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Reactivity of Differentially Substituted Bis(diazo) Esters in Rhodium(II) Mediated O-H Insertion Reactions

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Abstract: Selective catalysed decompositions of one diazo group in the presence of another are discussed. A range of bis(diazo) compounds was prepared in which the two diazo groups are differentially substituted. Rhodium(II) acetate catalysed decomposition in the presence of methanol resulted in exclusive O-H insertion reaction at the more reactive diazo group, the less reactive diazophosphonate remaining intact. With the more active rhodium(II) trifluoroacetamide as catalyst, both diazo groups decomposed simultaneously.

INTRODUCTION

Although α-bis(diazo) compounds, formed by dehydrogenation of the bis-hydrazones of 1,2-diketones, are relatively unstable and readily eliminate nitrogen to give alkynes,[1,2] other bis(diazo) compounds are isolable. Indeed the complex nature of their decomposition to give bis(carbenes) and their Wolff rearrangements have prompted many studies.[3-13] In particular, Trost used the decomposition of 1,3-diazoketones in the synthesis of cyclopropenones,[14] a method subsequently used by Chapman *et al.* in the generation of acenaphthyne.[15] The decomposition of 1,3-bis(diazo)indan-2-one has been widely studied,[16-23] and others, notably Maier and co-workers, have used the photochemical decomposition of bis- and tris-diazo compounds to synthesise unusual oxides of carbon, C_xO_y, and other reactive species.[24-27] Bis(diazo)silanes have been used in the formation of polysilicon containing species,[28-30] and Nakatani has exploited bis(diazoketones) in the synthesis of *trans*-hydro-2-inden-1-ones.[31,32] However very few of the above studies involve the transition-metal catalysed decomposition of bis(diazo) compounds,[23] although McKervey has used the copper(II) catalysed reaction of α,ω-bis(diazoketones) with 1,*n*-diols to construct macrocyclic oxo-crown ethers.[33]

Our own interest lies in the rhodium(II) catalysed reactions of diazocarbonyl compounds, in particular O-H insertion reactions, and we have described studies on the effect of catalyst and the nature of the diazo compound on the reaction.[34-37] In pursuit of the synthesis of naturally occurring polyether toxins containing cyclic ethers of various ring size, we have also studied intramolecular O-H insertion reactions,[38-41] and attempted to extend this work to the synthesis of fused oxepanes **2** using two *simultaneous* O-H insertion reactions (Scheme 1). Unfortunately, although the symmetrical bis(diazo) compound **1** could be readily prepared, its rhodium(II) catalysed decomposition failed to give the required double O-H insertion product **2**.[42] Therefore we considered using *sequential* O-H insertion reactions of differently substituted diazo groups. This would require the selective catalysed decomposition of one diazo group in the presence of another, and we decided to investigate whether this was indeed possible. The results of our studies are described herein.

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† *DJM would like to dedicate this paper to the memory of his former friend and teacher, Richard Michael Scrowston (Hull University), who died on 31 July 1997.*

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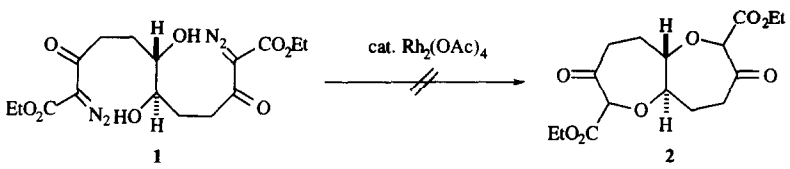


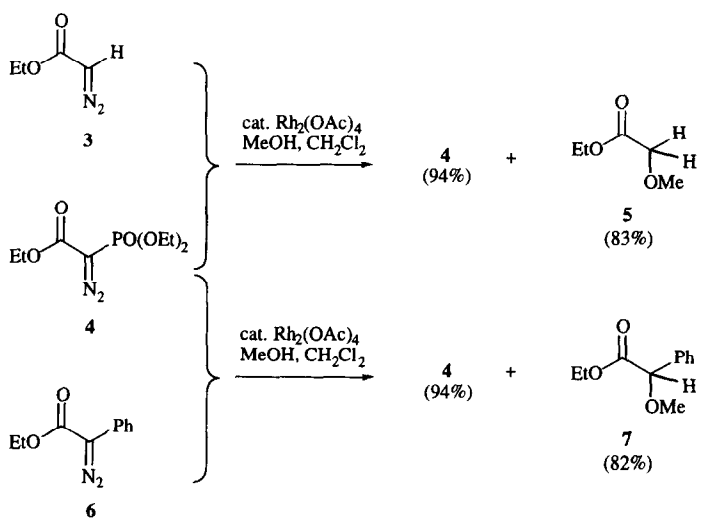
1 2

Scheme 1

RESULTS AND DISCUSSION

In a previous paper we demonstrated a marked difference in the reactivity of diazo compounds in which the diazo group is stabilised by a carbonyl group compared to a phosphonate group.[35] Whatever the cause of such an effect, it was clear that the differences in reactivity of diazocarbonyl compounds and diazophosphonates are remarkable and hence might be exploited in synthesis if suitable bis(diazo) compounds containing two different diazo groups could be obtained.

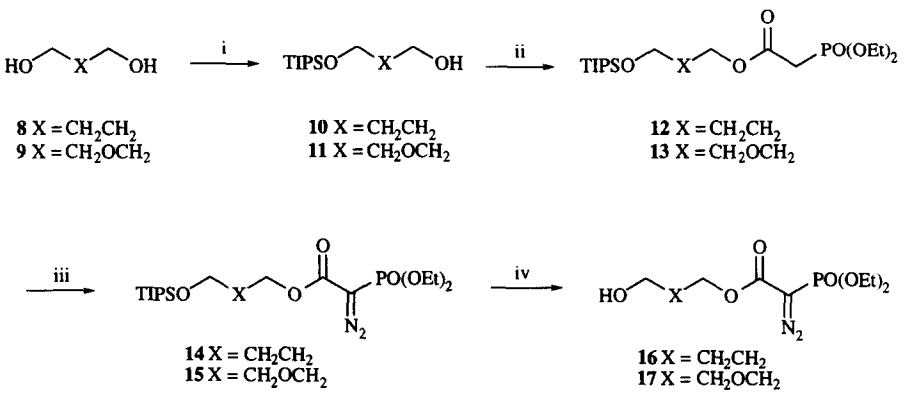
Initial studies were carried out on pairs of readily available individual diazo compounds. When ethyl diazoacetate **3**, a relatively reactive diazoester, was decomposed using rhodium(II) acetate in the presence of triethyl diazophosphonoacetate **4**, a highly stabilised diazo compound, and methanol (2 equiv.), the deep yellow colour of **3** (*cf.* the extremely pale yellow colour of **4**) dissipated within a few minutes and TLC analysis of the reaction mixture indicated its complete consumption. Separation of the reaction mixture showed that **3** had indeed undergone rhodium(II) catalysed O-H insertion in high yield to afford ethyl methoxyacetate **5**, whereas the diazophosphonate **4** remained essentially unchanged (Scheme 2). When the reaction was repeated with ethyl phenyldiazoacetate **6** in place of **3**, a very similar result was observed (Scheme 2); again the diazophosphonate **4** was recovered with the diazoester **6** undergoing selective reaction to give the α-methoxyester **7**.



