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[4+2] and [2+2] Photocycloadditions of 1,2-diketones to glycal and hydroxyglycal esters☆

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Abstract—Photocycloadditions of phenanthrenequinone **1** and acenaphthenequinone **16** to 3,4,6-tri-*O*-acetyl-D-glucal proceeded with distinctly different regioselectivities: **1** preferentially adds with both carbonyl oxygens to give the [4+2] cycloadduct, a 1-*O*,2-*O*-annelated α-D-glucoside (50% [*Chem. Ber.* **1952**, *85*, 531]), while **16** reacts with only one carbonyl group to exclusively yield the [2+2] addition product, a 1-*C*,2-*O*-oxetano-α-D-glucoside (86%). 2-Hydroxyglucal esters **11** and **12** also undergo photoadditions with **1** to give the *cis*-1,4-dioxane-fused cycloadducts **13** and **14**, whilst **16** fails to react. Structural and configurational assignments rest on NMR data and an X-ray analysis of spiro-pyranooxetane **18**.
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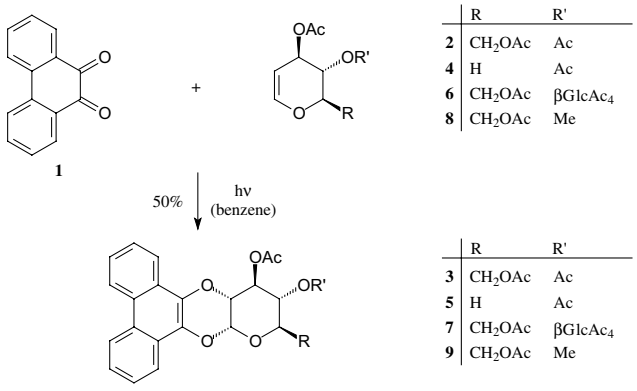
1. Introduction

The synthetic potential of photocycloadditions of carbonyl compounds to sugars carrying an olefinic double bond was first realized by Helferich et al.,[2] who in 1952—undoubtedly stimulated by the pioneering photochemical investigations of Schönberg and co-workers[3]—performed the UV-promoted cycloaddition of phenanthrenequinone **1** to tri-*O*-acetyl-D-glucal **2** to give the [4+2] cycloaddition product **3**, a phenanthro-dioxenopyran with an α-D-*gluco*-configuration at the pyran position, in 50% yield.[4] Ozonolysis of **3** led to 3,4,6-tri-*O*-acetyl-D-glucose,[4a] thus providing an overall method of stereoselectively hydroxylating the double bond of the glycal. Analogous products, each in crystalline form, were obtained from di-*O*-acetyl-D-xylal (**4** → **5**), hexa-*O*-acetyl-cellobial (**6** → **7**),[5] 3,6-di-*O*-acetyl-4-*O*-methyl-D-glucal (**8** → **9**)[6] and tri-*O*-acetyl-D-galactal (Scheme 1).[5]



	R	R'
2	CH_2OAc	Ac
4	H	Ac
6	CH_2OAc	βGlcAc$_4$
8	CH_2OAc	Me

	R	R'
3	CH_2OAc	Ac
5	H	Ac
7	CH_2OAc	βGlcAc$_4$
9	CH_2OAc	Me

Scheme 1.

The transfer of this intrinsically simple photocycloaddition to the readily accessible[7] 2-hydroxyglycal esters **10** should—provided the [4+2] cycloadducts are similarly preferred over their [2+2] pyrano-oxetane analogs—lead to products of type **11**, in which a pyranoid 2-ketohexose is bis-glycosidically linked to the vicinal diol group of the aglycone. In as much as there are various natural products containing a pyrano-dioxane structure of this type, such as the cardioactive cardenolides asclepin, calactin and uscharidine[8] or the antibiotic spectinomycin,[9] and since the double-glycosidic annulation of 2-ketosugars to steroidal or cyclohexanoid diols is all but satisfactorily solved synthetically,[10] we have chosen to probe the feasibility of the photocycloaddition of 1,2-diketones to hydroxyglycal esters **10** → **11** (Scheme 2). Herein we report the results of this study.

☆ Part 34 of the series 'Sugar-Derived Building Blocks'. Part 33. see Ref. 1.

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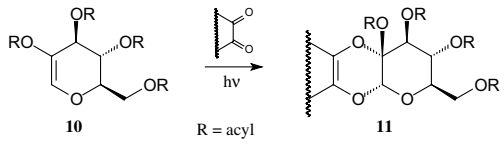
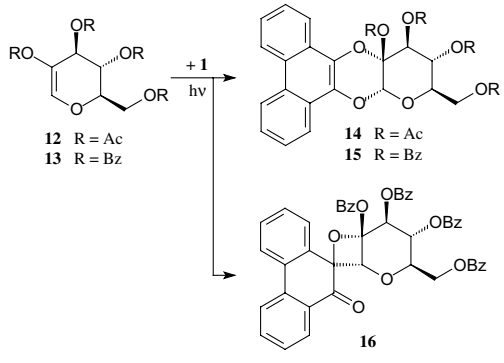


Scheme 2.

