2(3*H*)-Oxazolones from α-Hydroxy Amides and Keteneylidenetriphenylphosphorane via a Phoshorus Ylide Cascade

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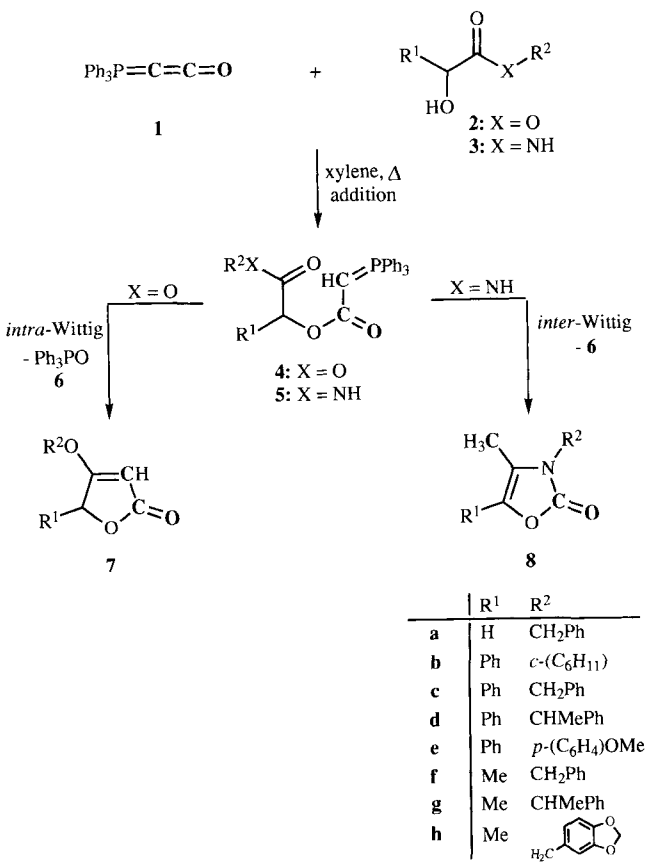
Upon heating in xylene α-hydroxyamides **3** react with the cumulated phosphorus ylide **1** to give the substituted 2(3*H*)-oxazolones **8** in 40–80% yield. The reaction proceeds via an addition/cyclization/*inter*molecular-Wittig olefination sequence, which implies three different types of phosphorus ylides of increasing "ylide activity". Evidence for the proposed mechanism is provided by trapping the intermediate ylide species with suitable carbonyl compounds. This technique may also be used to exclusively prepare the 2,4-oxazolidinediones **13** in good yields.

We recently reported on the synthesis of tetronates **7** from keteneylidenetriphenylphosphorane **1**[1] and α-hydroxyesters **2** by an addition/*intra*molecular-Wittig olefination sequence[2]. This reaction was extended meanwhile to esters bearing OH, SH, or NHR groups in α-, β-, or γ-position, which provides an easy access to the corresponding five- to seven-membered β-alkoxy-substituted heterocycles[3]. In the context of ongoing applications to the synthesis of natural products we then used amides **3** instead of the esters **2**, anticipating formation of the corresponding β-amino substituted butenolides because similar Wittig olefination reactions with the carbonyl group of amides are well-known[4]. However, what we eventually found were the 4-methyl-2-(3*H*)-oxazolones **8** (Scheme 1).



	R¹	R²
a	H	CH_2Ph
b	Ph	*c*-(C_6H_{11})
c	Ph	CH_2Ph
d	Ph	CHMePh
e	Ph	*p*-(C_6H_4)OMe
f	Me	CH_2Ph
g	Me	CHMePh
h	Me	

Yields lay between 40 and 80% when the reactions were carried out in refluxing xylene over a period of 8 h (or in a sealed glass ampulla at 165°C for 2 d in the cases of **8a** and **8g**). If amides **9** with a tertiary alcohol function were employed, then different products resulted. Compound **9a** for instance, featuring relatively small methyl residues, gave rise to a virtually inseparable mixture of 4-methylene-2-oxazolidinone **10a** (65%) and 2,4-oxazolidinedione **11a** (25%). Bulkier groups in α-position, such as the two phenyl rings in **9b**, led to the exclusive formation of 2,4-oxazolidinediones like **11b** (ca. 60% yield) as is shown in Scheme 2.

