

Deoxygenation of diarylmethanols with dilute mineral acid

Kyle A. Hope-Ross and John F. Kadla

Abstract: A new mild and efficient method for the deoxygenation of diarylmethanols is reported. The reaction employs catalytic hydrochloric acid in ethanol at reflux for 48 h. This reaction works on a variety of diarylmethanol substrates and mitigates the need for expensive and toxic reagents such as stannanes and silanes used in alternative procedures. In addition, this reaction can be used in tandem with the deprotection of acid-sensitive silyl ether protecting groups in a one-pot procedure.

Key words: deoxygenation, diarylmethanols, reduction, silyl ether deprotection.

Résumé : On rapporte une nouvelle méthode douce et efficace de désoxygénation des diarylméthanol. La réaction fait appel à une quantité catalytique d'acide chlorhydrique, dans l'éthanol au reflux, pendant 48 h. La réaction donne de bons résultats avec une variété de substrats diarylméthanol et elle atténue le besoin pour des réactifs toxiques et dispendieux, tels les stannanes et les silanes utilisés dans des méthodes alternatives. De plus, cette réaction peut être utilisée en tandem avec la déprotection d'éthers silylés sensibles aux acides utilisés comme groupes protecteurs dans des méthodes monotonnes.

Mots-clés : désoxygénation, diarylméthanol, réduction, déprotection d'éther silylé.

Introduction

Diarylmethane is a reoccurring structural motif in numerous natural products, including alangifolioside,¹ itoside K,² mastigophorene C,³ and terrestrols F–H⁴ (**2–4**, **5a–5c**, Fig. 1).

A possible synthetic route towards these natural products is the deoxygenation of diarylmethanols, which could be achieved in a number of ways, including the Grignard reaction.⁵ As such, the deoxygenation of secondary alcohols is an important transformation in synthetic organic chemistry. Unfortunately, few conditions for this transformation, which are both mild and widely applicable, have been reported.

Perhaps the most well-known example is the Barton–McCombie reaction, developed in 1975.⁶ In this reaction the alcohol is converted to a thiocarbonyl derivative that, upon treatment with tributylstannane and the radical initiator AIBN (azobisisobutyronitrile), affords the corresponding hydrocarbon.⁷ Unfortunately, this reaction involves the homolytic cleavage of the C–O bond, and because of the radical nature of the reaction, this somewhat limits the substrate scope. Additionally, the use of stoichiometric amounts of toxic heavy metals such as tin limits the industrial applications of such reactions.

More recently, variants of this reaction have been reported using silanes⁸ or dialkyl phosphites⁹ as hydrogen donors, and trialkyl boron–oxygen or peroxides as radical initiators.¹⁰

For the specific case of diarylmethanols (benzhydrols),

one reported deoxygenation involves treatment of the alcohol with triflic acid followed by triethyl silane.¹¹

Herein, we report a new mild and efficient deoxygenation of diaryl methanols to their corresponding diaryl methanes. This method uses dilute mineral acid in ethanol and proceeds without the use of silanes or toxic heavy metals. A variety of substrates were examined, and it was found that the reaction proceeds exclusively for diarylmethanols, but not for the other secondary alcohols examined.