3 4 6

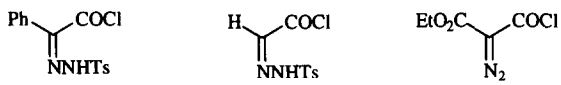
Scheme 2

It is clear that when rhodium(II) acetate is used as the catalyst in these reactions, there is a very marked difference between the relative reactivities of diazoesters **3** and **6** compared with diazophosphonate **4**. The fact that the products of the selective insertion reactions could be obtained in good yields, with virtually complete recovery of the diazophosphonate, led us to synthesise a range of bis(diazo) substrates in which the two different diazo groups are joined by a long tether, thereby lowering the possibility of an intramolecular interaction between them. The synthesis started with the inexpensive diols **8** and **9** (Scheme 3); these diols could be monoprotected in good yield using triisopropylsilyl chloride, pyridine in dichloromethane and an excess of the diol. The mono hydroxyl compounds **10** and **11** could then be esterified using (diethoxyphosphoryl)acetic acid, DCC, DMAP and pyridine leading to **12** and **13**. The active methylene groups of **12** and **13** were then converted to diazo groups using the commercially available diazo transfer reagent azidotris(diethylamino)phosphonium bromide[43] leading to the protected diazo alcohols **14** and **15**. Deprotection using dilute aqueous hydrochloric acid gave the key diazo alcohols **16** and **17** (Scheme 3).



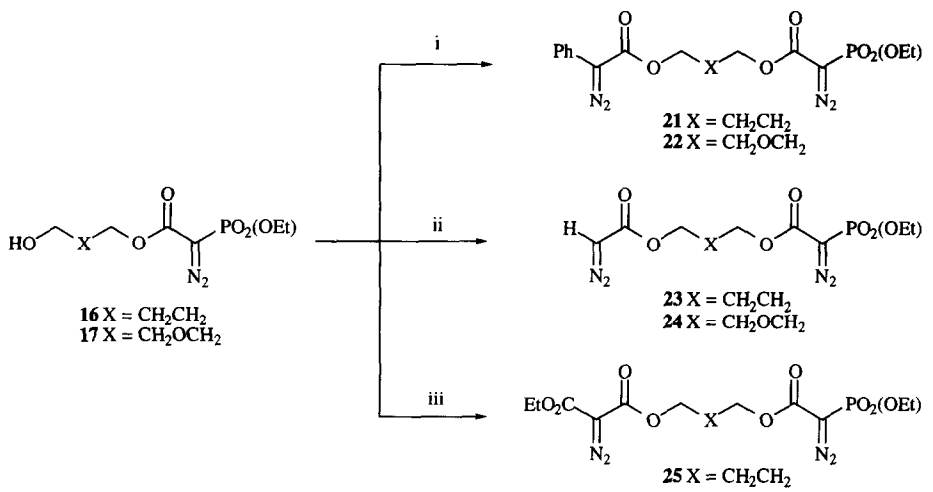
Scheme 3. *Reagents and Conditions:* (i) TIPSCl, py, CH_2Cl_2, 10 equiv. diol, 90% for **10**, 98% for **11**; (ii) $(EtO)_2POCH_2CO_2H$, DCC, DMAP, py, CH_2Cl_2, 81% for **12**, 65% for **13**; (iii) $(Et_2N)_3PN_3Br$, THF, *t*-BuOK, 84% for **14**, 79% for **15**; (iv) 0.01 M HCl, 50 °C, 82% for **16**, 81% for **17**.

From the two diazo alcohols **16** and **17** various bis(diazo) compounds were prepared by acylation reactions using the sulfonylhydrazone acid chlorides **18**[44] and **19**,[45] and the diazo acid chloride **20**[46] (Scheme 4).



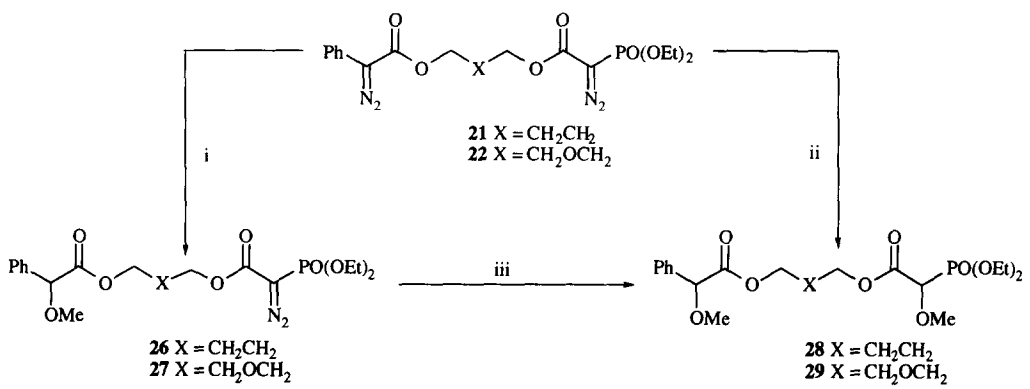
18 **19** **20**

The sulfonylhydrazones were used in the synthesis of the bis(diazo) compounds **21** and **23** using the procedure of Corey and Myers.[47] By this method, a mixture of the alcohol **16** and either **18** or **19** is treated first with *N,N*-dimethylaniline to initiate the acylation reaction before triethylamine is added to unmask the diazo group *via* a Bamford-Stevens reaction. The step-wise addition of reagents avoids the formation of sulfonate esters as by-products. The bis(diazo) compound **25** was prepared from the diazo acid chloride **20** using triethylamine as base. The corresponding bis(diazo) substrates (**22** and **24**) with an ether linker separating the two diazo esters were prepared from the diazo alcohol **17** (Scheme 4). In most cases the two $C{=}N_2$ stretching absorptions of the differentially stabilised diazo groups could be observed in the infra-red spectra of these compounds. For example, in the case of the diazo substrate **22** the absorption of the phosphonate diazo ester group was observed at 2089 cm^{-1} whereas the stretching band for the non-phosphonate stabilised diazo was at 2131 cm^{-1}.



