

Similar bridging is not found in the parent  $H_4Ru_4(CO)_{12}$ ; thus, if this were the favored conformation in methanol solution for the  $H_3Ru_4(CO)_{12}^-$  and  $H_3Os_4(CO)_{12}^-$  anions, the unusually slow back-reaction may reflect this added conformational change.

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- (5) Hieber, W.; Hübel, W. B. Z. *Elektrochem.* **1953**, *57*, 235. This work shows that in methanol  $H_2Fe(CO)_4$  is 465 times stronger than acetic acid, for which  $pK_a = 9.60$  in methanol.<sup>6</sup> The estimate of  $pK_2$  for  $H_2Fe(CO)_4$  follows from the lack of a second break in the titration curve (Hieber and Hübel), and the fact that salts such as  $Na_2Fe(CO)_4$  can be prepared in alcohols.
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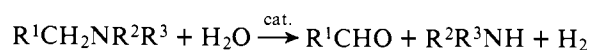
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## Palladium Catalyzed Hydrolysis of Tertiary Amines with Water

Sir:

Although catalytic hydrolysis of tertiary amines is principally of importance with respect to biological deamination processes<sup>1-2</sup> and energy-transfer systems for solar energy conversion,<sup>3</sup> there has been no report on catalytic hydrolysis with metal catalysts. We report a novel palladium catalyzed hydrolysis of tertiary amines, which is superior in certain cases to current procedures that require stoichiometric amount of oxidants.<sup>4</sup> The reaction involves insertion of palladium coordinated to the nitrogen lone pair into the carbon-hydrogen bond adjacent to nitrogen, giving iminium ion (1) and enamine complexes (2). The key step is the activation of hydrogen at saturated carbon to which much attention has been devoted recently.<sup>5-8</sup>



When a mixture of tributylamine (2 mmol), hydrochloric

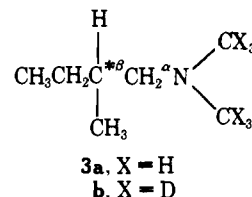
**Table I.** The Hydrolysis of Tertiary Amines with Water<sup>a</sup>

tertiary amines	convn, %	product, <sup>b</sup> % yield <sup>c,d</sup>	
		secondary amines	carbonyl compounds
tributylamine	30	dibutylamine, 97	butanal, 98 <sup>e</sup>
<i>N</i> -hexylpyrrolidine	61	pyrrolidine, 98	hexanal, 89 <sup>e</sup>
<i>N</i> -cyclohexylhexa-methylenimine	25	hexamethylenimine (90)	cyclohexanone (95)
<i>N</i> -cyclopentyl-morpholine	50	morpholine (85)	cyclopentanone (90)
<i>N,N</i> -dimethyl- $\alpha$ -methylbenzylamine	30	dimethylamine	acetophenone (80)
nicotine	67	pseudooxynicotine (85)	

<sup>a</sup> A mixture of an amine (2 mmol), HCl (0.7 mmol), palladium black (0.8 mmol), and water (40 mmol) was allowed to react with stirring at 200 °C for 40 h. <sup>b</sup> Identified by IR, <sup>1</sup>H NMR spectroscopy, and elemental analysis. <sup>c</sup> GLC yield based on the amine. <sup>d</sup> Isolated yield in parentheses. <sup>e</sup> Yield of 2,4-dinitrophenylhydrazone.

acid (0.7 mmol), palladium black (0.8 mmol), and 2,4-dinitrophenylhydrazine (2 mmol) in water (40 mmol) was heated with stirring under argon for 40 h at 200 °C, dibutylamine and the 2,4-dinitrophenylhydrazone of butanal were obtained in 98 and 92% yields, respectively.<sup>9</sup> The catalytic hydrolysis of tertiary amines proceeded generally and efficiently with palladium catalysts.<sup>10,11</sup> Examples of this simple reaction system for the hydrolysis of tertiary amines using palladium black and hydrochloric acid catalysts<sup>12</sup> are shown in Table I. The carbon-nitrogen bond of a tertiary amine is cleaved more readily in the order methine > methylene > methyl. Typically, hydrolysis of nicotine gave the relatively unstable pseudooxynicotine<sup>13</sup> exclusively in 85% isolated yield.