Experimental

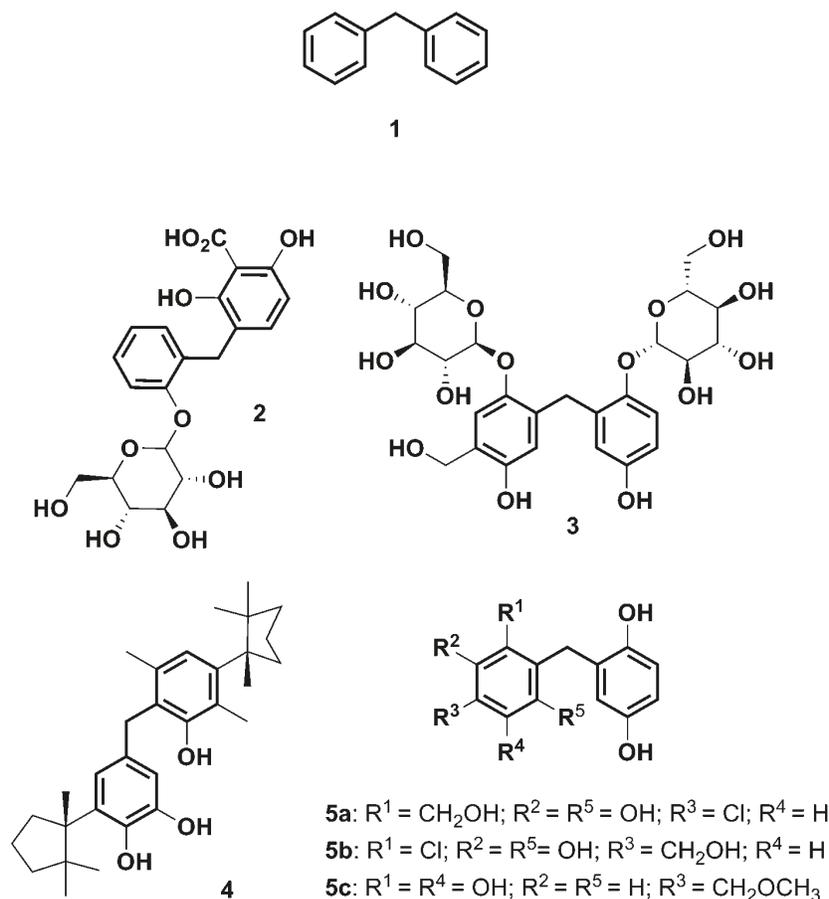
All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. Solvents were purchased from Fisher Scientific and used as received. All reactions were monitored by TLC, which was performed on Merck Alumafol 60 Å TLC plates with an UV indicator. Flash chromatography was performed on 60 Å, 70–230 mesh silica gel purchased from Fisher Scientific. ¹H and ¹³C NMR spectra were recorded using a 300 MHz Bruker Avance Ultrashield NMR spectrometer (300.13 and 75.03 MHz, respectively) and referenced to CDCl₃ (7.28 ppm). IR spectra were recorded using a PerkinElmer Spectrum One FT-IR spectrometer. Melting points were determined using a Mel-Temp melting point apparatus and are uncorrected. Boiling points were determined using differential scanning calorimetry (DSC) (TA Instruments Q1000) at 101.1 kPa according to ASTM E1782.¹²

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Fig. 1. Natural products containing the diarylmethane (**1**) moiety: alangifolioside (**2**), itoside K (**3**), mastigophorene C (**4**), and terrestrols F–H (**5a–5c**).



General procedure for the attempted deoxygenation of aryl methanols **6**, **7**, and **8**

To a solution of aryl methanol (0.50 g) in ethanol (50 mL) at 0 °C was added concentrated HCl (1.0 mL) as a solution in ethanol. The solutions were heated to reflux for 48–120 h, and the reactions were monitored by TLC (hexanes/ethyl acetate, 3:1). After cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO_3 (25 mL), mixed well, and extracted with CH_2Cl_2 (2 × 100 mL). The combined organics were washed with water (200 mL), dried over MgSO_4 , filtered, and solvent removed in vacuo to afford the starting materials quantitatively.

1-[4-(*tert*-Butyl-dimethylsiloxy)phenyl]ethanol (**7**) was prepared according to the literature.¹³ Yield: 1.38 g, 91%. ^1H NMR (300 MHz, CDCl_3) δ : 7.22 (d, $J = 8.20$ Hz, 2H), 6.80 (d, $J = 8.20$ Hz, 2H), 4.82 (m, 1H), 1.76 (s, 1H), 1.47 (d, $J = 6.28$, 3H), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.82, 138.35, 126.43, 119.86, 70.07, 25.81, 25.11, –4.21. ^1H NMR and ^{13}C NMR spectra are in agreement with those previously reported.¹³

4-(1-Hydroxyethyl)phenol (**8**)

