The Synthesis of Novel *p*-Quinone Methides: *O*-Dealkylation of 5-(*p*-Alkyloxyaryl)-10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-ols and Related Compounds

Benjamin Taljaard,*[a] Jana H. Taljaard[a] Christopher Imrie[a] and Mino R. Caira[b]

Keywords: Cleavage reactions / Conjugation / Dealkylation / Medium-ring compounds / Quinone methides / Dienones

The synthesis of a series of novel tricyclic *p*-quinone methides (*p*-QMs) from 5-(*p*-alkyloxyaryl)-10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-ol and related substrates in moderate-to-good yields is reported. The reaction is proposed to proceed under mild acidic conditions by *O*-dealkylation of the *p*-alkoxy group on the *p*-position of the pendant 5-aryl ring on the B-ring of the tricyclic system.The effect of different alkyl groups on the oxygen atom, as well as substituent groups on the phenyl ring flanking the *O*-alkyl group has also been investigated The mechanism of the reaction is discussed in terms of the relatively high intermediate cation stabilities, the possible intermediacy of a hemiketal, as well as conformational effects. Various modifications to the central seven-membered B-ring to introduce more rigidity to the tricyclic system have been made and the scope of the reaction further elaborated. Furthermore, the single crystal structure of dienone **14** has been determined and the *p*-quinone methide shown to be non-planar, which would account for the relative conformational rigidity of these systems and their ability to accommodate the planar cyclohexa-2,5-dienone moiety and thus explain the stability of these systems relative to their 5- and six-membered B-ring counterparts. These compounds may be useful for the synthesis of novel dyes or compounds which may exhibit photochromic and thermochromic properties.

Introduction

p-Quinone methides (*p*-QMs) are important intermediates in the biosynthesis of lignin,[1] as well as various other biological processes,[2–5] and were also identified as key intermediates in the formation of the toxic butylated hydroxytoluene found in food preservatives.[6] They occur in plants and were implicated as transient intermediates in the biosynthesis of chemical constituents of various natural products.[7–9] *p*-Quinone methides, which are usually intensely coloured, form the backbone of various cationic dyes and pH-sensitive indicators, such as fluorescein, which has found application as a diagnostic aid for cornea trauma, as well as analytical reagents such as bromophenol blue, a pH-sensitive indicator, and eosin, a wool dye and a histological staining agent for muscular fibers.[10–14] Synthetic flavylium salts can be utilized as molecular level switches driven by pH changes accompanied by dramatic colour changes as a result of the intermediacy of quinone methides,[15,16] whereas *p*-QMs and overcrowded bistricyclic aromatic alkenes have been shown to have thermochromic properties and thus used as thermochromic dyes.[17–23] Para-extended *p*-QMs have also been synthesized and studied as electron acceptors for the production of organic conducting materials.[24]

The synthesis of *p*-QMs derived from triarylmethyl (trityl) systems, the fuchsones, by the *O*-demethylation of methoxyphenyl trityl alcohols or chlorides under strongly acidic conditions at relatively high temperatures has been reported more than a century ago.[25–27] More recently Wada and co-workers, using trifluoroacetic acid instead of conc. sulfuric acid, obtained considerably higher yields of these useful dienones under much milder reaction conditions.[28] However, the synthesis of tricyclic *p*-QMs from ring systems containing seven-membered central B-rings under the above reaction conditions, has not as yet been reported.

The theoretical and stereochemical aspects, the UV and IR spectra of simple *p*-QMs derived from trityl systems had been studied in detail, but their synthetic uses or chemical reactions have surprisingly not been that well documented.[29–35] Furthermore, the simplest *p*-QM, 4-methylene-cyclohexa-2,5-dienone, has eluded isolation until only fairly recently, when it was trapped by complex formation with metals.[36,37]

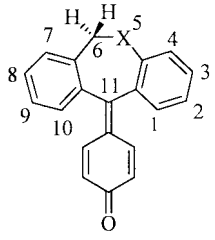
Tricyclic analogues based on fluorene and xanthene, have also not as yet been successfully synthesized by any of these

[a] Department of Chemistry, University of Port Elizabeth, P. O. Box 1600, Port Elizabeth 6000, South Africa
Fax: +27-41-5042573
E-mail: benjamin.taljaard@nmmu.ac.za
[b] Department of Chemistry, University of Cape Town, Rondebosch 7701, Cape Town, South Africa
E-mail: xraymino@science.uct.ac.za

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

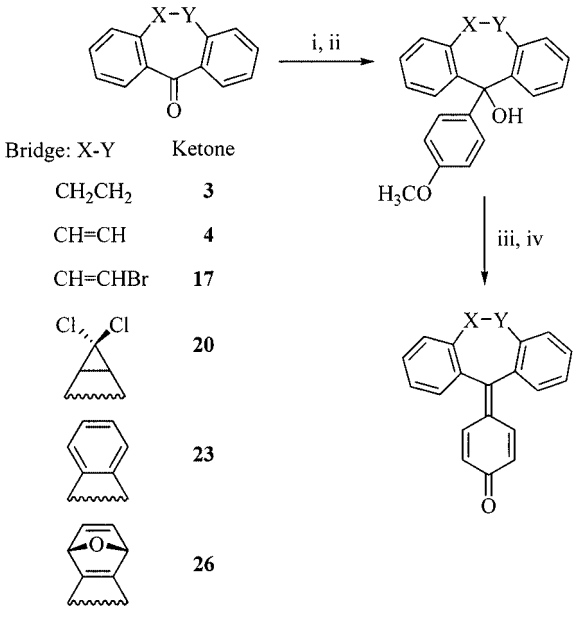
acid-mediated methods, although fluorenyl derivatives were prepared using Wittig reaction methodology, as well as by oxidative methods, requiring either anhydrous or rather drastic reaction conditions.[38,39] However, the synthesis of 4-(dibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2,5-dienone (**14**) by deprotonation of the 5-(*p*-hydroxyphenyl)dibenzo[*a*,*d*]cyclohepten-5-ylium salt with triethylamine, has been reported.[40]

We have previously reported the synthesis of the two novel tricyclic seven-membered B-ring *p*-QMs, 4-(6*H*-dibenzo[*b*,*e*]thiepin-11-ylidene)cyclohexa-2,5-dienone (**1**) and its oxygen analogue **2** under relatively mild reaction conditions (Figure 1).[41] We now report on the synthesis of a range of novel tricyclic *p*-QMs containing central seven-membered rings where, in the latter compounds, the heteroatoms in **1** and **2** have been substituted by carbon atoms and a couple of carbocyclic ring systems. A few trityl analogues have also been included to illustrate the versatility of this mild synthetic procedure and we also elaborate further on aspects of the mechanism previously proposed for the



X = S : **1**
X = O : **2**

Figure 1. 4-(6*H*-dibenzo[*b*,*e*]thiepin-11-ylidene)cyclohexa-2,5-dienone and its oxygen analogue.



Scheme 1. Synthesis of novel tricyclic *p*-quinone methides. Reagents and reaction conditions: i. *p*-$MeOC_6H_4MgBr$, THF; ii. aqueous NH_4Cl; iii. trifluoroacetic acid, H_2O, 2 days, room temp.; iv. aqueous NaOH work-up.

O-dealkylation reaction outlined in Scheme 1. In addition, the single crystal structure of the *p*-QM, **14** has been determined (Figure 2).

Results and Discussion

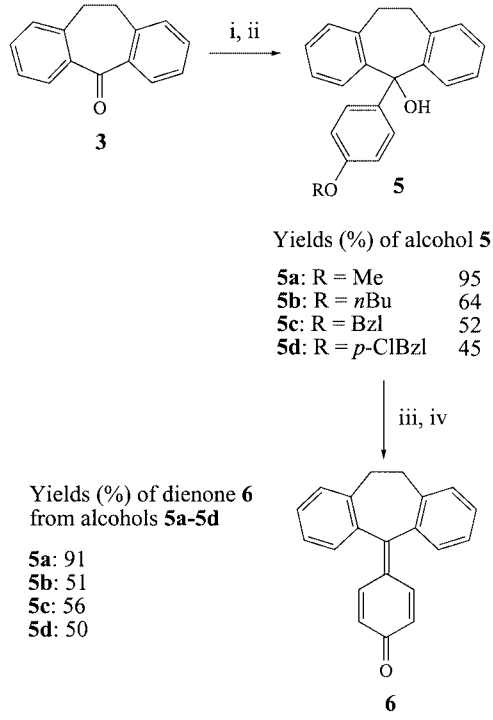
Following our good results on the synthesis of compounds **1** and **2**, it was decided to focus on a systematic study of the synthesis of these interesting novel compounds in order to determine the scope of the reaction, starting with relatively easily accessible starting materials. The ketones **3** and **4** (Scheme 1) were either purchased or synthesized in our laboratories by well-established protocols[42–44] and these and other ketones derived from **4** synthesized and subsequently converted into the corresponding *p*-methoxyaryl alcohols using Grignard reaction methodology.[45,46]

In some cases, Grignard reactions gave modest yields of the corresponding tertiary benzylic alcohols as pure gums, which could not be induced to crystallize. Substantial amounts of the aryl–aryl coupling product, 4,4′-dimethoxy-1,1′-diphenyl, were isolated from the latter reaction mixtures. These aryl coupling products have also previously been obtained in Grignard reactions and the synthetic utility of these aryl couplings exploited.[47,48] Moreover, structurally similar tricyclic alcohols are known to form enclathration compounds with both diethyl ether and THF, the reaction solvents employed in the classical preparations of the Grignard reagents, thus accounting for the reluctance of these alcohols to crystallize.[49–51]

Treatment of these alcohols with trifluoroacetic acid, in the presence of a small amount of water, at ambient temperature for 2 days, followed by aqueous alkaline work-up and preparative thin-layer chromatographic (PLC) separation, gave the *p*-QMs in poor-to-excellent non-optimised yields. The relatively modest yields of *p*-QMs in some cases may be attributed to mechanical losses due to the extensive PLC separations necessary for the isolation of the required substrates from the complex reaction mixtures.

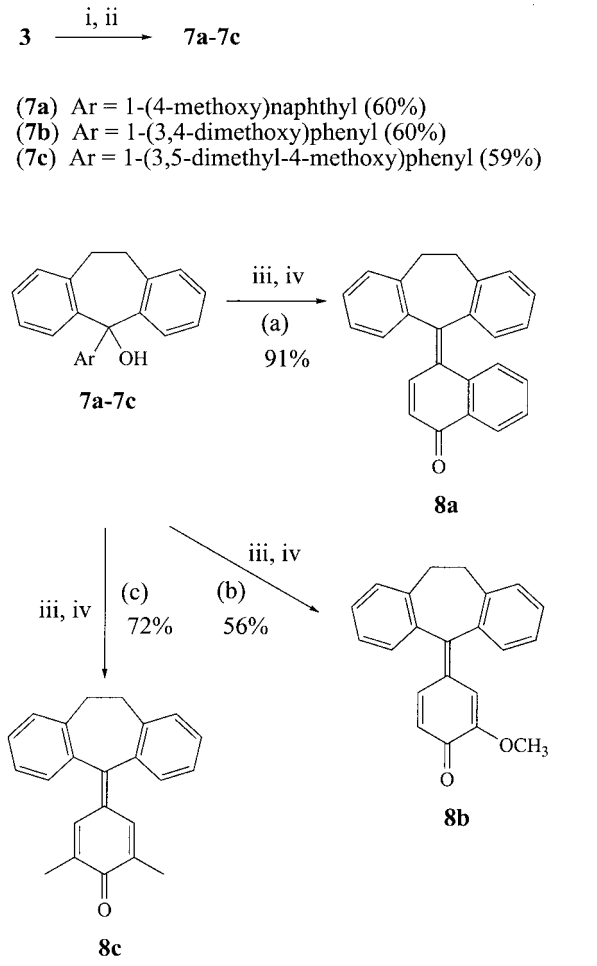
In order to assess the effect of groups other than methoxy on the *para*-position of the pendant 5-aryl group on the *O*-dealkylation reaction, various alkyl leaving groups were introduced into **3** as model compound (**5a**–**5d**, Scheme 2). It was surmised that the higher cation stability of the leaving benzyl and *p*-chlorobenzyl groups would enhance the yields of *p*-QM **6** if the mechanism involved nucleophilic attack on the departing alkyl group due to the relatively high stability of the benzyl cations. However, even though yields were not optimised, the methoxy group gave the best overall yield (Scheme 2), further suggesting the formation of a hemiketal intermediate during the course of the reaction. Furthermore, as appropriate *p*-methoxyphenyl derivatives are more accessible and cheaper than other alkoxyl substituents, these derivatives were selected as the reagents of choice for our synthetic studies.

