Reactions of Complex Ligands, LXXXIII[◇]

Photochemical Activation of (α-*exo*-Alkylidene-2-oxacyclopentylidene)-chromium Complexes for Benzannulation☆

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2,3-Dihydro-5-benzofuranols are synthesized by photochemical benzannulation of pentacarbonyl[(5-methylene or 5-benzylidene)-2-oxacyclopentylidene]chromium complexes **2** and **3** with a series of terminal and symmetrical or unsymmetrical internal alkynes. No benzannulation reaction, however, is observed under the standard thermal conditions.

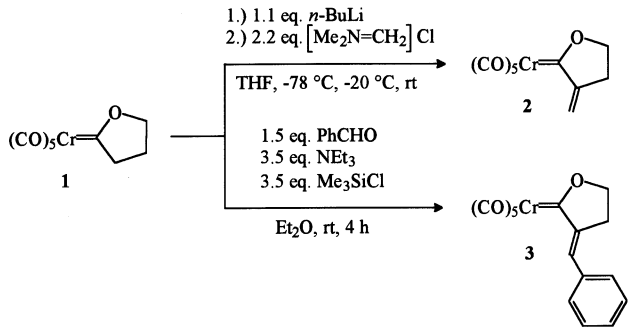
Introduction

A decade after their discovery by E. O. Fischer[2] carbonyl carbene complexes started to become valuable reagents in synthetic organic chemistry[3]. In particular, the chromium-mediated [3+2+1] cycloaddition of alkoxy(aryl or vinyl)carbene, alkyne and carbonyl ligands[4] provides a straightforward access to densely substituted oxygenated arenes and has been applied to the synthesis of various natural products.[5] It occurs at moderate temperatures under neutral conditions and is compatible with a wide variety of functional groups within the alkyne. Modifications of the standard protocol such as dry-state adsorption on silica gel[6] or photochemical initiation[7] have also been reported. Exploring the synthetic potential of (α-*exo*-alkylidene-2-oxacyclopentylidene)chromium complexes we focused on their benzannulation with alkynes. The benzannulation reaction is expected to provide a direct route to the 2,3-dihydro-5-benzofuranol[8] skeleton which is part of a variety of natural products and biologically active compounds.

Results and Discussion

Surprisingly, the (α-*exo*-alkylidene-2-oxacyclopentylidene)chromium complexes **2** and **3** did not undergo benzannulation with alkynes under the thermal standard conditions. Refluxing of **2** and **3** in both *tert*-butyl methyl ether and tetrahydrofuran in the presence of 3-hexyne neither led to any benzannulation product nor to decomposition within the first three hours. However, when complex **2** was refluxed in di-*n*-butyl ether in the presence of 3-hexyne, decomposition was observed after about two hours. The generally accepted mechanism of the benzannulation reaction[9] involves in the first step a decarbonylation which may be achieved by either thermal or photochemical means. In 1983, Geoffroy et al.[10] reported on the photochemistry of pentacarbonyl(1-methoxybenzylidene)tungsten(0), the formation of alkyne(tetracarbonyl)tungsten intermediates and their decomposition reactions leading to indenes. We studied the photochemical activation of (α-*exo*-alkylidene-2-oxacyclopentylidene)chromium complexes for benzannulation, and we now report on the synthesis of 2,3-dihydro-5-benzofuranols. Pentacarbonyl(2-oxacyclo-pentylidene)-chromium(0) (**1**) and its α-*exo*-methylene derivative **2** were prepared by the methods reported previously.[11][12] When complex **1** was treated with benzaldehyde in the presence of triethylamine and trimethylsilyl chloride[13] at room temperature (5-benzylidene-2-oxacyclopentylidene)pentacarbonylchromium(0) (**3**) was obtained in 85% yield. As previously reported by Aumann et al.[13] this protocol is expected to generate the *E* configuration of the α-*exo*-benzylidene unit of **3** (Scheme 1).

