Reaction of Alkynes with Iodine Monochloride Revisited

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Experimental Section

General Methods

Precoated Merck 60 F₂₅₄ aluminum silica gel sheets were used for TLC analyses. GLC analyses were performed using two types of capillary columns: an Alltech AT-35 bonded FSOT column (30 m × 0.25 mm i.d.) and an Alltech AT-1 bonded FSOT column (30 m × 0.25 mm i.d.). Purifications by MPLC were performed using silica gel Merck 60 (particle size 0.015–0.040 mm). NMR spectra were recorded at room temperature. The ¹H NMR spectra were referenced to the residual CHCl₃ proton of CDCl₃ at 7.260 ppm downfield of TMS and the ¹³C NMR spectra were referenced to the central line of the triplet at 77.02 ppm for CDCl₃. The structures of compounds **2a-d** and **3a-e** were assigned on the basis of their ¹H and ¹³C NMR spectra recorded at 600 and 150 MHz, respectively, in CDCl₃ solution and by a combination of 2D NMR techniques which included ¹H-¹³C HSQC (Heteronuclear Single Quantum Coherence) and ¹H-¹³C HMBC (Heteronuclear Multiple Bond Correlation). The structure and stereochemistry of compounds (*E*)-**5a-d**, (*E*)-**6** and (*Z*)-**7a-e** were assigned on the basis of their ¹H and ¹³C NMR spectra recorded at 600 and 150 MHz, respectively, in CDCl₃ solution and by a combination of 2D NMR techniques which included ¹H-¹H COSY, ¹H-¹H NOESY (mixing time: 400 ms), ¹H-¹³C HSQC and ¹H-¹³C HMBC. All reactions of air- and water sensitive materials were performed in flame-dried glassware under argon, by standard syringe, cannula and septa techniques. The following compounds were prepared by published procedures: 6-undecyn-5-ol (**2d**)² and 1-phenyl-1-heptyn-3-ol (**3a**)³. 2-Butyn-1-ol (**2a**), propargyl alcohol (**4**) and 1-phenyl-1-propyne (**3g**) were commercially available.

Experimental details

Methyl (but-2-ynloxy)acetate (2b). A 60 % dispersion of NaH in mineral oil (2.52 g, 63.4 mmol) was washed with pentane (2 × 30 mL) under an argon atmosphere and the residue was diluted with THF (40 mL). A solution of 2-butyn-1-ol (**3a**) (3.16 mL, 42.25 mmol) in THF (10 mL) was then added dropwise during 10 min and the resulting mixture was stirred at room temperature. After evolution of hydrogen had ceased a solution of methyl iodoacetate (10.1 g, 50.7 mmol) in THF (20 mL) was added dropwise during 0.5 h and the resulting mixture was stirred at room temperature for 66 h and then concentrated at room temperature under reduced pressure (200 mbar). The residue was diluted with water (50 mL) and extracted with Et₂O (3 × 40 mL). The organic extract was dried over Na₂SO₄ and fractionally distilled to give **2b** (3.74 g, 56 % yield) as a colourless liquid. Bp 115–117 °C/100 mbar. EI-MS: *m/z* (%) 127 (4), 83 (25), 82 (11), 74 (100), 54 (87). IR (neat): ν 2220, 1754, 1438, 1383, 1356, 1213, 1140, 1115, 915 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 1.86 (3 H, t, *J* = 2.6 Hz, H-4'), 3.77 (3 H, s, OCH₃), 4.20 (2 H, s, H-2), 4.26 ppm (2 H, m, H-1'). ¹³C NMR (150 MHz, CDCl₃): δ 3.6 (C-4'), 51.9 (OCH₃), 58.9 (C-1'), 66.0 (C-2), 73.8 (C-2'), 83.8 (C-3'), 170.4 ppm (C-1). Anal. Calcd. for C₇H₁₀O₄: C, 53.16; H, 6.37; Found: C, 53.07; H, 6.25.

Methyl (1-butylhept-2-ynloxy)acetate (2c). This compound, which was purified by MPLC on silica gel with a mixture of petroleum ether and Et₂O (95 : 5) as eluent, was prepared in 67 % yield starting from methyl iodoacetate and 6-undecyn-5-ol (**2d**) according to the same procedure employed for the synthesis of **2b**. Compound **2c** was a pale yellow liquid. EI-MS: *m/z* (%) 198 (10), 183 (57), 167 (26), 125 (59), 41 (100). IR (neat): ν 2235, 1758, 1743, 1621, 1466, 1436, 1207, 1130, 987 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.87 (3 H, t, *J* = 7.2 Hz, H-1'), 0.87 (3 H, t, *J* = 7.2 Hz, H-11'), 1.30 (2 H, m, H-2'), 1.35 (2 H, m, H-10'), 1.39 (2 H, m, H-3'), 1.43 (2 H, m, H-9'), 1.66 (1 H, m, H-4'), 1.72 (1 H, m, H-4'), 2.17 (2 H, m, H-8'), 3.70 (3 H, s, OCH₃), 4.17 (1