The effect of various groups flanking the methoxyl group on the *p*-position of the pendant phenyl ring have been in-



Scheme 2. Synthesis of alcohols **5a**–**5d**: Effect of various alkyl groups on the aryl-oxygen atom on the *O*-dealkylation reaction. Reagents and conditions: i. *p*-ROC_6H_4MgBr (R = methyl, *n*-butyl) or *p*-ROC_6H_4MgCl (R = benzyl, *p*-chlorobenzyl), THF, reflux; ii. aqueous NH_4Cl; iii. CH_2Cl_2, CF_3CO_2H, H_2O, room temp., 2 days; iv. aqueous NaOH work-up.

vestigated next (Scheme 3). In all cases, good-to-excellent yields of *p*-QMs were obtained and, although lower overall yields of dienones **8a**–**8c** were obtained, the methoxy leaving group still gave the best results (see compounds **5a** and **8a**). No evidence could be obtained for demethylation of the *meta*-methoxy group on the phenyl ring linked to the 5-position. This result would suggest that the generation of an incipient stable benzylic carbocation at the latter carbon atom is the pivotal intermediate step for *p*-QM formation and that the *O*-demethylation reaction of the *p*-methoxy group is driven by the added stabilization of this cation incurred on demethylation, introducing more conjugation to form a very stable dienone ring. In contrast to the planar fluorenyl[52] and reasonably planar and conformationally more mobile 9*H*-xanthenyl, 9*H*-thioxanthenyl, 9*H*-thioxanthenyl-10,10-dioxide, *N*-benzyl-9,10-dihydroacridinyl, and 9,10-dihydroanthracenyl tricyclic moieties, where the formed cyclohexa-2,5-dienone ring is expected to be subjected to more severe steric interactions as a result of *peri*-1,8-hydrogen interactions of the annulated A and B benzene rings, the seven-membered ring systems may assume conformations in which the dienone ring may readily be accommodated.[53–55] In contrast, in the open ring system of diphenyl(*p*-methoxyphenyl)methanols (tritanols), the aryl rings are twisted out of plane and the assumed conformations of the formed *p*-QM may also readily accommodate the formed cyclohexa-2,5-dienone moiety, but may also relatively easily revert back to the phenolic structure, whereas in the seven-membered B-ring systems, the conformational barriers are suggested to be much higher and hence would account for the higher stability and reluctance of these systems to revert to the phenolic forms in basic medium.

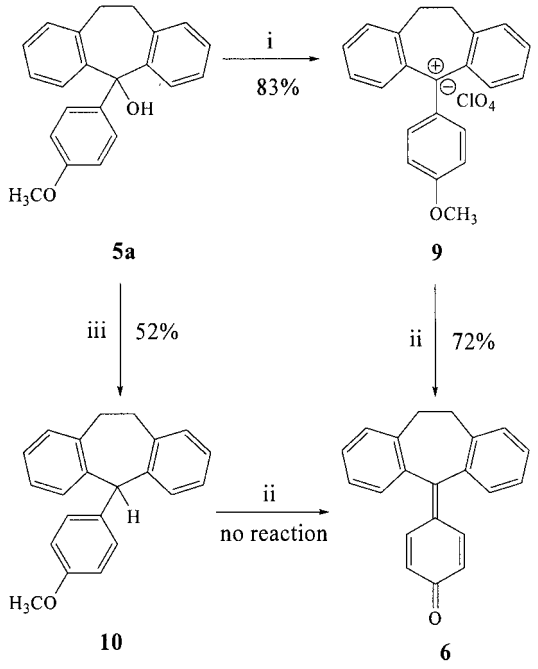


Scheme 3. The effect of different *O*-aryl groups at C-5 of 5-(4′-*O*-alkylaryl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol on *p*-QM formation. Reagents and conditions: i. ArMgBr, THF, 5 h reflux; ii. aqueous NH_4Cl; iii. CF_3CO_2H, H_2O, CH_2Cl_2, room temp., 2 days; iv. aqueous NaOH work-up.

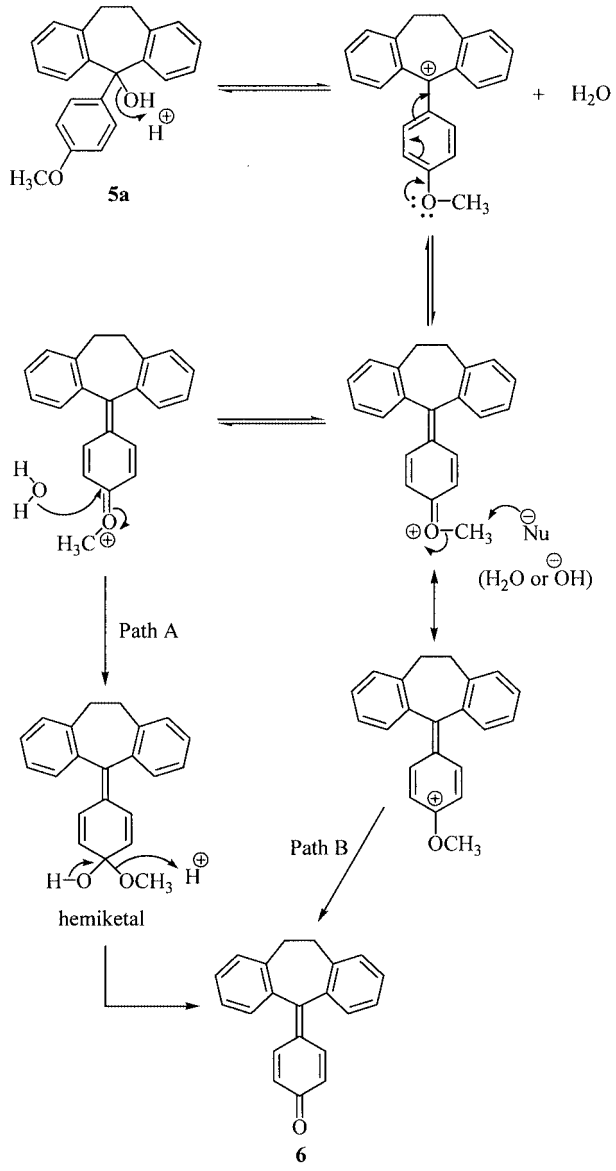
The alcohol **7a** dealkylated smoothly to give the *p*-QM, **8a** in excellent yield. This compound was targeted as a possible key intermediate for our planned annulation of the dienone system for the synthesis of tricyclic strained alkenes, as it already has a phenyl ring annulated to the dienone system.

In order to provide further evidence for our proposal of the importance of the formation of a stable cation at C-5 (structure **9**, Scheme 4) as driving force for the demethylation, alcohol **5a** was reduced to the corresponding hydrocarbon, thereby inhibiting the cation formation capability at this position of the substrate (Scheme 4).

The pivotal role of the formation of a carbocation at C-5 was demonstrated by the conversion of the alcohol **5a** to the corresponding hydrocarbon **10** (Scheme 4). The hydride ion, being a very poor leaving group, especially in acid medium, expectedly, did not result in the formation of the in-



Scheme 4. The effect of a stable carbocation at C-5 of compound **5a** on the *O*-dealkylation reaction. Reagents and conditions: i. $HClO_4/Ac_2O/CH_2Cl_2$, ether and petroleum ether added to precipitate the perchlorate salt; ii. CF_3CO_2H, H_2O, room temp., 2 days; iii. HCO_2H, Na_2CO_3, reflux for 1 h.



Scheme 5. Proposed mechanism for the *O*-dealkylation of 5*H*-(5-*p*-methoxyphenyl)dibenzo-10,11-dihydro[*a,d*]cyclohepten-5-ol (**5a**). Reagents and conditions: CF_3CO_2H, H_2O, 2 days stirring at ambient temperature, aqueous basic work-up.

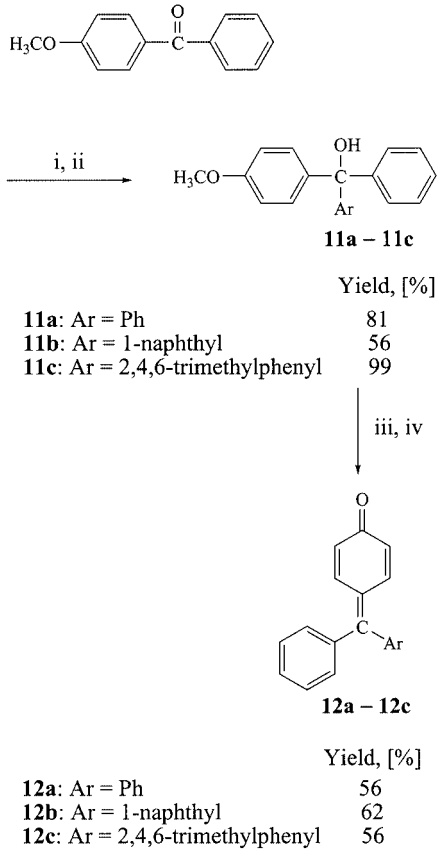
tensively coloured cation under the prevailing low pH conditions of the dealkylation reaction. Subsequently no evidence could be obtained for *p*-QM formation. However, on treatment of the anhydrous perchlorate salt **9**,[56] immediately after its synthesis, with aqueous trifluoroacetic acid, afforded *p*-QM **6** in 72% yield. As had been suggested previously,[41] the reaction proceeds either by the intermediacy of a hemiketal intermediate, followed by elimination of methanol to form the *p*-QM, or via direct attack of a nucleophile on the protonated *O*-methoxy carbon atom (Scheme 5, pathway B).

Clearly, both conformational and steric effects play a significant role in the formation and stablity of the *p*-QM, accounting for the more conformationally restricted tricyclic systems to form stable *p*-QMs.

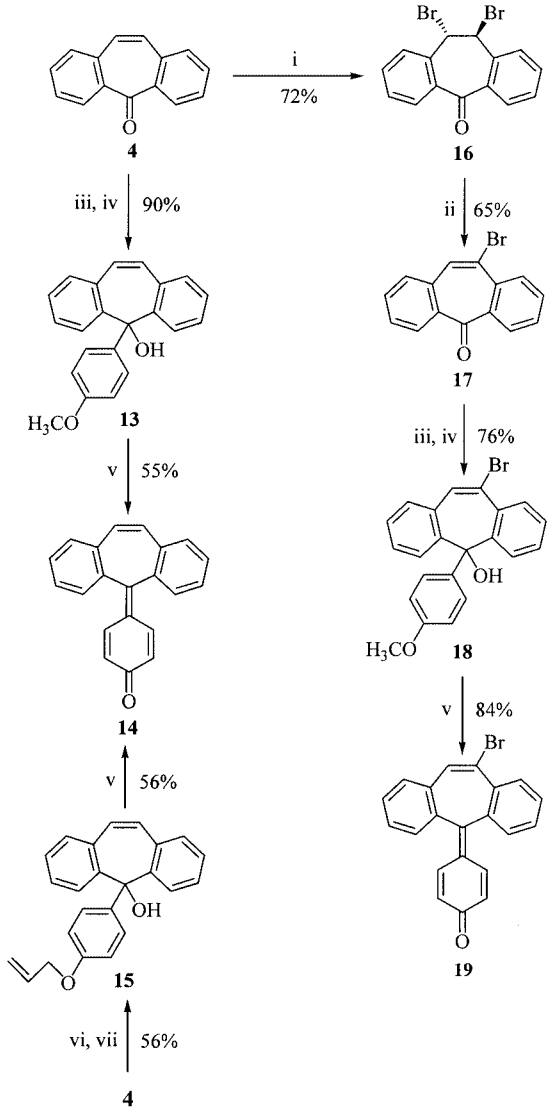
Furthermore, no evidence could be obtained for interconversion of the coloured dienone to the corresponding colourless phenolic form in aqueous basic medium, as had been reported to occur in trityl systems.[14,15,37] Although low yields of fuchsones were expected due to losses of product on work-up as consequence of this phenomenon, a few of the latter compounds were synthesized under the present reaction conditions. Quite acceptable yields of the *p*-quinones (fuchsones) were obtained even in spite of this reported rapid keto-enol interconversion occurring in the latter conformationally more mobile trityl systems. These yields are depicted in Scheme 6.

The more rigid tricyclic systems used in our investigations are non-planar and energy barriers for the interconversion of the various conformations are surmised to be much higher, resulting in a greater reluctance of these *p*-QMs to undergo reversion to the phenolic form in the presence of aqueous sodium hydroxide.

The 300-MHz ^{1}H-NMR spectra of the oxygen and sulfur analogues **1** and **2**, respectively, showed no change on recording the spectra over the temperature range –50 °C to +120 °C. This behaviour contrasts sharply with that of the alcohol precursors where the doublet AB coupling systems, assigned to the non-equivalent benzylic protons in the central B-ring α to the heteroatom, coalesced to broad singlets on heating, further supporting our proposal for relatively high energy barriers to conformational interchange to be present in these *p*-QMs.[57] No changes were observed in the ^{1}H NMR spectra of the *p*-QMs reported here over the specified temperature range.



Scheme 6. Synthesis of fuchsones under *O*-dealkylation reaction conditions. Reagents and reaction conditions: i. ArMgBr, THF, 18 h, reflux; ii. aqueous NH_4Cl; iii. trifluoroacetic acid, H_2O, room temp., 2 days; iv. aqueous NaOH work-up.

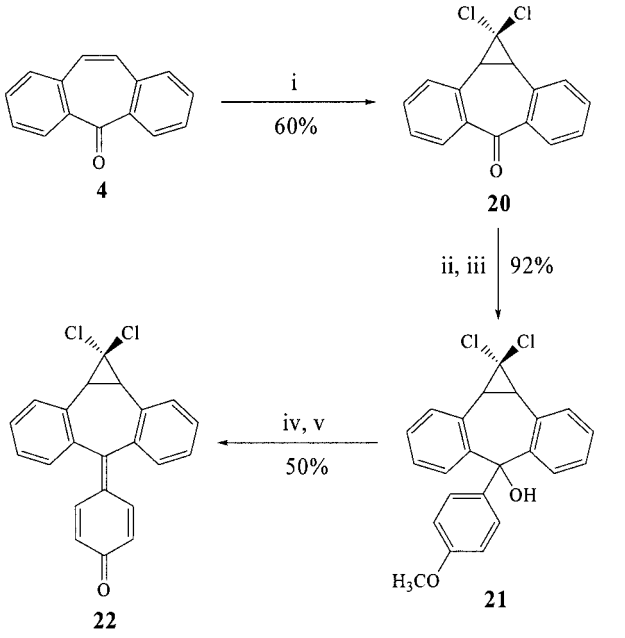


Scheme 7. Effect of the introduction of a double bond at the 10,11-position of 5-(*p*-methoxyhenyl)-10,11-dihydro[*a,d*]cyclohepten-5-ol on the demethylation reaction. Reagents and reaction conditions: i. Br_2, AcOH, room temp., overnight stirring; ii. KOH, MeOH, 2 h reflux; iii. *p*-$MeOC_6H_4MgBr$, THF, reflux, 16 h; iv. aqueous NH_4Cl; v. trifluoroacetic acid, H_2O, room temp., 2 days, aqueous NaOH work-up; vi. allylmagnesium bromide, THF, 16 h reflux; vii. aqueous NH_4Cl.

