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One-pot N-acylation and N-alkylation of *o*-nitroaniline with saturated hydrocarbons in the presence of carbon monoxide

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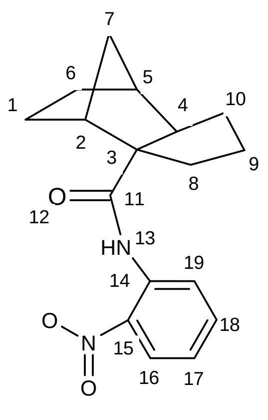
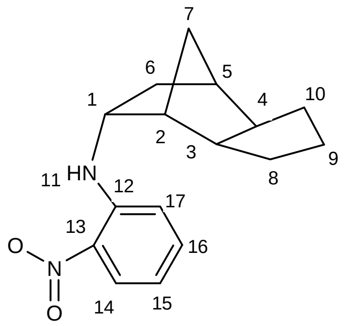
Experimental

The experiments were carried out under atmospheric CO pressure with $CBr_4{\cdot}2AlBr_3$ (E) in anhydrous CH_2Br_2 according to the typical procedures that are given in the paper. All NMR spectra were recorded on a Bruker Avance (^{1}H NMR 400 MHz; ^{13}C NMR 100 MHz, δ from Me_4Si in $CDCl_3$, *J*, Hz). The GC – MS spectra were carried out on a Finnigan Polaris GCO Plus.



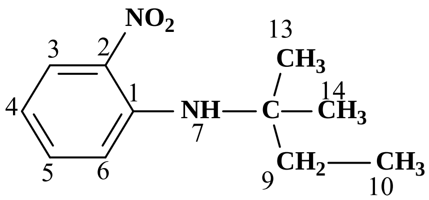
(**1**)

^{1}H NMR: 1.13 – 2.02, 2.04 – 2.16 (m, 12H, ^{5}C**H**, $^{1,6\text{-}10}$,C**H**$_2$); 2,03 (bs, 1H, ^{10}C**H**); 2.42 (bs, 1H, ^{4}C**H**); 2.51 (t, 1H, ^{2}C**H**, $^3J_{HH}$ =5.8, $^3J_{HH}$ = 5.8); 7.12 (t, 1H, ^{17}C**H**, $^3J_{HH}$ =8.5, $^3J_{HH}$ =8.5); 7.61 (t, ^{18}C**H**, , $^3J_{HH}$ =8.5, $^3J_{HH}$ =7.1); 8.21 (d, 1H, ^{19}C**H**, $^3J_{HH}$ = 7.1); 8.76 (d, 1H. ^{16}C**H**, $^3J_{HH}$ =8.5); 10.54 (bs, 1H, N**H**). ^{13}C NMR: 25.35 (^{6}C); 25.94 (^{1}C); 27.56 (^{10}C); 32.72 (^{1}C); 34.76 (^{4}C); 38.65 (^{7}C); 41.55 (^{5}C); 44.23 (^{2}C); 48.73 (^{4}C); 116.72 (^{16}C); 118.62 (^{17}C); 125.99 (^{19}C); 131.8 (^{14}C); 135.48 (^{18}C); 135.5 (^{15}C); 176.74 (^{11}C). MS**:** 300, M^+ (21); 265 (9)**;** 207, (6); 164 (9); 163, $C_{10}H_{15}CO^+$ (68); 138 (3); 136 (34); 135, $C_{10}H_{15}^+$ (100); 133 (5); 122 (4); 121 (6); 119 (4); 108 (4); 107 (9); 106 (7); 105 (9); 95, $C_7H_{11}^+$ (20); 93 (36); 92 (9); 91 (27); 90 (84); 81 (17); 80 (8); 79 (34); 78 (15); 77 (28); 69 (18); 68 (10); 67 (100); 66 (10); 64 (7); 63 (8); 55 (15); 53 (16)**.**



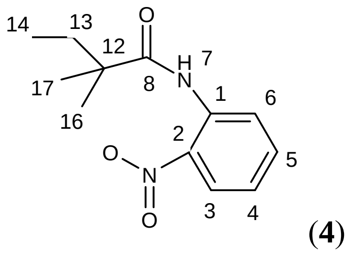
(2)

