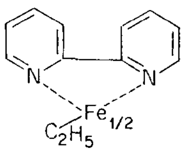


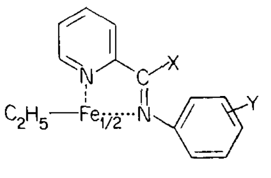
FIG. 6. Cyclotrimerization of butadiene as a function of the aluminum-to-nickel mole ratio.

num-to-nickel ratio of 2. Figures 5 and 6 give conversion and selectivity values as a function of PBA-to-nickel and aluminum-to-nickel ratio, respectively. The Ni(acac)$_2$ was the best nickel compound to use for this reaction; most other nickel salts gave poorer yields. Triethylaluminum was the best reducing agent, triisobutylaluminum gave a less active catalyst and $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, or $Al_2(C_2H_5)_3Cl_3$ resulted in completely inactive systems. For all of the catalysts that were active the reaction mixture had to be heated to 125 ± 10°C before the reaction commenced. Holding the reaction mixture at 100°C resulted in the slow conversion of butadiene to mainly 4-vinylcyclohexene.



Diethylbis (2,2'-dipyridyl) iron

(VI)



X = H, CH$_3$, phenyl
Y = H, CH$_3$, OCH$_3$ etc.

Iron-Schiff Base Complex

(VII)

Analysis of glc of the reaction products obtained using PBA as the ligand and authentic samples revealed that the (cyclododecatriene) CDT produced by this process consisted of 72.3% *trans,trans,-trans-* 12.7% *cis,trans,trans-* and 15.1% *cis,cis,trans*-1,5,9 isomers. There was no polymer formation with this catalyst and the only by-products of significance were 10% of VCH and 5% of 1,5-cyclooctadiene (COD). The composition of the CDT did not change with the Schiff base.

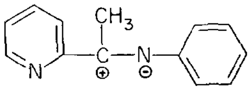
The main difference noted with the different Schiff bases was changes in reaction rates. However, because it was more difficult to handle butadiene, quantitative rate data were not obtained as was done with isoprene.

Discussion

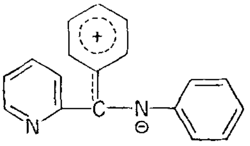
Yamamoto and co-workers (*6*) recently reported the preparation of diethylbis(2,2'-dipyridyl) iron and showed that this complex is an active catalyst for the cyclodimerization of butadiene and isoprene. It is likely that the catalyst complexes formed by the Schiff bases with iron are similar in structure. However, there is a difference in the bonding of 2,2'-dipyridyl (and most common nitrogen ligands) compared to the Schiff bases. With 2,2'-dipyridyl the majority of the bonding is sigma, σ. The —C=N— (anil) linkage of the Schiff bases can result in a combination of π and σ bonding upon coordination with iron. However, it is not possible to quantitatively determine the relative π and σ contributions to the bonding and in turn use this information to explain the variations in rate data given in Table 2.

From the data in Table 2 the following trends are apparent. (1) Replacing hydrogen at position *X* (structure VII) with an alkyl group results in an order of magnitude rate increase and replacing the alkyl group with phenyl at the same position results in another order of magnitude rate increase. (2) For a given structure, electron donating groups at (*Y*) results in moderate rate increases, (3) 2,6-NPX gives an unusually high reaction rate, and (4) as the rate of isoprene conversion increases so does the selectivity to cyclodimer.

The rate variations of (1) and (2) can be explained as follows: replacing the anil hydrogen (NPA) with an alkyl group such as CH_3 (PMA) or C_2H_5 (PEA) would increase the electron density at the anil nitrogen by an inductive effect, where (VIII) would be a major contributing resonance structure. The further increase in rate by replacing



(VIII)



(IX)

an alkyl group with a phenyl group (PBA) would result in a benzyl amine structure giving maximum resonance stability with IX being a major resonance structure. This rate increase in going from alkyl to phenyl is analogous to the higher rate of benzyl chloride hydrolysis compared to ethyl chloride where the formation of a resonance stabilized benzyl cation intermediate is cited to explain the difference (*14*). Substituting electron donating groups at *Y* would also be expected to increase electron density at the anil nitrogen by an inductive effect. This is shown by comparing rate data from using NPT, NPAn and 2,4-NPX with NPA and PBAn and PBT with PBA. As expected, the effect of substitution at (*Y*) on the rate is not as pronounced as the variations by substitution at (*X*).

An increase in electron density at the nitrogen would result in increased electron density at the iron atom upon coordination. An increased electron density at the iron atom should enhance its capability for bonding with a diolefin which in turn results in a greater reaction rate. An analogous situation has been reported where the catalytic rate increased for the oligomerization of olefins as the electron density of the nickel atom increased (*15*). Also, Rund and Claus (*9*) reported that the rate for the metal catalyzed decarboxylation of β-keto acids increased with increasing basicity of the substituted 1,10-phenanthroline ligands. They reported a linear relationship between the rate constant and the availability of the electrons on the nitrogen.

The high activity obtained using 2,6-NPX cannot be accounted for by electronic effects; a suggested explanation is steric effects. Having methyl groups at the 2 and 6 positions could result in considerable steric interference upon coordination of two ligands to iron. The steric interference is somewhat relieved in the case of 2,4-NPX. The forced steric configuration could result in a very active catalyst analogous to enzymatic catalysis.

