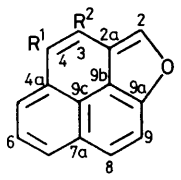
Preparation, Properties, and Some Chemical Reactions of Phenaleno[1,9-*bc*]furan

Gamini Weeratunga, Mona Austrup, and Russell Rodrigo *
Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

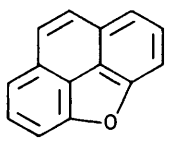
The synthesis of hitherto unknown phenaleno[1,9-*bc*]furan (**1**), in 11% overall yield from 2-naphthol, has been achieved. Its ^{1}H and ^{13}C n.m.r. spectra have been fully assigned by means of heteronuclear 2D correlations. The furanoid moiety of (**1**) displays Diels–Alder diene reactivity in its reactions with benzyne, dimethyl acetylenedicarboxylate, and singlet oxygen. The furan ring of (**1**) also suffers oxidation by *m*-chloroperbenzoic acid and undergoes catalytic hydrogenation. This chemistry appears to be more characteristic of naphtho[1,2-*c*]furan than of naphtho[1,2-*b*]furan although both structural units co-exist in structure (**1**).

The phenaleno[1,9-*bc*]furan ring system (**1**) has been largely ignored by organic chemists and neglected by Nature. This is in stark contrast to the other monofuranoid analogue of pyrene, phenanthro[4,5-*bcd*]furan (**2**), well known as part of the morphine alkaloid ring system and also as the parent heterocycle.[1] The chemical literature contains citations to only two distant relatives of (**1**), the synthetic compound (**3**)[2] and the natural product[3,4] salvelinone (**4**). Nothing is known about the parent heterocycle (**1**) or any of its close derivatives. A simple extension of our recent benzofuran synthesis[5] seemed to offer an easy route to this unknown ring system and an opportunity to study its chemistry. We now report our results.

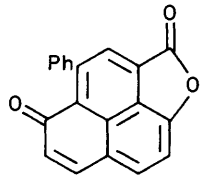
The dihydronaphthofuran ester (**5**)[5] was saponified and cyclised through the acid chloride (**6**) with aluminium chloride in methylene dichloride to provide the tetracyclic ketone (**7**) [55% from (**5**)]. Reduction with sodium borohydride gave the C-4 equatorial alcohol (**8**) (δ 5.3, q, after D_2O, J 11.2, 4.4 Hz, 4-H) as the sole product. This was followed by dehydrogenation with dichlorodicyano-*p*-benzoquinone (DDQ) in refluxing benzene. This reaction produced a mixture of the expected alcohol (**9**) (48%), the phenalenofuran (**1**) (8%), and the ketone (**7**) (19%). These were separated by column chromatography (silica gel; ethyl acetate–hexane) and the ketone (**7**) was recycled. The dehydrogenation was also attempted with compound (**7**) as the substrate but the results were even less encouraging; considerable decomposition was observed and none of the expected 4-hydroxyphenalenofuran (**10**) was found, probably because it was unstable under the conditions. Even the alcohol (**9**) was a sensitive compound. A mild, neutral method of dehydration had to be employed, and after some experimentation a suitable method was eventually found. An 80% yield of compound (**1**) was obtained by refluxing the alcohol (**9**) in anhydrous benzene with carbonyldi-imidazole for 24 h. This reagent had been previously used[6] for the dehydration of aldoximes to nitriles, but this appears to be the first instance of its application to the dehydration of alcohols. The entire sequence provides the target compound (**1**) in 24% overall yield from the ester (**5**) (11% from 2-naphthol in eight steps). The procedure permits substitution at C-4 and C-3 and the specifically deuteriated analogues (**11**) and (**12**) were also prepared; the former by using sodium borodeuteride to reduce the ketone (**7**) to alcohol (**13**) and the latter by deuteriation[5] of the initial naphthofuran ester (**5**). C-4 and C-3-alkylated derivatives of (**1**) should also be available by similar methods.