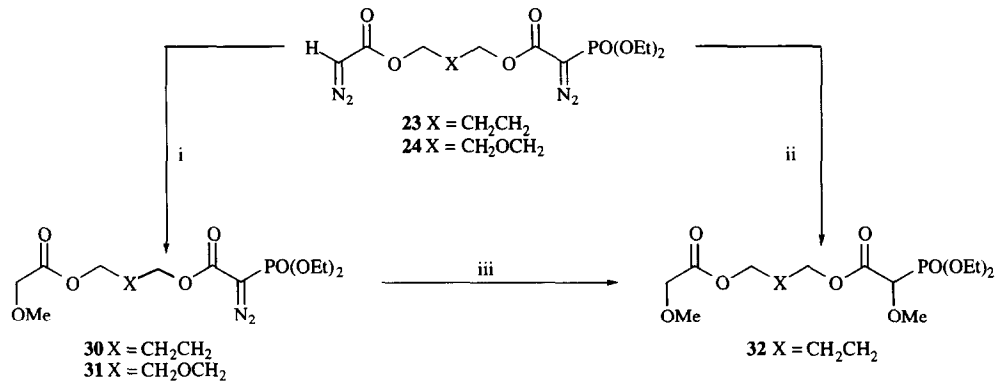
Scheme 4. *Reagents and Conditions:* (i) **18**, *N,N*-dimethylaniline, then NEt_3, 86% for **21**, 71% for **22**; (ii) **19**, *N,N*-dimethylaniline, then NEt_3, 90% for **23**, 45% for **24**; (iii) **20**, NEt_3, 86%.

With these bis(diazo) substrates in hand we were ready to attempt selective rhodium(II) catalysed insertion reactions. Thus, the substrate **21**, as a solution in dichloromethane, was treated with methanol (2 equiv.) and rhodium(II) acetate (2 mol%). The mono diazo compound **26**, could be obtained, but only in modest yield (Scheme 5). This mono diazo compound **26**, upon treatment with methanol and rhodium(II) trifluoroacetamide, a more active rhodium(II) catalyst,[48] in refluxing toluene was converted into the dimethoxy compound **28**. Furthermore, **21** could be transformed into **28** directly, by treatment with methanol and rhodium(II) trifluoroacetamide in refluxing toluene. Perhaps not surprisingly, the bis(diazo) substrates with an ether tether acted in an analogous fashion. Thus, **22** could be selectively converted into either the methoxy diazo compound **27** or the dimethoxy compound **29**, depending on the choice of conditions employed. Furthermore, **27** could be converted into **29** by using rhodium(II) trifluoroacetamide (Scheme 5).



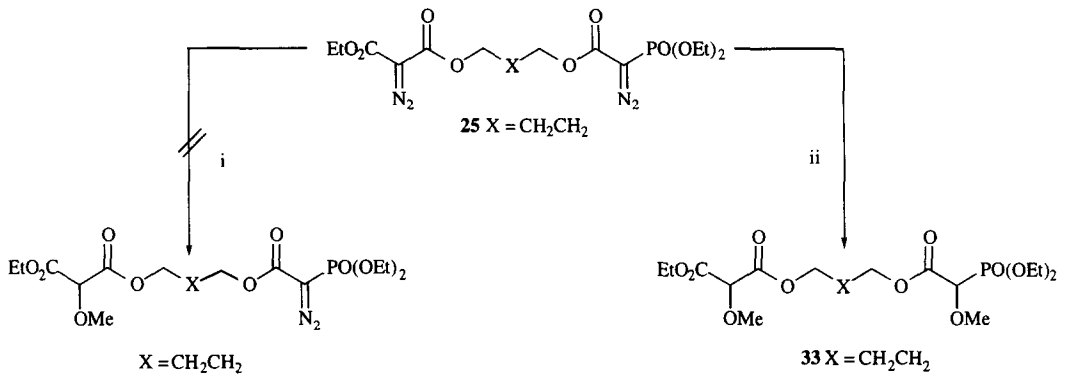
Scheme 5. *Reagents and Conditions:* (i) $Rh_2(OAc)_4$ (2 mol%), MeOH (2 equiv.), 25 °C, CH_2Cl_2, 36% for **26**, 60% for **27**; (ii) $Rh_2(NHCOCF_3)_4$ (2 mol%), MeOH (2 equiv.), 110 °C, toluene, 88% for **28**, 77% for **29**; (iii) as for (ii), 61% for **28**, 74% for **29**.

In a similar sense, the bis(diazo) ester **23** was transformed either into the monodiazo compound **30** or the dimethoxy compound **32** (Scheme 6). Likewise, **24** could be transformed into **31** using rhodium(II) acetate and **30** could be converted into **32** with rhodium(II) trifluoroacetamide.



Scheme 6. *Reagents and Conditions:* (i) $Rh_2(OAc)_4$ (2 mol%), MeOH (2 equiv.), 25 °C, CH_2Cl_2, 90% for **30**, 57% for **31**; (ii) $Rh_2(NHCOCF_3)_4$ (2 mol%), MeOH (2 equiv.), 110 °C, toluene, 63%; (iii) as for (ii), 76%.

Finally, the bis(diazo) substrate **25** could be converted into the dimethoxy derivative **33** in moderate yield. However, when **25** was treated with rhodium(II) acetate in the presence of methanol, a complex mixture of products resulted (Scheme 7).



Scheme 7. *Reagents and Conditions:* (i) $Rh_2(OAc)_4$ (2 mol%), MeOH (2 equiv.), 25 °C, CH_2Cl_2; (ii) $Rh_2(NHCOCF_3)_4$ (2 mol%), MeOH (2 equiv.), 110 °C, toluene, 55%.

The chemistry described above has clearly shown that in a molecule containing two differentially substituted diazo groups, the more reactive diazo system can undergo selective rhodium(II) mediated O-H insertion reaction leaving the other intact when rhodium(II) acetate is used as the catalyst. With rhodium(II) trifluoroacetamide, a more active catalyst, both diazo groups react.

EXPERIMENTAL

General experimental details

For general experimental details see references 35 and 37. NMR spectra were recorded at 250 MHz (1H) or 62.9 MHz (13C) in $CDCl_3$ unless otherwise stated. Although diazo compounds were chromatographically homogeneous, no satisfactory microanalyses could be obtained.

Competition experiments between pairs of diazo substrates

Triethyl phosphonoacetate *versus* ethyl diazoacetate

$Rh_2(OAc)_4$ (8.8 mg, 2 mol%) was added to a stirring mixture of dichloromethane (50 ml), methanol (64 mg, 2 mmol, 2 equiv.), triethyl diazophosponoacetate (250 mg, 1 mmol) and ethyl diazoacetate (114 mg, 1 mmol). After *ca.* 15 min the deep yellow colour of the diazoacetate had dissipated and TLC analysis indicated that this substrate had been totally consumed. The solvent was removed *in vacuo* at < 40 °C, and the residue was separated by column chromatography to give ethyl methoxyacetate **5** (98 mg, 83%) and unchanged triethyl diazophosphonoacetate (244 mg, 94%).

