and the trifluoromethanesulfonates. In our opinion, CF_3SO_2OCl is the most electrophilic chlorine compound ever prepared and is probably more electrophilic than $ClOSO_2F$.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

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A Direct, Selective, and General Method for Reductive Deamination of Primary Amines

Sir:

We wish to report the first direct, selective, and general method for replacement of organic primary amino groups by hydrogen. This method is apparently applicable to a variety of structural types, including amines containing other functionalities.[1]

$$RNH_2 \xrightarrow[OH^-,\ 0\ °C]{NH_2OSO_3H\ (2\text{-}3\ mol)} RH + N_2 + SO_4^{2-}$$

In a representative example, 6-aminocaproic acid (2.62 g, 20 mmol) is dissolved in 40 mL of 2.5 M aqueous NaOH in a flask connected to a gas buret. To this is added hydroxylamine-*O*-sulfonic acid (HOS, 4.52 g, 95% pure, 38 mmol) and the mixture is stirred (magnetic stirrer) in an ice bath. After 35 min, an additional 2.26 g of HOS (19 mmol) and 20 mL of 2.5 M NaOH is added and stirring is continued until gas evolution almost stopped (90 min, volume of gas evolved was 110% of theory). Acidification with sulfuric acid, extraction with diethyl ether, and distillation of the extract gives 1.22 g (55% of theory) of caproic acid, bp 205–207 °C, characterized by elemental analysis and ^1H NMR. Table I lists other examples of the method conducted under similar conditions. The outline of a mechanism (shown in Scheme I) is suggested. N-Amination of amines to hydrazines by HOS under basic conditions (employing in general 3-5 mol of amine/mol of HOS) is a general reaction with established preparative utility.[3] Formation of nitrene NH: from HOS with base has been proposed from successful trapping experiments with butadiene to yield pyrroline.[4] The facile conversion of RN=NH to RH and N_2 is well recognized.[5] Further evidence for the above mechanism was provided by treatment of benzylhydrazine or *p*-hydrazinobenzoic acid with HOS under the conditions described above, to furnish toluene (73% yield, besides 10% bibenzyl) or benzoic acid (41%), respectively.[6]

Scheme I

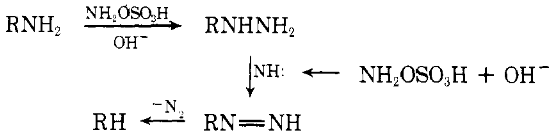
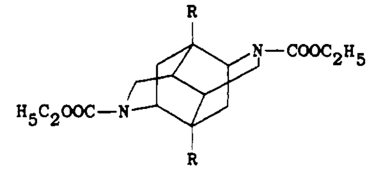


Table I

Substrate	Product	% yield[a]
2-Aminobenzoic acid	Benzoic acid[b]	72
2-Amino-3-methylbenzoic acid	3-Methylbenzoic acid	26[c]
Benzylamine	Toluene	65[d]
3-Aminopropionic acid	Propionic acid	50[d]
Alanine	Propionic acid	50[d]
L-Alanyl-L-phenylalanine	*N*-Propionyl-L-phenylalanine	51
1[e]	**2**[f]	49

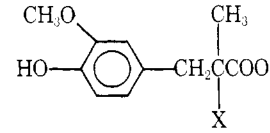
[a] Yields are those of pure, isolated products, unless otherwise noted. [b] Reaction finished at 90 °C. [c] 47% of starting material was recovered. [d] Yields were estimated by ^1H NMR analysis of reaction mixture. [e] See Figure 1.[2] [f] Figure 1.



1, R = CH_2NH_2 (Ref. 2) **2**, R = CH_3

Figure 1.

