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A New Free Radical Route To Oximes Using Alkyl Halides, Hexabutylditin and Readily Available Nitrite Esters

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Abstract: Reaction of alkyl radicals (generated from alkyl iodides or benzyl bromides with hexabutylditin) in the presence of alkyl nitrites affords oximes as products in good yields.
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The free radical chemistry of nitrite esters came to the fore as a result of two reactions. The Barton nitrite ester reaction[1] was a landmark not only in the development of free radicals as valuable intermediates in synthetic chemistry but also in allowing the functionalisation of remote and unactivated positions within steroids. The rigidity of the steroid nucleus permitted efficient hydrogen atom transfer in many cases from an axial methyl group to the intermediate oxyl radical, formed on photolysis of the nitrite ester. The second and related reaction involved the photolysis of nitrite esters of γ,δ-unsaturated alcohols[2]. These were valuable starting reagents for the formation of oximes following cyclisation of the oxyl radical onto the alkene. Currently, there is a renewed interest in nitrite esters and related derivatives as potential vectors of nitric oxide[3] in biological systems. However, the availablility of nitrite esters makes them attractive reagents for expanding the general repertoire of synthetic reactions.

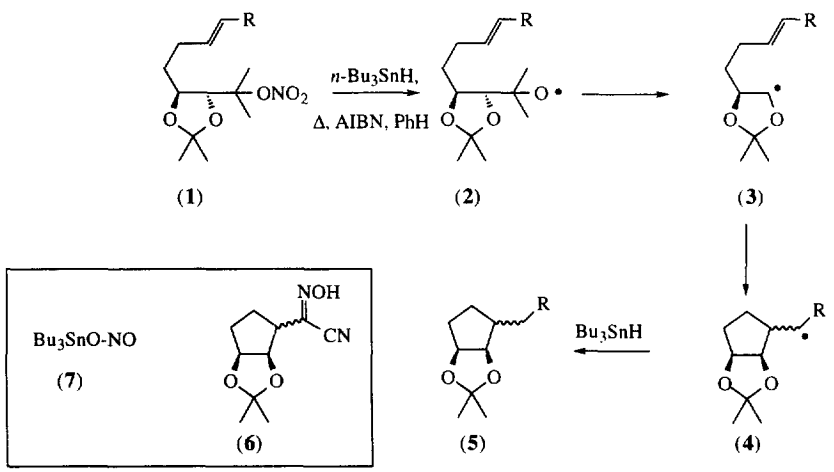


Figure 1

To contrast with nitrite esters, nitrate esters[4] have been long used as protecting groups in sugar chemistry. Nitrate esters are robust and easily formed, and the apparent harsh conditions for their formation are in fact compatible with sensitive functional groups. They can be removed with tributyltin hydride/AIBN[5] or by

photochemical means[4]. It has become apparent that nitrite esters also contrast with nitrate esters in another important way: the products of reaction of nitrate esters do not incorporate nitrogen oxide units into the product. In many cases, this is a positive advantage, and caused us to adopt nitrate esters for a number of our projects[6,7]. One of these involved studies[6] on the reaction of alkyl nitrates (**1**) with tri-n-butyltin hydride (Figure 1); the intermediate oxyl radicals (**2**) fragmented to afford the dioxolanyl radicals (**3**) which cyclised efficiently ultimately affording the products (**5**). However, one substrate (**1**, R=CN), behaved anomalously giving not only the expected nitrile products (**5**, R=CN), but also a minor product, oxime (**6**) in 6% yield, as a pair of geometric isomers. Pondering the origin of this product has now led to development of a new route to oximes[8].

One possible explanation for the formation of (**6**) involved tri-n-butyltin nitrite (**7**), formed during the tributyltin radical-induced nitrate ester decomposition. The proposed reaction sequence for nitrate ester decomposition under these thermal conditions is shown below:

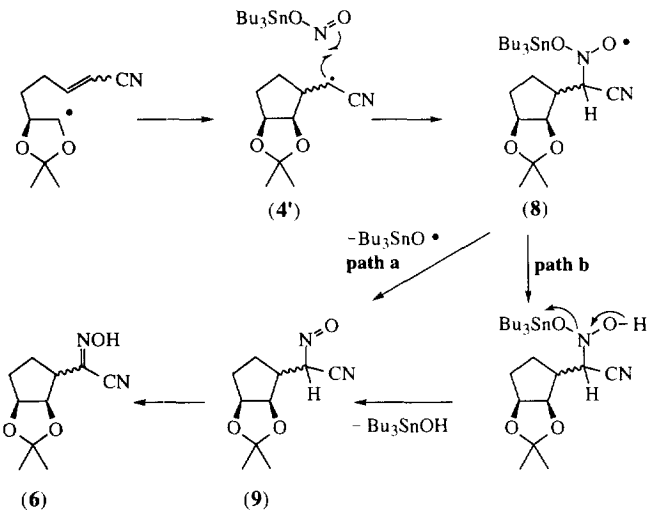


Figure 2

In the reaction of (**1**, R=CN), the oxime (**6**) could arise from the trapping of intermediate radical (**4'**) by NO (itself formed by the thermal decomposition of tributyltin nitrite[9]). However, it is also possible that the cyanomethyl radical (**4'**), reacts directly with tributyltin nitrite (Figure 2) giving radical (**8**). This intermediate could break down to the nitroso compound (**9**) either by a homolytic route (Figure 2, path a) or, following hydrogen atom abstraction, by heterolytic means (Figure 2, path b). It is reasonable that nitrite esters (RONO) should react well with carbon-centred radicals in view of the excellent trapping properties of nitroso compounds (R-NO).

To test this proposed sequence of events *tert*-butyl nitrate (**10**) was prepared from *tert*-butyl alcohol and reacted with tri-n-butyltin hydride and AIBN so as to give tributyltin nitrite (**11**) (Figure 3). This unpurified product was then irradiated together with benzyl bromide and hexabutylditin using a Philips Ultrafil lamp (300W) for 3 hours. The product from this reaction was benzaldoxime (**12**) (63%). In this case, the photolysis cleaves hexabutylditin to form tributyltin radicals which react in the normal way with the benzyl bromide to afford benzyl radicals, trapping of which leads to the oxime.