2. Results and discussion

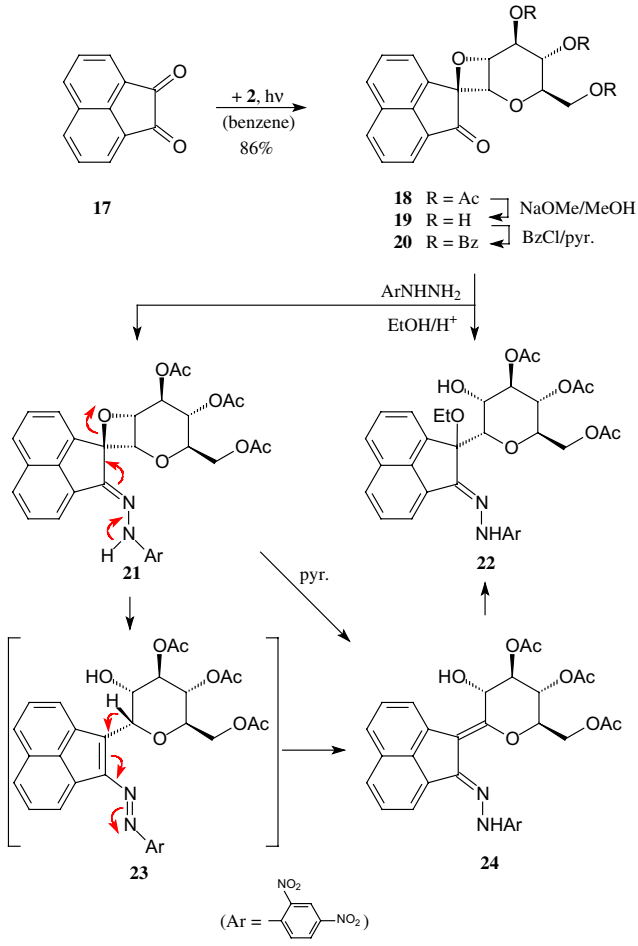
On reinvestigation of the photocycloaddition of phenanthrenequinone **1** to triacetyl-D-glucal **2**,[4b] it was found that exposure of their benzene solution to light from a standard 300 W lamp for 3 d and inducing the mixture to a gentle reflux, was as effective as the use of a high pressure mercury lamp, providing the [4+2] cycloadduct **3** in comparable yield (50%). In either case, the mother liquor contained several other products as evidenced by TLC, which due to only partial separation by column chromatography, were not identified unequivocally. Based on the NMR data of a minor fraction enriched with one of the side products, the ketooxetane isomer, resulting from [2+2] cycloaddition to only one carbonyl group, had also been formed. Such a course was not unexpected though, as [4+2] and [2+2] cycloadducts have been observed in the photoreactions of phenanthrenequinone with a variety of olefines[11] and, notably, with the glucal-analogous 1,4-dioxene.[12]

When irradiating a benzene solution of phenanthrenequinone and 2-acetoxy-D-glucal triacetate **12** for 3 d at 50 °C, the α-*cis*-annulated pyranodioxane **14** was the major cycloadduct and could be isolated from the reaction mixture, which contained several minor components (TLC), in 43% yield. However in the case of the benzoylated analogue **13**, both the [4+2] as well as [2+2] cycloadducts **15** and **16**, respectively, could be obtained in their crystalline forms, but only in moderate to modest yields (32% and 11%, respectively) (Scheme 3).



Scheme 3.

Attempts to induce analogous photocycloadditions onto hydroxyglucal esters **12** and **13** with in situ-generated *o*-benzoquinone, its tetrachloro derivative as well as 1,2-naphthoquinone failed to generate any products upon irradiation for up to 3 d with either a standard 300 W or a mercury high pressure lamp. The closely related acenaphthenequinone **17** though, being an aromatically substituted diketone rather than an *o*-quinone, reacted sluggishly with the hydroxyglucal esters **12** and **13**, resulting in product mixtures that were difficult to separate. However, when **16** was exposed to triacetyl-D-glucal **2** under analogous conditions, smooth and an essentially quantitative [2+2] cycloaddition took place to give keto-pyranooxetane **18**, isolable as well-formed plates or clustered needles in 86% yield (Scheme 4).

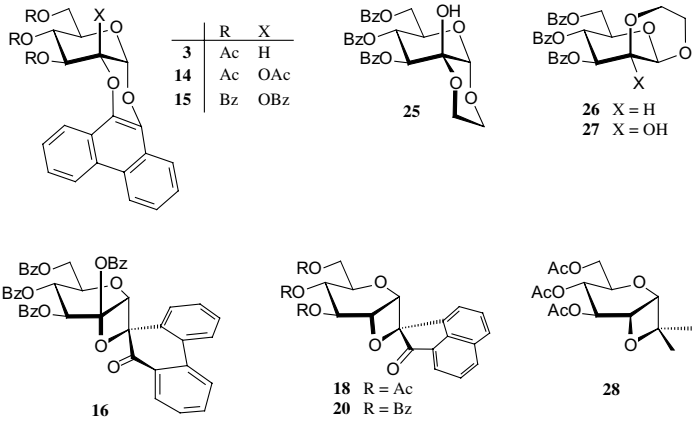


Scheme 4.

