PERKIN 1

Reactions of triene-conjugated diazo-compounds: reaction paths from *o*-(1,3-dienyl)aryldiazomethanes to 3,8-methano-1,2-diazocines and to pyrrolo[2,1-*a*]phthalazines *via* intramolecular (3 + 2) and 1,1-cycloaddition reactions

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The reaction paths followed by the triene-conjugated diazo-compounds **7**, which have α,β aromatic and γ,δ; ε,ζ olefinic unsaturation, depend strongly on the nature of the substituents R^1 and R^2. Those with $R^1,R^2 = (CH_2)_3$, **7a**–**e**, react at room temperature *via* an intramolecular (3 + 2) cycloaddition reaction of unprecedented regioselectivity to give the bridged benzodiazocines **18a**–**e** in high yield. Those with R^1 = Me and R^2 = Ph, **7f** and **7g**, react at 80 °C to give the hydrocarbons **19f**,**g** and, *via* new chemistry, the pyrrolo[2,1-*a*]phthalazines **24f**,**g**. The structures of compounds **18a**, **19a** and **24f** have been determined by X-ray crystallography.

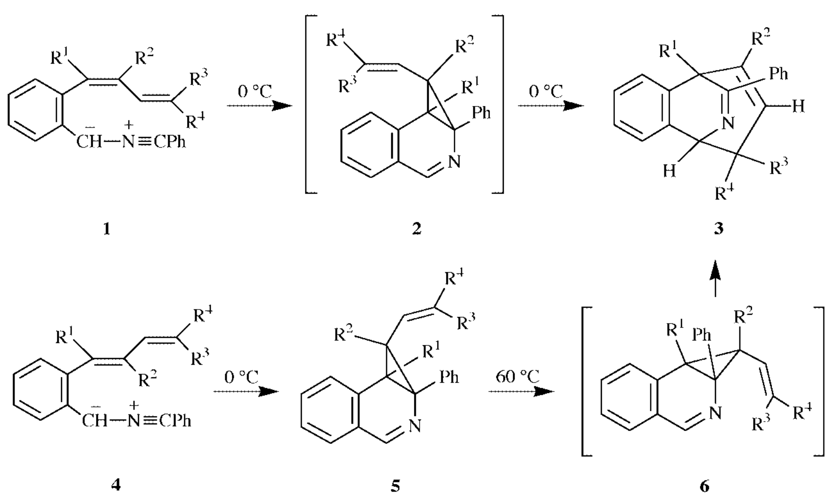
Introduction

We have recently reported the first investigations into the reactions of triene-conjugated 1,3-dipolar intermediates. This work[1] was done on nitrile ylides **1** and **4** which, with either a *cis* or *trans* γ,δ bond, react to give 1,4-prop[2]enoisoquinolines **3**. The first step in both cases is a stereospecific 1,1-cycloaddition reaction to give cyclopropa[*c*]isoquinolines in which the *cis* reactants **1** give the *endo* isomers **2** and the *trans* reactants **4** give the *exo* isomers **5** (Scheme 1). The *endo* isomers rearrange spontaneously at 0 °C *via* an aza-Cope rearrangement to give **3**, while the latter, **5**, are stable at room temperature because of their stereostructure but isomerise on heating to give **3** *via* **6**.

This work is of interest because it provides an easy route to the bridged isoquinoline system **3** which has the basic skeleton of the isopavine alkaloids and because the methodology could, in principle, be extended to similar non-natural analogues which incorporate other heteroatoms. One way of achieving this would be to utilise other 1,3-dipolar moieties in place of the nitrile ylide and the objective of the work reported here was to study the reactions of the analogous triene-conjugated diazo-compounds **7**. As in the cases of **1** and **4**, many possible intramolecular 1,3-dipolar reaction paths are possible *via* either electrocyclisation or cycloaddition reactions but here there is the added possibility of carbene reactions *via* loss of nitrogen. Diazo compounds are formally similar to nitrile ylides in structure and in many aspects of their chemistry and the reactions of **7** could in principle lead to **9**, the diaza analogue of **3**, *via* **8** (Scheme 2). Diazo compounds are known to react in some 1,1-cycloaddition reactions[2a–c] but in general this is a less favoured mode of reaction than it is for nitrile ylides and nitrile imines. Thus, in the reactions of the diene-conjugated systems **10** to give 2,3-benzodiazepines **12**,[3] species such as **13** have never been detected although they could in principle be in equilibrium with the quinonoid intermediates **11**, and indeed studying the chemistry of **7** would provide a test for the accessibility of **13**. At the outset therefore it was impossible to make an accurate prediction of the preferred reaction path for **7** and so an exploratory investigation was undertaken.

Results and discussion

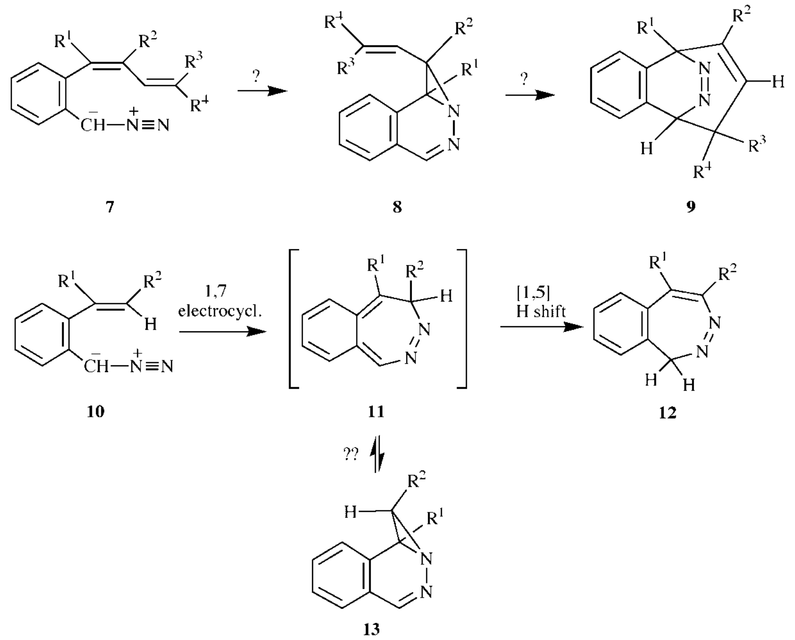
All the work in this paper is concerned with the reactions of the γ,δ-*cis* triene systems **7** (substituents identified in Table 1). They



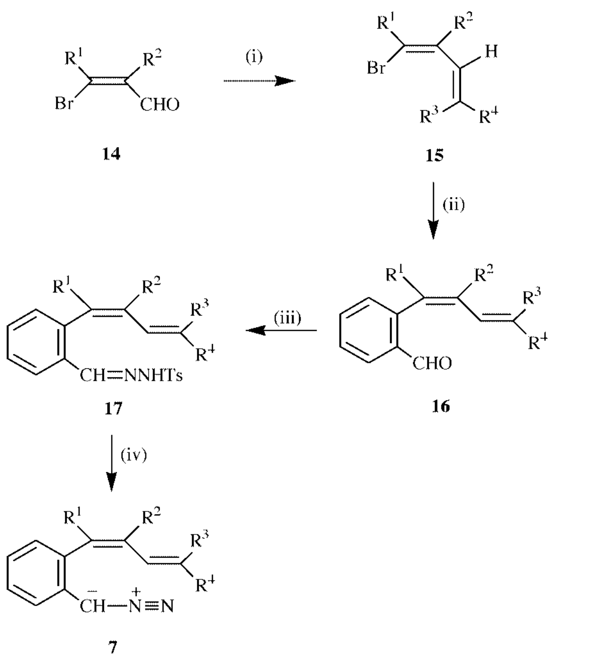
Scheme 1

Table 1 Identification of substituents for structures **7**, **15**–**19**, **24**

Compound							R^1	R^2	R^3	R^4
7a	**15a**	**16a**	**17a**	**18a**	**19a**		–$(CH_2)_3$–		H	Ph
7b	**15b**	**16b**	**17b**	**18b**			–$(CH_2)_3$–		H	H
7c	**15c**	**16c**	**17c**	**18c**			–$(CH_2)_3$–		H	Me
7d	**15d**	**16d**	**17d**	**18d**			–$(CH_2)_3$–		Me	Me
7e	**15e**	**16e**	**17e**	**18e**			–$(CH_2)_3$–		H	CO_2Me
7f	**15f**	**16f**	**17f**		**19f**	**24g**	Me	Ph	H	Ph
7g	**15g**	**16g**	**17g**		**19g**	**24g**	Me	Ph	H	*p*-Me-C_6H_4
7h	**15h**	**16h**	**17h**		**19h**		–$(CH_2)_4$–		H, Ph (*E*/*Z* mixture)	



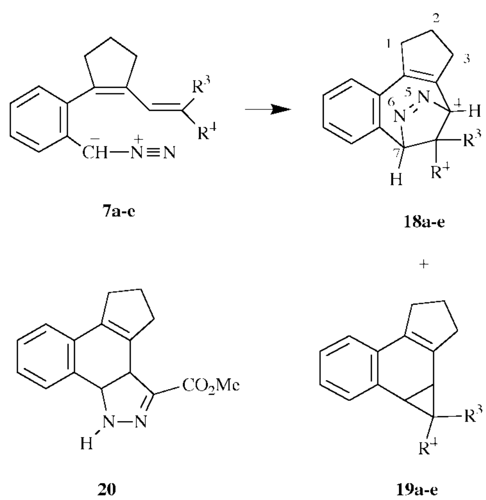
Scheme 2



Scheme 3 *Reagents*: i, $R^3R^4CH_2P^+Ph_3$ X^- or $R^3R^4CH_2P(O)(OEt)_2$/base; ii, 2-formylphenylboronic acid/Pd$(PPh_3)_4$/Na_2CO_3; iii, $TsNHNH_2$/H^+; iv, Na salt in DME.