These findings strongly suggest the following mechanistic proposal. Addition of the hydroxy group of **3** to the ylide **1** furnishes the ester ylide **5**, which (unlike **4**) does not undergo an *intra*molecular Wittig olefination but rather cyclizes to the 2,4-oxazolidinedione **13** by attack of the amide nitrogen atom on the ester carbonyl group and subsequent expulsion of methylenetriphenylphosphorane **12**. In an *inter*molecular Wittig reaction, **12** then olefinates **13** at the keto group in 4-position (amide type), which is more reactive than the keto group in 2-position (urethane type), to give the *exo*-methylene compound **14**. Normally, a quick tautomerization to give the product heterocycles **8** ensues and only amides **9**, lacking α-protons, furnish unrearranged 4-methylene-2-oxazolidinones like **10a** besides the unolefinated ketone **11a**. In the case of sterically demanding α-resi-

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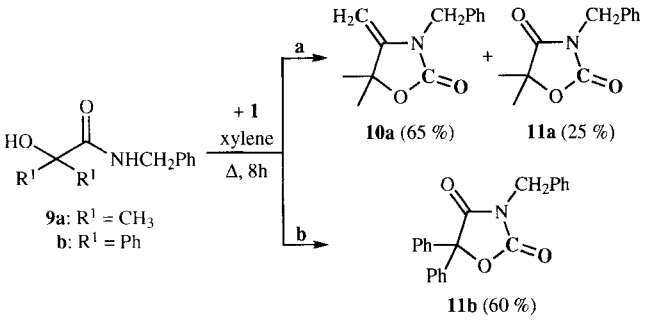
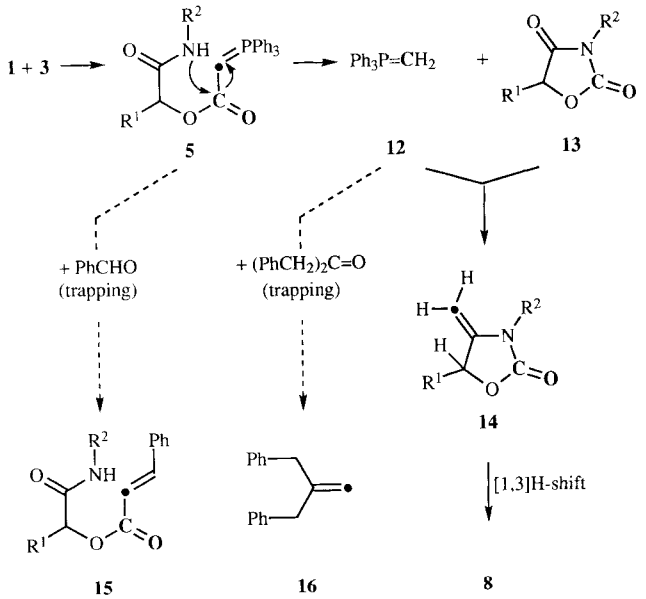


dues only the keto compounds like **11b** are found. Minor quantities (5–20%) of the intermediate 2,4-oxazolidinediones **13** are frequently found as by-products to **8** as well, but can be easily separated by column chromatography.



Although a couple of similar heterocyclization reactions with possible extrication of methylenetriphenylphosphorane have been reported in the literature[5–7], our reaction sequence is unusual insofar as it implies three different types of phosphorus ylides with increasing "Wittig reactivity". The cumulated ylide **1** reacts only sluggishly with aldehydes; the stabilized esterylides **5** should react quickly with aldehydes but rather slowly with ketones and **12** is known to form olefins even with ketones within a couple of minutes. These differences in the ylide reactivities can be used to trap the relevant intermediates **5** and **12**. If benzaldehyde is added to the mixture of **1** and **3** prior to heating, the esterylide **5** is formed as usual in refluxing xylene but then does not cyclize to **13** but undergoes an *inter*molecular Wittig olefination with benzaldehyde to the cinnamoate **15** and phosphane oxide **6**. Heating mixtures of **1**, **3**, and diphenylacetone under standard conditions results in the formation of **6** together with 2,4-dioxooxazolidines **13** and 1,1-dibenzylethene **16**, which is the Wittig product of **12** and the ketone added. This is not only strong evidence for the occurence of free ylide **12** but also a preparative route to **13**. Alternative moderate-yield syntheses of diones **13** and **11** based on the vigorous pyrolysis of carbonate esters of α-hydroxyamides are described in the literature[8]. Such diones are of considerable interest because of their analgetic, hypnotic, or anticonvulsant activity, for instance in the treatment of petit mal epilepsy[9–11].

