Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic supplementary information

An unexpected epoxidation of benzil derivatives in their reaction with a germene

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General Procedures.

All manipulations were carried out under N_2 or Ar using standard Schlenk techniques with solvents freshly distilled from sodium benzophenone. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AC 200, AC 250 and Avance 300 instruments at 200.13, 250.13 and 300.13 MHz (^1H), and 50.10, 62.89 and 75.47 MHz (^{13}C) respectively. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV and on a Nermag R10-10 spectrometer by CI (NH_3). Melting points were determined on a Leitz microscope heating stage 250. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse".

General procedure for the reaction of 1 with substituted benzils

A solution of substituted benzil (2.1 mmol) in Et_2O (10 mL) was added by syringe to the crude solution of **1** (prepared from 1.00 g of fluorogermane $Mes_2Ge(F)CHR_2$ (2.02 mmol) and one equivalent of *tert*-butyllithium). The initially orange reaction mixture turned light yellow by warming to room temperature. After removal of LiF by filtration, Et_2O was evaporated under vacuum and replaced by pentane ; a fractional crystallization at – 20°C afforded crystals of adducts **2**.

2b 1.11 g (76%), mp = 220 °C.

δ_H (300.18 MHz): 2.24 and 2.34 (2s, 2 x 3H, *p*-Me of Mes), 0.50 – 3.40 (extremely broad s ($\Delta\nu_{1/2}$ = 260 Hz) 12H, *o*-Me of Mes), [6.29 – 6.33 (m, 4H), 6.70 – 7.10 (very broad s, 4H),

6.90 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.19 – 7.44 (m, 7H), 7.62 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.68 (d, $^3J_{HH}$ = 7.5 Hz, 2H)] (arom H).

δ_C (75.47 MHz): 20.89 and 21.03 (*p*-Me of Mes), 22.78 and 23.61 (*o*-Me of Mes), 60.84 (CR_2), 77.90 (R_2CCO), 91.62 (GeOCO), 113.26 and 114.69 (2d, $^2J_{CF}$ = 21.1 Hz, *m*-CH of C_6H_4F), 120.08, 120.14, 125.25, 125.40, 126.95, 126.97, 128.77, 128.81, 128.92, 129.09, 130.14 and 130.25 (arom CH), 128.43, 128.65, 132.13, 132.17, 132.42, 133.30, 139.35, 139.44, 140.99, 141.51, 143.44, and 144.96 (arom C), 160.48 (d, $^2J_{CF}$ = 98.1 Hz, CF), 164.75 (d, $^2J_{CF}$ = 98.9 Hz, CF).

MS (60 eV, m/z) : 722 (M, 10), 627 (M – C_6H_4F, 10), 599 (M – C_6H_4F – CO, 8), 476 ($Mes_2Ge{=}CR_2$, 25), 451 (M – CR_2 – CC_6H_4F, 30), 394 (M – Mes_2GeO, 45), 311 (Mes_2Ge – 1, 38), 270 ($R_2CCC_6H_4F$ – 1, 45), 123 (FC_6H_4CO, 100).

Anal. Calcd for $C_{45}H_{38}F_2GeO_2$ (722.205) C, 74.92; H, 5.31; F, 5.27% . Found : C, 75.02; H, 5.10; F, 5.30%.

2c 1.01 g (67%), mp = 158 °C.

δ_H (300.18 MHz): 2.27 and 2.38 (2s, 2 x 3H, *p*-Me of Mes), 2.70 (extremely broad s ($\Delta\nu_{1/2}$ = 150 Hz) 12H, *o*-Me of Mes), 3.26 and 3.60 (2s, 2 x 3H, OMe), 2.40 – 3.10 (extremely broad s due to coalescence, *o*-Me of Mes), 6.12 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H of Ph), [6.01 – 6.03 (m, 1H), 6.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.35 – 6.39 (m, 1H), 6.55 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.78 – 6.94 (m, 6H), 7.19 – 7.42 (m, 6H), 7.52, 7.63, 7.69 and 7.78 (4d, $^3J_{HH}$ = 7.6 Hz, 4 x 1H)] (arom H).

δ_C (75.47 MHz): 20.91 and 21.04 (*p*-Me of Mes), 23.29 and 23.66 (*o*-Me of Mes), 54.84 and 55.09 (OMe), 61.02 (CR_2), 78.46 (R_2CCO), 91.90 (GeOCO), 112.41, 112.87, 113.95 and 114.32 (arom CH in ortho position in relation to COMe), 119.97, 120.06, 121.38, 125.46, 125.49, 126.76, 126.85, 126.95, 127.00 and 127.13 (other arom CH), 132.59, 133.52, 134.31, 137.98, 139.24, 139.33, 141.09, 141.56, 143.79 and 145.18 (arom C), 157.56 and 158.93 (*C*OMe).

