ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 603 (2000) 240–243

Journal of Organometallic Chemistry

Reaction of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes with sodium borohydride under microwave conditions

Joseph Akisanya, Timothy N. Danks *, Russell N. Garman

Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK

Received 20 January 2000; received in revised form 11 March 2000

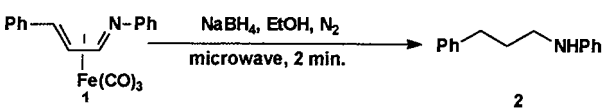
Abstract

Reaction of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes with sodium borohydride under microwave irradiation leads to formation of saturated secondary amines. When sodium borodeuteride is used for the reaction the products are 1,2,3-trideutero secondary amines. When this reaction is performed under thermal conditions the complexes are inert to reduction by sodium borohydride.

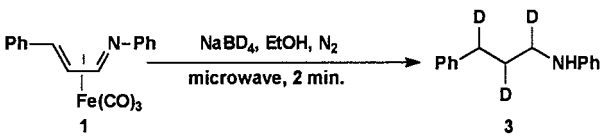
Keywords: (1-Azabuta-1,3-diene)tricarbonyliron(0); Reduction; Sodium borohydride; Microwave

1. Introduction

In recent years, the application of microwave irradiation for the promotion of organic reactions has received increasing attention. The technique has been used to assist in transfer hydrogenations [1] oxidations [2], aromatic substitutions [3], pericyclic reactions [4] and many other processes of significance to organic chemistry [5]. In addition, the technique has also found applications in the areas of inorganic and solid state synthesis [6]. The application of microwave irradiation to chemical reactions has been shown to significantly enhance the rate of these processes and in some cases has been used to promote reactions previously not observed under conventional thermal activation [7]. Our interest in the application of microwaves for the promotion of chemical reactions led us to investigate whether it was possible to replace the highly reactive reagent lithium aluminiumhydride with the less reactive sodium borohydride for reductions in which the latter reagent is ineffective.



Scheme 1.

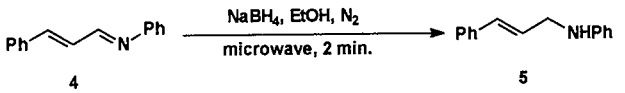


Scheme 2.

In past papers we described how tricarbonyliron(0) complexes of 1-azabuta-1,3-dienes and 1-oxabuta-1,3-dienes react with lithium aluminiumhydride to yield saturated amines and alcohols, respectively [8]. In these studies we demonstrated that the complexes were inert to reaction with sodium borohydride even when the reactions were performed at high temperatures for several hours [8]. We also illustrated that when lithium aluminiumdeuteride was used the reaction products contained three deuterium atoms in a 1,2,3-relationship [8]. In our search to find an alternative procedure to effect these reductions where it may be possible to use reagents other than lithium aluminiumhydride we decided to investigate the effect of microwave irradiation on the reaction between (1-azabuta-1,3-diene)tricarbonyliron(0) complexes and sodium borohydride.

* Corresponding author. Fax: +44-01483-876851.

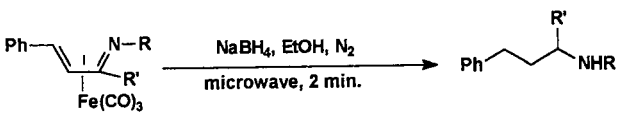
0022-328X/00/$ - see front matter
PII: S0022-328X(00)00194-7



Scheme 3.

Table 1
Reaction of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes with $NaBH_4$under microwave conditions

Entry	Complex	R	R′	Product	Yield (%)
1	**1**	Ph	H	2	90
2	**5**	Ph	CH_3	6	90
3	**7**	$Ph(CH_3)CH$	H	8	90
4	**9**	p-$CH_3OC_6H_4$	H	10	85
5	**11**	p-$CH_3OC_6H_4$	CH_3	12	70
6	**13**	$(CH_3)_2CH$	CH_3	14	0



Scheme 4.

2. Results and discussion

Initially the reaction between (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) (**1**) and sodium borohydride in ethanol was studied. A solution of complex **1** and sodium borohydride in ethanol was irradiated for 2 min in a domestic microwave oven [9] (500 W) to yield a dark mixture. Filtration of this mixture through alumina followed by removal of the solvent under reduced pressure lead to formation of a yellow oil identified as saturated amine on the basis of its spectroscopic and analytical date (Scheme 1).

When this reaction was carried out using sodium borodeuteride under identical conditions the reaction product obtained was confirmed as 1,2,3-trideutero secondary amine **3** from its ^{1}H-, ^{2}H-NMR and mass spectra [8]. Clearly, this result shows that the mechanism of the microwave-assisted reduction is likely to follow a similar reaction path to that carried out using lithium aluminiumhydride at 0°C (Scheme 2).

