

Unexpected formation of 4-arylcyclopentane-1,1,3,3-tetracarboxylates in GaCl₃-catalyzed reaction of 2-arylcyclopropane-1,1-dicarboxylates with tetrasubstituted 1-pyrazolines

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Tetramethyl 4-(3-bromophenyl)cyclopentane-1,1,3,3-tetracarboxylate 4d. The title compound was prepared according to the general procedure in 80% yield. Thick colorless oil. ¹H NMR (CDCl₃, 400.1 MHz): δ 2.59 [ddd, 1H, H_a(5), ²J 13.4 Hz, ³J 6.8 Hz, ⁴J 1.4 Hz], 2.80 [dd, 1H, H_b(5), ²J 13.4 Hz, ³J 13.1 Hz], 2.96 [dd, 1H, H_a(2), ²J 14.5 Hz, ⁴J 1.4 Hz], 3.17 [d, 1H, H_b(2), ²J 14.5 Hz], 3.25, 3.75, 3.76 and 3.80 (all s, 4×3H, 4OMe), 4.07 [dd, 1H, H(4), ³J 13.1 and 6.8 Hz], 7.14 [t, 1H, H(5'), C₆H₄, ³J 7.9 Hz], 7.28 [br.d, 1H, H(4') or H(6'), C₆H₄, ³J 7.9 Hz], 7.36 [ddd, 1H, H(4') or H(6'), C₆H₄, ³J 7.9 Hz, ⁴J 1.7 and 1.0 Hz], 7.47 [t, 1H, H(2'), C₆H₄, ⁴J 1.7 Hz]. ¹³C NMR (CDCl₃, 100.6 MHz): δ 38.7 [CH₂(5)], 41.4 [CH₂(2)], 48.9 [CH(4)], 52.4, 53.0, 53.1 and 53.2 (4OMe), 58.6 [C(1)], 64.5 [C(3)], 122.2 (CBr), 127.5 [CH(4') or CH(6'), C₆H₄], 129.7 [CH(5'), C₆H₄], 130.6 [CH(4') or CH(6'), C₆H₄], 131.7 [CH(2'), C₆H₄], 140.5 (*i*-C), 170.3, 170.9, 171.6 and 171.9 (4COO). MS (*m/z*, %): 458 (14) and 456 (15) [M]⁺, 427 (4) and 425 (4) [M–OMe]⁺, 398 (41) and 396 (44) [M–HCO₂Me]⁺, 367 (20), 366 (93), 365 (21), 364 (93), 338 (39), 336 (39), 310 (20), 309 (100), 308 (37), 307 (100), 279 (33), 277 (34), 198 (30), 155 (26), 141 (29), 140 (28), 139 (50), 128 (38), 115 (58), 113 (47), 77 (21), 59 (100). HRMS calcd for C₁₉H₂₁⁷⁹BrO₈, *m/z*: [M+Na]⁺, 479.0312. Found, *m/z*: 479.0304.

Tetramethyl 4-(4-methylphenyl)cyclopentane-1,1,3,3-tetracarboxylate 4e. The title compound was prepared according to the general procedure in 57% yield. Thick colorless oil. ¹H NMR (CDCl₃, 400.1 MHz): δ 2.34 (s, 3H, Me), 2.62 [ddd, 1H, H_a(5), ²J 13.5 Hz, ³J 6.7 Hz, ⁴J 1.6 Hz], 2.89 [dd, 1H, H_b(5), ²J 13.5 Hz, ³J 13.2 Hz], 3.00 [dd, 1H, H_a(2), ²J 14.5 Hz, ⁴J 1.6 Hz], 3.16 [s, 3H, CO₂Me at C(3)], 3.20 [d, 1H, H_b(2), ²J 14.5 Hz], 3.77, 3.79 and 3.81 (all s, 3×3H, 3OMe), 4.15 [dd, 1H, H(4), ³J 13.2 and 6.7 Hz], 6.95–7.05 (m, 4H, C₆H₄).