MS (60 eV, m/z) : 746 (M, 5), 639 (M – C_6H_4OMe, 20), 491 ($OGeMes_2CR_2$, 17), 476 ($Mes_2Ge{=}CR_2$, 15), 418 (M – Mes_2GeO, 100), 311 (Mes_2Ge – 1, 45), 135 ($MeOC_6H_4CO$, 51).

Anal. Calcd for $C_{47}H_{44}GeO_4$ (746.245) C, 75.73; H, 5.95%. Found : C, 75.92; H, 6.10%.

2d 1.12 g (74%), mp = 135 °C.

δ_H (300.18 MHz): 2.10 and 2.20 (2s, 2 x 3H, *p*-Me of Mes), the *o*-Me of the Mes groups could not be seen due to coalescence, 3.29 and 3.66 (2s, 2 x 3H, OMe), [6.04 and 6.17 (2d, $^3J_{HH}$ =

8.1 Hz, 2 x 2H), 6.51 – 6.80 (m, 4H), 6.64 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.07 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.08 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.15 – 7.27 (m, 4H), 7.30 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.48 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.56 (d, $^3J_{HH}$ = 7.5 Hz, 2H)] (arom H).

δ_C (75.47 MHz): 20.89 and 21.04 (*p*-Me of Mes), 23.23 and 23.61 (*o*-Me of Mes), 54.67 and 55.15 (OMe), 61.17 (CR_2), 77.97 (R_2CCO), 91.90 (GeOCO), 111.55, 113.00, 119.95, 119.98, 125.50, 125.70, 126.81, 126.88, 126.99, 128.77, 129.78, 132.43 and 132.70 (arom CH), 125.13, 128.72, 132.79, 133.59, 139.12, 139.23, 141.04, 141.50, 143.92 and 145.35 (arom C)**,** 157.91 and 159.40 (*C*OMe).

MS (60 eV, m/z) : 639 (M – C_6H_4OMe, 2), 491 ($OGeMes_2CR_2$, 5), 418 (M – Mes_2GeO, 30), 311 (Mes_2Ge – 1, 15), 271 (M – Mes_2GeCR_2, 25), 135 ($MeOC_6H_4CO$, 100).

Anal. Calcd for $C_{47}H_{44}GeO_4$ (746.245) C, 75.73; H, 5.95%. Found : C, 75.62; H, 6.01%.

2e 1.01 g (70%), mp = 176 °C.

δ_H (300.18 MHz): 1.86, 2.11, 2.19 and 2.20 (4s, 4 x 3H, *p*-Me of Mes and Me of C_6H_4Me), 2.10 – 3.10 (extremely broad s ($\Delta\nu_{1/2}$ = 150 Hz) 12H, *o*-Me of Mes), [6.15 and 6.30 (2d, $^3J_{HH}$ = 8.1 Hz, 2 x 2H), 6.50 – 6.85 (m, 4H), 6.92 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.03 – 7.28 (m, 6H), 7.30, 7.48, 7.54 and 7.59 (4dt, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 0.9 Hz, 4 x 1H)] (arom H).

δ_C (75.47 MHz): 20.89, 21.02 and 21.25 (*p*-Me of Mes and *p*-Me of C_6H_4Me), 23.23 and 23.60 (*o*-Me of Mes), 61.19 (CR_2), 78.25 (R_2CCO), 91.93 (GeOCO), 119.88, 119.91, 125.49, 125.56, 126.73, 126.78, 126.82, 126.95, 127.33, 128.28128.32, 128.41, 128.82 and 129.08 (arom CH)**,** 130.01, 132.82, 133.60, 133.65, 135.96, 137.62, 139.10, 139.21, 140.99, 141.51, 143.90 and 145.28 (arom C).

MS (60 eV, m/z) : 714 (M, 2), 623 (M – PhMe, 5), 475 ($Mes_2Ge{=}CR_2$ – 1, 10), 386 (M – Mes_2GeO, 35), 311 (Mes_2Ge– 1, 52), 119 (Mes, 100).

Anal. Calcd for $C_{47}H_{44}GeO_2$ (714.255) C, 79.12; H, 6.22%. Found : C, 79.02; H, 6.10%.