The data in Table 2 shows that the catalysts which exhibit the highest isoprene conversion rates also give selectivities greater than 90%. These results indicate that once a correct balance of electronic and steric requirements are fulfilled in the catalyst complex, isoprene is rapidly and selectively converted.

It was interesting to find that the $Fe(acac)_3$–TEA–2,2′-dipyridyl catalyst of Misono and co-workers (*4*) was different than the $Fe(acac)_3$–TEA–PBA catalyst. At a PBA-to-iron ratio of 1 and at room temperature, there was immediate cyclodimerization of isoprene. However, with 2,2′-dipyridyl and under the same conditions, there was no reaction. This catalyst had to be heated to approximately 40–50°C before the reaction commenced. Thus, the $Fe(acac)_3$–TEA–TBA catalyst is approximately 20–25°C more active than the $Fe(acac)_3$–TEA–2,2′-dipyridyl catalyst.

The difference in reactivity between isoprene and butadiene with the $Fe(acac)_3$–TEA–PBA catalyst was not surprising since Misono and co-workers also reported (*4*) this difference using the $Fe(acac)_3$–TEA–2,2′-dipyridyl catalyst. However, there are again differences between these two catalysts. Even though the cyclodimerization of isoprene and butadiene takes place at different temperatures with the $Fe(acac)_3$–TEA–PBA catalyst, the ultimate yields are about the same, 92 and 90%, respectively. With the $Fe(acac)_3$–TEA–2,2′-dipyridyl catalyst, there was not only a pronounced difference in reactivity but a great difference in ultimate yield. For example, at 50°C after 60 min the yield of isoprene cyclodimers was reported to be

96% whereas at the same temperature and after 240 min the butadiene cyclodimer yield was only 45%. These results indicate that not only slight variations in the coordination strength of the ligand can have a marked effect on reactivity but slight differences in the substrate structure can result in large reactivity differences. These results also suggest that the catalyst most likely involves a ligand–iron–diene complex and the slight change in going from isoprene to butadiene changes this catalyst complex with respect to the temperature needed for activation.

All of the Ni(acac)$_2$–TEA–Schiff base systems were selective catalysts for the conversion of butadiene to cyclododecatriene. A 30% yield of cyclododecatriene has been reported when the complex diethyl(2,2′-dipyridyl)nickel is used as the catalyst (*2*). We obtained a 43% yield of cyclododecatriene, using a catalyst prepared by reacting Ni(acac)$_2$ with TEA in the presence of 2,2′-dipyridyl. The low yields of cyclododecatriene when 1,10-phenanthroline or 2-cyanopyridine are used as the ligand shows that not any bidentate nitrogen compound complexed to nickel results in an active catalyst for this reaction.

All of the nickel-Schiff base catalysts gave predominantly the *trans,trans,trans*-cyclododecatriene isomer, which is in agreement with what others have reported using nickel catalysts (*16*). Ziegler-type catalysts yield predominantly the *trans,trans,cis*-isomer (*17*). The mechanism and stereochemistry for the formation of cyclododecatriene using nickel complex catalysts has been reported by Wilke (*18*) and most likely also applied to the nickel–Schiff base catalysts.

The main difference noted varying the Schiff base in the cyclotrimerization of butadiene was the reaction rate. Although quantitative rate data were not obtained, it was noted that the reaction rate was much faster when PBAn, PBT, and PBA were used compared to NPA or NPT. This is shown by the conversion data given in Table 3. These differences were greater at half the reaction time. For example, with NPA after 1 hr only 30% of the butadiene was converted whereas with PBA the conversion was 75% after the same time. The higher activity of catalysts made from PBA-type ligands compared to catalysts made from NPA-type ligands is the same trend as quantitatively shown for iron–Schiff base isoprene cyclodimerization catalysts. The data in Table 3 also show that the Schiff base ligands that give the highest conversions after 4 hr also result in the highest selectivities. This was also found for the cyclodimerization of isoprene, using the iron–Schiff base catalysts.

The Schiff base–nickel cyclododecatriene catalyst most likely involves one Schiff base ligand coordinated to the metal with the other coordination sites occupied by two ethyl groups. This is suggested based on the isolation of diethyl(2,2′-dipyridyl) nickel which exhibits catalytic activity for the cyclooligomerization of butadiene to cyclododecatriene (*5*). The active catalysts produced by ligand-to-iron mole ratios less than one is probably due to a concentration effect where a lower concentration of 1:1 ligand-to-nickel and ligand-to-iron catalysts is giving almost complete conversion during the reaction time used. It is hoped that this will be clarified by experiments in progress attempting to isolate, identify and test the catalytic activities of Schiff–base metal catalyst complexes.

The nickel–Schiff base catalysts did not catalyze the cyclotrimerization of isoprene. This was not surprising for no accounts have been found where nickel catalysts catalyze isoprene cyclotrimerization. Wilke reported a chromium catalyst that gave low yields of trimethylcyclododecatriene isomers (*19*). Steric hindrance was cited as the reason for the difficulty to cyclotrimerize isoprene. This is most likely the reason why the nickel–Schiff base catalysts gave little or no isoprene cyclotrimers.

In summary, this paper has shown that Schiff bases coordinated to iron and nickel results in very active diolefin cyclooligomerization catalysts. These Schiff bases like 2-cyanopyridine, phenyl-2-pyridylacetonitrile, and 2-pyridine aldoxime represent a different type of nitrogen ligand than previously used to selectively catalyze diolefin cyclooligomerization reactions. Evidence has also been given showing that structural changes in the ligand have a pronounced effect on reaction rate.

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