H, m, H-2), 4.18 (1 H, t, $J = 6.5$ Hz, H-5'), 4.21 ppm (1 H, m, H-2). ^{13}C NMR (150 MHz, CDCl_3): δ 13.4 (C-11'), 13.9 (C-1'), 18.2 (C-8'), 21.8 (C-10'), 22.3 (C-2'), 27.3 (C-3'), 30.6 (C-9'), 35.5 (C-4'), 51.6 (OCH_3), 65.1 (C-2), 70.2 (C-5'), 77.9 (C-6'), 87.3 (C-7'), 170.9 ppm (C-1). Anal. Calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_3$: C, 69.96; H, 10.06. Found: C, 69.89; H, 10.00.

Methyl (1-butyl-3-phenylprop-2-ynoxy)acetate (3b). This compound, which was purified by MPLC on silica gel with a mixture of hexane and Et_2O (95 : 5), as eluent was prepared in 60 % yield from 1-phenyl-1-heptyn-3-ol (**3a**) and methyl iodoacetate according to the same procedure used for the synthesis of **2b**. Compound **3b** was a pale yellow liquid. EI-MS: m/z (%) 203 (15), 187 (53), 145 (100), 128 (42), 115 (68). IR (neat): ν 2226, 1755, 1490, 1441, 1284, 1210, 1120, 757, 691 cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ 0.93 (3 H, t, $J = 7.2$ Hz, H-7'), 1.30 (1 H, m, H-2), 1.39 (2 H, m, H-6'), 1.53 (2 H, m, H-5'), 1.84 (1 H, m, H-4'), 1.90 (1 H, m, H-4'), 3.74 (3 H, s, OCH_3), 4.33 (1 H, m, H-2), 4.33 (1 H, m, H-2), 4.48 (1 H, t, $J = 6.7$ Hz, H-3'), 7.29 (1 H, m, H-4''), 7.31 (2 H, m, H-3'' and H-5''), 7.42 ppm (2 H, m, H-2'' and H-6''). ^{13}C NMR (150 MHz, CDCl_3): δ 13.9 (C-7'), 22.3 (C-6'), 27.3 (C-5'), 35.3 (C-4'), 51.7 (OCH_3), 65.4 (C-2), 70.5 (C-3'), 86.6 (C-1'), 87.0 (C-2'), 122.4 (C-1''), 128.2 (C-3'' and C-5''), 128.4 (C-4''), 131.7 (C-2'' and C-6''), 170.8 ppm (C-1). Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.81; H, 7.74. Found: C, 73.69; H, 7.68.

Methyl 6-phenylhex-5-ynoate (3c). A stirred solution of 5-hexynoic acid (5.22 g, 46.55 mmol) and *p*-toluenesulfonic acid (0.58 g, 0.30 mmol) in methanol (8.5 mL) and CH_2Cl_2 (17 mL) was refluxed for 26 h. The mixture was then cooled to 20 $^\circ\text{C}$ and a 10 % aqueous NaHCO_3 solution (40 mL) was added and the resulting mixture was extracted with Et_2O (4 $\times$ 50 mL). The organic extract was dried over Na_2SO_4 and fractionally distilled to give methyl 5-hexynoate (4.64 g, 79 % yield) as a colourless liquid. Bp 104–106 $^\circ\text{C}$ /130 mbar (bp 98–100/70 mm Hg).⁴ Deaerated iodobenzene (6.41 g, 31.43 mmol) and a deaerated solution of methyl 5-hexynoate (4.65 g, 34.57 mmol) in acetonitrile (5 mL) were sequentially added to a deaerated mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.47 g, 0.67 mmol), CuI 80.25 g, 1.34 mmol) and Et_3N (14 mL) in acetonitrile (9 mL) and the resulting mixture was stirred at room temperature for 1.5 h. It was then treated with a saturated aqueous NH_4Cl solution (80 mL) and extracted with AcOEt (4 $\times$ 60 mL). The organic extract was dried over Na_2SO_4 , filtered through Celite and concentrated under reduced pressure. The residue was fractionally distilled to give **3c** (5.32 g, 79 % yield) as an orange liquid. Bp 97–98 $^\circ\text{C}$ /0.1 mbar. EI-MS: m/z (%) 202 (12), 143 (16), 141 (11), 128 (100), 115 (49). IR (neat): ν 2230, 1737, 1598, 1490, 1438, 1222, 1161, 758, 693 cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ 1.94 (2 H, m, H-3), 2.49 (2 H, m, H-4), 2.52 (2 H, m, H-2), 3.69 (3 H, s, OCH_3), 7.27 (2 H, m, H-3' and H-5'), 7.29 (1 H, m, H-4'), 7.39 ppm (2 H, m, H-2' and H-6'). ^{13}C NMR (150 MHz, CDCl_3): δ 18.9 (C-4), 23.9 (C-3), 32.9 (C-2), 51.6 (OCH_3), 81.47 (C-6), 88.8 (C-5), 123.8 (C-1'), 127.7 (C-4'), 128.2 (C-3' and C-