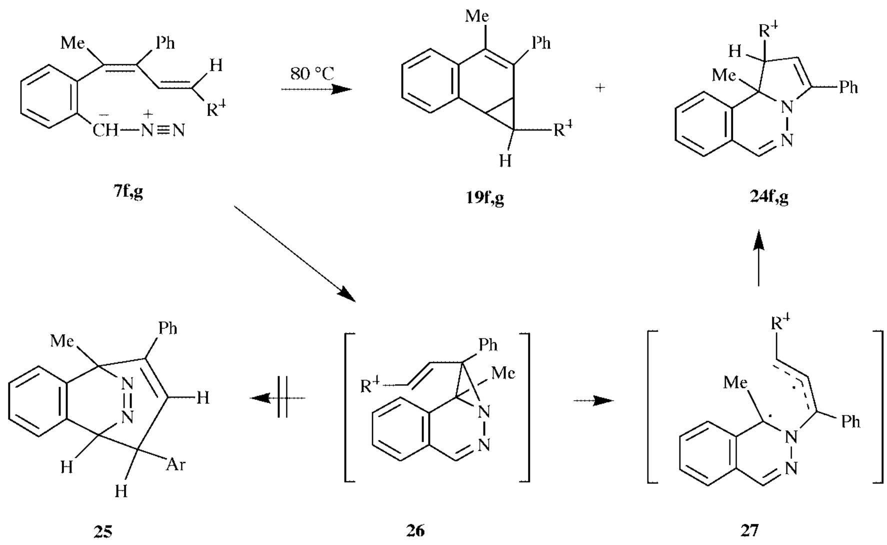
were generated, as in earlier work,[3] by the thermal decomposition of the tosylhydrazone sodium salts **17** under aprotic conditions in 1,2-dimethoxyethane (DME) as solvent (Scheme 3). The aldehydes **16** were prepared by Suzuki coupling reactions of 2-formylphenylboronic acid with the appropriate bromodiene **15**. The bromodienes were prepared *via* Arnold's bromoformylation reaction[4a,b] of ketones to give the bromoacryl aldehydes **14** and subsequent Wittig or Wadsworth–Emmons olefination.

The reaction paths followed by the diazo-compounds were split clearly into two types, that taken by reactants **7a**–**e** which have a cyclopentyl ring fused at the γ,δ position, shown in Scheme 4, and that followed by the others, shown in Scheme 5.



Scheme 4

The reactants **7a**–**e** gave products of three types, the bridged benzodiazocines **18** and the hydrocarbons **19**, and, for **7e** only, the indazole **20**. The product yields are shown in Table 2. It can



Scheme 5

Table 2 Product yields

Reactant	Temp./°C	Product yields (%) 18	19	20	24
17a	80	27	46		
17a	RT	67	19		
17b	RT	86			
17c	RT	75			
17d	RT	88			
17e	RT	28		59	
17f	RT/80		54		22
17g	RT/80		49		21
17h	80		59		

be seen that the bridged benzodiazocines **18** were the sole or major products from **7a–d** when the reactions were carried out at room temperature. These represent a new heterocyclic system and the identity of compound **18a** was confirmed by X-ray crystallography (Fig. 1). The structures of **18b–e** followed from comparison of their ^{1}H and ^{13}C NMR spectra and their mass spectra with those of **18a**. The ^{1}H NMR spectra of **18a–c,e** were at first sight unusual in that no coupling was seen between the protons on C-4 and C-7 and the bridgehead proton *trans* to the azo group ($R^3 = H$) but in **18b** (R^3, $R^4 = H$) the other bridgehead proton was coupled strongly (*J* 7–8 Hz). This confirms that in **18c,e** the hydrogen atoms at C-4 and C-12 have the same relative stereochemistry as in **18a** (Fig. 1). The first reaction to generate **7a** was carried out by heating the tosylhydrazone salt at *ca.* 80 °C in DME as solvent, *i.e.* at the usual temperature required to induce thermal decomposition of the salt. This gave **18a** (27%) and **19a** (46%), whose structure was also confirmed by X-ray crystallography (Fig. 2). In principle the latter could be formed either by loss of nitrogen from **7a** followed by intramolecular carbene addition to the terminal double bond, or *via* the extrusion of nitrogen from **18a**. The viability of the second pathway was shown by a control experiment, monitored by NMR, which showed that **18a** readily extrudes nitrogen at this temperature to give **19a** as the only product. In an attempt to minimise this thermolysis the reaction temperature for the decomposition of the tosylhydrazone salt was progressively reduced and, surprisingly, it was found that the reaction was complete in *ca.* 48 h at room temperature to give **18a** in enhanced yield (67%). It is most unusual for a tosylhydrazone salt to decompose at this low temperature and its occurrence must be ascribed primarily to steric acceleration due to the bulky *ortho* substituent and perhaps also to the effect of the diene conjugation in stabilising the resulting diazo-

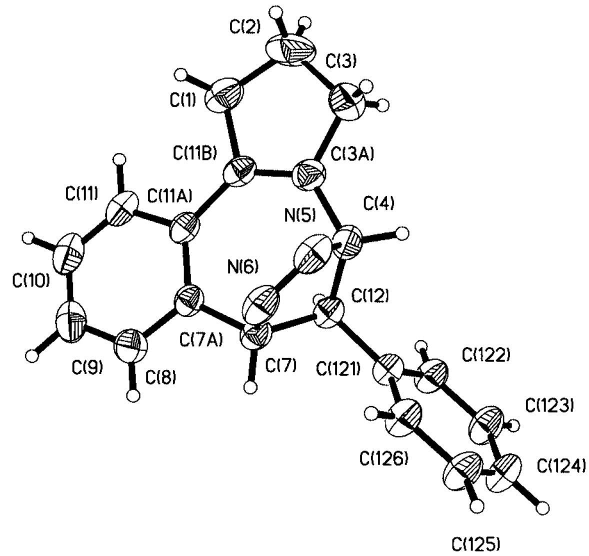


Fig. 1 Crystal structure of compound **18a**.

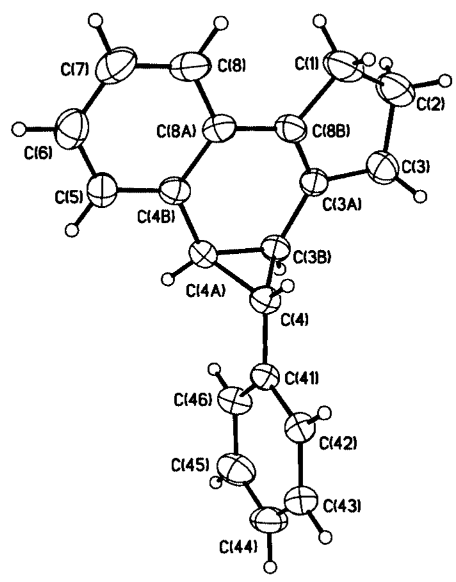
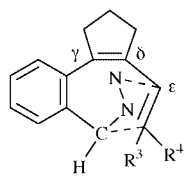


Fig. 2 Crystal structure of compound **19a**.

compound. In support of this argument it is notable that the decomposition temperature of trisylhydrazone salts[5] (trisyl = 2,4,6-triisopropylphenylsulfonyl) is markedly reduced by the bulk of the 2,4,6-triisopropylbenzenesulfonyl group. The subsequent generation of **7b–d** was carried out at room temperature and these reactions gave **18b–d** as the only isolated products in high yields (Table 2). In all of these cases the diazo-compounds **7a–e** were not present in detectable concentration during the reaction but reacted as they were formed.

The most straightforward interpretation of these results is that the products **18** were formed by concerted (3 + 2) cycloaddition reactions *via* a helical transition state as illustrated in structure **21**. This is consistent with the retention of the relative



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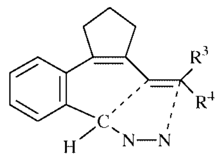

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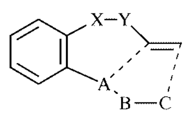


23

stereochemistry at the reaction sites for the cyclisation of **7a**,**c** and **e**. However it was unexpected that the cycloaddition should show this regioselectivity rather than that in structure **22**. This was primarily because all previous examples of the cycloadditions of propargyl-allenyl† 1,3-dipoles in systems such as **23** have reacted with the regioselectivity shown[6] and also because, in intermolecular reactions of diazo-compounds, monosubstituted alkenes react with the opposite regioselectivity to that observed here for **7b**. In this work the only example to show some reaction *via* the expected regioselectivity was **7e** which gave **20** as the major product (59%) together with **18e** (R^3 = H, R^4 = CO_2Me) (28%). Compound **20** was identified primarily from the similarity of its NMR spectra to those of the corresponding nitrile ylide adduct.[1] It would appear that the strong activating and regio-directing effect of the methoxycarbonyl group[6] serves to selectively stabilise transition state **22**.

Only three examples of analogues which lack the cyclopentenyl ring in the γ,δ position have been studied, **7f**,**g** and **h**. The reactions of **7f**,**g** (R^4 = Ph and *p*-tolyl respectively) are shown in Scheme 5. They proved to be quite different from those discussed above in that the tosylhydrazone salts, when subjected to the same reaction conditions (stirring in DME at room temperature for 48 h), did not give cycloadducts analogous to **18** and **20** but gave only the diazo-compounds **7f**,**g** in virtually quantitative yield. On heating at 80 °C in DME the diazo-compounds decomposed (Scheme 5) to give the cyclopropanaphthalenes **19f**,**g** as the major products (54 and 49%) and the pyrrolo[2,1-*a*]phthalazines **24f**,**g** (22 and 21%). The former are the expected carbene addition products but the reaction path to the pyrrolophthalazines **24f**,**g** is new. The reaction was carried out first with **7f** (R^4 = Ph) and the identity of the product as **24f** (R^4 = Ph) was confirmed by X-ray crystallography (Fig. 3). Having seen the unusual nature of the product, it seemed important for mechanistic reasons to be able to differentiate between the two phenyl groups in **24f** so the reaction was repeated with **7g** (R^4 = *p*-tolyl) with the result shown. The most likely reaction mechanism involves a two-step process, firstly 1,1-cycloaddition to give **26** as the primary product which subsequently rearranges as shown to give **24**. Analogous rearrangements of simpler vinylaziridines are well known[7,8] but usually require more forcing conditions. That **26** should rearrange to give **24** rather than take the expected aza-Cope route to give **25** is probably because the latter is thermodynamically disfavoured by the presence of the low bond-energy azo-group. A 1,1-cycloaddition reaction leading directly from **7** to **26** is proposed here, rather than an indirect route analogous to **10**→**11**→**13**, because of earlier work[3] which

† IUPAC name for propargyl is prop-2-ynyl.