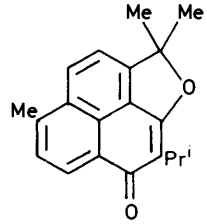
(**1**) $R^1 = R^2 = H$
(**10**) $R^1 = OH$, $R^2 = H$
(**11**) $R^1 = D$, $R^2 = H$
(**12**) $R^1 = H$, $R^2 = D$



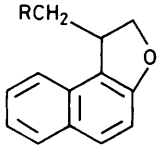
(**2**)



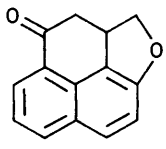
(**3**)



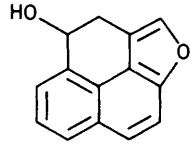
(**4**)



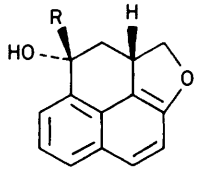
(**5**) R = CO_2Et
(**6**) R = COCl



(**7**)



(**9**)



(**8**) R = H
(**13**) R = D

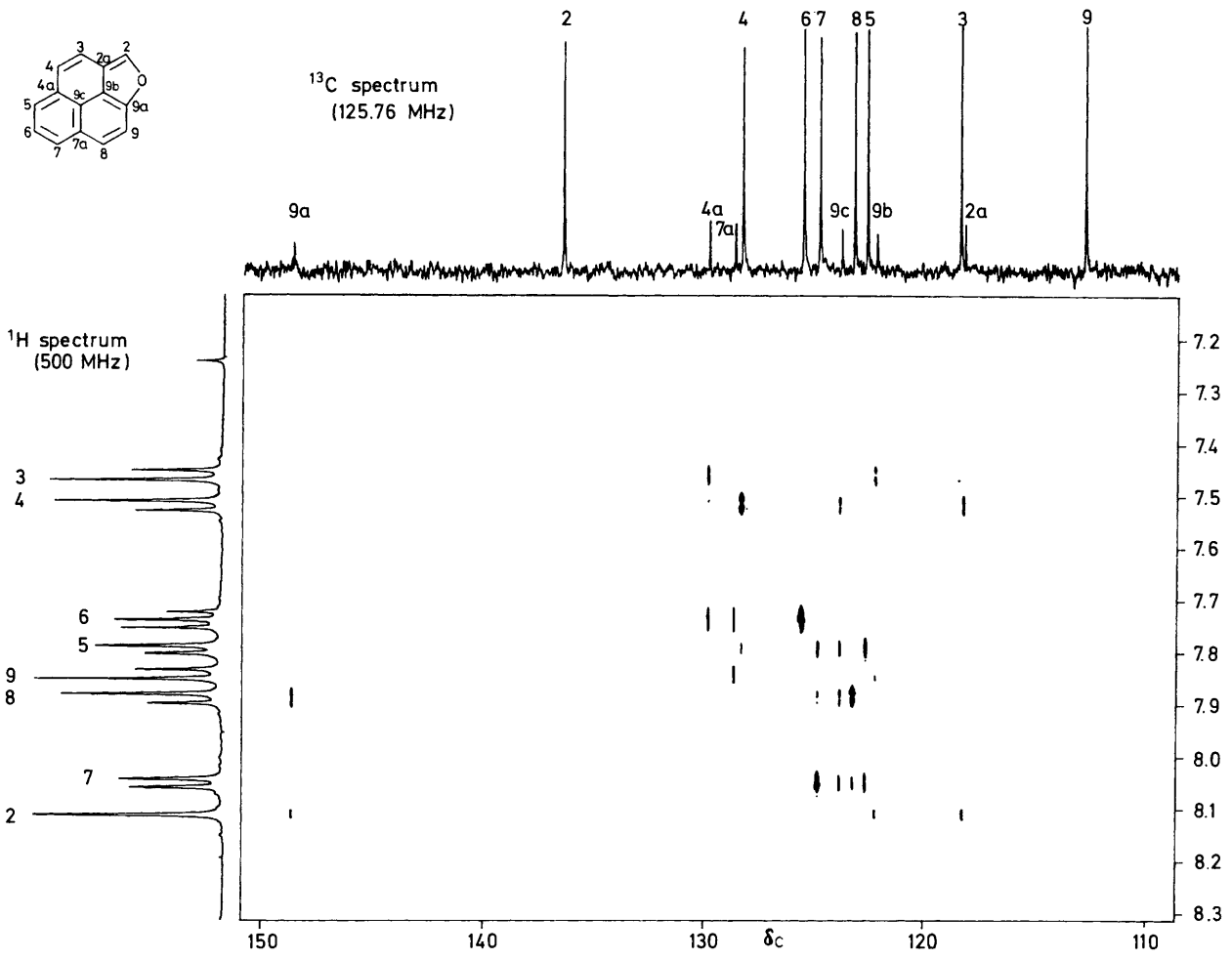


Figure. Heteronuclear chemical-shift correlation tuned to long-range ^{13}C–^{1}H couplings

Substitution at the C-5 to C-9 positions will depend on the availability of the corresponding 2-naphthol starting material.