To a solution of 1-[4-(*tert*-butyl-dimethylsiloxy)phenyl]ethanol (**7**, 0.50 g, 1.98 mmol) in ethanol (50 mL) at 0 °C was added concd. HCl (1.0 mL) as a solution in ethanol (9.0 mL). The reaction was heated to reflux for 48 h. After

cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO_3 (25 mL), added to water (150 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The combined organics were washed with water (200 mL), dried over MgSO_4 , filtered, and the solvent removed in vacuo. Crystallization from hexanes afforded **8** as a white powdery solid. Yield: 0.24 g, 90%; mp 136–139 °C (hexanes) (lit.¹³ 134–138 °C). ^1H NMR (300 MHz, CDCl_3) δ : 7.27 (d, $J = 8.28$ Hz, 2H), 6.82 (d, $J = 8.79$ Hz, 2H), 4.86 (q, $J = 6.37$ Hz, 1H), 4.82 (s, 1H), 1.72 (s, 1H), 1.53 (d, $J = 6.38$ Hz, 3H). ^1H NMR spectrum is in agreement with that previously reported.¹³

Diphenylmethanol (**10**)

To a solution of benzophenone (2.50 g, 13.72 mmol) in freshly distilled THF (50 mL) was added sodium borohydride (1.00 g, 27.44 mmol). The solution was heated to reflux for 18 h. After cooling to room temperature, the reaction mixture was poured into water (125 mL) and extracted with CH_2Cl_2 (2 × 200 mL). The combined organics were washed with water (200 mL), dried over MgSO_4 , filtered, and the solvent removed in vacuo to afford **10** as a white crystalline solid. Yield: 2.23 g, 88%; mp 65–68 °C (CH_2Cl_2) (lit.¹⁴ 65–66 °C). ^1H NMR (300 MHz, CDCl_3) δ : 7.43–7.26 (m, 10H), 5.87 (d, $J = 3.41$ Hz, 1H), 2.25 (d, $J = 3.49$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ : 143.81,

128.51, 127.59, 126.55, 76.29. ^1H NMR and ^{13}C NMR spectra are in agreement with those previously reported.¹⁴

Diphenylmethane (11)

To a solution of diphenylmethanol (**10**, 1.00 g, 5.43 mmol) in ethanol (50 mL) at 0 °C was added concd. HCl (1.0 mL) as a solution in ethanol (9.0 mL). The solution was heated to reflux for 72 h. After cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO_3 (25 mL) and water (100 mL) was added. The material was extracted with CH_2Cl_2 (2 \times 100 mL), washed with water (200 mL), dried over MgSO_4 , filtered, and the solvent removed in vacuo to afford a clear, colourless oil that crystallized on standing. Yield: 0.64 g, 72%; mp 24–26 °C (CH_2Cl_2) lit.¹⁵ 25–26 °C. ^1H NMR (300 MHz, CDCl_3) δ : 7.26–7.30 (m, 4H), 7.18–7.21 (m, 6H), 3.98 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ : 141.31, 129.07, 128.66, 126.29, 42.11. ^1H NMR and ^{13}C NMR spectra are in agreement with those previously reported.¹⁵

[4-(*tert*-Butyl-dimethylsilyloxy)phenyl]-4-(octyloxy)phenylmethanol (**12a**)

