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THE ROLE OF SODIUM BOROHYDRIDE IN NICKEL CATALYSED REACTIONS OF ACTIVE HYDROGEN COMPOUNDS AND BUTADIENE

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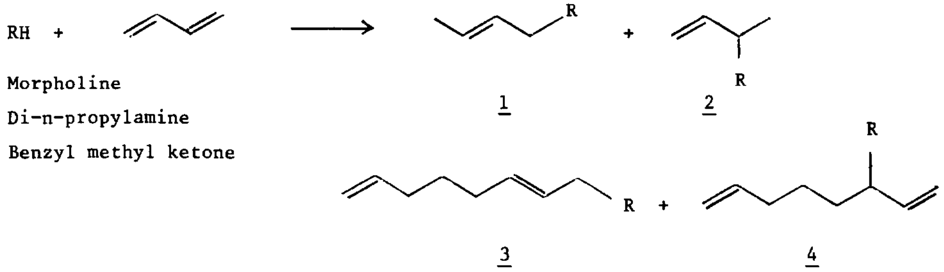
Previous studies have been reported of nickel-complex catalysed reactions between 1,3-dienes and active hydrogen compounds;[1-3] a system comprising Ni(acac)$_2$-PhP(i-OPr)$_2$-NaBH$_4$ being employed. Although the importance of reduction of Ni(II) to Ni(0) was stressed, a number of factors were clearly important. Sodium borohydride, although used consistently, has now been shown not to be essential except in a few specific cases. The scope of the reactions with amines has also been widened considerably by the enhanced reactivity of the system using other nickel salts.



a, RH = Morpholine
b, = Di-n-propylamine
c, = Benzyl methyl ketone

Reaction of morpholine (0.05 mole) with butadiene (0.15 mole) in presence of NiBr$_2$ (1mmole) PhP(i-OPr)$_2$ (1.1mmole) at 100°C for 30 mins gave a 79% conversion to a mixture of 1a(32%), 2a(33%), 3a(33%) and 4a(2%).* With Ni(acac)$_2$, however, only trace reaction is found unless sodium borohydride (0.3mmole) is present[2]. Borohydride is also required to effect good conversions on reaction with primary amines in the presence of Ni(acac)$_2$, but not with secondary amines such as di-n-propylamine, and active methylene compounds. At 100°C for 16 hours di-n-propylamine (0.05mole) and butadiene (0.15mole) with Ni(acac)$_2$(1mmole)-PhP(i-OPr)$_2$ (1.1mmole)-EtOH(5ml) gives 84% overall conversion to butenyl and octadienyl adducts, <u>1b</u>(34%), <u>2b</u>(0%), <u>3b</u>(66%), <u>4b</u>(0%). Benzyl methyl ketone at 75°C for 16 hours gives 82% reaction, comprising <u>1c</u>(13%), <u>2c</u>(8%), <u>3c</u>(74%), <u>4c</u>(5%). This behaviour is peculiar to Ni(acac)$_2$ since reaction with other nickel salts such as NiBr$_2$, NiCl$_2$, Ni(acetate)$_2$, and Ni(laurate)$_2$ proceeds smoothly with all amines irrespective of the presence of borohydride. n-Butylamine gives a quantitative yield of mono- and di-alkylated products with the NiBr$_2$ system at 100°C after 1 hour. This difference in reactivity of Ni(acac)$_2$ is directly attributable to its known ability to form complexes with amines[4,5]. It is evident that the stability of such complexes is one of degree, the morpholine adduct being especially stable. Ni(acac)$_2$ (morpholine)$_2$ has been prepared and used as a catalyst giving 75% conversion (16 hours) in presence of borohydride and only trace reaction in its absence. Thus the complex formation from Ni(acac)$_2$ and reagent morpholine competes with the reduction process of Ni(II) to Ni(0) by alkoxyphosphine. Addition of borohydride, therefore, breaks down or prevents complex formation. In cases where borohydride is not essential its addition nevertheless results in marginal rate enhancement. This may be due to assisted reduction of the nickel salt by alkoxyphosphine together with borohydride. Evidence for this is provided by the active butadiene oligomerisation system NiCl$_2$ (10mmole), PPh$_3$ (20mmole) and NaBH$_4$(40mmole)[6], which has been used to yield 73% reaction in 6 hours: <u>1a</u>(8%), <u>2a</u>(8%), <u>3a</u>(65%), <u>4a</u>(19%) from telomerisation of morpholine (0.13mole) and butadiene (0.4mole) at room temperature. Here, sodium borohydride assumes the exclusive role of reduction since triphenylphosphine does not reduce Ni(II) salts but acts simply as a stabilising ligand.