To assess whether tributyltin nitrite (**7**) was a special case, the photochemical reaction was repeated using the more readily available *iso*amyl nitrite. Thus, benzyl bromide, isoamyl nitrite and hexabutylditin were irradiated

with a Philips Ultrafil lamp for 4 h. After purification benzaldoxime (**12**) was isolated in an excellent 84% yield, showing that simple nitrite esters function very well in this reaction. Similarly, irradiation of cyclohexyl iodide with isoamyl nitrite and hexabutylditin resulted in cyclohexanone oxime (**13**) (71%). However, when cyclohexyl bromide was substituted for cyclohexyl iodide under the same conditions no oxime product was obtained, only cyclohexyl bromide being recovered.

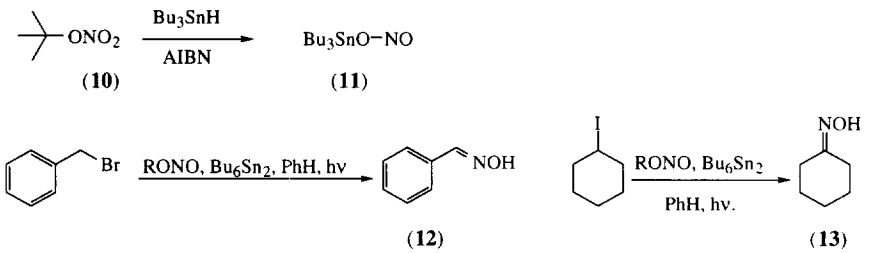
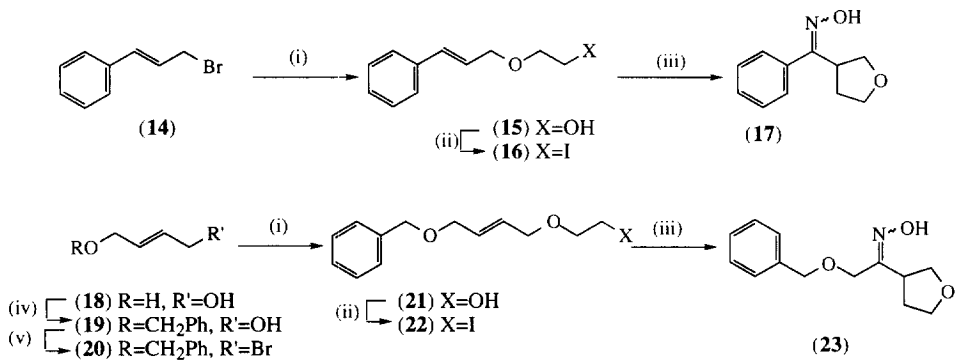


Figure 3

The failure of the cyclohexyl bromide reaction may indicate that the tributyltin radicals are reacting with the isoamyl nitrite faster than with the alkyl bromide. The benzyl bromide would of course be expected to have a weaker C-Br bond than a secondary alkyl bromide and hence the success of the benzyl bromide is not anomalous. A "blank" experiment in which cyclohexyl iodide and isoamyl nitrite were subjected to Philips Ultrafil lamp irradiation in the absence of tri-n-butyltin hydride and AIBN led to recovery of cyclohexyl iodide and no formation of oxime. This confirms that tributyltin radicals are playing an intimate part in the reaction.

In order to extend the scope of this chemistry more complicated substrates (**16**) and (**22**) were prepared (Figure 4). Cinnamyl bromide (**14**) and ethylene glycol were reacted in dimethylsulfoxide in the presence of potassium hydroxide to give alcohol (**15**). Iodination of the alcohol afforded iodide (**16**) (67%).

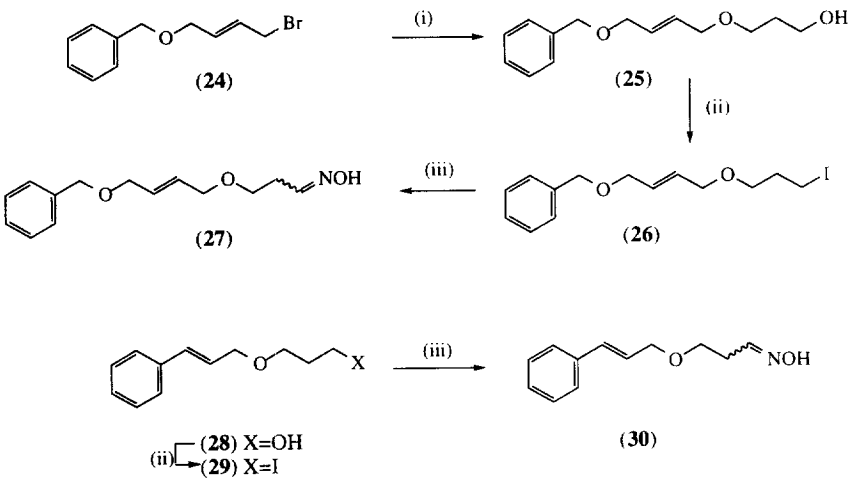


Reagents and Conditions: (i) KOH, DMSO, $(CH_2OH)_2$, (ii) I_2, imidazole, PhMe, (iii) iAmONO, Bu_6Sn_2, C_6H_6, hv, (iv) $PhCH_2Br$, NaH, DMF, THF, (v) NBS, Ph_3P, DCM.

Figure 4

The iodide (**22**) was approached in similar manner. Hence, mono-protection of *cis*-2-butene-1,4-diol (**18**) with benzyl bromide gave allylic alcohol (**19**). This was brominated to yield the bromide (**20**) which was reacted with ethylene glycol in dimethylsulfoxide in the presence of potassium hydroxide to give alcohol (**21**), iodination of which gave the iodide (**22**).

The irradiation of (**16**), isoamyl nitrite and hexabutylditin gave cyclised oxime (**17**) (73%) as a mixture of (*E*)-and (*Z*)-isomers. The two isomers were separable by column chromatography. That this result was not due to the special nature of the styrene double bond, was demonstrated by the reaction of (**22**). This gave an inseparable mixture of (***E***)- and (***Z***)-isomers of oxime (**23**) in total 61% yield. Thus substrates (**16**) and (**22**) cyclised very cleanly in a 5-*exo* mode, prior to termination. To investigate the scope of the reaction and in particular to learn whether 6-membered rings could be prepared by this route, homologues (**26**) and (**29**) were prepared (Figure 5).



Reagents and Conditions: (i) KOH, DMSO, $HO(CH_2)_3OH$, (ii) I_2, imidazole, PhMe, (iii) iAmONO, Bu_6Sn_2, C_6H_6, hv.

