Electronic supplementary materials *Mendeleev Commun*., 2011, **21**, 323–325

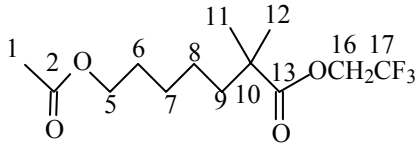
Superelectrophilic sp^3 C-H carbonylation of *n*-octyl acetate as a way to new bifunctional *neo*-octanes

Irena S. Akhrem*, Dzhul'etta V. Avetisyan, Lyudmila V. Afanas'eva, Alexander V. Orlinkov, Nikolai D. Kagramanov and Pavel V. Petrovskii

The experiments with *n*-octyl acetate (**I**) and *n*-hexyl acetate (**II**) were carried out under atmospheric CO pressure with $CBr_4 \cdot 2AlBr_3$ (**E**) in anhydrous CH_2Br_2 according to the typical procedure presented in the paper. All NMR spectra were recorded on a Bruker Avance spectrometer (^{1}H 400 MHz; ^{13}C 100 MHz, δ from $CDCl_3$, *J*, Hz). The GC-MS spectra were carried out on a Finnigan Polaris GCO Plus instrument.

1. Synthesis of $AcO(CH_2)_5C(Me)_2COOCH_2CF_3$

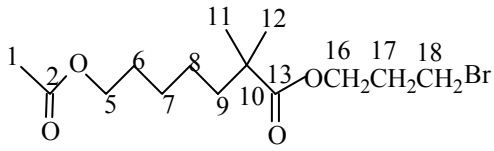
I (0.25 g, 1.47 mmol), E (2.16 g, 2.5 mmol), CH_2Br_2 (1.8 ml), CF_3CH_2OH (0.6 ml). Yield 75%.



^{1}H NMR: 1.19 (6H, s., $^{11,12}CH_3$), 1.13 – 1.73 (8H, m., $^{6\text{-}9}CH_2$); 2.01 (3H, s., $^1CH_3$); 4.02 (2H, t., $^3J_{HH}$ 6.6, $^5CH_2$); 4.44 (2H, q., $^3J_{HF}$, 8,0, $^{16}CH_2$) ^{13}C NMR: 20.78 ($^1CH_3$); 24.75 ($^{11,12}CH_3$); 26.05 ($^8CH_2$); 27.26 ($^7CH_2$); 28.85 ($^6CH_2$); 40.04 ($^9CH_2$); 42.23 (^{10}C); 59.90 (q., $^3J_{CF}$ 32.2, $^{16}CH_2$); 64.15 ($^5CH_2$); 124.24 (q., $^2J_{CF}$ 286.1 ($^{17}CF_3$); 170.91 (^{2}CO); 175.97 (^{13}C). MS: 299, $M^+ + H$ (6); 239 (6); 199 (6); 194 (4); 195 (6); 184 (7); 183 (9); 181 (6); 171 (9); 170 (86); 169 (16); 168 (4); 163 (4); 156 (5); 155 (25); 153 (4); 151 (4); 150 (12); 149 (14); 141 (11); 138 (5); 137 (5); 136 (6); 135 (56); 128 (4); 127 (5); 125 (4); 123 (10); 121 (6); 113 (4); 112 (4); 111 (36); 110 (14); 109 (23); 108 (4); 107 (7); 105 (5); 100 (4); 97 (5); 96 (9); 95 (28); 94 (4); 93 (8); 83 (18); 82 (15); 81 (27); 86 (5); 79 (14); 77 (10); 71 (4); 70 (8); 69 (100); 68 (6); 67 (49); 65 (5); 61 (6); 55 (40).

2. Synthesis of $AcO(CH_2)_5C(Me)_2COO(CH_2)_3Br$

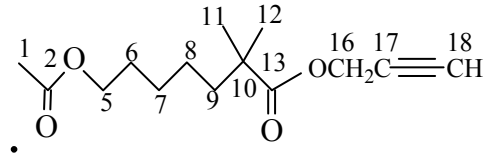
I (0.33 g, 1.90 mmol), E (2.79 g, 3.23 mmol), CH_2Br_2 (2.3 ml), $HO(CH_2)_3Br$ (0.6 ml). Yield 63%.