An order of reactivity of nickel salts has been established in the butadiene-amine-dialkoxyphenylphosphine system as:

$$NiBr_2 \simeq NiCl_2 > Ni(acetate)_2 \simeq Ni(laurate)_2 \gg Ni(acac)_2$$

In analogous reactions with active methylene compounds it was found:

$$NiBr_2 \simeq NiCl_2 > Ni(acac)_2 > Ni(acetate)_2 \simeq Ni(laurate)_2$$

TABLE

Reactions of butadiene with morpholine and benzyl methyl ketone[a]

Active hydrogen compound	Nickel salt	Time (hr)	Temp	Conversion (%)	Products (%)	
					butenyl	Octadienyl
Morpholine	$NiBr_2$	1	100°C	96	90	10
Morpholine	$Ni(acetate)_2$	1	100°C	85	42	58
Morpholine	$Ni(laurate)_2$	1	100°C	84	44	56
Morpholine	$Ni(acac)_2+NaBH_4$[b]	1	100°C	trace		
Morpholine	$Ni(acac)_2+NaBH_4$[b]	16	100°C	95	43	57
$PhCH_2COCH_3$[c]	$NiBr_2$	16	75°C	93	53	47
$PhCH_2COCH_3$[c]	$Ni(acetate)_2$	16	75°C	23	42	58
$PhCH_2COCH_3$[c]	$Ni(laurate)_2$	16	75°C	30	34	66
$PhCH_2COCH_3$[c]	$Ni(acac)_2$	16	75°C	32	21	79

a Ni salt (1mmole) - $PhP(i\text{-}OPr)_2$ (1.1mmole) - Active hydrogen compound (0.05mole) - Butadiene (0.15mole) - EtOH(5ml)

b $NaBH_4$ (0.3mmole)

c PhONa (1.4mmole) used as cocatalyst in all $PhCH_2COCH_3$ reactions.

The marked decrease in reactivity of $Ni(acac)_2$ with amines compared to active methylene compounds is in line with the tendency for complex formation with amines. Ethanol was used as solvent for these reactions since more effective conversions are found in the presence of a protic solvent. This is generally accompanied by a greater proportion of butenyl adduct in the product compared to that in the absence of solvent. The origin of this effect might arise from ethanol acting as a stabilising ligand and blocking available co-ordination sites for butadiene, or providing a source of protons with a consequent favouring of the butenyl pathway.

Studies on the reaction of morpholine and butadiene in presence of other dialkoxyphenylphosphines reveals the reactivity trend

$$PhP(i\text{-}OPr)_2 > PhP(OEt)_2 > PhP(OMe)_2$$

The observation that the nature of the alkoxy group in these phosphines is critical in determining reactivity has also been demonstrated by Rose with diethylamine-butadiene- nickel laurate reactions[7]. Under his conditions no reaction was reported with $PhP(OEt)_2$ and $PhP(OMe)_2$, but it is clear that this is attributable to the lower reactivity of diethylamine compared to morpholine. Current work reveals that reaction of morpholine and butadiene catalysed by nickel bromide (nickel laurate) for 1 hour at 100°C leads to 96%(84%), 59%(45%), 18%(2%) conversions with $PhP(i\text{-}OPr)_2$, $PhP(OEt)_2$ and $PhP(OMe)_2$, respectively. In the choice of an appropriate phosphine for these reactions it is clear that both the ability of phosphine to reduce Ni(II) to Ni(O)[8] and steric effects of the phosphine are important. Steric considerations governing instability and hence reactivity of an intermediate nickel-ligand species has recently been stressed[9,10] and adequately explains the present results.

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* Separation of the products was achieved by fractional distillation and G.L.C. All physical data were fully consistent with the assigned structures.

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