Figure 5

Iodides (**26**) and (**29**) were reacted with isoamyl nitrite and hexabutylditin in benzene by using irradiation with a Philips Ultrafil lamp. The reaction of iodide (**26**), did not lead to a cyclised product, but rather to a mixture of two inseparable isomeric acyclic oximes (**27**) (70%). Similarly, reaction of (**29**) under similar conditions gave a mixture of two inseparable isomeric acyclic oximes (**30**) (70%). The formation of acyclic oximes in these case reflects the substantially slower cyclisation rate for formation of 6-membered rings compared the their 5-membered ring counterparts.

In conclusion, investigations into anomalous products from nitrate and nitrite ester fragmentations have led to a new route to oximes from alkyl iodides. The chemistry extends to reactive benzyl bromides. The simplicity of the starting materials, the ability to use a liquid nitrite ester rather than gaseous NO, and the general familiarity of synthetic chemists with trialkyltin reagents suggest that this chemistry will have useful applications. This transformation to oximes adds to the rapidly expanding arsenal of radical methods for C-N bond formation[3a,10,11].

Experimental Section

General Information

Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Microanalyses were determined using a Perkin-Elmer 240B elemental analyser. IR spectra were measured using a Perkin-Elmer 1600 series FTIR spectrometer. UV spectra were recorded on a Philips PU8720 instrument. ^1H NMR were

recorded at 250 MHz with a digital resolution of 0.25 Hz / point on a Bruker WM250, at 270 MHz with a digital resolution of 0.33 Hz / point or at 400 MHz with a digital resolution of 0.31 Hz / point on a Bruker AM400 machine. ^{13}C NMR were recorded at 67.8 MHz on a Jeol EX270 or at 100 MHz on a Bruker AM400 machine. These were run as decoupled spectra and assigned using DEPT and correlation spectroscopy. All NMR experiments were carried out with tetramethylsilane as internal reference. Chemical shifts are quoted in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz). In several cases, where mixtures of diastereomers were obtained, the overlapping signals have been reported as multiplets, unless the coupling constant of each isomer could be ascertained. In cases where more than one isomer was formed in excess, wherever possible signals exclusively due to one isomer has been marked as follows: major isomer (**), minor isomer (*). The following abbreviations have been used to assign the multiplicity of the signals observed in the ^{1}H NMR and ^{13}C NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad
Mass spectra [electron impact (EI), chemical ionization (CI) and fast atom bombardment (FAB)] were recorded on VG AE1 MS902, VG Micromass 70E or VG Autospec spectrometers at Nottingham or at the EPSRC Mass Spectrometry Service Centre, Swansea.
THF was dried over sodium wire, and distilled freshly from potassium-benzophenone. Dichloromethane was distilled from calcium hydride. DMSO was dried over 4Å sieves, and vacuum distilled. Benzene was dried over sodium wire. All light petroleum was of boiling range 40-60°C and was distilled before use. Hexane was a mixture of isomeric hexanes, and was distilled before use. Flash column chromatography was performed using Sorbsil C60 (May & Baker), Kieselgel 60 (Art 9385) or Kieselgel HF254 silica gels. Photolysis reactions were performed with a 300W Philips Ultrafil lamp, type no. KL2866.

*tert-Butyl nitrate (**10**)*
Acetic anhydride (35.1ml, 372mmol, 3.4eq) was cooled to 0°C and concentrated fuming nitric acid (6.75ml, 168mmol, 1.5eq) added dropwise with stirring. Stirring was continued for 10 minutes, during which time *tert*-butyl alcohol (4.5g, 60.8mmol, 1.0eq) was dissolved in acetic anhydride (5ml), and also cooled to 0°C. The nitrating mixture was then added dropwise to this solution, which was allowed to react for 15 min. The resulting mixture was quenched by pouring into saturated aqueous sodium bicarbonate (100ml) with vigorous stirring for 1 h. The product was extracted into diethyl ether (3x100ml), and the combined organic extracts dried over magnesium sulphate and evaporated *in vacuo*. The product residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give *tert*–butyl nitrate as a yellow oil (2.5g, 24mmol, 40%). This compound (which was found to be volatile) was used directly for the next step.

*Formation of benzaldehyde oxime (**12**) using tributyltin nitrite (Bu_3SnONO).*
To a solution of *tert*-butyl nitrate (1g, 9.70mmol, 5.0eq) in dry benzene (30ml) was added tributyltin hydride (2.83g, 2.57ml, 9.70mmol, 5.0eq) and azoisobutyronitrile (318mg, 1.94mmol, 1.0eq). The resulting mixture was refluxed under nitrogen for 2 h. To this solution, benzyl bromide (332mg, 0.23ml, 1.94mmol, 1.0eq) and bis(tributyltin) (1.12g, 0.98ml, 1.94mmol, 1.0eq) was added and the mixture was irradiated (and hence refluxed) under nitrogen with a Philips Ultrafil lamp for 1 h. The crude mixture was evaporated *in vacuo* to yield a white solid. The residue was purified by column chromatography on silica gel eluted with 90% hexane/10% ethyl acetate to give the benzaldoxime (**12**) as white crystals (150mg, 1.23mmol, 63%); m.p.: 34-35°C. lit.[12] 35°C. (Found: C, 68.97; H, 6.12; N, 11.51%. C_7H_7ON requires: C, 69.39; H, 5.83; N, 11.57%). [Found: M^+ (EI), 121.0528. C_7H_7ON requires: M, 121.0527]; ν_{max}/cm^{-1} (film) 3312, 1632; δ_H (250 MHz, $CDCl_3$) 7.35 (3H, m, ArH), 7.55 (2H, m, ArH), 8.10 (2H, br s, ArCH=NOH); δ_C (67.8 MHz, $CDCl_3$) 126.6 (d), 128.3 (d), 129.7 (d), 131.4 (s), 150.0 (d) ppm; m/z (EI) 121 (M^+, 52%), 103 (100), 76 (68), 51 (32).

Formation of benzaldehyde oxime (12) using isoamyl nitrite

To a solution of isoamyl nitrite (1.2g, 10mmol, 5.0eq) in dry benzene (25ml) was added benzylbromide (350mg, 2.0mmol, 1.0eq) and bis(tributyltin) (5.95g, 10mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 4 h. The crude mixture was evaporated *in vacuo* to yield a white solid. The residue was purified by column chromatography on silica gel eluted with 90% hexane/10% ethyl acetate to give the benzaldoxime (**12**) as white crystals (297mg, 2.45mmol, 84%), identical to an authentic sample.