Scheme 1. α-*exo*-Alkylidene functionalization of 2-oxacyclopentylidene complex **1**



Tetrahydrofuran solutions of complexes **2** and **3** were irradiated at −20°C for 2 h in the presence of 5 equivalents of 1-pentyne. Chromatographic workup afforded 2,3-dihydro-6-propyl-5-benzofuranol (**4**) and 2,3-dihydro-4-phenyl-6-propyl-5-benzofuranol (**6**) in 24 and 37% yield,

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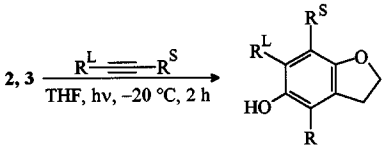
  1434−193X/98/0909−1739 $ 17.50+.50/0

respectively, as the only detectable regioisomers. Better yields than those obtained for the terminal alkyne were observed for the reaction with internal alkynes. Complexes **2** and **3** reacted with 3-hexyne to give 6,7-diethyl-2,3-dihydro-5-benzofuranol (**5**) and 6,7-diethyl-2,3-dihydro-4-phenyl-5-benzofuranol (**7**) in 35 and 81% yield, respectively (Scheme 2).

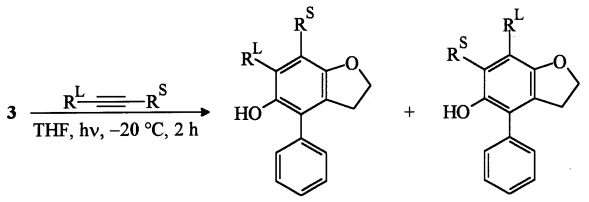
Scheme 2. Photochemical benzannulation of **2** and **3** with 1-pentyne and 3-hexyne



	R^L	R^S	R
4	Pr	H	H
5	Et	Et	H
6	Pr	H	Ph
7	Et	Et	Ph

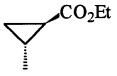
In general, unsymmetrically substituted alkynes form both possible regioisomers, and their ratio approaches unity with a decreasing difference in steric demand of the two alkyne substituents.[14] As a rule, the larger substituent is preferentially incorporated adjacent to the phenolic group orginating from the former carbonyl ligand; only terminal alkynes are known to afford a single regioisomer.[14] In order to investigate the extent of regioselectivity for the photochemical benzannulation complex **3** was treated with two different unsymmetrically substituted alkynes. Following the experimental protocol described above, reaction of **3** with 2-decyne gave a 3:1 ratio of the two possible regioisomers **8a/b** in a total yield of 40%; the regioisomeric ratio was determined on the basis of the ^{1}H-NMR signals for the methyl groups at C-7 (**8a**) and at C-6 (**8b**). The benzannulation of **3** with ethyl *trans*-2-(phenylethynyl)cyclopropanecarboxylate[15] under the same conditions as described before resulted in 66% yield of a mixture of regioisomers **9a/b** (Scheme 3).

Scheme 3. Photochemical benzannulation of **3** with unsymmetric internal alkynes



8a, 9a **8b, 9b**

8: R^L = Hept; R^S = Me

9: R^L = Ph; R^S = 

Column chromatography on silica gel using petroleum ether/diethyl ether (3:1) as eluent gave a 2:1 ratio of pure regioisomers **9a/b**; the stereochemistry of the major isomer expected **9a** was assigned according to a previous report[16] based on X-ray structure elucidation. The 2:1 ratio for **9a/b** contrasts that observed for the benzannulation of pentacarbonyl(1-methoxybenzylidene)chromium(0) with ethyl *trans*-2-(phenylethynyl)cyclopropanecarboxylate which resulted in the formation of a single regioisomer bearing the phenyl substituent as the "larger" substituent (R^L) adjacent to the phenolic group.[16]

Conclusions

Thermostable carbenechromium compounds such as *exo*-alkylidene-2-oxacyclopentylidene complexes **2** and **3** can be photoactivated towards benzannulation upon reaction with alkynes. Exploiting this approach 4,6,7-trisubstituted 2,3-dihydro-5-benzofuranols are accessible in moderate to good yields. For example, 2,3-dihydro-6-propyl-5-benzofuranol **(4)** – an active compound for the antioxidant-based inhibition of leukotriene biosynthesis[8b] – was prepared in a three-step synthesis exclusively utilizing commercially available compounds. The incorporation of terminal alkynes proceeds with complete regioselectivity, while the reaction with unsymmetrically substituted alkynes results in mixtures of regioisomers. In contrast to the thermal standard protocol no tricarbonylchromium complexes can be isolated; this result reflects the well-documented photolability[17] of arene(tricarbonyl)chromium complexes. The photoinduced benzannulation presented here leads to a *para*-alkoxyphenol skeleton, and thus complements the approach reported by Merlic et al.[18] which is based on a photocyclization reaction of dienylcarbene complexes generating *ortho*-alkoxy-substituted phenols.

