Supplementary Material

Engineering Reactions in Crystalline Solids: Preparation of α-Carbonyl Radicals in Crystals of Dialkyl-1,3-acetonedicarboxylates

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Materials and Methods: Solvents were distilled over CaH_2. Commercial reagents of the highest purity available were used without further purification. Gas chromatography(GC) was conducted on a 0.2mm x 25m x 0.11μm Hp-1 (cross linked methyl silicone gum) capillary column. ^1H and ^{13}C NMR spectra were obtained with a Bruker ARX400 spectrometer in $CDCl_3$. IR spectra were obtained with a Perkin-Elmer spectrometer either in KBr disks or as neat oils. Spectral data of compounds **2a-c** in $CHCl_3$ contained a 5-10% contribution of the enol form. The spectra data provided for these three compounds are for the keto form.

General Procedure for the Preparation of Ketodiesters 2a-c (Procedure A). A sample of commercially available diethyl 1,3-acetonedicarboxylate **1** and the desired alcohol in m-xylene was heated in a round bottom flask equipped with a Vigreux distillation column. The temperature of the oil bath was maintained between 110 …Cand 150 °C. As the reaction progressed, ethanol was distilled off. The reaction was stopped as soon as the solution reached the boiling point of m-xylene (139 ¡C).

General Procedure for the Preparation of Tetramethylketodiesters 3a-c (Procedure B). Potassium hydride was washed with freshly distilled hexane, dried with a stream of argon and weighed in a round bottom flask. THF was added to give a suspension. The 1,3-acetonedicarboxylate derivative in THF was added dropwise, and the resulting yellow solution was stirred for 30 min at room temperature. Three equivalents of methyl iodide were added into the reaction mixture which was allowed to stir for an additional 30 min. The reaction mixture was then refluxed for 30 min followed by the addition of three equivalents of methyl iodide. After two additional hours of reflux, the reaction was cooled in an ice bath and worked up after addition of saturated NH_4Cl. The organic components were extracted twice with diethyl ether, and the

combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent *in vacuo* afforded the desired diester.

General Procedure for the Preparation of Isobutyrates 5a-c (Procedure C). To a solution of the corresponding alcohol in CH_2Cl_2 was added isobutyryl chloride and pyridine. The resulting solution was stirred overnight at room temperature. The reaction mixture was worked up after addition of a 5% $NaHCO_3$ solution. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the corresponding ester.

General Procedure for Preparation of Methacrylates 6a-c (Procedure D). To a solution of the corresponding alcohol in toluene was added methacrylic anhydride and 4-dimethylamino pyridine. The resulting solution was heated at 70^{o}C for overnight. The reaction mixture was worked up after addition of a 5% $NaHCO_3$ solution. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the corresponding ester.

General Procedure for Photolysis in Benzene (Procedure E). Samples of ketodiesters **3a-c** were dissolved in anhydrous benzene (1 mg/ml) and 1 ml of these solutions were transferred to dry Pyrex NMR tubes. Each sample was deoxygenated by bubbling argon for 15 minutes. The NMR tube was placed behind a 306 nm filter and the solution irradiated with a medium pressure Hg Hannovia lamp. The solution was analyzed by GC after various times and the retention times of disproportionation products were compared to those of the authentic samples.

General Procedure for Photolysis in the Solid State (Procedure F). Powdered solid samples of ketodiesters **3a**,**c** were placed between two microscope slides screened by a λ>305 nm cutoff filter in the photolysis chamber. The sample was irradiated with the Hg lamp and small amounts of sample were removed at various times, dissolved in diethyl ether, and analyzed by GC. When low temperature photolysis was desired for samples of **3b**, the microscope slides containing the samples were secured in a DOW Ziploc brand freezer plastic bag which was placed on a surface with good thermal contact with an isopropanol-dry ice bath (-70¡C).