Triethyl phosphonoacetate *versus* ethyl phenyldiazoacetate

$Rh_2(OAc)_4$ (8.8 mg, 2 mol%) was added to a stirring mixture of dichloromethane (50 ml), methanol (64 mg, 2 mmol, 2 equiv.), triethyl diazophosponoacetate (250 mg, 1 mmol) and ethyl diazophenylacetate (190 mg, 1 mmol). After *ca.* 15 min the deep yellow colour of the diazophenylacetate had dissipated and TLC analysis indicated that this substrate had been totally consumed. The solvent was removed *in vacuo* , and the residue was separated by column chromatography to afford ethyl α-methoxyphenylacetate **7** (158 mg, 82%) and unchanged triethyl diazophosphonoacetate **4** (244 mg, 94%).

Preparation of the bis(diazo) substrates

4-(Triisopropylsiloxy)butanol 10

A solution of triisopropylsilyl chloride (9.46 g, 50 mmol) in dichloromethane (100 ml) was added dropwise over a period of 1 h to a rapidly stirring mixture of pyridine (4.35 g, 55 mmol), butane-1,4-diol (22.53 g, 250 mmol) and dichloromethane (250 ml) at room temperature. The mixture was allowed to stir overnight before water (250 ml) was added. The aqueous layer was extracted with dichloromethane before the combined extracts were washed with brine (3 x 100 ml) and the solvent was removed *in vacuo*. The crude product was distilled (Kugelrohr; b.p. 125 °C at 0.5 mbar) to yield the *title compound* as a colourless oil (11.2 g, 90%), (Found: MH^+, 247.2093. $C_{13}H_{30}O_2Si$+H requires 247.2093); υ_{max} (neat)/cm^{-1} 3348, 2943, 2892, 2867, 1464, 1107, 1065, 1026, 1014, 996 and 883; δ_H 0.98-1.15 (21 H, m, OSiC*H*Me_2 and CH*Me*$_2$), 1.57-1.71 (4 H, m, CH_2CH_2), 2.83 (1 H, br s, OH), 3.66 (2 H, t, *J* 5.7, CH_2OSi), 3.75 (2 H, t, *J* 5.7, C*H*$_2$OH); δ_C (100 MHz) 11.8 (CSi), 17.8 (*Me*$_2$CSi), 29.9 (CH_2), 30.5 (CH_2), 62.5 (CH_2OSi) and 63.7 (CH_2OH); *m/z* (CI) 247 (MH^+, 100%), 148 (11) and 136 (8).

2-(2-Triisopropylsiloxyethoxy)ethanol 11

Prepared as described above; the crude product was distilled (Kugelrohr; b.p. 170 °C at 3.5 mbar) to yield the title compound as a colourless oil (98%); υ_{max} (neat)/cm^{-1} 3407, 2943, 2892, 2867, 1464, 1113, 1069, 883, 680, 659 and 643; δ_H 1.02-1.06 (21 H, m, OSiC*H*Me_2 and CH*Me*$_2$), 2.45 (1 H, br s, OH), 3.58-3.63 (4 H, m, OCH_2), 3.68-3.72 (2 H, m, CH_2O) and 3.81-3.85 (2 H, m, OCH_2); δ_C 11.5 (CSi), 17.8 (*Me*$_2$CSi), 61.8 (OCH_2), 63.0 (OCH_2), 72.4 (OCH_2), and 72.6 (OCH_2); *m/z* (CI) 280 ($M+NH_4^+$, 100%) and 263 (MH^+, 30).

4-(Triisopropylsilyloxy)butyl (diethoxyphosphoryl)acetate 12

DCC (1 mol equiv.), DMAP (1 mol equiv.) and pyridine (1 mol equiv.) were added sequentially to a stirred mixture of the alcohol **10** and (diethoxyphosphoryl)acetic acid (each 1 mol equiv.) in dichloromethane. The

reaction mixture was stirred at room temperature for *ca.* 40 h before TLC analysis showed no remaining starting material. The white precipitate was filtered off before the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) then distilled (Kugelrohr; b.p. 240 °C at 0.1 mbar) to yield the *title compound* as a colourless oil (81%), (Found: MH^+, 425.2488. $C_{19}H_{41}O_6SiP$ + H requires 425.2488); υ_{max} (neat)/cm^{-1} 2943, 2894, 2867, 1740, 1465, 1269, 1110, 1054, 1027, 996, 972, and 883; δ_H (400 MHz) 1.03-1.12 (21 H, m, OSiC*H*Me_2 and CH*Me*$_2$), 1.35 (6 H, t, *J* 7.1, OCH_2*Me*), 1.57-1.63 (2 H, m, CH_2CH_2), 1.74-1.78 (2 H, m, CH_2CH_2), 2.97 (2 H, d, J_{HP} 21.6, PCH_2), 3.70 (2 H, t, *J* 5.7, CH_2OSi), 4.14-4.22 (6 H, m, OCH_2Me and $OCOCH_2$); δ_C 11.8 (CSi), 16.1 (Me), 16.2 (Me), 17.9 (*Me*$_2$CSi), 25.0 (CH_2), 29.3 (CH_2), 34.2 (d, J_{CP} 134.2, PCH_2), 62.4 (CH_2OSi), 62.6 (OCH_2Me), 65.5 ($OCOCH_2$) and 166.7 (C=O); *m/z* (CI) 425 (MH^+, 100%), 381 (12), 247 (18), 229 (16), 225 (11) and 49 (17).

2-(2-Triisopropylsiloxyethoxy)ethyl (diethoxyphosphoryl)acetate 13

Prepared from **11** and (diethoxyphosphoryl)acetic acid as described above; the crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) then distilled (Kugelrohr; b.p. 185 °C at 0.7 mmHg) to yield the *title compound* as a colourless oil (65%), (Found: M^+, 440.2361. $C_{19}H_{41}O_7PSi$ requires 440.2359); υ_{max} (neat)/cm^{-1} 2943, 2894, 2867, 1742, 1464, 1270, 1113, 1055, 1028, 997, 970, 883, 681 and 651; δ_H 0.98 (3 H, br s, OSiC*H*Me_2), 0.99 (18 H, br s, CH*Me*$_2$), 1.27 (6 H, t, *J* 7.1, OCH_2*Me*), 2.92 (2 H, d, J_{HP} 21.5, PCH_2), 3.51 (2 H, m, OCH_2), 3.67 (2 H, m, OCH_2), 3.75 (2 H, m, OCH_2), 4.10 (4 H, q, *J* 7.1, OCH_2Me) and 4.21 (2 H, m, OCH_2); δ_C 11.8 (CSi), 16.1 (Me), 16.2 (Me), 17.9 (*Me*$_2$CSi), 34.0 (d, J_{CP}134.5, PCH_2), 62.5 (CH_2O), 62.6 (CH_2O), 62.9 (OCH_2), 64.6 (OCH_2), 68.9 (OCH_2) and 77.6 (OCH_2); no C=O observed; *m/z* (CI) 458 ($M+NH_4^+$, 100%), 441 (MH^+, 35), 295 (15), and 280 (25).

