A New Method for the Synthesis of *Z*-Enediones via IBX-Mediated Oxidative Rearrangement of 2-Alkynyl Alcohol Systems

Benedikt Crone, Stefan F. Kirsch*

Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

Supporting Information

General experimental details and characterization data for compounds **2b**−**2n**.

(5 Pages)

General experimental details: Alkynyl alcohols **3** were prepared according to published procedures by alkynylation of oxiranes [Li−C≡C−R (1 equiv.), $BF_3 \cdot OEt_2$ (1 equiv.), −78 °C, THF].[1] DMSO was obtained from Fluka and contained less than 0.005% of water. IBX was prepared according to a procedure developed by Santagostino and co-workers.[2]

^{1}H NMR spectra were obtained on a Bruker 360 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 90.6 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); etc.; br (broad); app (apparent). High resolution mass spectra and EI were determined on a Finnigan MAT 95S and MAT 8200. Flash chromatography was performed with E. Merck silica gel (43−60 μm). The eluent used is reported in parentheses. Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F_{254}), and components were visualized by observation under UV light or by treating the plates with $KMnO_4/H_2SO_4$ followed by heating.

Facile isomerization of *Z*-enediones **6** on silica during column chromatography is likely responsible for the moderate yield in the reaction **3**→**6**. After column chromatography, varying amounts of the corresponding *E*-enediones were sometimes obtained, which were not observed in the ^{1}H NMR of the crude reaction mixture.

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[1] Yamaguchi, M.; Hirao, I. *Tetrahedron Lett.* **1983**, *24*, 391−394.
[2] Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org.Chem.* **1999**, *64*, 4537−4538.

General procedure for the IBX-mediated synthesis of *Z*-enediones 6.

(*Z*)-1-Phenylhex-2-ene-1,4-dione (6b):[3] IBX (0.66 mmol, 184 mg) was added to a solution of alcohol **3b** (115 mg, 0.66 mmol) in DMSO (1.3 mL) and the reaction vial was sealed, protected from light and stirred at room temperature. After 30 min, additional IBX (0.66 mmol, 184 mg) was added. After stirring for 1 h at room temperature, a third equivalent of IBX (0.66 mmol, 184 mg) was added. The reaction mixture was then stirred at room temperature for 22 h (until TLC analysis indicated complete consumption of starting material and of intermediary occurring ketone **7b**), diluted with CH_2Cl_2 (20 mL), and stirring was continued for 30 min to precipitate the insoluble byproduct, which was removed by filtration. The precipitate was washed with CH_2Cl_2 (2 × 5 mL), and the combined filtrate was subsequently diluted with water (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were washed brine (30 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography on silica (20% EtOAc/pentane) to afford the title compound **6b** as a pale yellow oil (80 mg, 0.43 mmol, 65%): R_f 0.20 (20% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.3 Hz, 3 H), 2.59 (q, *J* = 7.3 Hz, 2 H), 6.58 (d, *J* = 12.0 Hz, 1 H), 6.85 (d, *J* = 12.0 Hz, 1 H), 7.48 (t, *J* = 7.1 Hz, 2 H), 7.57 (tt, *J* = 7.3, 1.4 Hz, 1 H), 7.93−7.95 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.4, 35.9, 128.6, 128.7, 133.5, 135.3, 135.6, 136.0, 193.5, 202.1; LRMS (EI) 188 (5%) [M^+], 159 (100%), 105 (72%). HRMS 188.0837 [188.0837 calcd for $C_{12}H_{12}O_2$ (M^+)].

(*Z*)-1-Phenylpent-2-ene-1,4-dione (6c).[3] 54% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.27 (20% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 6.56 (d, *J* = 12.0 Hz, 1 H), 6.87 (d, *J* = 12.0 Hz, 1 H), 7.48 (t, *J* = 7.3 Hz, 2 H), 7.59 (tt, *J* = 7.5, 1.2 Hz, 1 H), 7.93−7.95 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 29.8, 127.8, 128.6, 128.8, 133.7, 135.3, 136.5, 193.3, 199.3; LRMS (EI) 174 (9%) [M^+], 149 (20%), 105 (100%), 77 (49%). HRMS 174.0679 [174.0681 calcd for $C_{11}H_{10}O_2$ (M^+)].

[3] A. Del Zotto, W. Baratta, G. Verardo, P. Rigo, *Eur. J. Org. Chem.*, 2000, 2795.