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Experimental Section

General: All reactions, manipulations, and purifications involving organometallics were performed under dry argon using Schlenk techniques. Solvents were dried by distillation from sodium hydride (diethyl ether), calcium hydride (petroleum ether, bp. 40–60°C), and potassium/sodium alloy (tetrahydrofuran) and saturated with argon. Silica gel (Merck, type 60, 0.063–0.200 mm) was degassed at high vacuum and stored under argon. – ^{1}H NMR: Bruker AM-250 (250 MHz), Bruker AM-400 (400 MHz) and Bruker DRX-500 (500 MHz). – ^{13}C NMR: AM-250 (62.8 MHz), Bruker AM-400 (100.6 MHz) and Bruker DRX-500 (125.7 MHz). All NMR spectra were recorded in $CDCl_3$ with $CHCl_3$ at δ_H = 7.26 as internal standard. – FT-IR: Nicolet Magna 550. – Elemental analysis: Heraeus CHN-Rapid. – MS: Kratos MS 50 (EI, 70 eV). – M.p.: Büchi SMP 20; the reported melting points are uncorrected. – TLC: 0.25 mm Merck silica gel plates 60 F_{254}.

(5-Benzylidene-2-oxacyclopentylidene)pentacarbonylchromium(0) (**3**)*:* To a solution of 850 mg (3.2 mmol) of 2-oxacyclopentylidene complex **1** in 15 ml of diethyl ether 1.5 equiv. (520 mg, 0.5 ml, 4.9 mmol) of benzaldehyde, 3.5 equiv. (1.23 g, 1.44 ml, 11.4 mmol) of trimethylsilyl chloride and 3.5 equiv. (1.15 g, 1.58 ml, 11.4 mmol) of triethylamine were added. The reaction mixture was stirred for 4 h at room temperature while the color changed from yellow to purple. After evaporation of the solvent, the residue was chromatographed on silica gel using petroleum ether/diethyl ether (1:1) as eluent to give 965 mg (2.76 mmol, 85%) of **3** as a purple solid, m.p. 99–100°C. – R_f = 0.78 (petroleum ether/diethyl ether,

1:1). – ^{1}H NMR (500 MHz): δ = 3.01 (td, ^3J = 7.63 Hz, ^4J = 2.75 Hz, 2 H, 4-H), 4.99 (t, ^3J = 7.63 Hz, 2 H, 3-H), 7.47–7.53 (m, 3 H, Ar-H), 7.6–7.64 (m, 2 H, Ar-H), 8.15 (t, ^4J = 2.75 Hz, 1 H, vinylic H). – ^{13}C NMR (125.7 MHz): δ = 26.73 (C-4), 82.70 (C-3), 129.12 (*meta*-Ar-C), 130.80 (*ortho*-Ar-C), 130.89 (*para*-Ar-C), 135.21 (*ipso*-Ar-C), 150.16 (vinylic CH), 150.27 (C-5), 217.49 (*cis*-CO), 224.24 (*trans*-CO), 320.97 (*carbene*-C). – FT-IR (hexane): $\tilde{\nu}$ = 2060 cm^{-1} (w, A_1^1), 1989 (w, B), 1964 (m, A_1^2), 1949 (vs, E). – MS (EI, 70eV); *m/z* (%): 350 (13) [M$^+$], 322 (4) [M$^+$ – CO], 294 (11) [M$^+$ – 2CO], 266 (12) [M$^+$ – 3CO], 238 (29) [M$^+$ – 4CO], 210 (100) [M$^+$ – 5CO]. – HRMS: calcd. for $C_{16}H_{10}CrO_6$ [M$^+$] 349.9882; found 349.9874. – $C_{16}H_{10}CrO_6$ (350.25): calcd. C 54.87, H 2.88; found C 55.19, H 3.26.