4-(Triisopropylsiloxy)butyl (diethoxyphosphoryl)diazoacetate 14

Prepared according to the literature procedure for diazotisation reactions using $(Et_2N)_3PN_3.Br$.[43] The crude product was purified by column chromatography (silica gel, ether) to yield the *title compound* as a pale yellow oil (84%), (Found: MH^+, 451.2393. $C_{19}H_{39}N_2O_6PSi$ + H requires 451.2393); υ_{max} (neat)/cm^{-1} 2957, 2944, 2895, 2867, 2129, 1707, 1289, 1164, 1106, 1049 and 1025; δ_H 1.02-1.06 (21 H, m, OSiC*H*Me_2 and CH*Me*$_2$), 1.35 (6 H, t, *J* 7.1, OCH_2*Me*), 1.53-1.64 (2 H, m, CH_2CH_2), 1.65-1.84 (2 H, m, CH_2CH_2), 3.69 (2 H, t, *J* 5.9, CH_2OSi), 4.14-4.24 (6 H, m, OCH_2Me and $OCOCH_2$); δ_C 11.8 (CSi), 15.98 (Me), 16.00 (Me), 17.9 (*Me*$_2$CSi), 25.3 (CH_2), 29.0 (CH_2), 62.5 (CH_2OSi), 63.5 (OCH_2Me), 63.6 (OCH_2Me) and 65.6 ($OCOCH_2$); no C=O observed; *m/z* (CI) 452 (MH^+, 12%), 451 (44), 425 (39), 247 (36), 245 (67), 229 (100), 196 (48) and 179 (53).

2-(2-Triisopropylsiloxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 15

Prepared as described above; the crude product was purified by column chromatography (silica gel, 1:1 ether-light petroleum graduating to ether) to yield the title compound as a pale yellow oil (79%); υ_{max} (neat)/cm^{-1} 2944, 2894, 2867, 2130, 1712, 1464, 1282, 1146, 1112, 1026, 979, 961, 883, 744 and 682; δ_H 1.03-1.07 (21 H, m, OSiC*H*Me_2 and CH*Me*$_2$), 1.34 (6 H, t, *J* 7.1, OCH_2*Me*), 3.56 (2 H, t, *J* 5.1, OCH_2), 3.72 (2 H, t, *J* 4.8, OCH_2), 3.81 (2 H, t, *J* 5.5, OCH_2), 4.04-4.26 (4 H, m, OCH_2Me), and 4.32 (2 H, t, *J* 4.8, OCH_2); δ_C 11.8 (CSi), 15.96 (Me), 16.08 (Me), 17.8 (*Me*$_2$CSi), 63.0 (CH_2O), 63.6 (OCH_2Me), 63.7 (OCH_2Me), 64.7 (OCH_2), 72.7 (OCH_2) and 76.5 (OCH_2); no C=O observed; *m/z* (CI) 484 ($M+NH_4^+$, 35%), 483 (100), and 466 (M^+, 30).

4-(Hydroxy)butyl (diethoxyphosphoryl)diazoacetate 16

The silyl ether was taken up into an excess of aqueous hydrochloric acid (0.01 M) and allowed to stir at 50 °C until TLC analysis indicated that all of the starting material had been consumed. The product was then extracted into ether (3 x 100 ml) and the combined extracts were washed successively with water (3 x 100 ml)

and brine (3 x 100 ml) before being dried ($MgSO_4$). The solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the *title compound* as a pale yellow oil (82%), (Found: MH^+, 295.1059. $C_{10}H_{19}N_2O_6P$ + H requires 295.1059); υ_{max} (neat)/cm^{-1} 3438, 2984, 2941, 2915, 2895, 2872, 2130, 1706, 1391, 1282, 1164, 1125, 1097, 1023 and 981; δ_H 1.35 (6 H, t, *J* 7.2, $OCH_2\mathit{Me}$), 1.67 (2 H, m, $CH_2\mathit{CH_2}$), 1.73 (2 H, m, $\mathit{CH_2}CH_2$), 3.68 (2 H, t, *J* 6.1, $\mathit{CH_2}OH$) and 4.17-4.27 (6 H, m, $O\mathit{CH_2}Me$ and $OCOCH_2$); δ_C 16.0 (Me), 16.1 (Me), 25.0 (CH_2), 28.9 (CH_2), 61.9 (CH_2O), 63.56 ($O\mathit{C}H_2Me$), 63.65 ($O\mathit{C}H_2Me$, 65.6 ($OCO\mathit{C}H_2$) and 164.7 (C=O); *m/z* (CI) 312 ($M+NH_4^+$, 54%), 295 (MH^+, 95), 269 (34), 196 (86), 179 (100), 156 (61), 108 (61), 88 (100), 71 (54) and 44 (57).

2-(2-Hydroxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 17

Prepared as described directly above; the crude product was purified by column chromatography (silica gel, 5% methanol in ethyl acetate) to yield the title compound as a pale yellow oil (81%); υ_{max} (neat)/cm^{-1} 3435, 2985, 2938, 2911, 2872, 2133, 1709, 1445, 1392, 1370, 1282, 1218, 1164, 1125, 1097, 1023, 981, 798 and 746; δ_H 1.31 (6 H, t, *J* 6.9, $OCH_2\mathit{Me}$), 2.69 (1 H, br s, OH), 3.52-3.56 (2 H, m, CH_2O), 3.65-3.70 (4 H, m, OCH_2), 4.10-4.22 (4 H, m, $O\mathit{CH_2}Me$) and 4.29-4.33 (2 H, m, OCH_2); δ_C (100 MHz) 18.6 (Me), 18.7 (Me), 64.1 (CH_2O), 66.27 ($O\mathit{C}H_2Me$), 66.33 ($O\mathit{C}H_2Me$), 67.1 (OCH_2), 71.4 (OCH_2), 75.0 (OCH_2) and 166.0 (d, J_{CP}12.4, C=O); *m/z* (CI) 328 ($M+NH_4^+$, 100%) and 311 (MH^+, 15).

