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208. Reaction of Aminoalcohols with Butadiene Catalyzed by Palladium Complexes

Preliminary Communication

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Summary

The aminoalcohols **1**, react with 2 equivalents of butadiene in the presence of catalytic quantities of bis(acetylacetonato)palladium/triphenylphosphine to give exclusively the corresponding *N*-octadienyl aminoalcohols. In the presence of excess butadiene, subsequent *O*-octadienylation occurs only for *N*-octadienyliminodiethanol **2g**, affording the monoether **4g**. *O*-octadienylation of **2a–f** and **4g** can be effected by the addition of molar quantities of triethylamine to the reaction mixture.

The palladium or nickel catalyzed reaction of active hydrogen compounds with 1,3-butadiene has been reported for alcohols, amines, carboxylic acids, phenols, active methylene and methyne compounds, oximes, hydrazones and *Schiff* bases [1]. Generally, for the palladium catalyzed reaction, the major products are octadienyl derivatives of the active hydrogen compounds, with smaller amounts of the corresponding butenyl compounds.

The recent publication of two patents [2] [3] prompts us to report our own results on the palladium-catalyzed reaction of butadiene with a number of multifunctional active-hydrogen compounds, viz. alkanolamines. The reactions provide a highly selective synthetic route to a number of long chain tertiary amino alcohols that are useful intermediates for a variety of applications.

Table 1. *Reaction*[a]) *of Butadiene with Alkanolamines, catalyzed by* $Pd(acac)_2 + 2PPh_3$

Alkanolamine **1**	Time (h)	Alkanolamine Conversion %	**2**[b])	**3**[c])	Other[d])
$CH_3NHCH_2CH_2OH$ (**a**)	16	100	98	2	
$C_2H_5NHCH_2CH_2OH$ (**b**)	16	100	98.5	1.5	
n-$C_4H_9NHCH_2CH_2OH$ (**c**)	16	95	98	2	
t-$C_4H_9NHCH_2CH_2OH$ (**d**)	16	100	99	-	1
$C_6H_5NHCH_2CH_2OH$ (**e**)	2½	99	93	-	7
$C_6H_5CH_2NHCH_2CH_2OH$ (**f**)	4	100	97	3	
$NH(CH_2CH_2OH)$ (**g**)	16	95	96	4	

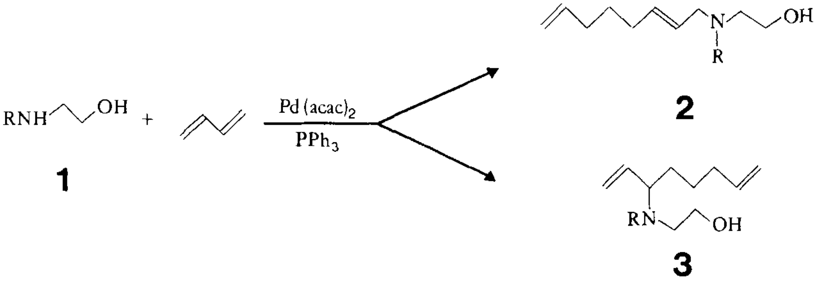
[a]) Reaction conditions: 0.25 mmol $Pd(acac)_2$; 0.50 mmol PPh_3; 0.25 mol alkanolamine, 0.5 mol butadiene, 80°, glass autoclave.

[b]) The IR., ^1H-NMR. and mass spectra are in agreement with the assigned structure.

[c]) Structure assigned by GC./MS.

[d]) Unidentified, high molecular weight products.

Scheme 1

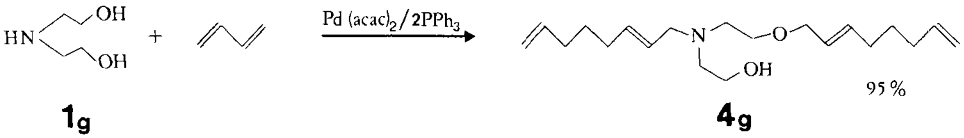


In all cases, preferential formation of *N*-octadienylated products occurred *(Table 1)*, which reflects the greater nucleophilicity of the amine group as compared to the alcohol function.

The reaction of excess butadiene with the amino alcohols afforded the *N*-octadienyl amino alcohols and 1,3,7-octatriene in high yield.

In only one case, that of the diol diethanolamine (**1g**), did any significant ether formation occur[1]) *(Scheme 2)*. However only one hydroxy group could be etherified. Thus it would appear that the catalytic system studied here is not able to catalyze the formation of octadienyl ethers from amino alcohols that contain one free hydroxy group.

Scheme 2



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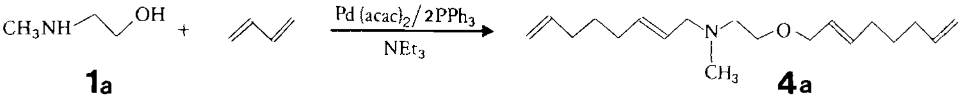
[1]) Reaction conditions: **1g**/butadiene/$Pd(acac)_2$/PPh_3 200:1800:1:2. Excess butadiene was converted to 1,3,7-octatriene.
The IR., ^1H-NMR. and mass spectra are in agreement with the assigned structure **4g**.

Scheme 3



Octadienyl ether formation can be induced, however, by the addition of triethylamine to the reaction mixture. Thus **1a**, reacted with a 5-fold excess of butadiene in the presence of Pd(acac)$_2$, triphenylphosphine and triethylamine to afford **2a** (33.6%), **3a** (0.4%), **4a** (29%) and 1,3,7-octatriene (37%).

The competition between the various *Lewis* bases in the reaction mixture for coordination or association to the catalyst and subsequent directivity of reaction is extremely sensitive to subtle influences, as has been recently demonstrated by *Heimbach et al.* [4] for the case of nickel-catalyzed oligomerisation of butadiene with various active-hydrogen compounds. In the reaction studied here, triethylamine can direct the formation of octadienyl ethers from amino monoalcohols, whereas the tertiary allylic amino group, which is itself present in the amino alcohol, cannot. The presence of a second intramolecular free hydroxyl group (case of diethanolamine **1g** or its *N*-octadienyl derivative **2g**) also results in etherification and in this respect plays a similar role to the triethylamine.

Our studies are continuing to elucidate this effect.

General Procedure. - A mixture of bis(acetylacetonato)palladium (77 mg, 0.25 mmol), triphenylphosphine (131 mg, 0.5 mmol), *N*-ethyl-aminoethanol (22.25 g, 0.25 mol) and butadiene (27 g, 0.5 mol) was heated, with stirring, for 16 h at 80° in a 250 ml glass autoclave. The developed pressure rose to a maximum of 5 kgcm^{-2} after 30 min. After 16 h the pressure was -0.5 kgcm^{-2}. A sample of the yellow-brown solution (after silylation with $(CH_3)_3SiCl$), was analyzed by GLC./MS. and shown to contain *N*-ethyl-aminoethanol (trace), **2b** (98.5%), **3b** (1.5%) and octa-1,3,7-triene (trace). Fractional distillation of the reaction mixture gave a first fraction containing mainly octa-1,3,7-triene and starting material (0,3 g), b.p. 25-70°/13 Torr. Further distillation afforded a second fraction containing **2b** and **3b** (47,9 g), b.p. 125-130°/13 Torr.

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