Substitution of primary amino groups contained in natural products (e.g., in amino acids, amino sugars, peptides, and proteins) by hydrogen (deuterium, tritium) appears to be an especially attractive field for application of this method. **3** ((*S*)-4-hydroxy-3-methoxy-α-methylphenylalanine[7]) was "deuterodeaminated" to give **4** in 31% yield. The labile protons of **3** and HOS were first exchanged for deuterium with D_2O (20 vol of D_2O was employed, followed by evaporation in vacuo to dryness; this treatment was repeated). NaOD in D_2O was obtained from Merck-Canada. **4:** ^1H NMR δ 1.16 (s, α-CH_3), 2.6 (d, J = 7 Hz, β-H), 2.94 (d, J = 7 Hz, β-H), 3.82 (s, OCH_3), 6.5–6.9 (m, aromatic H); mass spectrum *m/e* 211, 137 (4-hydroxy-3-methoxybenzyl), <2% of *m/e* 138. Reductive deamination of **3** in H_2O gave **5**, with $[\alpha]_D$ +2.1 ± 0.5° (*c* 1, in $CHCl_3$). Reductive deamination of **3** in methanol–$(CH_3)_4N^+OH^-$ (instead of H_2O–NaOH) gave **5** with $[\alpha]_D$ +5.6 ± 0.5° (*c* 1, in $CHCl_3$). This dependence of stereoselectivity on experimental conditions, as well as the low degree of stereoselectivity,[8] suggests complex mechanism. **5:** ^1H NMR δ 1.16 (d, J = 7 Hz, α-CH_3), 2.32–3.06 (m, α-H and β-H), 3.82 (s, CH_3O–), 6.5–6.9 (m, aromatic H); mass spectrum *m/e* 210, 137.



3, X = NH_2
4, X = D
5, X = H

The name "hydrodeamination" is proposed for this method.

References and Notes

(1) (a) Transformation of some *unsubstituted* primary amines into the corresponding hydrocarbons by reaction with difluoroamine HNF_2 has already

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been described: C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85,** 97 (1963). The need for vacuum-line techniques and the explosive nature of HNF_2 apparently discouraged development of this very interesting reaction. (b) A. Nickon and A. S. Hill (*J. Am. Chem. Soc.*, **86,** 1152 (1964)) showed that sulfonamides of primary amines give alkanes and arenes by treatment with 8–58 mol of hydroxylamine-*O*-sulfonic acid in boiling strongly basic aqueous systems. Also, *N,N*-disulfonimides, derived from unhindered amines, provide alkanes upon displacement with hydride anions at 150 °C: R. O. Hutchins, F. Cistone, B. Goldsmith, and P. Heuman, *J. Org. Chem.*, **40,** 2018 (1975).

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(6) Addition of trace amounts of Cu^{2+} exerts striking influence on this reaction:

$$C_6H_5CH_2NH_2 \xrightarrow[OH^-]{HOS} C_6H_5CHO + C_6H_5CH{=}NCH_2C_6H_5 + C_6H_5CH_2CH_2C_6H_5$$

Benzylhydrazine under similar conditions still gives the normal product—toluene—with a small amount of bibenzyl, suggesting that in the presence of Cu^{2+} benzylhydrazine is not an important intermediate.

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Reduction of Nitric Oxide by Carbon Monoxide in the Presence of Aqueous Palladium(II) and Copper(II)

Sir:

While highly favored thermodynamically, the reduction

$$CO + 2NO \rightarrow CO_2 + N_2O \qquad (1)$$

of nitric oxide by carbon monoxide does not proceed even at 450 °C.[1] Heterogeneous systems (metals and their oxides) are used for catalysis of this reaction, but typically elevated temperatures (400 °C) are required.[1] Homogeneous catalysis of reaction 1 at 23 °C has been recently reported by Eisenberg and co-workers.[2] The only system investigated in depth thus far employs the rhodium(I)-rhodium(III) couple.[2] The objective of our study is to determine first whether other transition metals may be used for homogeneous catalysis of the NO-CO reaction at room temperature and whether new insights on pathways for this reaction may be derived from these studies. Herein we report the utilization of the palladium(0)-palladium(II) system coupled with the copper(II)-copper(I) system, analogous to the Wacker system, for the catalysis of reaction 1 at room temperature.

The reactions of NO (350 Torr) and CO (360 Torr) in a 125-mL reaction vessel containing 25 mL of aqueous solutions of $PdCl_2$, $CuCl_2$, or CuCl and 2.0 M HCl were studied using a dual column Varian Aerograph A-350-B gas chromatograph. The yields of CO_2 and N_2O are given in Table I. A molecular sieves 5A column was used to separate the reactants CO and NO and a column packed with Poropak Q was used to separate the products N_2O and CO_2.