Preparation of Di-(–)-isobornyl 1,3-Acetonedicarboxylates (2a). Following procedure A, diethyl 1,3-acetonedicarboxylate (2.03 g, 10 mmol) was transesterified with racemic (–)-isoborneol (3.39 g, 22 mmol) in xylene (20 ml). After removing the solvent under reduced pressure, the excess isoborneol was removed by sublimation to give 4.1 g (98%) of **2a**. ^{1}H

NMR: δ 0.83 (s, 6H), 0.84 (s, 6H), 0.96 (s, 6H), 1.02-1.17 (m, 6H), 1.49-1.59 (m, 2H), 1.64-1.91 (m, 8H), 3.57 (s, 4H), 4.69-4.72 (m, 2H). ^{13}C NMR: δ 11.35,11.41, 19.80, 20.01, 26.92, 33.66 , 38.62, 44.93, 46.92, 48.73 , 49.24 , 82.51, 166.17, 195.37; IR (neat): 2965, 2877, 1730, 1710, 1465, 1380, 1151.

Preparation of 2,2,4,4-Tetramethyl di-(–)-isobornyl 1,3-Acetonedicarboxylate (3a). Following Procedure B, methylation was achieved by addition of compound **2a** (1.0 g, 2.4 mmol) in THF (10 mL) to a suspension of KH (0.43g, 10.7 mmol) in 20 mL of THF, followed by addition of methyl iodide (2.04 g, 14.04 mmol). Recrystallization of crude yellow solid in ether-hexane afforded 0.92g (80%) of **3a**. m.p. = 105-115 ^{o}C; ^{1}H NMR: δ 0.81 (s, 12H), 0.91 (s, 6H),1.05-1.13 (m, 6H), 1.37 (s, 12H), 1.49-1.59 (m, 2H), 1.65-1.89 (m, 6H), 4.56-4.59 (dd, J = 7.96, 3.20 Hz, 2H). ^{13}C NMR: δ 11.57, 19.81, 20.04, 23.23, 26.96, 33.73, 38.55, 44.98, 46.92, 48.84, 55.36, 82.20, 172.70, 204.32. IR (KBr): 2960, 2881, 1739, 1728, 1709, 1464, 1454, 1386, 1366, 1258, 1150 .

Preparation of Di-(-)-bornyl 1,3-Acetonedicarboxylate (2b). Following Procedure A, diethyl 1,3-acetonedicarboxylate (2.03 g, 10 mmol) was transesterified with (-)-borneol (3.4 g, 22 mmol) in xylene (20 mL) . After removing the solvent under reduced pressure, the excess (-)-borneol in the crude product was removed by sublimation to give 4.1 g of **2b** (98%). ^{1}H NMR: δ: 0.85 (s, CH_3, 6H), 0.87 (s, CH_3, 6H), 0.90 (s, CH_3, 6H), 1.00-1.04 (m, CH, 2H), 1.22-1.25 (m, CH, 6H), 1.66-1.91(m, CH_2&CH,6H), 2.33-2.38 (m, CH, 2H), 3.63 (s, CH_2, 4H), 4.93-4.97 (m, CH, 2H); ^{13}C NMR: δ 13.48 (CH_2), 18.81 (CH_3), 19.67 (CH_3), 26.98 (CH_2), 27.95 (CH_3), 36.56 (C), 44.80(CH_3), 47.89 (C), 48.86 (C), 49.27 (CH_2), 81.47(CH), 166.98, 195.53; IR (neat, cm^{-1}): 2955, 2881, 1737, 1718, 1474, 1454, 1326, 1240, 1184, 1114, 1022.

Preparation of 2,2,4,4-Tetramethyl Di-(-)-bornyl 1,3-Acetonedicarboxylate (3b). Following Procedure B, methylation was achieved by addition of **2b** (1.0 g, 2.4mmol) in THF (10ml) to a suspension of KH in 20ml THF, followed by additioon of methyl iodide (2.04 g, 14.4 mmol). Recrystallization of crude product in ether-hexane afforded 0.90g (80%) of **3b** ^{1}H NMR: δ 0.76 (s, 6H), 0.81 (s, 6H), 0.83 (s, 6H), 0.87-0.91 (dd, J= 13.79, 3.38 Hz, 2H), 1.12-1.35 (s, 6H), 1.37 (s, 6H), 1.38 (s, 6H),1.61-1.79 (m, 6H), 2.24-2.30 (m, 2H), 4.77-4.81 (m, 2H). ^{13}C NMR: δ 13.41, 18.69, 19.47, 23.36, 23.40, 26.82, 27.84, 36.29, 44.66, 47.70, 48.74, 55.30, 80.96, 173.32, 204.57; IR (neat. cm^{-1}): 2956, 2875, 1728, 1710, 1455, 1387, 1262, 1153.

