Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Acylation of Electrophilic Olefins via Decatungstate Photocatalyzed Activation of Aldehydes.

Silvia Esposti, Daniele Dondi, Maurizio Fagnoni*, and Angelo Albini.

Supporting information

Photochemical acylation of olefins.

Procedure A. A solution (30 ml) of an aldehyde (**1a-f**, 3 mmol, 0.1 M), and an olefin (**2a-f**, 0.1 M) in the presence of 200 mg of TBADT[S1] (2×10^{-3} M) in MeCN was poured in two quartz tubes and purged for 10 minutes with argon, serum capped and irradiated with six 15-W phosphor-coated lamps (emission centered at 310). The photolyzed solution was concentrated under reduced pressure and the products purified by bulb to bulb distillation.

Synthesis of 2-heptanoyl succinic acid dimethyl ester. (3) From 440 μL (0.1 M, 3 mmol) of heptanaldehyde (**1a**), 370 μL (3 mmol) of dimethylmaleate and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 488 mg of **3**, (oil, 63% yield). Spectroscopic data in accordance with literature data.[S2] Anal. Calcd. For $C_{13}H_{22}O_5$: C, 60.45; H, 8.58; found: C, 60.2; H, 8.5.

Synthesis of 4-oxo-decanenitrile. (4) From 440 μL (0.1 M, 3 mmol) of heptanaldehyde (**1a**), 200 μL (3 mmol) of acrylonitrile and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 287 mg of **4**, (oil, 57% yield). Spectroscopic data in accordance with literature data.[S3] Anal. Calcd. For $C_{10}H_{17}NO$: C, 71.81; H, 10.25; found: C, 71.9; H, 10.5.

Synthesis of 3-heptanoyl-cyclohexanone. (5)[S4] From 440 μL (0.1 M, 3 mmol) of heptanaldehyde (**1a**), 300 μL (3 mmol) of 2-cyclohexenone and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 354 mg of **5**, (oil, 56% yield).

5: ^{1}HNMR (δ, $CDCl_3$): 0.9 (t, 3H), 1.2-1.3 (m, 6H), 1.5-1.8 (m, 4H), 2.0-2.2 (m, 2H), 2.25-2.6 (m, 6H), 2.8-2.95 (m, 1H); ^{13}CNMR (δ, $CDCl_3$): 13.9 (CH_3), 22.4 (CH_2), 23.5 (CH_2), 24.9 (CH_2), 27.3 (CH_2), 28.8 (CH_2), 31.5 (CH_2), 40.8 (CH_2), 41.1 (CH_2), 42.5 (CH_2), 50.1 (CH), 210.1, 210.7; IR (neat) ν/cm^{-1}: 2931, 1712, 1451, 1225. Anal. Calcd. For $C_{13}H_{22}O_2$: C, 74.24; H, 10.54; found: C, 74.0; H, 10.7.

Synthesis of undecane-2,5-dione. (6) From 440 μL (0.1 M, 3 mmol) of heptanaldehyde (**1a**), 240 μL (3 mmol) of 2-butenone and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 331 mg of **6**, (oil, 60% yield). Spectroscopic data in accordance with literature data.[S5] Anal. Calcd. For $C_{11}H_{20}O_2$: C, 71.70; H, 10.94; found: C, 71.5; H, 10.7.

Synthesis of 4-oxo-decanoic acid methyl ester. (7) From 440 μL (0.1 M, 3 mmol) of heptanaldehyde (**1a**), 270 μL (3 mmol) of methyl acrylate and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 348 mg of **7**, (oil, 58% yield). Spectroscopic data in accordance with literature data.[S3] Anal. Calcd. For $C_{11}H_{20}O_3$: C, 65.97; H, 10.07; found: C, 65.8; H, 10.0.

Synthesis of 2-(3,3-Dimethyl-butyryl)-succinic acid dimethyl ester. (8) From 400 μL (0.1 M, 3 mmol) of 3,3-dimethylbutanal (**1b**), 370 μL (3 mmol) of dimethylmaleate and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 381 mg of **8**, (oil, 52% yield).

8: ^{1}HNMR (δ, $CDCl_3$): 0.95 (s, 9H), 2.5 (m, 2H), 2.7-2.95 (AB part of an ABX system, 2H), 3.6 (s, 3H), 3.65 (s, 3H), 3.8-3.95 (X part of an ABX system, 1H); ^{13}CNMR (δ, $CDCl_3$): 29.2 (CH_3), 29.9, 31.8 (CH_2), 51.6 (CH_3), 51.8 (CH_3), 54.3 (CH_2), 55.0 (CH), 168.7, 171.6, 202.7; IR (neat) ν/cm^{-1}: 2955, 1740, 1263, 1164, 1010; Anal. Calcd. For $C_{11}H_{20}O_5$: C, 59.00; H, 8.25; found: C, 59.0; H, 8.4.

