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NICKEL-CATALYZED AMINATION OF BUTADIENE

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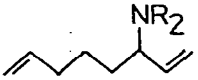
SUMMARY Dialkyloctadienylamines are formed selectively and in high yields upon reaction of secondary amines with butadiene in the presence of catalytic amounts of nickel(II) acetylacetonate, triphenylphosphine and triethylaluminium. Similar results are obtained by using a catalyst prepared by adding a Lewis acid, e.g. triethylaluminium or boron trifluoride etherate, to bis(1,5-cyclooctadiene)nickel(0) and triphenylphosphine. Support for a mechanism involving positively charged nickel complexes is presented.

The nickel-catalyzed amination of 1,3-dienes has been studied by several groups[1-8]. Although complex product mixtures have frequently been obtained, this reaction has considerable synthetic potential.

We were interested in preparing octadienylamines I-III, preferably I. Heimbach has reported [8] that reasonable yields of the compound II [R_2=$(CH_2CH_2)_2O$] can be obtained at room temperature using a nickel-triethyl phosphite catalyst. It therefore seemed interesting to try to increase the scope of the reaction and also to investigate its mechanism.

I

II



III

RESULTS

We have now studied the reactions of secondary amines with butadiene, using a catalyst made by reacting Ni(II) acetylacetonate with excess triethylaluminium in the presence of one equivalent of triphenylphosphine. Diethylamine reacted smoothly at room temperature in toluene to give the octadienylamine I (R=Et) in good yield together with a small amount of the isomer III. Some other secondary amines also gave good yields of octadienylamines. Dimethylamine, however, gave only a small amount of the isomers I and III (R=Me) and primary amines gave only trace amounts of octadienylamines. We therefore tried to find conditions that would permit amination with dimethylamine. We have also worked on optimizing the yields in the reactions of other secondary amines.

The reaction temperature was found to be very important. While, e.g. diethylamine gave about 70% yield at 20°C (Table 1), this was reduced to 30% at 40°C and only trace quantities at 80°C (*cf.* ref 8). However, at the lower temperature -60°C 85% yield was obtained. The yield of dimethyloctadienylamine was raised from 5% to 65% when the temperature was decreased from 20°C to -60°C and a similar but less dramatic increase was observed for the other amines (Table 2). At room temperature the yield of compound I (R=Et) could be improved to 86% by using a better coordinating solvent, tetrahydrofuran. A further increase, to 92%, was observed when the phosphine-nickel ratio was raised from 1:1 to 2:1. Finally, an essentially quantitative yield was obtained when bis(triphenylphosphine)nickel(II) chloride and a twentyfold excess of triethylamine were used to

TABLE 1

REACTIONS OF DIETHYLAMINE AND BUTADIENE CATALYZED BY NICKEL(II) SALTS, TRIETHYLALUMINIUM AND PHOSPHINES

Ni-salt	Ligand	L/Ni-ratio	Solvent	Temp (^{o}C)	Yield of I (%)[a]
Ni(acac)$_2$	PPh$_3$	1:1	Toluene	60	15[b]
Ni(acac)$_2$	PPh$_3$	1:1	Toluene	40	30[c]
Ni(acac)$_2$	PPh$_3$	1:1	Toluene	20	72[d]
Ni(acac)$_2$	PPh$_3$	1:1	Toluene	-60	85[d]
Ni(acac)$_2$	PPh$_3$	1:1	THF	20	86[d]
Ni(acac)$_2$	PPh$_3$	2:1	THF	20	92[d]
NiCl$_2$x2PPh$_3$		2:1	THF	20	100[d]
Ni(acac)$_2$	PBu$_3$	1:1	Toluene	20	70[d]
Ni(acac)$_2$	P(OPh)$_3$	1:1	Toluene	20	5[d]

[a] Yields determined by GLC. [b] Reaction time 20 min. [c] Reaction time 2h, the yields do not increase with longer reaction times. [d] Reaction time 20 h.

generate the catalyst. The catalytic turnover with these systems was about 400 mol/mol catalyst.

The structure of the coordinating ligand appears to be more important under our conditions than might be expected from earlier work using hydrides as reducing agents. Triphenylphosphine and tributylphosphine promoted the formation of octadienylamines, while triphenyl phosphite and tris(o-biphenylyl) phosphite were ineffective.