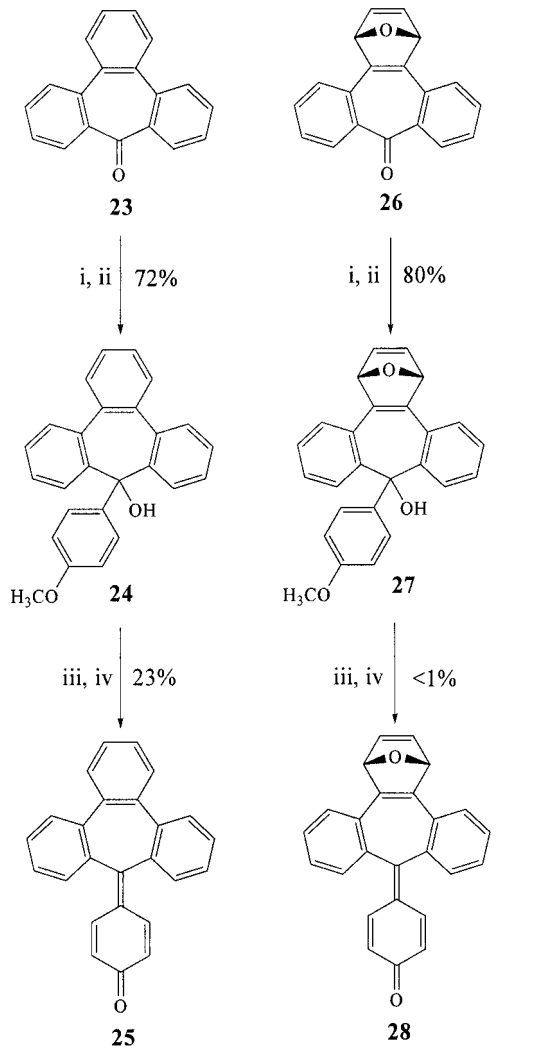
In order to further restrict the conformational lability of the molecule and to broaden the scope of the reaction, a double bond and other substituents were systematically introduced into the central seven-membered ring (Schemes 7–9). Introduction of a double bond at C-10–C-11, gave *p*-QM **14** in 55% yield (Scheme 7). Dealkylation of the *p*-allyloxyphenyl alcohol **15** also afforded **14** in 56% yield, the allyloxy leaving group showing no distinct advantage over the *p*-methoxy substituent. Introduction of a bromine atom on a double bond carbon atom of the bridge, gave the corresponding *p*-QM **19** in excellent yield (84%, see Scheme 7).

The introduction of a cyclopropyl moiety annulated to the 10,11-carbons, gave an acceptable yield of *p*-QM **22** (Scheme 8). The cyclopropyl moiety, despite introducing additional steric strain in the system,[58] does not seem to impart a significant effect on the yield of product **22.** Although the stereochemistry of the precursor alcohol and the dienone, respectively, have not been determined, modelling studies suggest that the conformation in which the *cis*-fused cyclopropyl ring is in an *anti*-orientation with respect to to the cyclohexadienone moiety on the seven-membered B-ring, to be the most stable.

The ketones **23** and **26** were synthesized next by well-established methods,[59–61] converted into the corresponding alcohols, and, subsequently to the *p*-QMs in the usual way (Scheme 9). The additional benzene ring at the 10,11-position intoduced additional strain into the molecule as a result of *peri*-interactions of the 1,8-aryl hydrogen atoms of the tricyclic system with the planar cyclohexadienone ring, thereby increasing the energy barrier for conformational inversion of the molecule. Although good yields of the alcohols **24** and **27** were obtained, the tetracyclic alcohol **24** gave the corresponding *p*-QM in low yield (23%). This may be attributed to the relatively low stability of the formed cation due to the decreased stabilization as a result of the aromatic system twisted out of plane, whereby resonance stabilization is inhibited.[61] The tetracyclic compound **27** however, gave <1% of dienone and a plethora of side-products, attributed to the instability of the latter alcohol in acid



Scheme 8. Synthesis of 4-(1,1-dichloro-1,1*a*,6,10*b*-tetrahydrodibenzo[*a,e*]cyclopropa[*c*]dibenzo[*a,d*]cyclohepta-5-ylidene)cyclohexa-2,5-dione. Reagents and conditions: i. CCl_3CO_2Et, powdered NaOMe, benzene/petroleum ether, 0–5 °C; ii. *p*-$MeOC_6H_4MgBr$, 16 h; iii. aqueous NH_4Cl; iv. CF_3CO_2H, H_2O, 2 days, room temp.; v. aqueous NaOH work-up.



Scheme 9. Synthesis of 4-(tribenzo[*a,c,e*]cyclohepten-9-ylidene)cyclohexa-2,5-dione. Reagents and reaction conditions: i. *p*-$MeOC_6H_4MgBr$, 5 h; ii. aqueous NH_4Cl; iii. CF_3CO_2H, H_2O, 2 days, room temp.; iv. aqueous NaOH work-up.

medium. Reducing the reaction time of the alcohol **27** with trifluoroacetic acid to 2 h, gave **28** in 20% yield, as well as starting material (65%). However, treatment of *p*-QM, **19**, with KO*t*Bu in ethereal furan by published methods,[59,60] afforded an improved yield of **28** (54%).

In order to explain the relatively high stability of the tricyclic seven-membered *p*-QMs as compared to the corresponding 5- and six-membered systems, the X-ray crystal structure of dienone **14** was determined (Figure 2 and Figure 3). These clearly show that the molecule may assume a conformation which will allow for the dienone system to be accommodated without much steric interaction. In the respective conformationally more labile and essentially planar xanthenyl and planar fluorenyl systems, respectively, steric interactions are expected to hinder formation of the planar cyclohexadienone ring, which would also account for the resistance of these systems to *O*-demethylate under the prevailing mild reaction conditions employed in our investigations.

Figure 2 shows the structure and conformation of **14** determined by X-ray analysis. The molecular point symmetry deviates only slightly from C_s. Atoms C10, C11, C14, and C15 form a plane with the remaining atoms of the seven-membered ring located above it. The endocyclic torsion angles around bonds C10–C11 and C14–C15 are 4.1(2) and 0.0(2)°, respectively, and ring symmetry is reflected in the remaining pairs of torsion angles viz. those about C11–C12, C13–C14 [34.3(2), –35.6(2)°] and about C9–C10, C9–C15 [–65.2(1), 62.9(1)°]. A formal double bond is confirmed for C12–C13, 1.338(2) Å, and the torsion angle around this bond is –0.6(2)°. As a result of the conformation adopted

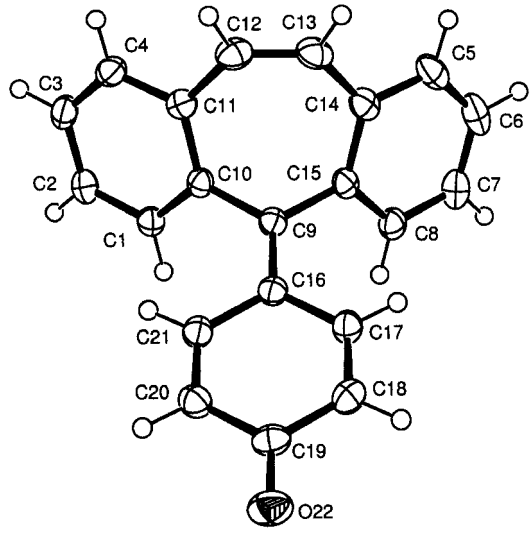


Figure 2. X-ray structure of **14** showing atomic numbering and thermal ellipsoids at the 50% probability level.

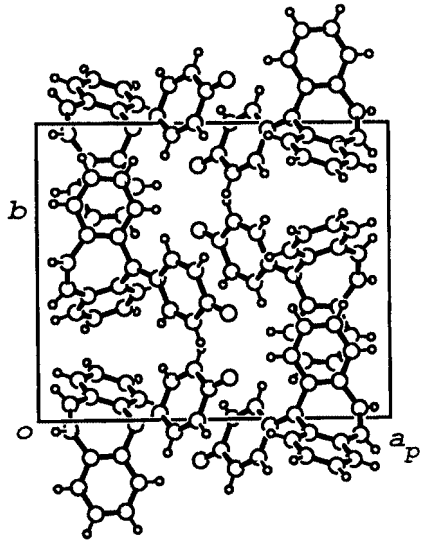


Figure 3. Projection of the crystal structure of **14** down (001).

by the central ring, the tricyclic system has a concave shape with a dihedral angle between the phenyl ring planes of 58.2(1)°.

The ring C16 through C21 is planar (max. deviation from the LS-plane = 0.004 Å) and is confirmed as a cyclohexadiene system with bonds C17–C18 and C20–C21 equal 1.344(2), 1.340(2) Å and significantly shorter than the remaining four bonds [range 1.455(2)–1.460(2) Å]. Double bond character for C9–C16, 1.367(2) Å, is also confirmed. Slight deviation from C_s symmetry is indicated by non-zero values for the torsion angles C15–C9–C16–C17, 6.4(2)° and C10–C9–C16–C21, 1.6(2)°.

Crystal packing is shown in Figure 3. Two crystallographically distinct π-π interactions stabilise the crystal structure. One of these involves the cyclohexadienone moiety and its centrosymmetric counterpart (Figure 3, centre), with centroid-centroid distance 3.643 Å. This interaction is complemented by a weak intermolecular hydrogen bond involving the carbonyl oxygen atom (C1–H···O22i with C···O 3.451(2) Å and C–H···O angle 152°, i = 1 – x, 1 – y, 1 – z).The other π-π interaction is between phenyl ring C1→C10 and its *c*-glide related counterpart (overlapping rings in Figure 3), with centroid-centroid distance 3.825 Å.

Conclusions

An efficient synthesis for a series of novel *p*-quinone methides under mild reaction conditions has been developed.The mechanism of the *O*-dealkylation reaction has been discussed in terms of carbocation stability, conformational and steric effects and the possible formation of a transient ketal intermediate. Furthermore, the X-ray structure confirmed the conformation of a model compound, showing the conformational twisting in the tricyclic system in order to accommodate the planar cyclohexen-2,5-dienone moiety, thus explaining their relative stabilities. This study also sheds more light on the inability of 5- and six-membered tricyclic B- ring analogues to demethylate to form stable, isolable, *p*-quinone methides under the prevailing mild acidic reaction conditions. Furthermore, these compounds should provide an entry into new photochromic and thermochromic materials and dyes.

Further investigations of reactions of these interesting compounds, as well as the scope of the dealkylation reaction are currently being pursued.

Experimental Section

Melting points were determined on an Electrothermal IA900 series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 Series Fourier Transform Spectrometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer. All spectra were recorded in $CDCl_3$, unless otherwise stated and chemical shifts are expressed in ppm relative to TMS as internal standard.

High resolution mass spectra (EI, 70 eV) were determined on a Kratos MS80RF instrument in the analytical laboratories of the Cape Technikon, Cape Town, South Africa and the X-ray structure determination was done by the X-ray unit at the University of Cape Town, South Africa.

Preparative thin-layer chromatography (PLC) separations were carried out using glass plates (40 cm × 20 cm or 20 cm × 20 cm) coated with Merck silica gel 60 F_{254} (1.5–2.0 mm layer thickness). Petroleum ether refers to the fraction boiling between 40 °C and 60 °C.

Synthesis of Ketones

The ketones, **3**, **4**, and 4-methoxybenzophenone were either obtained commercially or synthesized. Ketones **23** and **26** have previously been synthesized in these laboratories by established methods.[51,58,59]

***trans*-10,11-Dibromo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (16):** 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one (**4**, 50 g, 0.242 mol) in glacial acetic acid (400 mL), was treated with bromine (20 mL) in acetic acid (250 mL) at ambient temperature. The mixture was left to stand at room temperature for 15 h, filtered, the precipitate washed with small quantities of petroleum ether, and dried under reduced pressure, affording white crystals of **16** (63.8 g, 72%), m.p. 208–209.8 °C (ref.[44] m.p. 210–211 °C). IR (nujol): $\tilde{\nu}$ = 1639 cm^{-1} (s, *C*=O), 1589, 1577, 1463, 1379, 1337, 1298, 1245, 1185, 1147, 1103, 929. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82 (s, 2 H, H-10, 1-H), 7.20–8.71 (m, 6 H, Ar-*H*), 8.12 (d, J = 7.6 Hz, 2 H, 4-H, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.2 (C-10, C-11), 130.0, 131.4, 131.9, 133.1 (Ar, *C*-H), 137.1 138.4, 170.4 (quat. Ar), 192.6 (*C*=O). EI HRMS (70 eV): 367.90497 (0.83%), 365.90700 ($C_{15}H_{10}{}^{81}Br_2O$, 1.67%), 363.91141 ($C_{15}H_{10}{}^{79}Br_2O$, M$^+$, 0.86%), 284.99259 ($C_{15}H_{10}{}^{79}BrO$, 91.77%), 206.07329 ($C_{15}H_{11}O$, 100%), 178.07859 ($C_{14}H_{10}$, 82.26%), 176.06326 (25.97%), 89.03928 (C_7H_5, 28.43%). $C_{15}H_{10}{}^{79}Br_2O$: calcd. 363.90984; found 363.91141.