The oxetane ring in cycloadduct **18** proved to be stable towards basic conditions, such that de-*O*-acetylation could be effected under Zemplén conditions (NaOMe/MeOH) to give triol **19** as an amorphous powder. Subsequent benzoylation converted **19** into the highly crystalline tribenzoate **20**.

Under acidic conditions, however, for example, while attempting to prepare the 2,4-dinitrophenylhydrazone of **20** using the standard reagent solution (DNP/EtOH/H_2SO_4),[13] two DNP derivatives were obtained, one being the expected product **21** isolated in 33% yield, and the other compound **22**, in which the oxetane ring had been opened by ethanol. Its formation, presumably is initiated by an acid-promoted fission of the spiro-oxetane ring (arrows in **21**), followed by elaboration of ole-

Table 1. Structurally relevant ^{1}H NMR and rotational data for *cis*-fused pyranodioxanes and spiro-pyranooxetanes



Compound	^{1}H NMR ($CDCl_3$)								$[\alpha]_D^{20}$ ($CHCl_3$)
	H-1	H-3	H-4	H-5	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	
3	5.76	5.28	5.43	4.51	3.3	9.7	9.7	10.0	+85.0[4a]
14	6.37	5.43	5.62	4.53	—	—	9.4	9.8	+9.2
15	6.75	6.21	6.28	4.94	—	—	9.6	9.2	+24.2
25[14]	4.80	6.20	5.88	4.60	—	—	9.7	9.8	+8.8
26[14]	4.97	5.37	5.96	4.06	0.9	3.3	10.2	10.0	−17.3
27[14]	4.85	5.24	5.86	4.10	—	—	10.0	10.0	−7.1
16	6.32	6.18	6.56	4.80	—	—	10.8	9.9	+441
18	5.04	5.48	5.09	4.62	5.0	3.2	7.8	6.7	+188
20	5.25	6.02	5.63	4.97	4.9	3.4	7.9	6.6	+190
28[15]	4.48	4.72	5.34	4.97	5.5	4.0	8.8	6.5	+54.1

fine **24** through intermediate **23** and is concluded by addition of ethanol. This course is substantiated by the quantitative isolation of **24** on exposure of **21** to pyridine at ambient temperature, and its conversion into **22** with ethanol containing a trace of sulfuric acid.

2.1. Structural and configurational assignments

For the phenanthrenequinone/triacetyl-glucal cycloadduct **3**, the pyrano-dioxene structure and α-D-*gluco*-configuration—that is, α-*cis*-annulation in the photoaddition—had already been proven by chemical degradation,[4] and is corroborated by its ^{1}H NMR data, most notably the coupling constants of the pyranoid hydrogens (cf. Table 1). This analogous α-*cis*-fusion of pyran and dioxene rings, which prevailed in the hydroxyglycal ester cycloadducts **14** and **15**, followed from the following pieces of evidence: (i) IR and ^{13}C NMR data provide no evidence of a ketonic carbonyl function (as required for the pyranooxetane isomer, e.g., **16**); (ii) the chemical shifts for H-5 are in the 4.5–4.9 ppm range for **3**, **14**, **15** and the differently prepared[14] α-*cis*-annulated analogue **25** (cf. Table 1); by contrast, in β-D-mannopyranoside **26** and its equally β-*cis*-fused 2-hydroxy analogue **27**, H-5 occurs substantially downfield (4.1 ppm) as expected for β-D-glycosides and (iii) the rotational values for the α-*cis* products are comparatively small and uniformly positive versus negative values for the β-*cis*-fused analogues **26** and **27** (cf. Table 1).

By contrast, the specific rotations of the spiro-pyranooxetanes **16** and **18**–**22**, resulting from [2+2] photocycloaddition, are positive throughout and unusually large; the case of **16** even reached a value of +441. Conclusive evidence for the α-*cis*-fusion of pyran and oxetane rings is provided by the pyranoid couplings of the acenaphthenequinone adducts **18** and **20**, that correlate well with those of acetone adduct **28** of an established configuration,[15] yet differ from the couplings obtained for the β-*cis*-fused D-mannoside **26** (Table 1). In the pyranooxetane cycloadducts, the (*S*)-configuration at the spiro carbon atom was derived from an X-ray structural analysis of **18**, the acenaphthone carbonyl pointing away from the pyranoid ring oxygen (Fig. 1). Two other features are unusual in the solid state structure of **18**: the oxetane ring is all but planar showing a deviation of −16.3° from planarity, and the acetoxymethyl and two acetoxy groups of the pyranoid ring are in *trans*-diaxial orientation each, as evidenced by dihedral angles of 156.9°, −156.8° and 166.5°, respectively. This entails adoption of an unusually distorted pyran ring geometry best described as a hybrid conformation between the $^5H_4$ and $^0H_5$ half-chair forms.

In solution, however, as evidenced by the comparatively large $J_{3,4}$ and $J_{4,5}$ coupling constants of **18** (as well as **16**, **20** and **28**) (cf. Fig. 1), the pyranoid ring adopts a conformation approximating the $^4H_5$ half-chair, that is, nearly inverse to that in the solid state.