The parent heterocycle (**1**) is a crystalline solid (m.p. 112—114 °C) which can be stored in the freezer in the absence of light and air for long periods with only slight darkening of the material. The low-resolution e.i. mass spectrum displayed the molecular ion as the base peak at *m/z* 192 with isotope peaks at *m/z* 193 (14.5) and 194 (1.24) corresponding to the molecular formula $C_{14}H_8O$, confirmed by elemental analysis. The only other ions of any significance were found at *m/z* 164 (91) and 163 (60) corresponding to the extrusion of CO and CHO fragments respectively, cleavages characteristic of the furan ring and observed also in both benzofuran [7] and isobenzofuran.[8] The u.v. spectrum of compound (**1**) bore a greater similarity to the spectrum of pyrene than to that of (**2**) [1] and was unaffected by the addition of a few drops of trifluoroacetic acid to the u.v. sample.

Complete assignment of both the ^{1}H (500 MHz) and ^{13}C (125.76 MHz) were also completed. After recourse to spectra of the deuteriated analogues (**11**) and (**12**) and with the aid of a homonuclear COSY experiment the ^{1}H assignments were secured except for the 5-H and 7-H doublets. This ambiguity was settled by a ^{13}C, ^{1}H heteronuclear chemical-shift correlation tuned to long-range (^{3}J) couplings (Figure). The carbon resonance at δ_C 128.3, assigned unequivocally to C-4 from the ^{13}C spectrum of (**11**), is seen to correlate with 5-H at δ_H 7.79 (*peri*-naphthalene [9] coupling ^{3}J, C-4–5-H); C-8 assigned subsequently to the signal δ_C 123.3 shows a similar long-range correlation with 7-H at δ_H 8.05. The ^{13}C signals of the protonated carbons were rapidly assigned by a similar 2D heteronuclear correlation involving one-bond ^{13}C, ^{1}H couplings. The long-range (^{2}J and ^{3}J) 2D correlation displayed in the Figure confirmed these assignments. Thus it can be easily seen that C-2, C-3, C-6, and C-9 are not subject to such long-range interactions with ^{1}H nuclei but C-4 (with 5-H), C-5 (with 7-H), C-7 (with 5-H and 8-H), and C-8 (with 7-H) do interact ($^{3}J_{C-H}$) as expected. The quaternary carbons 2a, 9a, and 9b are furanoid; C-2a correlates with 4-H, C-9a with 8-H, and C-9b with 3-H and 9-H. In addition to these *meta* benzenoid couplings all three show ^{2}J (for C-2a) and ^{3}J (for C-9a and C-9b) furanoid interactions with 2-H; similar ^{2}J and ^{3}J interactions in furan, benzofuran, and isobenzofuran [10] have been recognised before. The remaining quaternaries are coupled as expected, C-4a (to 3-H and 6-H), C-7a (to 6-H and 9-H), and C-9c (to 4-H, 5-H, 7-H, and 8-H). All n.m.r. assignments for (**1**) are found in the Table.

The chemical behaviour of compound (**1**) was investigated next (Scheme). Interestingly enough, this turned out to be more naphtho[*c*]furanoid [11] than naphtho[*b*]furanoid although both structural units are present in structure (**1**). For example, the furan ring of (**1**) has detectable diene character (C-2, -2a, -9b, -9a). Thus Diels–Alder reactions with spontaneous aromatisation of the adducts were observed with dimethyl acetylenedicarboxylate (DMAD) and with benzyne. In the former instance the pyrene diester (**14**) was obtained and characterised

