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Approaches to Cyclopropazulenes: Transannular Aldol Reactions of Some Derivatives of 1,10-Dibromobicyclo[8.1.0]undecane-3,8-dione

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This paper describes synthetic approaches to potential precursors to cyclopropazulenes, a novel class of nonbenzenoid cycloproparenes. The acid-catalysed transannular aldol reaction of 1,10-dibromobicyclo[8.1.0]undecane-3,8-dione (**10**) gives a single ketol **13** possessing the cyclopropane moiety fused to the five-membered ring. Similar behaviour is observed in the aldol reaction of **27**, a benzo-fused analogue of **10**. In the transannular aldol reaction of dione **45**, the epoxy bridge forces the reaction in the desired sense to give a ring system (**47** and **48**) in which the cyclopropane ring is fused to the seven-membered ring. The α,β-unsaturated ketone **47** was elaborated into the benzofulvene derivative **51** but conversion of this into the benzocyclopropazulene **58** by overall deoxygenation and debromination could not be achieved. The diones used in this study were generally obtained in good yield by ozonolysis of an appropriate cyclic alkene. In the case of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (**26**), an alkene possessing methylene groups that are both allylic and benzylic, ozone effected overall dehydrogenation instead of cleavage of the alkene.

Introduction

The chemistry of benzocyclopropene (**1**) and its benzo-fused derivatives has been studied extensively from synthetic, spectroscopic and computational viewpoints, largely in order to assess the effects of fusion of the strained three-membered ring on the properties of the aromatic moiety.[1] On the other hand, our knowledge of nonbenzenoid cycloproparenes is much more limited.[2]

For some years we have been interested in devising synthetic routes to cyclopropazulenes, key members of this latter class of theoretically interesting molecules. Cyclopropa fusion to the bonds of the non-alternant blue hydrocarbon azulene (**2**) can in principle generate three aromatic cyclopropazulenes: 1*H*-cycloprop[*a*]azulene (**3**), 1*H*-cycloprop[*e*]-azulene (**4**) and 1*H*-cycloprop[*f*]azulene (**5**). Geometric factors should make **3** more strained and hence presumably more reactive than benzocyclopropene (**1**), but isomers **4** and **5** should be stable and isolable (Figure 1).

Reduced derivatives of 1*H*-cycloprop[*e*]azulene (**4**) are found in nature as members of the aromadendrane sesquiterpenoids. (+)-Aromadendrene (**6**), a constituent of the essential oil extracted from the wood of *Eucalyptus* species was the first reported natural product having this skeleton.[3] Aromadendrenes have also been isolated from red algae, soft corals, marine sponges, liverworts and a variety of plants.[4] Of particular interest is 1(10),2,4-aromadendratriene (**7**) which was isolated from the soft coral *Parerythropodium fulvum fulvum*, and is thought to be responsible for the organism's yellow colour.[5] Interestingly, this molecule requires only two more double bonds to form the fully aromatic system **8**. As the biosynthesis of naturally occurring azulenes is believed to proceed by aromatisation of hydrazulenes,[6] the occurrence of such a highly unsaturated compound raises the possibility that **8** may well be an as yet undiscovered natural product. However, prior to our studies,[2,7] no fully aromatic cyclopropazulenes, either of synthetic or natural origin, appear to have been reported.

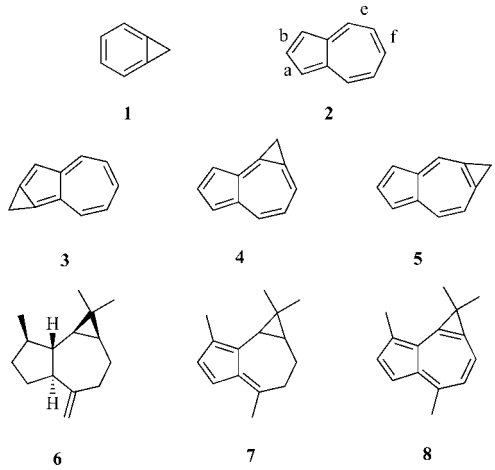

Figure 1. Theoretically possible cyclopropazulenes **3**, **4**, and **5** and examples of naturally occurring reduced cycloprop[*e*]azulenes **6** and **7**.

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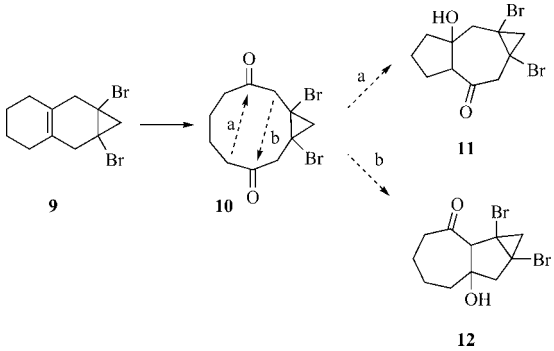
We considered that one possible approach to precursors to fully aromatic cyclopropazulenes could involve as a key step the intramolecular aldol reactions of the dione **10**, available by careful ozonolysis of **9**, the Diels–Alder adduct of 1,2-dimethylidenecyclohexane and 1,2-dibromocyclopropene.[8] We were particularly interested in obtaining the aldol product **11**, because this could in principle be transformed into the relatively unstrained 1*H*-cycloprop[*f*]azulene (**5**). In the event, treatment of **10** with base failed to deliver either **11** or **12** and gave instead products resulting from dehydrobromination, including an unusual cyclopenta[*b*]pyran derivative formed by extensive molecular reorganisation.[8] In the current paper we describe the outcome of acid-catalysed transannular aldol reactions of dione **10** and two of its benzo-fused derivatives **27** and **45** (see later).

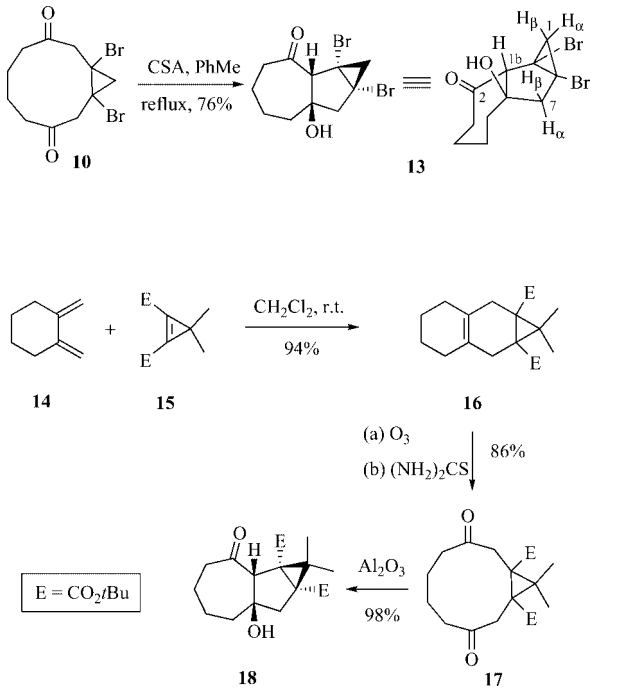
Results and Discussion

Treatment of the dione **10** with a catalytic amount of camphor-10-sulfonic acid in refluxing toluene[9] gave in high yield a single ketol formulated as **13** on the basis of its spectroscopic properties. The ^{1}H NMR spectrum of the product showed a singlet for 1b-H and, in addition to the cyclopropyl protons, only one further isolated methylene group, ruling out structure **11** (Scheme 1) which possesses two such groups. The proximity of the C-7 methylene group to the cyclopropyl methylene group was evident from the presence of a long-range coupling of 2.0 Hz between 1-H$_\alpha$, the proton *syn* to the bromine substituents, and 7-H$_\alpha$. Molecular models show that these protons are in an ideal coplanar W arrangement which is known to favour four-bond coupling in rigid systems.[10] The relative configuration at the ring junction positions was not established unambiguously but is assumed to be as depicted because of the similarities in the ^{1}H NMR spectral features of **13** with those of the benzo-fused analogue **33** (see later), the structure of which was confirmed by an X-ray diffraction study (Scheme 2).



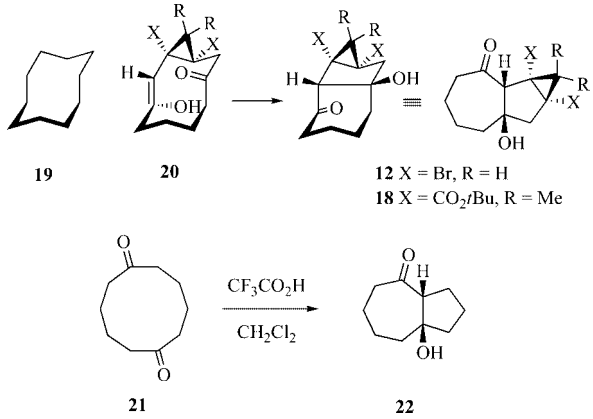
Scheme 1. Possible modes for the transannular aldol reaction of dione **10**.