General Procedure for the Photochemical Benzannulation of Carbene Complexes **2** *and* **3**: A solution of 1 mmol of carbene complex and 5 mmol of alkyne in 60 ml of tetrahydrofuran was irradiated for 2 h at −20°C using a mercury vapor lamp (Phillips 125 HPK) and special quartz glassware. A color change from purple to brownish yellow occurred. After evaporation of the solvent, the residue was chromatographed on silica gel using petroleum ether/diethyl ether (3:1) as eluent to give the pure 2,3-dihydro-5-benzofuranols.

2,3-Dihydro-6-propyl-5-benzofuranol (**4**) was prepared from **2** in 24% yield (43 mg, 0.24 mmol) as a white solid, m.p. 75°C. – R_f = 0.28 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (400 MHz): δ = 0.96 (t, ^3J = 7.44 Hz, 3 H, CH_3), 1.61 (pseudo-sext, ^3J = 7.44 Hz, 2 H, $CH_2CH_2CH_3$), 2.51 (t, ^3J = 7.44 Hz, 2 H, $CH_2CH_2CH_3$), 3.14 (t, ^3J = 8.61 Hz, 2 H, 3-H), 4.30 (s, 1 H, OH), 4.51 (t, ^3J = 8.61 Hz, 2 H, 2-H), 6.56 (s, 1 H, 4-H), 6.66 (s, 1 H, 7-H). – ^{13}C NMR (100.6 MHz): δ = 13.99 (CH_3), 23.06 ($CH_2CH_2CH_3$), 30.06 (C-3), 32.29 ($CH_2CH_2CH_3$), 71.18 (C-2), 110.11 (C-4), 112.14 (C-7), 125.04, 127.58 (C-6, C-3a), 147.18 (C-5), 152.04 (C-7a). – FT-IR (KBr): $\tilde{\nu}$ = 3450 (vs, br., ν_{O-H}), 2963 (vs, ν_{C-H}), 2930 (vs, ν_{C-H}), 2874 (vs, ν_{C-H}), 2855 (vs, ν_{C-H}). – MS (EI, 70eV); *m/z* (%): 178 (52) [M$^+$], 149 (100) [M$^+$ – CH_3]. – HRMS: calcd. for $C_{11}H_{14}O_2$ [M$^+$] 178.0994; found 178.0991.

6,7-Diethyl-2,3-dihydro-5-benzofuranol (**5**) was prepared from **2** in 35% yield (67 mg, 0.35 mmol) as a white solid, m.p. 86–87°C. – R_f = 0.50 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (500 MHz): δ = 1.15 (t, ^3J = 7.50 Hz, 3 H, CH_3), 1.16 (t, ^3J = 7.50 Hz, 3 H, CH_3), 2.60 (q, ^3J = 7.50 Hz, 2 H, CH_2CH_3), 2.63 (q, ^3J = 7.50 Hz, 2 H, CH_2CH_3), 3.13 (t, ^3J = 8.15 Hz, 2 H, 3-H), 4.50 (t, ^3J = 8.15 Hz, 2 H, 2-H), 6.54 (s, 1 H, 4-H). – ^{13}C NMR (125.7 MHz): δ = 14.63 (CH_3), 14.73 (CH_3), 19.27 (CH_2CH_3), 19.90 (CH_2CH_3), 30.40 (C-3), 70.55 (C-2), 109.44 (C-4), 123.77, 124.73 (C-6, C-3a), 127.36 (C-7), 147.32 (C-5), 152.44 (C-7a). – FT-IR (KBr): $\tilde{\nu}$ = 3548 cm^{-1} (sh, ν_{O-H}), 3313 (vs, br., ν_{O-H}), 2973 (vs, ν_{C-H}), 2932 (vs, ν_{C-H}), 2874 (vs, ν_{C-H}), 1481 (vs, δ_{C-H}), 1445 (vs, δ_{C-H}), 1436 (vs, δ_{C-H}), 1211 (vs), 1111 (vs, ν_{Ar-O-C}), 858 (vs, γ_{Ar-H}). – MS (EI, 70eV); *m/z* (%): 192 (23) [M$^+$], 177 (100) [M$^+$ – CH_3]. – HRMS: calcd. for $C_{12}H_{16}O_2$ [M$^+$] 192.1150; found 192.1149.