4-(Phenyldiazoacetoxy)butyl (diethoxyphosphoryl)diazoacetate 21

The title compound was prepared according to the procedure of Corey and Myers[47] using the tosyl hydrazone of phenylglyoxylic acid chloride **18**.[44] The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the *title compound* as a pale yellow oil (86%), (Found: $M+NH_4^+$, 456.1648. $C_{18}H_{23}N_4O_7P$ + NH_4 requires 456.1648); υ_{max} (neat)/cm^{-1} 2984, 2965, 2930, 2088, 1704, 1247, 1163, 1113, 1096, 1047 and 979; δ_H 1.34 (6 H, t, *J* 6.7, $OCH_2\mathit{Me}$), 1.76-1.78 (4 H, m, CH_2CH_2), 4.08-4.31 (8 H, m, 2 x OCH_2 and $O\mathit{CH_2}Me$, including 4 H, t, *J* 6.1), 7.13-7.19 (1 H, m, ArH), 7.32-7.39 (2 H, m, ArH) and 7.43-7.47 (2 H, m, ArH); δ_C 16.0 (Me), 16.1 (Me), 25.3 (2 C, CH_2CH_2), 63.5 (CH_2O), 63.6 (CH_2O), 64.1 (CH_2O), 64.9 (CH_2O), 123.9 (ArCH), 125.75 (ArC), 125.8 (ArCH), 128.9 (ArCH) and 165.0 (C=O, only one signal observed); *m/z* (CI) 456 ($M+NH_4^+$, 64%), 411 (68), 196 (100), 179 (92), 172 (67) and 105 (48).

2-(2-Phenyldiazoacetoxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 22

The title compound was prepared according to the procedure detailed directly above. The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the title compound as a pale yellow oil (71%); υ_{max} (neat)/cm^{-1} 2984, 2131, 2089, 1706, 1702, 1500, 1450, 1393, 1379, 1366, 1340, 1282, 1248, 1216, 1164, 1139, 1121, 1097, 1053, 1024, 979, 757 and 693; δ_H 1.35 (6 H, t, *J* 6.8, $OCH_2\mathit{Me}$), 3.71-3.77 (4 H, m, OCH_2), 4.14-4.23 (4 H, m, $O\mathit{CH_2}Me$), 4.33-4.42 (4 H, m, OCH_2) and 7.17-7.49 (5 H, m, ArH); δ_C (100 MHz) 16.45 (Me), 16.51 (Me), 64.0 (OCH_2), 64.1 (OCH_2), 64.8 (OCH_2), 69.3 (OCH_2), 69.5 (OCH_2), 77.1 (OCH_2), 124.4 (ArCH), 125.7 (ArC), 126.3 (ArCH), 129.3 (ArCH), 163.6 (d, J_{CP} 49.2, C=O) and 165.3 (C=O); a satisfactory mass spectrum could not be obtained.

4-(Diazoacetoxy)butyl (diethoxyphosphoryl)diazoacetate 23

Prepared according to the procedure of Corey and Myers,[47] using the tosylhydrazone acid chloride **19**.[45] The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the *title compound* as a pale yellow oil (90%), (Found: $M+NH_4^+$, 380.1335. $C_{12}H_{19}N_4O_7P$ + NH_4 requires 380.1335); υ_{max} (neat)/cm^{-1} 2986, 2966, 2128, 2115, 1700, 1398, 1357, 1340, 1282, 1220, 1186, 1167, 1113, 1095 and 1023; δ_H 1.32 (6 H, t, *J* 7.1, $OCH_2\mathit{Me}$), 1.68-1.73 (4 H, m, CH_2CH_2), 4.10-4.22 (8 H, m, 2 x OCH_2 and $O\mathit{CH_2}Me$, including 4 H, t, *J* 6.1), 4.73 (1 H, s, N_2=CH); δ_C 16.0 (Me), 16.1 (Me), 25.2 (2 C, CH_2CH_2), 46.0 (N_2=CH), 63.5 (CH_2O), 63.6 (CH_2O), 64.0 (CH_2O), 64.9 (CH_2O), 166.6 (C=O) and

165.0 (C=O); *m/z* (CI) 380 ($M+NH_4^+$, 0.5%), 335 (28), 266 (29), 196 (34), 179 (36), 108 (92) and 105 (48).

2-(Diazoacetoxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 24

The title compound was prepared according to the procedure detailed directly above. The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the title compound as a pale yellow oil (45%); υ_{max} (neat)/cm^{-1} 2984, 2130, 2117, 1708, 1702, 1698, 1455, 1393, 1388, 1370, 1349, 1282, 1215, 1191, 1164, 1121, 1097, 1022, 980 and 742; δ_H 1.37 (6 H, t, *J* 7.1, $OCH_2\mathit{Me}$), 3.68-3.74 (4 H, m, OCH_2), 4.16-4.24 (4 H, m, $OC\mathit{H}_2Me$), 4.25-4.37 (4 H, m, OCH_2) and 4.82 (1 H, br s, $HC=N_2$); δ_C 16.0 (Me), 16.1 (Me), 46.2 (br s, $HC=N_2$), 63.5 (OCH_2), 63.7 (OCH_2), 64.3 (OCH_2), 68.7 (OCH_2), 69.1 (OCH_2), 163.9 (C=O) and 164.9 (C=O); *m/z* (CI) 350 ($M-N_2$, 100%).

4-(Ethoxycarbonyldiazoacetoxy)butyl (diethoxyphosphoryl)diazoacetate 25

Prepared from the alcohol **16** and the diazo acid chloride **20**.[46] The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in ether) to yield the *title compound* as a pale yellow oil (86%), (Found: $M+NH_4^+$, 452.1546. $C_{15}H_{23}N_4O_9P + NH_4$ requires 452.1546); υ_{max} (neat)/cm^{-1} 2985, 2941, 2909, 2135, 1759, 1736, 1702, 1324, 1282, 1217, 1166, 1094, 1047, 1022 and 979; δ_H 1.27-1.36 (9 H, m, $OCH_2\mathit{Me}$), 1.72-1.77 (4 H, m, CH_2CH_2), and 4.12-4.32 (10 H, m, 2 x OCH_2 and $OC\mathit{H}_2Me$); δ_C 14.2 (Me), 16.0 (Me), 16.1 (Me), 25.1 (CH_2), 25.2 (CH_2), 61.7 (OCH_2Me), 63.5 (OCH_2Me), 63.6 (OCH_2Me), 64.7 (CH_2O), 64.8 (CH_2O), 160.97 (C=O), and 161.01 (C=O, only 2 signals observed); *m/z* (CI) 452 ($M+NH_4^+$, 36%), 407 (27), 214 (24), 196 (100), 179 (84), 156 (28) and 71 (34).