5'), 131.6 (C-2' and C-6'), 173.7 ppm (C-1). Anal. Calcd. for $C_{13}H_{14}O_2$: C, 78.48; H, 6.59: Found: C, 78.37; H, 6.48.

1-Phenyl-1-octyne (3d). To a deaerated mixture of iodobenzene (8.99 g, 44.06 mmol) and $Pd(PPh_3)_4$ (1.53 g, 1.32 mmol) in pyrrolidine (130 mL), which was stirred at room temperature under an argon atmosphere, was added 1-octyne (9.71 g, 88.11 mmol). After stirring at room temperature for 1.5 h the mixture was treated with a saturated aqueous NH_4Cl solution (300 mL) and extracted with Et_2O (5×70 mL). The organic extract was washed with cold 5 % sulfuric acid (3×30 mL) and water (50 mL), dried over Na_2SO_4 and filtered through Celite. The filtrate was concentrated under reduced pressure and the residue was fractionally distilled to give **5d** (7.70 g, 94 % yield) as a pale yellow liquid. The spectral properties of this compound were in agreement with those previously reported.⁵

1-(1-Butyl-3-phenylprop-2-ynoxy)-1-butane (3e). A 60 % dispersion of NaH in mineral oil (0.63 g, 14.51 mmol) was washed with pentane (2×30 mL) under an argon atmosphere and to the residue was added in one portion a solution of 1-phenyl-1-heptyn-3-ol (**3a**) 81.82 g, 9.67 mmol) in triglyme (14 mL). After evolution of hydrogen had ceased, a solution of iodobutane 82.13 g, 12.76 mmol) in triglyme (5 mL) was added dropwise during 15 min. After stirring the mixture at room temperature for 64 h, water (120 mL) was added and the mixture was extracted with Et_2O (4×50 mL). The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by MPLC on silica gel with a mixture of hexane and Et_2O (99 : 1) as eluent to give **3e** (0.73 g, 31 % yield) as a colourless liquid. EI-MS: m/z (%) 244 (M^+ , 1), 187 (49), 131 (100), 129 (13), 103 (10). IR (neat): ν 1598, 1490, 1465, 1336, 1258, 1119, 1094, 756, 691 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$): δ 0.94 (3H, t, $J = 7.3$ Hz, H-4'), 0.95 (3 H, t, $J = 7.5$ Hz, H-4''), 1.37 (2 H, m, H-3'), 1.43 (2 H, m, H-3''), 1.50 (2 H, m, H-2'), 1.61 (2 H, m, H-2''), 1.78 (1 H, m, H-1'), 1.83 (1 H, m, H-1''), 3.44 (1 H, dt, $J = 9.2$ and 6.6 Hz, H-1'''), 3.81 (1 H, dt, $J = 9.2$ and 6.6 Hz, H-1'''), 4.22 (1 H, t, $J = 6.7$ Hz, H-1), 7.30 (3 H, m, H-3''', H-4''' and H-5'''), 7.44 ppm (2 H, m, H-2''' and H-6'''). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.9 (C-4''), 14.0 (C-4'), 19.4 (C-3''), 22.5 (C-3'), 27.6 (C-2'), 31.8 (C-2''), 35.7 (C-1'), 68.7 (C-1''), (C-1), 85.2 (C-3), 89.0 (C-2), 123.1 (C-1'''), 128.1 (C-4'''), 128.2 (C-3''' and C-5'''), 131.7 ppm (C-2''' and C-6'''). Anal. Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.47; H, 9.79.