^{1}H NMR: 1.07 (6H, s., $^{11,12}CH_3$), 1.14 – 1.22 (4H, m., $^{8,9}CH_2$); 1.40 – 1.72 (4H, m, $^{6,7}CH_2$) 1.95 (3H, s., $^{1}CH_3$); 2.09 (2H, pent., $^{3}J_{HH}$ 6.20, $^{17}CH_2$); 3.42 (2H, t., $^{3}J_{HH}$ 6.48, $^{18}CH_2$);, 3.75 (2H, t., $^{3}J_{HH}$ 6.5, $^{5}CH_2$.); 4.00 (2H, t, $^{3}J_{HH}$ 6.5, $^{16}CH_2$); ^{13}C NMR: 20.78 ($^{1}CH_3$); 24.27 ($^{8}CH_2$); 24.81 ($^{11,12}CH_3$); 26.01 ($^{7}CH_2$); 28.09 ($^{6}CH_2$); 29.32 ($^{18}CH_2$); 30.29 ($^{17}CH_2$); 40.20 ($^{9}CH_2$); 41.90 (^{10}C); 61.62 ($^{16}CH_2$); 64.12 ($^{5}CH_2$); 170.56 (^{2}CO); 177.31 (^{13}CO). MS: 255, M^+ + H (34); 195 (3); 167 (5); 157 (5); 138 (8); 133 (4); 127 (5); 125 (12); 123 (6); 121 (11); 119 (4); 112 (12); 111 (80); 110 (7); 109 (17); 107 (10); 105 (5); 99 (5); 97 (8); 95 (17); 93 (15); 91 (12); 83 (21); 82 (5); 81 (19); 80 (6); 79 (27); 77 (12); 70 (12); 69 (100); 68 (4); 67 (38); 66 (4); 65 (7); 59 (5); 57 (4).

3. Synthesis of $AcO(CH_2)_5C(Me)_2COOCH_2C{\equiv}CH$

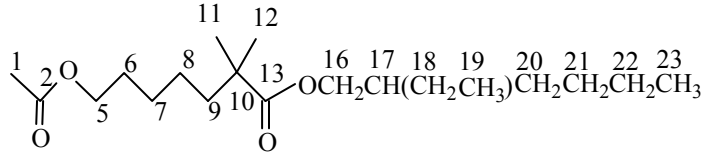
I (0.37 g, 2.15 mmol), E (3.16 g, 3.66 mmol), CH_2Br_2 (2.6 ml), $HOCH_2C{\equiv}CH$ (0.8 ml). Yield 78%.



^{1}H NMR: 1.10 (6H, s., $^{11,12}CH_3$), 1.0 – 1.68 (8H, m., $^{6-9}CH_2$); 1.96 (3H, s., $^{1}CH_3$); 2.41 (1H, bs, ^{18}CH); 3.95 (2H, t., $^{3}J_{HH}$ 6.6, $^{5}CH_2$); 4.58 (2H, s., $^{3}J_{HH}$, $^{16}CH_2$) ^{13}C NMR: 20.78 ($^{1}CH_3$); 24.18 ($^{8}CH_2$); 24.77 ($^{11,12}CH_3$); 26.00 ($^{7}CH_2$); 28.11 ($^{6}CH_2$); 40.21 ($^{9}CH_2$); 41.92 (^{10}C); 51.52 ($^{16}CH_2$); 64.18 ($^{5}CH_2$); 74.38 (^{18}CH); 76.59 (^{17}C); 170.89 (^{2}CO); 176.70 (^{13}C). MS: 255, M^+ + H (34); 195 (3); 167 (5); 157 (5); 138 (8); 133 (4); 127 (5); 125 (12); 123 (6); 121 (11); 119 (4); 112 (12); 111 (80); 110 (7); 109 (17); 107 (10); 105 (5); 99 (5); 97 (8); 95 (17); 93 (15); 91 (12); 83 (21); 82 (5); 81 (19); 80 (6); 79 (27); 77 (12); 70 (12); 69 (100); 68 (4); 67 (38); 66 (4); 65 (7); 59 (5); 57 (4).