The formation of a single (undesired) regioisomer **13** in the transannular aldol reaction was unexpected, and we examined the behaviour of the related dione **17**, obtained by ozonolysis of adduct **16**, under aldol reaction conditions. Treatment of **17** with basic alumina in dichloromethane



Scheme 2. Outcomes of the transannular aldol condensation of the diones **10** and **17**.

gave in high yield a single diastereomer, formulated as **18** on the basis of its NMR spectroscopic properties. Thus, both **10** and **17** undergo preferential cyclisation in direction b rather than a (Scheme 1) to give the presumably more strained products **13** and **18** possessing the cyclopropyl moiety fused to the five- rather than the seven-membered ring. This outcome can be rationalised if the (*E*)-enol **20** (or its corresponding enolate), having a conformation closely resembling that of the lowest-energy conformation **19** of cyclodecane,[11,12] is the product-determining intermediate. We note also that the acid-catalysed transannular aldol condensation[13] of cyclodecane-1,6-dione (**21**) gives **22** which has been shown to possess a *cis* configuration at the ring junction (Scheme 3).[14]



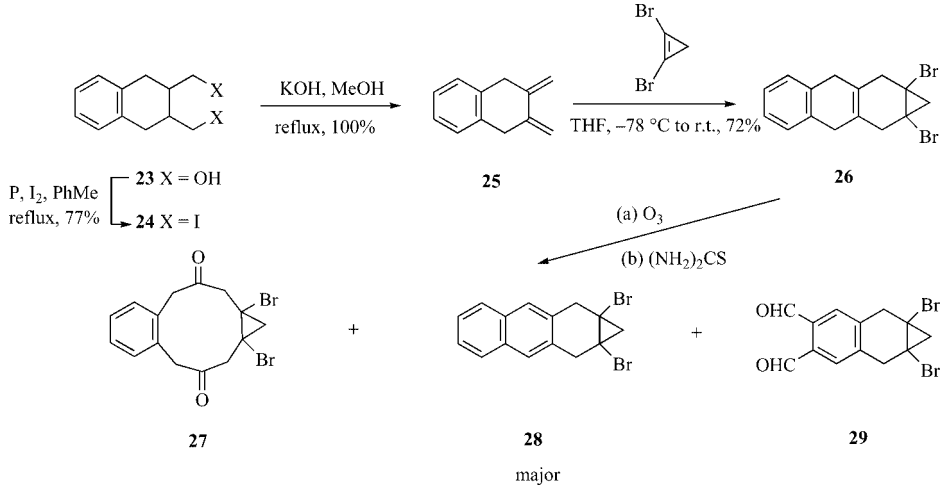
Scheme 3. Rationalisation for the formation of aldol products **12** and **18** and the stereochemical outcome of the transannular aldol reaction of cyclodecane-1,6-dione (**21**).

In an attempt to force the transannular aldol reaction into the desired direction as shown in Scheme 1, we prepared a benzo-fused derivative of **10**. Treatment of the diene **25**, prepared by a modification of published procedures,[15,16] with 1,2-dibromocyclopropene gave the adduct **26** in good yield. By analogy with the behaviour of the alkenes **9** and **16**, we expected **26** to deliver the dione **27** on ozonolysis. Surprisingly, this reaction gave predominantly the aromatised product **28**, accompanied in some runs by small amounts of the dialdehyde **29** and the dione **27**. When the disappearance of **26** was carefully monitored by TLC, the cycloprop[*b*]anthracene **28** could be isolated in high yield as the only product. A related outcome was reported without further comment by Jung who found that the ozonolysis of 1,2,4,5-tetramethylcyclohexa-1,4-diene yielded 1,2,4,5-tetramethylbenzene in addition to the expected cleavage product.[17] The aromatic products **28** and 1,2,4,5-tetramethylbenzene in Jung's reaction presumably arise by a radical pathway in which ozone abstracts a benzylic/allylic hydrogen atom to give a radical pair [R¨OOOH] which then collapses by hydrogen-atom transfer to give the arene and HOOOH, as has been demonstrated for the ozonisation of reactive C–H bonds in other substrates such as cumene.[18]

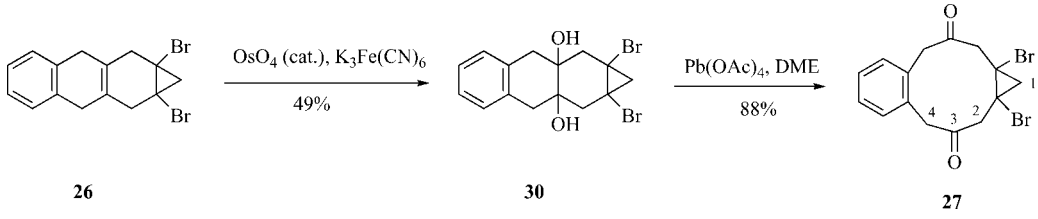
In view of the unusual behaviour of **26** towards ozone (Scheme 4), a two-step oxidation of the double bond was used to obtain the dione **27**. The adduct **26** was first *cis*-dihydroxylated to give the diol **30** using catalytic osmium tetroxide and potassium ferricyanide. The reaction was sluggish, but the rate could be improved by the addition of tetrabutylammonium acetate, which is thought to accelerate the hydrolysis of osmoic esters;[19] nevertheless, the reaction took several days. The use of catalytic ruthenium tetroxide and sodium periodate gave the diol **30** within 1 d, although purification was more difficult. This reaction is unusual as oxidations of alkenes with ruthenium tetroxide normally result in cleavage of the intermediate glycol[20] and should have converted **30** into **27** in the present case. However, glycol formation has also been observed in other systems.[21] The diol **30** was then cleaved using lead tetraacetate to give the highly crystalline dione **27** in good yield (88%).

The ^{1}H NMR spectrum of the dione **27** (Scheme 5) shows three AX patterns for the chemically distinct methylene groups and a multiplet for the aromatic protons. The AX pattern due to 1-H_α and 1-H_β has a coupling constant of 8.6 Hz, a value characteristic of geminal couplings in similarly substituted cyclopropyl rings. The coupling constants for the cyclodecane methylene groups 2-H_α, 2-H_β (14.0 Hz) and 4-H_α, 4-H_β (16.2 Hz) are typical of geminal coupling constants of methylene groups next to a carbonyl group.

The molecular and crystal structures of **27** are shown in Figures 2 and 3. The conformation of the ten-membered core of the dione is reminiscent of the conformation of cyclodeca-3,8-diene-1,6-dione (**31**) as postulated by Grob and Schiess (Figure 4),[22] but unlike that observed for the saturated analogue cyclodecane-1,6-dione (**32**).[23] In the ^{1}H NMR spectrum of **27** there is a small ^4J(H,H) coupling (1.6 Hz) between a hydrogen atom of C-2 and a hydrogen



Scheme 4. Preparation and abnormal ozonolysis of the alkene **26**.



Scheme 5. Preparation of dione **27**.

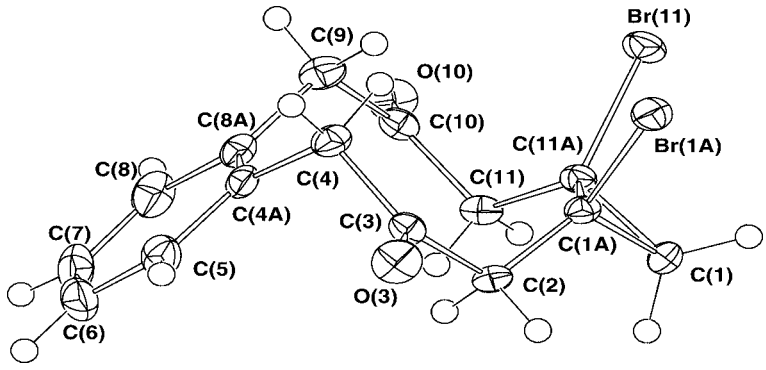


Figure 2. Molecular projection of 1a,11a-dibromo-1a,2,4,9,11,11a-hexahydro-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (**27**). Interplanar dihedral angles [°] (arabic numerals only: carbon atoms; roman numerals: planes): 4,4a,5,6,7,8,8a,9(I)/2,3,4,9,10,11(II) 85.64(8), 1a,2,11,11a(III)/(II) 77.8(1), 1,1a,11a(IV)/(III) 3.9(2), 2–4,O(3)(V)/(II) 7.02(9), 9–11,O(10)(VI)/(II) 1.66(9), (V)/(VI) 8.6(1), 1,1a,Br(1,1a)/(III),(IV) 50.5(1), 56.0(2). Distances [Å]: C–O: 1.214(3), 1.216(3); C–Br: 1.940(2), 1.935(2); C(1a)–C(11a): 1.532(3); C(1)–C(1a,11a): 1.500(3), 1.501(3). Angles [ ]: C(2)–C(1a)–C(11a): 124.3(2); C(1a)–C(11a)–C(11): 124.5(2).

atom of C-4 (and C-11), indicating a possible W relationship between these C–H bonds, as observed in the crystal structure. This suggests that the predominant conformation of **27** in solution may be similar to that observed in the solid state, wherein the tidy packing array is undoubtedly influenced by the parallel stacking of inversion-related aromatic rings (Figure 3).

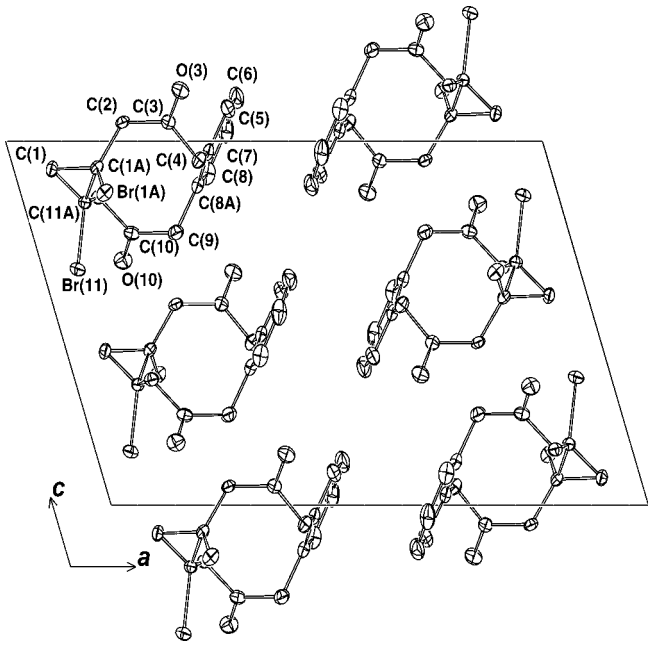
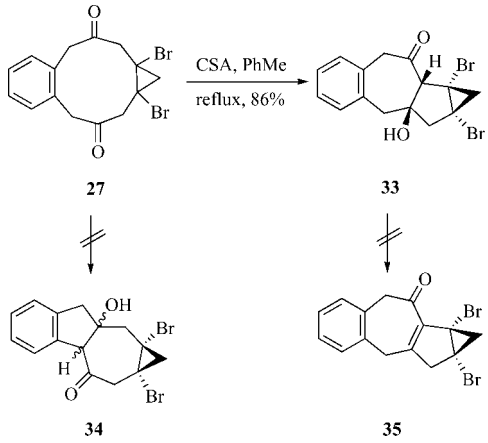


Figure 3. Unit cell contents of **27**, projected along *b*, showing the parallel packing of inversion-related aromatic rings.