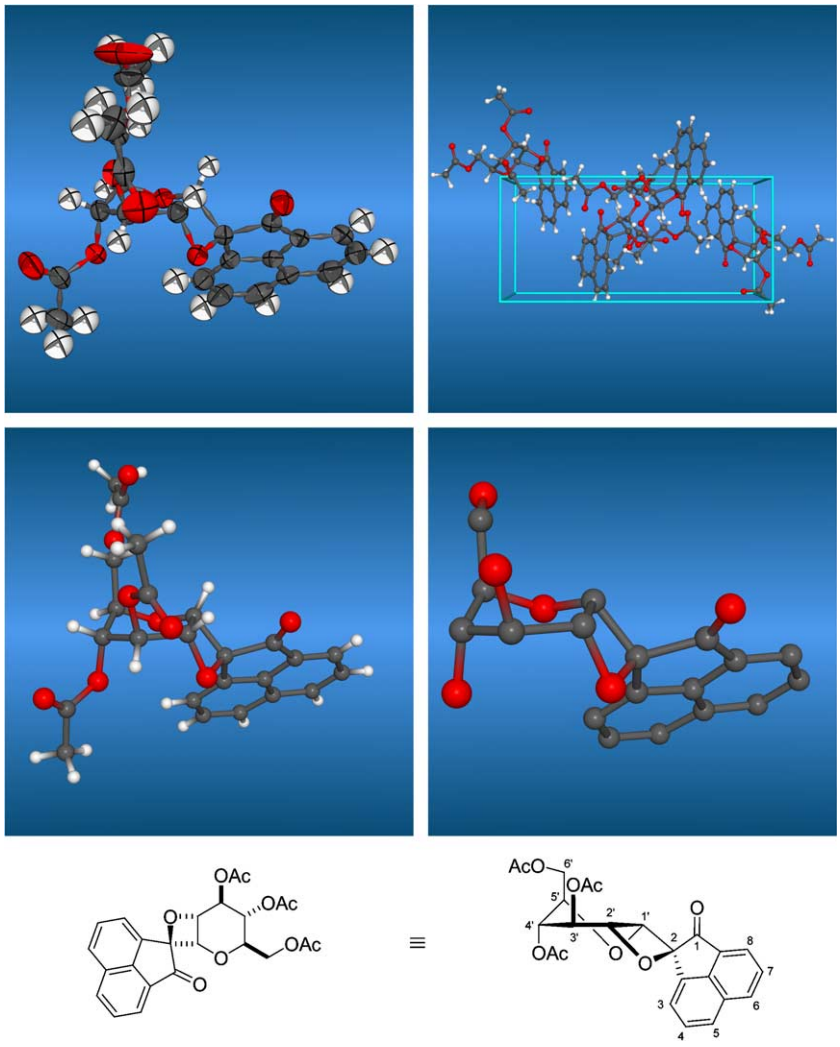


Figure 1. X-ray structure of acenaphthenone-2,2-ylidene-pyranooxetane **18** displayed by the anisotropic thermal ellipsoids (top left) and a single unit cell of the crystal structure (top right). In the centre row, a ball-and-stick mode representation with hydrogens and acetoxy groups (centre left) and without (centre right) is given, showing more clearly the pentacyclic ring skeleton.[16] For simplicity, pyran ring and acenaphthenone portions are numbered separately. Selected dihedral angles [°]: C1–C2–O2–C2′ +17.5, O2–C2–C1′–C2′ −16.3, O2–C2–C1′–O5′ +93.2, O2–C2′–C3′–O3′ +156.9, O3′–C3′–C4′–O4′ −156.8, O4′–C4′–C5′–C6′ +166.5, O5′–C1′–C2′–C3′ −25.5.[17]

3. Conclusion

In conclusion, we have shown that the photocycloadditions of phenanthrenquinone **1** and acenaphthenequinone **17**, onto 3,4,6-tri-*O*-acetyl-D-glucal **2** proceed with distinctly different regioselectivity. Compound **1** predominantly adds in a [4+2] fashion to give a 1-*O*,2-*O*-dioxane annulated α-D-glucoside **3**, isolable in 50% yield,[4] whereas **17** also reacts in an α-*cis* addition manner, yet with one carbonyl group only, to afford the [2+2] cycloadduct **18**, a 1-*C*,2-*O*-oxetano-glucoside, with high preference (86% isolated yield). 2-Hydroxyglucal esters such as **12** and **13** similarly reacted with phenanthrenequinone to give the analogous [4+2] cycloadducts **14** and **15**, respectively, yet the acenaphthenequinone **17** failed to give any products. Whilst a clear rationalization of this distinctly different photoaddition behaviour of two closely related aromatic 1,2-diketones is unavailing on the basis of the few preparative results available, the underlying reasons must be related to the sterically different fixation of the two carbonyl functions—and the radical intermediates generated therefrom in the course of the cycloaddition—those in **1** obviously being more suited to cycloadditions with both carbonyl oxygens than the wider spread ones in **17**.

4. Experimental

4.1. General

Melting points, determined with a Bock hot-stage microscope, are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 20 °C using a cell of 1 dm path length; concentration (*c*) in g/100 mL and solvent are given in parentheses. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 spectrometer in the solvents given. Mass spectra were acquired on Varian MAT 311 and MAT 212 spectrometers. Microanalyses were determined on a Perkin–Elmer 240 elemental analyzer. Analytical thin layer chromatography (TLC) was performed on precoated

Merck plastic sheets (0.2 mm silica gel 60 F_{254}) with detection by UV (254 nm) and/or spraying with H_2SO_4 (50%) and heating. Column and flash chromatography was carried out on Fluka silica gel 60 (70–230 mesh) using the specified eluents.