4. Synthesis of $AcO(CH_2)_5C(Me)_2COOCH_2CH(Et)Bu$

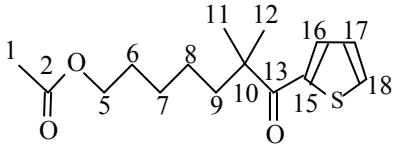
I (0.20 g, 1.17 mmol), E (1.72 g, 1.99 mmol), CH_2Br_2 (1.3 ml), 2-ethylhexanol-1 (4 mmol). Yield 75%.



^{1}H NMR: 0.84 – 0.90 (6H, м., $^{19,23}CH_3$), 1.29 (6H, s., $^{11,\ 12}CH_3$); 1.15-1.74 (15H, m., rest CH_2, ^{17}CH.); 2.01 (3H, s., $^{1}CH_3$); 3.98 (2H, t., $^{3}J_{HH}$ 6.7, $^{5}CH_2$); 3.98 (2H, t., $^{3}J_{HH}$,6.7, $^{16}CH_2$) ^{13}C NMR: 10.83 ($^{19}CH_3$); 13.83 ($^{23}CH_3$); 20.76 ($^{1}CH_3$); 22.77 ($^{22}CH_2$); 24.55 ($^{18}CH_2$); 24.58 ($^{8}CH_2$); 24.99 ($^{11,12}CH_3$); 26.24 ($^{7}CH_2$); 28.31 ($^{21}CH_2$); 28.71 ($^{6}CH_2$); 30.31 ($^{20}CH_2$); 38.59 (^{17}CH); 40.47 (^{9}CH); 42.17 (^{10}C); 64.26 ($^{5}CH_2$); 66.21 ($^{16}CH_2$); 170.89 (^{2}CO); 177.77 (^{13}CO). MS: 329, $M^+ + H$ (22); 299 (2); 287 (2); 279 (2); 269 (3); 217 (3); 199 (2); 171 (3); 167 (6); 158 (3); 157 (15); 156 (3); 149 (21); 139 (3); 129 (4); 128 (6); 127 (3); 123 (3); 113 (6); 112 (10); 111 (77); 110 (16); 109 (8); 108 (3); 102 (8); 101 (4); 97 (7); 95 (14); 89 (4); 88 (56); 87 (7); 84 (9); 83 (15); 82 (11); 81 (8); 79 (4); 73 (30); 71 (14); 70 (26); 69 (100); 68 (4); 67 (26); 65 (4); 59 (4); 57 (18); 55 (47).

5. Synthesis of $AcO(CH_2)_5C(Me)_2COC_4H_3S$

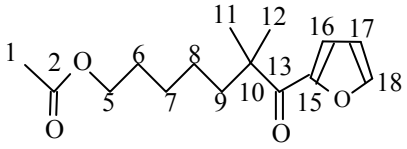
I (0.21 g, 1.21 mmol), E (1.78 g, 2.07 mmol), CH_2Br_2 (1.6 ml), thiophene (4.2 mmol). Yield 75%.