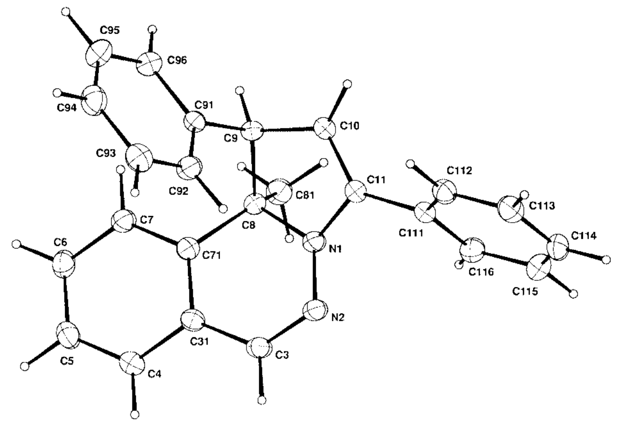
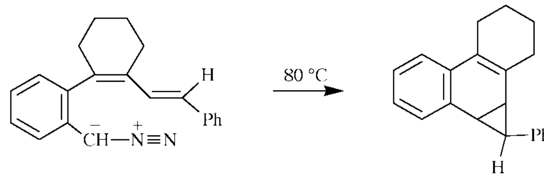


Fig. 3 Crystal structure of compound **24f**.

showed that 1,7-electrocyclisation of diazo-compounds is strongly inhibited by *cis* substituents on the δ carbon atom which are larger than a hydrogen atom. This chemistry thus provides the first evidence for the occurrence of a 1,1-cycloaddition reaction in systems of this type.

The analogue **7h** with a cyclohexene ring in the γ,δ position also showed a different pattern of reactivity to the analogues **7a–e** containing a cyclopentene ring. On reaction at room temperature, **7h** gave a mixture of products which could not be separated, but whose NMR spectrum indicated the absence of a cycloadduct analogous to **18**. Reaction at 80 °C gave only the hydrocarbon product **19h** (Scheme 6), in moderate yield (59%).



Scheme 6

Comparing the results for the diazo-compounds **7a–e** (Scheme 4), which cyclise rapidly at room temperature to give **18**, with those for **7h** (Scheme 6), which does not undergo a similar reaction, and **7f**,**g** (Scheme 5), which are stable at room temperature, it is clear that the presence of the cyclopentene ring in **7a–e** serves in some way to expedite the cycloaddition reaction *via* the transition state **21**. This effect is reminiscent of earlier observations when it was shown that the presence of a cyclopentene ring had a profound effect on 1,5- *vs*. 1,7-*peri*-selectivity in electrocyclisation reactions.[9] The use of Dreiding models shows that, as noted in the earlier work, the presence of the cyclopentene ring has the effect of expanding the exocyclic bond angles at the γ and δ positions. On a simple model this brings the ε atom of the alkene in **21** closer to the terminal N of the diazo group and takes it further away from the C of the diazo group in **22**. This probably provides the basis for rationalising the unique reactivity and regioselectivity observed in the reactions of **7a–e**, but a detailed explanation is not possible without modelling calculations of the two transition states.

Experimental

All proton NMR spectra were run at 250 MHz and all carbon NMR spectra at 62.9 MHz using $CDCl_3$ as solvent unless otherwise stated. Chemical shifts are recorded as δ values; *J* values are given in Hz. In the ^{13}C spectra carbon multiplicity was established by single frequency off-resonance decoupling or by DEPT. Mass spectra were obtained using electron ionisation at 70 eV unless otherwise stated. Preparative chromatography[10] was carried out on silica gel by the flash column method (Merck Kieselgel 60, 230–400 mesh), the 'dry-column flash' method (15 µm, Fluka Kieselgel G) or the 'medium pressure' (MPLC) technique using 100 × 2.5 cm columns (Merck Kieselgel 60, 230–400 mesh), and eluting solvents based on hexane admixed with ether or ethyl acetate. Ether refers to diethyl ether. 'Evaporation' of solvents indicates evaporation under reduced pressure using a rotary evaporator. All drying of solutions was done with anhydrous magnesium sulfate. Tetrahydrofuran (THF) was distilled from sodium and benzophenone as required. Ether was dried over sodium wire. 1,2-Dimethoxyethane (DME) was passed through a column of activated alumina and stored over molecular sieves 4 Å.

Preparation of the bromodienes 15a–h

(*E*)- and (*Z*)-3-Bromo-2-phenylbut-2-enal,[4] 1-bromo-2-formylcyclopentene,[4] 1-bromo-2-formylcyclohexene,[4] (*E*,*E*)-4-bromo-1,3-diphenylpenta-1,3-diene[4] **15f** and (*E*)-1-bromo-2-(2-phenylethenyl)cyclopentene[4] **15a**, 1-bromo-2-(2-phenylethenyl)cyclohexene **15h** as a mixture of (*E*) and (*Z*) isomers,[4] methyl 3-(2-bromocyclopent-1-enyl)propenoate[1] **15e** were prepared by known routes.

1-Bromo-2-ethenylcyclopentene 15b. *n*-Butyllithium (16.5 cm^3, 2.6 M in hexanes, 34.4 mmol) was added dropwise at 0 °C to a suspension of methyltriphenylphosphonium bromide (12.31 g, 34.5 mmol) in ether (100 cm^3). The reaction was stirred for 1 h at 0 °C and then a solution of 1-bromo-2-formylcyclopentene (6 g, 34.5 mmol) in ether (10 cm^3) was added. The mixture was stirred for 1 h at 0 °C, then 2 h at room temperature. Hydrolysis with ammonium chloride solution (10% w/v, 150 cm^3) and an extractive work up with ether (2 × 150 cm^3) gave, after evaporation of the solvent, a brown oil. Flash chromatography (silica, hexane 100%) gave 1-bromo-2-ethenylcyclopentene (2.4 g, 41%) as a colourless oil (Found: $(M + 1)^+$, 172.9950, 174.9941. $C_7H_9{}^{79}Br$ and $C_7H_9{}^{81}Br$ require $(M + 1)^+$, 172.9966, 174.9945); δ_H 1.65–1.77 (m, 2 H, CH_2), 2.23–2.29 (m, 2 H, CH_2), 2.58–2.64 (m, 2 H, CH_2), 5.12 (d, 1 H, CH, *J* 11.0), 5.26 (d, 1 H, CH, *J* 17.5), 6.88 (dd, 1 H, CH, *J* 17.5 and 11.0); δ_C 21.9 (CH_2), 26.6 (CH_2), 37.4 (CH_2), 114.7 (olefinic CH_2), 124.9, 132.1 (quaternary (quat.) olefinic), 136.9 (olefinic CH); *m*/*z* (FAB) 175 ($^{81}Br(M + 1)$, 41%), 173 ($^{79}Br(M + 1)$, 41), 115 (15), 95 (32), 81 (20), 79 (17), 55 (100).

1-Bromo-2-(prop-1-enyl)cyclopentene as a 2:1 mixture of (*E*) and (*Z*) isomers 15c. *n*-Butyllithium (16.82 cm^3, 2.05 M in hexanes, 34.48 mmol) was added dropwise to a suspension of ethyltriphenylphosphonium bromide (12.80 g, 34.48 mmol) in ether (100 cm^3). The reaction was stirred for 1 h at 0 °C and then a solution of 1-bromo-2-formylcyclopentene (6 g, 34.48 mmol) in ether (10 cm^3) was added and the reaction was stirred for 1 h at 0 °C, then 4 h at room temperature. The usual work up gave a yellow oil. Flash chromatography (silica, hexane) gave a mixture of (*E*)- and (*Z*)-1-bromo-2-(prop-1-enyl)cyclopentene (3.52 g, 55%) which could not be separated (Found: M^+, 186.0041, 188.0021. $C_8H_{11}{}^{79}Br$ and $C_8H_{11}{}^{81}Br$ require M^+, 186.0044, 188.0024); δ_H 1.75 (br d, 3 H, CH_3, *J* 6.6), 1.9–2.0 (m, 2 H, CH_2), 2.3–2.4 (m, 2 H, CH_2), 2.65–2.75 (m, 2 H, CH_2), 5.4–5.75 (m, 2′-H), 6.07 [br d, 1′-H ((*Z*) isomer), *J* 11.4], 6.29 [br d, 1′-H ((*E*) isomer), *J* 15.8] (*E*:*Z* ratio 2:1); δ_C 14.2, 16.4 (CH_3), 21.4, 22.3 (CH_2), 33.5, 36.4 (CH_2), 39.0, 40.1 (CH_2), 124.4, 125.6 (olefinic CH), 136.5, 136.7, 136.3, 137.8 (quat. olefinic CH); *m*/*z* (FAB) 188 ($^{81}Br(M)$, 42%), 186 ($^{79}Br(M)$, 43), 145 (52), 115 (67), 81 (49), 79 (51), 55 (100), 41 (78).

1-Bromo-2-(2-methylprop-1-enyl)cyclopentene 15d. Potassium *tert*-butoxide (3.86 g, 34.48 mmol) in dry THF (10 cm^3) was added dropwise to a suspension of isopropyltriphenylphosphonium iodide (14.9 g, 34.48 mmol) in dry THF (100 cm^3) at 0 °C. The reaction was stirred at 0 °C for 1 h and then a solution of 1-bromo-2-formylcyclopentene (6 g, 34.48 mmol) in THF was added and the mixture was stirred at room temperature for 4 h. The usual work up gave a brown oil. Flash chromatography (silica (Brockmann grade 3), hexane), gave 1-bromo-2-(2-methylprop-1-enyl)cyclopentene (4.1 g, 59%) as a colourless oil (Found: M^+ 200.0210, 202.0179. $C_9H_{13}{}^{79}Br$ and $C_9H_{13}{}^{81}Br$ require M^+ 200.0201, 202.0181); δ_H 1.80 (s, 3 H, CH_3), 1.82 (s, 3 H, CH_3), 1.90–2.01 (m, 2 H, CH_2), 2.57–2.66 (m, 4 H, CH_2), 5.95 (s, 1 H, olefinic CH); δ_C 19.7 (CH_3), 22.3 (CH_2), 27.6 (CH_3), 34.2 (CH_2), 39.4 (CH_2), 120.1 (olefinic CH), 118.8, 136.7, 137.4 (quat. olefinic); *m*/*z* (FAB) 202 (^{81}BrM, 49%) 200 (^{79}BrM, 50), 146 (76), 122 (54), 81 (87), 79 (94), 57 (100).