2,3-Dihydro-4-phenyl-6-propyl-5-benzofuranol (**6**) was prepared from **3** in 37% yield (94 mg, 0.37 mmol) as a pale yellow oil. – R_f = 0.59 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (250 MHz): δ = 0.99 (t, ^3J = 7.33 Hz, 3 H, CH_3), 1.65 (pseudo-sext, ^3J = 7.50 Hz, 2 H, $CH_2CH_2CH_3$), 2.60 (t, ^3J = 7.63 Hz, 2 H, $CH_2CH_2CH_3$), 3.00 (t, ^3J = 8.54 Hz, 2 H, 3-H), 4.49 (t, ^3J = 8.54 Hz, 2 H, 2-H), 4.61 (s, 1 H, OH), 6.61 (s, 1 H, 7-H), 7.36–7.44 (m, 3 H, Ar-H), 7.46–7.54 (m, 2 H, Ar-H). – ^{13}C NMR (62.8 MHz): δ = 14.06 (CH_3), 23.02 ($CH_2CH_2CH_3$), 29.90 (C-3), 32.68 ($CH_2CH_2CH_3$), 71.18 (C-2), 109.74 (C-7), 123.36 (C-4), 124.83, 128.43 (C-6, C-3a), 128.07 (*para*-Ar-C), 129.34 (*ortho*-Ar-C), 129.41 (*meta*-Ar-C), 135.41 (*ipso*-Ar-C), 144.16 (C-5), 153.15 (C-7a). – FT-IR (film): $\tilde{\nu}$ = 3560 cm^{-1} (m, ν_{O-H}), 3456 (m, ν_{O-H}), 3059 (w, ν_{Ar-H}), 2959 (vs, ν_{C-H}), 2930 (vs, ν_{C-H}), 2921 (s, ν_{C-H}), 2915 (s, ν_{C-H}), 2872 (vs, ν_{C-H}), 1458 (s, δ_{C-H}), 1448 (s, δ_{C-H}), 1423 (vs, δ_{C-H}), 1247 (s), 1180 (vs), 1126 (vs, ν_{Ar-O-C}), 986 (s), 953 (*s*), 896 (m, γ_{Ar-H}), 743 (vs, γ_{Ar-H}), 704 (vs, γ_{Ar-H}). – MS (EI, 70eV); *m/z* (%): 254 (100) [M$^+$], 225 (93) [M$^+$ – CH_2CH_3], 210 (33) [M$^+$ – $CH_2CH_2CH_3$]. – HRMS: calcd. for $C_{17}H_{18}O_2$ [M$^+$] 254.1307; found 254.1307.

6,7-Diethyl-2,3-dihydro-4-phenyl-5-benzofuranol (**7**) was prepared from **3** in 81% yield (217 mg, 0.81 mmol) as a pale yellow oil. – R_f = 0.63 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (500 MHz): δ = 1.19 (t, ^3J = 7.70 Hz, 3 H, CH_3), 1.21 (t, ^3J = 7.55 Hz, 3 H, CH_3), 2.66 (q, ^3J = 7.50 Hz, 2 H, CH_2CH_3), 2.70 (q, ^3J = 7.40 Hz, 2 H, CH_2CH_3) 3.01 (t, ^3J = 8.55 Hz, 2 H, 3-H), 4.49 (t, ^3J = 8.55 Hz, 2 H, 2-H), 4.71 (s, 1 H, OH), 7.37–7.41 (m, 3 H, Ar-H), 7.47–7.51 (m, 2 H, Ar-H). – ^{13}C NMR (125.7 MHz): δ = 14.63 (CH_3), 14.66 (CH_3), 19.62 (CH_2CH_3), 19.87 (CH_2CH_3), 30.13 (C-3), 70.56 (C-2), 122.19 (C-4), 122.29, 124.37 (C-6, C-3a), 127.84 (*para*-Ar-C), 127.89 (C-7), 129.27 (*ortho*-Ar-C), 129.49 (*meta*-Ar-C), 135.55 (*ipso*-Ar-C), 144.20 (C-5), 151.63 (C-7a). – FT-IR (film): $\tilde{\nu}$ = 3543 cm^{-1} (w, ν_{O-H}), 3058 (*s*, ν_{Ar-H}), 2944 (vs, ν_{C-H}), 2927 (vs, ν_{C-H}), 1433 (vs, δ_{C-H}), 1238 (vs, ν_{Ar-O-C}), 995 (m), 884 (m), 812 (m), 759 (m, γ_{Ar-H}), 712 (m, γ_{Ar-H}). – MS (EI, 70eV); *m/z* (%): 268 (100) [M$^+$], 253 (39) [M$^+$ – CH_3], 224 (19) [M$^+$ – CH_2CH_3]. – HRMS: calcd. for $C_{18}H_{20}O_2$ [M$^+$] 268.1463; found 268.1460.