O-H Insertion Reactions

(a) Using rhodium(II) acetate

4-(α-Methoxyphenylacetoxy)butyl (diethoxyphosphoryl)diazoacetate 26

Rhodium acetate (5.05 mg, 2 mol%) was added to a vigorously stirring solution of the bis(diazo) compound **21** (250 mg, 5.71 x 10^{-4} mol), methanol (1.13 x 10^{-3} mol, 2 equiv.). When TLC analysis showed complete consumption of the starting material, the solvent was removed *in vacuo* and the residue was purified by column chromatography (silica, 1:1 ethyl acetate-ether) to afford the *title compound* as a colourless oil (90 mg, 36%), (Found: $M+NH_4^+$, 460.1849. $C_{19}H_{27}N_2O_8P + NH_4$ requires 460.1849); υ_{max} (neat)/cm^{-1} 2984, 2963, 2933, 2131, 1750, 1735, 1707, 1702, 1466, 1455, 1391, 1370, 1281, 1201, 1176, 1108, 1075, 1022, 981, 797, 743 and 699; δ_H 1.25-1.31 (6 H, m, *J* 6.7, $OCH_2\mathit{Me}$), 1.50-1.62 (4 H, m, CH_2CH_2), 3.34 (3 H, s, OMe), 4.04-4.19 (8 H, m, 2 x OCH_2 and $OC\mathit{H}_2Me$), 4.69 (1 H, s, PhC*H*) and 7.20-7.38 (5 H, m, ArH); δ_C 16.2 (Me), 16.3 (Me), 25.75 (CH_2), 24.81 (CH_2), 57.2 (OMe), 63.9 (CH_2O), 64.0 (CH_2O), 64.2 (CH_2O), 65.8 (CH_2O), 82.4 (Ph*C*H), 127.1 (ArCH), 128.6 (ArCH), 128.7 (ArCH), 137.0 (ArC), 170.6 (C=O), and 174.7 (C=O); *m/z* (CI) 460 ($M+NH_4^+$, 8%), 434 (12), 417 (15), 256 (22), 196 (36), 184 (100) and 121 (47).

2-(α-Methoxyphenylacetoxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 27

Prepared from **22** as described above. The residue was purified by column chromatography (silica, 1:9 ethyl acetate-ether to afford the *title compound* as a colourless oil (60%), (Found: M^+, 458.1449. $C_{19}H_{27}N_2O_9P$ requires 458.1450); υ_{max} (neat)/cm^{-1} 2986, 2954, 2941, 2934, 2131, 1751, 1733, 1710, 1455, 1393, 1376, 1369, 1280, 1208, 1202, 1179, 1112, 1106, 1077, 1022, 981, 743 and 699; δ_H 1.33-1.37 (6 H, m, $OCH_2\mathit{Me}$), 3.41 (3 H, s, OMe), 3.48-3.68 (4 H, m, CH_2O), 4.18-4.27 (8 H, m, 2 x OCH_2 and $OC\mathit{H}_2Me$), 4.80 (1 H, s, PhC*H*) and 7.34-7.46 (5 H, m, ArH); δ_C 16.1 (Me), 16.2 (Me), 57.3 (OMe), 63.7 (CH_2O), 63.8 (CH_2O), 64.1 (CH_2O), 64.4 (CH_2O), 64.7 (CH_2O), 68.8 (CH_2O), 82.7 (Ph*C*H), 127.2 (ArCH), 128.8 (ArCH), 128.9 (ArCH), 136.1 (ArC), 163.2 (d, J_{CP} 12.3, C=O), and 170.6 (C=O); *m/z* (CI) 476 ($M+NH_4^+$, 100%) and 328 (60).

4-(Methoxyacetoxy)butyl (diethoxyphosphoryl)diazoacetate 30

Prepared from **23** according to the procedure described above. The crude product was purified by column chromatography (silica gel, 5% ethyl acetate in ether) to yield the *title compound* as a colourless oil (90%), (Found: MH^+, 367.1270. $C_{13}H_{23}N_2O_8P$ + H requires 367.1270); υ_{max} (neat)/cm^{-1} 2984, 2964, 2934, 2131, 1755, 1733, 1705, 1450, 1393, 1282, 1212, 1193, 1165, 1129, 1022, 979 and 747; δ_H 1.30 (6 H, t, *J* 7.1, OCH_2*Me*), 1.66-1.72 (4 H, m, CH_2CH_2), 3.38 (3 H, s, OMe), 3.97 (2 H, s, C*H*$_2$OMe) and 4.07-4.21 (8 H, m, 2 x OCH_2 and OC*H*$_2$Me); δ_C 16.5 (Me), 16.6 (Me), 25.4 (CH_2), 25.7 (CH_2), 59.8 (MeO), 64.0 (CH_2O), 64.5 (CH_2O), 65.3 (CH_2O), 67.0 (CH_2O), 70.1 (CH_2O), 167.7 (d, J_{CP} 49.2, C=O), and 170.0 (C=O); *m/z* (CI) 367 (MH^+, 13%), 358 (14), 341 (24), 196 (46), 179 (38), 178 (100) and 71 (45).

2-(Methoxyacetoxyethoxy)ethyl (diethoxyphosphoryl)diazoacetate 31

Prepared from **24** as detailed above. The product was purified by column chromatography (silica, 1:9 ethyl acetate-ether) to afford the *title compound* as a colourless oil (57%); (Found: $M+NH_4^+$, 382.1140. $C_{13}H_{23}N_2O_9P$ requires 382.1141); υ_{max} (neat)/cm^{-1} 2986, 2132, 1750, 1710, 1455, 1371, 1281, 1209, 1202, 1178, 1115, 1108, 1077, 1023, 981, 742 and 699; δ_H (400 MHz) 1.35-1.39 (6 H, m, OCH_2*Me*), 3.46 (3 H, s, OMe), 3.71-3.73 (4 H, m, CH_2O), 4.07 (2 H, s, C*H*$_2$OMe), 4.17-4.27 (4 H, m, OC*H*$_2$Me) and 4.28-4.37 (4 H, m, CH_2O); δ_C (100 MHz) 16.1 (Me), 16.2 (Me), 59.4 (OMe), 63.6 (CH_2O), 64.4 (CH_2O), 68.6 (CH_2O), 68.87 (CH_2O), 68.89 (CH_2O), 69.7 (CH_2O), 77.4 (MeO*C*H$_2$), 163.3 (d, J_{CP}12.1, C=O), and 170.2 (C=O); *m/z* (CI) 400 ($M+NH_4^+$, 100%), 383 (MH^+, 45), and 328 (25).

(b) Using rhodium(II) trifluoroacetamide: general procedure

The diazo phosphonate (1 mmol) was taken up into dry toluene (50 ml) and to this was added methanol (2 mmol; or 4 mmol for bis(diazo) compounds) and rhodium(II) trifluoracetamide (2 mol%). The mixture was heated to reflux overnight and upon cooling, the solvent was removed *in vacuo* before the crude material was purified by column chromatography.

