# *Communications*

## Reduction of Organic Compounds with Solutions of Ytterbium in Liquid Ammonia[1]

Summary: A solution of ytterbium in liquid ammonia reduces aromatic systems to 1,4-dihydroaromatics, α,β-unsaturated ketones to saturated ketones, and alkynes to trans alkenes.

Sir: Solutions of alkali metals and certain alkaline earths in liquid ammonia are widely employed for the reduction of a variety of organic functional groups.[2] The efficiency of the process can be attributed to the large reducing potential of these metals and to the effectiveness of ammonia as a supporting medium for electron transfer.[3] The lanthanide metals are also strongly electropositive, and consideration of the physicochemical characteristics of ytterbium ($4f^{14}6s^2$) in particular suggested that it should possess reducing properties similar to those of lithium and sodium by virtue of the transformation shown in eq 1.[4]

$$Yb^0 + NH_3 \rightarrow Yb^{2+} + 2e^-(NH_3)_n \qquad (1)$$
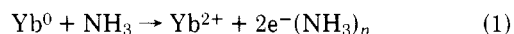
It has been shown that ytterbium dissolves in liquid ammonia to yield a blue solution containing the ammoniated electron.[5] This solution which, at high concentration, takes on a bronze luster similar to that observed with lithium–ammonia, is stable for several hours at -33 °C. We now report that the ytterbium–ammonia system is a powerful reducing agent, effective toward aromatic nuclei, α,β-unsaturated ketones, and alkynes.

Addition of an aromatic compound dissolved in a 10:1 mixture of THF–*tert*-butyl alcohol to an ytterbium–ammonia solution, followed by an aqueous workup and removal of ytterbium salts,[6] results in a generally good yield of the 1,4-dihydroaromatic system (Table I).[7] As in the Birch reduction,[2] substituents exert a pronounced effect on the rate of reduction of aromatic rings with ytterbium–ammonia. Thus, benzoic acid is reduced instantaneously, whereas aromatic rings substituted with alkyl and alkoxy groups are reduced more slowly. Durene, which is reduced with difficulty using lithium–ammonia,[8] was recovered unchanged upon exposure to ytterbium–ammonia under the same conditions. Naphthalenes are reduced efficiently and, in the case of the 1,7-dimethoxy derivative, there is a clear preference for reduction of the benzenoid ring containing the β substituent[9] giving, after hydrolysis, the corresponding tetralone. Anthracenes are also reduced rapidly to their 9,10-dihydro derivatives; the parent hydrocarbon gave 11% further reduction to 1,4,9,10-tetrahydroanthracene.[10] The reduction of estrone methyl ether (1)

1, R_1, R_2 = O
3, R_1 = OH; R_2 = H

2, R_1, R_2 = O
4, R_1 = OH; R_2 = H
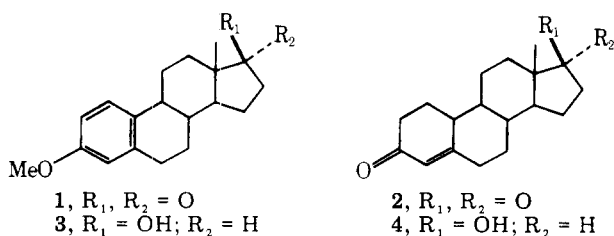
was complicated by the formation of pinacol-type dimeric products from reductive coupling at C-17 and, after acidic hydrolysis, gave only 22% of nortestosterone (2).[11] A 25% yield of estradiol methyl ether (3) was also produced. In contrast, treatment of 3, prepared by reduction of 1 with lithium alu-

### Table I. Ytterbium–Ammonia Reduction of Aromatic Compounds, α,β-Unsaturated Ketones, and Alkynes

compd	reaction time, h	product (% yield)
anisole	2.5	1-methoxy-1,4-cyclohexadiene (80)[a]
p-cresyl methyl ether	2.0	1-methoxy-4-methyl-1,4-cyclohexadiene (64)
benzoic acid	0.5	1,4-dihydrobenzoic acid (56)
durene	8.5	none[b]
naphthalene	8.0	1,4,5,8-tetrahydronaphthalene (88)
1,7-dimethoxynaphthalene	0.75	8-methoxy-β-tetralone (80)[c]
anthracene	0.5	9,10-dihydroanthracene (64)
9,10-dimethylanthracene	1.25	9,10-dihydro-9,10-dimethylanthracene (94)[d]
mesityl oxide		4-methylpentan-2-one (40)[a]
trans-4-phenyl-3-buten-2-one	0.3	4-phenylbutan-2-one (58)[a]
3-methyl-2-cyclopentenone	0.3	3-methylcyclopentanone (23)[a]
1-acetylcyclohexene	0.3	acetylcyclohexane (48)[a]
1-acetyl-2,6,6-trimethylcyclohexene	0.75	1-acetyl-2,6,6-trimethylcyclohexane (81)[e]
diphenylacetylene	0.5	*trans*-stilbene (75)
4-octyne	0.5	*trans*-4-octene (85)[a]
1-phenylpentyne	0.5	phenylpentane (67)[a,f]