To a solution of 1-bromo-4-(octyloxy)benzene (1.46 g, 5.12 mmol) in freshly distilled THF (60 mL) at –78 °C under an Ar atmosphere was added *tert*-butyl lithium (6.02 mL of a 1.7 mol/L solution in pentane, 10.24 mmol) dropwise. After the mixture was allowed to stir for 1 h, a solution of 4-(*tert*-butyl-dimethylsilyloxy)benzaldehyde (1.21 g, 5.12 mmol) in freshly distilled THF (10 mL) was added dropwise. The solution was warmed to room temperature and stirred for 20 h. The reaction mixture was quenched with brine (10 mL) and extracted with a 50:50 mixture of ether/petroleum ether (3 \times 80 mL). The combined organic fractions were washed with water (3 \times 100 mL), dried over MgSO_4 , filtered, and the solvent removed in vacuo. Flash chromatography (ether/petroleum ether, 10:1) afforded **12a** as a clear, light orange oil. Yield: 1.33 g, 59%; bp 435 °C (determined from DSC). ^1H NMR (300 MHz, CDCl_3) δ : 7.28 (d, J = 8.34 Hz, 2H), 7.23 (d, J = 8.43 Hz, 2H), 6.87 (d, J = 8.63 Hz, 2H), 6.81 (d, J = 8.51 Hz, 2H), 5.77 (s, 1H); 3.96 (t, J = 6.51 Hz, 2H), 1.79 (quin., J = 6.80 Hz, 2H), 1.53–1.20 (m, 10H), 1.00 (s, 9H), 0.91 (m, 3H), 0.20 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.57, 155.01, 136.88, 136.10, 127.77, 127.70, 119.92, 114.37, 75.50, 68.03, 31.92, 29.66, 29.63, 29.60, 29.58, 29.40, 29.34, 29.28, 26.05, 25.67, 22.69, 18.18, 14.12, –4.42. Anal. calcd. for $\text{C}_{31}\text{H}_{50}\text{O}_3\text{Si}$: C, 74.73; H, 10.10. Found: C, 74.71; H, 9.96.

[4-(*tert*-Butyl-dimethylsilyloxy)phenyl]-4-(dodecyloxy)phenylmethanol (**12b**) was prepared in a method analogous to **12a**. Yield: 3.53 g, 56%; bp 443 °C (determined from DSC). ^1H NMR (300 MHz, CDCl_3) δ : 7.27 (m, 2H), 7.23 (d, J = 10.04 Hz, 2H), 6.87 (d, J = 8.16 Hz, 2H), 6.81 (d, J = 7.98 Hz, 2H), 5.77 (s, 1H), 3.95 (t, J = 6.33 Hz, 2H), 2.07 (s, 1H), 1.78 (quin., J = 7.02 Hz, 2H), 1.51–1.21 (m, 18H), 0.99 (s, 9H), 0.90 (t, J = 6.42 Hz, 3H), 0.20 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.57, 155.01, 136.88, 136.10, 127.77, 127.70, 119.92, 114.37, 75.50, 68.03, 31.92, 29.68, 29.64, 29.60, 29.58, 29.40, 29.35, 29.29, 26.05, 25.67, 22.70, 18.18, 14.12, –4.42. Anal. calcd. for $\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si}$: C, 73.25; H, 9.56. Found: C, 73.21; H, 9.46.

[4-(*tert*-Butyl-dimethylsilyloxy)phenyl]-4-(hexadecyloxy)phenylmethanol (**12c**) was prepared in a method analogous to **12a**. Yield: 3.54 g, 50%; bp 450 °C (determined from DSC). ^1H NMR (300 MHz, CDCl_3) δ : 7.27 (d, J = 8.21 Hz, 2H), 7.23 (d, J = 8.48 Hz, 2H), 6.87 (d, J = 8.67 Hz, 2H), 6.81 (d, J = 8.53 Hz, 2H), 5.77 (d, J = 3.39 Hz, 1H), 3.95 (t, J = 6.55 Hz, 2H), 2.07 (d, J = 3.58 Hz, 1H), 1.78 (quin., J = 6.89 Hz, 2H), 1.54–1.23 (m, 26H), 0.99 (s, 9H), 0.94–0.87 (m, 3H), 0.20 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.57, 155.01, 136.88, 136.10, 127.77, 127.70, 119.92, 114.37, 75.50, 68.03, 31.93, 29.69, 29.66, 29.60, 29.58, 29.40, 29.36, 29.29, 26.05, 25.67, 22.70, 18.19, 14.12, –4.42. Anal. calcd. for $\text{C}_{35}\text{H}_{58}\text{O}_3\text{Si}$: C, 75.75; H, 10.53. Found: C, 75.71; H, 10.46.