Cyclohexanone oxime (13)

To a solution of isoamyl nitrite (2.78g, 23mmol, 5.0eq) in dry benzene (25ml) was added cyclohexyl iodide (1g, 47mmol, 1.0eq) and bis(tributyltin) (2.76g, 47mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 2 h. The crude mixture was evaporated *in vacuo* to yield a white solid. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give cyclohexanone oxime (**13**) as a white crystalline solid (710mg, 6.28mmol, 71%); m.p.: 89-91°C. lit.[12] 90°C. (Found: C, 63.58; H, 10.12; N, 12.36%. $C_6H_{11}ON$ requires: C, 63.67; H, 9.8; N, 12.38%). [Found: M^+ (EI), 113.0837. $C_6H_{11}ON$ requires: M, 113.0840]. ν_{max}/cm^{-1} (film) 3248, 1667; δ_H (250 MHz, $CDCl_3$) 1.64 (6H, m, $CH_2CH_2CH_2$), 2.20 (2H, t, *J* 5.9 Hz, CH_2), 2.50 (2H, t, *J* 5.9 Hz, CH_2), 7.60 (1H, br, NOH); δ_C (67.8 MHz, $CDCl_3$) 24.3 (t), 25.4 (t), 25.7 (t), 26.7 (t), 31.9 (t), 160.5 (s) ppm; m/z (EI) 113 (M^+, 100%), 55 (65).

Reaction of cyclohexyl bromide with isoamyl nitrite

To a solution of isoamyl nitrite (3.59g, 4.12ml, 30.6mmol, 5.0eq) in dry benzene (30ml) was added cyclohexyl bromide (1g, 0.75ml, 6.1mmol, 1.0eq) and bis(tributyltin) (3.55g, 3.1mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 2 h. The residue was purified by column chromatography on silica gel eluted with 70% hexane/30% ethyl acetate to give recovered cyclohexyl bromide (952mg, 5.84mmol, 95%), identical to an authentic sample.

Reaction of cyclohexyl iodide with isoamyl nitrite in the absence of bis(tributyltin)

To a solution of isoamyl nitrite (2.78g, 3.2ml, 23.8mmol, 5.0eq) in dry benzene (30ml) was added cyclohexyl iodide (1g, 0.62ml, 4.76mmol, 1.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 2 h. The residue was purified by column chromatography on silica gel eluted with 70% hexane/30% ethyl acetate to give recovered cyclohexyl iodide (923mg, 4.39 mmol, 92%), identical to an authentic sample.

2-(3-Phenylprop-2-enyloxy)ethanol (15)

To a suspension of potassium hydroxide (1.13g, 20mmol, 2.0eq) in dimethylsulfoxide (30ml) were added cinnamyl bromide (2g, 10mmol, 1.0eq) and ethylene glycol (1.25g, 20mmol, 2.0eq). The mixture was stirred for 0.5 h, poured into water (100ml) and extracted with dichloromethane (3x100ml). The aqueous phase was acidified with aqueous hydrochloric acid (2N, 200ml) and extracted with more dichloromethane (2x150ml). The combined organic phases were washed with water (5x300ml), dried over sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel and eluted with 70% hexane/30% ethyl acetate to give *2-(3-phenylprop-2-enyloxy)ethanol* (**15**) as a colourless oil (1.67g, 9.38mmol, 92%). [Found: M^+ (EI), 178.0995. $C_{11}H_{14}O_2$ requires: M, 178.0994]; ν_{max}/cm^{-1} (film) 3408, 1494, 1448, 1356, 1315, 1115; δ_H (250 MHz, $CDCl_3$) 2.10 (1H, br, OH), 3.61 (2H, t, *J* 5.1 Hz, CH_2CH_2OH), 3.77 (2H, t, *J* 5.1 Hz, CH_2CH_2OH), 4.19 (2H, dd, *J* 6.1, 1.3 Hz, $CH{=}CHCH_2$), 6.29 (1H, td, *J* 6.1, 16.0 Hz, CH=CH), 6.61 (1H, d, *J* 16.0 Hz, CH=CH), 7.32 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 61.6 (t), 71.2 (t),

71.6 (t), 125.6 (d), 126.1 (d), 127.6 (d), 128.1 (d), 132.5 (d), 136.4 (s) ppm; m/z (EI) 178 (M^+, 12%), 117 (100), 149 (100), 91 (100).

3-[2-Iodoethoxy]propenyl)benzene (16)

2-(3-Phenylprop-2-enyloxy)ethanol (**15**) (1g, 5.6mmol, 1.0eq), triphenylphosphine (2.28g, 8.7mmol, 1.55eq) and imidazole (0.58g, 8.4mmol, 1.5eq) were dissolved in toluene (30ml). To the stirred mixture at 60°C was added iodine (1.79g, 7.0mmol, 1.25eq) and the resulting mixture was stirred at 60°C for 20 minutes, then cooled to room temperature. Saturated aqueous sodium bicarbonate (20ml) was added, followed by iodine until the coloration persisted. The phases were separated and the organic layer was dried over sodium sulfate and evaporated *in vacuo* to yield a colourless oil. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give (3-[2-iodoethoxy]propenyl)benzene[13] (**16**) as a yellow oil (1.085g, 3.78mmol, 67%). [Found: M^+ (EI), 288.0003. $C_{11}H_{13}IO$ requires: M^+, 288.0011]; ν_{max}/cm^{-1} (film) 1598, 1494, 1448, 1357; δ_H (250 MHz, $CDCl_3$) 3.28 (2H, t, *J* 6.9 Hz, CH_2CH_2I), 3.75 (2H, t, *J* 6.9 Hz, CH_2CH_2I), 4.20 (2H, dd, *J* 6.1, 1.3 Hz, CH=CHCH$_2$), 6.28 (1H, td, *J* 6.1, 15.9 Hz, CH=CH), 6.62 (1H, d, *J* 15.9 Hz, CH=CH), 7.21 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 2.9 (t), 70.5 (t), 71.2 (t), 125.4 (d), 126.4 (d), 127.7 (d), 128.4 (d), 132.7 (d), 136.3 (s) ppm; m/z (EI) 288 (M^+, 4%), 154 (87), 133 (86), 131 (100), 105 (81).