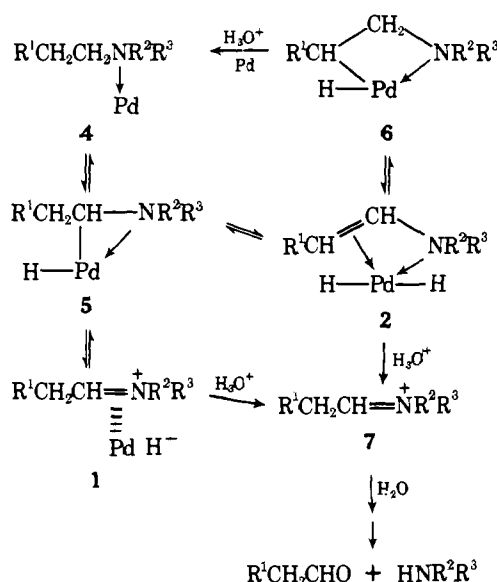
Catalysis of the hydrolysis of a tertiary amine by a proton exhibits a rate increase unless the proton is in excess of the amine, indicating that coordination of palladium to the lone pair of nitrogen competes with protonation. When optically active (*S*)-(+)-*N,N*-dimethyl-2-methylbutylamine (3a), ( $[\alpha]_D^{23}$  7.50°, 2.0 mmol) was treated with palladium in deuterium oxide (40 mmol) in the presence of  $CH_3CO_2D$  (0.7 mmol) at 190 °C for 14 h, the recovered amine lost its optical activity completely. The <sup>1</sup>H NMR analysis of recovered 3a



showed that  $\alpha$ -methylene,  $\beta$ -methine, and methyl groups were 63, 80, and 25% deuterated, respectively. Further when (*S*)-(+)-*N,N*-di(trideuteriomethyl)-2-methylbutylamine (3b) alone was treated with palladium catalyst at 200 °C for 16 h, deuterium distribution took place but with retention of the optical activity;<sup>7</sup> the  $\alpha$ -methylene,  $\beta$ -methine, and methyl groups of the recovered amine were 34, 17, and 67% deuterated, respectively. A <sup>13</sup>C NMR study<sup>14</sup> showed that the deuterium incorporation into the alkyl chain was limited to the  $\alpha$  and  $\beta$  positions of the tertiary amines under both amine exchange and hydrolysis conditions.<sup>15</sup>

A mechanism that may explain the above results is shown in Scheme I. The mechanism requires initial coordination of the nitrogen lone pair to metal followed by metal insertion into the adjacent carbon-hydrogen bond to form 5,<sup>7,8</sup> which comes to rapid equilibrium with the iminium ion (1)<sup>16-18</sup> and the enamine intermediate (2). In the absence of proton, the interconversions  $5 \rightleftharpoons 1$  and  $5 \rightleftharpoons 2 \rightleftharpoons 6$  proceed rapidly without losing the optical activity at the  $\beta$  position of 3. The exclusive

Scheme I



reaction pathway is a nucleophilic attack of the second molecule of the tertiary amine on the iminium ion complex **1**, resulting in the alkyl group exchange.<sup>7</sup> In contrast, under the hydrolysis condition, protonolysis of complexes **1** and **2** gives the non-metal-coordinated iminium ion **7**, which undergoes the usual acid-catalyzed hydrolysis steps of enamines to produce carbonyl compounds and secondary amines.<sup>19</sup> Protonolysis of intermediate **6** may cause the loss of the optical activity of recovered **3a** under the reaction conditions.