(*Z*)-1-Cyclohexyl-4-phenylbut-2-ene-1,4-dione (6d). 55% yield after flash chromatography on silica (10% Et_2O/pentane): R_f 0.31 (20% EtOAc/pentane). ^1H NMR (360 MHz, $CDCl_3$): δ = 1.24−1.37 (m, 5 H), 1.66-1.93 (m, 5 H), 2.48−2.54 (m, 1 H), 6.70 (d, *J* = 11.8 Hz, 1 H), 6.85 (d, *J* = 11.8 Hz, 1 H), 7.48 (t, *J* = 7.3 Hz, 2 H), 7.57 (tt, *J* = 7.5, 1.1 Hz, 1 H), 7.92−7.95 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 25.5, 25.8, 28.0, 50.2, 128.5, 128.7, 133.5, 135.3, 135.9, 136.1 193.8, 204.2; LRMS (EI) 242 (0.2%) [M^+], 160 (100%), 105 (15%).

(*Z*)-5-(Allyloxy)-1-phenylpent-2-ene-1,4-dione (6e). 43% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.41 (20% EtOAc/pentane). ^1H NMR (360 MHz, $CDCl_3$): δ = 4.04 (d, *J* = 5.7 Hz, 2 H), 4.18 (s, 2 H), 5.20 (d, *J* = 10.5 Hz, 1 H), 5.28 (dd, *J* = 17.3, 1.4 Hz, 1 H), 5.80−5.91 (m, 1 H), 6.72 (d, *J* = 12.3 Hz, 1 H), 7.00 (d, *J* = 12.3 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.93−7.96 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 72.4, 74.5, 118.0, 128.6, 128.7, 133.0, 133.6, 135.8, 137.2, 193.1, 199.8; LRMS (EI) 230 (0.2%) [M^+], 172 (38%), 149 (56%), 105 (100%).

(*Z*)-1,4-Diphenylbut-2-ene-1,4-dione (6f).[3] 59% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.40 (20% EtOAc/pentane). ^1H NMR (360 MHz, $CDCl_3$): δ = 7.17 (s, 2 H), 7.47 (t, *J* = 7.5 Hz, 4 H), 7.59 (tt, *J* = 7.5, 1.4 Hz, 2 H), 7.94−7.97 (m, 4 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 128.6, 128.7, 133.5, 135.6, 138.1, 192.4; LRMS (EI) 236 (40%) [M^+], 105 (100%), 77 (60%). HRMS 236.0835 [236.0837 calcd for $C_{16}H_{12}O_2$ (M^+)].

(*Z*)-1-*o*-Tolylhex-2-ene-1,4-dione (6g). 61% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.29 (20% EtOAc/pentane). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.1 Hz, 3 H), 2.40 (s, 3 H), 2.59 (q, *J* = 7.1 Hz, 2 H), 6.56 (d, *J* = 11.8 Hz, 1 H), 6.84 (d, *J* = 11.8 Hz, 1 H), 7.31−7.41 (m, 2 H), 7.69−7.76 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 21.3, 35.9, 125.9, 128.6, 128.9, 134.4, 135.5, 135.8, 135.9, 138.6, 193.7, 202.2; LRMS (EI) 202 (6%) [M^+], 173 (100%), 119 (68%). HRMS 202.0992 [202.0994 calcd for $C_{13}H_{14}O_2$ (M^+)].

(*Z*)-1-(4-*tert*-Butylphenyl)hex-2-ene-1,4-dione (6h). 60% yield after flash chromatography on silica (10% EtOAc/pentane): R_f 0.22 (10% EtOAc/pentane). ^1H NMR (360 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.3 Hz, 3 H), 1.35 (s, 9 H), 2.59 (q, *J* = 7.3 Hz, 2 H), 6.57 (d, *J* = 11.8 Hz, 1 H), 6.86

(d, J = 11.8 Hz, 1 H), 7.49 (d, J = 8.6 Hz, 2 H), 7.88 (d, J = 8.6 Hz, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 31.0, 35.2, 35.9, 125.7, 128.6, 133.3, 135.3, 135.9, 157.4, 193.0, 202.4; LRMS (EI) 244 (40%) [M^+], 229 (100%), 215 (62%), 161 (81%). HRMS 244.1467 [244.1463 calcd for $C_{16}H_{20}O_2$ (M^+)].

(*Z*)-1-(2-Methoxyphenyl)hex-2-ene-1,4-dione (6i). 35% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.40 (50% EtOAc/pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, J = 7.3 Hz, 3 H), 2.59 (q, J = 7.3 Hz, 2 H), 3.88 (s, 3 H), 6.33 (d, J = 12.0 Hz, 1 H), 6.92 (d, J = 12.0 Hz, 1 H), 6.95 (d, J = 8.4 Hz, 1 H), 7.03 (t, J = 7.7 Hz, 1 H), 7.49 (td, J = 8.4, 1.4 Hz, 1 H), 7.81 (dd, J = 7.7, 1.4 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.6, 35.6, 55.6, 111.7, 120.9, 126.9, 131.1, 134.4, 134.8, 136.9, 159.1, 192.9, 203.9; LRMS (EI) 218 (4%) [M^+], 179 (22%), 135 (100%). HRMS 218.0942 [218.0943 calcd for $C_{13}H_{14}O_3$ (M^+)].