Methyl 5-phenyl-4-pentynoate (3f). A stirred solution of 4-pentynoic acid (5.00 g, 58.90 mmol), *p*-toluenesulfonic acid (0.074 g, 0.39 mmol) in methanol (10.4 mL) and CH_2Cl_2 (22 mL) was refluxed for 23 h. The mixture was cooled to room temperature, a 10 % aqueous NH_4Cl solution (50 mL) was added and the resulting mixture was extracted with Et_2O (4×50 mL). The organic extract was dried over Na_2SO_4 and concentrated. The residue was fractionally distilled to give methyl 4-pentynoate (4.69 g, 71 % yield) as a colourless liquid. Bp 88 °C/142 mbar. Deaerated iodobenzene (7.31 g, 35.83 mmol) and a deaerated solution of methyl 4-pentynoate (4.42 g, 39.43 mmol) in acetonitrile (5 mL) were sequentially added to a deaerated mixture of $PdCl_2(PPh_3)_2$ (0.50 g, 0.72 mmol), CuI (0.27 g, 1.43 mmol) and Et_3N (15 mL). The resulting mixture was stirred under argon at room temperature for 1.5 h, then treated with a saturated aqueous NH_4Cl solution (100 mL) and extracted with AcOEt (3×70 mL). The organic extract was dried over Na_2SO_4 , filtered through Celite and concentrated under reduced pressure. The residue was fractionally distilled to give **3f** (3.71 g, 55 % yield) as a pale yellow liquid. Bp 87–90 °C/0.2 mbar. EI-MS: m/z (%) 188 (M^+ , 21), 173 (29), 160 (79), 145 (23), 128 (100). IR (neat): ν 2237, 1741, 1491, 1439, 1364, 1200, 1169, 758, 693 cm^{-1} . 1H NMR (600 MHz, $CDCl_3$): δ 2.63 (2 H, m, H-2), 2.73 (2 H, m, H-3), 3.71 (3 H, s, OCH_3), 7.26 (3 H, m, H-3', H-4', and H-5'), 7.38 ppm (2 H, m, H-2' and H-6'). ^{13}C NMR (150 MHz, $CDCl_3$): δ 15.3 (C-3), 33.4 (C-2), 51.7 (OCH_3), 81.1 (C-5), 87.9 (C-4), 123.5 (C-1'), 127.8 (C-4'), 128.2 (C-3' and C-5'), 131.6 (C-2' and C-6'), 172.3 ppm (C-1). Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43: Found: C, 76.49; H, 6.37.

General Procedure for the Addition of Iodine Monochloride to Alkynes 2 and 3. To a deaerated solution of an alkyne **3** or **5** (5.70 mmol) in dry 1,2-dichloroethane (30 mL) was added a 1 M CH₂Cl₂ solution of ICl (**1**) (5.70 mL, 5.70 mmol) and the mixture was stirred in the dark under argon at room temperature until completion of the reaction. It was then poured into a cold 10 % aqueous NaHCO₃ solution (50 mL) and extracted with CH₂Cl₂ (3 × 30 mL). The organic extract was washed with a 10 % aqueous Na₂S₂O₃ solution (20 mL) and water (30 mL), dried over Na₂SO₄, analyzed by GLC and GLC/MS, and concentrated under reduced pressure. The residue was purified by MPLC on silica gel. This procedure was used to prepare (*E*)-**5a**, (*E*)-**5c**, (*E*)-**5d** from **2a**, **2c** and **2d**, respectively, and to synthesize (*E*)-**7a–e** from **3a–e**. A similar procedure was employed to prepare (*E*)-**5b** from **2b**, but 1.4 equiv of ICl in CH₂Cl₂ solution were used. Compound **6** was prepared from **4** by a procedure similar to that used for the synthesis of compounds (*E*)-**5a**, (*E*)-**5c**, (*E*)-**5d**, and (*E*)-**7a–e**, but the reaction was performed in CH₂Cl₂ solution. It is worth mentioning that GLC analysis of the crude products which derived from the addition of iodine monochloride to **2b–d**, **3a–e** and **3g** showed that compounds (*E*)-**5b–d** and (*E*)-**7a–f** so obtained were stereoisomerically pure. On the other hand, GLC analysis of the crude product which derived from the addition of iodine monochloride to **2a** showed that compound (*E*)-**5a** so obtained was contaminated by less than 10 % of the corresponding (*Z*)-stereoisomer. Finally, it should be noted that a procedure similar to that used to prepare compounds (*E*)-**5** and (*E*)-**7** was employed to prepare compound **10** from **3f**, but in this last case the reaction was performed at 0 °C.

(*E*)-3-Chloro-2-iodo-2-buten-1-ol [(*E*)-5a]. The crude product, which was obtained by reaction of 2-butyne-1-ol (**2a**) with **1** at room temperature for 1.5 h, was purified by MPLC on silica gel with a mixture of petroleum ether and Et₂O (80 : 20) as eluent to give (*E*)-**5a** as an orange liquid in 75 % yield. EI-MS: *m/z* (%) 232 (M⁺, 13), 127 (8), 105 (18), 69 (19), 41 (100). IR (neat): ν 3301, 1624, 1427, 1376, 1231, 1081, 1017, 929, 678 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 2.41 (3 H, s, H-4), 4.45 ppm (2 H, s, H-2). ¹³C NMR (150 MHz, CDCl₃): δ 30.6 (C-4), 67.8 (C-1), 99.4 (C-2), 129.7 ppm (C-3). Anal. Calcd. for C₄H₆IO: C, 20.67; H, 2.60. Found: C, 20.61; H, 2.49.