Phenyl(tetrahydrofuran-3-yl)methanone oxime (17)

To a solution of isoamyl nitrite (1.63g, 13mmol, 5.0eq) in dry benzene (25ml) was added (3-[2-iodoethoxy]propenyl)benzene (**16**) (800mg, 2.7mmol, 1.0eq) and bis(tributyltin) (5.95g, 13mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 2 h. The crude mixture was evaporated *in vacuo* to yield a white solid. The residue was purified by column chromatography on silica gel eluted with 80% hexane/ 20% ethyl acetate to give *phenyl(tetrahydrofuran-3-yl)methanone oxime* (**17**) as white crystals and as a pair of isomers (2:1) (580mg, 3.31mmol, 73%). m.p.: 65-66°C; (Found: C, 69.05; H, 7.10; N, 7.36. $C_{11}H_{13}O_2N$ requires: C, 69.08; H, 6.86; N, 7.33%); [Found: $(M+H)^+$ (FAB) 192.1035. $C_{11}H_{13}O_2N$ requires: (M+H), 192.1024]; ν_{max}/cm^{-1} ($CHCl_3$) 3282, 1576, 1496, 1308, 961, 906; nmr data for the major isomer: δ_H (250 MHz, $CDCl_3$) 2.03-2.22 (2H, m, CHCH_2CH$_2$O), 3.73-3.88 (5H, m, C*H*CH$_2$CH_2OCH$_2$), 7.36-7.44 (5H, m, ArH), 9.47 (1H, br, NOH); δ_C (100 MHz, $CDCl_3$) 29.9 (t), 38.1 (d), 68.5 (t), 70.2 (t), 127.6 (d), 128.8 (d), 129.0 (d), 135.3 (s), 161.0 (s) ppm; m/z (FAB) 192 [$(M+H)^+$, 100%], 174 (23), 154 (18), 71 (13); nmr data for the minor isomer: δ_H (250 MHz, $CDCl_3$) 2.09-2.12 (2H, m, CHCH_2CH$_2$O), 3.36-3.94 (5H, m, C*H*CH$_2$CH_2OCH$_2$), 7.33-7.44 (5H, m, ArH); δ_C(67.8 MHz, $CDCl_3$) 29.9 (t), 45.5 (d), 69.8 (t), 70.2 (t), 127.5 (d), 128.4 (d), 129.1 (d), 135.4 (s), 161.1 (s) ppm.

4-(Phenylmethoxy)but-2-enol (19)

Sodium hydride (0.65g, 27mmol, 1.0eq) was washed with two portions of dry tetrahydrofuran (2x5ml) under nitrogen. Then, dry dimethylformamide (150ml) was added followed by slow addition of 2-butene-1,4-diol (**18**) (12g, 136mmol, 5.0eq). When bubbling of the solution had ceased and the sodium hydride appeared to have dissolved, benzyl bromide (4.66g, 27mmol, 1.0eq) was added and the solution left to stir overnight. A few drops of ether were then added to the solution. The dimethylformamide was removed *in vacuo* and the remaining products taken up into ether (200ml) and washed with water (2x100ml). The organic phase was dried over sodium sulfate and then ether removed to give a yellow oil. The residue was purified by column chromatography on silica gel eluted with 70% hexane/ 30% ethyl acetate to give 4-(phenylmethoxy)but-2-enol[14] (**19**) as a yellow oil (4.6g, 25.8mmol, 95%); [Found: $(M+H)^+$ (FAB), 179.1095. $C_{11}H_{14}O_2$ requires: (M+H),

179.1072]; ν_{max}/cm^{-1} (film) 3406, 1495, 1454, 1071, 1028; δ_H (250 MHz, $CDCl_3$) 1.88 (1H, t, *J* 5.7 Hz, OH), 4.10 (2H, d, *J* 5.5 Hz, $OCH_2CH=CH$), 4.18 (2H, dd, *J* 5.7, 5.7 Hz, $CH=CHCH_2OH$), 4.54 (2H, s, $ArCH_2$), 5.79 (2H, m, CH=CH), 7.35 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 58.0 (t), 65.3 (t), 72.1 (t), 127.52 (d), 127.56 (d), 127.6 (d), 128.2 (d), 132.3 (d), 137.6 (s) ppm; m/z (FAB) 179 [$(M+H)^+$, 52%], 154 (60), 137 (48), 91(100).

Bromo-4-(phenylmethoxy)but-2-ene (20)

4-(Phenylmethoxy)but-2-enol (**19**) (3g, 16.8mmol, 1.0eq) was dissolved in dry dichloromethane (100ml) and cooled to -30°C under nitrogen. To this magnetically stirred solution was added triphenylphosphine (5.29g, 20mmol, 1.2eq) followed by recrystallized N-bromosuccinimide (3.29g, 18mmol, 1.1eq). The course of the reaction was followed by tlc. Upon completion (3h), ether (200ml) was added and the organic phase was washed with saturated sodium bicarbonate (2x100ml) and saturated brine (100ml). The organic layer was dried over sodium sulphate, and concentrated to afford a yellow oil. The residue was purified by column chromatography on silica gel eluted with 70% hexane/30% ethyl acetate to give bromo-4-(phenylmethoxy)but-2-ene[13] (**20**) as a yellow oil (1.99g, 8.2mmol, 49%). [Found: $(M+H)^+$ (FAB), 241.0233 $C_{11}H_{13}OBr$ requires: (M+H), 241.0228]; ν_{max}/cm^{-1} (film) 1495, 1453, 1096; δ_H (250 MHz, $CDCl_3$) 3.99 (2H, d, *J* 8.3 Hz, $CH=CHCH_2Br$), 4.16 (2H, dd, *J* 6.2, 1.4 Hz, $OCH_2CH=CH$), 4.55 (2H, s, $ArCH_2$), 5.84 (2H, m, CH=CH), 7.36 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 26.4 (t), 64.7 (t), 64.9 (t), 127.6 (d), 127.8 (d), 128.2 (d), 128.3 (d), 130.9 (d), 137.8 (s) ppm; m/z (FAB) 241 [$(M+H)^+$, 11%], 239 (100), 154 (100).