31 **32**

Figure 4. Conformations of cyclodeca-3,8-diene-1,6-dione (**31**)[22] and cyclodecane-1,6-dione (**32**).[23]

The aldol reactions of the dione **27** (Scheme 6) were similar to those observed for **10**. Thus, treatment of **27** with camphor-10-sulfonic acid in refluxing toluene gave the aldol **33** in 86% yield.



Scheme 6. Transannular aldol reaction of dione **27**.

The structure of **33** was determined by 2D NMR techniques and a single-crystal X-ray structure study (Figure 5). This showed a *cis* configuration of the newly created fused 5–7 ring junction C-(2a)–C(9a), and that the bromo substituents are *trans* to the hydroxy group. The carbonyl group within the structure essentially is perpendicular to the average plane of the five-membered ring of the molecule, which has quasi-2 symmetry about a line through C(2a) and the midpoint of C(1a) and C(9b). The C–Br distances are appreciably shorter than in **27**. Again in **33** the crystal packing is tidy, dominated by hydrogen bonds between the hydroxy hydrogen atom and the carbonyl oxygen atoms of successive molecules in a string along crystallographic axis *a* [O(2a)···O(9′) 2.795(5) Å].

Longer exposure of **33** to camphor-10-sulfonic acid or higher reaction temperatures did not afford the enone **35** and only led to degradation. Like **10**, the dione **27** decomposed under basic conditions. The desired aldol product **34**

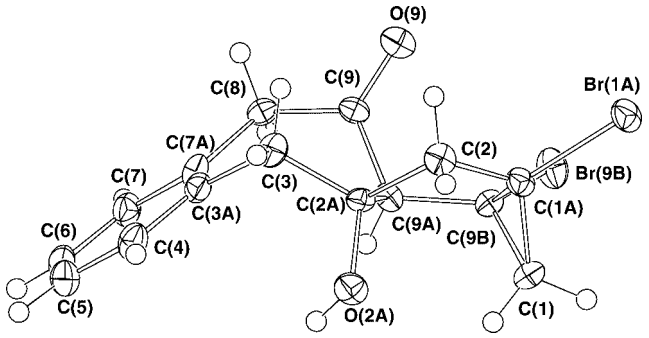
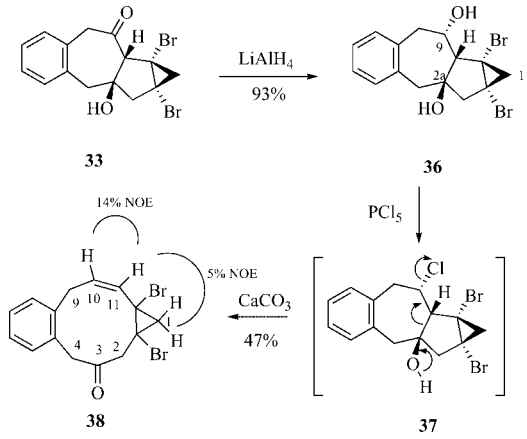


Figure 5. Molecular projection of (1aα,2aβ,9aβ,9bα)-1a,9b-dibromo-2a-hydroxy-1,1a,2,2a,3,8,9,9a,9b-octahydrobenzo[*f*]cycloprop[*a*]azulen-9-one (**33**). Distances [Å]: C–O: 1.428(5), 1.215(5); C–Br: 1.917(4), 1.913(4); C(1a)–C(9b): 1.502(5); C(1)–C(1a,9b): 1.506(6), 1.507(6). Angles [°]: C(2)–C(1a)–C(9b): 108.4(3); C(1a)–C(9b)–C(9a): 108.3(3).



Scheme 7. Fragmentation of chloro alcohol **37**.

was not observed under any of the conditions tested. The aldol **33** also was inert towards potential dehydrating agents such as basic alumina, trifluoroacetic anhydride/DMAP/triethylamine, Burgess' reagent[24] and phosphorus pentachloride/calcium carbonate.[25] Again, in **33** the crystal packing is tidy, dominated by hydrogen bonds between the hydroxy hydrogen atom and the carbonyl oxygen atoms of successive molecules in a string along crystallographic axis *a* [O(2a)···O(9′) 2.795(5) Å].

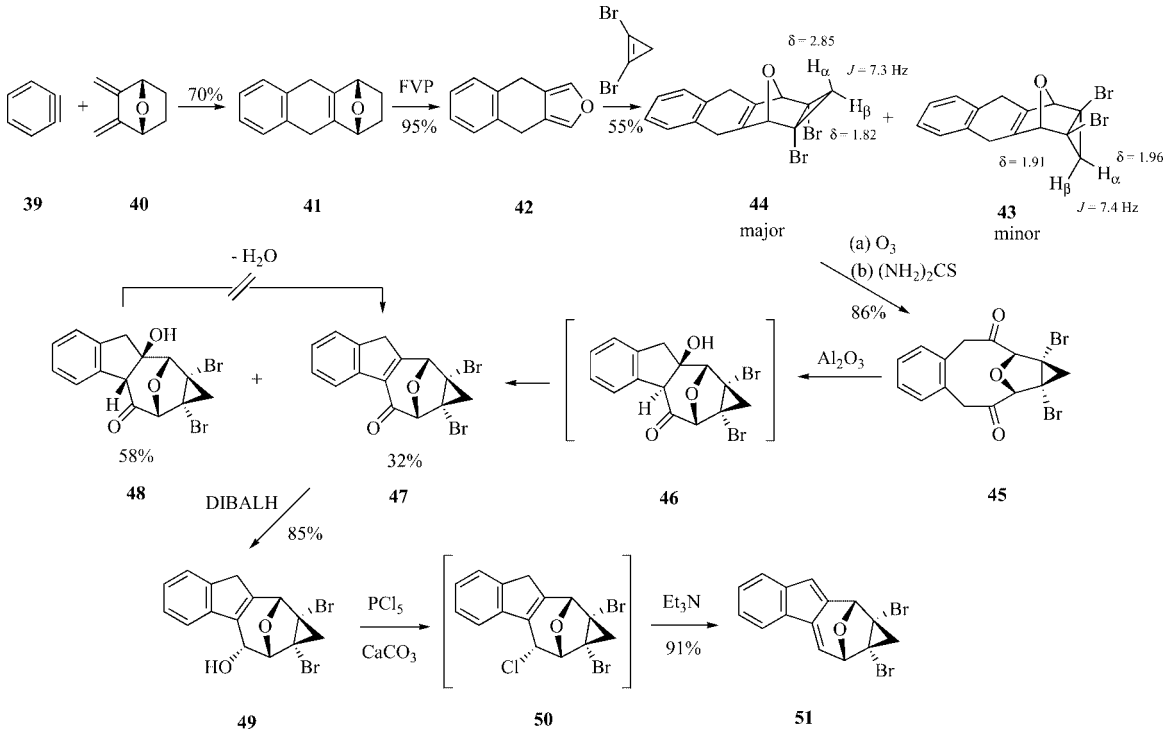
The single-crystal X-ray structure of the aldol **33** (Figure 5) can be used to rationalise some of the experimental observations summarised above. If the overall elimination of water to give **35** is to occur through an E2-type transition state, an antiperiplanar arrangement of 9a-H and the leaving group is required. As the H and OH substituents have a *cis* relationship, this structural requirement is lacking in **33** and may possibly explain why the enone **35** is not formed. The carbonyl group of **33** is almost perpendicular to the five-membered ring, and, due to poor alignment with the bridgehead C–H bond, this may impede the formation of an enol or enolate, which would have aided the elimination of water under acidic or basic conditions, respectively. The molecule also encapsulates the hydroxy group within a sterically congested environment as shown in Figure 5, preventing the generation of a good leaving group such as acetate, mesylate or chloride.

Reduction of **33** with lithium aluminium hydride gave the diol **36** as a single diastereomer. The relative configuration at the new stereogenic centre C-9 is assigned on the basis that the hydride addition is predicted to occur along the Bürgi–Dunitz trajectory (an angle of 109°)[26] to the less hindered face of the carbonyl group. This means that addition must occur from outside the concave ring system to deliver **36**. Alternatively, if the initial reaction of the reducing agent occurs at the C-2a hydroxy group to give an alkoxy-substituted alumino hydride, intramolecular transannular delivery of hydride to the carbonyl group would result in the same stereochemical outcome (Scheme 7).

The diol **36** was unreactive towards methanesulfonyl chloride/triethylamine, again providing evidence of the hindered nature of the hydroxy groups in this molecule. In an attempt to convert the hydroxy groups of **36** into chlorides, the diol was treated with phosphorus pentachloride and calcium carbonate. This gave an unexpected product having an ^{1}H NMR spectrum consisting of three AX patterns due to three isolated CH_2 groups, an allylic spin system and an aromatic multiplet. The molecule was unsymmetrical as the ^{13}C NMR spectrum showed fifteen signals, one of which was at δ = 206 ppm, arising from a ketonic carbonyl group. On this basis the product is formulated as the ketone **38**, and NOE difference experiments showed that the alkene had a *cis* configuration and was adjacent to the cyclopropyl ring.

This outcome can be rationalised as follows. The secondary hydroxy group of **36** reacts to give the chloride **37** with retention of stereochemistry, a known outcome of reactions of phosphorus pentachloride with alcohols.[25] The chloride leaving group of **37** is antiperiplanar to the hydroxy group and in the presence of calcium carbonate can afford the product **38** by a concerted fragmentation reminiscent of the Wharton fragmentation of hydroxy tosylates in the *cis*-decalin system.[27] The stereochemistry of the intermediate **37** demands that the *cis*-alkene be formed, as observed experimentally.

Thus, benzo fusion to the bicyclo[8.1.0]undecane-3,8-dione system, as exemplified in **27**, still resulted in the formation of undesired aldol product **33** (Scheme 6), despite the premise that the benzylic hydrogen atoms of **27** should possess enhanced kinetic acidity, which should favour formation of **34**. Clearly, geometric factors such as those suggested for **20** in Scheme 3 are of greater importance. We therefore envisaged that placement of an epoxy bridge between C-2 and C-9 should prevent enolisation towards these positions. The epoxy bridge within a structure such as **45** (Scheme 8) should also make the system more stable towards base compared to the diones **10** and **27**, as dehydrobromination should be precluded (Bredt's rule). This should permit the dione **45** to be subjected to basic as well as acidic aldol reaction conditions.