Methyl [(*E*)-3-chloro-2-iodobut-2-enyloxy]acetate [(*E*)-5b]. The crude product, which was obtained by reaction of **2b** with **1** at room temperature for 23 h, was purified by MPLC on silica gel with a mixture of hexane and Et₂O (65 : 35) as eluent to give (*E*)-**5b** as an orange liquid in 41 % yield. EI-MS: *m/z* (%) 269 (1), 231 (55), 215 (83), 177 (100), 119 (45). IR (neat): ν 1755, 1624, 1437, 1378, 1284, 1213, 1137, 1041, 679 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 2.44 (3 H, s, H-4'), 3.77 (3 H, s, OCH₃), 4.09 (2 H, s, H-2), 4.50 ppm (2 H, s, H-1'). ¹³C NMR (150 MHz, CDCl₃): δ 30.9 (C-4'), 52.0 (OCH₃), 66.5 (C-2), 74.8 (C-1'), 94.5 (C-2'), 132.3 (C-3'), 170.3 ppm (C-1). Anal. Calcd. for C₇H₁₀ClIO₃: C, 27.61; H, 3.31. Found: C, 27.53; H, 3.19.

Methyl (*E*)(1-butyl-3-chloro-2-iodohept-2-enyloxy)acetate [(*E*)-5c]. The crude product, which was obtained by reaction of **2c** with **1** at room temperature for 6 h, was purified by MPLC on silica gel with a mixture of petroleum ether and Et₂O (95 : 5) as eluent to give (*E*)-**5c** as an orange liquid in 58 % yield. EI-MS: *m/z* (%) 345 (18), 275 (23), 107 (14), 93 (25), 41 (100). IR (neat): ν 1758, 1608, 1437, 1378, 1284, 1208, 1120, 733, 685 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.89 (3 H, t, *J* = 7.2 Hz, H-1'), 0.94 (3 H, t, *J* = 7.4 Hz, H-11'), 1.24 (1 H, m, H-3'), 1.34 (2 H, m, H-2'), 1.34 (1 H, m, H-3'), 1.36 (2 H, m, H-10'), 1.51 (1 H, m, H-4'), 1.57 (2 H, m, H-9'), 1.70 (1 H, m, H-4'), 2.73 (2 H, m, H-8'), 3.74 (3 H, s, OCH₃), 3.83 (1 H, m, H-2), 4.05 (1 H, m, H-2), 4.13 ppm (1 H, t, *J* = 6.8 Hz, H-5'). ¹³C NMR (150 MHz, CDCl₃): δ 13.9 (C-11'), 14.0 (C-1'), 21.8 (C-10'), 22.5 (C-2'), 26.6 (C-3'), 29.1 (C-9'), 34.9 (C-4'), 43.1 (C-8'), 51.8 (OCH₃), 65.0 (C-2), 79.6 (C-5'), 105.4 (C-6'), 135.8 (C-7'), 170.5 ppm (C-1). Anal. Calcd. for C₁₄H₂₄ClIO₂: C, 43.48; H, 6.26. Found: C, 53.39; H, 6.20.

(E)-7-Chloro-6-iodoundec-6-en-5-ol [(E)-5d]. The crude product, which was obtained by reaction of **2d** with **1** at room temperature for 2.5 h, was purified by MPLC on silica gel with a mixture of petroleum ether and Et₂O (90 : 10) as eluent to give (E)-**5d** as an orange liquid in 65 % yield. EI-MS: *m/z* (%) 330 (M⁺, 5), 273 (83), 110 (22), 81 (26), 41 (100). IR (neat): ν 3359, 1612, 1464, 1379, 1108, 1031, 959, 732, 687 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.90 (3 H, t, *J* = 7.0 Hz, H-1), 0.94 (3 H, t, *J* = 7.5 Hz, H-11), 1.23 (1 H, m, H-3), 1.33 (1 H, m, H-3), 1.34 (2 H, m, H-2), 1.36 (2 H, m, H-10), 1.50 (1 H, m, H-4), 1.55 (1 H, m, H-4), 1.56 (2 H, m, H-9), 2.69 (2 H, m, H-8), 4.22 ppm (1 H, t, *J* = 6.9 Hz, H-5). ¹³C NMR (150 MHz, CDCl₃): δ 13.9 (C-11), 14.0 (C-1), 21.8 (C-10), 22.5 (C-2), 27.0 (C-3), 29.0 (C-9), 36.8 (C-4), 42.9 (C-8), 72.3 (C-5), 109.4 (C-6), 132.3 ppm (C-7). Anal. Calcd. for C₁₁H₂₀ClIO: C, 39.96; H, 6.10. Found: C, 39.85; H, 5.98