^{1}H NMR: 1.27 (2H, m., $^{8}CH_2$), 1.34 (6H, s., $^{11,12}CH_3$); 1.53 – 1.57 (4H, m., $^{7,9}CH_2$); 1.78 – 1.82 (2H, $^{6}CH_2$); 2.01 (3H, s., $^{1}CH_3$); 3.97 (2H, t., $^{3}J_{HH}$ 6.7, $^{5}CH_2$); 7.09 (1H, dd., $^{3}J_{HH}$ 4.9, $^{3}J_{HH}$ 3.0 ^{17}CH); 7.54 (1H, dd., $^{3}J_{HH}$ 4.9, ^{16}CH); 7.76 (1H, dd, $^{3}J_{HH}$ 3.0, ^{18}CH). ^{13}C NMR: 20.80 ($^{1}CH_3$); 24.24 ($^{8}CH_2$); 26.03 ($^{11,12}CH_3$); 26.31 ($^{7}CH_2$); 28.14 ($^{6}CH_2$); 41.28 (^{9}CH); 47.25 (^{10}C); 64.25 ($^{5}CH_2$); 127.49(^{17}CH); 131.36 (^{16}CH); 132.12 (^{18}C); 170.94 (^{2}CO); 198.39 (^{13}CO). MS: 282, M^+ (2); 222 (2); 208 (2); 207 (5); 193 (2); 180 (2); 179 (2); 168 (7); 167 (4); 166 (5); 156 (2); 155 (5); 154 (47); 153 (5); 152 (2); 151 (2); 149 (6); 140 (4); 139 (11); 134 (2); 126 (8); 125 (4); 113 (8); 112 (7); 111 (100); 110 (3); 109 (3); 97 (6); 95, $C_4H_3OCO^+$ (5); 85 (3); 83 (6); 84 (3); 83 (12); 81 (4); 70 (4); 69 (35); 67 (11); 55 (8).

6. Synthesis of $AcO(CH_2)_5C(Me)_2COC_4H_3O$

I (0.22 g, 1.30mmol), E (1.91 g, 2.22 mmol), CH_2Br_2 (1.6 ml), furan (4.2 mmol). Yield 75%.



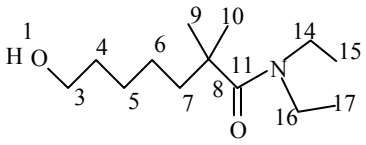
^{1}H NMR: 1.13 (2H, m., $^{8}CH_2$), 1.24 (6H, s., $^{11,12}CH_3$); 1.50 (2H, m., $^{7}CH_2$,); 1.74 (2H, m., $^{9}CH_2$); 1.93 (3H, s., $^{1}CH_3$); 1.96 (2H, м.,$^{6}CH_2$); 3.93 (2H, t., $^{3}J_{HH}$ 6.8, $^{5}CH_2$); 6.44 (1H, dd., $^{3}J_{HH}$ 3.5,^{17}CH); 7.14 (1H, d., $^{3}J_{HH}$ 3.5, ^{16}CH); 7.48 (1H, d, $^{3}J_{HH}$ 1.7, ^{18}CH). ^{13}C NMR: 20.74 ($^{1}CH_3$); 24.68 ($^{11,12}CH_3$); 26.25 ($^{7}CH_2$); 28.80 ($^{6}CH_2$); 39.62 (^{9}CH); 46.30 (^{10}C); 64.21 ($^{5}CH_2$); 111.48 (^{17}CH); 117.60 (^{16}CH); 144.69 (^{18}CH); 152.56 (^{15}C); 170.81 (^{2}CO); 194.33 (^{13}CO). MS: 267, M^+ + H (8); 192 (4); 191 (3); 163 (3); 152 (11); 151 (8); 150 (14); 149 (10); 139 (14); 138 (100); 137 (10); 136 (3); 0); 133 (4); 132 (5); 131 (5); 125 (4); 124 (18); 123 (40); 122 (4); 121 (5); 112 (3); 111 (16); 110 (15); 109 (8); 108 (3); 107 (4); 105 (4); 97 (9); 96 (18); 95, $C_4H_3OCO^+$ (61); 93 (4); 91 (5); 85 (3); 83 (8); 82 (6); 81 (11); 79 (8); 78 (4); 77 (5); 71 (29); 69 (29); 68 (9); 67, $C_4H_3O^+$ (27); 66 (4); 65 (5); 55 (19).