(*E*,*E*)-4-Bromo-1-(*p*-tolyl)-3-phenylpenta-1,3-diene 15g. *n*-Butyllithium (8.37 cm^3, 1.6 M in hexanes, 13.39 mmol) was added dropwise to a stirred suspension of 4-methylbenzyltriphenylphosphonium chloride (5.39 g, 13.39 mmol) in ether (50 cm^3) at 0 °C. The mixture was stirred for 1 h at 0 °C and then a solution of (*Z*)-3-bromo-2-phenylbut-2-enal (3 g, 13.39 mmol) in ether (10 cm^3) was added and the mixture was stirred for 1 h at 0 °C and then 3 h at room temperature. The usual work up gave a brown oil. Flash chromatography (silica, hexane 100%) gave the product as a colourless oil which on distillation gave (*E*,*E*)-4-bromo-1-(*p*-tolyl)-3-phenylpenta-1,3-diene (2.49 g, 59%) as colourless crystals, mp 61–62 °C (pentane) (Found: $(M + 1)^+$, 312.0516, 314.0486. $C_{18}H_{17}{}^{79}Br$ and $C_{18}H_{17}{}^{81}Br$ require $(M + 1)^+$, 312.0514, 314.0493); δ_H 2.24 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 6.01 (d, 1 H, CH, *J* 16.0), 7.09–7.47 (m, 9 H, aromatic CH), 7.51 (d, 1 H, CH, *J* 16.0); δ_C 21.1 (CH_3), 27.2 (CH_3), 126.5, 127.3, 128.3, 129.1, 129.4, 129.5, 134.1 (olefinic and aromatic CH), 122.6, 134.3, 137.5, 138.1, 138.9 (quat. olefinic and aromatic); *m*/*z* 314 ($^{81}Br(M)$, 58%), 312 ($^{79}Br(M)$, 58), 265 (59), 233 (100), 115 (30), 105 (28), 91 (90); ν_{max} (thin film)/cm^{-1} 1600 (diene).

Preparation of the 2-(1,3-dienyl)benzaldehydes 16a–f and their *p*-tosylhydrazones 17a–f

These compounds were prepared by the Suzuki coupling reactions of 2-formylphenylboronic acid with the appropriate bromodiene (Scheme 1). The *p*-tosylhydrazone derivatives were prepared, as in earlier work,[3] by the admixture of warm (40 °C) ethanolic equimolar solutions of the aldehyde and toluene-*p*-sulfonylhydrazide. The reaction mixtures were kept at 40 °C for 1 h then at room temperature overnight and then worked up. The methods are given in detail for the first example.

(*E*)-2-[2-(2-Phenylethenyl)cyclopentenyl]benzaldehyde 16a. A mixture of (*E*)-1-bromo-(2-phenylethenyl)cyclopentene **15a** (0.82 g, 3.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.115 g, 0.099 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.36 g, 3.5 mmol) and 2-formylphenylboronic acid (0.5 g, 3.3 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 1 h. The solvent was removed *in vacuo* and water (30 cm^3) was added. This mixture was extracted with DCM (3 × 50 cm^3) and the combined organic layers were dried and then passed through a pad of alumina. The solvent was removed *in vacuo* to give a yellow solid. Crystallisation gave (*E*)-2-[2-(2-phenylethenyl)cyclopentenyl]benzaldehyde (0.89 g, 91%), mp 102–103 °C from hexane (Found: C, 87.7; H, 6.6%. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); δ_H 2.04–2.19 (m, 2 H, CH_2), 2.81–2.99 (m, 4 H, CH_2), 6.54 (d, 1 H, =CH, *J* 16), 6.64 (d, 1 H, =CH, *J* 16), 7.11–8.02 (m, 9 H, aromatic CH), 10.02 (s, 1 H, CHO); δ_C 22.4 (CH_2), 33.3 (CH_2), 40.8 (CH_2), 122.7, 126.3, 127.4, 127.5, 127.6, 128.4, 129.7, 131.4, 133.7 (olefinic and aromatic CH), 134.1, 137.2, 138.1, 140.8, 142.3 (quat. olefinic and aromatic), 192.1 (CHO); ν_{max} (Nujol)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17a**. A solution of *p*-tosylhydrazide (0.36 g, 1.93 mmol) in ethanol (10 cm^3) was added to a solution of the aldehyde **16a** (0.5 g, 1.82 mmol) in ethanol (10 cm^3). The reaction mixture was heated at 40 °C for 1 h then cooled to room temperature and stirred for 12 h. The solvent was removed *in vacuo* to give a yellow oil. MPLC (silica, hexane–ether, 60:40) gave the *p*-tosylhydrazone **17a** as a colourless solid (0.57 g, 71%), mp 118–120 °C (hexane–ether) (Found: C, 73.3; H, 6.3; N, 6.2%; $(M + 1)^+$, 443.1792. $C_{27}H_{26}N_2SO_2$ requires C, 73.3; H, 5.9; N, 6.3%; $(M + 1)^+$, 443.1793); δ_H 2.04 (quin., 2 H, CH_2, *J* 7.4), 2.32 (s, 3 H, CH_3), 2.67–2.80 (m, 4 H, CH_2), 6.47 (d, 1 H, CH, *J* 16.0), 6.55 (d, 1 H, CH, *J* 16.0), 7.11–7.94 (m, 13 H, aromatic CH), 8.16 (br s, 1 H, NH); δ_C 21.4 (CH_3), 22.2 (CH_2), 33.0 (CH_2), 40.3 (CH_2), 123.2, 126.1, 126.2, 127.2, 127.6, 128.4, 129.1, 129.5, 129.9, 130.6, 146.8 (olefinic and aromatic CH), 130.9, 135.2, 137.3, 138.8, 139.1, 139.8, 143.8 (quat. olefinic and aromatic); *m*/*z* (FAB) 443 (M + 1, 40%), 393 (43), 322 (35), 252 (74), 228 (49), 202 (69), 178 (58), 115 (100).

2-(2-Ethenylcyclopentenyl)benzaldehyde 16b. A mixture of 1-bromo-2-ethenylcyclopentene **15b** (1.05 g, 6.1 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.211 g, 0.18 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred at room temperature for 1 h. Sodium carbonate (0.62 g, 6.1 mmol) and 2-formylphenylboronic acid (0.92 g, 6.1 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 3 h. The usual work up gave a yellow oil which on distillation gave 2-(2-ethenylcyclopentenyl)benzaldehyde (0.75 g, 62%), bp 210 °C/1 mmHg (Found: C, 84.5; H, 7.2%; M^+, 198.1054. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%; M^+, 198.1045); δ_H 2.05 (quin., 2 H, CH_2, *J* 6.5), 2.71 (t, 2 H, CH_2, *J* 6.5), 2.82 (t, 2H, CH_2, *J* 6.5), 5.1 (d, 1H, CH_2, *J* 10.3), 5.2 (d, 1H, CH_2, *J* 17.4), 6.13 (dd, 1 H, CH, *J* 17.4 and 10.3), 7.23–7.96 (m, 4 H, aromatic CH), 9.94 (s, 1 H, CHO); δ_C 22.1 (CH_2), 32.7 (CH_2), 40.6 (CH_2), 116.4 (CH_2), 127.3, 127.4, 129.5, 130.8, 133.6 (olefinic and aromatic CH), 133.9, 137.4, 141.1, 142.2 (quat. olefinic and aromatic), 192.1 (CHO); *m*/*z* 198 (M^+, 6%), 167 (18), 115 (24), 95 (77), 69 (70), 55 (100); ν_{max} (thin film)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17b.** Yield 67%, mp 83–84 °C (hexane) (Found: C, 69.2; H, 6.1; N, 7.5%; $(M + 1)^+$, 367.1487. $C_{21}H_{22}N_2SO_2$ requires C, 68.8; H, 6.05; N, 7.6%; $(M + 1)^+$, 367.1480); δ_H 1.8–2.0 (m, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.5–2.7 (m, 4 H, CH_2), 4.8 (d, 1 H, CH, *J* 10.7), 5.0 (d, 1 H, CH, *J* 17.4), 5.97 (dd, 1 H, CH, *J* 17.4 and 10.7), 6.60–7.49 (m, 8 H, aromatic CH), 7.79 (br s, 1 H, NH); δ_C 21.4 (CH_3), 21.9 (CH_2), 32.4 (CH_2), 40.0 (CH_2), 115.5 (CH_2), 125.9, 127.2, 127.7, 128.7, 129.5, 129.8, 131.3, 146.8 (olefinic and aromatic CH), 130.9, 135.3, 138.5, 138.8, 139.4, 143.9 (quat. olefinic and aromatic); *m*/*z* (FAB) 367 (M + 1, 99%), 269 (68), 251 (100), 197 (68), 178 (53), 152 (99), 91 (28).

2-[2-(Prop-1-enyl)cyclopentenyl]benzaldehyde 16c as a 2:1 mixture of (*E*) and (*Z*) isomers. A mixture of 1-bromo-2-(prop-1-enyl)cyclopentene as a mixture of (*Z*)- and (*E*) isomers **15c** (1.23 g, 6.62 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.229 g, 0.198 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.70 g, 7 mmol) and 2-formylphenylboronic acid (1 g, 6.62 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 4 h. The usual work up gave the product as a yellow oil. Distillation gave a mixture of the (*Z*) and (*E*) isomers of 2-[2-(prop-1-enyl)cyclopentenyl]benzaldehyde which proved impossible to separate (0.85 g, 63%), bp 160 °C/1 mmHg (Found: $(M + 1)^+$, 213.1065. $C_{15}H_{16}O$ requires $(M + 1)^+$, 213.1279); δ_H (* Indicates the major isomer) 1.66* (d, 3 H, CH_3, *J* 5.2), 1.73 (d, 3 H, CH_3, *J* 7.4), 1.97–2.12 (m, 2 H, CH_2), 2.68–2.93 (m, 4 H, CH_2), 5.63–5.77 [m, 2′ H and 1′ H ((*Z*) isomer)], 5.86 [d, 1′ H ((*E*) isomer), CH, *J* 15.5], 7.23–7.97 (m, 4 H, aromatic CH), 9.94 (s, 1 H, CHO), 9.95* (s, 1 H, CHO); δ_C 14.8 (CH_3), 18.3* (CH_3), 22.2* (CH_2), 23.2 (CH_2), 33.4* (CH_2), 36.8 (CH_2), 39.2 (CH_2), 40.4* (CH_2), 124.0, 125.5, 127.1, 127.2, 128.9, 129.3, 129.5, 133.6 (olefinic and aromatic CH), 133.8, 140.6, 140.7, 142.8, 142.9 (quat. olefinic and aromatic), 192.2 (CHO), 192.3* (CHO); *m*/*z* (FAB) 213 (M + 1, 15%), 147 (29), 91 (20), 69 (91), 55 (100), 41 (87); ν_{max} (thin film)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17c ((*E*) isomer).** Yield 69%, as colourless crystals, mp 138–139 °C (ethanol) (Found: C, 69.2; H, 6.4; N, 7.4%; $(M + 1)^+$, 381.1648. $C_{22}H_{24}N_2SO_2$ requires C, 69.45; H, 6.4; N, 7.4%; $(M + 1)^+$, 381.1637); δ_H 1.57 (br d, 3 H, CH_3, *J* 6.6), 1.95 (quin., 2 H, CH_2, *J* 7.5), 2.38 (s, 3 H, CH_3), 2.55–2.60 (m, 4 H, CH_2), 5.56–5.67 (dq, 1 H, CH, *J* 16.6 and 6.6), 5.73 (d, 1 H, CH, *J* 16.6), 7.06–7.36 (m, 5 H, aromatic CH), 7.68 (br s, 1 H, NH), 7.82–7.92 (m, 3 H, aromatic CH); δ_C 18.2 (CH_3), 21.4 (CH_3), 22.1 (CH_2), 33.1 (CH_2), 39.9 (CH_2), 125.8, 125.9, 127.0, 127.8, 128.2, 128.9, 129.5, 129.9, 147.0 (olefinic and aromatic CH), 130.8, 135.4, 139.1, 139.2, 144.0 (quat. aromatic and olefinic); *m*/*z* (FAB) 381 (M + 1, 100%), 380 (30), 279 (24), 225 (55), 195 (93), 167 (61), 115 (21).