10-Bromo-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (17): Dibromide **16** (18.40 g, 0.05 mol) and NaOH (6 g) in methanol (400 mL) were heated under reflux on a water-bath for 2 h. The hot solution was filtered, cooled and the precipitate re-crystallized from methanol to give white crystals of ketone **17** (9.3 g, 65%), m.p. 115.0–116 °C (ref.[44] m.p. 116 °C). IR ($CHCl_3$): $\tilde{\nu}$ = 1653 cm^{-1} (*C*=O), 1607, 1591, 1445, 1313, 1223, 1159, 1114, 933. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.6–8.1 (m, 9 H, Ar-*H* and H-11). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.0, 129.4, 130.6, 131.0, 131.4, 131.5, 133.2, 135.3

(Ar, *C*-H and C-11), 125.0, 133.3, 139.2, 139.7 (quat. Ar and C-10),194.7 (*C*=O). EI HRMS (70 eV); *m*/*z*: 285.98329 ($C_{15}H_9{}^{81}BrO$, M + 2, 97.14%), 283.98447 ($C_{15}H_9{}^{79}BrO$, M^+, 100%), 257.98702 ($C_{14}H_9{}^{81}Br$, 65.06%), 255.98905 ($C_{14}H_9{}^{79}Br$, 66.41%), 177.07034 ($C_{14}H_9$, 54.11%), 176.06310 (63.32%), 151.05460 ($C_{12}H_7$, 22.19%), 88.03161 (C_7H_4, 49.27%). $C_{15}H_9{}^{79}BrO$: calcd. 283.98368; found 283.98447.

1,1-Dichloro-1,1a,6,10b-tetrahydrodibenzo[*a*,*e*]cyclopropa[*c*]cyclohepten-6-one (20): To a stirred solution of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**4**, 6.0 g, 0.029 mol) in benzene **(CAUTION)** (100 mL) and petroleum ether (20 mL) at 0–5 °C was added, sodium methoxide powder (6.0 g, 0.03 mol), followed by ethyl trichloroacetate (20.0 g, 0.03 mol), dropwise, over 1 h. The suspension was stirred at 0–5 °C for 5 h, allowed to come to room temperature, water (20 mL) added, the separated benzene layer washed with water (3 × 20 mL), and dried (Na_2SO_4). Evaporation of the benzene under reduced pressure, gave an oil which crystallized from ethanol yielding colourless crystals of the ketone **20** (5.2 g, 60%), m.p. 132–133.1 °C (ref.[58] m.p. 131–133 °C). IR ($CHCl_3$): $\tilde{\nu}$ = 1656 cm^{-1} (*C*=O), 1597, 1491, 1446, 1293, 1159, 1108, 1050, 943. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.50 (s, 2 H, 1a-H, 10b-H), 7.21–8.60 (m, 6 H, Ar-*H*), 7.72 (d, *J* = 6.6 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.3 (C-1*a*, 10*b*), 128.7, 130.1, 132.5, 132.6 (Ar, *C*H), 131.6, 141.1 (quat. Ar), 197.8 (*C*=O). EI HRMS (70 eV); *m*/*z*: 290.00641 ($C_{16}H_{10}{}^{37}Cl_2O$, 4.80%), 288.01068 ($C_{16}H_{10}{}^{35}Cl_2O$, M^+, 7.37%), 255.04034 (33.44%), 253.04361 ($C_{16}H_{10}{}^{35}ClO$, 100%) 225.04728 ($C_{15}H_{10}{}^{35}Cl$, 15.70%), 218.07269 ($C_{16}H_{10}O$, 35.01%), 217.06498 ($C_{16}H_9O$, 13.61%), 189.07153 ($C_{15}H_9$, 34.52%), 165.06979 ($C_{13}H_9$, 6.95%), 63.02412 (C_5H_3, 3.90%). $C_{16}H_{10}{}^{35}Cl_2O$: calcd. 288.01087; found 288.01068.

Synthesis of Alcohols

General Procedure: A portion of a solution of 4-bromoanisole (2.8 g, 0.015 mol) in anhydrous THF (20 mL) was added to a stirred suspension of magnesium turnings (3.77 g, 0.76 mmol) in anhydrous THF (100 mL), a crystal of iodine added and the reaction flask warmed to initiate the reaction. The remainder of the 4-bromoanisole was then added dropwise at a rate as to maintain gentle refluxing of the solution. After 3 h, a solution of the ketone (1 mol-equiv.) in anhydrous THF (50 mL), was added slowly and the reaction mixture heated under reflux for 17 h, cooled, and poured into a 30% aqueous NH_4Cl solution (200 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), the organic layer washed with water (3 × 25 mL), dried (Na_2SO_4) and the solvent distilled off. The crude residue was then re-crystallized from benzene/petroleum ether (CAUTION) affording the pure alcohol.

5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (5a): (4.5 g, 95%), m.p. 126.1–126.9 °C (ref.[62] m.p. 121–123 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3595 cm^{-1} (vs), 3403 (br), 3086, 3013, 2834 (s), 1602, 1502, 1476, 1456, 1297, 1261, 1178, 1032, 999. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 1 H, O*H*), 2.60–2.80 (m, 2 H, CH_2), 2.81–2.98 (m, 2 H, CH_2), 3.74 (m, 3 H, OCH_3), 6.67 (d, *J* = 8.9 Hz, 2 H, Ar-*H*), 6.94 (d, *J* = 8.8 Hz, 2 H, Ar-*H*), 7.10 (m, 2 H, Ar-*H*), 7.17–7.31 (m, 4 H, Ar-*H*), 8.05 (dd, J_1 = 7.8, J_2 = 2.1 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.8 (*C*H_2*C*H_2), 55.7 (O*C*H_3), 79.3 (*C*-OH), 114.2, 114.2, 125.0, 125.9, 126.3, 127.9, 128.4, 130.9 (Ar *C*-H), 138.2, 141.3, 144.2, 159.4 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 316.14660 $C_{22}H_{20}O_2$, M^+, 23.52%), 315.13583 ($C_{22}H_{19}O_2$, 3.25%), 225.09120 ($C_{15}H_{13}O_2$, 10.77%), 135.04470 ($C_8H_7O_2$, 86.82%), 131.04969 (C_9H_7O, 10.86%), 108.05733 (C_7H_8O, 11.30%), 103.05487 (C_8H_7, 16.07%), 91.05474 (C_7H_7, 15.06%), 77 (C_6H_5, 18.00%). $C_{22}H_{20}O_2$: calcd. 316.14633; found: 316.14660.

5-(4-Butyloxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (5b): 1-Bromo(4-butyloxy)benzene (7.43 g, 36.4 mmol) in THF (100 mL), magnesium (0.81 g, 33.5 mmol) and ketone **3** (4.5 g, 21.6 mmol) yielded a crude residue that upon PLC separation with CH_2Cl_2 as mobile phase, afforded pure **5b** as a light-yellow gum, which could not be induced to crystallize (4.95 g, 64%). IR ($CHCl_3$): $\tilde{\nu}$ = 3604 cm^{-1} (OH), 3430 (OH), 3007, 1606, 1578, 1505, 1481, 1455, 1380, 1294, 1246, 1177, 1110, 1068. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.3 Hz, 3 H, -$CH_2CH_2CH_2CH_3$), 1.49 (sextet, *J* = 7.3 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.78 (quintet, *J* = 7.9 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 2.20 (s, 1 H, O*H*), 2.75 (m, 2 H, CH_2–CH_2), 2.94 (m, 2 H, CH_2–CH_2), 3.93 (t, *J* = 6.5 Hz, 2 H, -OC$H_2$$CH_2CH_2CH_3$), 6.76 (d, *J* = 8.8 Hz, 2 H, Ar-*H*), 6.95 (d, *J* = 8.7 Hz, 2 H, Ar-*H*), 7.11 (d, *J* = 7.0 Hz, 2 H, Ar-*H*), 7.30 (m, 4 H, Ar-*H*), 8.10 (d, *J* = 7.4 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (*C*H_3), 19.6 (*C*H_2), 31.4 (O*C*H_3), 31.7 (*C*H_2), 32.9 (*C*H_2), 68.1 (O*C*H_2), 114.8, 126.0, 126.3, 127.9, 128.3, 130.9 (Ar, *C*H), 138.2, 141.1, 144.3, 159.0 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 358.19429 ($C_{25}H_{26}O_2$, M^+, 17.48%), 267.13563 ($C_{18}H_{19}O_2$, 3.31%), 208.08821 ($C_{15}H_{12}O$, 100%), 191.08495 ($C_{15}H_{11}$, 7.48%), 181.10050 ($C_{14}H_{13}$, 11.21%), 177.09146 ($C_{11}H_{13}O_2$, 39.10%), 165.07122 ($C_{13}H_9$, 7.79%), 91.05423 (C_7H_7, 6.36%). $C_{25}H_{26}O_2$: calcd. 358.19328; found 358.19429.

5-(4-Benzyloxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (5c): 4-(Benzyloxy)-1-bromobenzene (9.48 g, 36.0 mmol) in THF (100 mL), magnesium (0.91 g, 37.2 mmol) and ketone **3** (5.0 g, 24.0 mmol), gave a crude residue that upon re-crystallization from benzene/petroleum ether, afforded alcohol **5c** (4.85 g, 52%), m.p. 97.0–98.9 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1} (OH), 3406 (OH), 2885, 1605, 1582, 1505, 1454, 1380, 1296, 1242, 1177, 1155, 1015, 911. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 1 H, O*H*), 2.75 (m, 2 H, CH_2-CH_2), 2.94 (m, 2 H, CH_2-CH_2), 5.04 (s, 2 H, Ar-CH_2-), 6.86 (d, J_1 = 2.2 Hz and J_2 = 8.9 Hz, 2 H, Ar-*H*), 6.97 (d, J_1 = 2.1 Hz and J_2 = 8.8 Hz, 2 H, Ar-*H*), 7.13 (d, *J* = 7.2 Hz, 2 H, Ar-*H*), 7.22–7.45 (m, 9 H, Ar-*H*), 8.12 (dd, J_1 = 1.7 Hz and J_2 = 7.7 Hz, 2 H, Ar-*H*): ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.9 (C-10, C-11), 70.4 (Ar-*C*H_2-), 115.2, 126.0, 126.3, 127.3, 127.9, 128.0, 128.4, 128.5, 129.0, 131.0 (Ar, *C*H), 137.2, 138.2, 141.6, 144.2, 158.6 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 392.17683 ($C_{28}H_{24}O_2$, M^+, 7.13%), 211.07657 ($C_{14}H_{11}O_2$, 12.94%), 209.09585 ($C_{15}H_{13}O$, 30.663%), 208.08952 ($C_{15}H_{12}O$, 55.20%), 180.09333 ($C_{14}H_{12}$, 5.73%), 165.07044 ($C_{13}H_9$, 5.12%), 131.04964 (C_9H_7O, 5.22%), 91.05438 (C_7H_7, 100%), 77.03800 (C_6H_5, 2.04%). $C_{28}H_{24}O_2$: calcd. 392.17636; found 392.17683.

5-[(4-Chlorobenzyloxy)phenyl]-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (5d): 1-Bromo-4-(4-chlorobenzyloxy)benzene (8.57 g, 28.8 mmol) in THF (100 mL), magnesium (0.72 g, 29.8 mmol) and ketone **3** (4 g, 19.2 mmol) yielded a crude residue that was separated by PLC (SiO_2/CH_2Cl_2) to give the pure alcohol **5d** (3.7 g, 45%), m.p. 58.1–59.4 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1} (OH), 3418 (OH), 1604, 1503, 1375, 1300, 1238, 1177, 1092, 1012, 911. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 1 H, O*H*), 2.70 (m, 2 H, CH_2-CH_2), 2.93 (m, 2 H, CH_2-CH_2), 5.00 (s, 2 H, Ar-CH_2-), 6.82 (d, *J* = 11.8 Hz, 2 H Ar-*H*), 6.95 (d, *J* = 11.7 Hz, 2 H, Ar-*H*), 7.11 (d, *J* = 7.1 Hz, 2 H, Ar-*H*), 7.21–7.43 (m, 8 H, Ar-*H*), 8.11 (dd, J_1 = 1.6 Hz and J_2 = 7.6 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.9 (*C*H_2-*C*H_2), 69.6 (Ar-*C*H_2-), 115.1, 125.9, 126.3, 128.0, 128.5, 129.2, 131.0 (Ar, *C*-H), 134.2, 135.7, 138.2, 141.8, 144.1, 158.3 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 428.13331 ($C_{28}H_{23}{}^{37}ClO_2$, M + 2, 4.37%), 426.13830 ($C_{28}H_{23}{}^{35}ClO_2$, M^+, 11.35%), 408.12823 ($C_{28}H_{21}{}^{35}ClO_2$, 1.32%), 245.03657 ($C_{14}H_{10}{}^{35}ClO_2$, 5.89%), 209.09394 (25.09%), 208.08920 ($C_{15}H_{12}O$, 86.74%), 127.01334 (32.07%), 125.01650 ($C_7H_6{}^{35}Cl$,

100%), 91.05485 (C_7H_7, 9.28%), 57.07199 (7.70%). $C_{28}H_{23}{}^{35}ClO_2$: calcd. 426.13866; found 426.13830.