In summary, an expedient method for the synthesis of 5-substituted 4-methyl-2(3*H*)-oxazolones and 2,4-oxazolidinediones from α-hydroxyamides has been found. So now α-hydroxycarboxylic esters can either be reacted directly with **1** to give tetronates or tetronic acid derivatives according to our previous findings, or they can be first aminolyzed to the amides to give the corresponding oxazolidine derivatives upon subsequent reaction with **1**. We are now trying to extend this reaction towards syntheses of six- and seven-membered heterocycles. β- and γ-hydroxy amides should open up a quick entry into the series of 1,3-oxazine-2-ones and 1,3-oxazepine-2-ones, which are heterocycles of basically considerable pharmaceutical relevance.

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Experimental Section

All reactions were set under a blanket of N_2. Solvents were purified as usual. Ylide **1**[1] was prepared as published; the amides **3** were prepared by aminolysis of the corresponding commercially available carboxylic esters. – Column chromatography: silica gel Si 60, Merck KGaA, Darmstadt, 63–200 μm. – The temperatures quoted are not corrected. – NMR: Jeol JNMX GX-400 (400 MHz and 100.5 MHz, for ^1H and ^{13}C, respectively). $CDCl_3$ as solvent, TMS as internal standard. The degree of substitution of the C atoms was determined by the DEPT-135, C–C coupling constants by the INADEQUATE method. δ is given in ppm – IR: Perkin-Elmer 1420. – MS: Varian MAT CH-4B (EFO-4B-source), Varian MAT 311A (EI/FD source). – MA: Heraeus Mikromat C–H–N.

1. *General Procedure for the Reaction of α-Hydroxy Amides* **3** *and* **9** *with Keteneylidenetriphenylphosphorane* **1**: A solution of 8.0 mmol of α-hydroxyamide **3** or **9**, 3.02 g (10.0 mmol) of keteneylidenetriphenylphosphorane **1**, and catalytic amounts of benzoic acid (for initial protonation of **1**) in 70 ml of xylene was refluxed for 8 h. For the syntheses of **8a** and **8g** this mixture was heated to 165 °C in a sealed glass tube for two days. The solvent was then evaporated and the residue chromatographed over silica gel with diethyl ether/*n*-pentane. Products **8** were always eluted as second fractions after various amounts of by-products **13** (5–20%) in each case.

1.1. *Synthesis of 4-Methyl-2(3H)-oxazolones* **8**

3-Benzyl-4-methyl-2(3H)-oxazolone (**8a**): 0.77 g (51%) from 1.32 g of **3a**, brown oil, b.p. 110–115 °C/0.09 Torr, eluted with diethyl ether/*n*-pentane (1:5). – IR (film): $\tilde{\nu}$ = 3140 cm^{-1}, 3020, 2920, 1740, 1650, 1390, 1060. – ^1H NMR: δ = 1.90 (s, 3H, CH_3), 4.77 (s, 2H, CH_2), 6.58 (s, 1H, 5-H), 7.24–7.37 (m, 5H, ArH). – ^{13}C NMR: δ = 9.0 (CH_3), 45.2 (CH_2), 123.4 (CH), 124.1 (C_q), 127.1, 128.0, 128.9 (ArCH), 136.1, 156.6 (C_q). – MS (70 eV); *m/z* (%) = 189 (40) [M^+], 91 (100) [$PhCH_2^+$]. – $C_{11}H_{11}NO_2$ (189.2): calcd. C 69.83, H 5.87, N 7.40; found C 69.85, H 5.88, N 7.47.