When the identical reaction was performed on the free 1-azabuta-1,3-diene **4** examination of the ^{1}H-NMR spectrum (300 MHz) of the product mixture indicated the presence of allylic amine **5** as the sole reaction product [10]. There was no evidence for the presence of saturated amine **2** in the product mixture even when the period of microwave irradiation was extended to 5 min. When the reaction times were extended to 10 min the reaction mixtures charred and failed to yield an identifiable product. Thus, it appears that, the application of microwaves for the reduction of these compounds cannot be used for their complete saturation (Scheme 3).

In order to explore the scope of this reaction a range of complexes bearing different substituents at nitrogen and C-2 of the coordinated 1-azabuta-1,3-diene were studied. The results from these experiments are summarised in Table 1 (Scheme 4).

In all cases when the substituent at nitrogen of the 1-azabuta-1,3-diene contains a phenyl group (Table 1 entries 1–5) the reaction results in formation of saturated amines. It is of interest however that when the substituent at nitrogen contained only an alkyl group (Table 1 entry 6**)** formation of saturated amines **14** was not observed and the reaction yields only starting complex **13**. In an attempt to promote a reaction between complex **13** and sodium borohydride the irradiation time was extended for period of up to 10 min. In each attempt the reaction resulted in charring and formation of unidentifiable products. When the reaction was attempted using lithium aluminiumhydride at 0°C for 3 h in accordance with previously reported conditions [8], reduction products were also not observed. It can be concluded therefore, that complex **13** is inert to reaction with hydride transfer reducing agents under thermal and microwave activation.

It has been shown that reaction of $LiAlH_4$ or $LiBEt_3H$ with (homodiene)tricarbonyliron(0) complexes leads to formation of anionic (η^3-allyl)tricarbonyliron complexes. This reaction has been shown to proceed via formation of an iron formyl intermediate. The possibility of the formation of iron formyl intermediates during the hydride transfer reduction of complexes **1** and **2** with sodium borohydride under microwave conditions cannot therefore be ignored [11].

By way of comparison the free 1-azabuta-1,3-dienes were also reacted with sodium borohydride under identical microwave conditions. In these cases the only products observed were allylic amines which resulted from 1,2-addition. In each example, there was no evidence for formation of the saturated amines even after prolonged (e.g. 5 min) microwave irradiation.

In conclusion, it has been shown that by the application of microwave irradiation sodium borohydride may be used in place of lithium aluminiumhydride for the reduction of tricarbonyliron(0) complexes of 1-azabuta-1,3-dienes. This not only allows a less hazardous reagent to be used but also considerably simplifies the 'work-up' procedure by allowing the reaction to be performed in the minimum quantity of solvent. It can also be concluded that the tricarbonyliron(0) moiety activates the 1-azabuta-1,3-diene to reduction by sodium borohydride under microwave conditions in a similar way to that previously reported for lithium aluminiumhydride at lower temperature [8]. It is of note however that the temperatures of these microwave reac-

tions could not be recorded, and it is therefore uncertain whether the activation of sodium borohydride is a result of rapid heating or a 'microwave effect'.

3. Experimental

Complexes **1** [12], **5**, **7** [13], **9** [14], **11**, and **13** [15] were synthesised by literature procedures. Melting points were recorded on a Kofler hot stage micro-melting-point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 300 instrument at 300 and 75.4 MHz, respectively. All chemical shifts are quoted in ppm relative to a tetramethylsilane standard. Chromatography was performed on Merck (40–63 μm) silica. Filtration through alumina was performed using deactivated Brockmann (grade iv) alumina. Elemental analyses was performed on a Leeman Laboratories CE 477 instrument.

3.1. Reaction of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) (**1**) with $NaBH_4$ under microwave conditions and the synthesis of N-phenyl-3-phenylproylamine (**2**)