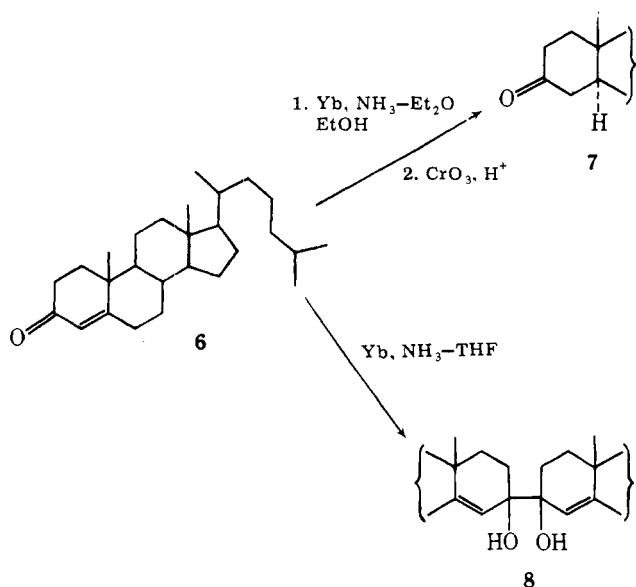[a] Yield determined by GLC using an internal standard. [b] Starting material was recovered quantitatively. [c] Product isolated after hydrolysis with aqueous NH_4Cl. [d] Determined by NMR to be a 1:1 mixture of cis–trans isomers [A. H. Beckett and R. G. Lingard, *J. Chem. Soc.*, 209 (1959)]. [e] Obtained as a mixture of cis and trans isomers in the ratio 12:88. [f] 1-Phenylpentyne (16%) was also obtained (2 equiv of ytterbium used).

minum hydride, with a tenfold molar excess of ytterbium in the absence of a proton donor, afforded a 52% yield of dihydrotestosterone 4.[12]

Solutions of ytterbium in ammonia are also effective in the reduction of α,β-unsaturated ketones (Table I). In this case, ether containing 1 molar equiv of *tert*-butyl alcohol as proton source is the preferred cosolvent and, under these conditions, a mixture of saturated ketone and the corresponding alcohol is invariably produced in a ratio dependent on both the substrate and the quantity of ytterbium. In the case of 4-phenylbutan-2-one, where a stabilized radical anion intermediate is generated, 10–20% of the β,β-coupled dimeric product 5 is

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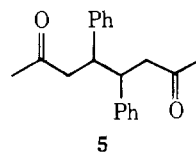
also formed. In order to facilitate isolation of the saturated ketone from the reduction medium, the crude reaction mixture was oxidized with Jones' reagent. Under these circumstances, yields compare favorably with those obtained by lithium–ammonia reduction of the same enones.[13] A more detailed study of the reduction of cholest-4-en-3-one (6) revealed that, whereas a 80% yield of cholestanone (7) was ob-

tained with ytterbium (in threefold excess) in ammonia containing alcohol (followed by oxidation with Jones' reagent),[14] the major product formed with THF as cosolvent and no proton source was the pinacol dimer **8**.[15] The presence of ytterbium enolates in these reductions is implied by the isolation of saturated ketones prior to oxidation and by analogy with lithium–ammonia reduction of similar systems.[13,16] It appears that ytterbium enolates, like their alkali metal counterparts, are stable in liquid ammonia and are appreciably less basic. However, an attempt to alkylate the ytterbium enolate from **6** with methyl iodide was not successful.[17]

Finally, the reduction of alkynes was demonstrated with diphenylacetylene and 4-octyne (THF cosolvent), affording the corresponding trans alkene (Table I). Interestingly, reduction of 1-phenylpentyne gave only a mixture of 1-phenylpentane and starting material, the proportions of which depended upon the quantity of ytterbium used. Apparently, certain double bonds can be saturated with this reagent,[18] a fact which was confirmed by the reduction of norbornadiene to bicyclo[2.2.1]heptene (eq 2) in 65% yield.[19]
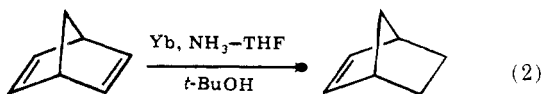
The ytterbium–ammonia system thus represents a useful reducing agent which resembles the analogous alkali metal solutions in potency. The ready availability of this lanthanide element,[20] in conjuction with its inertness to water and air (which necessitates no special precautions in its handling), and the fact that strongly basic hydroxides are avoided during workup, lends it certain advantages over the more reactive metals commonly used in electron-transfer chemistry.[21]