4.2. 1,2-*O*-(9,10-Phenanthrenediyl) 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 3

Following Helferich's et al. procedure,[4b] a suspension of phenanthrenequinone **1**, (6.24 g, 30 mmol) in a benzene solution of 3,4,6-tri-*O*-acetyl-D-glucal **2** (8.17 g, 30 mmol, in 400 mL) was irradiated with a watercooled quartz lamp for 15 h at rt. The quinone slowly dissolved and after 15 h the now clear solution was taken to dryness in vacuo, to give a syrup residue that crystallized on trituration with warm EtOH (100 mL). Recrystallization from EtOH afforded 7.20 g (50%) of **3** as colourless needles of mp 207–208 °C; $[\alpha]_D^{20} = +84.7$ (*c* 1, $CHCl_3$) lit.: mp 206–207 °C,[4a] 209–210 °C,[4b] $[\alpha]_D^{19} = +85.0$ (*c* 1, $CHCl_3$).[4a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.98, 2.05, 2.18 (three 1H-s, 3AcCH_3), 4.27, 4.44 (two 1H-dd, 6-H_2), 4.51 (ddd, 1H, 5-H), 4.69 (dd, 1H, 2-H), 5.28, 5.43 (two 1H-t, 3-H and 4-H), 5.76 (d, 1H, 1-H); $J_{1,2} = 3.3$, $J_{2,3} = 9.7$, $J_{3,4} = 9{,}7$, $J_{4,5} = 10.0$, $J_{5,6} = 2.1$ and 4.0, $J_{6,6} = 12.4$ Hz; phenanthrene-H: 7.60 (4H-m), 8.04, 8.25 (two 1H-m), 8.65 (2H-m). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.5, 20.7 (3AcCH_3), 61.5 (C-6), 67.6, 68.5, 69.6, 72.0 (C-2, C-3, C-4, C-5), 91.3 (C-1), 120-131 (phenanthrene-*C*), 169.5, 170.6 (Ac*C*O).

Irradiation could also be performed with a standard 300 W lamp (Osram Concentra) installed such that the reaction mixture is gently refluxing. The yield after 3 d was comparable.

4.3. 1,2-*O*-(9,10-Phenanthrenediyl) 2-acetoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 14

Finely powdered phenanthrenequinone (7.50 g, 36 mmol) was added to a solution of 12.0 g (36 mmol) of 3,4,6-tri-*O*-acetyl-2-acetoxy-1,5-anhydro-D-*arabino*-hex-1-enitol[7] **12** in benzene (500 mL) and the mixture irradiated with a standard 300 W lamp (Osram Concentra) resulting in a gentle reflux and gradual dissolution of the quinone. After 5 d, the solution was filtered through charcoal and evaporated to dryness in vacuo to leave a residue that was crystallized by trituration with MeOH and then recrystallized from the same solvent: 8.50 g (43%) of **14**; mp 187–191 °C (dec.); $[\alpha]_D^{20} = +9.2$ (*c* 1.1, $CHCl_3$). UV (benz- ene): λ_{max}(lg ε) = 327 nm (2.84), 343 (3.07), 361 (3.14); the solution shows an intense light-blue fluorescence when exposed to UV light of 254 nm. ^{1}H NMR (300 MHz, $CDCl_3$), pyranoid protons:[18] δ 2.01, 2.10, 2.17, 2.29 (four 3H-s, 4AcCH_3), 4.29, 4.39 (two 1H-ddd, 6-H_2), 4.53 (ddd, 1H, 5-H), 5.43 (t, 1H, 4-H), 5.62 (d, 1H, 3-H), 6.37 (s, 1H, 1-H), $J_{3,4} = 9.4$, $J_{4,5} = 9.8$, $J_{5,6} = 2.6$, 4.8, $J_{6,6} = 12.4$ Hz; phenanthrene-H: δ = 7.55–7.68 (4H-m), 8.03, 8.23 (two 1H-m), 8.61 (2H-m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 20.5, 20.7, 21.9 (4AcCH_3), 61.7 (C-6), 66.6, 67.1, 70.4 (C-3, C-4, C-5), 90.1 (C-1), 96.6 (C-2), 120–130 (Aryl-C), 168–170 (Ac*C*O). MS (FD): *m*/*z* = 538 [M^+]. Anal. Calcd for $C_{28}H_{26}O_{11}$ (538.5): C, 62.45; H, 4.87. Found C, 62.39; H, 4.78.

The methanolic mother liquor remaining after isolation of **14** contained several other products that could only partially be separated by column chromatography. ^{1}H NMR data of a minor fraction though indicated the presence of the [2+2] cycloadduct analog.