2-[4-(Phenylmethoxy)but-2-enyloxy]ethanol (21)

To a suspension of potassium hydroxide (0.84g, 14mmol, 2.0eq) in dimethylsulfoxide (30ml), bromo-4-(phenylmethoxy)but-2-ene (**20**) (2g, 10mmol, 1.0eq) and ethylene glycol (0.93g, 14mmol, 2.0eq), were added. The mixture was stirred for 0.5 h, poured into water (100ml) and extracted with dichloromethane (3x100ml). The aqueous phase was acidified with hydrochloric acid (2N, 200ml) and extracted with more dichloromethane (2x150ml). The combined organic phases were washed with water (5x300ml), dried over sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel eluted with 70% hexane/30% ethyl acetate to give *2-[4-(phenylmethoxy)but-2-enyloxy]ethanol* (**21**) as a colourless oil (1.1g, 4.9mmol, 66%). [Found: $(M+H)^+$ (FAB), 223.1323. $C_{13}H_{18}O_3$ requires: (M+H), 223.1334]; ν_{max}/cm^{-1} (film) 3438, 1496, 1454, 1330, 1246, 1206, 1070; δ_H (250 MHz, $CDCl_3$) 2.10 (1H, br, OH), 3.52 (2H, t, *J* 4.8 Hz, OCH_2CH_2OH), 3.72 (2H, t, *J* 4.8 Hz, OCH_2CH_2OH), 4.08 (4H, m, $OCH_2CH=CHCH_2O$), 4.52 (2H, s, $ArCH_2$), 5.79 (2H, m, CH=CH), 7.32 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 61.4 (t), 65.4 (t), 66.5 (t), 71.3 (t), 72.0 (t), 127.5 (d), 127.6 (d), 127.9 (d),128.2 (d), 129.2 (d), 137.8 (s) ppm; m/z (FAB) 223 [$(M+H)^+$, 15%], 154 (15), 54 (36).

(2-Iodoethoxy)-4-(phenylmethoxy)but-2-ene (22)

2-[4-(Phenylmethoxy)but-2-enyloxy]ethanol (**21**) (1g, 4.5mmol, 1.0eq), triphenylphosphine (1.83g, 6.9mmol, 1.55eq) and imidazole (0.46g, 6.7mmol, 1.5eq) were dissolved in toluene (30ml). To the stirred mixture at 60°C was added iodine (1.43g, 5.6mmol, 1.25eq) and the resulting mixture was stirred at 60°C for 20 min, then cooled to room temperature. Saturated aqueous sodium bicarbonate (20ml) was added, followed by iodine until the coloration persisted. The phases were separated and the organic layer was dried over sodium sulfate and evaporated *in vacuo* to yield a colourless oil. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give *(2-iodoethoxy)-4-(phenylmethoxy)but-2-ene* (**22**) as a yellow oil (1.17g, 3.0mmol, 78%). [Found: $(M+H)^+$ (FAB), 333.0361. $C_{13}H_{17}O_2I$ requires: (M+H), 333.0352]; ν_{max}/cm^{-1} (film) 1658, 1495, 1453, 1329, 1262, 1089; δ_H (250 MHz, $CDCl_3$) 3.24 (2H, t, *J* 6.7

Hz, CH_2CH_2I), 3.71 (2H, t, *J* 6.7 Hz, CH_2CH_2I), 4.10 (4H, 2 x d, *J* 4.9 Hz, $OCH_2CH{=}CHCH_2O$), 4.53 (2H, s, $ArCH_2$), 5.78 (2H, m, CH=CH), 7.33 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 2.8 (t), 65.5 (t), 66.2 (t), 70.6 (t), 72.1 (t), 127.6 (d), 127.7 (d), 128.3 (d), 128.9 (d), 129.7 (d), 137.9 (s) ppm; m/z (FAB) 333 [$(M+H)^+$, 30%], 154 (80), 136 (90), 91 (100).

*2-(Phenylmethoxy)(tetrahydrofuran-3-yl)ethanone oxime (**23**)*

To a solution of isoamyl nitrite (1.76g, 15mmol, 5.0eq) in dry benzene (25ml) was added (2-iodoethoxy)-4-(phenylmethoxy)but-2-ene (**23**) (1g, 3.0mmol, 1.0eq) and bis(tributyltin) (8.76g, 15mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 2 h. The crude mixture was evaporated *in vacuo* to yield a white solid. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give *2-(phenylmethoxy)(tetrahydrofuran-3-yl)ethanone oxime* (**23**) as white crystals as a inseparable pair of isomers (2:1) (612mg, 2.6mmol, 61%). m.p.: 84-85°C; [Found: $(M+H)^+$ (FAB), 236.1309. $C_{13}H_{17}O_3N$ requires: (M+H), 236.1287]; ν_{max}/cm^{-1} (film) 3311, 1453, 1072; δ_H (400 MHz, $CDCl_3$) 2.09-2.22 (2H, m, $CHCH_2CH_2O$), 3.28-3.34 [1H, tt, *J* 7.3, 7.3 Hz, $CHCH_2O$**], 3.62-4.16 [m, CH_2C=NOH* and $CHCH_2OCH_2$** and $CHCH_2OCH_2$ (minor)], 4.41 (2H, s, OCH_2C=NOH), 4.51* (2H, s, $ArCH_2$), 4.54 (2H, s, $ArCH_2$), 7.29-7.39 (5H, m, ArH), 7.90 (1H, br, OH), 8.0* (1H, br, OH); δ_C (67.8 MHz, $CDCl_3$) 28.8 (t), 29.4 (t), 36.9 (d), 40.5 (d), 64.5 (t), 67.8 (t), 68.0 (t), 69.1 (t), 69.5 (t), 70.6 (t), 72.3 (t), 73.3 (t), 127.6 (d), 127.7 (d), 128.3 (d), 137.3 (s), 137.4 (s), 157.3 (s), 159.0 (s) ppm; m/z (FAB) 236 [$(M+H)^+$, 59%], 234 (11), 91 (100), 71 (23).

