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NICKEL-CATALYZED REACTION OF BUTADIENE.
FORMATION OF 2-METHYLENEVINYLCYCLOPENTANE AND ADDITION OF AMINE TO BUTADIENE

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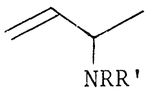
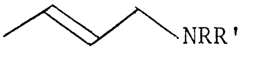
The cyclodimerization of butadiene catalyzed by bis(tri-*n*-butylphosphine)dibromonickel combined with sodium borohydride was investigated, using amines as protonic solvents. At 80°C a large amount of amine-adducts to butadiene was obtained together with 2-methylenevinylcyclopentane. The adducts were formed exclusively at room temperature.

We have already reported the formation of 2-methylenevinylcyclopentane *via* the selective cyclodimerization of butadiene by some nickel complexes.$^{1)}$ In this case presence of alcohol is essential for the reaction. Alcohol participates in the reaction of the nickel catalysts and in the proton-initiated cyclization. Acid, phenol and amine are less effective as protonic reagents. 2-Methylenevinylcyclopentane(III) is formed only in 10 % yield in the presence of morpholine, when $(n\text{-}Bu_3P)_2NiCl_2$ and butyllithium are used as the catalyst. A large amount of butadiene remains unchanged. It has now been found that in amine $(n\text{-}Bu_3P)_2NiBr_2$, combined with sodium borohydride, is highly effective for the cyclodimerization and the reaction of butadiene with amines at 80°C. The nickel-catalyzed reaction of butadiene with amines has been reported recently by Baker *et al.*, who employed nickel-phosphite and sodium borohydride as the catalyst in a molar ratio 1:0.1 and obtained butenyl- and octadienyl-substituted morpholines in a ratio 47:53 as the major products, accompanied by a small amount of the dimers of butadiene.$^{2)}$

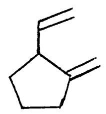
The results are summarized in Table. Butenyl-substituted amines(I and II) and III were the major products. The other products consisted of octadienyl-substituted amines, which were formed in yields lower than 20 %. Dimers other than III were not formed. At room temperature the reaction of amines occurred exclusively to produce butenyl-substituted amines. The product distribution was dependent on the kind of amines used. No reaction occurred when *tert*-butylamine or dicyclohexylamine was used.



I



II



III

Addition of excess sodium borohydride (>1:1 molar ratio of $NaBH_4$:Ni) suppressed the reaction and a large amount of butadiene remained unchanged.

According to Baker's report, the substituent on phosphorus of the ligand has a great influence on the reaction; i.e., alkoxyphosphines were effective but other phosphines such as triphenylphosphine did not accomplish the results. In our system triphenylphosphine, tri-n-butylphosphine and diethylphenylphosphine were also effective as the auxiliary ligand. Diphosphine, e.g., bis(diphenylphosphino)ethane was ineffective. Other phosphine complexes of nickel salts such as chloride were also effective, though the product distribution was somewhat different. Only a nickel bromide complex, $(\underline{n}\text{-}Bu_3P)_2NiBr_2$, showed some catalytic activities without using sodium borohydride. It is to note that the product distributions vary with the reaction time. Higher temperature and longer reaction time favor the formation of II. For example, butenylamine (I) of piperidine was isomerized to II almost quantitatively at 80°C for 24 hr.

In connection with a catalytic species, a comparison with the results of Baker et al., is interesting to note. They attribute the dependence of alkoxyphosphine on the catalysis to the ability to reduce the Ni^{II} salt to a Ni^0 species, which is active for the reaction. In the present work an equimolar amount of the nickel salt to sodium borohydride was used. It is assumed from the results of Green³⁾ that the nickel salt can not be reduced by 1 mole of sodium borohydride to Ni^0 species but to $H\text{-}Ni^{II}$. This is the difference from the ordinary Ni^0 catalysts, which are prepared by the reduction with an excess of a reducing agent, and give linear dimers of butadiene in protonic solvent such as alcohol or amine.⁴⁾ When the nickel salt was combined with an excess of sodium borohydride (more than 1 mole) in alcohols⁵⁾ or in ethers,⁶⁾ the linear dimerization occurred. On the contrary, when less than 1 mole of sodium borohydride was used, the cyclodimerization occurred to give III.⁷⁾

Reaction of Butadiene by $(\underline{n}\text{-}Bu_3P)_2NiBr_2$ and $NaBH_4$

Amine 2 ml	Reaction °C	Reaction hr	Yield (%) I	Yield (%) II	Yield (%) III
Morpholine	80	48	43	14	18
Piperidine	80	48	11	31	28
n-Propylamine	80	48	14	10	49
Diethylamine	80	48	—	32	63
Morpholine	20	36	77	4	—
Piperidine	20	36	51	3	—

$[Ni] = [NaBH_4] = 1$ mmole, [Butadiene] = 24 mmole.

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