Homogeneous Catalyzed Reduction of Nitro Compounds. III. Synthesis of Aliphatic Amines

John F. Knifton

Beacon Research Laboratories, Texaco Inc., Beacon, New York 12508

Received September 16, 1974

Herein we describe the novel application of homogeneous catalysis to the selective hydrogenation of nitroalkanes to amines (eq 1), in good yields and conversions,

$$\begin{matrix} R' \\ \diagdown \\ \quad CH{-}NO_2 \\ \diagup \\ R \end{matrix} + 3H_2 \longrightarrow \begin{matrix} R' \\ \diagdown \\ \quad CH{-}NH_2 \\ \diagup \\ R \end{matrix} + 2H_2O \quad (1)$$

using a broadly defined class of ligand-stabilized ruthenium complexes. While the aim of this research has been to evaluate homogeneous catalysts for selective RNO_2 reduction,[1] in this work, particular attention has been given to tris(triphenylphosphine)ruthenium(II) chloride as a catalyst precursor, in view of (a) its proved activity for hydrogenation catalysis,[2] (b) its stability in basic media, where the formation of the more reactive nitroalkane anion should be favored,[3] and (c) the previous history of the iron-group metal complexes for catalyzing transformations of the C–NO_2 function.[4]

Nitroalkane hydrogenation catalyzed by solutions of $RuCl_2(PPh_3)_3$ has been demonstrated here in oxygen-free 1:1 benzene–ethanol mixtures (see Table I). Advantages of this technique over existing methods for reducing nitroalkanes *via* homogeneous catalysis[3,4] include the good (up to 88 mol %) yields of alkylamine obtained, with improved catalyst turnover, without the need for stringent reaction conditions or for an aqueous, acidic media which could result in competing Nef-type hydrolysis. In this work, no amine formation was detected in the absence of ruthenium complex; neither does reduction proceed in the absence of hydrogen (expt 6) even though primary alcohols are reportedly good hydrogen donors for the $RuCl_2(PPh_3)_3$ complex.[5] Preferred reaction conditions for the amine synthesis (50–150 atm of H_2, 90–130°, excess alkali) should in fact favor the formation of the intermediate hydrochlorotris(triphenylphosphine)ruthenium(II) complex[2] (eq 2), and this is

$$RuCl_2(PPh_3)_3 + H_2 + B: \rightleftharpoons RuHCl(PPh_3)_3 + B{\cdot}HCl \quad (2)$$

consistent with the observed similar hydrogenation rates for $RuHCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ (expt 9 and 10), induction periods prior to hydrogenation with $RuCl_2(PPh_3)_3$, and the spectra of recovered catalyst samples (ν(Ru–H) 2020 cm^{-1}). Basic reaction conditions should also favor deprotonation of the nitroalkane to its anionic form,[3] by shifting the equilibrium of eq 3 further to the right. The

$$RR'CHNO_2 + B: \rightleftharpoons (RR'CNO_2)^- + BH^+ \quad (3)$$

formation of this anion has been confirmed spectroscopically.[1a] Here the effect of added alkali and triethylamine is seen primarily to improve catalyst selectivity and amine yields, rather than to increase the rate of hydrogenation (expt 2, 8, and 9). The addition of pyridine leads to catalyst deactivation,[2] as does the presence of the strongly coordinating CO molecule (expt 7 and 15).

The suggested mechanism for nitroalkane hydrogenation to amine (eq 4–6) contains several points in common with

$$RuHCl(PPh_3)_3 \rightleftharpoons RuHCl(PPh_3)_2 + PPh_3 \quad (4)$$

$$RuHCl(PPh_3)_2 + (RR'CNO_2)^- \longrightarrow RuCl(PPh)_2(RR'CNO) + OH^- \quad (5)$$

$$RuCl(PPh_3)_2(RR'CNO) + 3H_2 \longrightarrow RuHCl(PPh_3)_2 + RR'CHNH_2 + H_2O \quad (6)$$

that proposed earlier for alkene hydrogenation.[6] Initial dissociation of $RuHCl(PPh_3)_3$ to give the *trans*-hydrochlorobis(triphenylphosphine)ruthenium(II) complex[6,7] is consistent with the observed inhibition by excess triphenyl-

Table I
Hydrogenation of Nitrododecane[a,b]