*3-[4-(Phenylmethoxy)but-2-enyloxy]propanol (**25**)*

To a suspension of potassium hydroxide (1.08g, 19mmol, 2.0eq) in dimethylsulfoxide (30ml), bromo-3-(phenylmethoxy)but-2-ene (**24**) (2.3g, 9.5mmol, 1.0eq) and 1,3-propanediol (1.45g, 19mol, 2.0eq), were added. The mixture was stirred for 0.5 h, poured into water (100ml) and extracted with dichloromethane (3x100ml). The aqueous phase was acidified with aqueous hydrochloric acid (2N, 200ml) and extracted with more dichloromethane (2x150ml). The combined organic phases were washed with water (5x300ml), dried over sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel and eluted with 70% petrol/ 30% ethyl acetate to give *3-[4-(phenylmethoxy)but-2-enyloxy]propanol* (**25**) as a colourless oil (1.93g, 81mmol, 85%). [Found: $(M+H)^+$ (FAB), 237.1508. $C_{14}H_{20}O_3$ requires: (M+H), 237.1491]; ν_{max}/cm^{-1} (film) 3426, 2862, 1454, 1330,1093; δ_H(250 MHz, $CDCl_3$) 1.80 (2H, tt, *J* 5.7, 5.7 Hz, $OCH_2CH_2CH_2OH$), 2.20 (1H, t, *J* 5.2 Hz, OH), 3.60 (2H, t, *J* 5.7 Hz, $OCH_2CH_2CH_2OH$), 3.70 (2H, td, *J* 5.3, 5.3 Hz, $OCH_2CH_2CH_2OH$), 4.01 (2H, d, *J* 5.0 Hz, $OCH_2CH{=}CH$), 4.08* (2H, d, *J* 5.0 Hz, $OCH_2CH{=}CH$), 4.50 (2H, s, $ArCH_2$), 7.1 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 32.0 (t), 60.9 (t), 65.4 (t), 66.5 (t), 68.7 (t), 72.0 (t), 127.5 (d), 127.6 (d), 128.2 (d), 129.1 (d), 129.3 (d), 137.8 (s) ppm; m/z (FAB) 237 [$(M+H)^+$, 45%], 91 (100), 69 (18).

*1-(3-Iodopropoxy)-4-(phenylmethoxy)but-2-ene (**26**)*

3-[4-(Phenylmethoxy)but-2-enyloxy]propanol (**25**) (1.3g, 5.5mmol, 1.0eq), triphenylphosphine (2.24g, 8.5mmol, 1.55eq) and imidazole (0.56g, 8.2mmol, 1.5eq) were dissolved in toluene (30ml). To the stirred mixture at 60°C was added iodine (1.74g, 6.8mmol, 1.25eq) and the resulting mixture was stirred at 60°C for 20 min, then cooled to room temperature. Saturated aqueous sodium bicarbonate (20ml) was added, followed by iodine until the coloration persisted. The phases were separated and the organic layer was dried over sodium sulfate and evaporated *in vacuo* to yield a colourless oil. The residue was purified by column chromatography on silica gel eluted with 80% petrol/20% ethyl acetate to give *1-(3-iodopropoxy)-4-(phenylmethoxy)but-2-ene*

(**26**) as a yellow oil (1.54g, 4.4mmol, 82%). (Found: C, 48.56; H, 5.53; I, 36.76; $C_{14}H_{19}O_2I$ requires: C, 48.57, 5.53; I, 36.66); [Found: $(M+H)^+$ (FAB), 347.0517. $C_{14}H_{19}O_2I$ requires: (M+H), 347.0508]; ν_{max}/cm^{-1} (film) 2858, 1453, 1099; δ_H (270 MHz, $CDCl_3$) 2.0 (2H, tt, *J* 6.0, 6.0 Hz, $OCH_2CH_2CH_2I$), 3.28 (2H, t, *J* 6.0 Hz, $OCH_2CH_2CH_2I$), 3.45 (2H, t, *J* 6.0 Hz, $OCH_2CH_2CH_2I$), 4.0 (2H, d, *J* 6.0 Hz, $CH=CHCH_2$), 4.10* (2H, d, *J* 6.0 Hz, $CH=CHCH_2$), 4.5 (2H, s, $ArCH_2$), 5.7 (2H, m, CH=CH), 7.1 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 3.3 (t), 33.1 (t), 65.5 (t), 66.4 (t), 69.3 (t), 72.0 (t), 127.5 (d), 127.9 (d), 128.2 (d), 129.2 (d), 129.2 (d), 137.9 (s) ppm; m/z (FAB) 347 [$(M+H)^+$, 23%], 91 (100).

3-[4-(Phenylmethoxy)but-2-enyloxy]propanal oxime (27)

To a solution of isoamyl nitrite (1.7g, 14.4mmol, 5.0eq) in dry benzene (25ml) was added 1-(3-iodopropoxy)-4-(phenylmethoxy)but-2-ene (**26**) (1g, 2.9mmol, 1.0eq) and bis(tributyltin) (8.35g, 14.4mmol, 5.0eq). The mixture was refluxed under nitrogen with a Phillips Ultrafil lamp for 6 h. The crude mixture was evaporated *in vacuo* to yield a yellow oil. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give *3-(4-[phenylmethoxy]but-2-enyloxy)propanal oxime* (**27**) as a yellow oil, an inseparable pair of isomers (1:1) (501mg, 2.0mmol, 70%). [Found: $(M+H)^+$ (FAB), 250.1449. $C_{14}H_{19}O_3N$ requires: (M+H), 250.1443]; ν_{max}/cm^{-1} (film) 3344, 1651, 1454, 1331, 1093; δ_H (250 MHz, $CDCl_3$) 2.45 (2H, dt, *J* 6.3, 6.3 Hz, $CH_2CH=NOH$), 2.65* (2H, dt, *J* 6.3, 6.3 Hz, $CH_2CH=NOH$), 3.50 (2H, t, *J* 6.3 Hz, $OCH_2CH_2CH=NOH$), 4.02 (2H, dd, *J* 5.2, 2.6 Hz, $OCH_2CH=CHCH_2$), 4.08 (2H, d, *J* 5.2 Hz, $OCH_2CH=CHCH_2$), 4.50 (2H, s, $ArCH_2$), 5.70 (2H, m, CH=CH), 6.80* (1H, t, *J* 5.2 Hz, $CH_2CH=NOH$), 7.30 (5H, m, ArH), 7.40 (1H , t, *J* 5.2 Hz, $CH_2CH=NOH$), 7.60 (1H, br, NOH); δ_C (67.8 MHz, $CDCl_3$) 25.7 (t), 29.5 (t), 29.9 (t), 58.2 (t), 65.4 (t), 66.3 (t), 66.4 (t), 66.6 (t), 72.0 (t), 72.2 (t), 127.5 (d), 127.6 (d), 127.8 (d), 128.0 (d), 128.2 (d), 129.1 (d), 129.2 (d), 129.3 (d), 132.1 (d), 137.8 (d), 149.1 (d), 149.5 (s) ppm; m/z (FAB) 350 [$(M+H)^+$, 17%], 91 (100).