Scheme 8. Synthesis of the epoxy-bridged benzocyclopropazulene derivative **51**.

Although previously synthesised by Garratt and Neoh,[28] 4,9-dihydronaphtho[2,3-*c*]furan (**42**) was obtained more conveniently by an alternative method. Addition of benzyne (**39**) to the diene **40**[29] gave the 7-oxabicyclo[2.2.1]-hept-2-ene derivative **41**, which upon flash vacuum pyrolysis (FVP) at 350 °C gave the pure furan **42** in 95% yield. The cycloaddition between the furan **42** and 1,2-dibromocyclopropene gave mainly *exo* adduct **44** in 55% yield, with the *exo*/*endo* ratio being greater than 19:1 on the basis of the ^{1}H NMR spectrum of the crude product (here the term *exo* refers to the isomer where the cyclopropyl methylene group is *cis* to the epoxy bridge). The assignment of the configurations of the adducts **43** and **44** is based on comparisons of their cyclopropyl proton chemical shifts with those of the analogous adducts obtained by the cycloaddition of 1,2-dibromocyclopropene and furan, where the chemical shift difference between 1-H$_\alpha$ and 1-H$_\beta$ is greater in the *exo* adduct ($\Delta\delta$ = 1.06 ppm) than in the *endo* adduct ($\Delta\delta$ = 0.31 ppm), arising from deshielding caused by the proximity of 1-H$_\alpha$ to the bridging oxygen atom in the former adduct.[30] The chemical shift difference ($\Delta\delta$ = 1.03 ppm) between the analogous hydrogen atoms in the major adduct derived from **42** and 1,2-dibromocyclopropene is therefore consistent with the assigned *exo* configuration.

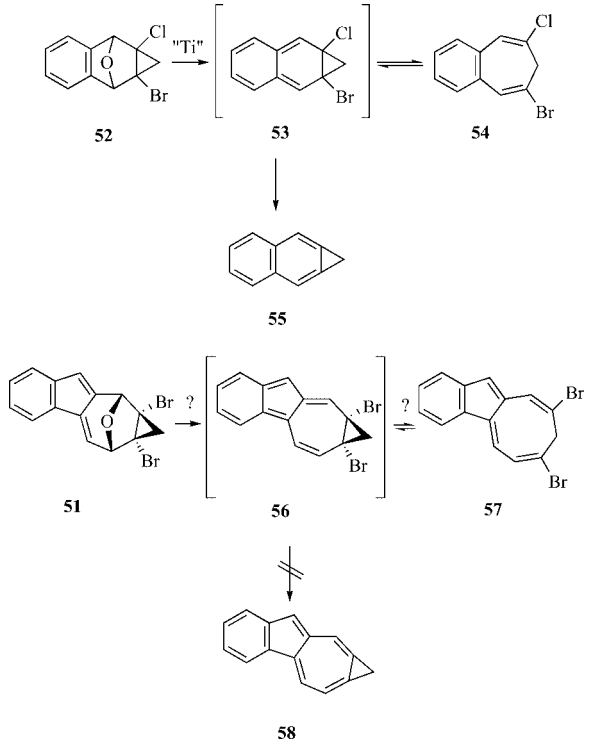
Unlike the previous system (Scheme 4) where the action of ozone resulted in the overall oxidation of the adduct **26** to the naphthalene derivative **28**, the double bond of **44** was cleanly ozonised to give the dione **45** in 86% yield. A signal at δ = 204.0 ppm in the ^{13}C NMR spectrum and an absorption at 1710 cm^{-1} in the IR spectrum confirmed the presence of the keto groups. The alkene π-bond within **44** is electron-rich as a consequence of strain and possible pyramidalisation,[31] and hence is readily attacked by ozone in the normal 1,3-dipolar cycloaddition fashion required for overall double-bond cleavage.

The dione **45** was observed to be stable towards weak bases such as triethylamine. However, treatment of **45** with basic alumina in refluxing 1,2-dichloroethane for 90 min gave the enone **47** (58%) and the aldol **48** (32%), which were easily separated by radial chromatography. Longer reaction times led to degradation. The isolated aldol product **48** was inert to further treatment with alumina and was *not* converted into the enone **47**, raising the possibility that two aldol products **46** and **48** are formed during the reaction. Although the stereochemistry of the isolated aldol at the newly formed ring junction has not been established rigorously, we suggest that it is *cis*, and that only **46**, having a *trans* arrangement of H and OH, dehydrates to afford the enone **47**.

The enone **47** was reduced with DIBALH to give an alcohol as a single diastereomer, depicted as **49** on the basis that hydride transfer occurs to the less hindered face of the carbonyl group. The hindered nature of the hydroxy group of **49** was apparent as mesylation using methanesulfonyl chloride and triethylamine was unsuccessful. Treatment of **49** with phosphorus pentachloride and calcium carbonate gave the chloride **50**, which was not isolated but dehydrochlorinated with triethylamine to give the benzofulvene **51** as yellow crystals in good yield (91%).

Generation of compound **58** (Scheme 9), the benzannelated derivative of 1*H*-cycloprop[*f*]azulene, from the benzofulvene **51** requires overall debromination and deoxygenation. Müller and Schaller showed that compounds related

to **51**, such as the adduct **52** derived from isobenzofuran and 1-bromo-2-chlorocyclopropene, could be converted into cycloproparenes using a low-valent titanium reagent, generated by adding methyllithium or lithium aluminium hydride to titanium trichloride.[32] Although the mechanism for aromatisation is not fully understood, the authors proposed the sequence shown in Scheme 9. The low-valent titanium reagent deoxygenates **52** to form the reactive *o*-xylylene **53**, which is in equilibrium with the benzocycloheptatriene **54**. Dehalogenation of **53** by the reducing agent then gives the cycloproparene **55**.[32]



Scheme 9. Failure of **51** to deliver the target aromatic benzocyclopropazulene **58**.

When the benzofulvene **51** was subjected to these reaction conditions, no recognisable products were identified. If the deoxygenation of **51** had occurred, the highly reactive benzo[*c*]fulvene species **56** would have been formed; this could rapidly isomerise to **57** and react further to give decomposition products. As the blue colour characteristic of azulenes was not observed during the reaction, formation and subsequent degradation of the cyclopropazulene **58** cannot be implied.

In an attempted cleavage of the epoxy bridge, the benzofulvene **51** was treated in separate experiments with boron trichloride and aluminium trichloride in dichloromethane at low temperatures. In both cases only complex mixtures were obtained, and the ^{1}H NMR spectra of the crude products suggested that the reaction mixtures contained ring-opened products, as there was an absence of high-field proton resonances.

Although further experimentation may well lead to the discovery of conditions for the conversion of **51** into **58**, this approach was discontinued as a viable approach to cyclopropazulenes through the photolysis of azulenopyrazoles was developed at this stage.[7,33]

Conclusion

Transannular aldol reaction of the symmetrical dione 1,10-dibromobicyclo[8.1.0]undecane-3,8-dione (**10**) and its derivatives **17** and **27** surprisingly give products in which the cyclopropane moiety is fused to the five-membered ring. In the epoxy-bridged dione **45**, transannular reaction is forced to occur in the other regiochemical sense, and the resulting enone **47** was converted into the benzofulvene **51**, a potential precursor of the benzo-fused cyclopropazulene **58**.

Experimental Section

General: Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were performed by M. H. W. Laboratories (Phoenix, Arizona). NMR spectra were measured at 200 MHz (^{1}H) with a Varian Gemini, 300 MHz (^{1}H), 75.5 MHz (^{13}C) with a Bruker AM 300 spectrometer, 500 MHz (^{1}H), 126 MHz (^{13}C) with a Bruker ARX 500 spectrometer and 600 MHz (^{1}H), 151 MHz (^{13}C) with a Bruker AV 600 spectrometer. ^{13}C assignments were made with the aid of DEPT experiments. Mass spectra were measured with a VG Autospec mass spectrometer. Only molecular ion peaks, and peaks registering above 10% relative abundance are reported. Infrared spectra were recorded using KBr discs with a Bio-Rad FTS45 FTIR spectrophotometer with absorption recorded ($\tilde{\nu}_{max}$ in cm^{-1}). Electronic spectra were recorded with a Milton Roy Array 3000 Spectrophotometer and are reported in wavelength (λ in nm). Analytical thin-layer chromatography (TLC) was carried out using Merck (Art. 554) silica gel 60 F_{254} pre-coated on aluminium sheets. The spots were first visualised using UV light (254 nm) and then spraying with 6% ceric sulfate in 2 N H_2SO_4 solution and heating for 30 s. Preparative radial chromatography was carried out using a Chromatotron Model 7924T (Harrison Research, Palo Alto, California) with Kieselgel 60 PF_{254} gipshaltig (Merk Art. 7749). Silica gel filtrations were performed using Fluka Kieselgel 60 as adsorbent packed dry under water aspirator vacuum on a sintered glass funnel. In both chromatographic techniques, increasing proportions of ethyl acetate in light petroleum were used as eluting solvents, unless stated otherwise. Fractions were monitored by TLC, and appropriate fractions were combined. Anhydrous tetrahydrofuran and diethyl ether were obtained by distillation from benzophenone potassium ketyl. All reactions requiring anhydrous reagents were carried out under nitrogen or argon. Light petroleum refers to the fraction of b.p. 65–70 °C. All organic extracts were dried with anhydrous magnesium sulfate. Tetra-*n*-butylammonium fluoride was dried by the following method: Tetra-*n*-butylammonium fluoride trihydrate was dissolved in anhydrous benzene. The benzene and water were co-distilled off under reduced pressure and the process repeated until the mass remained constant. The residual solid was then dried at room temperature under high vacuum.

