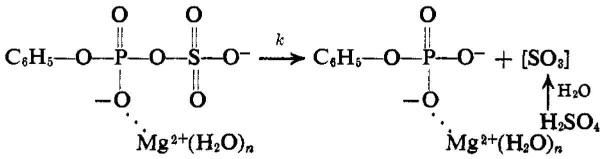
Mg^{2+} ion ($k_0 = 4.44 \times 10^{-4}$ sec^{-1}). These k_{max} and k_0 are dependent on both water and acid concentration, and the ratio (k_{max}/k_0) appears to increase linearly with decreasing water concentration, and exponentially with decreasing acid concentration,[8] at least in the range of $[H_2O] = 3$–8 *M* and $[HClO_4] = 0.3$–3×10^{-3} *M*.

The above observations suggest that the 1:1 complex of the ester and magnesium ion **1** is catalytically active, while the higher order complexes are stable and inert to hydrolysis. The absence of the salt effect[6] may eliminate the possibility that the inhibition at higher Mg^{2+} concentration is due to such an effect. Presumably, **1** decomposes unimolecularly to form a phosphate–magnesium ion complex and sulfur trioxide.[9]



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Much remains to be clarified in order to know the detailed mechanism of this magnesium ion catalysis, in particular to derive a reasonable rate law. Nevertheless, it may be of considerable importance to note that a change of medium alone causes a profound influence on the effectiveness of metal ion catalysis, even in the absence of a suitably located functional group for coordination with metal ion.

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(8) Preliminary experiments showed that the plots of log k_{obsd} *vs.* log $[HClO_4]$ are linear with slopes of 1.6 (when $[PPS] = [Mg(ClO_4)_2] = 1.8 \times 10^{-3}$ *M*) and 3.2 in the absence of $Mg(ClO_4)_2$, respectively, in a range of $[HClO_4] = 0.3$–3.0×10^{-3} *M*. The slope appears to be invariant to the change of water concentration from 4 to 6 *M*.

(9) Similar unimolecular fission of the S–O bond has been suggested in the acid-catalyzed hydrolysis of PPS.[2]

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Synthesis of Unsymmetrical Secondary and Tertiary Amines from Amines by Palladium Catalyst

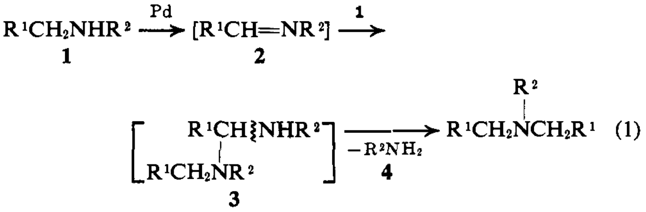
Sir:

Unsymmetrical amines are synthesized by Hofmann alkylation[1] or reductive alkylation[2] of either ammonia or amines and by modifications of these reactions.[3]

We wish to report a new process for the synthesis of unsymmetrical secondary and tertiary amines by dehydrogenation of primary or secondary amines by palladium black. The method is operationally simple, highly selective, and efficient, hence offers advantages over previous methods.

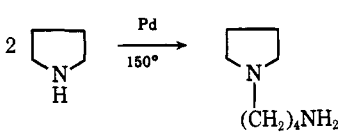
In a general procedure, a suspension of palladium black (5 wt%) in amines (5–10 g) was heated at 25–200° with stirring for 3–20 hr. After filtration of palladium the products were distilled. The distillate was analyzed by vpc, and the structure of the products was assigned by comparison of their spectral data with those of authentic samples.

Treatment of primary amines having activated α hydrogens with Pd at 25° afforded secondary amines and/or imines as shown in Table I. Thus, allylamine was converted to *N*-propylideneallylamine (95%), while benzylamine led to *N*-benzylidenebenzylamine (45%) and *N*,*N*-dibenzylamine (45%). These reactions can be illustrated by addition of the amine **1** to the intermediate imine **2** derived from dehydrogenation[4] of **1** followed by elimination of ammonia[5] (**4**, $R^2 = H$) as shown in eq 1.



