Acid-promoted Amination of Butadiene on Nickel(0)

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Summary In the reaction of butadiene with amine catalysed by bis(cyclo-octa-1,5-diene)nickel and tri-n-butylphosphine, trifluoroacetic acid enhances the amination of butadiene to give butenylamine at room temperature.

WE have recently reported the nickel-catalysed reaction of butadiene with amines,[1] a reaction in which the cyclodimerization and the amination of butadiene occur competitively. Several nickel catalysts have been used to effect the dimerization of butadiene with concomitant addition of amine to butadiene.[2] These nickel catalysts give a linear dimer of butadiene and a mixture of butenyl- and octadienyl-amines by incorporation of one and two units of butadiene, respectively. It has now been found that catalytic amounts of certain protic acids enhance the amination of butadiene.

Bis(cyclo-octa-1,5-diene)nickel, $Ni(cod)_2$, tri-n-butylphosphine, and trifluoroacetic acid were used as the catalyst in this study,[1] the reaction being carried out in morpholine. The results are shown in the Figure. The nickel complex with tri-n-butylphosphine gave octa-1,3,6-triene[3] in 80% yield. When 0·2 equiv. of trifluoroacetic acid was added to this system, a dramatic change was observed: octa-1,3,6-triene was no longer formed but octadienylamines† were produced in yields of 60%. When the ratio of added acid to nickel was 10:1, butenylamine was selectively formed. The catalyst of this composition is active even at room temperature, to give 3-(*N*-morpholino)but-1-ene as the major product, which isomerises to 1-(*N*-morpholino)but-2-ene.

The added acid has a promoting effect on the formation of nickel hydride.[4] The production of butenylamine can be explained by attack of the amino-group on the carbon atom of the π-allyl group, which is formed by the reaction of diene with nickel hydride.[5]

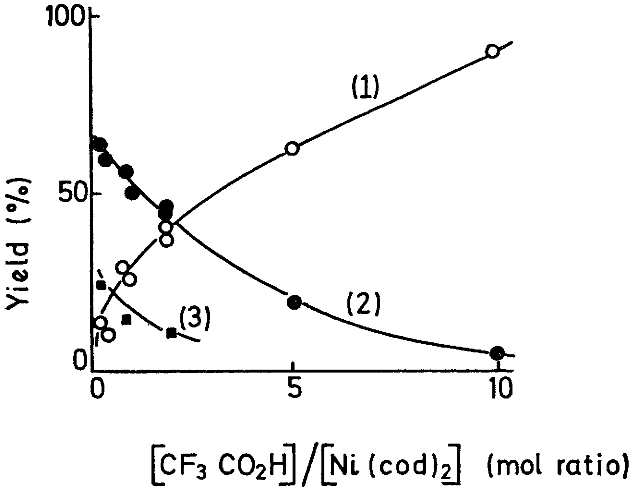

FIGURE. Effect of $[CF_3CO_2H]$ at 80° for 7 h. (1) butenylamine; (2) octadienylamine; (3) dimers of butadiene.
Conditions: $[Ni(cod)_2] = 0{\cdot}1$ mmol, $[Bu_3{}^nP] = 0{\cdot}3$ mmol, [morpholine] = [butadiene] = 10 mmol.

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† 1-(*N*-Morpholino)octa-2,7-diene and a small amount of 3-(*N*-morpholino)-octa-1,7-diene. P. Heimbach has reported in ref. 5 that an octa-2,6-dienyl derivative is formed in the absence of acid. From the present study it is evident that the presence of acid influences not only the reactivity but also the position of the double bond formed.

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[3] The dimerization of butadiene in amines has been reported: P. Heimbach, *Angew. Chem.*, 1968, **80**, 967.

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