4-(4-(Octyloxy)benzyl)phenol (**13a**)

To a solution of [4-(*tert*-butyl-dimethylsilyloxy)phenyl]-4-(octyloxy)phenylmethanol (**12a**, 1.00 g, 2.26 mmol) in ethanol (50 mL) at 0 °C was added concd. HCl (1.0 mL) as a solution in ethanol (10 mL). The solution was heated to reflux for 48 h. After cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO_3 (25 mL), mixed well, and extracted with hexanes (3 \times 50 mL) and ether (50 mL). The combined organics were washed with water (200 mL), dried over MgSO_4 , filtered, and the solvent removed in vacuo. Crystallization from 5% ether in petroleum ether afforded **13a** as a white, powdery solid. Yield: 0.56 g, 79%; mp 70–73 °C (5% ether in petroleum ether). ^1H NMR (300 MHz, CDCl_3) δ : 7.07 (t, J = 8.22 Hz, 4H), 6.83 (d, J = 8.52 Hz, 2H), 6.76 (d, J = 8.42 Hz, 2H), 3.94 (t, J = 6.60 Hz, 2H), 3.86 (s, 2H), 1.78 (quin., J = 6.93 Hz, 2H), 1.52–1.21 (m, 10 H), 0.90 (t, J = 5.97 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 157.48, 153.75, 133.93, 133.45, 129.94, 129.70, 115.24, 114.50, 68.07, 40.13, 31.83, 29.37, 29.33, 29.25, 26.07, 22.66, 14.10. Anal. calcd. for $\text{C}_{21}\text{H}_{28}\text{O}_2$: C, 80.73; H, 9.03; O, 10.24. Found: C, 80.31; H, 9.02; O, 10.67.

4-(4-(Dodecyloxy)benzyl)phenol (**13b**) was prepared in a method analogous to **13a**. Yield: 0.50 g, 68%; mp 80–83 °C (5% ether in petroleum ether). ^1H NMR (300 MHz, CDCl_3) δ : 7.07 (t, J = 8.20 Hz, 4H), 6.83 (d, J = 8.59 Hz, 2H), 6.76 (d, J = 8.48 Hz, 2H), 3.94 (t, J = 6.54 Hz, 2H), 3.86 (s, 2H), 1.78 (quin., J = 6.52 Hz, 2H), 1.51–1.21 (m, 14 H), 0.90 (t, J = 6.51 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 157.48, 153.73, 133.95, 133.46, 129.94, 129.70, 115.25, 114.52, 68.09, 40.14, 31.93, 29.67, 29.64, 29.61, 29.59, 29.42, 29.35, 29.34, 26.07, 22.70, 14.12. Anal. calcd. for $\text{C}_{25}\text{H}_{36}\text{O}_2$: C, 81.47; H, 9.85; O, 8.68. Found: C, 81.40; H, 9.81; O, 8.79.

4-(4-(Hexadecyloxy)benzyl)phenol (**13c**) was prepared in a method analogous to **13a**. Yield: 0.60 g, 78%; mp 83–90 °C (5% ether in petroleum ether). ^1H NMR (300 MHz, CDCl_3) δ : 7.07 (t, J = 8.20 Hz, 4H), 6.80 (dd, J_1 = 8.66 Hz, J_2 = 2.00 Hz, 4H), 4.56 (s, 1H), 3.94 (t, J = 6.58 Hz, 2H), 3.86 (s, 2H), 1.78 (quin., J = 6.58 Hz, 2H), 1.37 (m, 26H); 0.90 (t, J = 6.58 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 157.5, 153.7, 134.0, 133.4, 129.9, 129.7, 115.2, 114.5, 68.0, 40.1, 31.9, 29.7 (3), 29.6 (4), 29.4 (3), 29.3, 26.1, 22.7, 14.1. Anal. calcd. for $\text{C}_{29}\text{H}_{44}\text{O}_2$: C, 82.02; H, 10.44; O, 7.53. Found: C, 82.05; H, 10.48; O, 7.47.