Under conditions comparable with those previously employed, a 3-L sample of a CO-NO mixture over a stirred 10^{-2} M $PdCl_2$-0.20 M $CuCl_2$-2.0 M HCl (100 mL) solution resulted in conversion of CO to CO_2 at a more rapid rate than the Rh systems previously employed.[2a] No induction time was observed for formation of CO_2 and N_2O as was observed with the $RhCl_3$ and $RhCl_3$-HCl systems.[2a] The rate of N_2O formation was faster with the present $PdCl_2$-$CuCl_2$-HCl system than the rates previously reported for the $RhCl_3$ and $RhCl_3$-HCl systems, but slower than the system employing $Rh(CO)_2Cl_2^-$ catalyst.[2a] Experiments designed to elucidate aspects and significant species involved in the reaction are summarized in Table I.

Table I. Yield of Nitrous Oxide and Carbon Dioxide from Reaction of NO and CO at 25 °C[a]

Run	$PdCl_2$, M	Copper(II) or copper(I),[b] M	N_2O		CO_2, yield, %
			Torr	Yield, %	
1	0.010		152	76	88
2	0.010	0.20	140	75	100
3	0.100	0.20	151	80	100[c]
4	0.010	0.20	140	75	100[c]
5	10^{-3}	0.20	88	47	99[c]
6	10^{-4}	0.20	48	26	100[c]
7	10^{-3}	0.002	19	11	9.1
8	10^{-3}	0.020	41	23	29.4
9	10^{-3}	0.200	94	50	90
10	10^{-3}	0.600	47	25	100
11	10^{-3}	1.00	37	21	100
12	10^{-3}	2.00	23	13	100
13	10^{-3}	10^{-3} [b]	17	10	8.4
14	10^{-3}	0.010[b]	29	16	15.0
15	10^{-3}	0.100[b]	80	45	41
16	10^{-3}	1.00[b]	129	72	70

[a] Reaction time, 24 h. [b] Concentration of $CuCl_2^-$. [c] Reaction, 18 h.

Aqueous $PdCl_2$ (run 1) was shown to effect conversion of CO-NO to CO_2 and N_2O, but the rate of reaction was eventually decreased as metallic palladium was deposited. In the absence of CO there was negligible N_2O formation from the systems containing NO-$PdCl_2$-HCl and NO-$PdCl_2$-$CuCl_2$-HCl. Precipitation of palladium(0) can be obviated in the presence of $CuCl_2$-HCl (run 2) with formation of soluble $CuCl_2^-$ and oxidation of palladium(0). Conversion turnovers of up to 120 mol of N_2O/mol of palladium(II) were observed. The rate and yield of N_2O formation were increased with increasing palladium(II) concentration (runs 3-6). The rate of N_2O formation was first order with respect to partial pressure of NO, but the kinetic orders with respect to palladium(II) and copper(II) appear to be complex functions which are still under investigation. The yield of N_2O formation was unchanged with variation of HCl concentration at 4, 3, 2 and 1 M. At HCl concentrations lower than 1 M the rate of N_2O formation was greatly reduced with precipitation of CuCl and palladium(0). With H^+ maintained at 2 M (using $HClO_4$), the optimum yield of N_2O was obtained with 2.6 M Cl^-. The use of 0.20 M $CuBr_2$-2.0 M HBr gave a reduced N_2O yield (21%) compared with 47% obtained with the corresponding chloride solution. The N_2O yield was found to increase with increasing $CuCl_2$ concentration (0.002-0.200 M), but high concentrations of $CuCl_2$ gave lower yields of N_2O (runs 7-12). The typical Wacker conditions (0.03 M $PdCl_2$, 2.2 M $CuCl_2$, 3.3 M LiCl) gave lower N_2O yields than those shown in Table I. Solutions containing CuCl could be used instead of $CuCl_2$ and the yield of N_2O formation was enhanced by higher concentrations of $CuCl_2^-$ (run 13-16). The yield of N_2O (17%) from the reaction of NO with 0.20 M $CuCl_2^-$-2.0 M HCl, which was slightly less in the presence of CO, was increased to 55% for the reaction of NO with 1.0×10^{-3} M $PdCl_2$-0.20 M $CuCl_2^-$-2.0 M HCl. The presence of CO does not appreciably alter the rate of N_2O formation in the latter system.

The reactions leading to conversion of CO and NO to CO_2 and N_2O include

$$CO + Pd^{2+} + H_2O \rightarrow Pd^0 + CO_2 + 2H^+ \qquad (2)$$

$$Pd^0 + 2CuCl_2 \rightarrow Pd^{2+} + 2CuCl_2^- \qquad (3)$$

$$Pd^0 + 2NO + 2H^+ \rightarrow Pd^{2+} + N_2O + H_2O \qquad (4)$$