$$\underset{\mathbf{1}}{R^1CH_2NHR^2} \xrightarrow{Pd} \underset{\mathbf{2}}{[R^1CH{=}NR^2]} \xrightarrow{\mathbf{1}} \underset{\mathbf{3}}{\left[\begin{array}{l} \quad R^1CH\,NHR^2 \\ \quad\ | \\ R^1CH_2NR^2 \end{array}\right]} \xrightarrow[-R^2NH_2]{} \underset{\mathbf{4}}{R^1CH_2\overset{R^2}{\overset{|}{N}}CH_2R^1} \quad (1)$$

Analogous reactions were generally performed on secondary amines giving tertiary amines with two identical substituents. Reaction of *N*-methylbenzylamine with Pd afforded *N*-methyldibenzylamine in 85% yield in addition to methylamine. *N*-Methylaniline was also converted to *N*,*N*-dimethylaniline along with aniline. Liberation of amines such as methylamine and aniline in these reactions would be rationalized by cleavage[6] of the C–N bond of the intermediate **3**. This is clearly demonstrated by formation of 1-pyrrolidinebutylamine (**5**, 98%) on treatment of pyrrolidine with Pd at 150° for 5 hr.



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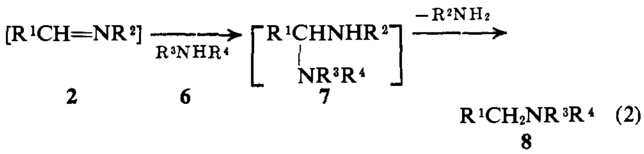
In analogy with formation of tertiary amines in eq 1, amine exchange reactions might be expected by introducing a primary amine (**6**, $R^4 = H$) or a secondary amine (**6**) at the stage of addition of the amine to the intermediate imine **2** followed by extruding R^2NH_2 (eq 2). Indeed, as shown in Table II, reaction of *N*-methylbenzylamine with aniline afforded *N*-phenylbenzylamine (48%) and *N*-benzylideneaniline (52%) by exchanging the methyl group for the phenyl group. Further, addition of a secondary amine to **2** to give **7** followed by extruding R^2NH_2 can also be achieved selectively. Thus, reaction of *N*-methylbenzylamine with *N*-methylbutylamine gave *N*-butyl-*N*-methyl-



$$\underset{\mathbf{2}}{[R^1CH{=}NR^2]} \xrightarrow[\underset{\mathbf{6}}{R^3NHR^4}]{} \underset{\mathbf{7}}{\left[\begin{array}{l} R^1CHNHR^2 \\ \quad | \\ \quad NR^3R^4 \end{array}\right]} \xrightarrow{-R^2NH_2} \underset{\mathbf{8}}{R^1CH_2NR^3R^4} \quad (2)$$

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(2) W. S. Emerson, *Org. React.*, **4**, 174 (1948).

(3) (a) R. F. Borch and H. D. Durst, *J. Amer. Chem. Soc.*, **91**, 3996 (1969); (b) H. Zimmer, *J. Org. Chem.*, **35**, 2826 (1970); (c) J. C. Richer and D. Perelman, *Can. J. Chem.*, **48**, 570 (1970); (d) R. A. W. Johnstone, *J. Chem. Soc. C*, 2223 (1969).

(4) A. A. Balandin and N. A. Vasyunia, *Dokl. Akad. Nauk SSSR*, **103**, 831 (1955).

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(6) Palladium must play an important role in the cleavage of the intermediate **3**, since thermal reaction of *N*-benzylidenemethylamine with *N*-methylbenzylamine without Pd led to *N*-benzylidenebenzylamine, but not to *N*-methyldibenzylamine, the ordinary product of the reaction of *N*-methylbenzylamine with Pd.

Table I. Products of the Reactions of Primary and Secondary Amines (Eq 1)

Amines $R^1CH_2NHR^2$		Temp, °C	Time, hr	Product yield (%)[a]		Conversion (%)[d]
R^1	R^2			$(R^1CH_2)_2NR^2$	$R^1CH{=}NCH_2R^1$	
C_6H_5	H	80	5	45	45	90
$CH_2{=}CH$	H	25	5		95[b]	95
C_6H_5	CH_3	120	20	85		28
H	C_6H_5	120	20	98		7
CH_3	C_6H_5	150	48	98		5
n-C_3H_7	CH_3	160	5	85[c]		70

[a] Yields based on unrecovered amines. [b] $CH_3CH_2CH{=}NCH_2CH{=}CH_2$. [c] Another product was $(n\text{-}C_4H_9)_3N$ (8%). [d] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