Expt	Complex	Added base	Mole ratio of $C_{12}H_{25}NO_2$:(Ru, Fe):base	H_2 pressure, atm	$C_{12}H_{25}NH_2$ yield,[c] mol %	Rel rate[d]
1	$RuCl_2(PPh_3)_3$	KOH	100:1:200	90	54	
2	$RuCl_2(PPh_3)_3$	KOH	10:1:20	90	88	1–1.5
3	$RuCl_2(PPh_3)_3$	KOH	3:1:6	90	81	
4	$RuCl_2(PPh_3)_3$	KOH	3:1:6	34	59	
5	$RuCl_2(PPh_3)_3$	KOH	3:1:6	1	<5	
6	$RuCl_2(PPh_3)_3$	KOH	10:1:20	0[e]	<1	
7	$RuCl_2(PPh_3)_3$	C_5H_5N	3:1:20	90	33	
8	$RuCl_2(PPh_3)_3$	Et_3N	10:1:20	90	83	0.90
9	$RuCl_2(PPh_3)_3$	None	10:1	90	57	1.00
10	$RuHCl(PPh_3)_3$	None	10:1	90	60	0.95
11	$RuCl_3(AsPh_3)_2$	None	10:1	90	79	2.1
12	$RuCl_2(SbPh_3)_3$	None	10:1	90	77	2.9
13	$RuCl_2(diphos)_2$[g]	None	10:1	90	57	1.1
14	$RuCl_2(PPh_3)_3 + 2PPh_3$	None	10:1	90	1.7	<0.1
15	$RuCl_2(CO)_2(PPh_3)_2$	KOH	10:1:20	90	23	
16	$Ru(CO)_3Cl_2$	KOH	10:1:20	90	67[f]	
17	$Fe(CO)_5$	KOH	1:1:2	90	67[f]	
18	$Fe(CO)_3(PPh_3)_2$	KOH	2:1:4	90	16	

[a] A mixture of isomers 2- through 6-nitrododecanes. [b] Run conditions: 0.001–0.02 *M* Ru, 120°, 1–6 hr. [c] $C_{12}H_{25}NH_2$ yield data refer to maximum dodecylamine yields, based upon nitrododecane charged, for reaction times up to 6 hr. The data were estimated by both ir and glpc techniques. [d] Relative rate data are based upon the maximum observed rates of nitrododecane reduction for each experiment, as determined by glpc, with expt 9 as the base (reference) case. [e] Run under N_2 (68 atm). [f] Extensive precipitation of ruthenium or iron complex. [g] diphos, = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

phosphine (expt 14) and increasing rate with decreasing ligand strength[8] (expt 9, 11, and 12) in the order PPh_3 < $AsPh_3$ < $SbPh_3$. However, related hydridoruthenium complexes[9] may also be involved here, and recovered catalyst samples often contain ruthenium carbonyl species (ν(C≡O) 1950 cm^{-1}) as a result of ethanol decarbonylation.[6] Samples may also show new maxima at 1580 cm^{-1} assignable to NO_2 vibrations of the coordinated $RR'CNO_2^-$ anion.[10] The dependence of the hydrogenation rate upon applied H_2 pressure and substrate concentration indicates (6) to include the rate-determining step. Deoxygenation of the coordinated nitroalkane anion[1b] (eq 5) might proceed *via* a nitrene-like intermediate,[4] but this seems unlikely in view of the lack of evidence for coupling products. A more detailed examination of C–NO_2 reduction by solubilized ruthenium complexes, embodying both selective and sequential hydrogenation, has been found possible with nitroaromatic substrates.[11]

A variety of ruthenium complexes with π-bonding ligands, capable of forming hydrido species of differing lability, have been screened and found active for hydrogenation of nitroalkanes[12] (expt 9–16). Bis(triphenylphosphine)iron tricarbonyl and iron pentacarbonyl both yielded some amine[4] but were generally less effective and showed lower stability in the alkali media.

Experimental Section

Hydrogenation (prepurified) was purchased from Matheson Co., dichlorotris(triphenylphosphine)ruthenium(II) was supplied by Strem Chemical Co., and other ruthenium complexes were prepared by published methods.[13] Nitrododecane (a mixture of 2 through 6 isomers) was synthesized by liquid–vapor phase nitration of *n*-dodecane.

Synthesis Procedure. A known weight of ruthenium complex (0.1–2 mmol) was dissolved, with stirring, in 100 ml of predried, N_2-saturated, equivolume benzene–ethanol, alkali metal hydroxide was added as required, and the mixture was heated to 120° in a glass-lined pressure reactor. Nitrododecane (1–100 mmol) was injected into the reaction mixture from a side ampoule, and the H_2 pressure was adjusted (1–90 atm). The course of the reduction may be monitored by withdrawing small (1–2 ml), clear liquid samples at regular time intervals and analyzing these by glpc or ir.

On cooling, the product liquid was concentrated under reduced pressure, and the amine product was isolated by solvent extraction. Dodecylamines were identified by ir, nmr, elemental analyses, and comparison with authentic samples.

Acknowledgment. The author thanks Texaco Inc. for permission to publish this paper and T. S. Strother for experimental assistance.