2-[2-(2-Methylprop-1-enyl)cyclopentenyl]benzaldehyde 16d. A mixture of 1-bromo-2-(2-methylprop-1-enyl)cyclopent-1-ene **15d** (1.32 g, 6.62 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.229 g, 0.198 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.7 g, 6.62 mmol) and 2-formylphenylboronic acid (1 g, 6.62 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 6 h. The usual work up gave an oil which on distillation gave 2-[2-(2-methylprop-1-enyl)cyclopentenyl]benzaldehyde as a yellow oil (0.96 g, 64%), bp 230 °C/0.05 mmHg (Found: C, 85.3; H, 8.0%; M^+, 226.1355. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%; M^+, 226.1358); δ_H (200 MHz, $CDCl_3$) 1.62 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 2.02–2.12 (m, 2 H, CH_2), 2.74–2.87 (m, 4 H, CH_2), 5.52 (br s, 1 H, CH), 7.23–7.93 (m, 4 H, aromatic CH), 9.92 (s, 1 H, CHO); δ_C 19.7 (CH_3), 23.3 (CH_2), 27.2 (CH_3), 37.0 (CH_2), 39.1 (CH_2), 119.9 (olefinic CH), 126.9, 127.0, 129.2, 133.5 (aromatic CH), 126.8, 133.7, 134.9, 136.3, 141.1 (quat. olefinic and aromatic), 192.3 (CHO); *m*/*z* 226 (M, 100%), 225 (40), 209 (71), 167 (75), 115 (26), 59 (25); ν_{max} (thin film)/cm^{-1} 1700 (CHO).

***p*-Tosylhydrazone 17d.** Yield 55%, mp 113–115 °C (hexane–ether) (Found: $(M + 1)^+$, 395.1779. $C_{23}H_{26}N_2SO_2$ requires $(M + 1)^+$, 395.1793); δ_H 1.68 (s, 6 H, 2 × CH_3), 2.17–2.30 (m, 2 H, CH_2), 3.06 (s, 3 H, CH_3), 3.14–3.34 (m, 4 H, CH_2), 5.11 (br s, 1′ H), 7.25–7.86 (m, 8 H, aromatic CH); δ_C 25.0 (CH_2), 27.1 (2 × CH_3), 30.6 (CH_2), 34.3 (CH_2), 50.4 (CH_3), 77.7 (quat. olefinic carbon), 114.7 (quat. olefinic carbon), 124.0, 124.1, 124.9, 125.6, 128.2 (aromatic CH), 129.5, 132.4, 139.5, 140.1, 141.1 (quat. olefinic and aromatic); *m*/*z* (FAB) 395 (M + 1, 66%), 237 (92), 209 (100), 165 (98), 141 (58), 115 (32), 77 (45), 43 (41).

(*E*)-2-[2-(2-Methoxycarbonylethenyl)cyclopentenyl]benzaldehyde 16e. A mixture of (*E*)-1-bromo-2-(2-methoxycarbonylethenyl)cyclopentene **15e** (0.76 g, 3.3 mmol) and tetrakis(triphenylphospine)palladium(0) (0.115 g, 0.099 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.34 g, 3.3 mmol) and 2-formylphenylboronic acid (0.5 g, 3.3 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 12 h. The usual work up gave a yellow solid which was crystallised to give (*E*)-2-[2-(2-methoxycarbonylethenyl)cyclopentenyl]benzaldehyde (0.47 g, 56%), mp 131–132 °C (hexane–ethanol) (Found: $(M + 1)^+$, 257.1170. $C_{16}H_{16}O_3$ requires $(M + 1)^+$, 257.1178); δ_H 2.05 (quin., 2 H, CH_2, *J* 7.2), 2.67 (t, 2 H, CH_2, *J* 7.2), 2.79 (t, 2 H, CH_2, *J* 7.2), 3.60 (s, 3 H, OCH_3), 5.82 (d, 1 H, CH, *J* 15.8), 7.01 (d, 1 H, CH, *J* 15.8), 7.06–7.96 (m, 4 H, aromatic

CH), 9.89 (s, 1 H, CHO); δ_C 22.2 (CH_2), 32.8 (CH_2), 41.5 (CH_2), 51.4 (OCH_3), 119.8, 137.9 (olefinic CH), 128.1, 128.6, 129.6, 133.8 (aromatic CH), 134.7, 137.9, 140.5, 147.6 (quat. olefinic and aromatic), 167.3 (C=O, ester), 191.2 (CHO); *m*/*z* (FAB) 257 (M + 1, 22.5%), 225 (49), 147 (44), 73 (100), 43 (63); ν_{max} (Nujol)/cm^{-1} 1730 (C=O, ester), 1690 (CHO).

***p*-Tosylhydrazone 17e.** Yield 77%, mp 153–154 °C (ethanol) (Found: C, 64.7; H, 5.8; N, 6.7%; $(M + 1)^+$, 425.1541. $C_{23}H_{24}N_2SO_4$ requires C, 65.1; H, 5.7; N, 6.6%; $(M + 1)^+$, 425.1535); δ_H 1.91–2.04 (m, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 2.57–2.68 (m, 4 H, CH_2), 3.63 (s, 3 H, OCH_3), 5.77 (d, 1 H, CH, *J* 15.7), 6.98–7.18 (m, 10 H, olefinic and aromatic CH), 8.78 (br s, 1 H, NH); δ_C 21.4 (CH_3), 21.9 (CH_2), 32.4 (CH_2), 40.9 (CH_2), 51.3 (OCH_3), 118.9, 126.5, 127.6, 127.8, 129.0, 129.4, 129.8, 138.6, 145.9 (olefinic and aromatic CH), 131.0, 135.3, 137.1, 137.6, 143.8, 149.5 (quat. olefinic and aromatic), 167.5 (C=O, ester); *m*/*z* (FAB) 425 (M + 1, 19%), 393 (28), 339 (51), 279 (100), 227 (30), 179 (48), 167 (53), 115 (38); ν_{max} (Nujol)/cm^{-1} 1730 (C=O).

(*E*,*E*)-2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)benzaldehyde 16f. A mixture of (*E*,*E*)-4-bromo-1,3-diphenylpenta-1,3-diene **15f** (0.5 g, 3.3 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.229 g, 0.194 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.38 g, 3.3 mmol) and 2-formylphenylboronic acid (0.5 g, 3.3 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 3 h. The usual work up gave a yellow oil which solidified on standing. Crystallisation gave (*E*,*E*)-2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)benzaldehyde (0.89 g, 82%), mp 61–62 °C (hexane) (Found: C, 88.3; H, 6.1%; M^+, 324.1523. $C_{24}H_{20}O$ requires C, 88.85; H, 6.2%; M^+, 324.1514); δ_H 1.96 (s, 3 H, CH_3), 5.96 (d, 1 H, CH, *J* 15.9), 6.60 (d, 1 H, CH, *J* 15.9), 6.99–8.05 (m, 14 H, aromatic CH), 10.24 (s, 1 H, CHO); δ_C 24.1 (CH_3), 126.0, 126.8, 127.0, 127.4, 127.6, 128.0, 128.1, 128.3, 129.4, 129.6, 132.0, 133.9 (olefinic and aromatic CH), 133.4, 133.5, 136.9, 138.6, 140.1, 146.8 (quat. olefinic and aromatic), 191.5 (CHO); *m*/*z* 324 (M, 47%), 229 (29), 202 (71), 178 (41), 115 (100), 102 (26); ν_{max} (Nujol)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17f.** Yield 78%, mp 134–136 °C (hexane–ether) (Found: C, 75.3; H, 6.0; N, 5.6%; M^+, 492.1870. $C_{31}H_{28}N_2SO_2$ requires C, 75.6; H, 5.7; N, 5.7%; M^+, 492.1871); δ_H 1.79 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 5.91 (d, 1 H, CH, *J* 16.0), 6.56 (d, 1 H, CH, *J* 16.0), 6.97–8.00 (m, 14 H, aromatic CH), 8.26 (br s, 1 H, NH); δ_C 21.4 (CH_3), 23.8 (CH_3), 126.0, 126.3, 126.9, 127.1, 127.3, 127.7, 128.3, 128.4, 128.8, 129.2, 129.6, 129.7, 130.4, 131.7, 146.5 (olefinic and aromatic CH), 130.6, 135.2, 137.3, 138.9, 139.5, 143.4, 144.0 (quat. olefinic and aromatic); *m*/*z* (FAB) 492 (M, 1%), 455 (31), 345 (94), 269 (70), 257 (76), 178 (44), 167 (67), 115 (100).