Tetramethyl 4-(4-chlorophenyl)cyclopentane-1,1,3,3-tetracarboxylate 4g. The title compound was prepared according to the general procedure in 69% yield. Thick colorless oil. ¹H NMR (CDCl₃, 400.1 MHz): δ 2.58 [ddd, 1H, H_a(5), ²J 13.4 Hz, ³J 6.7 Hz, ⁴J 1.5 Hz], 2.81 [dd, 1H,

H_b(5), ²J 13.4 Hz, ³J 13.2 Hz], 2.97 [dd, 1H, H_a(2), ²J 14.5 Hz, ⁴J 1.5 Hz], 3.15 [d, 1H, H_b(2), ²J 14.5 Hz], 3.22, 3.75, 3.76 and 3.80 (all s, 4×3H, 4OMe), 4.08 [dd, 1H, H(4), ³J 13.2 and 6.7 Hz], 7.24 and 7.28 (both m, 2×2H, C₆H₄). ¹³C NMR (CDCl₃, 100.6 MHz): δ 38.8 [CH₂(5)], 41.5 [CH₂(2)], 48.7 [CH(4)], 52.5, 53.0, 53.2 and 53.3 (4OMe), 58.7 [C(1)], 64.6 [C(3)], 128.3 (2 *m*-CH), 130.2 (2 *o*-CH), 133.4 (*p*-CCl), 136.6 (*i*-C), 170.5, 171.0, 171.7 and 171.9 (4COO). HRMS calcd for C₁₉H₂₁³⁵ClO₈, *m/z*: [M+Na]⁺, 435.0817. Found, *m/z*: 435.0812.

Tetramethyl 4-(4-bromophenyl)cyclopentane-1,1,3,3-tetracarboxylate 4h. The title compound was prepared according to the general procedure in 65% yield. Thick colorless oil. ¹H NMR (CDCl₃, 400.1 MHz): δ 2.57 [ddd, 1H, H_a(5), ²J 13.4 Hz, ³J 6.7 Hz, ⁴J 1.5 Hz], 2.80 [dd, 1H, H_b(5), ²J 13.4 Hz, ³J 13.1 Hz], 2.97 [dd, 1H, H_a(2), ²J 14.5 Hz, ⁴J 1.5 Hz], 3.15 [d, 1H, H_b(2), ²J 14.5 Hz], 3.22, 3.75, 3.76 and 3.80 (all s, 4×3H, 4OMe), 4.07 [dd, 1H, H(4), ³J 13.1 and 6.7 Hz], 7.22 and 7.39 (both m, 2×2H, C₆H₄). ¹³C NMR (CDCl₃, 100.6 MHz): δ 38.6 [CH₂(5)], 41.4 [CH₂(2)], 48.7 [CH(4)], 52.4, 53.0, 53.1 and 53.2 (4OMe), 58.6 [C(1)], 64.4 [C(3)], 130.4 and 131.2 (2 *o*-CH and 2 *m*-CH), 131.5 (CBr), 137.1 (*i*-C), 170.3, 171.0, 171.7 and 172.0 (4COO). MS (*m/z*, %): 458 (5) and 456 (5) [M]⁺, 427 (2) and 425 (2) [M-OMe]⁺, 398 (45) and 396 (48) [M-HCO₂Me]⁺, 338 (23), 336 (24), 307 (61), 306 (22), 305 (65), 279 (32), 277 (34), 184 (34), 182 (39), 141 (29), 139 (52), 128 (44), 115 (70), 113 (71), 77 (25), 59 (100). HRMS calcd for C₁₉H₂₁⁷⁹BrO₈, *m/z*: [M+Na]⁺, 479.0312; [M+K]⁺, 495.0051. Found, *m/z*: 479.0303, 495.0053.

Tetramethyl 4-(2-naphthyl)cyclopentane-1,1,3,3-tetracarboxylate 4j. The title compound was prepared according to the general procedure in 48% yield. Thick colorless oil. ¹H NMR (CDCl₃, 400.1 MHz): δ 2.69 [dd, 1H, H_a(5), ²J 13.5 Hz, ³J 6.7 Hz], 3.00 [ddd, 1H, H_b(5), ²J 13.5 Hz, ³J 13.1 Hz, ⁴J 1.5 Hz], 3.02 [dd, 1H, H_a(2), ²J 14.5 Hz, ⁴J 1.5 Hz], 3.03 [s, 3H, CO₂Me at C(3)], 3.25 [d, 1H, H_b(2), ²J 14.5 Hz], 3.773, 3.775 and 3.82 (all s, 3×3H, 3OMe), 4.30 [dd, 1H, H(4), ³J 13.1 and 6.7 Hz], 7.36–7.53 (m, 3H, 2-naphthyl), 7.62–7.89 (m, 4H, 2-naphthyl). ¹³C NMR (CDCl₃, 100.6 MHz): δ 38.9 [CH₂(5)], 41.6 [CH₂(2)], 49.4 [CH(4)], 52.3, 52.9, 53.1 and 53.3 (4OMe), 58.7 [C(1)], 64.5 [C(3)], 125.9, 126.1, 126.2, 127.1, 127.3, 127.5 and 127.9 (7CH, 2-naphthyl), 132.8, 133.7 and 135.5 (3C, 2-naphthyl), 170.6, 171.0, 171.9 and 172.0 (4COO).