3-Cyclohexyl-4-methyl-5-phenyl-2(3H)-oxazolone (**8b**): 1.00 g (48%) from 1.86 g of **3b**, yellow solid, m.p. 111–114 °C, eluted with

diethyl ether/*n*-pentane (1:1). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3020 cm^{-1}, 2910, 2840, 1730, 1350. – ^1H NMR: δ = 1.23–1.39 (m, 3H, CH_2), 1.68–1.91 (m, 5H, CH_2), 2.12–2.21 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 3.64–3.70 (m, 1H, NCH), 7.25–7.46 (m, 5H, ArH). – ^{13}C NMR: δ = 9.9 (CH_3), 24.9, 25.9, 30.0 (CH_2), 54.2 (CH), 118.8 (C_q), 125.2, 127.3 (ArCH), 128.4 (C_q), 128.5 (ArCH), 134.0, 154.1 (C_q). – MS (70 eV); *m/z* (%) = 257 (50) [M^+], 175 (100) [$M^+ - C_6H_{12}$]. – $C_{16}H_{19}NO_2$ (257.3): calcd. C 74.67, H 7.46, N 5.44; found C 74.70, H 7.48, N 5.50.

3-Benzyl-4-methyl-5-phenyl-2(3H)-oxazolone (**8c**): 1.51 g (71%) from 1.93 g of **3c**, yellow solid, m.p. 91 °C, eluted with diethyl ether/*n*-pentane (2:1). – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 1750, 1500, 1400, 1060. – ^1H NMR: δ = 2.10 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 7.24–7.48 (m, 10H, ArH). – ^{13}C NMR: δ = 9.6 (CH_3), 45.4 (CH_2), 119.0 (C-4), 125.0, 127.0, 127.5, 128.0 (ArCH), 128.3 (C-5), 128.7, 129.0 (ArCH), 134.3, 136.1 (C_q), 155.3 (C-2). – MS (70 eV); *m/z* (%) = 265 (45) [M^+], 118 (20), 105 (20) [$PhCH_2N^+$], 91 (100) [$PhCH_2^+$]. – $C_{17}H_{15}NO_2$ (265.3): calcd. C 76.98, H 5.66, N 5.28; found C 76.87, H 5.60, N 5.33.

4-Methyl-5-phenyl-3-(α-phenylethyl)-2(3H)-oxazolone (**8d**): 0.89 g (40%) from 2.04 g of **3d**, brown oil, b.p. 150 °C/0.09 Torr, eluted with diethyl ether/*n*-pentane (2:1). – IR (film): $\tilde{\nu}$ = 3020 cm^{-1}, 1730, 1650, 1340, 680. – ^1H NMR: δ = 1.89 (d, *J* = 7.33 Hz, 3H, CH_3), 2.01 (s, 3H, CH_3), 5.44 (q, *J* = 7.33 Hz, 1H, CH), 7.23–7.44 (m, 10H, ArH). – ^{13}C NMR: δ = 10.1, 18.4 (CH_3), 52.2 (CH), 119.0 (C_q), 125.2, 126.5, 127.5, 127.8 (ArCH), 128.3 (C_q), 128.6, 128.8 (ArCH), 134.4, 139.9, 154.9 (C_q). – MS (70 eV); *m/z* (%) = 279 (90) [M^+], 225 (80), 175 (100) [$M^+ - PhCH_2CH_3$], 120 (60) [$PhCHCH_3NH^+$], 106 (70) [$PhCH_2CH_3^+$]. – $C_{18}H_{17}NO_2$ (279.3): calcd. C 77.40, H 6.14, N 5.02; found C 77.51, H 6.07, N 5.19.

3-(p-Methoxybenzyl)-4-methyl-5-phenyl-2(3H)-oxazolone (**8e**): 1.18 g (50%) from 2.17 g of **3e**, viscid yellow oil, eluted with diethyl ether/*n*-pentane (1:1). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1730 cm^{-1}, 1500, 1160, 1020. – ^1H NMR: δ = 2.17 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 4.77 (s, 2H, CH_2), 6.84–6.89 (m, 2H, ArH), 7.22–7.46 (m, 7H, ArH). – ^{13}C NMR: δ = 9.5 (CH_3), 44.8 (CH_2), 55.2 (OCH_3), 114.2 (ArCH), 118.9 (C_q), 124.8, 127.4 (ArCH), 128.0, 128.2 (C_q), 128.5, 128.6 (ArCH), 134.2, 155.3, 159.2 (C_q). – MS (70 eV); *m/z* (%) = 295 (8) [M^+], 121 (100) [$CH_2(C_6H_4OCH_3^+$]. – $C_{18}H_{17}NO_3$ (295.3): calcd. C 73.21, H 5.81, N 4.74; found C 73.29, H 5.85, N 4.67.

