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Conversion of Alcohols into Unsymmetrical Secondary or Tertiary Amines by a Palladium Catalyst. Synthesis of N-Substituted Pyrroles

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Summary The palladium-induced reaction of arylmethanols or allyl alcohols with amines provides a useful method for synthesis of secondary or tertiary amines; N-substituted pyrroles can be prepared by the palladiumcatalysed reaction of but-2-ene-1,4-diol with primary amines in excellent yields.

We recently reported a ready amine-exchange reaction induced by palladium catalyst.¹ We now report an efficient process for synthesis of secondary or tertiary amines from the reaction of arylmethanols or allyl alcohols with primary or secondary amines with a palladium catalyst.



This method has certain advantages over the classical reductive amination of aldehydes and ketones, where high-pressure hydrogenation conditions are normally required, and yields are often $low.^2$

Reaction of benzyl alcohol (28 mmol) with n-hexylamine (30 mmol) in the presence of palladium black (0.2 g) under nitrogen at 110° for 6 h gave N-n-hexylbenzylamine in 98% yield. Other examples are in the Table.



N-Substituted pyrroles (5) can be prepared by a similar reaction. The palladium-catalysed reaction of *cis*-but-2ene-1,4-diol (6) with primary amines under mild condition gave the pyrroles (5) in excellent yields. Although many methods (*e.g.* condensation of primary amines with 2,5diketones,^{3,4} tetrabromobutanes,⁵ and 1,4-diaminobuta-1,3-dienes⁶) have been used for the synthesis of (5), they require 2,5-diketones or their derivatives which are normally difficult to be prepared, and the yields are often low.

In a typical case, a mixture of (6) (3.5 g), ethanolamine (1.2 g) and palladium black (0.1 g) was stirred at 120° for 18 h. Filtration followed by distillation gave (5a) (b.p. 120—130° at 90 mmHg) (87%); ν_{max} 3200 cm⁻¹; δ 6.50 (t, 2H, J 2 Hz), 6.00 (t, 2H), 3.67 (t, 2H, J 7 Hz, N-CH₂) 3.83 (t, 2H, O-CH₂), and 2.13 (s, H).

reaction (1), by analogy with the amine-exchange reaction.¹ Dehydration of the alcohol (1) would lead to the intermediate (2) which would react with (3) to give the corresponding Schiff base. Subsequent hydrogenation of the Schiff base with the palladium-hydride species would afford the product (4). The pyrroles (5) could be derived

TABLE. Reaction of alcohols with amines with a palladium catalyst						
R ¹ R ² CHOH		R ⁸ R ⁴ NH		m (60	Product amine	
D1	-X			Temp./°C	Conversion	Y teld
K-	Ľ.	Ľ,	К-	(time/n)	(70)	(%)
\mathbf{H}	\mathbf{Ph}	H	n-C ₆ H ₁₈	110(6)	35	98
н	\mathbf{Ph}	н	Ph	80(6)	28	$44(56)^{a}$
н	$CH_2 = CH$	H	$n-C_6H_{13}$	100(12)	40	87 ^b
Me	\mathbf{Ph}	H	n-C ₆ H ₁₃	120(18)	96	83(7)°
Me	\mathbf{Ph}	$-[CH_2]_4-$		110(26)	95	83

^a N-Benzylideneaniline. ^b N-Propylidenehexylamine. ^cα-Methylbenzylideneamine.

Similarly, reaction of (6) (120°; 14-20 h) with cyclohexylamine, n-hexylamine, and aniline gave (5b) (89%), (5c) (93%), and (5d) (46%), respectively. The trans-isomer of (6) reacts similarly with cyclohexylamine to give (5b) in 95% yield.

by a similar procedure; palladium-induced intramolecular cyclization of the initially formed 4-aminobut-2-en-1-ol would give (5).

These reactions can be rationalized by the mechanism in

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† Satisfactory spectroscopic and analytical data have been obtained for all compounds.

¹ N. Yoshimura, I. Moritani, T. Shimamura, and S.-I. Murahashi, J. Amer. Chem. Soc., 1973, 95, 3038.

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²W. S. Emerson, Org. Reactions, 1948, 4, 174.
³ R. Pips, Ch. Derappe, and Ng. Ph. Buu-Hoï, J. Org. Chem., 1960, 25, 390; A. Kreutzberger and P. A. Kalter, *ibid.*, p. 554.
⁴ A. P. Trenter, M. A. Volodina, N. L. Podlesiva, and N. E. Golubeva, Doklady. Akad. Nauk S.S.S.R., 1957, 114, 1036 (Chem. Abs., 1958, 52, 3767).

⁶ A. Treibs and O. Hitzler, Chem. Ber., 1957, 90, 787. ⁶ M. F. Feyley, N. M. Bortnick, and L. H. McKeever, J. Amer. Chem. Soc., 1957, 79, 4144.