5-(4-Methoxyphenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (13): (4.4 g, 93%), m.p. 136.8–137.9 °C; ref.[58] m.p. 137–139 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3604 cm^{-1} (vs), 3391 (br), 3054, 1591, 1460, 1440, 1316, 1165, 1112, 1005. ^1H NMR (300 MHz, $CDCl_3$); δ = 2.23 (s, 1 H, O*H*), 3.69 (s, 3 H, OCH_3), 6.49 (s, 4 H, 2× Ar, C*H*, 10-H,11-H), 6.69 (s, 2 H, Ar-*H*), 7.25–7.39 (m, 4 H, Ar-*H*), 7.42–7.52 (m, 2 H, Ar-*H*), 8.20 (d, *J* = 8.1 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$); δ = 55.1 (*C*H_3O), 78.3 (*C*-OH), 112.8, 124.1, 124.6, 126.5, 126.8, 127.6, 127.9, 128.0, 128.3, 128.6, 129 3, 130.1, 130.8, 131.0, 131.2, 131.5, (Ar, *C*-H), 133.2, 133.4, 138.1, 142.6, 158.7 (quat. *C*-atoms). EI HRMS (70 eV); *m*/*z*: 314.13128 ($C_{22}H_{18}O_2$, M^+, 100%), 313.12182 ($C_{22}H_{17}O_2$, 6.88%),297.12625 ($C_{22}H_{17}O$, 3.24%), 207.08123 ($C_{15}H_{11}O$, 23.64%), 178.07799 ($C_{14}H_{10}$, 32.70%), 165.07037 ($C_{13}H_9$, 3.50%), 152.06262 ($C_{12}H_8$, 5.34%), 135.04466 ($C_8H_7O_2$, 36.57%), 92.02633 (C_6H_4O, 6.35%). $C_{22}H_{18}O_2$: calcd. 314.13068; found 314.13128.

1,1-Dichloro-6-(4-methoxyphenyl)-1,1a,6,10b-tetrahydrodibenzo-[*a*,*e*]cyclopropa[*c*]cyclohepten-6-ol (21): (3.7 g, 92%), m.p. 247.1–249.1 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1}, 3413 (OH), 1605, 1508, 1484, 1298, 1250, 1179, 1038, 837. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 1 H, O*H*), 2.59 (s, 2 H, 1a-H, 10b-H), 3.82 (s, 3 H, OCH_3), 6.83 (d, *J* = 6.8 Hz, 2 H, Ar-*H*), 7.0 (d, *J* = 6.7 Hz, 2 H, Ar-*H*), 7.26–7.40 (m, 6 H, Ar-*H*), 7.99 (m, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.5 (C-1*a*, C-10*b*), 55.7 (O*C*H_3), 63.7 (quat., C-1), 114.5, 125.1, 127.9, 128.0, 128.6, 133.3 (*C*H, Ar), 129.8, 141.0, 146.3, 159.4 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 398.06798 (13.14%), 396.06846 ($C_{23}H_{18}{}^{35}Cl_2O_2$, M^+, 22.05%), 361.10057 ($C_{23}H_{18}{}^{35}ClO_2$, 40.26%), 325.12290 ($C_{23}H_{17}O_2$, 100%), 297.12693 ($C_{15}H_{18}{}^{35}ClO_2$, 16.45%), 290.13172 ($C_{20}H_{18}O_2$, 35.80%), 265.10012 ($C_{15}H_{18}{}^{35}ClO_2$, 19.39%), 253.04036 ($C_{16}H_{10}{}^{35}ClO$, 29.79%), 218.07236 ($C_{16}H_{10}O$, 27.77%), 77.03913 (C_6H_5, 20.97%). $C_{23}H_{18}{}^{35}Cl_2O_2$: calcd. 396.06839; found 396.06846.

10-Bromo-5-(4-methoxyphenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (18): (3.1 g, 76%), m.p. 145.5–146.6 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3606 cm^{-1} (OH), 3387 (OH), 2838, 1608, 1508, 1479, 1439, 1327, 1300, 1249, 1180, 1164, 1118, 1035. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 1 H, O*H*), 3.76 (s, 3 H, OCH_3), 6.69 (s, 4 H, Ar-*H*), 7.20–7.59 (m, 6 H, Ar-*H*), 7.87 (d, *J* = 7.5 Hz, 2 H, 11-*H*), 8.16 (dd, J_1 = 4.6 Hz and J_2 = 5.2 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6 (O*C*H_3), 113.7, 124.2, 124.8, 125.2, 127.1, 127.4, 127.9, 128.7, 130.0, 129.98, 134.3 (Ar. *C*H, C-11), 125.2, 132.5, 133.3, 137.9, 144.3, 144.4, 159.6 (quat. Ar, C-10). EI HRMS (70 eV); *m*/*z*: 394.03914 ($C_{22}H_{17}{}^{81}BrO_2$, M + 2, 0.25%), 392.03842 ($C_{22}H_{17}{}^{79}BrO_2$, M^+, 0.25%), 313.12325 ($C_{22}H_{17}O_2$, 100%), 295.11193 ($C_{22}H_{15}O$, 2.60%), 269.09456 ($C_{20}H_{13}O$, 2.79%), 252.09424 ($C_{20}H_{12}$, 4.86%), 189.07012 ($C_{15}H_9$, 2.58%), 135.04509 ($C_8H_7O_2$, 13.83%), 78.04645 (C_6H_6, 28.35%). $C_{22}H_{17}{}^{79}BrO_2$: calcd. 392.04119; found 392.03842.

9-(4-Methoxyphenyl)-9*H*-tribenzo[*a*,*c*,*e*]cyclohepten-9-ol (24): (2.65 g, 72%), m.p. 169.6–170.7 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3604 cm^{-1} (OH), 3391 (OH), 2838, 1606, 1582, 1508, 1438, 1298, 1248, 1178, 1124, 1035, 1020. ^1H (300 MHz, $CDCl_3$): δ = 2.21 (s, 1 H, O*H*), 3.62 (s, 3 H, OCH_3), 6.40 (d, *J* = 8.8 Hz, 2 H, Ar-*H*), 6.71 (d, *J* = 8.8 Hz, 2 H, Ar-*H*), 7.00–7.62 (m, 10 H, Ar-*H*), 8.19 (d, *J* = 7.8 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5 (O*C*H_3), 113.2, 123.7, 127.4, 127.6, 127.7, 128.5, 129.2, 130.4 (Ar, *C*H, C-9), 136.7, 137.6, 139.6, 146.9, 158.8 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 364.14597 ($C_{26}H_{20}O_2$, M^+, 20.17%), 229.10214 ($C_{18}H_{13}$, 59.53%), 228.09491 ($C_{18}H_{12}$, 52.69%), 135.04493 ($C_8H_7O_2$, 100%), 77.03919 (C_6H_5, 3.61%). $C_{26}H_{20}O_2$: calcd. 364.14633; found 364.14597.

3′′,6′′-Epoxy-11-(4-methoxyphenyl)-3′′,6′′-dihydro-tribenzo[*a*,*c*,*e*]-cycloheptatrien-11-ol (27): (3.0 g, 80%) m.p. 165.4–167.5 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1} (s, OH), 3481 (br., OH), 2838 (s), 1605, 1508, 1440, 1300, 1251, 1179, 1034. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 1 H, O*H*), 3.71 (s, 3 H, OCH_3), 5.64 (s, 2 H, 3′′-H, 6′′-H), 6.57 (s, 2 H, 4′′-H, 5′′-H), 7.10–7.57 (m, 10 H, Ar-*H*), 8.30 (d, *J* = 7.9 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5 (O*C*H_3), 79.2 (C-11), 85.5 (C-3′′, C-6′′), 113.4, 121.7, 126.0, 127.2, 127.9, 128.8 (Ar *C*-H, C-5, C-6), 131.5, 138.3, 139.7 (quat. Ar), 142.1 (Ar *C*-H), 148.9, 159.3 (Ar, *C*H, C-4′′, C-5′′). EI HRMS (70 eV); *m*/*z*: 380.14005 ($C_{26}H_{20}O_3$, M^+, 100%), 351.13889 ($C_{25}H_{19}O_2$, 30.57%), 244.08829 ($C_{18}H_{12}O$, 20.68%), 237.09117 ($C_{16}H_{13}O_2$, 25.25%), 215.08542 ($C_{17}H_{11}$, 38.65%), 135.04455 ($C_8H_7O_2$, 42.67%), 121.06561 (C_8H_9O, 12.22%). $C_{26}H_{20}O_3$: calcd. 380.14124; found 380.14005.

5-(4-Methoxynaphthalen-1-yl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (7a): 1-Bromo-4-methoxynaphthalene (4.30 g, 19.1 mmol) in THF (100 mL), magnesium (0.72 g, 29.6 mmol) and 5*H*-dibenzo-10,11-dihydro[*a*,*d*]cyclohepten-5-one **3** (2.65 g, 12.74 mmol) gave a sparingly soluble white solid, which, after washing with benzene and drying, afforded pure **7a** (3.2 g, 60%), m.p. 209.7–210.8 °C. IR (nujol): $\tilde{\nu}$ = 3526 cm^{-1} (OH), 1619, 1588, 1514, 1479, 1460, 1389, 1365, 1323, 1274, 1250, 1215, 1157, 1091, 1007, 968. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.76 (s, 1 H, O*H*), 2.62–2.86 (m, 4 H, 10-H, 11-H), 6.65 (d, *J* = 7.3 Hz, 1 H, Ar-*H*), 7.02–7.42 (m, 9 H, Ar-*H*), 8.03 (d, *J* = 8.7 Hz, 1 H, Ar-*H*), 8.10 (dd, J_1 = 7.9, J_2 = 1.3 Hz, 2 H, Ar-H), 8.30 (d, *J* = 10.6 Hz, 1 H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): 32.2 (2×*C*H_2), 55.9 (*C*H_3), 80.1 (quat., C-5), 102.6,122.8, 124.9, 125.3, 126.3, 126.58, 126.64 (Ar, *C*-H), 127.2 (quat. Ar), 127.7, 127.8, 131.0 (Ar, *C*-H), 131.6, 134.0, 137.2, 146.1, 156.1 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 366.16188 ($C_{26}H_{22}O_2$, M^+, 21.73%), 348.15093 ($C_{26}H_{20}O$, 3.94%), 209.09303 (26.64%), 208.08888 ($C_{15}H_{12}O$, 100%), 185.06017 ($C_{12}H_9O_2$, 36.43%), 178.07835 ($C_{14}H_{10}$, 6.13%), 165.07015 ($C_{13}H_9$, 5.68%), 158.07227 ($C_{11}H_{10}O$, 6.59%), 115.05423 (4.55%), 91.05498 (C_7H_7, 3.58%). $C_{26}H_{22}O_2$: calcd. 366.16198; found 366.16188.

5-(3,4-Dimethoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (7b): 1-Bromo-3,4-dimethoxybenzene (*p*-bromoveratrole) (7.82 g, 37.2 mmol) in THF (100 mL), magnesium (0.91 g, 37.2 mmol), and ketone **3** (5.0 g, 24.0 mmol) yielded a crude solid residue, which crystallized from benzene/petroleum ether affording white crystals of **7b** (5.0 g, 60%), m.p. 189.1–190.2 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1} (s, OH), 3410 (br., OH), 3010, 2837, 1601, 1509, 1482, 1464, 1410, 1326, 1256, 1138, 1026. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 1 H, O*H*), 2.74 (m, 2 H, CH_2–CH_2), 2.94 (m, 2 H, CH_2–CH_2), 3.63 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.55 (d, *J* = 7.0 Hz, 2 H, Ar-*H*), 6.72 (d, *J* = 7.0 Hz, 1 H, Ar-*H*), 7.03–7.40 (m, 6 H, Ar-*H*), 8.10 (dd, J_1 = 1.5 Hz and J_2 = 7.6 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.9 (C-10, C-11), 56.2 (O*C*H_3), 56.3 (O*C*H_3), 110.3, 111.1, 119.7, 125.9, 126.2, 128.0, 130.9 (Ar, *C*H), 138.3, 141.8, 144.1, 148.9, 149.3 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 346.15677 ($C_{23}H_{22}O_3$, M^+, 63.85%), 328.14640 ($C_{23}H_{20}O_2$, 8.88%), 255.10110 ($C_{16}H_{15}O_3$, 5.87%), 209.09502 ($C_{15}H_{13}O$, 39.20%), 208.08912 ($C_{15}H_{12}O$, 100%), 191.08552 ($C_{15}H_{11}$, 9.75%), 165.05694 ($C_9H_9O_3$, 54.20%), 91.05479 (C_7H_7, 8.36%). $C_{23}H_{22}O_3$: calcd. 346.15689; found 346.15677.

5-(4-Methoxy-3,5-dimethylphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-ol (7c): 4-Bromo-1-methoxy-2,6-dimethylbenzene (4.65 g, 21.6 mmol) in THF (100 mL), magnesium (0.54 g, 22.3 mmol) and ketone **3** (3.0 g, 14.4 mmol) yielded a solid, which crystallized from benzene/petroleum ether as **7c** (2.9 g, 59%), m.p.

208.5–210.7 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3603 cm^{-1} (OH), 3430 (OH), 3010, 1482, 1455, 1318, 1228, 1160, 1132, 1015. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 6 H, 2×CH_3), 2.36 (s, 1 H, O*H*), 2.74 (m, 2 H, CH_2-CH_2), 2.97 (m, 2 H, CH_2-CH_2), 3.70 (s, 3 H, OCH_3), 6.64 (s, 2 H, Ar-*H*), 7.08–7.40 (m, 6 H, Ar-*H*), 8.06 (d, *J* = 7.5 Hz, 2, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7 (2×*C*H_3), 32.8 (*C*H_2–*C*H_2), 79.4 (O*C*H_3), 125.8, 126.2, 127.4, 127.9, 130.9 (*C*H, Ar), 131.3, 138.1, 144.2, 156.8 (quat. Ar, C-5). EI HRMS (70 eV); *m*/*z*: 344.17852 ($C_{24}H_{24}O_2$, M^+, 52.03%), 326.16828 ($C_{24}H_{22}O$, 8.21%), 209.09529 ($C_{15}H_{13}O$, 45.95%), 208.08839 ($C_{15}H_{12}O$, 91.96%), 191.08528 ($C_{15}H_{11}$, 10.75%), 180.09344 ($C_{14}H_{12}$, 24.97%), 163.07499 ($C_{10}H_{11}O_2$, 100%), 136.08887 ($C_9H_{12}O$, 16.99%), 131.04960 (C_9H_7O, 9.99%). $C_{24}H_{24}O_2$: calcd. 344.17763; found 344.17852.