(*E*,*E*)-2-[1-Methyl-2-phenyl-4-(*p*-tolyl)buta-1,3-dienyl]benzaldehyde 16g. A mixture of (*E*,*E*)-4-bromo-3-phenyl-1-(*p*-tolyl)penta-1,3-diene **15g** (2.06 g, 6.62 mmol) and tetrakis-(triphenylphosphine)palladium(0) (0.229 g, 0.198 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.70 g, 7 mmol) and 2-formylphenylboronic acid (1 g, 6.62 mmol) in water (20 cm^3) were added and the mixture was heated at reflux for 3 h. The usual work up gave a viscous yellow oil which on distillation gave (*E*,*E*)-2-[1-methyl-2-phenyl-4-(*p*-tolyl)buta-1,3-dienyl]benzaldehyde (1.81 g, 81%), bp 245 °C/1 mmHg (Found: M^+, 338.1669. $C_{25}H_{22}O$ requires M^+, 338.1671); δ_H 1.96 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 5.96 (d, 1 H, CH, *J* 15.8), 6.58 (d, 1 H, CH, *J* 15.8), 6.87–8.07 (m, 13 H, aromatic CH), 10.25 (s, 1 H, CHO); δ_C 21.0 (CH_3), 24.3 (CH_3), 126.1, 127.0, 127.5, 127.6, 127.8, 128.3, 129.0, 129.6, 129.9, 132.2, 134.4 (olefinic and aromatic CH), 133.1, 133.6, 134.4, 137.1, 139.0, 140.4, 147.2 (quat. olefinic and aromatic), 191.8 (CHO); *m*/*z* (FAB) 338 (M, 28%), 279 (23), 205 (39), 121 (56), 105 (100), 91 (47); ν_{max} (thin film)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17g.** Yield 92%, mp 140–141 °C (hexane–ether) (Found: $(M + 1)^+$, 507.2124. $C_{32}H_{30}N_2SO_2$ requires $(M + 1)^+$, 507.2106); δ_H 1.80 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 5.92 (d, 1 H, CH, *J* 15.9), 6.56 (d, 1 H, CH, *J* 15.9), 6.92–8.07 (m, 17 H, aromatic CH); δ_C 125.9, 126.1, 126.8, 127.1, 127.5, 128.0, 128.2, 128.9, 129.1, 129.4, 129.6, 131.5, 146.5 (olefinic and aromatic CH), 130.2, 130.6, 134.5, 135.1, 136.8, 138.9, 139.5, 143.5, 143.8 (olefinic and aromatic CH); *m*/*z* (APCI CV = 35) 507.2 (M + 1, 85%).

2-[2-(2-Phenylethenyl)cyclohexenyl]benzaldehyde 16h as a 1.7 : 1 mixture of (*E*) and (*Z*) isomers. A mixture of 1-bromo-2-(2-phenylethenyl)cyclohexene **15h**, as a mixture of the (*E*) and (*Z*) isomers (1.73 g, 6.62 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.229 g, 0.194 mmol, 3% mol catalyst) in DME (20 cm^3) was stirred for 1 h at room temperature. Sodium carbonate (0.74 g, 7 mmol) and 2-formylphenylboronic acid (1 g, 6.62 mmol) in water (20 cm^3) were added and the mixture was heated at reflux overnight. The usual work up gave a yellow oil which on distillation gave 2-[2-(2-phenylethenyl)-cyclohexenyl]benzaldehyde as an inseparable mixture of the (*E*) and (*Z*) isomers (1.31 g, 69%), bp 240 °C/1 mmHg (Found: M^+, 288.1513. $C_{21}H_{20}O$ requires M^+, 288.1514); δ_H 1.70–1.90 (m, 4 H, CH_2), 2.16–2.55 (m, 4 H, CH_2); 4 olefinic protons 5.81 (d, *J* 12.2), 6.15 (d, *J* 12.2), 6.49 (d, *J* 16.2), 6.58 (d, *J* 16.2); 6.98–8.03 (m, 9 H, aromatic CH), 2 × C*H*O 10.02 (s), 10.04 (s); δ_C 22.5, 22.6, 22.7, 25.1, 28.6, 31.4, 33.5, 34.7 (CH_2), 126.2, 126.8, 127.0, 127.1, 127.3, 127.8, 128.3, 128.4, 129.2, 129.7, 129.9, 130.6, 133.9, 134.8 (olefinic and aromatic CH), 133.1, 133.6, 137.4, 137.8, 147.4, 147.8 (quat. olefinic and aromatic), 192.1, 192.2 (CHO); *m*/*z* (FAB) 288 (M, 28%), 271 (35), 197 (45), 105 (35), 91 (100); ν_{max} (thin film)/cm^{-1} 1690 (CHO).

***p*-Tosylhydrazone 17h as a mixture of (*E*) and (*Z*) isomers.** Yield 59%, mp 117–119 °C (hexane–ether) (Found: $(M + 1)^+$, 457.1938. $C_{28}H_{28}N_2SO_2$ requires $(M + 1)^+$, 457.1950); δ_H (* Indicates the major isomer) 1.68–1.82 (m, 4 H, CH_2), 2.16 and 2.29* (s, 3 H, CH_3), 2.33–2.42 (m, 4 H, CH_2), 6.43 (d, 1 H, CH, *J* 16.3), 6.45 (d, 1 H, CH, *J* 16.3), 7.06–7.91 (m, 14 H, olefinic and aromatic CH); δ_C 21.4 (CH_3), 22.5 (CH_2), 22.7 (CH_2), 25.0 (CH_2), 34.0 (CH_2), 125.9, 126.2, 126.5, 127.0, 127.7, 128.2, 128.3, 128.9, 129.3, 129.5, 130.2, 146.6 (olefinic and aromatic CH), 130.5, 132.3, 135.2, 137.1, 137.5, 143.6, 143.9 (quat. olefinic and aromatic); *m*/*z* (APCI CV = 35) 457.3 (M + 1, 100%); *m*/*z* (FAB) 456 (M, 8%), 301 (28), 272 (30), 220 (38), 165 (73), 115 (57), 91 (100).

Generation and reactions of the 2-(1,3-dienyl)phenyldiazomethanes 7a–h

These intermediates were generated, as in earlier work,[3] by the thermal decomposition of the sodium salts of the corresponding *p*-tosylhydrazones **17a**–**h** under aprotic conditions in DME as solvent. All reactions were carried out under nitrogen and in the dark. The method is given in detail for the first example.

(*E*)-2-[2-(2-Phenylethenyl)cyclopentenyl]phenyldiazomethane 7a. *(i) At 80 °C.* An ethanolic solution of sodium ethoxide (2 5 cm^3, 0.435 M, 1.09 mmol) was added to a solution of the *p*-tosylhydrazone **17a** (0.5 g, 1.15 mmol) in dry ethanol (10 cm^3). The reaction mixture was stirred for 1 h then the solvent was removed on a rotary evaporator at room temperature to leave the sodium salt. The latter was dried in the evaporation flask at room temperature under high vacuum over phosphorus pentaoxide in a desiccator for 12 h. Dry DME (50 cm^3) was added to the flask and the mixture was heated under reflux for 3 h. After cooling to room temperature the reaction mixture was filtered through a pad of Celite and the solvent was removed *in vacuo* to give an orange oil which was shown by TLC (silica, hexane–ether, 80:20) to contain two components. Dry-column flash chromatography (silica, hexane–ether, 80:20 to 0:100) gave (a) 1,1a,2,3,4,8b-hexahydro-1-phenylcyclopenta-[*a*]cyclopropa[*c*]naphthalene **19a** (0.142 g, 46%), mp 106–107 °C (hexane) (Found: C, 92.6; H, 7.11%; M^+, 258.1406. $C_{20}H_{18}$ requires C, 93.0; H, 7.0%; M^+, 258.1408); δ_H 1.13 (t, 1 H, CH, *J* 4.2), 1.98–2.18 (m, 2 H, CH_2), 2.41 (dd, 1 H, CH, *J* 3.9 and 8.0), 2.64–2.75 (m, 4 H, CH_2), 2.76 (dd, 1 H, CH, *J* 4.2 and 8.0), 6.99–7.46 (m, 9 H, aromatic CH); δ_C 22.5 (CH_2), 26.2 (CH), 28.6 (CH), 31.0 (CH_2), 33.3 (CH), 36.0 (CH_2), 123.8, 125.1, 125.3, 126.0, 128.1 (aromatic CH), 128.3 (2 × aromatic CH), 130.1, 130.6, 134.7, 139.8, 143.1 (quat. aromatic and olefinic CH); and (b) 2,3,4,7-tetrahydro-4,7-methano-12-phenyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18a** (0.069 g, 27%), mp 121–123 °C (hexane–ethanol) (Found: $(M + 1)^+$, 287.1542. $C_{20}H_{18}N_2$ requires $(M + 1)^+$, 287.1548); δ_H (360 MHz, $CDCl_3$) 1.49–1.65 (m, 2 H, CH_2), 2.28–2.56 (m, 3 H, CH_2), 2.79–2.92 (m, 1 H, CH_2), 3.28 (s, 1 H, H-12), 5.26 (s, 1 H, CH), 5.71 (s, 1 H, CH), 6.80–7.27 (m, 9 H, aromatic CH); δ_C 21.0, 36.3, 39.6 (3 × CH_2), 42.5 (benzylic CH), 90.6, 98.4 (2 × CH), 126.2, 126.9, 128.0, 128.4, 128.7, 129.7, 131.3 (aromatic CH), 132.8, 135.3, 135.8, 140.1, 141.9 (quat. olefinic and aromatic); *m*/*z* (FAB) 287 (M + 1, 87%), 286 (14), 258 (100), 228 (37), 189 (50), 178 (49), 167 (55), 115 (46). The structures of both products were confirmed by X-ray crystallography (Figs. 1 and 2).

(ii) At room temperature. The sodium salt from the *p*-tosylhydrazone **17a** (0.5 g, 1.15 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature and in the dark. Monitoring by TLC showed that reaction was complete after 48 h. A similar work up and chromatography gave 1,1a,2,3,4,8b-hexahydro-1-phenylcyclopenta[*a*]cyclopropa[*c*]naphthalene **19a** (0.049 g, 19%) and 2,3,4,7-tetrahydro-4,7-methano-12-phenyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18a** (0.175 g, 67%) both identical in all respects to the products obtained in the experiment above.

Thermal decomposition of 2,3,4,7-tetrahydro-4,7-methano-12-phenyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine 18a. The reactant **18a** (15 mg, 0.052 mmol) in perdeuteriotoluene (0.5 cm^3) in an NMR tube was heated at 78 °C. Monitoring by NMR showed that 1a,2,3,4,8b-pentahydro-1-phenylcyclopenta[*a*]cyclopropa-[*c*]naphthalene **19a** was the only product.