4-[Hydroxyl(4-(octyloxy)phenyl)methyl]phenol (**14a**)

To a solution of [4-(*tert*-butyl-dimethylsilyloxy)phenyl]-4-(octyloxy)phenylmethanol (**12a**, 2.50 g, 5.65 mmol) in freshly distilled THF (20 mL) at 0 °C was added a solution of tributyl ammonium fluoride trihydrate (TBAF, 3.57 g, 11.30 mmol) in freshly distilled THF (20 mL). The solution was allowed to stir for 1 h, warmed to room temperature, and then stirred for 2 h. The reaction mixture was poured into water (50 mL), mixed well, and then separated. The aqueous phase was extracted with a 50:50 mixture of ether/petroleum ether (2 × 100 mL), and the combined organics were washed with water (250 mL), dried over MgSO₄, filtered, and the solvent removed in vacuo. Crystallization from 5% ether in petroleum ether afforded **14a** as a white, powdery solid. Yield: 1.02 g, 55%; mp 81–86 °C (5% ether in petroleum ether). ¹H NMR (300 MHz, CDCl₃) δ: 7.27 (d, *J* = 8.44 Hz, 2H), 7.25 (d, *J* = 8.37 Hz, 2H), 6.87 (d, *J* = 8.71 Hz, 2H), 6.81 (d, *J* = 8.62 Hz, 2H), 5.78 (s, 1H), 4.77 (s, 1H), 3.95 (t, *J* = 6.57 Hz, 2H), 1.78 (quin., *J* = 6.57 Hz, 2H), 1.52–1.24 (m, 10H), 0.90 (t, *J* = 6.72 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 158.60, 154.86, 136.58, 136.05, 127.99, 127.72, 115.22, 114.42, 75.41, 68.05, 31.81, 29.35, 29.27, 29.23, 26.05, 22.65, 14.09. Anal. calcd. for C₂₁H₂₈O₃: C, 76.79; H, 8.59; O, 14.61. Found: C, 77.38; H, 7.80; O, 14.82.

4-[Hydroxy(4-(hexadecyloxy)phenyl)methyl]phenol (**14c**) was prepared in a method analogous to **14a**. Yield: 0.53 g, 50%; mp 95–101 °C (5% ether in petroleum ether). ¹H NMR (300 MHz, CDCl₃) δ: 7.28 (d, *J* = 8.11 Hz, 2H), 7.26 (d, *J* = 8.66 Hz, 2H), 6.87 (d, *J* = 8.49 Hz, 2H), 6.81 (d, *J* = 8.32 Hz, 2H), 5.78 (s, 1H), 4.69 (s, 1H), 3.95 (t, *J* = 6.51 Hz, 2H), 1.78 (quin., *J* = 6.53 Hz, 2H), 1.54–1.20 (m, 26H), 0.90 (t, *J* = 6.57 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 158.59, 154.84, 136.58, 136.05, 128.39, 127.92, 115.22, 114.46, 75.41, 68.07, 31.81, 29.35, 29.29, 29.25, 26.06, 22.66, 14.10. Anal. calcd. for C₂₉H₄₄O₃: C, 79.04; H, 10.06; O, 10.89. Found: C, 78.43; H, 10.47; O, 11.10.

4-(4-(Octyloxy)benzyl)phenol (**13a**)

To a solution of 4-[hydroxyl(4-(octyloxy)phenyl)methyl]phenol (**14a**, 0.20 g, 0.61 mmol) in ethanol (50 mL) °C was added concd. HCl (0.5 mL) as a solution in ethanol (9.5 mL). The solution was allowed to stir for 1 h and then heated to reflux for 48 h. After cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO₃ (25 mL), mixed well, and then extracted with petroleum ether (3 × 50 mL) and ether (50 mL). The combined organics were washed with water (200 mL), dried over MgSO₄, filtered, and the solvent removed in vacuo to afford 4-(4-(octyloxy)benzyl)phenol as a white powdery solid. Yield: 0.17 g, 90%; mp 70–73 °C (ether/petroleum ether). ¹H NMR (300 MHz, CDCl₃) δ: 7.07 (t, *J* = 8.22 Hz, 4H), 6.83 (d, *J* = 8.52 Hz, 2H), 6.76 (d, *J* = 8.42 Hz, 2H), 3.94 (t, *J* = 6.60 Hz, 2H), 3.86 (s, 2H), 1.78 (quin., *J* = 6.93 Hz, 2H), 1.52–1.21 (m, 10 H), 0.90 (t, *J* = 5.97 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.48, 153.75, 133.93, 133.45, 129.94, 129.70, 115.24, 114.50, 68.07, 40.13, 31.83, 29.37, 29.33, 29.25, 26.07, 22.66, 14.10. Anal. calcd. for C₂₁H₂₈O₂: C, 80.73; H, 9.03; O, 10.24. Found: C, 80.01; H, 9.46; O, 10.53.