A suspension of complex **1** (0.05 g, 0.14 mmol) and sodium borohydride (0.025 g, 0.65 mmol) in ethanol (0.05 ml) was irradiated at full power for 2 min in a 500 W domestic microwave oven. A saturated solution of sodium chloride (1 × 10 ml) was added and the organic fraction was extracted into diethyl ether (3 × 10 ml) and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure to leave yellow oil. This oil was identified as saturated amine **2** (0.03 g, 90%). B.p. 150–152°C at 1 mmHg. Found: m/z 211.1360. $C_{15}H_{17}N$ requires 211.1361. IR (cm^{-1}) (liquid film) ν_{max}: 3410 broad (NH). ^{1}H-NMR (300 MHz; $CDCl_3$): 1.91 (2H, m, $CH_2CH_2CH_2$), 2.21 (2H, t, J 9.0 Hz, $PhCH_2CH_2$), 3.12 (2H, t, J 9.0 Hz, $HNCH_2CH_2$), 3.40 (1H, broad, NH), and 6.50–7.50 (10H, m, 2 × aryl-H). ^{13}C-NMR: (100.6 MHz; $CDCl_3$), 30.8 (C-2), 33.1 (C-3), 43.1 (C-1), 112.51, 116.93, 125.70, 128.17, 128.98, 141.45, and 148.13 (aromatics); EIMS m/z: 211 [M^+, 27%], 106 [100, $M - PhCH_2CH_2$], and 91 [20, $M - 120$, C_7H_7].

3.2. N-Phenyl-4-phenyl-2-butylamine (**6**)

M.p. 140–142°C; (0.028 g, 90%). Found: C, 84.9; H, 8.5; N, 6.1. $C_{16}H_{19}N$ Calc. C, 85.3; H, 8.5; N, 6.2%. IR (cm^{-1}) (Nujol) ν_{max}: 3390 (NH). ^{1}H-NMR (300 MHz; $CDCl_3$): 1.95 (3H, d, J 7.0 Hz, CH_3CH), 1.89 (2H, m, CH_2CH_2CH), 2.75 (2H, t, J 8.0 Hz, $PhCH_2CH_2$), 3.54 (1H, br, NH), 3.55 (1H, m, $CHCH_3$) and 6.50–7.50 (10H, m, aryl-H). ^{13}C-NMR (75.4 MHz; $CDCl_3$): 20.69 (CH_3), 32.36 (C-2), 36.67 (C-1), 47.70 (C-3), 113.03, 116.79, 125.73, 128.24, 128.33, 129.17, 141.67, 147.43 (2 × Ph). EIMS: m/z 255 [M^+, 80%], 150 [100, $M - 105$] and 91 [75, C_7H_7].

3.3. N-(1-phenylethyl)-3-phenylpropylamine (**8**)

B.p. 150–152°C at 1 mmHg; (0.030 g, 90%). Found: C, 85.3; H, 8.7; N, 6.0. $C_{17}H_{21}N$. Calc. C, 85.3; H, 8.8; N, 5.9%. IR (cm^{-1}) (liquid film) ν_{max}: 3320m (NH). ^{1}H-NMR (300 MHz; $CDCl_3$): 1.37 (3H, d, J 7.0 Hz, CH_3CH), 1.58 (1H, broad, NH), 1.81 (2H, m, J 8.0 Hz, $CH_2CH_2CH_2$), 2.60 (4H, m, $PhCH_2CH_2CH_2$), 3.78 (1H, q, J 7.0 Hz, $CHCH_3$) and 7.10–7.50 (10H, m, 2 × aryl-H). ^{13}C-NMR (100.6 MHz $CDCl_3$): 24.16 (CH_3CH), 31.76 (C2), 33.35 (C3), 47.22 (C1), 58.19 ($CHCH_3$), 125.57, 126.43, 126.70, 128.15, 128.26, 142.08, and 145.67 (aromatics). EIMS: m/z 239 [M^+, 23%], 224 [62, $M–CH_3$] and 105 [100, $M - 134$, $CH(CH_3)Ph$].

3.4. N-(4-methoxyphenyl)-3-phenylpropylamine (**10**)

M.p. 45–46°C; (0.029 g, 85%). Found: C, 79.5; H, 8.0; N, 5.7. $C_{16}H_{19}NO$. Calc. C, 79.6; H, 7.9; N, 5.8%. IR (cm^{-1}) (Nujol) ν_{max}: 3410 (NH). ^{1}H-NMR (400 MHz; $CDCl_3$): 1.96 (2H, dt, J 7.0 and 7.5 Hz, $CH_2CH_2CH_2$), 2.75 (2H, t, J 7.5 Hz, $PhCH_2CH_2$), 3.12 (2H, t, J 7.0 Hz, CH_2CH_2NH), 3.35 (1H, m, NH), 3.76 (3H, s, OCH_3) and 6.50–7.40 (9H, m, 2 × aryl-H). ^{13}C-NMR (75.4 MHz; $CDCl_3$): 31.06 (C2), 33.31 (C3), 44.31 (C1), 55.69 (OCH_3), 113.94, 114.77, 123.78, 128.27, 141.61, 142.50 and 151.90 (aromatics). EIMS m/z 241 [M^+, 45%] and 136 [100, $M–PhCH_2CH_2CH$].