^{1}H NMR: 0.87 – 0.97, 1.13 – 1.26, 1.27 – 1.37, 1.57 – 1.66, 1.74 – 1.92 (m. 14H, $^{2-10}$C**H**, C**H$_2$**); 3.30 (m.,1H, ^{1}C**H**); 5.88 (bs. 1H, ^{11}N**H)**; 6.63 (t., 1H, ^{15}C**H**, , $^{3}J_{HH}$ =8.4, $^{3}J_{HH}$ =7.8); 6.82 (d., 1H, ^{17}C**H**, $^{3}J_{HH}$ =8.4); 7.30 (t., ^{16}C**H**, , $^{3}J_{HH}$ =8.6, , $^{3}J_{HH}$ =7.8); 8.04 (d., 1H, ^{14}C**H**, $^{3}J_{HH}$ = 8.6). ^{13}C NMR: 27.35 (^{9}C); 29.65 (^{7}C); 31.86 (^{8}C); 32.71 (^{5}C); 35.57 (^{10}C); 39.19 (^{2}C); 40.15 (^{6}C); 40.86 (^{3}C); 51.21 (^{4}C); 53.66 (^{1}C); 114.56 (^{15}C); 118.65 (^{17}C); 126.55 (^{14}C); 135.85 (^{16}C). MS: 272, M^+ (46); 255, M^+-17 (53)**;** 238 (17); 237 (31); 226, M^+-NO_2 (13); 209 (15); 197 (18): 185, $C_{11}H_9N_2O^+$ (24); 171 (40); 169 (40); 157 (27); 156 (32); 148, $C_7H_4N_2O_2^+$ (49); 135 (37); 134 $C_{10}H_{14}^+$ (45); 133 (44); 131 (97); 119, $C_9H_{11}^+$ (60); 107, $C_8H_{11}^+$ (54); 106 (84); 105 (86); 93, $C_7H_9^+$ (46); 92 (31); 91 (91); 79 (100); 77 (61); 67, $C_5H_7^+$ (20); 65 (36); 53 (98).



(3)

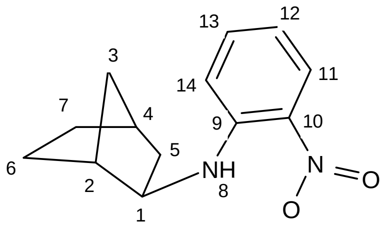
^{1}H NMR: 0.91 (t, 3H, $^{3}J_{HH}$ = 7.0, ^{10}C**H$_3$**); 1.43 (s, 6H, ^{13,14}C**H$_3$**); 1.81 (q, 2H, $^{3}J_{HH}$=7.0, ^{9}C**H$_2$**); 6.28 (bs, 1H, ^{7}C**H$_2$**); 6.65 (bt, 1H, ^{4}C**H**); 6.85 (d, 1H, $^{3}J_{HH}$=8.4, ^{6}C**H**); 7.33 (bt, 1H, ^{5}C**H**); 8.06 (d, 1H, $^{3}J_{HH}$=8.2, ^{3}C**H**). ^{13}C NMR: 7.99 (^{10}C); 27.09 (^{13,14}C); 33.89 (^{9}C); 54.19 (^{8}C); 115.50 (^{4}C); 118.59 (^{6}C); 126.99 (^{3}C); 135.36 (^{5}C); 144.70 (^{2}C); 144.90 (^{1}C). MS: M^+, 208 (26); 193 (16); 180 (19); 179 (100); 146 (2); 139 (4); 138 (43); 133 (9); 132 (16); 130 (5); 123 (3); 122 (8); 121 (4); 120 (4); 119 (10); 118 (4); 117 (9); 108 (5); 107 (4); 93 (6); 92 (27); 90 (5); 82 (4); 80 (5); 78 (4); 77 (12); 76 (7): 71 (19); 70 (9); 65 (18); 64 (5); 63 (7); 55 (22).



(**4**)

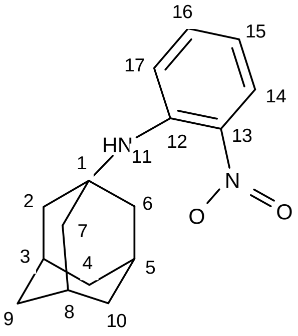
^{1}H NMR: 0.97 (t, 3H, $^{3}J_{HH}$ = 7.3, ^{14}C**H**$_3$); 1.32 (s, 6H, ^{16,17}C**H**$_3$); 1.69 (q, 2H, $^{3}J_{HH}$=7.3, ^{13}C**H**$_2$); 7.15 (bs, 1H, ^{7}C**H**$_2$); 7.63 (bt, 1H, ^{4}C**H**); 8.20 (d, 1H, $^{3}J_{HH}$=8.0, ^{6}C**H**); 7.33 (bt, 1H, ^{5}C**H**); 8.80 (d, 1H, $^{3}J_{HH}$=7.95, ^{3}C**H**). ^{13}C NMR: 8.91 (^{14}C); 24.49 (^{16,17}C); 33.63 (^{13}C); 47 .(^{12}C); 121.75 (^{3}C); 122.74 (^{4}C); 125.44 (^{6}C); 125.66 (^{1}C); 135.71 (^{2}C); 177. 07 (^{8}C). MS: 236, M^+ (7); 208 (7); 190 (1); 179 (1); 137 (33); 122 (1); 108 (1); 99 (6); 92 (4); 71 (100); 55 (10).