Synthesis of 3-(3-phenyl-propionyl)-cyclohexanone. (9) From 400 μL (0.1 M, 3 mmol) of 3-phenylpropanal (**1c**), 300 μL (3 mmol) of 2-cyclohexenone and 200 mg of TBADT in 30 mL of MeCN irradiated for 24h. Purification afforded 415 mg of **9**, (oil, 60% yield).

9: ^{1}H NMR (δ, $CDCl_3$): 1.55-1.80 (m, 2H), 1.95-2.10 (m, 2H), 2.2-2.6 (m, 4H), 2.7-3.0 (m, 5H), 7.1-7.3 (m, 5H); ^{13}CNMR (δ, $CDCl_3$): 24.7 (CH_2), 27.0 (CH_2), 29.5 (CH_2), 40.8 (CH_2), 42.3 (CH_2), 42.5 (CH_2), 50.2 (CH), 126.1 (CH), 128.2 (CH), 128.4 (CH), 140.4, 209.2, 209.4; IR (neat) ν/cm^{-1}: 3028, 2943, 1711, 1604, 751, 701. Anal. Calcd. For $C_{15}H_{18}O_2$: C, 78.23; H, 7.88; found: C, 78.3; H, 7.9.

Synthesis of 3-cyclohexanecarbonyl-cyclopentanone (12) and 3-cyclohexyl-cyclopentanone (13)[S6] From 240 μL (0.1 M, 2 mmol) of cyclohexancarboxyaldehyde (**1e**), 165 μL (2 mmol) of 2-cyclopentenone and 130 mg of TBADT in 20 mL of MeCN irradiated for 7h. Purification by column chromatography (from cyclohexane:ethyl acetate 98:2 to 96:4 as the eluant) afforded 149 mg of **12**, (oil, 45% yield) and 83 mg of **13**, (oil, 25% yield).

12: ^{1}H NMR (δ, $CDCl_3$): 1.1-1.5 (m, 6H), 1.55-2.05 (m, 6H), 2.1-2.6 (m, 5H), 3.3-3.5 (m, 1H); ^{13}CNMR (δ, $CDCl_3$): 25.4 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 26.2 (CH_2), 28.1 (CH_2), 28.5 (CH_2), 37.4 (CH_2), 40.6 (CH_2), 45.7 (CH), 49.9 (CH), 213.8 (CO), 216.9 (CO); IR (neat) ν/cm^{-1}: 2930, 2854, 1744, 1702, 732; Anal. Calcd. For $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; found: C, 74.1; H, 9.2.

13: Spectroscopic data in accordance with literature data.[S6] Anal. Calcd. For $C_{11}H_{18}O$: C, 79.46; H, 10.91; found: C, 79.4; H, 10.8.

The same reaction carried out in capped test tubes immersed in a cooling bath at -20 °C by using a 125 W high-pressure mercury arc through Pyrex as an external source yielded after 7h of irradiation compounds **12** (46%) and **13** (< 1%) as determined by GC technique.

Synthesis of 2-*t*-butyl-succinic acid dimethyl ester. (14) From 325 μL (0.1 M, 3 mmol) of pivalaldehyde (**1f**), 370 μL (3 mmol) of dimethylmaleate and 200 mg of TBADT in 30 mL of MeCN irradiated for 48h. Purification afforded 422 mg of **14**, (oil, 70% yield). Spectroscopic data in accordance with literature data.[S7] Anal. Calcd. For $C_{10}H_{18}O_4$: C, 59.39; H, 8.97; found: C, 59.2; H, 9.0.

Procedure B. A solution of the aldehyde (0.1 M) and the olefin (0.1 M) in the presence of TBADT (2×10^{-3} M) was irradiated in an immersion-well apparatus by using a 125 W high-pressure mercury arc through Pyrex, while maintaining a nitrogen flux. The end products were separated by column chromatography (cyclohexane/ethyl acetate as eluants).

Synthesis of 2-(2-ethyl-butyryl)-succinic acid dimethyl ester (10) and 2-(1-ethylpropyl)-succinic acid dimethyl ester. (11) A solution of 910 μL (0.1 M, 7 mmol) of 2-ethylbutyrraldehyde (**1d**), 860 μL (7 mmol) of dimethylmaleate and 465 mg of TBADT in 70 mL of MeCN was irradiated for 9h. After evaporation of the solvent, the residue was purified by column chromatography (cyclohexane:ethyl acetate 95:5 as the eluant) yielding 256 mg of **10** (15%, oil) and 514 mg of **11** (34%, oil).