(E)-2-Chloro-3-iodoprop-2-en-1-ol [(E)-6]. The crude product, which was obtained by reaction of **4** with **1** at 0 °C for 0.5 h, was purified by MPLC on silica gel with a mixture of CH₂Cl₂ and petroleum ether (70 : 30) as eluent to give (E)-**6** as an orange liquid in 46 % yield. EI-MS: *m/z* (%) 218 (M⁺, 77), 183 (100), 153 (13), 127 (95), 91 (90). IR (neat): ν 3295, 1600, 1443, 1219, 1052, 1025, 967, 790, 671 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 4.46 (2 H, s, H-1), 6.52 ppm (1 H, s, H-3). ¹³C NMR (150 MHz, CDCl₃): δ 66.1 (C-1), 74.1 (C-3), 136.0 ppm (C-2). Anal. Calcd. for C₃H₄ClIO: C, 16.50; H, 1.85. Found: C, 16.41; H, 1.75.

(E)-1-Chloro-2-iodo-1-phenylhept-1-en-3-ol [(E)-7a]. The crude product, which was obtained by reaction of **3a** with **1** at room temperature for 3 h, was purified by MPLC on silica gel with a mixture of petroleum ether and Et₂O (80 : 20) as eluent to give (Z)-**7a** as a pale yellow solid in 70 % yield. Mp 62–64 °C. EI-MS: *m/z* (%) 350 (M⁺, 4), 223 (25), 131 (49), 102 (82), 41 (100). IR (KBr): ν 3396, 1623, 1592, 1460, 1129, 1061, 970, 862, 653 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.96 (3 H, t, *J* = 7.0 Hz, H-7), 1.42 (2 H, m, H-6), 1.47 (2 H, m, H-5), 1.67 (2 H, m, H-4), 4.37 (1 H, t, *J* = 6.9 Hz, H-2), 7.34 (2 H, m, H-2' and H-6'), 7.38 (1 H, m, H-4'), 7.40 ppm (2 H, m, H-3' and H-5'). ¹³C NMR (150 MHz, CDCl₃): δ 14.1 (C-7), 22.6 (C-6), 27.1 (C-5), 36.9 (C-4), 72.6 (C-3), 111.6 (C-2), 128.4 (C-5' and C-3'), 128.6 (C-1), 129.0 (C-2' and C-6'), 129.1 (C-4'), 141.4 ppm (C-1'). Anal. Calcd. for C₁₃H₁₆ClIO: C, 44.53; H, 4.60. Found: C, 44.45; H, 4.52.

Methyl (E)(1-butyl-3-chloro-2-iodo-3-phenylprop-2-enyloxy)acetate [(E)-7b]. The crude product, which was obtained by reaction of **3b** with **1** at room temperature for 4 h, was purified by MPLC on silica gel with a mixture of hexane and Et₂O (90 : 10) as eluent to give (E)-**7b** as a yellow solid in 83 % yield. Mp 42–44 °C. EI-MS: *m/z* (%) 333 (3), 295 (20), 277 (34), 275 (100), 163 (23). IR (KBr): ν 1756, 1591, 1443, 1377, 1282, 1209, 1122, 768, 707 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.96 (3 H, t, *J* = 7.1 Hz, H-7'), 1.41 (1 H, m, H-5'), 1.42 (2 H, q, *J* = 7.1 Hz, H-6'), 1.50 (1 H, m, H-5'), 1.67 (1 H, m, H-4'), 1.83 (1 H, m, H-4'), 3.79 (3 H, s, OCH₃), 4.01 (1 H, m, H-2), 4.19 (1 H, m, H-2), 4.30 (1 H, t, *J* = 6.8 Hz, H-3'), 7.34 (2 H, m, H-2'' and H-6''), 7.38 (1 H, m, H-4''), 7.41 ppm (2 H, m, H-3'' and H-5''). ¹³C NMR (150 MHz, CDCl₃): δ 14.0 (C-7'), 22.6 (C-6'), 26.8 (C-5'), 35.1 (C-4'), 51.9 (OCH₃), 65.4 (C-2), 79.9 (C-3'), 107.7 (C-2'), 128.4 (C-3'' and C-5''), 128.9 (C-2'' and C-6''), 129.2 (C-4''), 132.0 (C-1'), 141.4 (C-1''), 170.4 ppm (C-1). Anal. Calcd. For C₁₆H₂₀IO₂: C, 47.25; H, 4.96. Found: C, 47.12; H, 4.83.

