

THE NICKEL-CATALYSED REACTION OF DIETHYLAMINE WITH  
BUTADIENE

---

by D. Rose

HENKEL & Cie. GmbH, D 4 Düsseldorf, Postfach 1100

---

(Received in UK 30 August 1972; accepted for publication 7 September 1972)

Since our work on the nickel-catalysed reaction between butadiene and secondary amines was completed, a short communication reporting a similar study has appeared. The catalytic reaction between primary or secondary amines with butadiene using a Ni(II)-acetylacetonate- $\text{NaBH}_4$ - $\text{PhP}(\text{OiPr})_2$  catalyst system to yield both octadienyl and butenyl-substituted amines was described<sup>1</sup>. It was suggested by these authors that the success of these reactions was dependent upon the ability of the alkoxy-phosphine to reduce the Ni(II) salt to a Ni(0) species. Their basis for this claim was the work of Gray et al.<sup>2</sup> who showed that  $\text{PhP}(\text{OMe})_2$  and  $\text{PhP}(\text{OEt})_2$  were able to reduce Ni(II) salts to the corresponding Ni(0) complexes,  $\text{Ni}(\text{Lig})_4$ .

We have confirmed the results of Baker et al.<sup>1</sup> but also wish to report further results concerning the butadiene - diethylamine reaction using  $\text{NaBH}_4$  and other reducing agents together with an extended series of ligands, which show that the ability of the ligand to reduce Ni(II) salts to Ni(0) complexes is not the deciding factor. Results obtained for various ligands are summarised in Table I.

Table I

ligand	yield of octadienyl- amines +)	yield of butenyl- amines +)	ligand	yield of octadienyl- amines +)	yield of butenyl- amines+)
$\text{PhP}(\text{OCH}(\text{CH}_3)_2)_2$	59 %	5 %	$\text{Ph}_2\text{P}(\text{OCH}(\text{CH}_3)_2)$	10 %	2 %
$\text{PhP}(\text{OC}_6\text{H}_{11})_2$	67 %	5 %	$\text{Ph}_2\text{P}(\text{OC}_6\text{H}_{11})$	25 %	5 %
$\text{PhP}(\text{OCH}(\text{CH}_3)(\text{C}_2\text{H}_5))_2$	65 %	10 %	$\text{Ph}_2\text{P}(\text{OCH}(\text{CH}_3)(\text{C}_2\text{H}_5))$	2.4 %	4 %
$\text{PhP}(\text{OCH}(\text{CH}_3)(\text{C}_3\text{H}_7))_2$	62 %	10 %	$\text{Ph}_2\text{P}(\text{OCH}(\text{CH}_3)(\text{C}_3\text{H}_7))$	13 %	15 %
$\text{PhP}(\text{O}(\text{CH}_2)_4\text{CH}_3)_2$	10 %	11 %	$\text{Ph}_2\text{P}(\text{O}(\text{CH}_2)_4\text{CH}_3)$	25 %	12 %

No products were found with the following ligands:

$\text{PhP}(\text{OC}(\text{CH}_3)_3)_2$ ,  $\text{MeP}(\text{OCH}(\text{CH}_3)_2)_2$ ,  $\text{PhP}(\text{OCH}(\text{Ph})_2)_2$ ,  $\text{PhP}(\text{OCH}(\text{CH}_2\text{Cl})_2)_2$ ,  $\text{PhP}(\text{OCH}(\text{Me})(\text{Ph}))_2$ ,  $\text{PhP}(\text{OCH}(\text{CH}_3)(\text{CO}_2\text{C}_2\text{H}_5))_2$ ,  $\text{PhP}(\text{OCH}_3)_2$ ,  $\text{PhP}(\text{OC}_2\text{H}_5)_2$ .

Reaction conditions:

1 g Ni(II) Laurate, 0,1 g  $\text{NaBH}_4$  0,5 Moles Diethylamine,

1 mole Butadiene: 90°, 4 hours

Nickel : Ligand Ratio, 1 : 1.

+) yields reported are total yields of isomeric butenyl or octadienylamines.

The observation that no products were found when  $\text{PhP}(\text{OCH}_3)_2$  or  $\text{PhP}(\text{OC}_2\text{H}_5)_2$  were used as ligands, shows that the ability of the ligand to reduce Ni(II) to a Ni(0) species is not the deciding factor as to whether the ligand is effective or not, as has been suggested by both Baker et al <sup>1</sup> and Shields and Walker <sup>3</sup> From the results given in Table I it can be seen that the type of ligand which is effective is extremely limited, and only those ligands of the type  $\text{RP}(\text{OR})_2$  which possess, a) an aryl group directly attached to phosphorus, and b)

which have two alkoxy groups derived from secondary alcohols also attached to the phosphorus atom, show good catalytic activity. Replacement of only one of the sec. alcohol alkyl groups by phenyl, as in  $\text{PhP}(\text{OCH}(\text{Me})(\text{Ph}))_2$  results in loss of catalytic activity. We are unable at present to explain this remarkable ligand specificity, but it could be that some kind of interaction between the metal and the secondary hydrogen atom of the alkoxy group occurs. An indication that a Ni hydride is the active species is found by comparing the yields of products obtained with (sec.  $(\text{C}_4\text{H}_9)_2$ ) AlH and  $\text{Al}(\text{Et})_3$  as reducing agents. In the former case a 53 % yield of octadienylamines + 12 % butenylamines was found, whereas with  $\text{Al}(\text{Et})_3$  only a 16 % yield of octadienylamines was found. It is to be expected that nickel hydride formation should be considerably easier with the former ligand.

We have confirmed that butenylamines are also formed during this reaction, as found in the case of the morpholine-butadiene reaction <sup>1</sup>. However, we have further found that the distribution of octadienyl and butenylamines can be largely controlled by varying the Ni : Ligand ratio. The results obtained for the ligand  $\text{PhP}(\text{OCH}(\text{CH}_3)_2)_2$  are shown in Table II.

Table II

Ni : Ligand ratio	$(\text{C}_2\text{H}_5)_2\text{N C}_8\text{H}_{13}$ : $(\text{C}_2\text{H}_5)_2\text{N C}_4\text{H}_7$ ratio
1 : 1	50 : 1
1 : 2	2, 2 : 1
1 : 3	0, 7 : 1
1 : 4	0, 3 : 1
1 : 8	0, 02 : 1

Reaction conditions:

1 g Ni Laurate, 0,1 g  $\text{NaBH}_4$ , 0,5 Moles Diethylamine 0,5 Moles Butadiene,  $90^\circ$ , 4 hours

It is apparent that blockage of a second co-ordination site on the nickel atom prevents co-ordination of a second molecule of butadiene, a necessary step before insertion to give a C<sub>8</sub>-chain can occur.

References

- 1 R. Baker, D.E. Halliday and T.N. Smith, Chem. Comm., 1971, 1583
- 2 A.A. Ario, B.B. Chastain and H.B. Gray, Inorg. Chim. Acta, 1969, 3, 8
- 3 T.C. Shields and W.E. Walker, Chem. Comm., 1971, 173