4-(α-Methoxyphenylacetoxy)butyl (diethoxyphosphoryl)methoxyacetate 28

The residue was purified by column chromatography (silica, 1:9 ethyl acetate-ether) to afford the *title compound* as a colourless oil (88%); (Found: M^+, 446.1706. $C_{20}H_{31}O_9P$ requires 446.1705); υ_{max} (neat)/cm^{-1} 2984, 2962, 2934, 2914, 1749, 1455, 1331, 1261, 1186, 1179, 1119, 1050, 777, 732 and 700; δ_H (400 MHz) 1.31-1.35 (6 H, m, OCH_2*Me*), 1.61-1.71 (4 H, m, CH_2CH_2), 3.40 (3 H, s, MeO), 3.52 (3 H, s, MeO), 4.14-4.24 (9 H, m, C*H*OMe, 2 x OCH_2, and OC*H*$_2$Me), 4.76 (1 H, s, C*H*OMe) and 7.32-7.44 (5 H, m, ArH); δ_C (100 MHz) 18.2 (2 C, Me), 25.0 (CH_2), 25.1 (CH_2), 57.3 (OMe), 60.4 (d, J_{CP} 51.6, PCHO*Me*), 63.7 (OCH_2), 63.8 (OCH_2), 64.5 (O*C*H$_2$Me), 65.0 (O*C*H$_2$Me), 77.5 (d, J_{CP}175.6, P*C*HOMe), 82.6 (Ph*C*HOMe), 127.2 (ArCH), 128.9 (ArCH), 130.0 (ArCH), 136.3 (ArC), 162.7 (C=O), and 170.7 (C=O); *m/z* (CI) 464 ($M+NH_4^+$, 100%), 447 (MH^+, 35), and 328 (40).

2-(α-Methoxyphenylacetoxyethoxy)ethyl (diethoxyphosphoryl)methoxyacetate 29

The residue was purified by column chromatography (silica, 1:9 ethyl acetate-ether) to afford the *title compound* as a pale yellow oil (77%); (Found: M^+, 462.1673. $C_{20}H_{31}O_{10}P$ requires 462.1655); υ_{max} (neat)/cm^{-1} 2984, 2954, 2932, 1751, 1456, 1261, 1190, 1119, 1027, 978 and 733; δ_H 1.26-1.37 (6 H, m, OCH_2*Me*), 3.41 (3 H, s, MeO), 3.51 (3 H, s, MeO), 3.57-3.66 (4 H, m, CH_2O), 4.15-4.30 (9 H, m, 2 x OCH_2, C*H*OMe and OC*H*$_2$Me), 4.80 (1 H, s, C*H*OMe) and 7.31-7.49 (5 H, m, ArH); δ_C 16.2 (Me), 16.3 (Me), 57.2 (OMe), 60.3 (d, J_{CP}13.0, PCHO*Me*), 63.57 (OCH_2), 63.62 (OCH_2), 63.67 (OCH_2), 63.73 (OCH_2), 64.0 (OCH_2), 64.4 (OCH_2), 78.1 (d, J_{CP} 157.3, P*C*HOMe), 82.3 (Ph*C*HOMe), 127.1 (ArCH), 128.5 ArCH), 128.7 (ArCH), 136.0 (ArC), 167.1 (C=O), and 170.5 (C=O); *m/z* (EI) 462 (M^+, 50%), 447 (95) and 121 (100).

4-(Methoxyacetoxy)butyl (diethoxyphosphoryl)methoxyacetate 32

Prepared according to the procedure outlined above. The crude product was purified by column chromatography (silica gel, ethyl acetate) to yield the *title compound* as a colourless oil (63%), (Found: MH^+, 371.1417. $C_{14}H_{27}O_9P$ + H requires 371.1471); υ_{max} (neat)/cm^{-1} 2957, 2925, 2854, 1750, 1464, 1455, 1261, 1190, 1124, 1049, 1024 and 976; δ_H 1.25-1.31 (6 H, m, $OCH_2\mathit{Me}$), 1.68-1.74 (4 H, m, CH_2CH_2), 3.38 (3 H, s, OMe), 3.45 (3 H, s, OMe), 3.96 (2 H, s, CH_2OMe) and 4.08-4.22 (9 H, m, 2 x OCH_2, OCH_2Me and PC*H*OMe); δ_C 16.2 (Me), 16.3 (Me), 25.0 (CH_2), 25.1 (CH_2), 59.3 (MeO), 60.4 (d, J_{CP}12.9, PCHO*Me*), 63.5 (CH_2O), 63.7 (CH_2O), 64.1 (CH_2O), 65.0 (CH_2O), 69.7 (CH_2OMe), 78.3 (d, J_{CP}157.5, PC*H*OMe), 167.2 (C=O), and 170.2 (C=O); *m/z* (CI) 388 ($M+NH_4^+$, 46%), 371 (MH^+, 100), 180 (4), 156 (7), 139 (5), 108 (6), 45 (7) and 44 (16).

4-(Ethoxycarbonyl-1-methoxyacetoxy)butyl (diethoxyphosphoryl)methoxyacetate 33

The residue was purified by column chromatography (silica, 1:9 ethyl acetate-ether) to afford the *title compound* as a pale yellow oil (55%); (Found: $M+NH_4^+$, 442.1604. $C_{17}H_{31}O_{11}P$ requires 442.1604); υ_{max} (neat)/cm^{-1} 2984, 2938, 1746, 1330, 1260, 1191, 1122, 1027, 978 and 733; δ_H 1.25-1.34 (9 H, m, $OCH_2\mathit{Me}$), 1.73-1.78 (4 H, m, CH_2CH_2), 3.48 (3 H, s, MeO), 3.49 (3 H, s, MeO), 4.514-4.29 (11 H, m, 2 x OCH_2, OCH_2Me and PC*H*OMe) and 4.37 (1 H, s, C*H*OMe); δ_C 14.0 (Me), 16.2 (Me), 16.3 (Me), 24.87 (CH_2), 24.93 (CH_2), 59.6 (OMe), 60.4 (d, J_{CP}12.8, PCHO*Me*), 62.0 (OCH_2), 63.5 (OCH_2), 63.7 (OCH_2), 64.9 (OCH_2Me), 65.2 (OCH_2Me), 77.5 (d, J_{CP}157.4, PCHOMe), 80.3 (*C*HOMe), 167.0 (C=O), 178.1 (C=O), and 179.7 (C=O); *m/z* (CI) 460 ($M+NH_4^+$, 100%), 443 (MH^+, 35), 316 (20), 258 (25), and 180 (25).

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