4-(4-(Hexadecyloxy)benzyl)phenol (**13c**) was prepared in

a method analogous to 4-(4-(octyloxy)benzyl)phenol. Yield: 0.18 g, 79%; mp 83–90 °C (ether/petroleum ether). ¹H NMR (300 MHz, CDCl₃) δ: 7.07 (t, *J* = 8.20 Hz, 4H), 6.80 (dd, *J*₁ = 8.66 Hz, *J*₂ = 2.00 Hz, 4H), 4.56 (s, 1H), 3.94 (t, *J* = 6.58 Hz, 2H), 3.86 (s, 2H), 1.78 (quin., *J* = 6.58 Hz, 2H), 1.37 (m, 26H), 0.90 (t, *J* = 6.58 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.5, 153.7, 134.0, 133.4, 129.9, 129.7, 115.2, 114.5, 68.0, 40.1, 31.9, 29.7 (3), 29.6 (4), 29.4 (3), 29.3, 26.1, 22.7, 14.1. Anal. calcd. for C₂₉H₄₄O₂: C, 82.02; H, 10.44; O, 7.53. Found: C, 82.05; H, 10.48; O, 7.47.

Bis(4-(dodecyloxy)phenyl)methanol (**15**)

A solution of 4,4'-bis(dodecyloxy)benzophenone (0.30 g, 0.55 mmol) and sodium borohydride (0.046 g, 1.20 mmol) in ethanol (40 mL) was allowed to reflux for 1 h. After cooling to room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH₂Cl₂ (2 × 100 mL). The combined organics were washed with water (2 × 200 mL), dried over MgSO₄, filtered, and the solvent removed in vacuo. Crystallization from hexanes afforded **15** as a white powdery solid. Yield: 0.23 g, 76%; mp 37–39 °C (hexanes). ¹H NMR (300 MHz, CDCl₃) δ: 7.28 (d, *J* = 8.55 Hz, 4H), 6.88 (d, *J* = 8.55 Hz, 4H), 5.78 (d, *J* = 3.40 Hz, 1H), 3.95 (t, *J* = 6.58 Hz, 4H), 2.06 (d, *J* = 3.40 Hz, 1H), 1.78 (quin. *J* = 6.58 Hz, 4H), 1.52–1.19 (m, 36 H); 0.90 (t, *J* = 6.58 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ: 158.55, 136.16, 127.71, 114.39, 75.46, 68.04, 31.92, 29.66, 29.63, 29.60, 29.58, 29.40, 29.35, 29.28, 26.05, 22.69, 14.12. Anal. calcd. for C₃₇H₆₁O₃: C, 80.23; H, 11.10; O, 8.67. Found: C, 80.31; H, 11.03; O, 8.66.

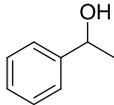
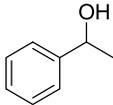
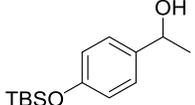
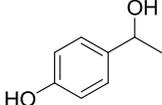
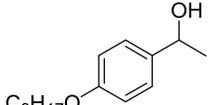
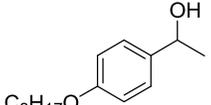
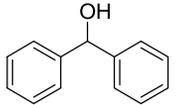
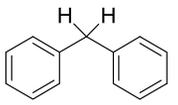
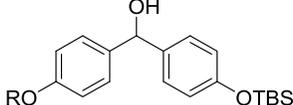
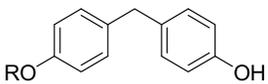
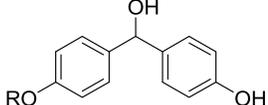
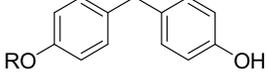
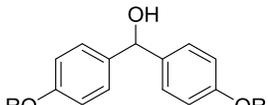
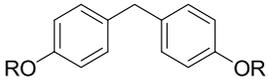
Bis(4-(dodecyloxy)phenyl)methane (**16**)