Registry No.—2-Nitrododecane, 53119-34-9; 3-nitrododecane, 53608-64-3; 4-nitrododecane, 53608-65-4; 5-nitrododecane, 53608-66-5; 6-nitrododecane, 53199-35-0; 2-dodecylamine, 13865-46-8; 3-dodecylamine, 53608-67-6; 4-dodecylamine, 19031-73-3; 5-dodecylamine, 53608-68-7; 6-dodecylamine, 53608-69-8; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuHCl(PPh_3)_3$, 19631-00-6; $RuCl_3(AsPh_3)_2$, 41685-48-7; $RuCl_2(SbPh_3)_3$, 15709-80-5; $RuCl_2$(diphos)$_2$, 53608-63-2; $RuCl_2(CO)_2(PPh_3)_2$, 14564-35-3; $[Ru(CO)_3Cl_2]_2$, 22594-69-0; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_3(PPh_3)_2$, 21255-52-7.

References and Notes

(1) Parts I and II: (a) J. F. Knifton, *J. Org. Chem.*, **38**, 3296 (1973); (b) J. F. Knifton, *J. Catal.*, **33**, 289 (1974).
(2) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).
(3) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N.Y., 1966, Chapter 14.
(4) See for example (a) F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970); (b) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965); (c) H. Alper, *Inorg. Chem.*, **11**, 976 (1972).
(5) Y. Sasson and J. Blum, *Tetrahedron Lett.*, 2167 (1971).
(6) B. R. James, *Inorg. Chim. Acta, Rev.*, **4**, 73 (1970).
(7) B. R. James and L. D. Markham, *Inorg. Chem.*, **13**, 97 (1974).
(8) G. Hendrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **10**, 105 (1971).
(9) T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970).
(10) A. G. Lee, *Spectrochim. Acta, Part A*, **28**, 133 (1972).
(11) J. F. Knifton and R. M. Suggitt, French Patent 2,127,970 (1972).
(12) J. F. Knifton, U.S. Patent 3,766,271 (1973).
(13) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

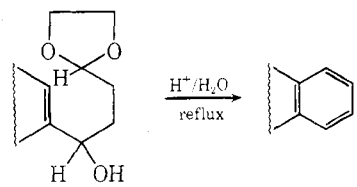
A Short Route to Functionalized Naphthalenes

Hubert J. J. Loozen

Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

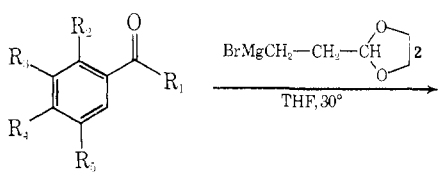
Received September 20, 1974

In recent work the synthesis of benzothiophenes and benzimidazoles from thiophenes and imidazoles, respectively, was presented.[1,2] Typical was the introduction of a suitably functionalized four-carbon atom fragment on the heterocyclic system, followed by acid-catalyzed formation of the benzene moiety as indicated below. This type of

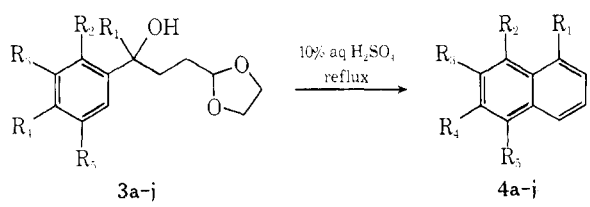


reaction seemed to be extendible to ring systems which are susceptible toward electrophilic substitution reactions.

This approach applied in the synthesis of naphthalenes proved to be successful. Reaction of the strongly activated 3,4,5-trimethoxybenzaldehyde (**1a**) with Grignard derivative **2**[3] gave alcohol **3a**, which upon treatment with refluxing 10% aqueous sulfuric acid for 1 hr afforded 2,3,4-trimethoxynaphthalene (**4a**) nearly quantitatively.[4]



1a–j



3a–j 4a–j

In the same way products **4b–f** were obtained in excellent yields. Naphthols **4g** and **h** could be obtained under the same conditions on allowing hydroxybenzaldehydes **1g** and **h** to react with 2 equiv of **2** and following this with cyclization. Formation of the less activated products **3i** and **j** leading to 2-methylnaphthalene and naphthalene required prolonged reaction times (6 and 16 hr, respectively). It should be mentioned that in the cases where cyclization could take place at two different positions (**3c, 3e, 3f, 3h,** and **3i**) more than 90% regiospecificity was observed, leading to the least hindered products.

A particular case is presented by the synthesis of naphthol **6.** Treatment of **3a** with manganese dioxide[5] in refluxing benzene gave ketone **5.** Under the assumption that the deactivation of the keto group on the benzene ring was