***o*-$C_4H_9NHC_6H_4NO_2$ (5).** MS: 195, M^++1 (4); M^+, 194 (34); 180 (10); 179 (95); 139 (8); 138 (100); 133 (4); 132 (17); 130 (3); 122 (8); 121 (7); 120 (6); 119 (7); 118 (3); 117 (8); 108 (8); 107 (4); 91 (11); 90 (8); 82 (8); 80 (10); 77 (10); 76 (5); 66 (5); 57 (61); 56 (8); 51 (12).



(**6**)

^{1}H NMR: 1.19 (m, 1.08 – 1.22, 3H, $^{3',7'\,7''}$C**H**); 1.31 (m, 1.28- 1.34, 1H, $^{5'}$C**H**); 1.52 (m, 1.44 - 1.62, 3H, $^{6',6'',3''}$C**H**); 1.84 (m, 1.82 – 1.86, 1H,$^{5''}$C**H**); 2.29 (2.27 – 2.32, 2H, ^{2,4}C**H**); 3.35 (m, 3.31 – 3.37, ^{1}C**H**); 6.62 (dd, 1H, $^{3}J_{HH}$=8.6, $^{3}J_{HH}$=7.1, ^{12}C**H**); 6.81 (dd, 1H, $^{3}J_{HH}$=7.9, $^{4}J_{HH}$=1 0, ^{14}C**H**); 7.28 (dd, 1H, $^{3}J_{HH}$=7.9, $^{3}J_{HH}$=7.1, ^{13}C**H**); 7.81 (bs, 1H, N**H**); 8.02 (d, 1H, $^{3}J_{HH}$=8.6, ^{11}C**H**). ^{13}C NMR: 25.98 ($^{6}CH_2$); 28.06 ($^{7}CH_2$); 35.32 ($^{3}CH_2$); 35.44 (^{4}CH); 40.74 ($^{5}CH_2$); 41.41 (^{2}CH); 55.67 (^{1}C); 114.48 (^{14}CH); 118.59 (^{12}CH); 125.59 (^{11}CH); 131.38 (^{13}CH), 144.42 (^{9}C); 144.64 (^{10}C). MS: 232, M^+ (100); 217 (12); 203 (16); 191 (15); 185 (25); 177 (23); 171 (20); 169 (26); 157 (18); 156 (20); 151 (21); 149 (22); 148 (44), 147 (24); 145 (20); 139 (20); 138 (73); 135 (46); 134 (44); 133 (20); 132 (37); 131 (98); 130 (34); 129 (21); 123 (21); 122 (18); 119 (54); 118 (19); 117 (16); 111 (26); 109 (41); 108 (58); 107 (45); 106 (75); 105 (43); 97 (28); 92 (52); 93 (42); 92 (49); 91 (46); 85 (12); 83 (23); 81 (70); 80 (63); 79 (85); 71 (25); 67 (50); 65 (76); 63 (25); 55 (33).



(**7**)

^{1}H NMR: 1.73 (t, 6H, $^{4,\ 9,10}$C**H$_2$**, $^{3}J_{HH}$ =2.4); 2.08 (d, 6H, ^{2,6,7}C**H$_2$**, $^{3}J_{HH}$ =2.4); 2.17 (sept, 3H, ^{3,5,8}C**H,** $^{3}J_{HH}$ =2.4); 6.07 (bs, NH, ^{11}N**H**); 6.56 (t, 1H, ^{16}C**H**); 7.17 (d, 1H, ^{17}C**H**, $^{3}J_{HH}$ = 8.7.); 7.32 (td, 1H, $^{3}J_{HH}$ = 8.7, $^{3}J_{HH}$ = 8.6, $^{4}J_{HH}$ = 1.7, ^{15}C**H**); 8.16 (dd, 1H, $^{3}J_{HH}$ = 8.6., $^{4}J_{HH}$ = 1.7, ^{14}C**H**). ^{13}C NMR: 29.43 (^{3,5,8}C); 36. 17 (^{4,9,10}C); 42.26 (^{2,6,7}C); 52.65 (^{1}C); 114,54 (^{15}C); 116.65 (^{17}C); 127.30 (^{14}C); 132.32 (^{13}C); 134.91 (^{16}C); 144.78 (^{12}C). MS: 272, M^{+} (16); 243 (6); 215 (12); 181 (5); 180 (10), 148 (6); 135 (100); 107 (8); 106 (3); 93 (20); 92 (5); 91 (8); 90 (3); 81 (7); 79 (24); 78 (5); 77 (10); 69 (3); 67 (12); 65 (5); 55 (9); 53 (6).

1-AdCONHC$_6$H$_4$NO$_2$-*o* (8). MS: 300, M^{+} (5); 254 (3); 163 (6); 135 (100); 107 (4); 105 (2); 93 (13); 92 (3); 91 (6); 81 (5); 79 (18); 78 (3); 77 (8); 69 (2); 67 (7); 65 (3); 55 (6); 53 (3).