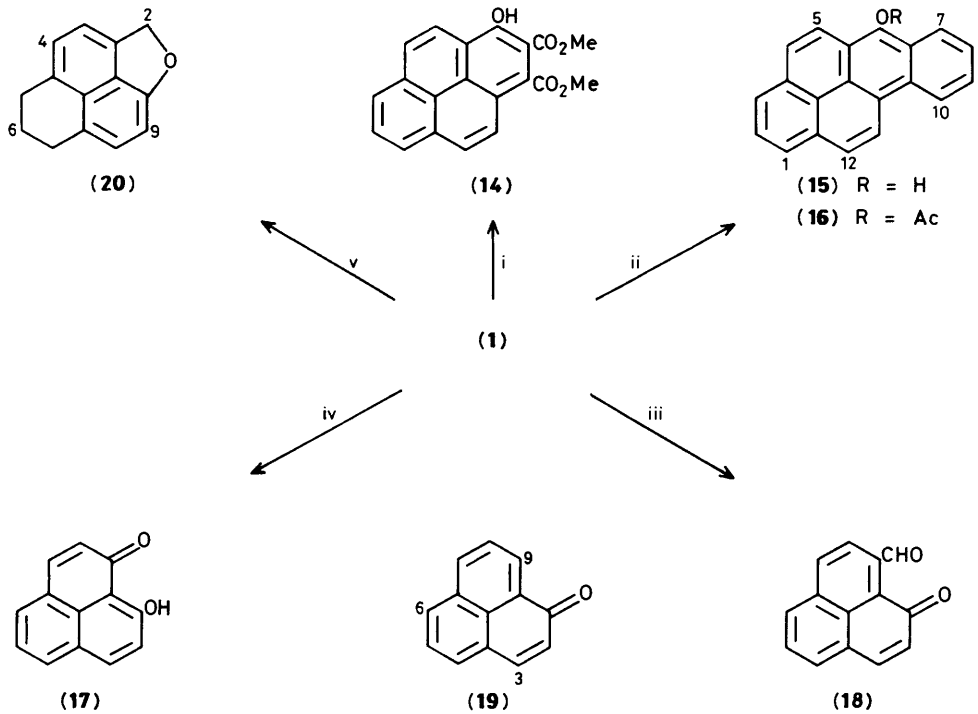
by low- and high-resolution mass spectrometry (h.r.m.s.), i.r., and ^{1}H n.m.r. spectroscopy. Benzo[*a*]pyren-6-ol (**15**), the product of benzyne addition to (**1**) and subsequent aromatisation of the adduct, is a much studied[12] material of some significance to the mechanism of *in vivo* detoxification of benzopyrene. Furthermore, it is known[13] to undergo autoxidation very easily through a 6-oxyl radical to form various benzopyrene diones. The n.m.r. spectrum of our sample of compound (**15**) was very unsatisfactory. The broadened signals in this spectrum were probably a consequence of such an autoxidation. The formation of compound (**15**) was confirmed, however, by h.r.m.s. and by acetylation to the known[14] 6-acetoxybenzopyrene (**16**). Singlet oxygen [Rose Bengal; tetrahydrofuran (THF); 20 °C] reacts with compound (**1**), to provide the well known 9-hydroxyphenalenone (**17**) in high yield. The strongly chelated hydroxy proton of compound (**17**) is found very far downfield at δ_H 16.5 in its ^{1}H n.m.r. spectrum and the symmetry of the molecule is clearly reflected in its ^{1}H and ^{13}C spectra.[15] We were not able to observe any reaction between compound (**4**) and *p*-benzoquinone. The diene character of compound (**1**) seems sufficient for reaction with only the best dienophiles. Bond-angle strain in the five-membered ring of (**1**) might be one of the contributing factors to the unusual reactivity. It has been observed[3] that the internal angles at C-2a (107°), -9a (109°), and -9b (103°) in compound (**4**) show considerable distortion from the ideal trigonal state. Moreover, the occurrence of these Diels–Alder reactions in compound (**1**) result in only a minimal loss of aromaticity; the fact that two rings can still be benzenoid in oxygen-bridged adducts (not isolated) might be a major factor. We are trying to grow suitable crystals of compound (**1**) for an accurate low-temperature *X*-ray study in order to obtain more information about its bond lengths and angles.

The furan ring of structure (**1**) is also sensitive to peroxy acids. With *m*-chloroperbenzoic acid (MCPBA) in methylene dichloride at room temperature, oxidative cleavage was completed in 15 min with formation of the 9-formylphenalenone (**18**) in 71% yield. The structure of the product was established by h.r.m.s., i.r., and ^{1}H n.m.r. [in comparison with the published spectrum[16] of phenalenone (**19**)] analysis. The aldehyde proton was found at δ_H 10.8 and the ring-proton chemical shifts showed a close similarity to those of the phenalenone with the exception of 8-H which was at δ_H 8.3 [7.67 in (**19**)], deshielded by the aldehyde at C-9. The mass spectrum [M^+, 208 (31)] had prominent ions at *m/z* 180 (49) and 152 (100), representing the sequential elimination of two molecules of CO with the latter corresponding to the acenaphthylene radical cation $[C_{12}H_8]^{\bullet+}$.