(1aα,1bβ,6aβ,7aα)-1a,7a-Dibromo-6a-hydroxy-1,1a,1b,3,4,5,6,6a,7,7a-decahydro-1*H*-cycloprop[*a*]azulen-2-one (13): A solution of 1,10-dibromobicyclo[8.1.0]undecane-3,8-dione[8] (50 mg, 0.15 mmol) and camphor-10-sulfonic acid (2 mg) in toluene

(15 mL) was heated under reflux for 2 h. The reaction mixture was adsorbed onto silica and subjected to rapid silica filtration. Elution with ethyl acetate/hexane (1:9) gave the title compound as colourless prisms (38 mg, 76%), m.p. 128–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 1 H, 1b-H), 2.66 (dd, J = 14.0, 2.0 Hz, 1 H, 7-H$_\alpha$), 2.53 (m, 2 H, CH_2), 2.43 (d, J = 7.0 Hz, 1 H, 1-H$_\beta$), 2.34 (d, J = 14.0 Hz, 1 H, 7-H$_\beta$), 1.97–1.59 (m, 9 H, 4 × CH_2, OH), 1.54 (dd, J = 7.0, 2.0 Hz, 1 H, 1-H$_\alpha$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 207.6 (CO), 80.4 (C), 69.3 (CH), 50.4 (CH_2), 42.9 (CH_2), 40.7 (CH_2), 40.4 (C), 40.1 (C), 30.8 (CH_2), 22.7 (CH_2), 22.4 (CH_2) ppm. IR (KBr disk): $\tilde{\nu}$ = 3400, 1700 cm^{-1}. $C_{11}H_{14}Br_2O_2$ (338.04): calcd. C 39.08, H 4.18; found C 39.33, H 4.26.

Di-*tert*-butyl 1a,2,3,4,5,6,7,7a-Octahydro-1,1-dimethyl-1*H*-cyclopropa[*b*]naphthalene-1a,7a-dicarboxylate (16): A solution of 1,2-bis(methylene)cyclohexane[35] (760 mg, 7.0 mmol) and di-*tert*-butyl 3,3-dimethylcyclopropene-1,2-dicarboxylate[36] (970 mg, 3.6 mmol) in dichloromethane (5 mL) was flushed with argon and kept at room temperature overnight. The solvent was evaporated and the residue subjected to rapid silica filtration. Elution with ethyl acetate/hexane (1:9) gave the title adduct as a clear oil (1.27 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.50 (br. d, J = 16.5 Hz, 2 H, 2-H and 7-H), 1.98 (br. d, J = 16.5 Hz, 2 H, 2-H and 7-H), 1.93–1.67 (m, 4 H, 2CH_2), 1.65–1.48 (m, 4 H, 2 CH_2), 1.42 (s, 18 H, 2 CO_2tBu), 1.28 (s, 3 H, CH_3), 0.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.6 (CO), 124.9 (C), 80.0 (C), 34.8 (C), 30.4 (CH_2), 29.7 (CH_2), 28.6 (C), 28.1 (CH_3), 23.3 (CH_2), 19.9 (CH_3), 16.4 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 1719 cm^{-1}. MS (EI): m/z (%) = 264 (12) [M – 2 C_4H_8], 247 (24), 246 (13), 221 (24), 220 (18), 219 (100), 218 (17), 203 (32), 177 (19), 173 (19), 159 (12), 131 (12), 91 (20). An analytical sample was obtained by distillation (kugelrohr, 150 °C, 0.01 Torr). $C_{23}H_{36}O_4$ (376.54): calcd. C 73.37, H 9.64; found C 73.16, H 9.64.

Di-*tert*-butyl 11,11-Dimethyl-3,8-dioxobicyclo[8.1.0]undecane-1,10-dicarboxylate (17): Ozonised oxygen was bubbled through a stirred cooled (–78 °C) solution of the adduct **16** (100 mg, 0.27 mmol) in a 1:5 mixture of anhydrous methanol/dichloromethane (15 mL) containing sodium hydrogen carbonate (30 mg) until the mixture turned blue. The excess of ozone was displaced by bubbling nitrogen through the cold mixture. The mixture was then added dropwise to a mixture of thiourea (25 mg, 0.33 mmol) and sodium hydrogen carbonate (15 mg) in dichloromethane (5 mL) at ice-bath temperature and stirring was continued for 1 h. The mixture was washed with water (2 × 20 mL) and the combined aqueous layers were extracted with dichloromethane (2 × 10 mL). The combined organic layers were dried and concentrated to a small volume. Addition of hexane (ca. 1 mL) deposited the title compound as colourless crystals (93 mg, 86%); m.p. 131–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (d, 2 × A part of AB, J = 17.1 Hz, 2 H, 2-H and 9-H), 2.70–2.57 (m, 2 H), 2.49 (d, 2 × B part of AB, J = 17.1 Hz, 2 H, 2-H and 9-H), 2.41–2.38 (m, 4 H), 1.40 (s, 18 H, 2 × CO_2tBu), 1.30 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 211.3 (CO), 169.0 (CO), 81.3 (C), 42.5 (CH_2), 41.2 (CH_2), 38.1 (C), 27.9 (C), 28.8 (CH_3), 24.8 (CH_2), 20.8 (CH_3), 18.3 (CH_3) ppm. IR (Nujol): $\tilde{\nu}$ = 1722, 1692 cm^{-1}. MS (EI): m/z (%) = 296 (25) [M – 2 C_4H_8], 279 (31), 261 (10), 252 (17), 251 (100), 238 (12), 234 (17), 233 (31), 223 (21), 215 (16). $C_{23}H_{36}O_6$ (408.54): calcd. C 67.62, H 8.88; found C 67.60, H 8.73.

Di-*tert*-butyl 6a-Hydroxy-1,1-dimethyl-2-oxo-1,1a,1b,3,4,5,6,6a,7,7a-decahydro-1*H*-cycloprop[*a*]azulene-1a,7a-dicarboxylate (18): A mixture of the dione **17** (98 mg, 0.24 mmol) and alumina (Woelm basic activity III, 1.0 g) in anhydrous dichloromethane (10 mL) was stirred at room temperature under argon for 16 h. The alumina was removed by filtration, washed with several portions of dichloromethane and the combined filtrates were concentrated under reduced pressure to give the title compound as colourless prisms (96 mg, 98%); m.p. 136–139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.01 (s, 1 H, 1b-H), 2.64 (ddd, J = 14.1, 11.9, 2.7 Hz, 1 H), 2.60 (d, J = 14.6 Hz, 1 H, 7-H$_\alpha$), 2.54 (ddd, J = 11.4, 8.5, 2.9 Hz, 1 H), 2.37–2.28 (m, 1 H), 2.09 (d, J = 14.6 Hz, 1 H, 7-H$_\beta$), 1.93–1.58 (m, 6 H), 1.48 (s, 9 H, CO_2tBu), 1.42 (s, 12 H, CO_2tBu, CH_3), 1.40 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.8 (CO), 169.2 (CO), 168.4 (CO), 85.8 (C), 81.5 (C), 80.9 (C), 68.1 (CH), 49.3 (C), 45.9 (CH_2), 44.8 (C), 42.2 (CH_2), 41.1 (CH_2), 34.1 (C), 28.1, (CH_3), 28.0 (CH_3), 25.4 (CH_2), 23.4 (CH_2), 20.1 (CH_3), 18.2 (CH_3) ppm. IR (Nujol): $\tilde{\nu}$ = 3440, 1718, 1700 cm^{-1}. MS (EI): m/z (%) = 296 (43) [M – 2 × C_4H_8], 279 (54), 278 (13), 261 (12), 260 (20), 252 (17), 251 (100), 250 (20), 239 (11), 238 (76), 234 (46), 233 (65), 232 (14), 220 (58), 216 (17), 215 (31), 192 (50), 145 (10), 199 (12), 91 (12). $C_{23}H_{36}O_6$ (408.54): calcd. C 67.62, H 8.88; found C 67.45, H 8.79.

2,3-Bis(methylene)-1,2,3,4-tetrahydronaphthalene (25): Iodine (7.77 g, 61.9 mmol) was added to a mixture of red phosphorus (0.7 g, 23 mmol) in toluene (20 mL) and the mixture heated under reflux for 30 min. A solution of 1,2,3,4-tetrahydronaphthalene-2,3-dimethanol[34] (5.37 g, 28 mmol) in toluene (50 mL) was added to the phosphorus/iodine solution which was then heated under reflux for 3 h, during which the dark solution cleared. The solution was cooled, washed with saturated sodium hydrogen carbonate solution and brine, dried and concentrated under reduced pressure to give 2,3-bis(iodomethyl)-1,2,3,4-tetrahydronaphthalene as a colourless oil (8.22 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09–7.20, (m, 4 H, ArH), 3.29, (dd, J = 9.7, 4.8 Hz, 2 H), 3.07 (dd, J = 9.7, 9.6 Hz, 2 H); 3.00, (dd, J = 16.7, 5.4 Hz, 2 H), 2.80 (dd, J = 16.7, 7.2 Hz, 2 H), 2.43–2.56 (m, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 133.6 (C), 129.3 (CH), 126.3 (CH), 40.8 (CH), 33.5 (CH_2), 7.3 (CH_2) ppm. 2,3-Bis(iodomethyl)-1,2,3,4-tetrahydronaphthalene (4.12 g, 10 mmol) was added to a solution of potassium hydroxide (1.68 g, 30 mmol) in anhydrous methanol (20 mL) and the mixture was vigorously stirred under reflux under argon for 3 h. The mixture was cooled, poured into water and extracted with light petroleum (3 × 50 mL). The extract was washed with brine, dried, and concentrated to give the crude diene as a clear oil (1.72 g, 100%), The ^{1}H NMR spectrum is identical to that described.[34] The diene was used immediately in the next step.

1a,9a-Dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (26): Tetra-*n*-butylammonium fluoride (2.61 g, 10 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise to a stirred solution of 2,3-bis(methylene)-1,4-dihydronaphthalene (1.22 g, 7.82 mmol) and 1,1,2-tribromo-2-(trimethylsilyl)cyclopropane (2.30 g, 6.56 mmol) in anhydrous tetrahydrofuran (10 mL) at –78 °C. After 1 h, the mixture was allowed to stand at –20 °C for 15 h and then at room temperature for 1 h. The solution was concentrated under reduced pressure and the residue was taken up in diethyl ether/water and extracted with diethyl ether (3 × 10 mL). The combined ethereal extracts were washed with water (2 × 20 mL), dried and concentrated under reduced pressure to give a yellow solid which was subjected to silica filtration. Elution with light petroleum gave the title adduct as a colourless solid (1.67 g, 72%) which recrystallised from light petroleum as colourless prisms, m.p. 149–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.26 (m, 4 H, ArH), 3.11–3.31 (m, 6 H), 2.90 (d, J = 14.7 Hz, 2 H), 1.65, (d, J = 7.5 Hz, 1 H), 1.45 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 133.3 (C), 127.9 (CH), 126.1 (CH), 124.4 (C), 41.1 (CH_2), 38.4 (C), 34.3 (CH_2), 26.1 (CH_2) ppm. $C_{15}H_{14}Br_2$ (354.09): calcd. C 50.88, H 3.99; found C 50.68, H 8.94.

