

A Simple and Convenient One Step Method for the Reductive Deoxygenation of Aryl Ketones to Hydrocarbons

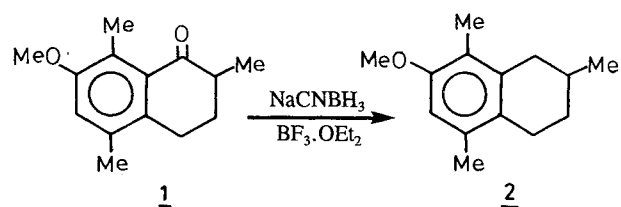
A. Srikrishna,* J. A. Sattigeri, R. Viswajanani and C. V. Yelamagga

Department of Organic Chemistry, Indian Institute of Science, Bangalore – 560 012, India.

Received 12 October 1994

Abstract: A one step, clean and efficient, conversion of arylaldehydes, ketones and ketals into the corresponding hydrocarbons using ionic hydrogenation conditions employing sodium cyanoborohydride in the presence of two to three equivalents of $\text{BF}_3 \cdot \text{OEt}_2$ is described.

Conversion of aryl ketones into the corresponding hydrocarbons is a frequently encountered reaction in organic synthesis. Among the relatively few direct one step methods available¹ for this transformation, the ionic hydrogenation² using trialkylsilanes in the presence of Bronsted or Lewis acids has a special place for its convenience and efficiency. In our search for finding an alternative to trialkylsilane in ionic hydrogenation reaction, we have discovered that sodium cyanoborohydride in the presence of boron trifluoride etherate reduces the aromatic aldehydes, ketones and ketals very cleanly and efficiently into the corresponding hydrocarbons.



Reaction of the tetralone **1**³ in the presence of three equivalents of $\text{BF}_3 \cdot \text{OEt}_2$ with sodium cyanoborohydride in dry THF at room temperature for four hours, cleanly furnished the tetralin **2**³ in 81% yield, whose structure was established from its spectral data. In an analogous manner various aryl aldehyde and ketones, **3–13** were reductively deoxygenated into the corresponding hydrocarbons **14–23**,⁴ using sodium cyanoborohydride in the presence of two to three equivalents of $\text{BF}_3 \cdot \text{OEt}_2$ in dry THF either at room temperature or at reflux temperature, and the results are summarised in table 1. All the reactions were clean and the structures of all the

TABLE 1.^a Reductive deoxygenation using NaCNBH_3 and $\text{BF}_3 \cdot \text{OEt}_2$

entry	Starting Material	Product	Temp. Time	Yield %	entry	Starting Material	Product	Temp./ Time	Yield %
(1)			RT/4 hr	81	(10)			65°C/5 hr	81 ^b
(2)			RT/12 hr	94	(11)			65°C/4 hr	95 ^b
(3)			RT/12 hr	71	(12)			65°C/12 hr	55 ^c
(4)			RT/1 hr	95	(13)			RT/3 hr	82
(5)			RT/8 hr	90	(14)			RT/3 hr	70
(6)			RT/1 hr	95	(15)			65°C/2 hr	90
(7)			65°C/18 hr	86 ^b	(16)			65°C/4 hr	74
(8)			65°C/8 hr	88 ^b	(17)		—	65°C/24 hr ^d	---
(9)			65°C/5 hr	84 ^b	(18)		—	65°C/24 hr ^d	---

(a) Yields (unoptimised) refer to isolated and chromatographically pure products. All the products exhibited spectral data consistent with their structures. (b) Only alcohols were obtained when the reaction was carried out at room temperature. (c) Low yield is probably due to the partial hydrolysis of the ester to acid. (d) No reaction was observed even with 5 equivalents of $\text{BF}_3 \cdot \text{OEt}_2$.

products were established from their spectral data. Mechanistically the reaction may be proceeding as in other ionic hydrogenation reactions, *via* the reduction of the carbocations. The intermediacy of carbocation is clearly revealed by the ease of the reaction with substrates containing electron donating groups at para position. The intermediacy of the corresponding benzylic alcohols (or equivalent) in the reaction is evident from the isolation of the corresponding benzylic alcohols when the reactions were carried out at room temperature instead of at reflux temperature with the ketones **8-11**. Reductive deoxygenation of the benzyl alcohol **24** to the hydrocarbon **25** employing the same procedure further established the intermediacy of benzyl alcohols in the reaction. Interestingly even the corresponding acetate **26** was cleanly transformed into the hydrocarbon **25** using the present procedure. Reductive deoxygenation of the ketals **27** and **28** to the hydrocarbons **19** and **20** (entries 15 and 16) further extended the scope of this methodology. Even though, quite expectedly, the THP ether was cleaved to the corresponding phenol (entry 5), surprisingly the benzyl ether of phenol was found to be resistant to reductive cleavage (entry 6) under these conditions. Both esters as well as acids were found to be inert (entries 17 and 18) pointing to the chemoselectivity of the reaction conditions.