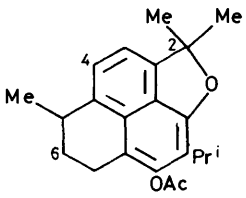
Catalytic hydrogenation of compound (**1**) (5% Pd–charcoal; ethyl acetate; 60 lb in^{-2}) proceeded smoothly to the tetrahydro derivative (**20**) whose structure was assigned by mass spectrometry and ^{1}H n.m.r. spectroscopy. The mass spectrum shows ions at *m/z* 196 [M^+ (100)], 195 (57), and 167 (13), the last two being characteristic of the dihydrofuran unit of structure (**20**). The presence of three contiguous methylene groups (C-5—C-7) was indicated by the presence of two multiplets at δ_H 2.07 (2 H) and δ_H 2.98 (4 H) in the 250 MHz n.m.r. spectrum and the C-2 methylene group appeared as a two-proton singlet at δ_H 5.75. The signals from the *ortho*-coupled naphthalene protons were unexceptional. A similar tetrahydrophenalenofuran (**21**) was formed as a product of reduction

Table. ^{13}C and ^{1}H Chemical shifts (δ) for compound (**1**) in $CDCl_3$

	δ			δ	
Atom	^{13}C	^{1}H	Atom	^{13}C	^{1}H
2	136.4	8.11	7	124.9	8.05
2a	118.2		7a	128.6	
3	118.4	7.46	8	123.3	7.89
4	128.3	7.52	9	112.8	7.84
4a	129.8		9a	148.8	
5	122.7	7.79	9b	122.2	
6	125.6	7.74	9c	123.9	



Scheme. The reactions of phenaleno[1,9-*bc*]furan. *Reagents and conditions:* i, DMAD; ii, benzyne; iii, MCPBA; iv, $^1O_2$; v, H_2, Pd/C, 60 lb in^{-2}



(21)

and acetylation of salvelinone (**4**). In the 90 MHz spectrum of that compound multiplets at δ_H 1.6—2.3 (6-H_2) and 2.6—2.9 (7-H_2) were assigned to the methylene groups at C-6 and C-7. Phenalenofuran (**1**) in common with furan, benzofuran, and isobenzofuran shows a characteristically large $^1J_{C-H}$ coupling (205 Hz) for the α-carbon (C-2) of the furan ring. Unlike the other three oxygen heterocycles, however, compound (**1**) could not be deprotonated at C-2. A variety of conditions, with various alkyl-lithiums, lithium di-isopropylamide, solvents, and temperatures were tried to no avail. The reason for the failure of this reaction is currently not clear.

Experimental

M.p.s were determined on a Fischer Mel Temp apparatus and are uncorrected. I.r. were obtained on a Perkin-Elmer 983 spectrophotometer and u.v. spectra on a Perkin-Elmer Lambda 5 instrument. N.m.r. spectra were run on Bruker AC 200, AM 250, or AM 500 spectrometers, for deuteriochloroform solutions with tetramethylsilane unless otherwise indicated. Low- and high-resolution mass spectra were measured on VG 7070 and VG ZAB-E spectrometers at the Regional Mass Spectrometry Centre at McMaster University, Hamilton, Ontario. Column chromatography was done with Silica gel (60—230 mesh) or neutral alumina (Brockman Activity 1, 80—200 mesh). Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario.

