Rate Enhancement of Diels-Alder Reactions in Aqueous Perfluorinated Emulsions

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Preparation of LiFOS

Water was purified by a Milli-Q Water-Purification System. The perfluorinated emulsions were prepared with LiFOS and PFH in water under sonication for 1 hr at ambient temperature. After the completion of the emulsion formation, the dispersion was partially applied for the measurement of the particle size distributions (NIKKISO Nanotrac UPA-EX150) at 25 °C.

3: 2,3,4a-Trimethyl-1,4,4a,9a-tetrahydro-anthraquinone

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 8.08-7.98 (2H, m), 7.76-7.70 (2H, m), 3.02 (1H, dd, $J=5.5$, 7.7), 2.60 (1H, d, $J=17.6$), 2.42 (1H, dd, $J=7.7$, 17.6), 2.17 (1H, dd, $J=5.5$, 17.6), 1.79 (1H, d, $J=17.6$), 1.63 (3H, s), 1.61 (3H, s) and 1.34 (3H, s); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ : 200.3, 198.6, 134.2, 134.0, 133.7, 133.1, 127.3, 126.6, 123.6, 122.7, 53.7, 48.5, 38.7, 31.2, 23.8, 18.9 and 18.6

5: 2,3-Dimethyl-1,4,4a,9a-tetrahydro-anthraquinone

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 8.04 (2H, dd, $J=3.4$, 5.8), 7.74 (2H, $J=3.4$, 5.8), 3.39-3.33 (2H, m), 2.50-2.40 (2H, m), 2.19-2.09 (2H, m), 1.64 (6H, s); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ : 198.4, 134.2, 134.1, 126.8, 123.5, 47.4, 30.7 and 18.9

8: 3a,4,9,9a-Tetrahydro-4-methyl-2-octyl-4,9[1',2']benzo-1H-benz[f]isoindole-1,3-(2H)-dione

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.41-7.34 (2H, m), 7.30-7.24 (2H, m), 7.24-7.08 (4H, m), 4.76 (1H, d, $J=3.2$), 3.21 (1H, dd, $J=3.2$, 8.3), 3.07 (2H, t, $J=7.3$), 2.80 (1H, d, $J=8.3$), 2.29 (3H, s), 1.36-1.01 (8H, m), 0.88 (3H, t, $J=7.1$) and 0.86-0.66 (4H, m) ; $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ : 176.67, 176.01, 144.60, 141.93, 141.20, 138.80, 126.76, 126.58, 126.42, 126.40, 124.90, 123.71, 122.13, 121.91, 50.31, 48.20, 45.49, 44.92, 38.31, 31.72, 28.96, 28.88, 27.07, 26.36, 22.57, 15.24 and 14.04 ; MS (EI) m/z (relative intensity %) 401 (M^+ , 4), 302 (23) and 192 (100) ; IR (KBr) 3068, 3039, 3023, 2923, 2871, 2852, 1772, 1708, 1465, 1438, 1398, 1361, 1338, 1174, 1141, 1022, 773, 763, 754 and 709 cm^{-1}

9: 5,6-Dimethyl-2-octyl-3a,4,7,7a-tetrahydro-isoindole-1,3-dione

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.39 (2H, t, $J=7.1$), 2.94 (2H, t, $J=2.4$), 2.38 (2H, d, $J=14.9$), 2.16 (2H, bd, $J=14.9$), 1.65 (6H, s), 1.42 (2H, quint, $J=7.3$) 1.28-1.00 (10H, m) and 0.81 (3H, t, $J=6.8$) ; $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ : 180.27, 126.81, 39.76, 38.77, 31.71, 30.74, 29.13, 29.08, 27.55, 26.42, 22.54, 19.15 and 13.99 ; HRMS calcd. for $\text{C}_{18}\text{H}_{29}\text{O}_2\text{N}$ m/z 291.2198 found m/z 291.2176 ; MS(EI) m/z (relative intensity %) 291(M^+ , 100), 276(5), 193(16), 108(58) and 82(2) ; IR (NaCl) 2927, 2856, 1768, 1700, 1438, 1400, 1371, 1349 and 1174 cm^{-1}