Methyl (*E*)-(6-chloro-5-iodo-6-phenylhex-5-enoate [(*E*)-7c]. The crude product, which was obtained by reaction of **3c** with **1** at room temperature for 7 h, was purified by MPLC on silica gel with a mixture of hexane and Et₂O (96 : 4) as eluent to give (*E*)-7c as a red liquid in 75 % yield. EI-MS: *m/z* (%) 237 (66), 205 (31), 177 (42), 141 (100), 115 (85). ¹H NMR (600 MHz, CDCl₃): δ 2.00 (2 H, dt, *J* = 7.5 and 7.3 Hz, H-3), 2.45 (2 H, t, *J* = 7.5 Hz, H-2), 2.91 (2 H, t, *J* = 7.3 Hz, H-4), 3.71 (3 H, s, OCH₃), 7.34 (2 H, m, H-2' and H-6'), 7.37 (1 H, m, H-4'), 7.38 ppm (2 H, m, H-3' and H-5'). ¹³C NMR (150 MHz, CDCl₃): δ 23.7 (C-3), 32.5 (C-2), 41.3 (C-4), 51.7 (OCH₃), 99.7 (C-5), 128.4 (C-3' and C-5'), 128.9 (C-4'), 129.1 (C-2' and C-6'), 129.4 (C-6), 141.8 (C-1'), 173.5 ppm (C-1). Anal. Calcd. for C₁₃H₁₄ClIO₂: C, 42.82; H, 3.87. Found: C, 42.75; H, 3.79.

(*E*)-1-Chloro-2-iodo-1-phenyloct-1-ene [(*E*)-7d]. The crude product, which was obtained by reaction of **3d** with **1** at room temperature for 2 h, was purified by MPLC on silica gel with hexane as eluent to give (*Z*)-7d as a pale yellow liquid in 93 % yield. EI-MS: *m/z* (%) 348 (M⁺, 13), 185 (8), 151 (47), 125 (21), 115 (100). IR (neat): ν 1594, 1488, 1443, 1377, 1121, 1029, 875, 769 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.93 (3 H, t, *J* = 6.9 Hz, H-1), 1.36 (2 H, m, H-3), 1.37 (2 H, m, H-2), 1.42 (2 H, m, H-4), 1.65 (2 H, m, H-5), 2.84 (2 H, m, H-6), 7.34 (1 H, m, H-4'), 7.35 (2 H, m, H-2' and H-6'), 7.38 ppm (2 H, m, H-3' and H-5'). ¹³C NMR (150 MHz, CDCl₃): δ 14.0 (C-1), 22.6 (C-2), 28.1 (C-4), 28.4 (C-5), 31.6 (C-3), 42.1 (C-6), 101.6 (C-7), 128.2 (C-8), 128.3 (C-3' and C-5'), 128.8 (C-4'), 129.2 (C-2' and C-6'), 142.1 ppm (C-1'). Anal. Calcd. for C₁₄H₁₈ClI: C, 48.23; H, 5.20. Found: C, 48.13; H, 5.09.

(*E*)-1-(1-Butyl-3-chloro-2-iodo-3-phenylprop-2-enyloxy)butane [(*E*)-7e]. The crude product, which was obtained by reaction of **3e** with **1** at room temperature for 1 h, was purified by MPLC on silica gel with a mixture of hexane and Et₂O (99 : 1) as eluent to give (*E*)-7e as a pale yellow liquid in 74 % yield. EI-MS: *m/z* (%) 406 (M⁺, 2), 349 (67), 293 (100), 275 (14), 131 (58). IR (neat): ν 1618, 1592, 1465, 1444, 1330, 1123, 1097, 709, 693 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 0.94 (3 H, t, *J* = 7.1 Hz, H-7), 0.96 (3 H, t, *J* = 7.4 Hz, H-4'), 1.38 (1 H, m, H-5), 1.39 (2 H, m, H-6), 1.46 (2 H, m, H-3'), 1.47 (1 H, m, H-5), 1.60 (1 H, m, H-4), 1.63 (2 H, m, H-2'), 1.71 (1 H, m, H-4), 3.33 (1 H, m, H-1'), 3.53 (1 H, m, H-1'), 4.04 (1 H, t, *J* = 6.8 Hz, H-3), 7.34 (2 H, m, H-2'' and H-6''), 7.38 (1 H, m, H-4''), 7.39 ppm (2 H, m, H-3'' and H-5''). ¹³C NMR (150 MHz, CDCl₃): δ 14.0 (C-7), 14.1 (C-4'), 19.6 (C-3'), 22.6 (C-6), 27.0 (C-5), 31.8 (C-2'), 35.1 (C-4), 68.6 (C-1'), 79.5 (C-3), 110.6 (C-2), 128.4 (C-3'' and C-5''), 128.99 (C-4''), 129.04 (C-2'' and C-6''), 130.1 (C-1), 141.71 ppm (C-1''). Anal. Calcd. for C₁₇H₂₄ClIO: C, 50.20; H, 5.95. Found: C, 50.09; H, 5.82.