3-Benzyl-4,5-dimethyl-2(3H)-oxazolone (**8f**)[12]: 1.31 g (81%) from 1.43 g of **3f**, white solid, m.p. 88–89 °C (ref.[12] 90–91 °C), eluted with diethyl ether/*n*-pentane (2:1). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2900 cm^{-1}, 1740, 1690, 1370. – ^1H NMR: δ = 1.82 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 4.72 (s, 2H, CH_2), 7.24–7.35 (m, 5H, ArH). – ^{13}C NMR: δ = 8.1, 9.8 (CH_3), 45.3 (CH_2), 117.3 (C_q), 127.3, 127.8, 128.8 (ArCH), 131.6, 136.5, 156.0 (C_q). – MS (70 eV); *m/z* (%) = 203 (40) [M^+], 91 (100) [$PhCH_2^+$].

4,5-Dimethyl-3-(α-phenylethyl)-2(3H)-oxazolone (**8g**): 0.69 g (40%) from 1.54 g of **3g**, brown oil, b.p. 95–100 °C/0.09 Torr, eluted with diethyl ether/*n*-pentane (2:1). – IR (film): $\tilde{\nu}$ = 3020 cm^{-1}, 1740, 1690, 1540, 690. – ^1H NMR: δ = 1.68 (s, 3H, CH_3), 1.81 (d, *J* = 7.70 Hz, 3H, CH_3), 1.98 (s, 3H, CH_3), 5.33 (q, *J* = 7.70 Hz, 1H, CH), 7.26–7.37 (m, 5H, ArH). – ^{13}C NMR: δ = 8.8, 9.7, 18.3 (CH_3), 51.8 (CH), 117.2 (C_q), 126.5, 127.6, 128.6 (ArCH), 131.7, 140.2, 155.6 (C_q). – MS (70 eV); *m/z* (%) = 217 (30) [M^+], 113 (60) [$M^+ - PhCCH_3$], 105 (100) [$PhCHCH_3^+$]. – $C_{13}H_{15}NO_2$ (217.3): calcd. C 71.85, H 6.97, N 6.45; found C 71.80, H 7.02, N 6.50.

4,5-Dimethyl-3-[3,4-(methylenedioxy)benzyl]-2(3H)-oxazolone (**8h**): 1.05 g (53%) from 1.78 g of **3h**, fine yellow needles, m.p. 82 °C, eluted with diethyl ether/*n*-pentane (2:1). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2920 cm^{-1}, 1750, 1690, 1480, 1430, 1030. – ^1H NMR: δ = 1.85 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 4.61 (s, 2H, NCH_2), 5.94 (s, 2H, CH_2), 6.70–6.76 (m, 3H, ArH). – ^{13}C NMR: δ = 8.1, 9.8 (CH_3), 45.2 (NCH_2), 101.2 (CH_2), 107.8, 108.4 (ArCH), 117.3 (C_q), 120.6 (ArCH), 130.4, 131.6, 147.3, 148.2, 156.0 (C_q). – MS (70 eV); *m/z* (%) = 247 (50) [M^+], 193 (35) [$CH_3C{=}CCH_3^+$], 150 (30) [$C_8H_8NO_2^+$], 135 (100) [$C_8H_7O_2^+$]. – $C_{13}H_{13}NO_2$ (247.2): calcd. C 63.15, H 5.31, N 5.67; found C 63.20, H 5.26, N 5.55.

1.2. *Synthesis of Oxazolidines* **10** *and* **11**

3-Benzyl-5,5-dimethyl-4-methyleneoxazolidine (**10a**)[13] *and 3-Benzyl-5,5-dimethyl-2,4-oxazolidinedione* (**11a**)[5] (inseparable mixture): 1.51 g (62 mol-% **10a**, 25 mol-% **11a**, acc. to NMR) from 1.54 g of **9a**, colourless oil, b.p. 100–105 °C/0.09 Torr, eluted with diethyl ether/*n*-pentane (1:1). – IR (mixture) (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3010, 2980, 2920, 1810, 1760, 1670. – ^1H NMR (**10a**): δ = 1.51 (s, 6H, 2 CH_3), 3.96 (d, *J* = 3.17 Hz, 1H, C*H*H′), 4.02 (d, *J* = 3.17 Hz, 1H, CH*H*′), 4.65 (s, 2H, NCH_2), 7.25–7.36 (m, 5H, ArH). – ^{13}C NMR (**10a**): δ = 27.9 (CH_3), 45.2, 80.6 (CH_2), 82.3 (C_q), 127.1, 127.7, 128.7 (ArCH), 135.3, 150.3, 155.9 (C_q). – ^1H NMR (**11a**): 1.54 (s, 6H, 2 CH_3), 4.66 (s, 2H, NCH_2), 7.25–7.36 (m, 5H, ArH). – ^{13}C NMR (**11a**): 23.5 (CH_3), 43.6 (CH_2), 83.8 (C_q), 128.4, 128.5, 128.9 (ArCH), 134.9, 154.4, 175.7 (C_q). – MS (mixture) (70 eV); *m/z* (%) = 219 (20) [M^+ (**11a**)], 217 (40) [M^+ (**10a**)], 91 (100) [$PhCH_2^+$].