Typical experimental procedure: Sodium cyanoborohydride (120 mg, 2 mmol) was added to a magnetically stirred solution of 2,5,8-trimethyl-7-methoxy-1-tetralone³ (**1**, 220 mg, 1 mmol) and BF₃.OEt₂ (0.39 ml, 3 mmol) in dry THF (3 ml) and the reaction mixture was stirred at room temperature for 4 hr. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with ether (10 ml), washed with saturated aqueous NaHCO₃ solution followed by brine and dried over anhydrous Na₂SO₄. Evaporation of the solvent and purification of the residue over a silica gel (4 gm) column using hexane as eluent furnished 2,5,8-trimethyl-7-methoxy-tetralin³ (**2**, 165 mg, 81%) as an oil. IR (neat): ν_{\max} 1595, 1580, 1480, 1465, 1295, 1120, 835 cm⁻¹. ¹H NMR (90 MHz, CDCl₃): δ 6.65 (1 H, s, aromatic), 3.8 (3 H, s, O-CH₃), 2.5-2.7 (4 H, m, 2 x ArCH₂), 2.24 (3 H, s, C₅-CH₃), 2.1 (3 H, s, C₈-CH₃), 1.75-2.05

(3 H, m, H-2 and 3), 1.1 (3 H, d, J = 7.2 Hz, *sec*-CH₃); ¹³C NMR (67.5 MHz, CDCl₃): δ 155.8 (C-7), 137.4, 134.7, 128.2, 122.6 (C-8), 110.9 (C-6), 56.5 (O-CH₃), 37.2 (C-1, 32.0, 29.8, 27.6, 23.0 (C₅-CH₃), 20.7 (C₈-CH₃), 11.5 (C₂-CH₃).

In conclusion, we have discovered a convenient and efficient procedure for the reductive deoxygenation of aryl aldehydes, ketones and ketals using ionic hydrogenation conditions employing sodium cyanoborohydride as the reducing agent and BF₃.OEt₂ as the Lewis acid. Currently, we are investigating the suitability of this reagent combination for further synthetically important transformations.

ACKNOWLEDGEMENTS. We thank Prof. G.S. Krishna Rao for the generous gift of some aryl ketones. RV and JAS thank the U.G.C., New Delhi; and I.I.Sc. respectively for the award of research fellowships.

REFERENCES AND NOTES

1. Eisch, J.J.; Liu, Z.-R.; Boleslawski, M.P. *J. Org. Chem.*, **1992**, *57*, 2143 and references cited therein.
2. Smonou, I. *Tetrahedron Lett.*, **1994**, *35*, 2071; Olah, G.A.; Wang, Q.; Surya Prakash, G.K. *Synlett*, **1992**, 647; Orfanopoulos, M; Smonou, I. *Synth. Commun.*, **1988**, *18*, 833 and references cited therein.
3. Iyer, W.A.; Humber, L.G.; Taylor, W.I. *J. Chem. Soc.*, **1954**, 3505.
4. (a) *Dictionary of Organic Compounds*, 5th ed., Chapman & Hall, New York, 1982; (b) Aldrich Catalog of Fine Chemicals, Aldrich Chemical Company Inc.: Milwaukee, 1992-93; (c) Munavalli, S. *Bull. Soc. Chim., Fr.*, **1965**, 785; (d) Dubois, J.E.; Balon, D. *Nouv. J. Chim.*, **1981**, *5*, 33; (e) Dev, S.; Guha, P.C. *J. Ind. Chem. Soc.*, **1948**, *25*, 13; (f) Klimusheva, G.V.; Kravers, M.; Struchkov-Yu, T.; Yatsenko, L.P. *Opt. Spektrosk.*, **1982**, *52*, 576; CA: 97: 63413k (g) Bouquet, M.; Guy, A.; Lemaire, M.; Guette, J.P. *Synth. Commun.*, **1985**, *15*, 1153.