8. Reaction of *n*-hexyl acetate with Et_2NH

II (0.125 g, 0.87 mmol), CBr_4 (0.51 g, 1.59 mmol), $AlBr_3$ (0.73 g, 2.78 mmol), CH_2Br_2 (1.9 ml), Et_2NH (2.4 mmol.) A molar ratio [$HOC_6H_{12}CONEt_2$]: [$AcOC_6H_{12}CONEt_2$] = 1 :3. Total yield 60%. **$HOC_6H_{12}CONEt_2$** (2 isomers: *neo*/*iso* = 1:7) MS (*iso*-isomer): 202, M^++ H, (1); 186, M^+ - Me (3); 170, M^+ - CH_2OH (4); 168, M^+ - Me –H_2O (5); 156 (10); 143 (5); 142 (39); 130 (11), 129, M^+ - NEt_2 (94); 114 (40); 100, $CONEt_2^+$ (44); 83 (10); 74 (10); 72, NEt_2^+(62); 71 (6); 70 (4); 69 (10); 59 (5); 58 (100; 55(49). **$AcOC_6H_{12}CONEt_2$** (2 isomers: *neo*/*iso* = 1:17). MS (*iso*-isomer): 243, M^++ H, (3); 228 (3); 200, M+ - Ac (5); 186 (9); 184 (25); 183 (6); 168 (8); 156 (10); 155 (3); 154 (10); 143 (8); 142 (52); 140 (4); 130 (8), 129, M^+ - (100); 128 (10); 127 (4); 126 (5); 115 (7); 114 (41); 111 (9); 101(9); 100, $CONEt_2^+$ (54); 83 (26); 74 (31); 72, NEt_2^+(66); 71 (5); 69 (7); 59 (5); 58 (88); 55(44).

9. Reaction of *n*-octyl acetate with Et_2NH

I (0.15 g, 0.87 mmol), E (1.14 g, 1.32 mmol), CH_2Br_2 (1.8 ml), Et_2NH (0.7g, 10 mmol.) At −15 ^{o}C (1 h), diethyl amine was involved to the *in situ* generated carbonylation product as a stream with CO. Yield of $HOC_8H_{16}CONEt_2$ 70%. MS of **$AcNEt_2$** (M^+ 115) is identical with that of N,N-diethyl acetamide (NIST 08: DB: repl: b, ID# 6286).



^{1}H NMR: 1.07 (6H, t, $^{3}J_{HH}$ 6.6, $^{15,17}CH_3$), 1.28 (6H, s., $^{9.10}CH_3$); 1.29 – 1.59 (8H, m., $^{4-7}CH_{2,}$); 2.35 (1H, bs, OH[1]); 3.43 (4H, m., $^{14,16}CH_2$); 3.67 (2H,t., $^{3}J_{HH}$ 6.6, $^{5}CH_2$). ^{13}C NMR: 13.20 ($^{15,17}CH_3$); 24.61 ($^{6}CH_3$); 26.18 ($^{5}CH_2$); 27.05 ($^{9,10}CH_3$); 32.41 (^{4}CH); 40.98 ($^{14,16}CH_2$); 41.31 ($^{7}CH_2$); 42.45 (^{8}C); 62.39 ($^{3}CH_2$); 175.63(^{11}C). MS: 230, M^++H (18); 228 (3); 214 (6); 212 (4); 200 (5); 198 (5); 186 (11); 185 (5); 173 (5); 170 (11); 169 (11); 159 (7); 158 (5); 157, $HOC_8H_{16}CO$ (14); 156 (25); 155 (4); 145 (5); 144 (8); 143, $H(Me)_2CONEt_2$ (60);142 (13); 140 (5); 129 (17) M^+ - $CONEt_2$ (); 128 (39); 126 (5); 116 (5); 115 (78); 114 (9); 111 (10); 110 (6); 102 (32); 101 (8); 100, $CONEt_2$ (96); 95 (12); 91 (5); 86 (25); 83 (12); 81 (10); 79 (8); 77 (8); 74 (12); 72, NEt_2 (100); 70 (8); 69 (98).