10: ^{1}H NMR (δ, $CDCl_3$): 0.8 (t, 3H), 0.9 (t, 3H), 1.3-1.55 (m, 2H), 1.55-1.75 (m, 2H), 2.65-2.75 (m, 1H), 2.8 (t, *J* = 7 Hz, 2H), 3.6 (s, 3H), 3.7 (s, 3H), 4.1 (t, *J* = 7 Hz, 1H); ^{13}CNMR (δ, $CDCl_3$): 12.5 (CH_3), 12.8 (CH_3), 24.1 (CH_2), 25.4 (CH_2), 33.1 (CH_2), 53.2 (CH_3), 53.8 (CH_3), 55.3 (CH_2), 55.6

(CH), 170.0, 172.9, 207.6. IR (neat) ν/cm^{-1}: 2965, 1743, 1710, 1267, 1016. Anal. Calcd. For $C_{11}H_{20}O_5$: C, 59.00; H, 8.25; found: C, 58.9; H, 8.1.

11: ^{1}H NMR (δ, $CDCl_3$): 0.9 (2t, 6H), 1.15-1.45 (m, 4H), 1.5-1.6 (m, 1H), 2.25-2.4 (A part of an ABX system, 1H), 2.65-2.8 (B part of an ABX system, 1H), 2.95-3.01 (X part of an ABX system, 1H), 3.65 (2s, 6H); ^{13}CNMR (δ, $CDCl_3$): 11.4 (CH_3), 11.6 (CH_3), 23.1 (CH_2), 23.5 (CH_2), 31.9 (CH), 42.8 (CH_2), 43.1 (CH), 51.5 (CH_3), 51.6 (CH_3), 173.0, 175.2; IR (neat) ν/cm^{-1}: 2963, 1739, 1167. Anal. Calcd. For $C_{11}H_{20}O_4$: C, 61.09; H, 9.32; found: C, 61.1; H, 9.4.

The same reaction carried out in capped test tubes immersed in a cooling bath at -20 °C by using a 125 W high-pressure mercury arc through Pyrex as an external source yielded after 7h of irradiation compounds **10** (40%) and **11** (5%) as determined by GC technique.

Photochemical reaction between pivalaldehyde (1f) and dimethyl maleate (2a) at -50 °C. A solution of **1f** (0.1 M), and **2a** (0.1 M) in the presence of TBADT (2×10^{-3} M) was irradiated for 6h in capped test tubes immersed in a cooling bath at -50 °C by using a 125 W high-pressure mercury arc through Pyrex as an external source. Accordingly, succinate **14** (48%) and the ketoester **15** (16%) was formed as determined by GC by comparison with authentic samples (see below for the synthesis of **15**).

Synthesis of 2-(2,2-dimethyl-propionyl)-succinic acid dimethyl ester. (15) A mixture of 1 mL of methyl-4,4-dimethyl-oxopentanoate and 0.6 mL of methylbromoacetate was added dropwise to a solution of sodium methylate in MeOH. The resulting solution was heated overnight under reflux under stirring, cooled and poured in water and then extracted with ether (4×25 mL). The organic phase was then washed with water (3×10 mL) and dried over $MgSO_4$. The title compound (740 mg, 51% yield) was isolated by column chromatography (cyclohexane:ethyl acetate from 98:2 to 94:6 as the eluant) as an oil.

15: ^{1}H NMR (δ, CD_3COCD_3): 1.2 (s, 9H), 2.5-3.0 (AB part of an ABX system, 2H), 3.6 (s, 3H), 3.7 (s, 3H) 4.4- 4.5 (X part of an ABX system, 1H); ^{13}CNMR (δ,CD_3COCD_3): 27.0 (CH_3), 34.4 (CH_2), 46.1, 49.2 (CH), 52.4 (CH_3), 53,1 (CH_3), 170.3, 172.3, 209.9 (CO); IR (neat) ν/cm^{-1}: 2957, 1740, 1709, 1232, 1163; Anal. Calcd. For $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; found: C, 57.4; H, 7.9.

[S1] D. Dondi, A. M. Cardarelli, M. Fagnoni, A. Albini, *Tetrahedron* **2006**, *62*, 5527-5535.

[S2] I. Kawenoki, D. Maurel, J. Kossanyi, *Bull. Soc. Chim. Fr.* **1982**, 385-390.

[S3] M. Yamashita, H. Tashika, M. Uchida, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1257-1261.

[S4] J. Lucchetti, A. Krief, *Synth. Commun.* **1983**, *13*, 1153-1162.

[S5] A. Pecunioso, R. Menicagli, *J. Org. Chem.* **1988**, *53*, 2614-2617.

[S6] D. Dondi, A. M. Cardarelli, M. Fagnoni, A. Albini, *Tetrahedron* **2006**, *62*, 5527-5535.

[S7] M. Mella, M. Fagnoni, A. Albini, *J. Org. Chem*, **1994**, *59*, 5614-5622.