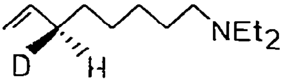
TABLE 2

RELATIVE AND TOTAL YIELDS OF OCTADIENYLAMINES FORMED IN NICKEL-CATALYZED REACTIONS OF DIALKYLAMINES WITH BUTADIENE IN TOLUENE[a]

Amine	Temp. (°C)	Relative yields of I	II	Total yields[b] (%)
Diethylamine	20	97.5	2.5	62 (72 GLC)
Dimethylamine	20	83	17	ca 5
Dimethylamine	-60	93	7	65
Dibutylamine	20	98.5	1.5	37
Piperidine	20	90	10	50
Piperidine	-60	95	5	75
Morpholine	20	80	20	70

[a] 0.5 mmol $Ni(acac)_2$, 0.5 mmol PPh_3, 2 mmol Et_3Al, 25 mmol amine and 75 mmol butadiene. [b] Yields of isolated products.

When N-deuterio-N,N-diethylamine was used in the amination reaction, compound Ia, deuterated only in the 6-position, was formed.



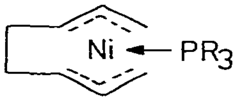
Ia

Butadiene does not react with diethylamine in the presence of catalytic amounts of bis(1,5-cyclooctadiene)nickel(0) and a phosphine [5]. However, when a catalytic amount of triethylaluminium was added, compound I (R=Et) was formed in 9% yield at room temperature. Again, by decreasing the temperature to -60°C, the yield was considerably improved (to 88%, relative yields of I:III = 1:39). We also found that some other Lewis acids could be used in place of triethylaluminium, e.g. boron trifluoride etherate and tin(IV) chloride, giving octadienylamines in 88% and 51% yield, respectively. On the other hand, aluminium(III) chloride and lithium(I) chloride were ineffective. A few per cent of butenylamines were formed along with the octadienylamines when tin(IV) chloride was used as the Lewis acid, probably due to the presence of some hydrogen chloride.

DISCUSSION

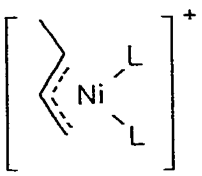
The amination reaction is quite sensitive to steric factors, as evidenced by the variation in the ratio between the two isomers I and III. Morpholine and dimethylamine, which have low steric requirements, gave III:I ratios of about 1:4 at 20°C, while the corresponding ratio for piperidine was 1:9, for diethylamine 1:39, and for the more bulky dibutylamine 1:66. Steric bulk also seems to decrease the yield since dibutylamine gave a low yield and diisoproplyamine none at all.

Earlier work by us on π-allylpalladium complexes [9] and by Furukawa et al. [6] on π-allylnickel hexafluorophosphate shows that charged π-allylmetal complexes are readily aminated. This is also indicated by theoretical calculations on π-olefin metal complexes [10]. The requirements for a charged species are demonstrated by the lack of reactivity of the bis-π-allyl complex IV, prepared from Ni(O), a phosphine and butadiene [5].

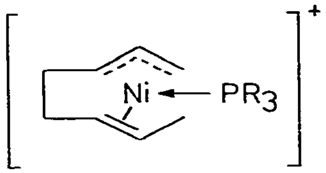


IV

Butenylamines very probably are formed via nickel hydride and π-crotylnickel. The charged π-crotylnickel complex V, prepared by protonating nickel(O) by trifluoroacetic acid in the presence of butadiene and a phosphine, could be a precursor of the butenylamines and octadienylamines. In fact, the work of Heimbach [8] seems to suggest such a mechanism, since the isomer II is that expected from the insertion of butadiene into the allyl-nickel bond, follwed by amination (V ⟶ VI ⟶ II). However, the results presented in

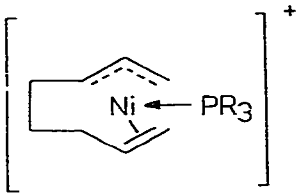


V



VI

ref.5 suggest that only I and III are formed as primary products. The same product pattern is found in our work. The formation of diethyloctadienylamine Ia, deuterated only in the 6-position, when N-deuterio-N,N-diethylamine is used, is further proof that a terminal double bond is formed in the primary product. A very reasonable mechanism for the formation of octadienylamines is that one of the π-allyl groups of complex IV is protonated by the amine-Lewis acid complex, forming a positively charged complex VII, which is aminated.



VII

It thus seems likely that both butenyl- and octadienylamines are formed *via* charged intermediates. However, while the butenylamines are probably formed *via* nickel(II) hydride and π-crotylnickel, the octadienylamines seem to form *via* nickel(0) and the π-allylnickel complexes IV and VII.