5-(4-Allyloxyphenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (15): 4-(Allyloxy)-1-bromobenzene (4.65 g, 21.8 mmol) in THF (100 mL), magnesium (0.55 g, 22.6 mmol) and ketone **4** (3.0 g, 14.5 mmol) gave a crude residue that upon re-crystallization from benzene/petroleum ether, afforded alcohol **15** (2.77 g, 56%), m.p. 107.0–108.0 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3602 cm^{-1} (OH), 3385 (OH), 1606, 1506, 1433, 1298, 1239, 1176, 1114, 1018, 917. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 1 H, O*H*), 4.44 (d, *J* = 5.4 Hz, 2 H, OCH_2), 5.24 (dd, J_1 = 1.3 Hz and J_2 = 10.5 Hz, 1 H, CH=CH_2), 5.39 (dd, J_1 = 1.5 Hz and J_2 = 17.3 Hz, 1 H, CH=CH_2), 6.0 (octet, *J* = 5.2 Hz, 1 H, C*H*=CH_2), 6.51–6.65 (m, 4 H, Ar-*H*), 6.73 (s, 2 H, H-10, H-11), 7.30–7.58 (m, 6 H, Ar-*H*), 8.2 (d, *J* = 7.9 Hz, 2 H, 4-H, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = ($CDCl_3$) 69.1 (benzyl *C*), 118.2, 114.8, 125.0, 127.0, 128.4, 128.5, 128.6, 129.1, 131.7, 133.6 (Ar, *C*H, alkene *C*), 133.7, 138.7, 143.0, 158.3 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 340.14668 ($C_{24}H_{20}O_2$, M^+, 100%), 300.11476 ($C_{21}H_{16}O_2$, 18.15%), 299.10853 ($C_{21}H_{15}O_2$, 30.31%), 281.09609 ($C_{21}H_{13}O$, 14.15%), 207.08053 ($C_{15}H_{11}O$, 17.46%), 179.08450 ($C_{14}H_{11}$, 17.93%), 178.07822 ($C_{14}H_{10}$, 32.12%), 161.06082 ($C_{10}H_9O_2$, 18.97%), 121.02869 ($C_7H_5O_2$, 7.92%). $C_{24}H_{20}O_2$: calcd. 340.14633; found 340.14668.

Synthesis of *p*-Quinone Methides

The *p*-methoxyaryl alcohol (10.8 mmol) in dichloromethane (100 mL) was treated with trifluoroacetic acid (7.5 g, 65.8 mmol) and water (2.0 g, 110 mmol), the mixture stirred at ambient temperature for 72 h., cooled, and treated with 20% aqueous NaOH (3×50 mL). The organic layer was separated, washed with water (3×30 mL), dried (Na_2SO_4), the solvent distilled off and the crude residue further purified by PLC (SiO_2/CH_2Cl_2). Re-crystallization of the solid, obtained from by elution of a bright yellow band from the PLC plates, from ethanol, afforded yellow crystals of the corresponding *p*-quinone methide.

4-(10,11-Dihydro-dibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2,5-dienone (6): (2.81 g, 91%), m.p. 158.0–159.7 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1632 cm^{-1} (C=O), 1524, 1478, 1233, 1160, 866. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.35 (dd, J_1 = 7.1 Hz and J_2 = 11.9 Hz, 2 H, CH_2CH_2), 2.95 (dd, J_1 = 7.1 Hz and J_2 = 11.8 Hz, 2 H, CH_2CH_2), 6.42 (d, *J* = 10.1 Hz, 2 H, CH=C*H*-C=O), 7.1–7.4 (m, 8 H, Ar-*H*), 7.49 (d, *J* = 10.1 Hz, 2 H, C*H*=CH-C=O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.7 (*C*H_2), 32.8 (*C*H_2), 115.9, 121.6, 126.0, 126.2, 127.8, 128.4, 129.3, 129.5, 129.6, 130.3, 130.9, 138.5 (Ar, *C*H, *C*H=*C*H-C=O and C-10, C-11), 138.2, 140.5, 144.5, 156.7, 161.5 (quat. Ar), 187.59 (*C*=O). EI HRMS (70 eV): *m*/*z*: 284.11995 ($C_{21}H_{16}O$, M^+, 73.24%), 239.08345 ($C_{19}H_{11}$, 18.24%), 215.0860 ($C_{17}H_{11}$, 8.80%), 191.08549 ($C_{15}H_{11}$, 32.64%), 178.0774 ($C_{14}H_{19}$, 8.50%), 50.94805 (100%). $C_{21}H_{16}O$: calcd. 284.12012; found 284.11995.

4-(Dibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2,5-dienone (14): (1.74 g, 55%), m.p. 180.0–181.0 °C (ref.[40] m.p.183–185°C). IR ($CHCl_3$): $\tilde{\nu}$ = 1633 cm^{-1} (C=O), 1525, 1433, 1383, 1224, 866. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.38 (d, *J* = 10.2 Hz, 2 H, CH=C*H*-C=O), 7.01 (s, 2 H, 10-H,11-H), 7.30 (d, *J* = 10.4 Hz, 2 H, C*H*=CH-C=O), 7.35–7.5 (m, 8 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.5, 128.8, 128.9, 129.6 138.0 (Ar, *C*-H, *C*H=*C*H-C=O and C-10, C-11), 134.5 136.1 156.8 (quat. Ar), 187.2 (*C*=O). EI HRMS (70 eV); *m*/*z*: 282.10474 ($C_{21}H_{14}O$, M+, 100%), 254.10536 ($C_{20}H_{14}$, 12.94%), 253.10136 ($C_{20}H_{13}$, 52.9%), 252.09411 ($C_{20}H_{12}$, 31.84%), 126.04597 ($C_{10}H_6$, 13.38%). $C_{21}H_{14}O$: calcd. 282.10447; found 282.10474.]

4-(10-Bromodibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2,5-dienone (19): (3.29 g, 84%), m.p. 184.1–188.9 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1633 cm^{-1} (C=O), 1561, 1531, 1480, 1431, 1383, 1206, 1164, 1103, 866. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.42 (d, *J* = 9.9 Hz, 2 H, CH=C*H*-C=O), 7.20–7.53 (m, 9 H, Ar-*H*, C*H*=CH-C=O), 7.62 (s, 1 H, 11-H), 7.88 (m, 1 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.2, 128.6, 128.7, 128.9, 129.0, 129.1, 130.0, 130.1, 130.4, 134.0, 137.6, 137.7 (Ar, *C*H, C-11, *C*H=*C*H-C=O), 125.0, 129.4, 133.7 137.3, 155.1 (quat. Ar, C-10), 187.22 (*C*=O). EI HRMS (70 eV); *m*/*z*: 362.01341 ($C_{21}H_{13}{}^{81}BrO$, M + 2, 99.84%), 360.01572 ($C_{21}H_{13}{}^{79}BrO$, M^+, 100%), 299.10527 (31.51%), 281.09543 ($C_{21}H_{13}O$, 35.16%), 253.10003 ($C_{20}H_{13}$, 45.05%), 252.09393 ($C_{20}H_{12}$, 63.14%), 250.07825 ($C_{20}H_{10}$, 27.23%), 226.07852 ($C_{18}H_{10}$, 15.44%), 126.04638 ($C_{10}H_6$, 25.98%), 125.03897 ($C_{10}H_5$, 20.28%), 113.03869 (C_9H_5, 26.02%). $C_{21}H_{13}{}^{79}BrO$: calcd. 360.01498; found 360.01572.

4-(1,1-Dichloro-1,1*a*,6,10*b*-tetrahydrodibenzo[*a*,*e*]cyclopropa[*c*]dibenzo[*a*,*d*]cyclohepta-5-ylidene)cyclohexa-2,5-dienone (22): (1.98 g, 50%), m.p. 222.5–225.7 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1633 cm^{-1} (C=O), 1579, 1532, 1484, 1446, 1383, 1219, 1175, 1162, 1107, 1041, 950. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.35 (s, 2 H, H-1a, H-10b), 6.44 (d, *J* = 10.1 Hz, 2 H, CH=C*H*-C=O), 7.16 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 7.24–7.50 (m, 6 H, Ar-H, CH=C*H*-C=O, 7.53 (d, *J* = 7.6 Hz, 2 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.3 (C-1a, C-10b), 61.8 (C-1), 128.0, 129.3 129.7 129.9 133.3 138.0 (Ar, *C*-H, *C*H=*C*H-CO), 130.0, 130.4, 140.2, 158.0 (quat. Ar), 187.4 (*C*=O). EI HRMS (70 eV); *m*/*z*: 366.04129 (68.09%), 365.04626 (23.29%), 364.04268 ($C_{22}H_{14}O^{35}Cl_2$, M^+, 100%), 331.06922 (18.85%) 329.07252 ($C_{22}H_{14}{}^{35}ClO$, 56.32%), 293.09555 ($C_{22}H_{13}O$, 38.56%), 265.10083 ($C_{21}H_{13}$, 61.17%), 263.08625 ($C_{21}H_{11}$, 29.69%), 252.093441 ($C_{20}H_{12}$, 12.53%), 202.07831 ($C_{16}H_{10}$, 17.06%), 113.03716 (C_9H_5, 4.70%). $C_{22}H_{14}{}^{35}Cl_2O$: calcd. 364.04217; found 264.04268. $C_{22}H_{14}Cl_2O$ (365.26): calcd. C 72.34, H 3.86; found C 72.25, H 3.65.

4-(Tribenzo[*a*,*c*,*e*]cyclohepten-9-ylidene)cyclohexa-2,5-dienone (25): (0.83 g, 23%), m.p. 264.4–265.5 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1632 cm^{-1} (C=O), 1579, 1559, 1537, 1471, 1431, 1384, 1273, 1226, 1162, 866. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.38 (d, *J* = 10.1 Hz, 2 H, CH=C*H*-C=O), 7.28–7.35 (m, 2 H, Ar-*H*), 7.40–7.55 (m, 8 H, Ar-*H*, C*H*=C*H*-C=O), 7.60–7.74 (m, 4 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.8, 127.9, 128.5 129.4 129.7, 130.1, 130.5 138.0 (Ar, *C*H, *C*H=*C*H-C=O), 137.5, 137.9, 140.8, 157.9 (quat. Ar), 187.4 (*C*=O). EI HRMS (70 eV); *m*/*z*: 332.12052 ($C_{25}H_{16}O$, M^+, 100%), 303.11607 ($C_{24}H_{15}$, 32.10%), 302.10970 ($C_{24}H_{14}$, 22.74%), 300.09353 ($C_{24}H_{12}$, 10.93%), 276.09466 ($C_{22}H_{12}$, 11.25%), 150.04618 ($C_{12}H_6$, 8.72%), 138.04649 ($C_{11}H_6$, 7.55%). $C_{25}H_{16}O$: calcd. 332.12012; found 332.12052.

4-(10,11-Dihydrodibenzo[*a*,*d*]cyclohepten-5-ylidene)-4*H*-naphthalen-1-one (8a): (3.3 g, 91%), m.p. 172.9–173.9 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1645 cm^{-1} (C=O), 1598, 1543, 1481, 1453, 1402, 1301, 1238, 1215,

1178, 1156, 1129, 1096, 1027. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 (m, 2 H, CH_2–CH_2), 3.54 (m, 2 H, CH_2–CH_2), 6.50 (d, J = 10.3 Hz, 1 H, CH=C*H*-C=O), 6.97 (d, J = 7.4 Hz, 1 H), 7.05–7.45 (m, 10 H, Ar-*H*), 7.74 (d, J = 10.3 Hz, 1 H, C*H*=CH-C=O), 8.26 (d, J = 7.7 Hz, 1 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.9 (*C*H_2–CH_2), 32.0 (CH_2–*C*H_2), 126.1, 126.8, 126.9, 127.2, 128.2, 128.4, 128.9, 129.1, 129.3, 129.4, 129.8, 130.6, 131.0, 136.8 137.9, 142.5 (Ar, *C*-H, *C*H=*C*H-C=O), 127.6, 141.2 154.3 (quat. Ar), 185.9 (*C*=O). EI HRMS (70 eV); *m*/*z*: 334.13540 ($C_{25}H_{18}O$, M^+, 100%), 303.11571 ($C_{24}H_{15}$, 6.03%), 291.11611 ($C_{23}H_{15}$, 8.88%), 289.10206 ($C_{23}H_{13}$, 15.36%), 191.08568 ($C_{15}H_{11}$, 29.57%), 145.05347 (8.93%), 138.04589 ($C_{11}H_6$, 7.91%). $C_{25}H_{18}O$: calcd. 334.13577; found 334.13540.