2-(2-Ethenylcyclopentenyl)phenyldiazomethane 7b. The sodium salt from the *p*-tosylhydrazone **17b** (0.40 g, 1.09 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h. The usual work up gave an orange oil. Dry-column flash chromatography (silica, hexane–ether 70:30) gave 2,3,4,7-tetrahydro-4,7-methano-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18b** as an orange solid (0.19 g, 86%), which could not be crystallised, mp 94–96 °C (Found: $(M + 1)^+$ 211.1244. $C_{14}H_{14}N_2$ requires $(M + 1)^+$, 211.1235); δ_H 1.75–2.01 (m, 4 H, cyclopentyl CH_2 and 12-CH_2), 2.68–2.91 (m, 3 H, CH_2), 3.02–3.14 (m, 1 H, CH_2), 5.28 (d, 1 H, CH, *J* 7.3), 5.66 (d, 1 H, CH, *J* 7.9), 7.05–7.56 (m, 4 H, aromatic CH); δ_C 21.0 (CH_2), 23.8 (CH_2), 36.4 (CH_2), 39.6 (CH_2), 82.7 (CH), 89.9 (CH), 127.8, 128.3, 129.5, 131.3 (aromatic CH), 133.2, 135.5, 136.2, 140.4 (quat. olefinic and aromatic); *m*/*z* (FAB) 211 (M + 1, 62), 183 (22), 182 (100), 181 (57), 167 (29), 152 (17), 115 (8).

2-[2-(Prop-1-enyl)cyclopentenyl]phenyldiazomethane 7c. The sodium salt of the *p*-tosylhydrazone **17c** (0.40 g, 1.05 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h. The usual work up gave an orange oil. Dry-column flash chromatography (silica, hexane–ether, 70:30) gave 2,3,4,7-tetrahydro-4,7-methano-12-methyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18c** as a viscous yellow oil (0.16 g, 75%) (Found: $(M + 1)^+$, 225.1380. $C_{15}H_{16}N_2$ requires $(M + 1)^+$, 225.1392); δ_H 0.91 (d, 3 H, CH_3, *J* 7.2), 1.84–2.10 (m, 2 H, CH_2), 2.32 (q, 1 H, CH, *J* 7.2), 2.69–2.90 (m, 3 H, CH_2), 3.02–3.09 (m, 1 H, CH_2), 4.93 (s, 1 H, CH), 5.29 (s, 1 H, CH), 7.21–7.49 (m, 4 H, aromatic CH); δ_C 18.0 (CH_3), 20.9 (CH_2), 30.5 (CH), 36.2 (CH_2), 39.6 (CH_2), 90.1 (CH), 97.6 (CH), 127.7, 128.1, 129.3, 131.2 (aromatic CH), 132.9, 135.0, 135.7, 139.8 (quat. olefinic and aromatic); *m*/*z* (FAB) 225 (M + 1, 35%), 197 (25), 196 (31), 195 (68), 181 (74), 179 (74), 167 (100), 115 (49), 91 (33).

2-[2-(2-Methylprop-1-enyl)]phenyldiazomethane 7d. The sodium salt of the *p*-tosylhydrazone **17d** (0.3 g, 0.76 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h. The usual work up gave an orange oil. Dry-column flash chromatography (silica, hexane–ether, 70:30) gave 2,3,4,7-tetrahydro-4,7-methano-12,12-dimethyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18d** (0.16 g, 88%), mp 87–89 °C as a pale yellow solid which could not be crystallised (Found: $(M + 1)^+$, 239.1550. $C_{19}H_{18}N_2$ requires $(M + 1)^+$, 239.1548); δ_H 0.95 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3), 1.87–2.07 (m, 2 H, CH_2), 2.72–2.97 (m, 3 H, CH_2), 3.00–3.16 (m, 1 H, CH_2), 4.80 (s, 1 H, CH), 5.14 (s, 1 H, CH), 7.16–7.57 (m, 4 H, aromatic CH); *m*/*z* (FAB) 239 (M + 1, 100%), 236 (30), 211 (13), 210 (92), 195 (35), 169 (44), 165 (43), 43 (70).

(*E*)-2-[2-(2-Methoxycarbonylethenyl)cyclopentenyl]phenyldiazomethane 7e. The sodium salt of the *p*-tosylhydrazone **17e** (0.4 g, 0.94 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h. The usual work up gave a yellow solid shown by TLC to contain two components. Dry-column flash chromatography (silica, hexane–ether, 70:30 to 0:100) gave (a) 2,3,4,7-tetrahydro-4,7-methano-12-methoxycarbonyl-1*H*-cyclopenta[*e*][2,3]benzodiazocine **18e** (0.07 g, 28%), mp 135–137 °C (hexane–ethanol) (Found: $(M + 1)^+$, 269.1290. $C_{16}H_{16}N_2O_2$ requires $(M + 1)^+$, 269.1290); δ_H 1.91–1.98 (m, 2 H, CH_2), 2.78–2.85 (m, 3 H, CH_2), 3.05–3.12 (m, 1 H, CH_2), 3.69 (s, 3 H, OCH_3), 5.59 (s, 1 H, CH), 6.00 (s, 1 H, CH), 7.25–7.57 (m, 4 H, aromatic CH); δ_C 21.0 (CH_2), 36.4 (CH_2), 39.5 (CH_2), 41.5 (CH), 52.4 (OCH_3), 85.6 (CH), 92.7 (CH), 128.3, 128.8, 129.8, 131.6 (aromatic CH), 132.8, 134.2, 137.0, 138.5 (quat. olefinic and aromatic); ν_{max} (Nujol)/cm^{-1} 1719 (C=O, ester); *m*/*z* (FAB) 269 (M + 1, 52%), 240 (10), 239 (22), 181 (100), 179 (21), 178 (25), 166 (16), 165 (16); and (b) 3-methoxycarbonyl-1,3a,4,5,6,10b-hexahydrobenzo[*g*]cyclopenta[*e*]-indazole **20** (0.15 g, 59%), mp 147–149 °C (hexane–ethanol) as a colourless solid (Found: C, 71.4; H, 6.2; N, 10.4%; $(M + 1)^+$, 269.1286. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.0; N, 10.4%; $(M + 1)^+$, 269.1290); δ_H (360 MHz, $CDCl_3$) 1.87–2.01 (m, 2 H, CH_2), 2.35–2.47 (m, 1 H, CH_2), 2.53–2.70 (m, 1 H, CH_2), 2.73–2.83 (m, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 4.16 (d, 1 H, CH, *J* 11.1), 4.96 (dd, 1 H, CH, *J* 10.6 and 3.3), 6.29 (br s, 1 H, NH), 7.11–7.33 (m, 4 H, aromatic CH); δ_C (90.55 MHz, $CDCl_3$) 22.0 (CH_2), 30.9 (CH_2), 34.4 (CH_2), 43.9 (CH), 52.1 (OCH_3), 65.9 (CH), 124.1, 126.5, 128.4, 128.9 (aromatic CH), 129.3, 131.9, 132.1, 134.6, 144.0 (quat. olefinic and aromatic); ν_{max} (Nujol)/cm^{-1} 1706 (C=O, ester); *m*/*z* (FAB) 269 (M + 1, 45%), 237 (59), 235 (57), 181 (37), 168 (34), 167 (100), 152 (20).

(*E*,*E*)-2-(1-Methyl-2,4-diphenylbuta-1,3-dienyl)phenyldiazomethane 7f. *(i) At room temperature.* The sodium salt of the *p*-tosylhydrazone **17f** (0.4 g, 0.81 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h. The usual work up gave (*E*,*E*)-2-(1-methyl-2,4-diphenylbuta-1,3-dienyl)phenyldiazomethane **7f** (0.26 g, 94%) as an orange oil which proved impossible to purify further; δ_H (200 MHz, $CDCl_3$) 1.75 (s, 3 H, CH_3), 4.91 (s, 1 H, CH), 5.88 (d, 1 H, CH, *J* 16.1), 6.63 (d, 1 H, CH, *J* 16.1), 7.01–7.53 (m, 15 H, aromatic CH); ν_{max} (Nujol)/cm^{-1} 2060 (C=N=N).

(ii) At 80 °C. A similar procedure was followed using the same amount of the *p*-tosylhydrazone **17f**. After standing for 48 h at room temperature the DME solution was heated at reflux for 3 h. The usual work up gave a yellow oil which contained two components (TLC, silica, hexane–ether 90:10). MPLC (silica, hexane–ether, 90:10) gave (a) 1a,7b-dihydro-3-methyl-1,2-diphenyl-1*H*-cyclopropa[*a*]naphthalene **19f** as a *ca.* 1:3 mixture of *cis* and *trans* isomers (0.135 g, 54%), bp 250 °C/1 mmHg (Found: M^+, 308.1572. $C_{24}H_{20}$ requires M^+, 308.1565); δ_H 1.51* (br t, CH, *J* 4.2), 1.87 (s, CH_3), 2.15* (s, CH_3), 2.54* (dd, CH, *J* 4 and 8.3), 2.69 (br t, CH, *J* 8.5), 2.83 (br t, CH, *J* 9.1), 2.92* (dd, 1 H, CH, *J* 4.4 and 8.3), 3.13 (dd, CH, *J* 8 and 9.2), 7.02–5.56 (m, 14 H, aromatic CH); δ_C 16.7 (CH_3), 28.2 (CH), 32.9 (CH), 33.0 (CH), 124.7, 125.2, 125.4, 126.1, 126.8, 126.9, 127.9, 128.2, 128.4, 129.0 (aromatic CH), 131.3, 132.5, 134.2, 136.0, 142.1, 142.5 (quat. olefinic and aromatic); *m/z* (FAB) 309 (M + 1, 66%), 308 (54), 294 (48), 231 (97), 229 (100), 218 (23), 215 (68), 191 (24), 91 (16) (* indicates the major isomer); and (b) 10b-methyl-1,3-diphenyl-1,10b-dihydropyrrolo[2,1-*a*]phthalazine **24f** (0.055 g, 22%), mp 154–156 °C (pentane–chloroform) (Found: $(M + 1)^+$, 337.1700. $C_{24}H_{20}N_2$ requires $(M + 1)^+$, 337.1705); δ_H (360 MHz, $CDCl_3$) 1.70 (s, 3 H, CH_3), 3.91 (d, 1 H, CH, *J* 3.5), 5.28 (d, 1 H, CH, *J* 3.5), 6.69–7.75 (m, 15 H, olefinic and aromatic CH); δ_C (90.55 MHz, $CDCl_3$) 31.1 (CH_3), 60.1 (CH), 66.0 (quat. carbon), 105.4 (CH), 124.2, 126.2, 126.5, 127.9, 128.0, 128.1, 128.5, 128.6, 129.2, 132.9 (aromatic CH), 124.3, 131.7, 132.4, 140.3, 146.3 (quat. olefinic and aromatic); *m/z* (FAB) 337 (M + 1, 100), 336 (15), 233 (16), 145 (11), 115 (12), 91 (11). The structure of this compound was confirmed by X-ray crystallography (Fig. 3).