11: Ethyl 8-hydroxy-2,3-dimethyl-7-oxo-1,4,4a,7-tetrahydronaphthalene-4a-carboxylate

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ :6.95 (1H, d, $J=9.9$), 6.50-6.45 (2H, m), 4.21-4.03 (2H, m), 3.35 (1H, d, $J=20.9$), 2.95 (1H, d, $J=20.9$), 2.93 (1H, d, $J=16.1$), 2.07 (1H, d, $J=16.1$), 1.70 (3H, s), 1.69 (3H, s) and 1.19 (3H, t, $J=7.0$); $^{13}\text{C-NMR}$ (CDCl_3) δ :180.4, 170.0, 149.4, 143.2, 128.0, 127.2, 123.9, 122.7, 62.1, 52.6, 41.0, 31.7, 18.8, 18.4 and 14.0 ; MS (EI) m/z (relative intensity %) 262 (M^+ ,82), 189 (84), 171 (100), 157 (73), 143 (71), 115 (36) and 91 (30); HRMS calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_4$ m/z 262.1205, found m/z 262.1200. IR(KBr): 3380(br), 2920, 1730, 1650, 1200 and 840 cm^{-1}

13a: Ethyl 8-hydroxy-3-(4-methylpent-3-enyl)-7-oxo-1,4,4a,7-tetrahydronaphthalene-4a-carboxylate

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ :6.96 (1H, d, $J=9.9$), 6.53-6.45 (2H, m), 5.51-5.43 (1H, m), 5.11-5.05 (1H, m), 4.13-4.05 (2H, m), 3.46 (1H, d, $J=21.2$), 3.05-2.95 (2H, m), 2.20-1.95 (5H, m), 1.72-1.53 (6H, m) and 1.46-1.13 (3H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ :180.3, 169.9, 149.5, 143.8, 134.6, 131.9, 127.2, 127.1, 123.8, 118.6, 62.2, 52.3, 38.2, 37.2, 26.0, 26.0, 25.6, 17.7 and 14.0 ; MS (EI) m/z (relative intensity %) 316 (M^+ , 62), 247 (43), 243 (68), 175 (88), 173 (100), 157 (23), 145 (32), 115 (24) and 69 (53); IR (NaCl): 3190, 2920, 2845, 2380, 1730, 1645, 1415, 1375, 1235, 1205 and 1180 cm^{-1}

13b: Ethyl 8-hydroxy-2-(4-methylpent-3-enyl)-7-oxo-1,4,4a,7-tetrahydronaphthalene-4a-carboxylate

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 6.98 (1H, d, $J=9.9$), 6.53-6.45 (2H, m), 5.51-5.43 (1H, m), 5.11-5.05 (1H, m), 4.27-4.13 (2H, m), 3.38 (1H, d, $J=20.9$), 3.11 (1H, dd, $J=5.5$, 16.1), 3.05-2.95 (1H, m), 2.20-1.95 (5H, m) and 1.72-1.53 (6H, m), 1.46-1.13 (3H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 150 MHz) δ : 180.3, 170.1, 149.8, 143.8, 136.7, 132.0, 127.4, 127.1, 123.6, 117.0, 62.2, 52.0, 36.6, 35.4, 29.0, 26.3, 25.6, 17.7 and 14.0; MS (EI) m/z (relative intensity %) 316 (M^+ , 82), 243 (40), 175 (100), 173 (87), 157 (24), 145 (20), 115 (22), 91 (13) and 69 (47); HRMS calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_4$ m/z 316.1675 found m/z 316.1665; IR (NaCl): 3382, 2920, 2845, 2380, 1730, 1645, 1415, 1375, 1235, 1205 and 1180 cm^{-1}

180.271

175

150

126.815

125

100

75

50

39.762

38.776

31.714

30.736

29.133

29.076

27.555

26.421

22.541

19.146

13.991

25

PPM