(*Z*)-1-(4-Phenoxyphenyl)hex-2-ene-1,4-dione (6j). 33% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.16 (50% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.09 (t, J = 7.3 Hz, 3 H), 2.58 (q, J = 7.3 Hz, 2 H), 6.55 (d, J = 11.8 Hz, 1 H), 6.82 (d, J = 11.8 Hz, 1 H), 7.00 (d, J = 8.9 Hz, 2 H), 7.08 (d, J = 8.9 Hz, 2 H), 7.21 (t, J = 7.5, 1 H), 7.40 (t, J = 7.7, 2 H) 7.91 (d, J = 8.9, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 36.0, 117.4, 120.3, 124,7 130.1, 130.6, 130.9, 135.4, 135.6, 155.5, 162.5, 192.0, 202.2; LRMS (EI) 280 (9%) [M^+], 251 (100%), 197 (59%). HRMS 280.1097 [280.1099 calcd for $C_{18}H_{16}O_3$ (M^+)].

(*Z*)-1-(4-Fluorophenyl)hex-2-ene-1,4-dione (6k). 52% yield after flash chromatography on silica (15% EtOAc/pentane): R_f 0.29 (10% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.08 (t, J = 7.3 Hz, 3 H), 2.58 (q, J = 7.3 Hz, 2 H), 6.58 (d, J = 12.0 Hz, 1 H), 6.78 (d, J = 12.0 Hz, 1 H), 7.16 (t, J = 8.9 Hz, 2 H), 7.97 (app. dd, J = 8.9, 2.0 Hz, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.4, 36.0, 116.0 (d, $^2J_{C,F}$ = 22 Hz), 131.2 (d, $^3J_{C,F}$ = 10 Hz), 132.4 (d, $^4J_{C,F}$ = 3 Hz), 135.5, 135.6, 166.0 (d, $^1J_{C,F}$ = 256 Hz), 192.2, 201.7; LRMS (EI) 206 (15%) [M^+], 177 (100%), 149 (48%). HRMS 206.0742 [206.0743 calcd for $C_{12}H_{11}FO_2$ (M^+)].

(*Z*)-1-(Thiophen-3-yl)hex-2-ene-1,4-dione (6l). 60% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.33 (20% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ =

1.12 (t, J = 7.3 Hz, 3 H), 2.59 (q, J = 7.3 Hz, 2 H), 6.54 (d, J = 11.8 Hz, 1 H), 6.80 (d, J = 11.8 Hz, 1 H), 7.34 (dd, J = 5.0, 3.0 Hz, 1 H), 7.56 (dd, J = 5.2, 1.4 Hz, 1 H), 8.04 (dd, J = 2.6, 1.1 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 35.8, 126.9, 127.0, 132.9, 133.2, 138.1, 141.5, 185.8, 203.4; LRMS (EI) 194 (8%) [M^+], 165 (100%), 111 (92%). HRMS 194.0400 [194.0402 calcd for $C_{10}H_{10}O_2S$ (M^+)].

(*Z*)-1-Cyclohexenylhex-2-ene-1,4-dione (6m). 50% yield after flash chromatography on silica (20% EtOAc/pentane): R_f 0.30 (20% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.09 (t, J = 7.3 Hz, 3 H), 1.61−1.68 (m, 4 H), 2.20−2.32 (m, 4 H), 2.52 (q, J = 7.3 Hz, 2 H), 6.38 (d, J = 12.0 Hz, 1 H), 6.59 (d, J = 12.0 Hz, 1 H), 6.81−6.83 (m, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 21.5, 21.7, 22.6, 26.2, 36.0, 134.3, 136.4, 139.5, 143.0, 194.7, 202.1; LRMS (EI) 192 (6%) [M^+], 153 (20%), 109 (100%). HRMS 192.1149 [192.1150 calcd for $C_{12}H_{16}O_2$ (M^+)].

(*Z*)-2-Methylocta-1,4-diene-3,6-dione (6n). 52% yield after flash chromatography on silica (20% Et_2O/pentane): R_f 0.14 (20% EtOAc/pentane). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.09 (t, J = 7.3 Hz, 3 H), 1.97 (s, 3 H), 2.53 (q, J = 7.3 Hz, 2 H), 5.84 (d, J = 1.4 Hz, 1 H), 5.87 (s, 1 H), 6.44 (d, J = 12.0 Hz, 1 H), 6.60 (d, J = 12.0 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 7.5, 16.9, 36.1, 126.4, 134.1, 136.9, 144.5, 195.9, 201.4; LRMS (EI) 152 (2%) [M^+], 123 (100%), 109 (30%).