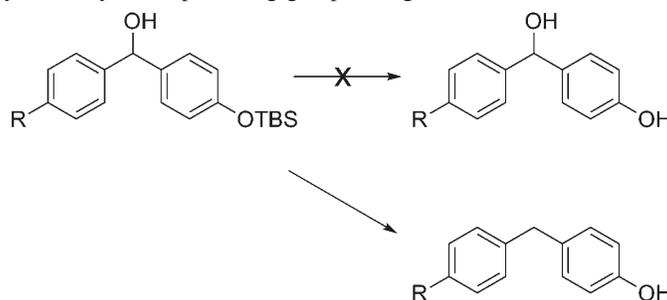
To a solution of bis(4-(dodecyloxy)phenyl)methanol (**15**, 0.25 g, 0.45 mmol) in ethanol (50 mL) at reflux was added a solution of concd. HCl (0.5 mL) in ethanol (9.5 mL). The solution was allowed to reflux for 48 h. After cooling to room temperature, the reaction mixture was poured into a saturated solution of NaHCO₃ (25 mL) and mixed well. Water (100 mL) was added and the mixture was extracted with petroleum ether (150 mL) and ether (100 mL). The combined organics were washed with water (200 mL), dried over MgSO₄, filtered, and the solvent removed in vacuo to afford bis(4-(dodecyloxy)phenyl)methane as a waxy white solid. Yield: 0.20 g, 83%; mp 30–33 °C (petroleum ether/ether). ¹H NMR (300 MHz, CDCl₃) δ: 7.08 (d, *J* = 8.59 Hz, 4H), 6.83 (d, *J* = 8.59 Hz, 4H), 3.94 (t, *J* = 6.57 Hz, 4H), 3.87 (s, 2H), 1.78 (quin., *J* = 6.56 Hz, 4H), 1.51–1.22 (m, 36H), 0.91 (t, *J* = 6.57 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.46, 133.54, 129.68, 114.44, 68.02, 40.14, 31.92, 29.66, 29.63, 29.60, 29.59, 29.41, 29.34, 29.33, 26.07, 22.69, 14.12. Anal. calcd. for C₃₇H₆₁O₂: C, 82.62; H, 11.43; O, 5.95. Found: C, 82.65; H, 11.48; O, 5.87.

Results and discussion

In our efforts towards the acidic hydrolysis of silyl ether protecting groups,¹⁶ we discovered an unexpected result: in addition to cleavage of the silicon–oxygen bond, we also observed deoxygenation of the diarylmethanol (Scheme 1).

Table 1. Deoxygenation of secondary alcohols using HCl/EtOH.

Entry	Reactant	Time (h)	Yield (%)	Product	
6		96	NR ^a	6 	
7		48	90	8 	
9		120	NR	9 	
10		48	72	11 	
12a		R = C ₈ H ₁₇	48	79	13a 
12b		R = C ₁₂ H ₂₅	48	68	
12c		R = C ₁₆ H ₃₃	48	78	
14a		R = C ₈ H ₁₇	48	90	13a 
14c		R = C ₁₆ H ₃₃	48	79	
15		R = C ₁₂ H ₂₅	48	83	16 

^a NR: no reaction**Scheme 1.** Attempted acidic hydrolysis of silyl ether protecting groups. Reagents and conditions: HCl, EtOH, reflux 48 h.

To further probe the generality of this reaction, we tested a number of substrates including secondary alcohols and diarylmethanols with different substitution patterns, with and without silyl ether protecting groups. Table 1 outlines the substrates examined and the results, including reaction time and yield. It was found that the reaction does not proceed for primary alcohols or secondary alcohols not bearing two aryl functionalities, nor was the presence of the silyl protect-

ing group required. The reaction proceeds in good yields (68%–90%) for substrates displaying a variety of substitution patterns.

Conclusions

A new mild and efficient method for the deoxygenation of diarylmethanols has been developed. This reaction mitigates

the need to use radical conditions or toxic heavy metals employed in the Barton–McCombie deoxygenation.

Acknowledgements

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