6-Heptyl-2,3-dihydro-7-methyl-4-phenyl-5-benzofuranol (**8a**) *and 7-Heptyl-2,3-dihydro-6-methyl-4-phenyl-5-benzofuranol* (**8b**) were prepared from **3** following the procedure described above. Chromatography gave 130 mg (0.4 mmol, 40%) of **8a/b** as a pale yellow oil as a 3:1 mixture of regioisomers which were not separated. – R_f (major regioisomer **8a**) = 0.68 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (500 MHz): δ = 0.89 (t, ^3J = 6.95 Hz, 3 H, CH_3), 1.24–1.38 (m, 6 H, 3 × CH_2), 1.38–1.45 (m, 2 H, CH_2), 1.50–1.57 (m, 2 H, CH_2), 2.21 (s, 3 H, Ar-CH_3), 2.64–2.68 (m, 2 H, Ar-CH_2), 3.02 (t, ^3J = 8.55 Hz, 2 H, 3-H), 4.49 (t, ^3J = 8.60 Hz, 2 H, 2-H), 4.68 (s, 1 H, OH), 7.37–7.41 (m, 3 H, Ar-H), 7.46–7.51 (m, 2 H, Ar-H). – ^{13}C NMR (125.7 MHz): δ = 11.83 (CH_3), 14.12 (Ar-CH_3), 22.69, 26.86, 29.24, 29.53, 30.01 (5 × CH_2), 30.30 (C-3), 31.88 (Ar-CH_2), 70.55 (C-2), 118.15 (C-4), 121.97, 122.12 (C-6, C-3a), 127.48 (C-7), 127.90 (*para*-Ar-C), 129.31 (*ortho*-Ar-C), 129.55 (*meta*-Ar-C), 135.63 (*ipso*-Ar-C), 144.22 (C-5), 151.99 (C-7a). – FT-IR (film): $\tilde{\nu}$ = 3572 cm^{-1} (m, ν_{O-H}), 3460 (m, ν_{O-H}), 3059 (w, ν_{Ar-H}), 2955 (vs, ν_{C-H}), 2927 (vs, ν_{C-H}), 2856 (*s*, ν_{C-H}), 1450 (vs, δ_{C-H}), 1414 (vs, δ_{C-H}), 1130 (vs, ν_{Ar-O-C}), 771 (m, γ_{Ar-H}), 708 (m, γ_{Ar-H}). – MS (EI, 70eV); *m/z* (%): 324 (94) [M$^+$], 239 (100) [M$^+$ – C_6H_{13}], 224 (76) [M$^+$ – C_6H_{13}, – CH_3], 77 (22) [Ph$^+$]. – HRMS: calcd. for $C_{22}H_{28}O_2$ [M$^+$] 324.2090; found 324.2090. – R_f (minor regioisomer **8b**) = 0.64 (petroleum ether/diethyl ether, 3:1). – ^{1}H NMR (500 MHz): δ = 0.90 (t, ^3J = 6.95 Hz, 3 H, CH_3), 1.24–1.38 (m, 6 H, 3 × CH_2), 1.38–1.45 (m, 2 H, CH_2), 1.50–1.57 (m, 2 H, CH_2), 2.22 (s, 3 H, Ar-CH_3), 2.60–2.64 (m, 2 H, Ar-CH_2), 3.00 (t, ^3J = 8.72 Hz, 2 H, 3-H), 4.47 (t, ^3J = 8.60 Hz, 2 H, 2-H), 4.68 (s, 1 H, OH), 7.37–7.41 (m, 3 H, Ar-H), 7.46–7.51 (m, 2 H, Ar-H). – ^{13}C NMR (125.7 MHz): δ = 11.77 (CH_3), 14.13 (Ar-CH_3), 22.69, 27.12, 29.26, 29.60, 29.89 (5 × CH_2), 30.20 (C-3), 31.92 (Ar-CH_2), 70.57 (C-2), 118.15 (C-4), 121.75, 122.05 (C-6, C-3a), 123.78 (C-7), 127.88 (*para*-Ar-C), 129.31 (*ortho*-Ar-C), 129.51 (*meta*-Ar-C), 135.69 (*ipso*-Ar-C), 144.44 (C-5), 151.77 (C-7a).