4-*Oxo*-2,2a,3,4-*tetrahydrophenaleno*[1,9-bc]*furan* (**7**).—The naphthofuran ester (**5**) (2 g, 7.81 mmol) was dissolved in methanol–THF (1:1; 50 ml) and the solution was stirred with aqueous sodium hydroxide (10%; 5 ml) for 6 h at room temperature. The solvents were removed under reduced pressure and the aqueous residue was acidified with 2M hydrochloric acid. The solution was extracted with ethyl acetate (3 × 50 ml), the extracts were dried, and the solvent was removed to leave an oil, which was crystallised from ether. The crystalline acid was dissolved in dry benzene (20 ml), and added to a solution of oxalyl chloride (1.13 ml, 13 mmol) in benzene (10 ml); the mixture was stirred at room temperature for 30 min and the benzene was removed under reduced pressure to leave the crude acid chloride (**6**) as an oil. The oil was dissolved in dry methylene dichloride (30 ml), anhydrous aluminium chloride (1.067 g, 8 mmol) was added, and the solution was stirred at room temperature for 3 h. Usual work-up followed by chromatography on silica gel in ethyl acetate–hexane (1:4) produced solid *ketone* (**7**), which was recrystallised from ether (0.9 g, 55%), m.p. 141—142 °C (Found: C, 79.7; H, 4.8. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%); $\nu_{max.}$($CHCl_3$) 1 680, 1 582, 1 523, and 1 474 cm^{-1}; δ_H(250 MHz) 2.71 (1 H, q, *J* 15, 12.9 Hz, 3-$H_{ax.}$), 3.22 (1 H, q, *J* 15, 5.7 Hz, 3-$H_{eq.}$), 4.14 (1 H, m, 2a-H), 4.31 (1 H, q, *J* 12, 8.4 Hz, 2-H), 5.14 (1 H, t, *J* 8.4 Hz, 2-H), 7.22 (1 H, d, *J* 8.8 Hz), 7.44 (1 H, t, *J* 7.8 Hz), 7.75 (1 H, d, *J* 8.8 Hz), and 8.05 (2 H, overlapping d, *J* 7.8 Hz); *m/z* 210 (M^+, 100%), 181 (44), 169 (21), and 152 (32).

2,2a,3,4-*Tetrahydrophenaleno*[1,9-bc]*furan*-4-*ol* (**8**).—Sodium borohydride (189 mg, 5 mmol) was added to a solution of the ketone (**7**) (2.1 g, 10 mmol) in dry methanol (20 ml) and the mixture was stirred at room temperature for 3 h. Usual work-up followed by crystallisation from ether gave the *alcohol* (**8**) (2 g, 95%) as white crystals, m.p. 132—133 °C (Found: C, 79.1; H, 5.85. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%); $\nu_{max.}$($CHCl_3$) 3 446, 1 646, and 1 471 cm^{-1}; δ_H(250 MHz) 1.78 (1 H, q, *J* 12.3, 11.6, 11.2 Hz, 3-$H_{ax.}$), 1.97 (1 H, d, *J* 8.5 Hz, OH exchanges with D_2O), 2.66 and 2.70 (1 H, 2 t, *J* 12.3, 4.6, 4.4 Hz, 3-$H_{eq.}$), 3.94 (1 H, m, 2a-H), 4.2 (1 H, q, *J* 12.1, 8.4 Hz, 2-H), 5.01 (1 H, t, *J* 8.4 Hz, 2-H), 5.3 (1 H, q when D_2O added, *J* 11.2, 4.4 Hz, 4-H), 7.09 (1 H, d, *J* 8.7 Hz), 7.32 (1 H, q, *J* 8.2, 7.2 Hz), 7.55 (1 H, d, *J* 7.2 Hz), 7.61 (1 H, d, *J* 8.7 (Hz), and 7.69 (1 H, d, *J* 8.2 Hz); *m/z* 212 (M^+, 100), 210 (8), 194 (11), 193 (42), 165 (28), and 164 (23).

The 4-deuterio analogue (**13**) was prepared in an identical manner with sodium borodeuteride. It had spectroscopic properties consistent with its structure.

3,4-*Dihydrophenaleno*[1,9-bc]*furan*-4-*ol* (**9**).—The alcohol (**8**) (1.06 g, 5 mmol) was dissolved in benzene (50 ml), DDQ (1.248 g, 5.5 mmol) was added, and the mixture was refluxed for 18 h. The solvent was removed under reduced pressure to leave an oil, which was chromatographed on a silica gel column with ethyl acetate–hexane (1:4) to give three products (**1**), (**7**), and (**9**) in order of elution. The *major constituent* (**9**) was sublimed at 80 °C (1 mmHg) to provide crystalline material (0.49 g, 48%), m.p. 104—105 °C (Found: C, 80.1; H, 5.15. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%); $\nu_{max.}$($CHCl_3$) 3 592, 1 659, and 1 451 cm^{-1}; δ_H(500 MHz) 3.37 (2 H, octet, *J* 16, 5.2, 1.1 Hz, 3-H_2), 5.41 (1 H, t, *J* 5.2 Hz, 4-H), 7.52 (1 H, q, *J* 7, 8.3 Hz, 6-H), 7.56 (1 H, br s, 2-H), 7.62 (1 H, d, *J* 8.9 Hz, 9-H), 7.64 (1 H, d, *J* 7 Hz, 5-H), 7.70 (1 H, d, *J* 8.9 Hz, 8-H), and 7.89 (1 H, d, *J* 8.3 Hz, 7-H); *m/z* 210 (M^+, 100), 193 (45), 182 (24), 181 (73), and 164 (32).