Ozonolysis of 1a,9a-Dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (26)

(1) Formation of 1a,9a-Dibromo-1a,2,9,9a-tetrahydro-1*H*-cycloprop[*b*]anthracene (28): Ozonised oxygen was bubbled through a cooled (–78 °C) solution of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (51 mg, 0.15 mmol) and sodium hydrogen carbonate (1 mg) in a mixture of dry methanol (5 mL) and dichloromethane (25 mL), and the progress of the reaction was carefully monitored by TLC. When all the starting material was consumed, the ozone was displaced by bubbling nitrogen through the cold reaction mixture. The resulting solution was added dropwise to a cooled (0 °C) suspension of thiourea (15 mg) and sodium hydrogen carbonate (30 mg) in dichloromethane (10 mL) and then stirred at 0 °C for 1 h. The reaction mixture was washed with water (2 × 20 mL) and the combined aqueous phases were extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with brine (1 × 20 mL) and concentrated under reduced pressure to afford 1a,9a-dibromo-1a,2,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene as a crystalline solid (50 mg, 100%) essentially pure by ^{1}H NMR analysis. An analytical sample was obtained by recrystallisation from light petroleum as colourless plates, m.p. 129–130 °C. MS (EI): *m*/*z* (%) = 352 (17) [M$^+$], 306 (25), 279 (11), 274 (17), 259 (15), 229 (43), 193 (17), 192 (100), 191 (80), 190 (12), 189 (26), 178 (11), 167 (24), 165 (24), 149 (60), 139 (34), 123 (17), 113 (11), 96 (16), 95 (18), 91 (12), 86 (41), 84 (63), 83 (19). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.73 (m, part of AA′BB′ system, 2 H), 7.53 (s, 2 H), 7.47–7.42, (m, part of AA′BB′ system, 2 H), 3.90, (d, *J* = 15.5 Hz, 2 H), 3.74 (d, *J* = 15.5 Hz, 2 H), 1.40 (d, *J* = 8.3 Hz, 1 H), 1.35 (d, *J* = 8.3 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 132.3 (C), 132.1 (C), 127.0 (CH), 126.6 (CH), 125.7 (CH), 40.9 (CH_2), 37.8 (C), 23.4 (CH_2) ppm. $C_{15}H_{12}Br_2$ (352.07): calcd. C 51.17, H 3.44; found C 50.91, H 3.30. In a control experiment, oxygen was bubbled through a solution of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (20 mg) in anhydrous methanol (1 mL) and dichloromethane (5 mL) at –78 °C for 15 min (longer than the average ozonolysis experiment). No reaction was observed by ^{1}H NMR spectroscopy.

(2) Typical Outcome in the Ozonolysis of 1a,9a-Dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (26): Ozonized oxygen was bubbled through a cooled (–78 °C) solution of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (100 mg, 0.28 mmol) and sodium hydrogen carbonate (2 mg) in a mixture of dry methanol/dichloromethane (1:5, 30 mL), until the reaction was complete as indicated by the blue colour of excess ozone. The ozone was displaced by bubbling nitrogen through the cold reaction mixture. The cold solution was then added dropwise to a cooled (0 °C) mixture of thiourea (30 mg, 0.35 mmol) and sodium hydrogen carbonate (2 mg) in dichloromethane (10 mL) and then stirred at 0 °C for 1 h. The reaction mixture was washed with water (2 × 20 mL) and the combined aqueous phases were extracted with dichloromethane (2 × 10 mL). The combined extracts were washed with brine (1 × 20 mL) and concentrated under reduced pressure to afford an oil which was subjected to radial chromatography. Elution with light petroleum and 10% ethyl acetate/light petroleum gave 1a,9a-dibromo-1a,2,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (**28**) (40 mg, 40%), 1a,7a-dibromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene-4,5-dialdehyde (**29**) (10 mg, 11%) and 1a,11a-dibromo-1a,2,4,9,11,11a-hexahydro-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (**27**) (7 mg, 8%). The ^{1}H NMR spectrum of **27** was identical to that described later.

1a,7a-Dibromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene-4,5-dialdehyde (29): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (s, 2 H, CHO), 7.67 (s, 2 H, ArH), 3.83 (d, *J* = 16.2 Hz, 2 H), 3.76 (d, *J* = 16.2 Hz, 2 H), 1.43 (d, *J* = 8.4 Hz, 1 H, cyclopropyl), 1.38 (d, *J* = 8.4 Hz, 1 H, cyclopropyl) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 191.5 (CH), 140.3 (C), 135.3 (C), 131.2 (CH), 40.7 (CH_2), 36.5 (C), 23.9 (CH_2) ppm.

(1aα,2aα,8aα,9aα)-1a,9a-Dibromo-1a,2,2a,3,8,8a,9,9a-octahydro-1*H*-cycloprop[*b*]anthracene-2a,8a-diol (30): A solution of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-1*H*-cycloprop[*b*]anthracene (**26**) (893 mg, 2.52 mmol) and tetra-*n*-butylammonium acetate (1.60 g, 5.30 mmol) in tetrahydrofuran (20 mL) and *tert*-butyl alcohol (20 mL) was stirred at room temperature, and a solution of potassium ferricyanide (2.49 g, 7.56 mmol) and potassium carbonate (1.05 g, 7.56 mmol) in water (30 mL) was added. Osmium tetroxide (ca. 10 mg) was added to the mixture which then was stirred for 3 d. Sodium sulfite was added to the brown solution and the mixture was stirred for 1 h. The brown solution was poured into water and extracted with diethyl ether (2 × 100 mL). The ethereal layer was washed with water (3 × 100 mL), dried, concentrated and subjected to silica gel filtration. Elution with light petroleum and 10% ethyl acetate/light petroleum gave starting material (293 mg, 33%) followed by the title diol (476 mg, 49%). An analytical sample was obtained by recrystallisation from dichloromethane/light petroleum to give colourless prisms, m.p. 197–202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09–7.21 (m, 4 H), 3.09 (d, *J* = 17.0 Hz, 2 H), 2.96 (d, *J* = 17.0 Hz, 2 H) 2.78 (d, *J* = 14.9 Hz, 2 H), 2.62 (dd, *J* = 14.9, 1.0 Hz, 2 H), 2.10 (d, *J* = 7.7 Hz, 1 H), 1.72 (br. s, 2 H, OH) 1.51 (ddd, *J* = 7.7, 1.0, 1.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 132.6 (C), 129.3 (CH), 126.7 (CH), 72.8 (C), 45.3 (CH_2), 40.4 (CH_2), 37.0 (C), 33.2 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 3448 (OH) cm^{-1}. $C_{15}H_{16}Br_2O_2$ (388.10): calcd. C 46.42, H 4.16; found C 46.43, H 4.26.

1a,11a-Dibromo-1a,2,4,9,11,11a-hexahydro-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (27): Lead(IV) acetate (101 mg, 0.23 mmol) was added portionwise over 20 min to a stirred solution of the diol **30** (58.9 mg, 0.15 mmol) and trichloroacetic acid (75 mg, 0.46 mmol) in anhydrous 1,2-dimethoxyethane (10 mL) at 0 °C under argon. The mixture was stirred until the reaction was complete according to TLC analysis (30 min). Water was added and the mixture was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (1 × 50 mL), dried and concentrated under reduced pressure to give the dione as a crystalline solid (51.9 mg, 88%). An analytical sample was obtained by recrystallisation from dichloromethane/light petroleum as colourless prisms, m.p. 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.21 (m, 4 H, ArH), 4.50, (d, *J* = 13.9 Hz, 2 H), 3.60, (dd, *J* = 13.9, 1.6 Hz, 2 H), 3.28, (dd, *J* = 16.3, 1.6 Hz, 2 H), 2.73, (d, *J* = 16.3 Hz, 2 H), 1.75 (d, *J* = 8.6 Hz, 1 H), 1.26 (d, *J* = 8.6 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 203.7 (CO), 131.9 (C), 130.8 (CH), 128.3 (CH), 49.4 (CH_2), 45.4 (CH_2), 38.6 (C), 31.2 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 1701 (CO) cm^{-1}. $C_{15}H_{14}Br_2O_2$ (386.09): calcd. C 46.67, H 3.66; found C 46.57, H 3.80.

(1aα,2aβ,9aβ,9bα)-1a,9b-Dibromo-2a-hydroxy-1,1a,2,2a,3,8,9,9a,9b-octahydrobenzo[*f*]cycloprop[*a*]azulen-9-one (33): A solution of dione **27** (305 mg, 0.79 mmol) and camphor-10-sulfonic acid (2 mg) in toluene (50 mL) under argon was heated under reflux for 24 h. The solution was concentrated and subjected to radial chromatography. Elution with 50% dichloromethane/light petroleum and dichloromethane gave the title aldol (264 mg, 86%). Recrystallisation from dichloromethane/light petroleum gave colourless prisms, m.p. 142–143 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.09 (m, 4 H, ArH), 4.02 (d, *J* = 19.0 Hz, 1 H, 8-H), 3.71 (d, *J* =

19.0 Hz, 1 H, 8-H), 3.41 (d, *J* = 0.9 Hz, 1 H, 9a-H), 3.03 (d, *J* = 14.4 Hz, 1 H, 3-H), 2.66 (d, *J* = 14.4 Hz, 1-H, 3-H), 2.56 (dd, *J* = 13.5, 2.0 Hz, 1 H, 2-H), 2.53 (d, *J* = 7.2 Hz, 1 H, 1-H), 2.43 (d, *J* = 13.5 Hz, 1 H, 2-H), 1.45 (dd, *J* = 7.2, 2.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 204.2 (C, C-9), 134.6 (C, C-3a), 133.3 (C, C-7a), 131.1 (CH, C-7), 130.6 (CH, C-4), 128.5 (CH, C-5 or C-6), 127.9 (CH, C-5 or C-6), 82.6 (C, C-2a), 66.5 (CH, C-9a), 50.4 (CH_2, C-8), 47.7 (CH_2, C-2), 44.9 (CH_2, C-3), 40.2 (C, C-9b), 38.7 (C, C-1a), 30.5 (CH_2, C-1) ppm. IR: $\tilde{\nu}_{max}$ = 3493 (OH), 1705 (CO) cm^{-1}. $C_{15}H_{14}Br_2O_2$ (386.09): calcd. C 46.67, H 3.66; found C 46.80, H 3.90.