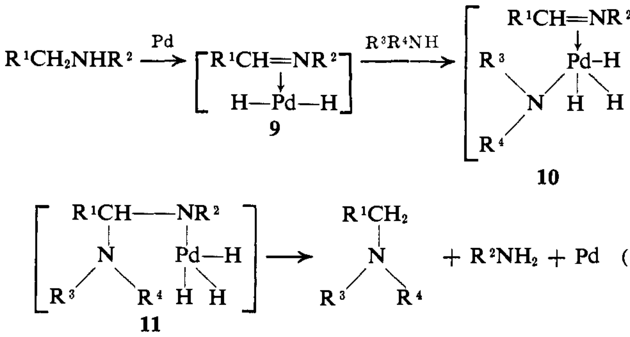
Table II. Reactions of Secondary Amines with Either Primary Amines or Secondary Amines (Eq 2)

Amines $R^1CH_2NHR^2$		R^3NHR^4		Temp, °C	Time, hr	Product yield (%)[a] R^1CH_2-NHR^3R^4	$R^1CH{=}NR^3$	Conversion (%)[b]
R^1	R^2	R^3	R^4					
C_6H_5	CH_3	n-C_6H_{13}	H	120	10	55	30	37
C_6H_5	CH_3	C_6H_{11}	H	120	10	10	90	40
C_6H_5	CH_3	C_6H_5	H	120	20	48	52	40
C_6H_5	CH_3	$H_2N(CH_2)_2$	H	120	10	95		24
H	C_6H_5	n-C_6H_{13}	H	120	40	98		5
n-C_3H_7	CH_3	n-C_6H_{13}	H	160	7	75		45
C_6H_5	CH_3	n-$CH_3(CH_2)_3$	CH_3	120	10	80		55
C_6H_5	CH_3	$(CH_2)_5$		130	10	97		90
C_6H_5	CH_3	$(CH_2)_4$		130	10	75		75
n-C_3H_7	CH_3	$(CH_2)_5$		160	5	98		85

[a] Yields based on unrecovered amines. [b] Conversions based on unrecovered amines are easily improved by prolonged reaction time or higher temperature.

benzylamine (95%), and on treatment of *N*-methylpropylamine with pyrrolidine led to *N*-propylpyrrolidine (98%).

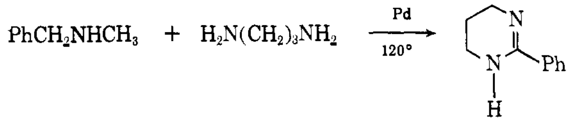
Secondary and tertiary amines are simply synthesized by reaction of various amines using a palladium catalyst. The conversion of these reactions is improved by using more active catalysts such as π-allylpalladium complexes or Wilkinson catalyst, although side reactions appear. The reaction can be envisioned as follows. The key step is the formation of a palladium π complex of Schiff base bearing a Pd–H bond (**9**) by dehydrogenation by palladium. Oxidative addition of an amine (R^3R^4NH) into **9** leading to **10**, followed by addition of the Pd–N across the N=C bond, would form **11** which subsequently cleaves to form products



(3)

reductively.[6] The palladium(II)-catalyzed additions of amines across carbon–carbon[7] or carbon–nitrogen[8] double bonds have been demonstrated.

Variations of this reaction can open new routes to heterocyclic compounds. For example, palladium-catalized reaction of *N*-methylbenzylamine with 1,3-propanediamine at 120° affords 2-phenyl-1,4,5,6-tetrahydropyrimidine (**12**) in 75% yield. Furthermore,



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treatment of allylamine with 1,3-propanediamine gives 2-ethylhexahydropyrimidine in 82% yield. We are currently exploring other applications of this reaction.

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^{207}Pb Pulse Fourier Transform Nuclear Magnetic Resonance. A Promising New Tool for Studies in Lead Chemistry

Sir:

The recent development of pulse Fourier transform approaches has made ^{13}C nmr spectroscopy a powerful, popular, and convenient tool for a wide range of chemical studies. We wish to report here that virtually the same techniques used for ^{13}C are also applicable to ^{207}Pb resonances and provide some preliminary data illustrating the promise and characteristics of high-resolution ^{207}Pb nmr. Although there have been earlier nmr studies of ^{207}Pb (21.1% naturally abundant, 9.13×10^{-3} as sensitive as ^1H for equal numbers of