3.5. N-(4-methoxyphenyl)-4-phenyl-2-butylamine (**12**)

M.p. 140–141°C; (0.025 g, 70%). Found. C, 79.8, H, 8.3, N, 5.5; $C_{17}H_{21}NO$. Calc. C, 80.0; H, 8.3; N, 5.5%. IR (cm^{-1}) (Nujol) ν_{max}: 3395m (NH). ^{1}H-NMR (300 MHz; $CDCl_3$): 1.16 (3H, d, J 6.3 Hz, $CHCH_3$), 1.64–1.89 (2H, m, $PhCH_2CH_2CH$), 2.69 (2H, t, J 6.3 Hz, $PhCH_2$), 3.37 (1H, m, $CHCH_3$), 3.70 (3H, s, OCH_3), 6.46–7.28 (9H, m, 2 × Ph). ^{13}C-NMR: (75.4 MHz; $CDCl_3$): 20.75 ($CHCH_3$), 32.39 ($PhCH_2CH_2CH$), 38.72 ($PhCH_2$), 48.77 ($CHCH_3$), 55.66 (OCH_3), 114.62, 114.81, 125.72, 128.27, 128.34, 141.67, 141.99, 121.72 (2 × Ph). FABMS: m/z 255 [M^+, 100%], 150 [70, $M - 105$] and 91 [25, C_7H_7].

Acknowledgements

We thank the University of Surrey for financial support.

References

[1] (a) R.M. Gordon, D.C. Gaba, K.A. Jebber, D.M. Zacaharias, Organometallics 12 (1993) 5020. (b) A.K. Bose, B.K. Banik, K.J. Barakat, M.S. Manhas, Synlett (1993) 575.

[2] R. Gedye, F. Smith, K. Westaway, A. Humera, L. Baldisera, L. Laberge, J. Roussell, Tetrahedron Lett. 26 (1986) 279.

[3] (a) R. Laurent, A. Laporteire, J. Dubac, Organometallics 13 (1994) 2493. (b) Y. Yuncheng, G. Dabin, J. Yulin, Synth. Commun. 22 (1992) 2117.

[4] (a) R.J. Giguere, T.L. Bray, S.M. Duncan, S.M. Majetich, Tetrahedron Lett. 27 (1986) 4945. (b) A. Srikrishna, S. Nagaraju, J. Chem. Soc. Perkin Trans. 1 (1992) 311.

[5] (a) S. Caddick, Tetrahedron 50 (1994) 10403. (b) J. Hamelin, P. Jacquault, A. Loupy, D. Mathe, A. Petit,. F. Texier-Boullet, Synthesis (1998) 1213.

[6] (a) D.M.P. Mingos, Adv. Mater. 5 (1993) 857. (b) D.M.P. Mingos, A.G. Whittaker, J. Chem. Soc. Dalton Trans. (1995) 2073. (c) N. Hanson, P. Riby, J.R. Parsonage, Abs. Pap. Am. Chem. Soc. 209 (1995) 24. (d) D.R. Baghurst, J. Barrett, E.E. Coleyshaw, W.P. Griffith, D.M.P. Mingos, Mineralog. Mag. 60 (1996) 821. (e) R.E. Douthwaite, M.L.H. Green, M.J. Rosseinsky, Chem. Mater. 8 (1996) 394.

[7] M. Chastrette, M. Soufiaoui, A. Stambouli, Tetrahedron Lett. 32 (1991) 1723.

[8] (a) T.N. Danks, Tetrahedron Lett. 35 (1994) 4177. (b) T.N. Danks, J. Labelled Compd. Radiopharm. 36 (1995) 393.

[9] Many workers have demonstrated the use of domestic microwave ovens for the promotion of chemical reactions. See for example: A.K. Bose, B.K. Banik, M.S. Manhas, E.W. Robb, Res. Chem. Intermed. 20 (1994) 1.

[10] N. De Kimpe, E. Stanoeva, R. Verhel, N. Schamp, Synthesis (1988) 587.

[11] M. Brookhart, S. Chang, P.S. White, Organometallics 9 (1993) 3636.

[12] S. Otsuka, T. Yoshida, A. Nakamura, Inorg. Chem. 6 (1967) 20.

[13] T.N. Danks, S.E. Thomas, J. Chem. Soc. Perkin Trans. 1 (1990) 761.

[14] G. Bellachioma, G. Cardaci, J. Chem. Soc. Dalton Trans. (1976) 1735.

[15] M.J. Ackland, T.N. Danks, M.E. Howells, J. Chem. Soc. Perkin Trans. 1 (1998) 813.