(1aα,2aβ,9α,9aβ,9bα)-1a,9b-Dibromo-1a,2,2a,3,8,9,9a,9b-octahydro-1*H*-benzo[*f*]cycloprop[*a*]azulene-2a,9-diol (36): The aldol **33** (170 mg, 0.44 mmol) in diethyl ether (30 mL) was added dropwise to a slurry of lithium aluminium hydride (25 mg, 0.66 mmol), in anhydrous diethyl ether (10 mL) at –10 °C under argon and stirred for 30 min. Saturated sodium sulfate solution (1 mL) was added and the resulting suspension was stirred for 10 min. The mixture was filtered, dried and concentrated under reduced pressure to give the title diol (159 mg, 93%). An analytical sample was obtained by recrystallisation from dichloromethane/light petroleum to give colourless plates, m.p. 135–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.11 (m, 4 H, ArH), 4.81 (ddd, *J* = 9.6, 2.9, 2.9 Hz, 1 H), 3.47 (d, *J* = 13.4 Hz, 1 H), 3.42 (dd, *J* = 9.6, 16.2 Hz, 1 H), 3.18, (dd, *J* = 16.2, 2.9 Hz,1 H), 2.69 (m, 2 H), 2.58 (d, *J* = 7.2 Hz, 1 H), 2.47 (d, *J* = 13.0 Hz, 1 H), 1.78 (d, *J* = 2.0 Hz, 1 H), 1.53 (dd, *J* = 7.2, 2.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.3 (C), 136.2 (C), 129.7 (CH), 129.3 (CH), 127.5 (CH), 127.0 (CH), 78.7 (C), 67.4 (CH), 57.8 (CH), 50.2 (CH_2), 46.1 (C), 43.7 (CH_2), 41.9 (C), 40.5 (CH_2), 31.2 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 3407 (OH), 3261 (OH) cm^{-1}. $C_{15}H_{16}Br_2O_2$ (388.10): calcd. C 46.42, H 4.16; found C 46.55, H 4.30.

Treatment of (1aα,2aβ,9α,9aβ,9bα)-1a,9b-Dibromo-1a,2,2a,3,8,9,9a,9b-octahydro-1*H*-benzo[*f*]cycloprop[*a*]azulene-2a,9-diol (36) with Phosphorus Pentachloride: The diol **36** (38.4 mg, 0.099 mmol) in anhydrous chloroform (1 mL) was added to a stirred suspension of phosphorus pentachloride (53 mg, 0.25 mmol) and anhydrous calcium carbonate (20.0 mg, 0.198 mmol) in anhydrous chloroform (8 mL) at 0 °C under argon. After 45 min, the mixture was washed with water and brine, dried and concentrated to give an oil which was subjected to radial chromatography. Elution with 5% ethyl acetate/light petroleum gave (*Z*)-1a,11a-dibromo-1,1a,2,4,9,11a-hexahydrobenzo[*a*]cyclopropa[*f*]cyclodecen-3-one (**38**) as a colourless crystalline solid (17.2 mg, 47%), which was recrystallised from dichloromethane/light petroleum, m.p. 165–167 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 4 H, ArH), 5.72 (ddd, *J* = 12.5, 10.5, 4.8 Hz, 1 H), 5.33 (dd, *J* = 10.5, 1.7 Hz, 1 H), 4.79 (d, *J* = 14.7 Hz, 1 H), 4.52 (dd, *J* = 14.0, 12.5 Hz, 1 H), 3.47 (d, *J* = 17.9 Hz, 1 H), 3.38 (d, *J* = 14.7 Hz, 1 H), 3.21 (ddd, *J* = 14.0, 4.8, 1.7 Hz, 1 H), 2.58 (d, *J* = 17.9 Hz, 1 H), 1.87 (d, *J* = 8.0 Hz, 1 H), 1.54 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 205.8 (CO), 139.2 (CH), 136.3 (C), 132.7 (C), 131.7 (CH), 129.9 (CH), 127.9 (CH), 127.4 (CH), 127.1 (CH), 54.2 (CH_2), 44.0 (CH_2), 38.9 (C), 36.7 (CH_2), 35.0 (C), 34.9 (CH_2) ppm. IR $\tilde{\nu}_{max}$ = 1704 (CO) cm^{-1}. $C_{15}H_{14}Br_2O$ (370.09): calcd. C 48.68, H 3.81; found C 48.49, H 4.00.

1,2,3,4,9,10-Hexahydro-1,4-epoxyanthracene (41): 2,3-Bis(methylene)-1,4-epoxycyclohexane,[29] 2-diazoniobenzoate[37] from anthranilic acid (1.4 g, 10 mmol), 1,2-epoxypropane (1 mL) in dichloroethane (60 mL) was slowly heated to reflux and maintained at that temperature for 25 min. The mixture was concentrated and subjected to silica gel filtration. Elution with 5% ethyl acetate/light petroleum gave the title adduct (1.38 g, 70%) which crystallised from light petroleum as prisms, m.p. 99–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 4 H, ArH), 4.99–4.93 (m, 2 H), 3.74–3.58 (m, 2 H), 3.44–3.28 (m, 2 H), 1.93–1.84 (m, 2 H), 1.31–1.22 (m, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 137.7 (C), 133.5 (C), 129.3 (CH), 126.1 (CH), 79.9 (CH), 26.6 (CH_2), 25.2 (CH_2) ppm. $C_{14}H_{14}O$ (198.27): calcd. C 84.81, H 7.12; found C 85.03, H 7.04.

4,9-Dihydronaphtho[2,3-*c*]furan (42): 1,2,3,4,9,10-Hexahydro-1,4-epoxyanthracene (**41**) (1.42 g) was placed at the sealed end of a silica tube (500 × 10 mm) and the tube was positioned horizontally in a Thermolyne 21100 tube furnace which had a heating zone of 400 mm. The tube was heated to 350 °C and the open end of the tube connected to the vacuum system (< 0.1 Torr). The tube was cooled with solid dry ice at the exit. The substrate was heated using a kugelrohr oven to effect passage into the hot zone. At the end of the pyrolysis the solid was scraped out from the cold zone to give pure title furan as a pale yellow solid (1.16 g, 95%), m.p 79–80 (ref.[28] 78 °C). The ^{1}H NMR spectrum is identical with that reported.[28]

(1aα,2β,9β,9aα)-1a,9a-Dibromo-1a,2,3,8,9,9a-hexahydro-2,9-epoxy-1*H*-cycloprop[*b*]anthracene (44): Tetra-*n*-butylammonium fluoride (2.66 g, 10.2 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise to a solution of 4,9-dihydronaphtho[2,3-*c*]furan (1.31 g, 7.7 mmol) and 1,1,2-tribromo-2-(trimethylsilyl)cyclopropane (2.97 g, 8.48 mmol) in anhydrous tetrahydrofuran (10 mL) at –78 °C and stirred for 1 h. The mixture was allowed to stand at –20 °C for 2 d and then at room temperature for 1 h. The mixture was poured into water and extracted with diethyl ether (2 × 75 mL). The combined ethereal extracts were washed with brine (1 × 50 mL), dried, and concentrated under reduced pressure. The solid (3.20 g) contained both *exo* and *endo* adducts in a ratio of 19:1 according to ^{1}H NMR analysis. The product was subjected to rapid silica filtration. Elution with light petroleum and 1% ethyl acetate/light petroleum gave the title *exo* adduct as a colourless crystalline solid (1.56 g, 55%), which recrystallised from light petroleum as prisms, m.p. 139–141 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (s, 4 H, ArH), 4.79 (s, 2 H), 3.83–3.62 (m, 4 H), 2.85 (d, *J* = 7.3 Hz, 1 H), 1.82 (d, *J* = 7.3 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 142.1 (C), 132.9 (C), 129.2 (CH), 126.3 (CH), 83.2 (CH), 44.3 (C), 36.9 (CH_2), 29.8 (CH_2) ppm. $C_{15}H_{12}Br_2O$ (368.07): calcd. C 48.95, H 3.29; found C 48.99, H 3.50.

Spectral Details for the *endo* Adduct (1aα,2α,9α,9aα)-1a,9a-Dibromo-1a,2,3,8,9,9a-hexahydro-2,9-epoxy-1*H*-cycloprop[*b*]anthracene (43): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.47–6.95 (m, 4 H ArH), 5.08 (s, 2 H), 3.80–3.28 (m, 4 H), 1.96 (d, *J* = 7.4 Hz, 1 H), 1.91 (d, *J* = 7.4 Hz, 1 H).

(1aα,2β,9β,9aα)-1a,11a-Dibromo-1a,2,4,9,11,11a-hexahydro-2,9-epoxy-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (45): Ozonised oxygen was bubbled through a cooled (–78 °C) mixture of 1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-2,9-epoxy-1*H*-cycloprop[*b*]anthracene (830 mg, 2.36 mmol) and sodium hydrogen carbonate (10 mg) in a mixture of dry methanol (5 mL) dichloromethane (25 mL), until the reaction was complete as indicated by the blue colour of excess ozone. The ozone was displaced by bubbling nitrogen through the cold reaction mixture. Then thiourea (230 mg) was added and the mixture stirred at 0 °C for 1.5 h. The reaction mixture was washed with water (100 mL) and brine (100 mL), dried and concentrated under reduced pressure to afford the dione as a crystalline solid (780 mg, 86%). The analytical sample was obtained by recrystallisation from dichloromethane/light petroleum to

give colourless rhombohedra, m.p. 234–236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–722 (m, 4 H, ArH), 4.55 (s, 2 H), 4.46 (br. d, J = 12.3 Hz, 2 H), 3.73 (br. d, J = 12.3 Hz, 2 H), 1.82 (d, J = 7.6 Hz, 1 H), 1.66 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 204.0 (CO), 132.7 (CH), 128.8 (C), 128.3 (CH), 89.7 (CH), 45.3 (CH_2), 40.2 (C), 37.2 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 1710 (CO) cm^{-1}. $C_{15}H_{12}Br_2O_3$ (400.07): calcd. C 45.03, H 3.02; found C 44.96, H 3.17.