EXPERIMENTAL

Gas chromatography was performed on a Pye 104 instrument using a 1 m x 6 mm column of 20% Apiezon L + 10% KOH on Chromosorb W. NMR spectra were recorded on a Bruker WP 200 spectrometer (TMS internal standard) and mass spectra on an LKB 9000 instrument.

Diethylamine, dibutylamine, piperidine and morpholine were distilled over KOH pellets and stored under nitrogen with molecular sieves. Nickel acetylacetonate was suspended in toluene, the water removed by azeotropic distillation with toluene, and the residue dried in vacuum at 80°C. Bis(triphenylphosphine)nickel chloride was prepared from $NiCl_2x6H_2O$ and triphenylphosphine [11]. Commercial samples of all other reagents were used without further purification. Triethylaluminium was dissolved in toluene (25% solutions) before use. PA grade toluene was dried with molecular sieves and tetrahydrofuran was distilled from potassium and benzophenone. All reactions were performed under purified nitrogen. A glove-bag was used for manipulations of bis(cyclooctadiene)nickel.

General procedure for the amination reaction

Starting from a Ni(II) salt

Nickel acetylacetonate (0.5 mmol) and triphenylphosphine (0.5-1 mmol) were placed in a Fisher and Porter glass autoclave equipped with a magnetic stirrer. The apparatus was flushed with nitrogen and cooled to approximately -75°C. Butadiene (50-75 mmol) was distilled into the apparatus. A solvent (toluene or THF, 5 ml), a secondary amine (25 mmol) and triethylaluminium (1-10 mmol) were added. The cooling bath was removed and the reaction mixture was left at room temperature for 20 h. The product mixtures were then analyzed by GLC. In a number of representative experiments the octadienylamines were also isolated by extraction followed by distillation. The yields of diethyloctadienylamines were determined by GLC using *p*-cymene as an internal standard.

In order to improve the yield of dimethyloctadienylamine, in particular, a modified procedure was also used. The reaction was run essentially as described above, but after mixing the reagents at -60°C, the reaction mixture was allowed to reach room temperature in 20 h. The products were then analyzed as described above.

Starting from bis(cyclooctadiene)nickel

Bis(cyclooctadiene)nickel (1–2 mmol) and triphenylphosphine (1–2 mmol) were placed in a Fisher and Porter glass autoclave. Butadiene (50–75 mmol), diethylamine (25 mmol) and triethylaluminium (1–2 mmol) were added at -60°C as described above. The reaction mixture was then allowed to reach room temperature in 20 h. The same procedure was used when boron trifluoride etherate or tin(IV) chloride was used in place of triethylaluminium, while solid Lewis acids were placed in the autoclave together with the nickel complex and triphenylphosphine.

The products were identified by combined GLC/MS and by NMR spectra of mixtures of the isomers I and III. The dimethyloctadienylamines I and III (R=Me) were also separated by preparative GLC using a 3 m x 19 mm column of 20% Apiezon L + 10% KOH on Chromosorb W. The NMR spectrum ($CDCl_3$) of isomer I shows absorptions at δ 5.80 (m, 1H), 5.53 (m, 2H), 4.9–5.1 (m, 2H), 2.85 (d, J=5.4 Hz, 2H), 2.21 (s, 6H), 2.06 (apparent quartet, J=7, 4H) and 1.48 ppm (quintet, J=7, 2H) and that of isomer III absorptions at δ 5.6–5.9 (m, 2H), 4.9–5.3 (m, 4H), 2.72 (ddd, J=4.3, 8.7 and 13, 1H), 2.27 (s, 6H), 2.15 (m, 2H), ca. 1.5 (AB-part of ABM_2X-spectrum) and 1.4 ppm (m, 2H).

Preparation of compound Ia

N-deuterium-*N*,*N*-diethylamine: Diethylamine (50 mmol) was dissolved in diethyl ether (50 ml) and a 2M solution of butyllithium (50 mmol) in hexane was added at 0°C. The reaction mixture was stirred for 0.5 h, deuterium oxide (50 mmol) was added and the precipitate removed by filtration. The solvent was evaporated and the product was distilled.

Compound Ia was then prepared using a catalyst prepared from nickel(II) acetylacetonate as described above.

The NMR spectrum of compound I shows a multiplet (δ 5.72 ppm) composed of 12 lines for the proton at C7, with coupling constants 10.3 and 17.1 (to the cis and trans vinylic protons at C8) and 6.6 Hz (to the methylene protons at C6), while 8 broadened lines are observed for the proton at C7 of compound Ia. The shift and coupling constants are the same as for compound I. The coupling to deuterium is ca. 1 Hz.

ACKNOWLEDGEMENTS

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