4-(10,11-Dihydrodibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2-methoxy-2,5-dienone (8b): (1.91 g, 56%), m.p. 211.1–212.5 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1626 cm^{-1} (C=O), 1570, 1528, 1479, 1453, 1425, 1369, 1251, 1224, 1203, 1130, 1093, 1013. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (m, 2 H, CH_2–CH_2), 3.38 (m, 2 H, CH_2–CH_2), 3.67 (s, 3 H, OCH_3), 6.49 (d, J = 9.9 Hz, 1 H, CH=C*H*-C=O), 6.66 (d, J = 2.3 Hz, 1 H, C*H*=CH-C=O), 7.14–7.37 (m, 8 H, Ar-*H*), 7.45 (dd, J_1 = 2.4 Hz and J_2 = 9.9 Hz, 1 H, CH=C*H*-C=O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.7 (*C*H_2–CH_2), 32.8 (CH_2–*C*H_2), 55.5 (O*C*H_3), 109.2, 126.0, 128.5, 129.1, 129.3, 129.3, 129.9, 130.1, 130.4, 137.8 (Ar, *C*H, *C*H=*C*H-C=O), 129.5, 138.5, 138.62, 139.0, 139.1, 153.1, 157.8 (quat. Ar, CH=*C*H(OCH_3)-C=O), 181.49 (*C*=O). EI HRMS (70 eV); *m*/*z*: 314.13075 ($C_{22}H_{18}O_2$, M^+, 100%), 296.11856 ($C_{22}H_{16}O$, 4.90%), 283.11210 ($C_{21}H_{15}O$, 7.33%), 239.08481 ($C_{19}H_{11}$, 14.61%), 215.08521 ($C_{17}H_{11}$, 10.67%), 191.08568 ($C_{15}H_{11}$, 47.60%), 113.03875 (C_9H_5, 7.38%), 91.05501 (C_7H_7, 5.89%). $C_{22}H_{18}O_2$: calcd. 314.13068; found 314.13075.

4-(10,11-Dihydrodibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclohexa-2,6-dimethyl-2,5-dienone (8c): (2.43 g, 72%), m.p. 210.4–212.2 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1637 cm^{-1} (C=O), 1608, 1532, 1479, 1446, 1428, 1375, 1340, 1221, 1093, 1029, 916. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.0 (s, 6 H, CH_3), 2.91 (m, 2 H, CH_2-CH_2), 3.35 (m, 2 H, CH_2-CH_2), 7.15–7.37 (m, 10, Ar-*H*, C*H*=C*H*-C=O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2 (2 × *C*H_3), 32.7 (*C*H_2-*C*H_2), 126.0, 129.1, 129.7, 130.1, 134.4 [Ar, *C*H, *C*H=C(OCH_3)-C=O], 129.1, 136.4, 138.4, 139.2, 156.7 [quat. Ar, CH=*C*(OCH_3)-C=O], 187.8 (*C*=O). EI HRMS (70 eV); *m*/*z*: 312.15200 ($C_{23}H_{20}O$, M^+, 100%), 297.12657 ($C_{22}H_{17}O$, 37.91%), 269.13110 ($C_{21}H_{17}$, 10.26%), 253.10108 ($C_{20}H_{13}$, 10.64%), 191.08531 ($C_{15}H_{11}$, 17.43%), 126.04689 ($C_{10}H_6$), 91.05490 (C_7H_7, 2.20%). $C_{23}H_{20}O$: calcd. 312.15142; found 312.15200.

***O*-Dealkylation of Alcohols Substituted with Various *p*-Substituents on the Pendant 5-Phenyl Ring** (Schemes 2 and 7)

5-(4-Butyloxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**5b**), demethylated according to the general method, gave dienone **6** (1.52 g, 51%).

5-(4-Benzyloxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**5c**), gave **6** (1.72 g, 56%).

5-[(4-Chlorobenzyloxy)phenyl]-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**5d**), gave **6** (1.54 g, 50%).

5-(4-Allyloxyphenyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**15**), gave **14** (1.7 g, 56%).

Synthesis of Trityl Alcohols

(4-Methoxyphenyl)diphenylmethanol (11a): Alcohol **11a** had previously synthesized in these laboratories in 81% yield,[49] m.p. 54–56 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3597 cm^{-1} (OH, s), 3458 (OH, br), 1609, 1585. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.37 (s, 1 H, br, OH), 3.85 (s, 3 H, *p*-CH_3O), 6.94 (d, J = 8.3 Hz, 2 H, Ar-*H*), 7.32 (d, J = 8.5 Hz, 2 H, Ar-*H*), 7.41 (s, 10 H, Ar-*H*). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 57.4 (*p*-*C*H_3O), 83.9 (*C*OH), 115.4, 129.3, 130.0, 130.1, 131.5 (Ar, *C*-H), 141.5 (quat. Ar), 149.4 (quat. Ar), 160.8 (C=O). EI LRMS: *m*/*z*; 290 (M^+, 37.21%), 274 (12.01%), 273 (12.64%), 214 (18.94%), 213 (100.00%), 185 (10.88%), 135 (28.36%), 105 (56.97%), 77 (46.76%). EI HRMS (70 eV): $C_{20}H_{18}O_2$: calcd. 290.1307; found 290.1306.

(4-Methoxyphenyl)naphthalen-1-ylphenylmethanol (11b): 1-Bromonaphthalene (4.33 g, 20.9 mmol) in anhydrous THF (100 mL), magnesium (0.53 g, 21.9 mmol) and 4-methoxybenzophenone (3.0 g, 14.1 mmol), afforded pure **11b** (2.69 g, 56%) as a light brown gum which could not be induced to crystallize. IR ($CHCl_3$): $\tilde{\nu}$ = 3597 cm^{-1} (OH), 3415 (OH), 2838, 1607, 1582, 1509, 1395, 1297, 1179. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50 (s, 1 H, O*H*), 3.85 (s, 3 H, OCH_3), 6.80–8.35 (m, 16 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.7 (O*C*H_3), 83.5 (*C*-OH), 113.8, 124.7, 125.8, 126.0, 127.6, 128.2, 128.5, 128.6, 128.7, 129.3, 129.5, 129.8 (Ar *C*-H), 131.9, 135.4, 130.8, 142.8, 147.7, 159.0 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 340.14547 ($C_{24}H_{20}O_2$, M^+, 43.17%), 323.14366 ($C_{24}H_{19}O$, 32.65%), 263.10792 ($C_{18}H_{15}O_2$, 49.69%), 232.0878 ($C_{17}H_{12}O$, 100%), 213.09192 ($C_{14}H_{13}O_2$, 68.13%), 135.04488 ($C_8H_7O_2$, 63.13%), 105.03417 (C_7H_5O, 54.27%). $C_{24}H_{20}O_2$: calcd. 340.14633; found 340.14547. In a duplicate synthesis, compound **11b** was obtained as white crystals in 62% yield, m.p. 131–133 °C. This failure of the alcohol to crystallize may be explained in terms of enclathration of the solvent THF by the host alcohol in the procedure reported above.[49]

(4-Methoxyphenyl)phenyl(2,4,6-trimethylphenyl)methanol (11c): 1-Bromo-2,4,6-trimethylbenzene (Bromomesitylene) (6.97 g, 35.0 mmol) in THF (100 mL), magnesium (0.90 g, 36.8 mmol) and 4-methoxybenzophenone (5.0 g, 23.6 mmol) afforded **11c** (7.05 g, 99%) as a chromatographically homogeneous yellow gum. IR ($CHCl_3$): $\tilde{\nu}$ = 3598 cm^{-1} (OH), 3004, 2837, 1607, 1508, 1446, 1295. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.91 (s, 6 H, 2 × CH_3), 2.31 (s, 3 H, *p*-CH_3), 2.77 (s, 1 H, O*H*), 3.84 (s, 3 H, OCH_3), 6.87 (d, J = 9.6 Hz, 4 H, Ar-*H*), 7.16 (s, 1 H, Ar-*H*), 7.19 (s, 1 H, Ar-*H*), 7.24–7.45 (m, 5 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 21.6, 24.7 (3 × *C*H_3), 55.7 (O*C*H_3), 83.7 (quat. *C*-OH), 113.8, 127.3, 127.6, 128.2, 128.5, 128.9, 129.2, 129.5, 130.4, 131.7 (Ar, *C*H), 136.6, 138.1, 138.5, 140.4, 141.8, 148.3, 159.2 (quat. Ar). EI HRMS (70 eV); *m*/*z*: 332.17764 ($C_{23}H_{24}O_2$, M^+, 32.62%), 315.17417 ($C_{23}H_{23}O$, 20.39%), 300.15146 ($C_{22}H_{20}O$, 15.89%), 255.13822 ($C_{17}H_{19}O_2$, 34.59%), 213.09120 ($C_{14}H_{13}O_2$, 100%), 149.09616 ($C_{10}H_{13}O$, 38.40%), 147.08066 ($C_{10}H_{11}O$, 63.82%), 105.03397 (C_5H_7O, 43.15%), 77.03912 (C_6H_5, 32.95%). $C_{23}H_{24}O_2$: calcd. 332.17763; found 332.17764.

Synthesis of Trityl *p*-Quinone Methides (Fuchsones)

4-Benzhydrylidenecyclohexa-2,5-diene (**12a**) was obtained as yellow crystals, 56%, had identical m.p., IR and ^{1}H NMR spectra as reported.[63] In addition, it had the following mass spectroscopic data. EI LRMS: *m*/*z*; 258 (M^+, 100.00%), 229 (49.76%), 228 (25.72%), 215 (20.31%), 202 (14.54%), 181 (6.20%), 165 (6.29%), 152 (11.03%), 101 (12.38%), 77 (4.70%).– EI HRMS (70 eV): $C_{19}H_{14}O$: calcd. 258.1045; found 258.1049.

4-[Naphthalen-1-yl(phenyl)methylene]cyclohexa-2,5-dienone (12b): Yield 2.08 g, 62%, m.p. 169.0–170.0 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1628 cm^{-1} (C=O), 1512, 1443, 1381, 1174, 866. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.31 (d, J = 9.9 Hz, 1 H, CH=C*H*-C=O), 6.55 (d, J = 10.3 Hz, 1 H, CH=C*H*-C=O), 7.00 (d, J = 9.9 Hz, 1 H, CH=C*H*-C=O), 6.82–8.10 (m, 13 H, Ar-*H* and C*H*=CH-C=O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.4, 126.3, 126.8, 127.5, 128.9, 130.5,

130.4, 131.6, 139.0, 139.9 (Ar, *C*H), 129.66, 132.4, 134.1, 137.9, 140.1, 159.3 (quat. Ar, *C*H=*C*H-C=O), 187.7 (*C*=O). EI HRMS (70 eV); *m*/*z*: 308.12046 ($C_{23}H_{16}O$, M^+, 100%) 280.12195 ($C_{22}H_{16}$, 13.37%), 279.11693 ($C_{22}H_{15}$, 36.10%), 277.10041 ($C_{22}H_{16}$, 13.37%), 276.09346 ($C_{22}H_{12}$, 16.0%), 231.08096 ($C_{17}H_{11}O$, 17.09%). $C_{23}H_{16}O$: calcd. 308.12012; found 308.12046.

4-[Phenyl(2,4,6-trimethylphenyl)methylene]cyclohexa-2,5-dienone (12c): Yield 1.93 g, 56%, m.p. 122.5–124.7 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1628 cm^{-1} (C=O), 1607, 1511, 1443, 1379, 1222, 1168. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 6.38 (dd, J_1 = 2.5 Hz and J_2 = 10.5 Hz, 1 H, CH=C*H*-C=O), 6.43 (dd, J_1 = 2.5 Hz and J_2 = 10.6 Hz, 1 H, CH=C*H*-C=O), 6.95 (m, 3 H), 7.23–7.44 (m, 5 H, Ar-H, C*H*=CH-C=O), 7.80 (dd, J_1 = 2.5 Hz and J_2 = 10.6 Hz, 1 H, CH=C*H*-C=O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (*C*H_3), 21.5 (2 × *C*H_3), 128.8, 129.1, 129.4, 129.5, 130.4, 131.7, 138.6, 139.1 (Ar, *C*-H, *C*H=*C*H-C=O), 130.8, 136.4, 136.8, 138.5, 139.0, 160.1 (quat. Ar), 187.7 (*C*=O). EI HRMS (70 eV): *m*/*z*; 300.15235 ($C_{22}H_{20}O$, M^+, 100%), 285.12743 ($C_{21}H_{17}O$, 8.70%), 257.13253 ($C_{20}H_{17}$, 13.48%), 242.10970 ($C_{19}H_{14}$, 12.19%), 229.10072 ($C_{18}H_{13}$, 3.78%), 215.08573 ($C_{17}H_{11}$, 5.40%), 179.08496 ($C_{14}H_{11}$, 4.73%), 165.07029 ($C_{13}H_9$, 4.86%). $C_{22}H_{20}O$: calcd. 300.15142; found 300.15235.

Synthesis of 5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohept-5-ylium Perchlorate (9): 5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**5a**, 1.0 g, 3.2 mmol) in acetic anhydride (50 mL) was cooled and 70% perchloric acid added dropwise until no further precipitation occurred.[56] The brown precipitate was filtered, washed with anhydrous ether and dried under reduced pressure. Re-crystallization from nitromethane/ether/petroleum ether gave the dark-yellow perchlorate salt **9** (1.1 g, 83%). IR ($CHCl_3$): $\tilde{\nu}$ = 3017 cm^{-1}, 1611, 1393, 1326, 1208 (s), 1107, 777 (vs), 744 (vs), 670 (vs). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.24 (s, 4 H, CH_2CH_2), 4.44 (s, 3 H, OCH_3), 7.30 (d, J = 8.5 Hz, 2 H, Ar-*H*, 3′-H, 5′-H), 7.38–7.62 (m, 8 H, Ar-*H*), 8.41 (d, J = 8.4 Hz, Ar-*H*, 4-H, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.4 (*C*H_2), 60.8 (O*C*H_3), 121.2, 127.0, 131.1, 132.5 (Ar, *C*-H), 133.0 (quat. Ar), 133.9 (Ar, *C*-H), 138.1, 140.0 (quat. Ar), 149.5 (Ar, *C*-H), 181.8, 201.2 (quat. Ar). The salt **9** was used immediately in the demethoxylation step.