4.4. 1,2-*O*-(9,10-Phenanthrenediyl) 2-benzoyloxy-3,4,6-tri-*O*-benzoyl-α-D-glucopyranoside 15

Phenanthrenequinone (1.50 g, 7.2 mmol) was added to a benzene solution of 3,4,6-tri-*O*-benzoyl-2-benzoyloxy-1,5-anhydro-D-*arabino*-hex-1-enitol[7] **13** (4.15 g, 7.2 mmol in 150 mL). The suspension was then irradiated with a standard 300 W lamp (Osram Concentra), resulting in a gentle reflux to give a clear solution after 30 min. After 3 d, the mixture was filtered through charcoal. The filtrate evaporated to dryness in vacuo and the residue, consisting of two main components [R_f = 0.28 (**15**) and 0.06 (**16**), in CH_2Cl_2/*n*-hexane/EtOAc (50:30:1)], subjected to chromatography on silica gel (2 × 30 cm column). Elution with CH_2Cl_2/*n*-hexane/EtOAc (50:30:1), collection of the first major fraction and removal of the solvents in vacuo and trituration with EtOAc gave **15** (1.80 g, 32%) as slightly yellowish crystals of mp 128–130 °C; $[\alpha]_D^{20} = +24.2$ (*c* 1.1, $CHCl_3$). UV (C_6H_6): λ_{max}(lg ε) = 326 nm (2.90), 3.53 (3.08), 361 (3.14). ^{1}H NMR (300 MHz, $CDCl_3$), pyran hydrogens:[18] δ 4.12, 4.16 (2H dd, 6-H_2), 4.94 (ddd, 1H, 5-H), 6.21 (d, 1H, 3-H), 6.28 (t, 1H, 4-H), 6.75 (s, 1H, 1-H), $J_{3,4} = 9.6$, $J_{4,5} = 9.2$, $J_{5,6} = 2.8$, 3.9, $J_{6,6} = 12.4$ Hz. MS (FD, 10 mA): *m*/*z* = 786 [M^+]. Anal. Calcd for $C_{48}H_{34}O_{11}$ (786.80): C, 73.27; H, 4.36. Found C, 73.13; H, 4.30.

4.5. (1*S*,3*R*,4*S*,5*R*,6*R*,8*S*)-4,5-Bis(benzoyloxy)-3-benzoyloxymethyl-8,8-(spiro-9-phenanthrone-10-ylidene)-2,7-dioxabicyclo [4.2.0]octane 16

After elution of pyranodioxene **15** (cf. above), the silica gel column was then eluted with the more polar *n*-hexane/EtOAc (3:2) to release the minor component, pyranooxetane **16**. Evaporation of the appropriate fractions in vacuo and digeration of the residue with *n*-hexane/EtOAc (1:1) gave 420 mg (11%) of **16** as a colourless, amorphous product; mp 125 °C; $[\alpha]_D^{20} = +441$ (*c* 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$), pyran protons:[18] δ 4.67 (m, 1H, 6-H_a), 4.80 (2H-m, 5-H, 6-H_b), 6.18 (d, 1H, 3-H), 6.32 (s, 1H, 1-H), 6.56 (t, 1H, 4-H), $J_{3,4} = 10.8$, $J_{4,5} = 9.9$ Hz. MS (FD, 10 mA): *m*/*z* = 786 [M^+]. Anal. Calcd for $C_{48}H_{34}O_{11}$ (786.80): C, 73.27; H, 4.36. Found C, 73.15; H, 4.33.

4.6. (1*S*,3*R*,4*S*,5*R*,6*R*,8*S*)-4,5-Bis(acetoxy)-3-acetoxymethyl-8,8-(spiro-1-acenaphthone-2-ylidene)-2,7-dioxabicyclo[4.2.0]octane 18

A suspension of acenaphthenequinone **17** (910 mg, 5 mmol) in a solution of glucal **2** (1.35 g, 5 mmol) in benzene (250 mL) was irradiated with a standard 300 W lamp for 3 d, whereby the temperature was kept at ~50 °C by a cooling finger. The orange-red suspension

gradually changed to a clear yellow solution generating a major product of $R_f = 0.28$ (*n*-hexane/EtOAc, 3:2) with only faint spots at $R_f = 0.22$ and 0.42. Filtration and removal of the solvent in vacuo gave a solid residue, which was purified by trituration with charcoal in boiling EtOAc. Evaporation of the filtrate to dryness and crystallization from Et_2O gave 1.95 g (86%) of **18**; mp 158.5 °C; $[\alpha]_D^{20} = +188$ (*c* 1, $CHCl_3$). Crystallization from *i*-propanol or EtOAc/cyclohexane afforded **16** as rectangular plates while from CCl_4 clustered needles are obtained. ^{1}H NMR (300 MHz, $CDCl_3$), pyran hydrogens:[17] δ 2.02, 2.13, 2.18 (three 3H-s, AcCH_3), 4.17, 4.31 (two 1H-dd, 6-H_2), 4.62 (ddd, 1H, 5-H), 5.04 (d, 1H, 1-H), 5.09 (t, 1H, 4-H), 5.48 (dd, 1H, 3-H), 5.55 (dd, 1H, 2-H; $J_{1,2} = 5.0$, $J_{2,3} = 3.2$, $J_{3,4} = 7.8$, $J_{4,5} = 6.7$, $J_{5,6} = 3.2$ and 6.4, $J_{6,6} = 12.3$ Hz; acenaphthene-H: 7.74 (2H-m), 7.99 (3H-m), 8.14 (1H-m); NOE showed the 8.14 signal in resonance with pyranoid H-5. ^{13}C NMR (75 MHz, $CDCl_3$):[18] δ 20.7, 20.8 (AcCH_3), 62.4 (C-6), 67.5 (C-4), 72.8 (C-3), 73.5 (C-5), 74.5 (C-1), 79.6 (C-2), 90.5 (quart. oxetane-C), 112-142 (10 Ar-C), 169.6, 169.7, 170.3 (Ac*C*O), 201.6 (CO. (FD, 5 mA): *m*/*z* = 454 [M^+]. Anal. Calcd for $C_{24}H_{22}O_9$ (454.5): C, 63.43; H, 4.88. Found C, 63.46; H, 4.85.