Preparation of Diadamantyl 1,3-Acetonedicarboxylate (2c). Following Procedure A, diethyl 1,3-acetonedicarboxylate (2.03 g, 10 mmol) was added to a soution of adamantanol (3.33 g, 22 mmol) in xylene (30 mL). After removal of solvent under reduced pressure, the excess adamantanol was removed by sublimation to give 4.06 g (98%) of **1**. ^{1}H NMR: δ 1.63 (s, CH_2, 12H), 2.08-2.09 (d, CH_2, 12H), 2.14 (s, CH, 6H), 3.46 (s, CH_2, 4H); ^{13}C NMR: δ 30.78 (CH_2), 36.05(CH), 41.17 (CH_2), 50.37 (CH_2), 82.30 (C), 165.62 (C=O), 197.79 (C=O); IR (neat, cm^{-1}): 2910, 2852, 1726, 1710, 1456, 1326, 1237, 1184, 1147, 1053.

Preparation of 2,2,4,4-Tetramethyl Diadamantyl 1,3-Acetonedicarboxylates (3c). Following Procedure B, compound **2c** (1.0 g, 2.4 mmol) in THF (10 ml) was added into a suspension of KH (0.43g, 10.7 mmol) in 20 mL THF dropwise, and the resulting enolate was reacted with methyl iodide (2.04 g,14.4 mmol). Recrystallization of crude yellowish solid in ether-hexane afforded 0.96 g of **3c.** m.p. =165-167 ^{o}C; ^{1}H NMR: δ 1.42-1.47 (m, CH_2,12H), 1.70 (s, CH_3, 12H), 1.96(s, CH, 6H), 2.16-2.17 (d, CH_2, 12H); ^{13}C NMR: δ 23.95 (CH_3), 30.85 (CH_2), 35.99 (CH), 41.05 (CH_2), 56.37 (C), 81.02 (C), 172.06 (C=O), 204.97 (C=O); IR (KBr, cm^{-1}): 2922, 2855, 1731, 1705, 1457, 1385, 1158, 1053 .

Preparation of 2,2,3,3-Tetramethyl Di-(–)-isobornyl Succinate (4a). Following Procedure E, 20 mg of a powder sample of compound **3a** were irradiated for 5 hours, and diester **4a** was obtained wth 100 % selectivity in 68 % yield. ^{1}H NMR: δ 0.84 (s, CH_3, 6H), 0.85 (s, CH_3, 6H), 0.93 (s, CH_3, 6H), 1.04-1.18 (s, CH_2, 4H), 1.23 (s, CH_3, 12H), 1.39-1.43 (m, CH, 2H), 1.39-1.43 (m, CH, 2H), 1.65-1.81 (m, CH_2&CH,8H), 4.60-4.64 (dd, J=3.82 Hz, 2H); ^{13}C NMR: δ 11.78 (CH_2), 15.28 (CH_3), 20.03(CH_3), 22.38 (C), 27.03 (CH_2), 33.90 (CH_3), 38.88 (CH_2), 45.02 (CH_3), 46.89 (CH), 47.29 (C), 48.68 (C), 81.41 (CH), 175.21; IR (neat, cm^{-1}): 2950, 2881, 1724, 1454, 1386, 1263, 1238, 1155, 1111, 1025 .

Preparation of (±)-Isobornyl Isobutyrate (5a). Following procedure C, acylation was accomplished by stirring a sample of racemic isoborneol (0.21g, 1.4mmol) in dichloromethane (5ml) with isobutyryl chloride (1.6 mL, 1.5 mmol) and pyridine (0.16mL, 2 mmol). Chromatography (hexane/CH_2Cl_2 = 3:1) of crude product gave 0.27 g of **5a** as a clear oil. ^{1}H NMR: δ 0.80 (s, 6H), 0.95 (s, 3H), 1.04-1.105 (m, 2H), 1.10-1.11 (d, J=3.45 Hz, 3H), 1.12-1.13 (d, J=3.47 Hz, 3H), 1.49-1.75 (m, 5H), 2.43-2.51 (m, 1H), 4.59-4.62 (m, 1H). ^{13}C NMR: δ 11.33, 18.87, 18.99, 19.88, 20.09, 27.02, 33.71, 34.31, 38.79, 44.99, 46.85, 48.64, 80.45, 176.36; IR (neat, cm^{-1}): 2956, 2878, 1732, 1470, 1198, 1157, 1071.