References and Notes

(1) Appropriately, 1978 marks the centenary of the discovery of ytterbium by Jean-Charles Galissard de Marignac at the University of Geneva; for an historical account see C. K. Jorgesen, *Chimia*, **32**, 89 (1978).
(2) A. J. Birch and G. Subba Rao in "Advances in Organic Chemistry, Methods and Results", Vol. 8, E. C. Taylor, Ed., Wiley Interscience, New York, N.Y., 1972, p 1.
(3) H. Smith "Organic Reactions in Liquid Ammonia", Interscience, New York, N.Y., 1963.
(4) The Yb²⁺ ion possesses the closed f shell electron configuration of Xe;

however, the divalent state is readily oxidized in air to Yb³⁺ ($E_{Yb^0 \to Yb^{3+}}$ is -2.27 V). The ionic radius of Yb²⁺ is intermediate between that of Li⁺ and Na⁺.

(5) S. Salot and J. C. Warf, *J. Am. Chem. Soc.*, **90**, 1932 (1968).
(6) The initial formation of Yb²⁺ in this process is indicated by a characteristic green color prior to workup. Addition of aqueous solutions results in the formation of a suspension of brown Yb³⁺ salts, which can be removed by filtration through Celite or may be dissolved in dilute mineral acid.
(7) All products, including those whose yields were determined by GLC, were characterized by means of their IR, NMR, and mass spectra and, where appropriate, by melting point. Comparisons with authentic samples were made where these were available, otherwise elemental composition was determined by exact mass measurement.
(8) Using a large excess of lithium and a 1:3 ratio of THF–NH₃ containing 3% *tert*-butyl alcohol, durene was reduced during 12 h to 1,2,4,5-tetramethylcyclohexa-1,4-diene in 72% yield (C. L. Kirkemo and J. D. White, unpublished observations).
(9) Cf. M. Kocor and W. K. Kotlarek, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, **19**, 219 (1971).
(10) R. G. Harvey and K. Urbery, *J. Org. Chem.*, **33**, 2570 (1968).
(11) B. J. Magerlein and J. A. Hogg, *J. Am. Chem. Soc.*, **80**, 2220 (1958).
(12) H. L. Dryden, G. M. Webber, R. L. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).
(13) D. Caine, *Org. React.*, **23**, 1 (1976).
(14) D. H. R. Barton, D. A. Ives, and B. R. Thomas. *J. Chem. Soc.*, 903 (1954).
(15) P. Bladon, J. W. Cornforth, and R. H. Jaeger. *J. Chem. Soc.*, 863 (1958).
(16) L. M. Jackman and B. C. Lange, *Tetrahedron*, **33**, 2737 (1977).
(17) See J. d'Angelo, *Tetrahedron*, **32**, 2979 (1976).
(18) G. W. Watt, *Chem. Rev.*, **46**, 325 (1950).
(19) B. R. Ortiz de Montellano, B. A. Loving, T. C. Shields, and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 3365 (1967).
(20) Ytterbium (99.9%, distilled) is available from Research Chemicals, P.O. Box 14588, Phoenix, Arizona 85063, at $0.90 per gram.
(21) This research was assisted financially by a grant (CHE77-04379) from the National Science Foundation.
(22) National Institutes of Health Research Career Development Awardee (1976–1981).
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Homoallyl–Cyclopropylcarbinyl Carbonium Ion Formation and Rearrangement under Strongly Basic Conditions

Summary: Treatment of the ethylene glycol ketal of 2,8-dibromocyclooctanone with sodium hydroxide produces the ethylene glycol ketal of 2,7-cyclooctadienone (71–76%) and a mixture of ethylene glyoxymethyl cyclohept-2-ene- and bicyclo[4.1.0]hept-7-ylorthocarboxylates (about 20%), indicating (in conjunction with the carbocation chemistry of the ethylene glycol ketal of 8-bromocyclooct-2-enone) that intermediate homoallyl–cyclopropylcarbinyl carbonium ions may be involved in the reactions leading to orthoester side products.

Sir: While the generation and reactions of carbonium ions in strongly acidic media are well documented,[1a] such is not the case for basic media.[1b,c] In this communication evidence is presented which implicates the novel formation and rearrangement of a homoallyl–cyclopropylcarbinyl carbonium ion system under *strongly alkaline conditions.*

The preparation of 2,7-cyclooctadienone is usually carried out according to the reaction sequence developed by Garbisch.[2] Cyclooctanone ethylene ketal (**1**) is treated with bromine to give (after recrystallization from methanol) *trans*-2,8-dibromocyclooctanone ethylene ketal (**2**), which is bisdehydrobrominated (with refluxing methanolic sodium hydroxide) to the diene ketal **3**, which in turn is hydrolyzed to **4**. It has now been discovered that there are interesting side reactions (apparently involving intermediate carbonium ions) which accompany the elimination reaction (**2 → 3**).