(E)-1-Chloro-2-iodo-1-phenylprop-1-ene [(E)-7f]. The crude product, which was obtained by reaction of 1-phenyl-1-propyne (**3g**) with **1** at room temperature for 2 h, was purified by MPLC on silica gel with petroleum ether as eluent to give (E)-**7f** as a pale yellow liquid in 77 % yield. EI-MS: *m/z* (%) 278 (M⁺, 82), 151 (11), 115 (100), 89 (12), 63 (7). ¹H NMR (200 MHz, CDCl₃): δ 2.74 (3 H, s, CH₃), 7.36 ppm (5 H, m, C₆H₅). Anal. Calcd. for C₈H₈ClI: C, 38.81; H, 2.89. Found: C, 38.77; H, 2.69.

5-Iodo-6-phenyl-3,4-dihydro-2H-pyran-2-one (9). The crude product, which was obtained by reaction of **3f** with **1** at 0 °C for 3 h, was purified by MPLC on silica gel with a mixture of hexane and Et₂O (80 : 20) as eluent to give **9** as a pale yellow solid in 41 % yield. Mp 32–34 °C. EI-MS: *m/z* 300 (M⁺, 51), 258 (11), 173 (25), 127 (10), 105 (100). IR (neat): ν 1775, 1695, 1675, 1596, 1449, 1288, 1194, 1072, 691 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 2.79 (2 H, m, H-3), 2.97 (2 H, m, H-4), 7.39 (1 H, m, H-4'), 7.40 (2 H, m, H-3' and H-5'), 7.57 ppm (2 H, m, H-2' and H-6'). ¹³C NMR (150 MHz, CDCl₃): δ 30.2 (C-3), 34.4 (C-4), 70.0 (C-5), 128.1 (C-3' and C-5'), 129.3 (C-2' and C-6'), 129.7 (C-4'), 134.4 (C-1'), 150.6 (C-6), 167.3 ppm (C-2). Anal. Calcd. for C₁₁H₉IO₂: C, 44.03; H, 3.02. Found: C, 43.94; H, 2.97.

Table 1. ¹³C Chemical shifts of the Acetylenic Carbon Atoms of some Alkyl Substituted Acetylenes and Propargyl Alcohol **2a-d**

$ \begin{array}{c} \alpha \quad \beta \quad \text{O-R}^1 \\ \text{Alkyl-C}\equiv\text{C-CH} \\ \quad \quad \quad \text{R} \\ \text{2a-d, 4} \end{array} $				δ_α	δ_β	$\Delta\delta_{(\text{C}\equiv\text{C})}$	Ref.
Compound							
Alkyl	R	R ¹					
4	H	H	OH	74.4	82.5	- 8.1	a
2a	Me	H	OH	81.6	78.5	+ 3.1	a
2b	Me	H	CH ₂ COOMe	83.8	73.8	+ 10.0	This work
2c	<i>n</i> -Bu	<i>n</i> -Bu	CH ₂ COOMe	87.4	78.0	+ 9.4	This work
2d	<i>n</i> -Bu	<i>n</i> -Bu	H	85.3	81.4	+ 3.9	This work

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Table 2. ¹³C Chemical shifts of the Acetylenic Carbon Atoms of some Phenyl Substituted Acetylenes **3a-e**

$ \begin{array}{c} \alpha \quad \beta \quad \text{R}^1 \\ \text{Ph-C}\equiv\text{C-CH} \\ \quad \quad \quad \text{R} \\ \text{3a-e} \end{array} $				δ_α	δ_β	$\Delta\delta_{(\text{C}\equiv\text{C})}$
Compound						
R	R ¹					
3a	<i>n</i> -Bu	OH		84.7	90.3	- 5.6
3b	<i>n</i> -Bu	OCH ₂ COOMe		86.6	87.0	- 0.4
3c	H	CH ₂ CH ₂ COOMe		81.5	88.8	- 7.3
3d	H	<i>n</i> -C ₅ H ₁₁		80.6	90.4	- 9.8
3e	<i>n</i> -Bu	O- <i>n</i> -Bu		85.2	89.0	- 3.8

Table 3. ^{13}C Chemical shifts of the Olefinic Carbon Atoms of Chloriodoalkenes

Compound	δ_α	δ_β
(E)-5a	129.8	99.4
(E)-5b	132.3	94.5
(E)-5c	135.8	105.4
(E)-5d	132.3	109.4
(E)-7a	128.6	111.6
(E)-7b	132.0	107.7
(E)-7c	129.4	99.7
(E)-7d	128.2	101.6
(E)-7e	130.1	110.6

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