Preparation of (±)-Isobornyl Methacrylate (6a). Following Procedure D, to a solution of (±)-isoborneol (0.23g, 1.5mmol) in toluene (8ml) was added methacrylic anhydride (0.28g, 1.8mmol) and 4-dimethylamino pyridine (0.036g, 0.3mmol). The crude product was purified by flash column (Hexane/ EtOAc = 4:1) to give 0.26 g of **6a** (80 %) as clear oil. ^{1}H NMR: δ 0.80 (s, 3H), 0.81 (s, 3H), 0.96 (s, 3H), 0.99-1.16 (m, 2H), 1.45-1.57 (m, 3H), 1.69-1.79 (m, 3H), 1.87 (s, 3H), 4.65-4.68 (dd, J=7.35, 3.05 Hz, 1H). 5.46-5.47 (m, 1H), 6.01-6.02 (m, 1H). ^{13}C NMR: δ 11.45, 18.18, 18.28, 19.87, 20.07, 27.01, 33.67, 38.81, 45.00, 46.88, 48.79, 81.08, 124.87, 136.80, 166.77. IR (neat): 2955, 2880, 1716, 1651, 1454, 1326, 1300, 1163.

Preparation of 2,2,3,3-Tetramethyl Diadamantnyl Succinate (4c). Following Procedure E, 20 mg of a powder sample of compound **3c** were irradiated for 8 hours and diester **13** was obtained with 100 % selectivity in 88% yield. mp = 187-191 ^{o}C; ^{1}H NMR: δ 1.18 (s, CH_3, 12H), 1.64 (d, CH_2, 12H), 2.10 (d, CH_2, 12H), 2.14 (s, CH, 6H); ^{13}C NMR: δ 22.44 (CH_3), 30.80 (CH_2). 36.26 (CH), 41,30 (CH_2), 47.44 (C), 80.43 (C), 175.04. IR (KBr. cm^{-1}): 2914, 2853, 1721, 1456, 1238, 1165, 1127, 1056.

Preparation of (-)-Bornyl Isobutyrate (5b). Following procedure C, acylation was accomplished by stirring a sample of (-)-Borneol (0.21g, 1.3 mmol) in dichloromethane (5mL) with isobutyryl chloride (1.6ml, 1.5mmol) and pyridine (0.16ml, 2 mmol). Chromatography (hexane:CH_2Cl_2 = 3:1) of crude product gave 0.27 g of **5b** as a clear oil. ^{1}H NMR: δ 0.76 (s, 3H), 0.81 (s, 3H), 0.84 (s, 3H), 0.85-0.89 (m, 1H), 1.09-1.10 (d, J=2.43 Hz, 3H), 1.11-1.12 (d, J=2.43 Hz, 3H), 1.13-1.25 (m, 2H), 1.59-1.61 (m, 1H), 1.67-1.70 (m, 1H), 1.87-1.93 (m, 1H), 2.25-2.31 (m, 1H), 2.45-2.52 (m, 1H), 4.79-4.83 (m, 1H). ^{13}C NMR: δ 13.41, 18.71, 18.77, 18.87, 19.61, 27.04, 27.99, 34.19, 36.79, 44.85, 46.85, 48.64, 79.28, 177.26; IR (neat, cm^{-1}): 2957, 2874, 1731, 1472,1451, 1441, 1197, 1155.

Preparation of Adamantyl Isobutyrate (5c). Following Procedure C, acylation was accomplished by addition of adamantanol (0.21g, 1.4mmol) in dichloromethane (5 ml) to isobutyryl chloride (1.6 ml, 1.5 mmol) in pyridine (0.16ml, 2 mmol). Crude product as purified by flash chromatography (hexane/CH_2Cl_2 = 3:1) to give 0.29 g of **7** as a clear oil. ^{1}H NMR: δ 1.03-1.05 (d, CH_3, 6H),1.59 (s, CH_2, 6H), 2.03 (s, CH_2, 6H), 2.09 (s, CH, 3H), 2.31-2.38 (s, CH, 1H). ^{13}C NMR: δ 19.01 (CH_3), 30.75 (CH_2), 36.07 (CH), 41.23 (CH_2), 45.23 (CH), 79.61 (C), 176.37. IR (neat, cm^{-1}): 2912, 2853, 1730, 1457,1351, 1194, 1161, 1058 .