Treatment of 1a,11a-Dibromo-1a,2,4,9,11,11a-hexahydro-2,9-epoxy-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (45) with Basic Alumina: 1a,11a-Dibromo-1a,2,4,9,11,11a-hexahydro-2,9-epoxy-1*H*-benzo[*a*]cyclopropa[*f*]cyclodecene-3,10-dione (730 mg, 1.82 mmol), basic alumina (Woelm activity III, 2.47 g) and dichloroethane (30 mL) were stirred under reflux under argon for 90 min. The mixture was cooled, filtered and the residue was washed with dichloromethane. The filtrate was concentrated to give a brown solid which was subjected to radial chromatography. Elution with 5% ethyl acetate/light petroleum gave (1aα,2β,9β,9aα)-1a,9a-dibromo-1,1a,2,8,9,9a-hexahydro-2,9-epoxybenzo[*a*]cycloprop[*f*]azulen-3-one (**47**) (423 mg, 58%) and 1a,9a-dibromo-8a-hydroxy-2,9-epoxy-1,1a,2,3a,8,8a,9,9a-octahydrobenzo[*a*]cycloprop[*f*]azulen-3-one (**48**) (230 mg, 32%), which did not form the dehydrated product on repeated alumina treatment.

(1aα,2β,9β,9aα)-1a,9a-Dibromo-2,9-epoxy-1,1a,2,8,9,9a-hexahydrobenzo[*a*]cycloprop[*f*]azulen-3-one (47): Recrystallised from dichloromethane/light petroleum as colourless prisms, m.p. 193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–7.27 (m, 4 H, ArH), 4.98 (s, 1 H), 4.50 (s, 1 H), 3.92 (d, J = 24.5 Hz, 1 H), 3.82 (d, J = 24.5 Hz, 1 H), 2.61 (d, J = 7.4 Hz, 1 H), 1.89 (d, J = 7.4 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 189.2 (CO), 164.9 (C), 141.5 (C), 138.5 (C), 134.8 (C), 127.2 (CH), 126.5 (CH), 123.8 (CH), 123.0 (CH), 83.1 (CH), 76.9 (CH), 43.6 (C), 41.3 (CH_2), 35.6 (C), 32.5 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 1685 (CO) cm^{-1}. $C_{15}H_{10}Br_2O_2$ (382.05): calcd. C 47.16, H 2.64; found C 47.39, H 2.59.

1a,9a-Dibromo-8a-hydroxy-1,1a,2,3a,8,8a,9,9a-octahydro-2,9-epoxybenzo[*a*]cycloprop[*f*]azulen-3-one (48): Recrystallised from dichloromethane/light petroleum as colourless prisms, m.p. 193–194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.47 (m, 1 H, ArH), 7.33–7.21 (m, 3 H, ArH), 4.41 (s, 1 H), 4.10 (s, 1 H), 3.81 (s, 1 H), 3.57 (d, J = 16.2 Hz, 1 H), 2.97 (d, J = 16.2 Hz, 1 H), 2.80 (s, 1 H, OH), 2.30 (d, J = 7.3 Hz, 1 H), 1.65 (d, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 199.6 (CO), 140.1 (C), 136.0 (C), 128.3 (CH), 127.6 (CH), 127.1 (CH), 125.0 (CH), 84.8 (CH), 81.3 (CH), 77.9 (CH), 62.8 (C), 44.3 (CH_2), 35.9 (C), 35.2 (C), 27.6 (CH_2) ppm. IR: $\tilde{\nu}_{max}$ = 3422 (OH), 1728 (CO) cm^{-1}. $C_{15}H_{12}Br_2O_3$ (400.07): calcd. C 45.03, H 3.02; found C 44.86, H 3.21.

(1aα,2β,9β,9aα)-1a,9a-Dibromo-1a,2,9,9a-tetrahydro-2,9-epoxy-1*H*-benzo[*a*]cycloprop[*f*]azulene (51): DIBALH in toluene (0.93 mL, 1.2 M, 1.11 mmol) was added dropwise to a stirred solution of 1a,9a-dibromo-1,1a,2,8,9,9a-hexahydro-2,9-epoxybenzo[*a*]cycloprop[*f*]azulen-3-one (286 mg, 0.74 mmol) in anhydrous dichloromethane (10 mL) under argon at 0 °C. The solution was stirred at 0 °C until the reaction was complete (TLC) and then quenched with methanol (1 mL) and water (0.5 mL) and filtered. The filtrate was washed with water and brine, dried, and concentrated under reduced pressure to give almost pure (1aα,2β,3α,9β,9aα)-1a,9a-dibromo-1a,2,3,8,9,9a-hexahydro-2,9-epoxy-1*H*-benzo[*a*]cycloprop[*f*]-azulen-3-ol (**49**) (244 mg, 85%). Recrystallisation from dichloromethane/light petroleum gave colourless prisms, m.p. 151–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.21 (m, 4 H, ArH), 5.40–5.29 (m, 1 H), 4.63 (s, 1 H), 4.55 (d, J = 5.0 Hz, 1 H) 3.79 (dd, J = 23.0, 2.5 Hz, 1 H), 3.52 (dd, J = 23.0, 3.4 Hz, 1 H), 2.51 (d, J = 12.3 Hz, 1 H, OH), 2.32 (d, J = 7.1 Hz, 1 H), 1.42 (d, J = 7.1 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.5 (C), 143.2 (C), 142.3 (C), 137.6 (C), 1265 (CH), 125.2 (CH), 123.7 (CH), 121.5 (CH), 77.1 (CH), 76.3 (CH), 70.6 (CH), 46.0 (C), 40.3 (CH_2), 34.5 (C), 29.0 (CH_2) ppm. The foregoing alcohol (208 mg, 0.54 mmol) in anhydrous chloroform (2 mL) was added to a cooled (0 °C) mixture of phosphorus pentachloride (146 mg, 0.7 mmol) and anhydrous calcium carbonate (54 mg, 0.54 mmol) in anhydrous chloroform (15 mL). After 10 min, triethylamine (0.5 mL, 5 mmol) was added dropwise to the solution and the mixture stirred at room temperature for 20 min. The reaction mixture was washed with ice-cold 1 M HCl solution and brine, dried and concentrated under reduced pressure to give a pale yellow solid which was subjected to radial chromatography. Elution with light petroleum and 2.5% ethyl acetate/light petroleum gave the title benzofulvene as a yellow crystalline solid (181 mg, 91%). An analytical sample was obtained by recrystallisation from dichloromethane/light petroleum as yellow plates, m.p. 133–135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.16 (m, 4 H, ArH), 7.02 (ddd, J = 4.3, 1.8, 0.6 Hz, 1 H), 6.67 (d, J = 1.8 Hz, 1 H), 5.03 (s, 1 H), 4.73 (d, J = 4.3 Hz, 1 H), 2.46 (d, J = 7.1 Hz, 1 H), 1.79 (d, J = 7.1 Hz, 1 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 143.1 (C), 139.0 (C), 134.3 (C), 133.1 (C), 128.7 (CH), 127.8 (CH), 126.7 (CH), 125.4 (CH), 121.4 (CH), 120.9 (CH), 77.4 (CH), 74.6 (CH), 44.0 (C), 40.5 (C), 31.1 (CH_2) ppm. $C_{15}H_{10}Br_2O$ (366.05): calcd. C 49.22, H 2.75; found C 49.28, H 2.60.

X-ray Crystallographic Analysis: For the single-crystal X-ray studies (**27**, **33**), full spheres of CCD area detector diffractometer data were measured at ca. 153 K (Bruker AXS instrument, ω-scans, $2\theta_{max}$ = 58°; monochromatic Mo-K_α radiation, λ = 0.71073 Å), $N_{t(otal)}$ reflections merging to N unique after "empirical"/multiscan absorption correction (R_{int} cited; proprietary software), N_o with $I > 2\sigma(I)$ considered "observed" and used in the full-matrix least-squares refinements on F^2, refining anisotropic displacement parameter forms for C, O, Br, $(x,y,z,\ U_{iso})_H$ being refined (**27**)/constrained at estimates (**33**), except for the hydroxy hydrogen atom in **33**, where they were allowed to refine freely. Neutral atom complex scattering factors were employed. Results are presented below and in the CCDC deposition and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. CCDC-613269 (**27**) and -613270 (**33**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal/Refinement Data for 27: $C_{15}H_{14}Br_2O_2$, M = 386.1. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a = 16.732(2), b = 8.274(1), c = 10.701(3) Å, β = 107.972(2)°, V = 1409 Å^3. $D_{calcd.}$ (Z = 4) = 1.82(0) g cm^{-3}. μ_{Mo} = 57 cm^{-1}; specimen: 0.30 × 0.22 × 0.05 mm; $T_{min/max}$ = 0.67. N_t = 15794, N = 3541 (R_{int} = 0.033), N_o = 2827; R = 0.025, R_w = 0.069.

Crystal/Refinement Data for 33: $C_{15}H_{14}Br_2O_2$, M = 386.1. Monoclinic, space group $P2_1/c$, a = 5.888(1), b = 9.516(2), c = 24.970(5) Å, β = 94.488(3)°, V = 1395 Å^3. $D_{calcd.}$ (Z = 4) = 1.83(8) g cm^{-3}. μ_{Mo} = 58 cm^{-1}; specimen: 0.30 × 0.25 × 0.15 mm; $T_{min/max}$ = 0.58. N_t = 15448, N = 3485 (R_{int} = 0.039), N_o = 2662; R = 0.039, R_w = 0.094.

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