3-(3-Phenylprop-2-enyloxy)propanol (28)

To a suspension of potassium hydroxide (4.54g, 81mmol, 2.0eq) in dimethylsulfoxide (30ml), cinnamyl bromide (8g, 10mmol, 1.0eq) and 1,3-propanediol (6.17g, 81mol, 2.0eq), were added. The mixture was stirred for 0.5 h, poured into water (100ml) and extracted with dichloromethane (3x100ml). The aqueous phase was acidified with aqueous hydrochloric acid (2N, 200ml) and extracted with more dichloromethane (2x150ml). The combined organic phases were washed with water (5x300ml), dried over sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel and eluted with 70% petrol/30% ethyl acetate to give *3-(3-phenylprop-2-enyloxy)propanol* (**28**) as a colourless oil (3.66g, 19mmol, 48%). [Found: M^+ (EI), 192.1162. $C_{12}H_{16}O_2$ requires: M, 192.1150]; ν_{max}/cm^{-1} (film) 3394, 2865, 1657, 1448, 1365, 1109, 967; δ_H (250 MHz, $CDCl_3$) 1.87 (2H, tt, *J* 5.8, 5.8 Hz, $OCH_2CH_2CH_2OH$), 2.40 (1H, br, OH), 3.67 (2H, t, *J* 5.8 Hz, $OCH_2CH_2CH_2OH$), 3.80 (2H, dt, *J* 5.8, 5.8 Hz, $OCH_2CH_2CH_2OH$), 4.15 (2H, dd, *J* 6.0, 1.4 Hz, $CH=CHCH_2$), 6.27 (1H, dt, *J* 6.1, 16.0 Hz, $ArCH=CH$), 6.59 (1H, d, *J* 16.0 Hz, $ArCH=CH$), 7.34 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 31.9 (t), 59.8 (t), 67.7 (t), 71.0 (t), 125.5 (d), 125.9 (d) 127.1 (d), 128.0 (d), 131.7 (d), 136.1 (s) ppm; m/z (EI) 192 (M^+, 36%), 118 (100), 92 (100).

[3-(3-Iodopropoxy)propenyl]benzene (29)

3-(3-Phenylprop-2-enyloxy)propanol (**28**) (3.66g, 19mmol, 1.0eq), triphenylphosphine (7.74g, 29.5mmol, 1.55eq) and imidazole (1.94g, 28.5mmol, 1.5eq) were dissolved in toluene (30ml). To the stirred mixture at 60°C was added iodine (6g, 23.7mmol, 1.25eq) and the resulting mixture was stirred at 60°C for 20 min, then cooled to room temperature. Saturated aqueous sodium bicarbonate (20ml) was added, followed by iodine until the coloration persisted. The phases were separated and the organic layer was dried over sodium sulfate and

evaporated in vacuo to yield a colourless oil. The residue was purified by column chromatography on silica gel eluted with 90% petrol/10% ethyl acetate to give *[3-(3-iodopropyloxy)propenyl]benzene* (**29**) as a yellow oil (2.76g, 9.2mmol, 48%). [Found: (EI), M^+ 302.0186.$C_{12}H_{15}OI$ requires: M, 302.0168]; ν_{max}/cm^{-1} (film) 2852, 1598, 1494, 1448, 1362, 1107, 966; δ_H (270 MHz, $CDCl_3$) 2.08 (2H, tt, *J* 6.6, 6.6 Hz, $OCH_2CH_2CH_2I$), 3.30 (2H, t, *J* 6.6 Hz, $OCH_2CH_2CH_2I$), 3.54 (2H, t, *J* 5.8 Hz, $OCH_2CH_2CH_2I$), 4.15 (2H, dd, *J* 5.9, 1.3 Hz, $CH{=}CHCH_2$), 6.28 (1H, td, *J* 6.1, 16.0 Hz, ArCH=CH), 6.61 (1H, d, *J* 16.0 Hz, ArCH=CH), 7.33 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 3.4 (t), 33.3 (t), 69.3 (t), 71.4 (t), 125.8 (d), 126.3 (d), 127.5 (d), 128.4 (d), 132.2 (d), 136.4 (s) ppm; m/z (EI) 302 (M^+, 55%), 131 (100), 105 (89).

3-(3-Phenylprop-2-enyloxy)propanal oxime (30)

To a solution of isoamyl nitrite (1.95g, 16.6mmol, 5eq) in dry benzene (25ml) was added [3-(3-iodopropyloxy)propenyl]benzene (**29**) (1g, 33.2mmol, 1.0eq) and bis(tributyltin) (9.63g, 16.6mmol, 5.0eq). The mixture was refluxed under nitrogen with a Philips Ultrafil lamp for 3 h. The crude mixture was evaporated *in vacuo* to yield a yellow oil. The residue was purified by column chromatography on silica gel eluted with 80% hexane/20% ethyl acetate to give 3-(3-phenylprop-2-enyloxy)propanal oxime (**30**) as a yellow oil and inseparable pair of isomers (1:1) (482mg, 2.4mmol, 70%). [Found: $(M+H)^+$ (FAB), 206.1182. $C_{12}H_{15}O_2N$ requires: (M+H), 206.1181];ν_{max}/cm^{-1} ($CHCl_3$) 3314, 1456, 1360, 1109, 988; δ_H (250 MHz, $CDCl_3$) 2.58 (2H, dt, *J* 6.2, 6.2 Hz, $CH_2CH{=}NOH$), 2.71* (2H , dt, *J* 6.2, 6.2 Hz, $CH_2CH{=}NOH$), 3.65 (2H, t, *J* 6.3 Hz, $OCH_2CH_2CH{=}NOH$), 4.17 (2H, m, $CH{=}CHCH_2$), 6.32 (1H, m, ArCH=CH), 6.74 (1H, d, *J* 15.0 Hz, ArCH=CH), 6.87 (1H, t, *J* 5.2 Hz, $CH_2CH{=}NOH$), 7.33 (5H, m, ArH), 7.53* (1H , t, *J* 5.8 Hz, $CH_2CH{=}NOH$); δ_C (67.8 MHz, $CDCl_3$) 25.5 (t), 25.8 (t), 27.6 (t) 30.1 (t), 66.4 (t), 71.5 (t), 125.6 (d), 126.4 (d), 127.4 (d), 127.6 (d), 128.2 (d), 128.4 (d), 128.7 (d), 132.5 (d), 136.5 (s), 149.4 (d), 149.7 (d) ppm; m/z (FAB) 206 [$(M+H)^+$, 2%], 115 (86), 91 (100).

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