Recently Laine has reported that deuterium exchange of triethylamine by deuterium oxide takes place easily with the homogeneous  $Rh_6(CO)_{16}$  catalyst<sup>20</sup> at the  $\beta$  position rather than the  $\alpha$  position, suggesting a mechanism which involves simultaneous insertion of three rhodiums of  $Rh_6(CO)_{16}$  into the  $\alpha$ - and  $\beta$ -carbon-hydrogen bonds. This is in contrast to the results obtained with heterogeneous palladium catalysts where deuterium exchange at  $\alpha$  position of tertiary amines exceeds that at the  $\beta$  position. When an equimolar mixture of tributylamine and deuterium oxide was treated with either palladium black or  $Rh_6(CO)_{16}$  at 150 °C for 20 h, the relative ratio of the deuterium content of the  $\alpha$  to  $\beta$  positions of the recovered tributylamine was 4:1 for palladium catalyst and 1:4 for  $Rh_6(CO)_{16}$  catalyst.<sup>21</sup> With the catalytic hydrolysis of tertiary amines, at least, it is doubtful whether the homogeneous metal cluster catalyst can be used to model heterogeneous catalytic reactions.<sup>22</sup> Work is in progress to investigate the full scope of the present reaction and to apply our method to other systems.

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- (9) In the absence of 2,4-dinitrophenylhydrazine, dibutylamine and *N,N*-dibutyl-2-butylamine, which are condensation products of dibutylamine and butanal, are obtained in 54 and 47% yield, respectively.
- (10) Palladium catalyst gave the best result among the metals examined. Other palladium compounds such as  $PdCl_2$  and  $Pd(OAc)_2$  gave similar results. Alternatively, soluble ruthenium catalysts such as  $RuCl_3$  can be used conveniently, giving similar results.
- (11) The reaction of tertiary amines such as tributylamine with water in the presence of acid catalysts does not take place at 200 °C without palladium catalyst.
- (12) The higher  $pK_a$  results in higher conversion of tertiary amines. The conversion of tributylamine increases in the order of  $CH_3CO_2H < ClCH_2CO_2H < Cl_3CCH_2CO_2H < NO_2C_6H_4SO_3H$ . When 0.3 equiv of *p*- $NO_2C_6H_4SO_3H$  is used under the same reaction condition, the conversion reaches to 80%.
- (13) 4-Methylamino-1-(3-pyridyl)butanone: IR (liquid film) 1655  $cm^{-1}$  (C=O), 3100 (N-H); NMR ( $CDCl_3$ )  $\delta$  1.55 (br t, 2 H), 2.20 (s, 3 H), 2.35 (m, 4 H). Wada, E. *Arch. Biochem. Biophys.* **1957**, *72*, 145.
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## Retention of Stereochemistry during Multipositional Isomerization of an Olefin by Diiron Nonacarbonyl

Sir:

The preponderance of evidence indicates that olefins rearrange in the presence of iron carbonyl catalysts by a sequence of 1,3-hydrogen shifts. Numerous reports have dealt with this reaction,<sup>1</sup> and a few have provided convincing arguments regarding the detailed nature of the rearrangement. Casey and Cyr have established that during  $Fe_3(CO)_{12}$  induced rearrangement of 3-ethyl-1-pentene-3-*d*<sub>1</sub> (**1**) to 3-ethyl-2-pentene, the deuterium label was scrambled randomly between the terminal methyl groups, as shown in **2**.<sup>2</sup> These results were interpreted in terms of rapidly equilibrating complex species, representatives of which are shown in Scheme I.

Only a small number of reports have concerned the stereochemistry of the hydrogen shift, and none have dealt with the stereochemistry of the hydrogen shift in purely hydrocarbon rearrangements. Ford and Strauss have shown that the rearrangement of the labeled *endo*-tricyclodecenol **3** proceeds stereospecifically to give the saturated ketone **4**, with the stereochemistry of the migrating deuterium as shown.<sup>3</sup> In another example, Green and Hughes found that the monoolefin-tetracarbonyliron complex **5** rearranged to the diene-tricarbonyliron complex **6**, with some of the optical activity of **5** remaining intact.<sup>4</sup>

Regarding the first example, it is difficult to envision another result, since it is essentially impossible for an iron species responsible for the hydrogen shift to approach the *endo* face of