10. Reaction of n-octyl acetate with Bu_2NH

I (0.39 g, 2.26 mmol), E (3.33 g, 3.85 mmol), CH_2Br_2 (2.7 ml), Bu_2NH (0.64, 5.0 mmol). Conversion of **I** 100%. GC –MS: MS of **$AcNBu_2$** (M^+ 171) is identical with that of *N*,*N*-dibutyl acetamide (NIST 08: DB: repl: b, ID# 10906.) **$AcOC_8H_{16}CONBu_2$.** MS: 328, M^+ (1); 327 (1); 284, M^+ – Ac(14); 268, M^+ –AcO (6); 252 (3); 242 (4); 226 (6); 224 (3); 213 (4); 212 (20); 199 (10); 198 (3); 170 (4); 158 (7); 157 (11); 156 (100); 143 (3); 130 (11); 128 (8); 121 (10); 119 (4); 114 (17); 112 (4); 111 (27); 109 (5); 100 (26); 99 (3); 86 (18); 83 (6); 72 (4); 70 (5); 69 (39); 67 (7); 57 (39); 55 (6).

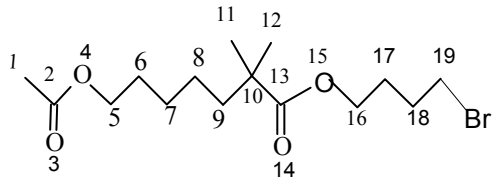
11. Reaction of *n*-octyl acetate with toluene

I (0.16 g, 0.95 mmol), E (1.39 g, 1.62 mmol), CH_2Br_2 (1 ml), C_6H_5Me (0.8 ml). Conversion of **I** is 92%, Molar ratio of mixtures of isomers $AcOC_8H_{16}C_6H_4Me$ (M = 262): $AcOC_8H_{16}C_6H_3(Me)(C_8H_{15})$ (372) = 10 : 1. GC-MS: **$AcOC_8H_{16}C_6H_4Me$** with isomer decreasing: (**1**) major isomer: 262, M^+ (0.5); 203, M^+-AcO (2); 202, M^+-AcOH (19); 187, M^+-AcOH-Me (4); 134 (12); 133, $MeC_6H_4C(Me)_2^+$ (100); 132 (7); 131 (4); 128, $CH_3C_8H_{16}^+$ (3); 119, $MeC_6H_4C_2H_4^+$ (5); 117 (8); 115 (9); 106 (9); 105, $MeC_6H_4CH_2^+$ (95); 103 (4); 93 (7); 91, $MeC_6H_5^+$(14); 79 (8); 77 (6) (*neo*). (**2**). 262, M^+ (1); 203, M^+-AcO (2); 159 (2); 147 (3); 145 (3); 134 (15); 133, $MeC_6H_4C(Me)_2^+$ (100); 132 (15); 131 (3); 129 (3); 128, $CH_3C_8H_{16}^+$ (3); 120 (8); 119, $MeC_6H_4C_2H_4^+$ (35); 118 (6); 117 (19); 115 (13); 106 (9); 105, $MeC_6H_4CH_2^+$ (91); 103 (5); 93 (6); 91, $MeC_6H_5^+$(26); 79 (6); 77 (8). (*neo*). (**3**) 262, M^+ (0.6); 202, M^+-AcOH (16); 187 (5); 173 (2), 159 (4); 147 (9); 146 (5); 145 (8); 133 (3); 132 (31); 131 (6); 120 (20); 119,