Phenaleno[1,9bc]*furan* (**1**).—The alcohol (**9**) (420 mg, 2 mmol) was refluxed with 1,1′-carbonyldi-imidazole (390 mg, 2.4 mmol) in dry benzene (30 ml) for 24 h. Removal of the solvent followed by column chromatography on neutral alumina with ethyl acetate–hexane (1:9) gave *compound* (**1**) (307 mg, 80%) which was sublimed at 80 °C (1 mmHg), m.p. 112—114 °C (Found: C, 87.9; H, 4.5. $C_{14}H_8O$ requires C, 87.5; H, 4.2%); $\nu_{max.}$($CHCl_3$) 1 521, 1 475, and 1 426 cm^{-1}; $\lambda_{max.}$(MeOH) 249, 257, 325sh, 341, and 359 nm (log ε 3.98, 4.05, 3.44, 4.75, and 4.86); $\lambda_{min.}$ 234, 254, 274, and 350 nm (log ε, 3.40, 3.94, 2.61, and 3.57). See Table for δ_H and δ_C; *m/z* 192 (M^+, 100%), 164 (91), and 163 (60).

Dimethyl 1-*hydroxypyrene*-1,2-*dicarboxylate* (**14**).—Phenalenofuran (**1**) (19.2 mg, 0.1 mmol) was dissolved in dry methylene dichloride (5 ml) and the solution was stirred with DMAD (0.2 ml) for 30 min. Removal of the solvent, followed by chromatography on silica gel with ethyl acetate–hexane (1:1), gave the *diester* (**14**) (22 mg, 65%), m.p. 152—154 °C (from ether) (Found: M^+, 334.0846. $C_{20}H_{14}O_5$ requires *M*, 334.0841); $\nu_{max.}$($CHCl_3$) 3 657, 1 722, 1 671, and 1 622 cm^{-1}; δ_H(250 MHz) 4.08 and 4.10 (each 3 H, s, CO_2Me), 7.77 (1 H, d, *J* 9.2 Hz), 7.87 (1 H, d, *J* 9.2 Hz), 7.98 (1 H, d, *J* 7.4 Hz), 8.03 (1 H, t, *J* 7.4 Hz), 8.10 (1 H, d, *J* 9.1 Hz), 8.14 (1 H, d, *J* 7.4 Hz), 8.55 (1 H, d, *J* 9.1 Hz), and 11.94 (1 H, s, OH exchanges with D_2O); *m/z* 334 (45%), 303 (*M* − OMe, 28) 302 (*M* − MeOH, 100, *ortho* effect), and 287 (19).

Benzo[a]*pyren*-6-*ol* (**15**) *and Benzo*[a]*pyren*-6-*yl Acetate* (**16**).—Butyl-lithium (2.5 M; 0.056 ml, 0.14 mmol) was cooled to −70 °C under nitrogen. A solution of phenalenofuran (**1**) (240 mg, 1.25 mmol) in dry ether (5 ml) was added during 5 min, followed [17] by a solution of *o*-dibromobenzene (0.0168 ml, 0.14 mmol) in dry ether (5 ml) during 10 min to the mixture at between −70 and −55 °C. The mixture was allowed to reach

0 °C during 3 h, water was added, and the aqueous mixture was extracted with ether. The extract was evaporated, column chromatography of the residue on silica gel in ethyl acetate–hexane (1:9) eluted phenalenofuran (**1**) (200 mg recovery) and the *benzopyrenol* (**15**) (33 mg, 60%) successively. Compound (**15**): [Found: M^+, 268.0896. $C_{20}H_{12}O$ requires M, 268.0904. (M − CHO), 239.0870. $C_{19}H_{11}$ requires m/z, 239.0879].