Reduction of 5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-ol (5a)

5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (10): 5-(4-Methoxyphenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**5a**, 5.0 g, 15.8 mmol) in 98% formic acid (100 mL) was treated with potassium carbonate (1.0 g), and the reaction mixture heated under reflux for 5 h and then cooled in ice. The precipitate was filtered, washed with cold water and re-crystallized from ethanol yielding **10** (2.47 g, 52%) as a white solid, m.p. 99.8–100.9 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3014 cm^{-1}, 1607, 1507, 1457, 1291, 1245, 1180, 1109, 1036, 853. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.75 (m, 2 H, CH_2-CH_2), 3.12 (m, 2 H, CH_2-CH_2), 3.77 (s, 3 H, OCH_3), 5.19 (s, 1 H, H-5), 6.70 (m, 4 H, Ar-*H*), 7.10–7.42 (m, 8 H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.6 (*C*H_2-*C*H_2), 57.6 (C-5), 58.0 (O*C*H_3), 113.0, 113.7, 126.5, 127.1, 127.6, 128.5, 128.6, 128.9, 130.3, 130.8, 131.2, 131.8 (Ar *C*H), 135.1, 138.1, 140.3, 140.9, 141.0, 158.0 (quat. Ar). EI HRMS (70 eV): *m*/*z*: 300.15136 ($C_{22}H_{20}O$, M^+, 50.07%), 298.13729 ($C_{22}H_{18}O$, 43.34%), 267.11657 ($C_{21}H_{15}$, 5.75%), 253.09925 ($C_{20}H_{13}$, 5.39%), 223.11145 ($C_{16}H_{15}O$, 15.42%), 193.09802 ($C_{15}H_{13}$, 48.01%), 192.09398 ($C_{15}H_{12}$, 100%), 165.07014 ($C_{13}H_9$, 11.33%), 77.03773 (C_6H_5, 3.14%). $C_{22}H_{20}O$: calcd. 300.15142; found 300.15136.

X-ray Crystallography: Crystallographic data for **14** are listed in Table 1. Intensity data were collected from a yellow, prismatic specimen mounted on a Nonius Kappa CCD diffractometer using Mo-*K*α radiation (λ = 0.71069 Å) with the crystal cooled in a stream of N_2 from a Cryostream cooler (Oxford Cryosystems, UK). The data-collection strategy indicated by the program COLLECT[64] involved suitable combinations of 1° φ- and ω-scans. Program DENZO-SMN[65] was used for cell refinement and data reduction. The structure was solved using program SHELXS86[66] and refined on F^2 with SHELXL97[67] with all non-hydrogens modelled anistropically. All H atoms were located in difference electron-density maps and were included in idealized positions in a riding model with isotropic thermal parameters equal to 1.2 times those of their parent atoms. In the final cycles of refinement, least-squares weights of the form $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.(F_o^2, 0) + 2F_c^2]/3$ were employed. Molecular parameters were calculated with PLATON[68] and program ZORTEP[69] was used for illustrations.

Table 1. Crystal data, data collection and refinement parameters for **14**.

Parameter	Value
Molecular formula	$C_{21}H_{14}O$
Molecular mass	282.32
Crystal size (mm)	0.40 × 0.30 × 0.25
Crystal system	monoclinic
Space group	$P2_1/c$
Temperature	173(2)
a [Å]	15.5662(3)
b [Å]	12.6808(2)
c [Å]	7.4708(1)
α [°]	90
β [°]	102.921(1)
γ [°]	90
V [Å^3]	1437.34(4)
Z	4
D_c [g cm^{-3}]	1.305
F(000)	592
μ [mm^{-1}]	0.079
2θ range [°]	1.27–27.48
Reflections collected/unique	8887/3306
R_{int}	0.018
Data completeness [%]	99.6
Max./min. transmission	0.9816/0.9692
Data/restraints/parameters	3306/0/199
Goodnessof-fit (*S*)	1.04
R [*F*, $I > 2\sigma(I)$]	0.0374
wR [F^2, all]	0.0994
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ [e·Å^{-3}]	0.18/–0.19

CCDC-186121 contains 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.

Supporting Information (see also the footnote on the first page of this article): Space-filling and stick models showing the packing in the crystal structure structure of **14**.

Acknowledgments

The authors thank the South African National Research Foundation and the Universities of Port Elizabeth and Cape Town for financial support and a bursary (J. H. T.). Thanks are also expressed

to Dr. P. Boshoff, Cape Technikon, for the recording of HRMS and Mr. H. Marchand for technical assistance.

[1] G. J. Leary, *Wood Sci. Technol.* **1980**, *14*, 21–24.
[2] D. C. Thompson, J. A. Thompson, M. Sugumaran, P. Moldéus, *Chem-Biol. Interact.* **1993**, *86*, 129–162.
[3] T. J. Monks, D. C. Jones, *Current Drug Metabolism* **2002**, *3*, 425–438.
[4] J. K. Myers, J. D. Cohen, T. S. Widlanski, *J. Am. Chem. Soc.* **1995**, *117*, 11049–11054.
[5] M.-R. Lee, K.-H. Baek, H. J. Jin, Y.-G. Jung, I. Shin, *Angew. Chem. Int. Ed.* **2004**, *43*, 1675–1678.
[6] J. L. Bolton, L. G. Valeno, Jr., J. A. Thompson, *Chem. Res. Toxicol.* **1992**, *5*, 816–822.
[7] B. D. Morris, M. R. Prinsep, *J. Org. Chem.* **1998**, *63*, 9545–9547.
[8] P. M. Dewick, *Medicinal Natural Products – A Biosynthetic Approach*, 2nd ed., John Wiley & Sons, **2002**, pp. 74, 77.
[9] I. C. Piña, M. L. Sanders, P. Crews, *J. Nat. Prod.* **2003**, *66*, 2–6.
[10] R. L. M. Allen, *Colour Chemistry*, Thomas Nelson & Sons, London, **1971**, p. 113.
[11] *The Merck Index, 12th ed.* (Ed.: S. Budavari), Merck & Co., Inc., Whitehouse Station, N. J., U. S. A., **1996**, pp. 705, 236, 610, 1604.
[12] D. C. Neckers, *J. Chem. Educ.* **1987**, *64*, 649–656.
[13] W. M. F. Fabian, S. Schuppler, O. S. Wolfbeis, *J. Chem. Soc., Perkin Trans. 2* **1996**, 853–856.
[14] T. Miura, Y. Urano, K. Tanaka, T. Nagano, K. Ohkubo, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 8666–8671.
[15] F. Pina, J. C. Lima, A. J. Parola, C. A. M. Afonso, *Angew. Chem. Int. Ed.* **2004**, *43*, 1525–1527.
[16] F. Pina, M. Measatri, V. Balzani, *J. Chem. Soc., Chem. Commun.* **1999**, 107–113.
[17] A. Levy, P. U. Biedermann, S. Cohen, I. Agranat, *J. Chem. Soc., Perkin Trans. 2* **2000**, 725–735.
[18] P. U. Biedermann, J. J. Stezowski, I. Agranat, *Eur. J. Org. Chem.* **2001**, 15–34.
[19] D. Villemin, M. Hachémi, M. Hammadi, *J. Chem. Res. (S)* **2003**, 260–261.
[20] C. Dugave, L. Demange, *Chem. Rev.* **2003**, *103*, 2475–2535.
[21] B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816.
[22] R. A. van Delden, N. Koumura, A. Schoevaars, A. Meetsma, B. L. Feringa, *Org. Biomol. Chem.* **2003**, *1*, 33–35.
[23] R. A. van Delden, M. K. J. ter Wiel, H. de Jong, A. Meetsma, B. L. Feringa, *Org. Biomol. Chem.* **2004**, *2*, 1531–1541.
[24] J. Zhou, A. Rieker, *J. Chem. Soc., Perkin Trans. 2* **1997**, 931–938.
[25] A. Bistrzycki, C. Herbst, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2333–2339.
[26] A. Baeyer, V. Villiger, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2774–2796.
[27] M. Gomberg, R. L. Jickling, *J. Am. Chem. Soc.* **1915**, *37*, 2575–2591.
[28] M. Wada, T. Watanabe, S. Natsume, H. Mishima, K. Kirishima, T. Erabi, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3233–3240.
[29] J. Velek, B. Kaitek, L. Musil, S. Vašicková, M. Souček, *Coll. Czech. Chem. Commun.* **1981**, *46*, 873–882.
[30] M. Racine-Weisbuch, *C. R. Acad. Sci. (Compt. Rend.), Ser. C* **1969**, *269*, 99–102.
[31] L. Musil, B. Koutek, J. Velek, M. Souček, *Coll. Czech. Chem. Commun.* **1984**, *49*, 1949–1964.
[32] L. Musil, B. Koutek, J. Velek, J. Krupička, M. Souček, *Coll. Czech. Chem. Commun.* **1983**, *48*, 2825–2839.
[33] L. Musil, B. Koutek, M. Pišová, M. Souček, *Coll. Czech. Chem. Commun.* **1981**, *46*, 1148–1159.
[34] B. Koutek, L. Musil, J. Velek, A. Lyčka, D. Šnobl, M. Synáčková, M. Souček, *Coll. Czech. Chem. Commun.* **1981**, *46*, 2540–2556.
[35] B. Koutek, M. Pišova, J. Krupička, A. Lyčka, D. Šnobl, M. Souček, *Coll. Czech. Chem. Commun.* **1982**, *47*, 1645–1653.
[36] N. Ashkenazi, A. Vigalok, S. Parthiban, Y. Ben-David, L. J. W. Shimon, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 8797–8798.
[37] O. Rabin, A. Vigalok, D. Milstein, *Chem. Eur. J.* **2000**, *6*, 454–462.
[38] H.-D. Becker, K. Gustafsson, *J. Org. Chem.* **1976**, *41*, 214–221.
[39] M. O. F. Goulart, J. H. P. Utley, *J. Org. Chem.* **1988**, *53*, 2520–2525.
[40] B. Föhlisch, P. Bürgle, D. Krockenberger, *Chem. Ber.* **1968**, *101*, 2717–2730.
[41] M. R. Jorgensen, C. W. McCleland, B. Taljaard, J. H. Taljaard, *J. Chem. Res. (S)* **2002**, 516–517.
[42] R. Weiss, *Org. Synth., Coll. Vol. 2*, John Wiley & Sons, New York, **1943**, p. 61.
[43] A. C. Cope, S. W. Fenton, *J. Am. Chem. Soc.* **1951**, *73*, 1673–1678.
[44] W. Treibs, H. J. Klinkhamer, *Chem. Ber.* **1951**, *84*, 671–679.
[45] M. Gomberg, L. H. Cone, *Justus Liebigs Ann. Chem.* **1909**, *370*, 142–208.
[46] R. L. Shriner, C. N. Wolf, *J. Am. Chem. Soc.* **1951**, *73*, 891–894.
[47] H. Hart, K. Harada, C-J. F. Du, *J. Org. Chem.* **1985**, *50*, 3104–3110.
[48] K. Šindelář, J. Holubek, E. Svátek, O. Matoušova, J. Metyšová, J. Metyšová, M. Protiva, *J. Heterocyclic Chem.* **1989**, *26*, 1325–1330.
[49] B. Barton, Ph. D. Thesis, Host-guest chemistry: The synthesis and assessment of host compounds based on the 9-arylxanthenyl and related systems, University of Port Elizabeth, South Africa, **1996**.
[50] B. Barton, M. R. Caira, C. W. McCleland, B. Taljaard, *J. Chem. Crystallogr.* **1999**, *29*, 1179–1186.
[51] B. Barton, M. R. Caira, C. W. McCleland, B. Taljaard, *J. Chem. Soc., Perkin Trans. 2* **2000**, 865–869.
[52] K. Albert, A. Rieker, *Chem. Ber.* **1977**, *110*, 1804–1822.
[53] S. V. McKinley, P. A. Grieco, A. E. Young, H. H. Freedman, *J. Am. Chem. Soc.* **1970**, *92*, 5900–5907.
[54] S. V. McKinley, J. W. Rakshys, Jr., A. E. Young, H. H. Freedman, *J. Am. Chem. Soc.* **1971**, *93*, 4715–4724.
[55] C.-T. Chen, S.-D. Chao, K.-C. Yen, C.-H. Chen, I.-C. Chou, S.-W. Hon, *J. Am. Chem. Soc.* **1997**, *119*, 11341–11342.
[56] H. J. Dauben, Jr., L. R. Honnen, K. M. Harmon, *J. Org. Chem.* **1960**, *25*, 1442–1445.
[57] M. R. Jorgensen, Ph. D. Thesis, Studies on 11-aryl-11-azido-6,11-dihydrodibenz[*b*,*e*]oxepins and their sulfur analogues, University of Port Elizabeth, South Africa, **1998**.
[58] W. Coyne, J. W. Cusic, *J. Med. Chem.* **1974**, *17*, 72–75.
[59] W. Tochtermann, K. Oppenländer, U. Walter, *Chem. Ber.* **1964**, *97*, 1318–1328.
[60] W. Tochtermann, K. Oppenländer, U. Walter, *Chem. Ber.* **1964**, *97*, 1329–1336.
[61] M. Nógrádi, *Acta Chim. Acad. Sci. Hung.* **1978**, *96*, 393–404.
[62] G. Berti, A. Da Settimo, *Ann. Chim. (Rome)* **1959**, *49*, 1237–1252.
[63] T. W. Lewis, D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1979**, *101*, 5717–5725.
[64] *COLLECT* data collection software: **2000**, Nonius BV, Delft, The Netherlands.
[65] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[66] G. M. Sheldrick, *SHELXS86*, in: *Crystallographic computing 3* (Eds.: M. Kruger, R. Goddard), Oxford, UK: Oxford University Press, **1985**, 175–178.
[67] G. M. Sheldrick, *SHELXL-97*, **1997**, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[68] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
[69] L. Zsolnai, H. Pritzkow, *ZORTEP*: **1994**, *ORTEP program for personal computer*, University of Heidelberg, Germany.

Received: October 22, 2004