Ethyl trans-2-(2′,3′-Dihydro-5′-hydroxy-4′,6′-diphenylbenzofuran-7′-yl)cyclopropanecarboxylate (**9a**) *and Ethyl trans-2-(2′,3′-Di-*

hydro-5′-hydroxy-4′,7′-diphenylbenzofuran-6′-yl)cyclopropanecarboxylate (**9b**) were prepared from **3** in 66% total yield. Chromatography gave 176 mg (0.44 mmol, 44%) of **9a** and 88 mg (0.22 mmol, 22%) of **9b** as pale yellow oils. − R_f (major regioisomer **9a**) = 0.24 (petroleum ether/diethyl ether, 3:1). − ^{1}H NMR (400 MHz): δ = 1.18 (t, ^3J = 7.24 Hz, 3 H, CH_3), 1.31 (ddd, $^3J_{cis}$ = 9.54 Hz, $^3J_{trans}$ = 5.18 Hz, $^3J_{trans}$ = 4.30 Hz, 1 H, 1-H or 2-H), 1.57 (ddd, $^3J_{cis}$ = 8.31 Hz, $^3J_{trans}$ = 6.94 Hz, $^3J_{trans}$ = 4.01 Hz, 1 H, 1-H or 2-H), 1.89 (ddd, ^2J = 4.70 Hz, ^3J = 8.22 Hz, ^3J = 5.09 Hz, 1 H, 3a-H or 3b-H), 2.14 (ddd, ^2J = 4.50 Hz, ^3J = 9.39 Hz, ^3J = 6.85 Hz, 1 H, 3a-H or 3b-H), 3.07 (t, ^3J = 8.61 Hz, 2 H, 3′-H), 3.94 (dq, ^2J = 10.57 Hz, ^3J = 7.14 Hz, 1 H, OC*H*HCH$_3$), 4.02 (dq, ^2J = 10.57 Hz, ^3J = 7.14 Hz, 1 H, OCH*H*CH$_3$), 4.51 (t, ^3J = 8.61 Hz, 2 H, 2′-H), 4.62 (s, 1 H, OH), 7.37−7.50 (m, 10 H, Ar-H). − ^{13}C NMR (100.6 MHz): δ = 14.20 (CH_3), 16.05 (C-3), 22.11 (2 C, C-1 and C-2), 29.92 (C-3′), 60.21 (O*C*H$_2$CH$_3$), 70.95 (C-2′), 119.14 (C-4′), 123.99, 126.34 (C-6′, C-3′a), 128.61 (C-7′), 129.00 (Ar-CH), 129.09 (Ar-CH), 129.43 (2 C, Ar-CH), 130.39 (2 C, Ar-CH), 135.64 (*ipso*-Ar-C), 135.82 (*ipso*-Ar-C), 143.61 (C-5′), 151.76 (C-7′a), 173.85 (*C*O$_2$Et). − FT-IR (film): $\tilde{\nu}$ = 3546 cm^{-1} (m, ν_{O-H}), 3087 (w, ν_{Ar-H}), 3030 (vs, ν_{C-H}), 2968 (vs, ν_{C-H}), 2927 (vs, ν_{C-H}), 2901 (*s*, ν_{C-H}), 1719 (vs, $\nu_{C=O}$), 1409 (vs, δ_{C-H}), 1192 (vs, ν_{Ar-O-C}). − MS (EI, 70eV); *m*/*z* (%): 400 (15) [M$^+$], 326 (9) [M$^+$ − CO$_2$Et, − H], 312 (9) [M$^+$ − CHCO$_2$Et, − H], 105 (100) [PhC$_2$H$_4^+$], 91 (13) [PhCH$_2^+$], 77 (6) [Ph$^+$]. − HRMS: calcd. for $C_{26}H_{24}O_4$ [M$^+$] 400.1675; found 400.1665. − R_f (minor regioisomer **9b**) = 0.17 (petroleum ether/diethyl ether, 3:1). − ^{1}H NMR (250 MHz): δ = 1.04 (ddd, $^3J_{cis}$ = 9.03 Hz, $^3J_{trans}$ = 8.42 Hz, $^3J_{trans}$ = 5.00 Hz, 1 H, 1-H or 2-H), 1.15 (t, ^3J = 7.08 Hz, 3 H, CH_3), 1.21−1.35 (m, 2 H, 3a-H and 3b-H), 1.76 (dpseudo-t, $^3J_{cis}$ = 8.30 Hz, $^3J_{trans}$ = 5.62 Hz, 1 H, 1-H or 2-H), 3.03 (ddd, ^2J = 15.87 Hz, ^3J = 9.40 Hz, ^3J = 7.32 Hz, 1 H, 3′a-H or 3′b-H), 3.13 (ddd, ^2J = 15.63 Hz, ^3J = 9.28 Hz, ^3J = 7.93 Hz, 1 H, 3′a-H or 3′b-H), 3.94 (dq, ^2J = 10.86 Hz, ^3J = 7.08 Hz, 1 H, OC*H*HCH$_3$), 4.05 (dq, ^2J = 10.86 Hz, ^3J = 7.08 Hz, 1 H, OCH*H*CH$_3$), 4.43 (dpseudo-t, ^2J = 8.30 Hz, ^3J = 9.52 Hz, 1 H, 2′a-H), 4.57 (ddd, ^2J = 8.92 Hz, ^3J = 9.34 Hz, ^3J = 7.33 Hz, 1 H, 2′b-H), 7.29−7.51 (m, 10 H, Ar-H). − ^{13}C NMR (62.8 MHz): δ = 14.11 (CH_3), 15.02 (C-3), 20.56 (C-1 or C-2), 20.86 (C-1 or C-2), 30.23 (C-3′), 60.00 (O*C*H$_2$CH$_3$), 70.97 (C-2′), 116.60 (C-4′), 125.44, 127.43 (C-6′, C-3′a), 127.65 (Ar-CH), 128.10 (C-7′), 128.46 (Ar-CH), 128.49 (Ar-CH), 128.54 (Ar-CH), 128.78 (2 C, Ar-CH), 129.56 (4 C, Ar-CH), 136.10 (2 C, *ipso*-Ar-C), 143.52 (C-5′), 153.15 (C-7′a), 172.10 (*C*O$_2$Et). − FT-IR (film): $\tilde{\nu}$ = 3560 cm^{-1} (m, ν_{O-H}), 3456 (m, ν_{O-H}), 3059 (w, ν_{Ar-H}), 2959 (vs, ν_{C-H}), 2930 (vs, ν_{C-H}), 2921 (s, ν_{C-H}), 2915 (s, ν_{C-H}), 2872 (vs, ν_{C-H}), 1423 (vs, δ_{C-H}), 1423 (vs, δ_{C-H}), 1423 (vs, δ_{C-H}), 1211 (vs, ν_{Ar-O-C}), 856 (vs, γ_{Ar-H}). − MS (EI, 70eV); *m*/*z* (%): 400 (100) [M$^+$], 326 (54) [M$^+$ − CO$_2$Et, − H], 312 (53) [M$^+$ − CHCO$_2$Et, − H]. − HRMS: calcd. for $C_{26}H_{24}O_4$ [M$^+$] 400.1675; found 400.1686.

☆ Dedicated to Professor *Reinhard Hoffmann* on the occasion of his 65th birthday.

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