The benzopyrenol (**15**) (33 mg) was stirred in a mixture of pyridine and acetic anhydride at room temperature. Usual work-up followed by column chromatography on silica gel in ethyl acetate–hexane (1:9) and crystallisation from ether gave the acetate (**16**) (27 mg, 70%) as yellow needles, m.p. 207—208 °C (lit.,[14] 209—210 °C); $\nu_{max.}$($CHCl_3$) 1 755, 1 599, 1 580, and 1 460 cm^{-1}; δ_H(200 MHz) 2.70 (3 H, s, OAc), 7.75—8.30 (9 H, m, ArH), 9.01 (1 H, d, J 9.2 Hz), and 9.05 (1 H, d, J 9.8 Hz); m/z 310 (M^+, 13%), 268 (M − CH_2CO, 100), and 239 (32).

9-*Hydroxyphenalen*-1-*one* (**17**).—A solution of compound (**1**) (28.8 mg, 0.15 mmol) in THF (10 ml) with Rose Bengal (5 mg) was exposed to a Sylvania 625 W sun lamp with oxygen bubbling through the solution for 20 min at 20 °C. Removal of the solvent under reduced pressure followed by column chromatography gave the title ketone (**17**) (21 mg, 71%), m.p. 199—200 °C (lit.,[15] 199—200 °C); $\nu_{max.}$($CHCl_3$) 3 600—2 500, 1 632, 1 591, and 1 481 cm^{-1}; δ_H(200 MHz) 7.18 (2 H, d, J 9.3 Hz, 2- and 8-H), 7.60 (1 H, t, J 7.7 Hz, 5-H), 8.02 (2 H, d, J 7.7 Hz, 4- and 6-H), 8.10 (2 H, d, J 9.3 Hz, 3- and 7-H), and 16.5 (1 H, s, OH); m/z 196 (M^+, 100), 168 (38), and 139 (39).

9-*Oxo*-9H-*phenalene*-1-*carbaldehyde* (**18**).—Phenalenofuran (**1**) (20 mg, 0.104 mmol) was dissolved in dry methylene dichloride (5 ml) and treated with MCPBA (24.7 mg, 0.114 mmol). The mixture was stirred at room temperature for 15 min. Usual work-up followed by column chromatography on silica gel in ethyl acetate–hexane (1:4) and recrystallisation from ether gave the *aldehyde* (**18**) (15 mg, 71%) as yellow needles, m.p. 160 °C (decomp.) (Found: M^+, 208.0539. $C_{14}H_8O_2$ requires M, 208.0542): $\nu_{max.}$($CHCl_3$) 1 691 and 1 634 cm^{-1}; δ_H(250 MHz) 6.79 (1 H, d, J 9.7 Hz, 2-H), 7.7 (1 H, q, J 7.9, 8.24 Hz, 5-H), 7.84 (1 H, d, J 9.7 Hz, 3-H), 7.87 (1 H, d, J 7.9 Hz, 4-H), 8.03 (1 H, d, J 8.3 Hz, 7-H), 8.08 (1 H, d, J 8.24 Hz, 6-H), 8.30 (1 H, d, J 8.3 Hz, 8-H), and 10.81 (1 H, s, C*H*O); m/z 208 (M^+, 31), 180 (49), and 152 (100).

2,5,6,7-*Tetrahydrophenaleno*[1,9-bc]*furan* (**20**).—A mixture of compound (**1**) (28.8 mg, 0.15 mmol) and palladium–charcoal (3 mg, 10%) in ethyl acetate (10 ml) was stirred under hydrogen (60 lb in $^{-2}$) for 12 h. The solution was filtered through Celite and the solvent was removed under reduced pressure to leave the *title compound* (**20**) as an oil (24 mg, 80%) (Found: M^+, 196.0895. $C_{14}H_{12}O$ requires M, 196.0888); $\nu_{max.}$($CHCl_3$) 1 587, 1 492, and 1 469 cm^{-1}; δ_H(250 MHz) 2.07 (2 H, m, 6-H_2), 2.98 (4 H, m, 5- and 7-H_2), 5.75 (2 H, s, 2-H_2), 6.58 (1 H, d, J 7.3 Hz, 9-H), 7.04 (1 H, d, J 7.3 Hz, 8-H), and 7.1 and 7.18 (each 1 H, d, J 7.0 Hz, 3- and 4-H); m/z 196 (M^+, 100), 195 (57), and 167 (13).

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