3-Benzyl-5,5-diphenyl-2,4-oxazolidinedione (**11b**)[14]: 0.93 g (60%) from 2.54 g of **9b**, yellow needles, m.p. 137 °C (ref.[14] 139–140 °C). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3040 cm^{-1}, 1805, 1730, 1400. – ^1H NMR: δ = 4.73 (s, 2H, CH_2), 7.24–7.47 (m, 15H, ArH). – ^{13}C NMR: δ = 44.1 (CH_2), 88.8 (C_q), 126.2, 127.1, 128.4, 128.4, 128.8, 128.9, 129.3 (ArCH), 134.5, 136.5, 154.2, 172.0 (C_q). – MS (70 eV); *m/z* (%) = 343 (45) [M^+], 194 (100) [$PhCCO^+$], 91 (60) [$PhCH_2^+$].

2. *General Procedure for the Synthesis of 2,4-Oxazolidinediones* **13**; *Trapping of Methylenetriphenylphosphorane* **12** *with Diphenylacetone:* A solution of 8.0 mmol of α-hydroxyamide **3**, 3.02 g (10.0 mmol) of keteneylidenetriphenylphosphorane **1**, 1.68 g (8.0 mmol) of diphenyl acetone, and catalytic amounts of benzoic acid in 70 ml of xylene was refluxed for 8 h. The solvent was then evaporated and the residue chromatographed over silica gel with diethyl ether/*n*-pentane (1:1), whereupon 1,1-dibenzylethene came off as the first fraction ($R_f \approx 0.8–0.9$), products **13** as the second fraction ($R_f \approx 0.4–0.5$), and phosphane oxide **6** stayed at the starting point.

3-Benzyl-2,4-oxazolidinedione (**13a**)[15]: 0.85 g (56%) from 1.32 g of **3a**, yellowish solid, m.p. 44 °C (ref.[15] 44–45 °C), eluted with diethyl ether/*n*-pentane (2:1). – IR (film): $\tilde{\nu}$ = 3010 cm^{-1}, 1800, 1720, 1430, 1140. – ^1H NMR: δ = 4.67 (s, 2H, CH_2), 4.68 (s, 2H, CH_2), 7.33–7.43 (m, 5H, ArH). – ^{13}C NMR: δ = 43.8 (NCH_2), 67.9 (CH_2), 128.6, 128.9, 129.0 (ArCH), 134.5, 155.7, 170.1 (C_q). – MS (70 eV); *m/z* (%) = 191 (40) [M^+], 100 (60) [$M^+ - PhCH_2$], 91 (100) [$PhCH_2^+$].

3-Cyclohexyl-5-phenyl-2,4-oxazolidinedione (**13b**): 1.13 g (54%) from 1.86 g of **3b**, yellow solid, m.p. 79 °C, eluted with diethyl ether/*n*-pentane (1:3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3020 cm^{-1}, 2920, 1800, 1730, 1400. – ^1H NMR: δ = 1.19–1.37 (m, 3H, CH_2), 1.65–1.88 (m, 5H, CH_2), 2.01–2.15 (m, 2H, CH_2), 3.90–3.98 (m, 1H, NCH), 5.63 (s, 1H, 5-H), 7.26–7.47 (m, 5H, ArH). – ^{13}C NMR: δ = 24.8, 25.6, 28.9 (CH_2), 53.1, 79.2 (CH), 126.0, 129.1, 129.7 (ArCH), 132.0, 154.9, 171.3 (C_q). – MS (70 eV); *m/z* (%) = 259 (25) [M^+], 178 (100) [$M^+ - C_6H_{11}$], 160 (60). – $C_{15}H_{17}NO_3$ (259.3): calcd. C 69.48, H 6.62, N 5.40; found C 69.51, H 6.60, N 5.38.