X-ray crystal data and structure refinement:[16] Space group P_{21}, monoclinic, unit cell dimensions $a = 9.117(4)$, $b = 19.857(3)$, $c = 11.934(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2160.5(11)$ Å^3, $Z = 4$, Dc = 1.397 g/cm^3, μ(Mo-K$_\alpha$) = 0.066 mm^{-1}, $1.71° < \theta < 24.02°$, F(0 0 0) = 952, crystal size $0.4 \times 0.2 \times 0.2$ mm, 6992 reflections collected | 3431 unique ($R_{int} = 0.0145$) data | parameters = 3431 | 597, Goof = 1.003, $R_{indices}$ ($I > 2\sigma\pm$): $R_1 = 0.0274$, $wR_2 = 0.0757$, $R_{indices}$ (all data): $R_1 = 0.0282$, $wR_2 = 0.0770$; Refinement method: full-matrix least-squares on F^2. Ball-and-stick mode stereostructure and selected torsional angles: Figure 1.

4.7. (1*S*,3*R*,4*S*,5*R*,6*R*,8*S*)-3-Hydroxymethyl-8,8-(spiro-1-acenaphthone-2-ylidene)-2,7-dioxabicyclo[4.2.0]octane-4,5-diol 19

A methanolic solution of **18** (450 mg, 1 mmol, in 50 mL), to which 1 mL of NaOMe in MeOH had been added, was kept for 3 h at rt, followed by neutralization (Amberlite IR 120, H^+ form), filtration and removal of the solvent in vacuo. Compound **19** (300 mg, 91%) as a colourless powder of mp 133 °C (dec.) was obtained; $[\alpha]_D^{20} = +176$ (*c* 1, MeOH). ^{1}H NMR (acetone-d_6/D_2O), pyran hydrogens:[18] δ 3.60 (dd, 1H, 4′-H), 3.66, 3.78 (two 1H-dd, 6-H_2), 4.11 (ddd, 1H, H-5), 4.38 (dd, 1H, 3′-H), 5.06 (d, 1H, 1′-H), 5.15 (t, 1H, 2′-H), $J_{1,2} = 5.4$, $J_{2,3} = 5.0$, $J_{3,4} = 9.8$, $J_{4,5} = 7.8$, $J_{5,6} = 3.0$ and 5.4, $J_{6,6} = 12.2$ Hz. MS (FD, 7 mA): *m*/*z* = 328 [M^+]. Anal. Calcd for $C_{18}H_{16}O_6$ [328.3]: C, 65.85; H, 4.91. Found C, 65.80; H, 4.87.

4.8. (1*S*,3*R*,4*S*,5*R*,6*R*,8*S*)-4,5-Bis(benzoyloxy)-3-benzoyloxymethyl-8,8-(spiro-1-acenaphthone-2-ylidene)-2,7-dioxabicyclo[4.2.0]octane 20

Benzoyl chloride (1.0 g, 7.1 mmol) was added to a cooled (0 °C) solution of **19** (230 mg, 0.7 mmol) in pyridine (20 mL) and the mixture kept at rt overnight followed by pouring into ice-water (50 mL). Extraction with $CHCl_3$ (3 × 30 mL), washing of the combined extracts with water (3 × 30 mL), drying and evaporation to dryness left a residue, which crystallized from *i*-propanol in the form of colourless needles: 400 mg (89%) of **20**; mp 176 °C; $[\alpha]_D^{20} = +190$ (*c* 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) for pyran hydrogens:[18] δ 4.59, 4.68 (two 1H-dd, 6-H_2), 4.97 (ddd, 1H, H-5), 5.25 (d, 1H, H-1), 5.63 (dd, 1H, H-4), 5.73 (dd, 1H, H-2), 6.02 (dd, 1H, H-3), $J_{1,2} = 4.9$, $J_{2,3} = 3.4$, $J_{3,4} = 7.9$, $J_{4,5} = 6.6$, $J_{5,6} = 3.9$ and 6.4, $J_{6,6} = 12.2$ Hz. MS (FD): *m*/*z* = 640 [M^+]. Anal. Calcd for $C_{39}H_{28}O_9$ (640.7): C, 73.12; H, 4.41. Found: C, 72.99; H, 4.35.

4.9. 2,4-Dinitrophenylhydrazone of 17:21

A solution of **18** (270 mg, 0.59 mmol) in EtOH (5 mL) was stirred into a solution of 2,4-dinitrophenylhydrazine (400 mg, 2 mmol) in a mixture of H_2SO_4 concd (2 mL), water (3 mL) and EtOH (10 mL),[13] resulting in a precipitate, which was collected after 15 min and washed with water. The orange-coloured solid consisted of two main products with $R_f = 0.44$ (**21**) and 0.26 (**22**, TLC in CH_2Cl_2/EtOAc, 10:1), which were separated by elution from a silica gel column with CH_2Cl_2/EtOAc (10:1).