(*E*,*E*)-2-[1-Methyl-2-phenyl-4-(*p*-tolyl)buta-1,3-dienyl]phenyldiazomethane 7g. The sodium salt of the *p*-tosylhydrazone **17g** (0.75 g, 0.79 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was stirred under nitrogen at room temperature for 48 h and then heated under reflux for 3 h. The usual work up gave a yellow oil shown by TLC to contain two components. MPLC (silica, hexane–ether, 90:10) gave (a) 1a,7b-dihydro-3-methyl-2-phenyl-1-(*p*-tolyl)-1*H*-cyclopropa[*a*]-naphthalene **19g** as a *ca.* 1:2 mixture of *cis* and *trans* isomers (0.24 g, 49%), bp 250 °C/1 mmHg (Found: $((M + 1)^+$, 323.1801. $C_{25}H_{22}$ requires $(M + 1)^+$, 323.1800); δ_H 1.55* (br t, CH, *J* 4.3), 1.97 (s, CH_3), 2.23 (s, 3 H, CH_3), 2.43* (s, CH_3), 2.57* (dd, CH, *J* 4.0 and 8.3), 2.70 (br t, CH, *J* 8.2), 2.82 (br t, CH, *J* 9), 2.93* (dd, CH, *J* 4.0 and 8.3), 3.11 (dd, CH, *J* 8.2 and 9.2), 6.86–7.62 (m, 13 H, aromatic CH) (* = major component); δ_C 16.2 (CH_3), 16.4 (CH_3), 17.4 (CH), 20.8 (CH), 20.9 (CH), 26.5 (CH_3), 27.9 (CH_3), 28.0 (CH), 32.6 (CH), 32.8 (CH), 123.8, 124.6, 125.0, 125.6, 126.0, 126.4, 126.5, 126.7, 126.8, 127.8, 127.8, 127.9, 128.1, 128.8, 129.0, 129.1, 129.4, 131.0 (aromatic CH), 128.6, 129.6, 131.5, 132.1, 132.2, 132.5, 134.3, 134.6, 134.8, 136.1, 139.2, 142.1, 142.9 (quat. olefinic and aromatic); *m/z* (APCI, CV = 20) 322.9 ((M + 1), 100%); and (b) 10b-methyl-3-phenyl-1-(*p*-tolyl)-1,10b-dihydropyrrolo[2,1-*a*]phthalazine **24g** as a yellow oil (0.11 g, 21%) (Found: $(M + 1)^+$, 351.1853. $C_{25}H_{22}N_2$ requires $(M + 1)^+$, 351.1861); δ_H (360 MHz, $CDCl_3$) 1.61 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 3.81 (d, 1 H, CH, *J* 3.3), 5.19 (d, 1 H, CH, *J* 3.3), 6.82–7.68 (m, 14 H, aromatic CH); *m/z* (APCI, CV = 20) 351 (M + 1, 100%).

2-[2-(2-Phenylethenyl)cyclohexenyl]phenyldiazomethane 7h. The sodium salt of the *p*-tosylhydrazone **17h** (0.5 g, 1.10 mmol) was prepared and dried as above. Its solution in dry DME (50 cm^3) was heated at reflux for 4 h. The usual work up gave a pale yellow oil. MPLC (silica, hexane–ether, 90:10) gave a colourless oil which was distilled to give 1a,2,3,4,5,9b-hexahydro-1-phenyl-1*H*-cyclopropa[*l*]phenanthrene **19h** (0.17 g, 59%), bp 215 °C/1 mmHg (Found: M^+, 272.1531. $C_{21}H_{20}$ requires M^+, 272.1565); δ_H 1.26 (t, 1 H, CH, *J* 4.2), 1.59–1.95 (m, 4 H, CH_2), 2.23 (dd, 1 H, CH, *J* 4.3 and 8.2), 2.31–2.60 (m, 4 H, CH_2), 2.75 (dd, 1 H, CH, *J* 4.3 and 8.2), 7.01–7.51 (m, 9 H, aromatic CH); δ_C 22.5 (CH_2), 22.9 (CH_2), 25.1 (CH_2), 27.2 (CH), 31.5 (CH_2), 32.5 (CH), 32.6 (CH), 122.5, 122.6, 125.0, 125.2, 125.8, 128.1, 128.2 (aromatic CH), 127.8, 132.1, 133.9, 134.0, 143.2 (quat. olefinic and aromatic); *m/z* (APCI, CV = 20) 271.9 (M, 100%).

A similar experiment carried out at room temperature gave multiple products which could not be separated.

The crystal structures of (i) 1,1a,2,3,4,8b-hexahydro-1-phenyl-cyclopenta[*a*]cyclopropa[*c*]naphthalene 19a, (ii) 2,3,4,7-tetra-hydro-4,7-methano-12-phenyl-1*H*-cyclopenta[*e*][2,3]benzo-diazocine 18a, and (iii) 10b-methyl-1,3-diphenyl-1,10b-dihydropyrrolo[2,1-*a*]phthalazine 24f

Diffraction data were collected in ω–θ mode on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device using Cu-Kα radiation.

(i) Compound 18a (Fig. 1). Crystal data for $C_{20}H_{18}N_2$, $M = 286.36$, orthorhombic, $a = 11.8635(8)$, $b = 13.2643(9)$, $c = 18.9431(14)$ Å, $V = 2980.9(4)$ Å^3, space group *Pbca*, $Z = 8$, $D_c = 1.276$ g cm^{-3}, $F(000) = 1216$, yellow rhombic, 0.59 × 0.35 × 0.27 mm^3, μ(Cu-Kα) = 0.579 mm^{-1}, 2θ range for data collection: 5–120°. The structure was solved by direct methods (SHELXS)[11] and refined by full-matrix least-squares against F^2 (SHELXL)[11] with anisotropic displacement parameters for all non-H atoms and H atoms refined with isotropic displacement parameters constrained to 1.2 times that of the atom to which they are bonded. The final $R(F) = 4.60\%$ [based on F and 1987 data with $F > 4\sigma(F)$] and $wR2 = 11.61\%$ (based on F^2 and all 2181 unique data) for 254 parameters. The final difference map max. and min. were 0.16 and −0.17 e Å^{-3}.

(ii) Compound 19a (Fig. 2). Crystal data for $C_{20}H_{18}$, $M = 258.34$, orthorhombic, $a = 18.699(2)$, $b = 22.045(2)$, $c = 6.8983(18)$ Å, $V = 2843.5$ Å^3, space group *Pccn*, $Z = 8$, $D_c = 1.207$ g cm^{-3}, $F(000) = 1104$, colourless block, μ(Cu-Kα) = 0.51 mm^{-1}, data were collected in the range $5 < 2\theta < 140°$. The structure was solved as described above and refined against F^2 (SHELXTL)[11] with H atoms in idealised positions and anisotropic displacement parameters for all non-H atoms. The final $R(F) = 5.63\%$ [based on F and 1209 data with $F > 4\sigma(F)$] and $wR2 = 14.52\%$ (based on F^2 and all 2090 unique data used for refinement) for 182 parameters. The final difference map max. and min. were 0.17 and −0.18 e Å^{-3}.

(iii) Compound 24f (Fig. 3). Crystal data for $C_{24}H_{20}N_2$, $M = 336.44$, monoclinic, $a = 17.0807(15)$, $b = 7.0507$, $c = 16.1161(16)$ Å, $\beta = 112.113(6)°$, $V = 1798.1$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.24$ g cm^{-3}, $F(000) = 713.74$, yellow block, 0.47 × 0.23 × 0.19 mm^3, μ(Cu-Kα) = 0.53 mm^{-1}, 2θ range for data collection: 5–120° (the peak profiles were quite broad, and diffraction was quite weak at high angle). The structure was solved by direct methods (SIR92)[12] and refined by full-matrix least-squares against F (CRYSTALS)[13] with H atoms in idealised positions and anisotropic displacement parameters for all non-H atoms. The final $R(F)$ was 4.51%, $R_w(F) = 4.75\%$ for 236 parameters using 2633 data with $F > 4\sigma(F)$ out of 3184 unique data. The final difference map max. and min. were 0.20 and −0.18 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **18a**, **19a** and **24f** have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference number 207/401. See http://www.rsc.org/suppdata/p1/a9/a909516k for crystallographic files in .cif format.

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References

1 J.-P. Strachan, J. T. Sharp and M. C. Crawshaw, *J. Chem. Soc.*, *Perkin Trans. 1*, 1999, 443.
2 (*a*) A. Padwa and H. Ku, *Tetrahedron Lett.*, 1980, **21**, 1009; (*b*) A. Padwa and A. Rodriguez, *Tetrahedron Lett.*, 1981, **22**, 187; (*c*) T. Miyashi, Y. Fujii, Y. Nishizawa and T. Mukai, *J. Am. Chem. Soc.*, 1981, **103**, 725.
3 D. P. Munro and J. T. Sharp, *J. Chem. Soc.*, *Perkin Trans. 1*, 1984, 849.
4 (*a*) Z. Arnold and A. Holy, *Collect. Czech. Chem. Commun.*, 1961, **26**, 3059; (*b*) I. R. Robertson and J. T. Sharp, *Tetrahedron*, 1984, **40**, 3095.
5 C. C. Dudman and C. B. Reese, *Synthesis*, 1982, 419.
6 *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley-Interscience, New York, 1984.
7 R. S. Atkinson and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 778.
8 R. S. Atkinson and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 772.
9 (*a*) R. H. Findlay, J. T. Sharp and P. B. Thorogood, *J. Chem. Soc.*, *Perkin Trans. 1*, 1975, 102; (*b*) K. L. M. Stanley, J. Dingwall and J. T. Sharp, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 1433.
10 J. T. Sharp, I. Gosney and A. G. Rowley, *Practical Organic Chemistry, a Student Handbook of Techniques*, Chapman and Hall, London, 1989, pp. 160 and 163.
11 G. M. Sheldrick, SHELXTL, version 5, Siemens Analytical X-ray Instruments, 1995.
12 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Gaicovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435
13 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Issue 10, Chemical Crystallography Laboratory, University of Oxford, 1996.

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