3-Benzyl-5-phenyl-2,4-oxazolidinedione (**13c**)[5]: 1.28 g (60%) from 1.93 g of **3c**, white solid, m.p. 116 °C (ref.[5] 118 °C), eluted

with diethyl ether/*n*-pentane (1:1). – IR (film): $\tilde{\nu}$ = 3040 cm^{-1}, 1810, 1740, 1400, 1150. – ^1H NMR: δ 4.70 (s, 2H, CH_2), 5.69 (s, 1H, 5-H), 7.32–7.40 (m, 10H, ArH). – ^{13}C NMR: δ = 44.0 (CH_2), 80.3 (C-5), 126.0, 128.5, 128.8, 128.9, 129.1, 129.8 (ArCH), 131.5, 134.6, 155.0, 170.9 (C_q). – MS (70 eV); *m/z* (%) = 267 (60) [M^+], 222 (30) [$M^+ - CO_2$], 118 (100) [$PhCHCO^+$].

5-Methyl-3-(α-phenylethyl)-2,4-oxazolidinedione (**13g**)[5]: 1.06 g (60%) from 1.54 g of **3g**, yellow oil, b.p. 85–90°C/0.09 Torr (ref.[5] 94–98°C/0.08 Torr), eluted with diethylether/*n*-pentane (1:1). – IR (film): $\tilde{\nu}$ = 3040 cm^{-1}, 3020, 2980, 1800, 1730, 1400, 1170. – ^1H NMR: δ = 1.53 (d, *J* = 7.08 Hz, 3H, CH_3), 1.86 (d, *J* = 7.08 Hz, 3H, CH_3), 4.72–4.78 (m, 1H, CH), 5.30–5.34 (m, 1H, 5-H), 7.26–7.47 (m, 5H, ArH). – ^{13}C NMR: δ = 16.7, 16.9 (CH_3), 51.9, 75.3 (CH), 127.4, 128.3, 128.7 (ArCH), 138.8, 154.6, 173.5 (C_q). – MS (70 eV); *m/z* (%) = 219 (80) [M^+], 146 (90) [CH_3COCO^+], 105 (70) [$PhCHCH_3^+$].

3. *Synthesis of N-Benzyl-α-Cinnamoyloxyphenylacetamide* (**15c**); *Trapping of Ester Ylide* **5c** *with Benzaldehyde:* A solution of 1.93 g (8.0 mmol) of α-hydroxyamide **3c**, 3.02 g (10.0 mmol) of keteneylidenetriphenylphosphorane **1**, 0.85 g (8.0 mmol) of benzaldehyde, and catalytic amounts of benzoic acid in 70 ml of xylene was refluxed for 8 h. The solvent was then evaporated and the residue chromatographed over silica gel with ethylacetate/*n*-pentane (1:2). 2.08 g (70%) as yellow solid, m.p. 125–130°C. – IR (film): $\tilde{\nu}$ = 3300 cm^{-1}, 3050, 1740, 1720, 1660, 1150. – ^1H NMR: δ = 4.41–4.51 (m, 2H, CH_2), 6.26 (s, 1H, CH), 6.51 (d, *J* = 15.95 Hz, 1H, PhCH=C*H*), 6.72 (s, 1H, NH), 7.00–7.70 (m, 15H, ArH), 7.74 (d, *J* = 15.95 Hz, 1H, PhC*H*=CH). – ^{13}C NMR: δ = 43.2 (CH_2), 75.5, 116.6 (CH), 127.4, 127.6, 128.2, 128.6, 128.7, 128.9, 128.9 (ArCH), 130.7 (C_q), 133.9 (ArCH), 135.6, 137.7 (C_q), 146.6 (CH), 168.4, 169.3 (C_q). – MS (70 eV); *m/z* (%) = 371 (2) [M^+], 265 (10) [$M^+ - NHCH_2Ph$], 238 (100) [$M^+ - CONCH_2Ph$], 223 (25) [$M^+ - Ph(CH)_2CO_2H$]. – $C_{24}H_{21}NO_3$ (371.4): calcd. C 77.61, H 5.71, N 3.77; found C 77.63, H 5.75, N 3.80.

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