The fraction eluted first (for next fraction containing **21** cf. below), upon removal of the solvents in vacuo, gave 125 mg (33%) of **21**; $[\alpha]_D^{20} = -65.7$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$):[17] δ 1.90, 2.15, 2.24 (three 3H-s, AcCH_3), 4.00, 4.21 (two 1H-dd, 6′-H_2), 4.36 (ddd, 1H, 5′-H), 4.98 (dd, 1H, 4′-H), 5.50 (2H m, 1′-H, 2′-H), 6.28 (m, 1H, 3′-H), 7.73–9.18 (6 m, 9 Ar-H), 12.79 (s, 1H, NH), $J_{3,4} = 10.3$, $J_{4,5} = 2.9$, $J_{5,6} = 2.9$, 5.9, $J_{6,6} = 12.4$ Hz. MS (FD): *m*/*z* = 634 [M^+]. Anal. Calcd for $C_{30}H_{26}N_4O_{12}$ (634.6): C, 56.79; H, 4.13; N, 8.83. Found C, 56.70; H, 4.05; N, 8.77.

4.10. (1*R*)-1-Ethoxy-1-(3′,4′,6′-tri-*O*-acetyl-α-*C*-glucopyranosyl)-acenaphth-2-one 2,4-dinitrophenylhydrazone 22

The fractions eluted after separation of those of **21** (cf. above) contained **22** ($R_f = 0.26$, CH_2Cl_2/EtOAc, 10:1). Their evaporation to dryness in vacuo afforded 165 mg (41%) of an orange-coloured solid; mp 211 °C; $[\alpha]_D^{20} = -460.7$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (3H-t, EtCH_3), 1.88, 1.90, 2.21 (three 3H-s, 3AcCH_3), 3.08, 3.35 (two 1H-dq, EtCH_2), 3.80 (m, 1H, 6′-H_a), 3.96 (d, 1H, 1′-H), 4.19 (m, 1H, 2′-H), 4.48 (m, 2H, 5′-H, 6′-H_b), 4.74 (t, 1H, 4′-H), 4.80 (d, 1H, OH), 5.12 (t, 1H, 3′-H), 7.6–9.2 (5 m, Ar-H), 13.0 (s, 1H, NH); $J_{1,2} = 1.5$, $J_{2,3} = 3.0$, $J_{4,5} = 3.3$, $J_{2,OH} = 3.4$ Hz. The OH-signal could be exchanged by D_2O, the NH signal remained. MS (FD): *m*/*z* = 680 [M^+]. Anal. Calcd for $C_{32}H_{32}N_4O_{13}$ (680.6): C, 56.47; H, 4.74; N, 8.23. Found C, 56.39; H 4.77; N 8.15.

4.11. 2-(3′,4′,6′-Tri-*O*-acetyl-D-glucopyranos-1′,1′-ylidene)-1-acenaphthone 2,4-dinitrophenylhydrazone 24

A solution of **21** (90 mg, 0.14 mmol) in pyridine (15 mL) was kept at rt overnight, followed by evaporation to

dryness in vacuo and two subsequent co-evaporations with toluene. Purification by elution from a short silica gel column with CH_2Cl_2/EtOAc (10:1) and removal of the solvents from the eluates containing **24** (TLC) gave 85 mg (94%) of a deeply red solid; dec. ~185 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00, 2.20, 2.22 (three 3H-s, 3AcCH_3), 4.49, 4.62 (two 1H-d, 6′-H_2), 4.90 (ddd, 1H, 5′-H), 5.21 (dd, 1H, 4′-H), 5.33 (t, 1H, 3′-H), 5.76 (d, 1H, 2′-H), 7.6–8.7 (5 m, ArH), 11.85 (s, 1H, NH), $J_{2',3'} = 2.6$, $J_{3',4'} = 3.6$, $J_{4',5'} = 9.6$, $J_{5',6'} = 2.3$, 5.8, $J_{6',6'} = 12.6$ Hz. MS (FD): $m/z = 643$ [M^+]. Anal. Calcd for $C_{30}H_{26}N_4O_{12}$ (634.6): C, 56.79; H, 4.13; N, 8.83. Found C, 56.73; H, 3.98; N, 8.79.

Due to the intense colour of even very dilute solutions, the rotational value of **24** could not be determined.

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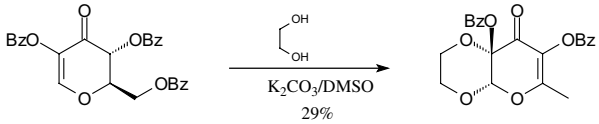

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17. CCDC-242771 contains the supplementary crystallographic data for **18**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk.
18. For easier comparison of ^{1}H and ^{13}C NMR data, the pyranoid hydrogens of Paterno–Büchi ([2 + 2]) and Schönberg ([4 + 2]) cycloadducts are both numbered according to carbohydrate usage, that is, H-1 (anomeric proton) through H-6 and C-1–C-6.