$MeC_6H_4CH(CH_3)^+$ (100); 118 (10); 117 (39); 116 (3); 115 (16); 105 (24); 103 (3); 91 (43); 83 (4); 79 (5); 77 (5).(*tert*-isomer). **$AcOC_8H_{16}C_6H_3(Me)(C_8H_{15})$** (M=372) (3 isomers with close concentrations and similar mass-spectra). The MS of two of them is following: (1).M^+, 372 (0.2); 304 (19); 303, M^+ - C_5H_9 (76); 244 (4); 243 (7); 207 (7); 201 (6); 188 (8); 187 (42); 175 (15); 174 (12); 173 (74); 171 (4); 161 (9); 160 (11); 159, $C_6H_4(Me)C_5H_8^+$ (69); 158 (4); 157 (7); 147 (6); 146 (9); 145, $C_6H_5C_5H_8^+$ (100); 134 (9); 133 (78); 132 (7); 131 (46); !30 (5); 129 (10); 128 (5); 119 (9); 117 (8); 112 (7); 111 (72); 105 (19); 119 (13); 91 (6); 69 (37). (2). M^+, 372 (5); 303, M - C_5H_9 (32); 289 (7); 244(6); 243 (23); 229 (7); 207 (4); 201 (6); 187 (15); 174 (8); 173 (48); 161 (19); 160 (18); 159, $C_6H_4(Me)C_5H_8^+$ (100); 157 (7); 144 (5); 143 (5); 133 (9); 132 (8); 131 (69); !30(4); 129 (7); 119 (15); 117 (12); 115 (5); 111, $C_8H_{15}^+$ (25); 105 (13); 91 (8); 69 (15).

12. THF ring-opening by *n*-octyl acetate, CO, and $CBr_4 \cdot 2AlBr_3$

I (0.30 g, 1.75 mmol), E (2.57 g, 2.97 mmol), CH_2Br_2 (2 ml), THF (0.5 ml). Yield 72%.



^{1}H NMR: 1.11 (6H, s., $^{11,12}CH_3$); 1.14 -1.22 (4H, m, $^8CH_2$), 1.49 (2H, m., $^7CH_2$,); 1.61 (2H, m., $^6CH_2$); 1.78 (2H,., $^{18}CH_3$); 1.93 (2H, м.,$^{17}CH_2$); 2.03 (3H, $^1CH_2$); 3.42 (2H, t., $^3J_{HH}$ 6.6, $^{19}CH_2$); 4.02 (2H, t., $^3J_{HH}$ 6.7, $^5CH_2$); 4.07 (2H, t, $^3J_{HH}$ 6.4, $^{16}CH_2$). ^{13}C NMR: 20.68 ($^1CH_3$); 24.32 ($^8CH_2$), 24.85 ($^{11,12}CH_3$); 26.05 ($^7CH_2$); 27.02 ($^{18}CH_2$); 28.14 ($^6CH_2$); 29.06 ($^{17}CH_2$); 32.74 ($^{19}H_2$); 40.22 ($^9CH_2$); 41.91 (^{10}C); 62.96 ($^5CH_2$); 63.94 ($^{16}CH_2$); 170.79 (^{2}C); 177.46 (^{13}C). MS: 351, 353 , M^+ + H (7); 271, M - Br (1); 171, $MeCOOC_8H_{16}^+$ (3); 137, 135, $C_4H_8Br^+$ (52); 112, $C_8H_{16}^+$ (6); 111 (51); 110 (4); 95, $C_4H_3OCO^+$ (10); 82 (4); 81 (3); 70 (5); 69 (100); 67, $C_4H_3O^+$ (19); 65 (3); 55 (43). **$HOC_8H_{16}COOC_4H_8Br$** (small amount). MS: 309, 311 , M^+ + H (2); 157, $HOC_8H_{16}CO^+$ (5); 137, 135, $C_4H_8Br^+$ (50); 136, 138 , $C_4H_9Br^+$ (2); 112, $C_8H_{16}^+$ (4); 111 (24); 109 (3); 95, $C_4H_3OCO^+$ (6); 88 (3); 83 (3); 82 (5); 79, 81, Br^+ (4); 73 (7); 70 (9); 69 (100); 67, $C_4H_3O^+$ (18); 67 (3); 55 (57).