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THE ADDITION OF BENZOCYCLOBUTENYLIDENE TO BENZENE

THE FACILE REARRANGEMENT OF SPIRO[BENZOCYCLOBUTENE-1,7'-CYCLOHEPTA-1',3',5'-TRIENE] TO 9a,10-DIHYDROBENZ[*a*]AZULENE

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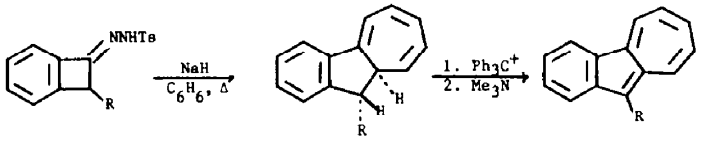
Abstract—Thermal decomposition of the sodium salts of benzocyclobutenone tosylhydrazone and 2-methylbenzocyclobutenone tosylhydrazone in benzene affords 9a,10-dihydrobenz[*a*]azulene **4** and *trans*-10-methyl-9a,10-dihydrobenz[*a*]azulene **3**, respectively. A mechanism involving initially the addition of the carbene benzocyclobutenylidene, or its 2-Me derivative, to the benzene ring is postulated. A proposed intermediate in the reaction, spiro[benzocyclobutene-1,7'-cyclohepta-1',3',5'-triene] **12** has been synthesised, and shown to give rise to **4** under the reaction conditions. The rate of rearrangement of **12** → **4** has been measured, and the activation energy determined: $E_a = 125.9 \pm 0.8$ KJ mol^{-1} and $A = 1.38 \times 10^{14}$ sec^{-1}. The mechanism for the rearrangement must involve ring opening of the benzocyclobutene moiety of **12** to give an *o*-xylylene intermediate which is postulated to possess considerable diradical character. At 71.8°, this ring opening is 2.7×10^6 times faster than the ring opening of the parent benzocyclobutene molecule. The decomposition of the sodium salt of 2-(7'-cyclohepta-1',3',5'-trienyl)benzaldehyde tosylhydrazone has also been investigated, and is shown to yield 4a,10-dihydrobenz[*a*]azulene, 9,10-dihydrobenz[*a*]azulene and 8,9-benzotricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene. A mechanism involving intramolecular 1,3-dipolar addition of a diazo grouping to a cycloheptatriene Π-bond, followed by decomposition of the resulting pyrazoline intermediate, is proposed

The addition of benzocyclobutenylidene and 2-methylbenzocyclobutenylidene to benzene

We have shown previously that decomposition of the sodium salt of 2-methylbenzocyclobutenone tosylhydrazone **1** in tetrahydrofuran leads to products derived from intermolecular reactions of the carbene 2-methylbenzocyclobutenylidene.[1] In an attempt to suppress insertion of the carbene into the C–H bonds of the solvent, we investigated the thermolysis of the sodium salt of **1** in benzene. This reaction afforded in 42% yield a hydrocarbon formulated as *trans*-10-methyl-9a,10-dihydrobenz[*a*]azulene **3** (Scheme 1).[2] An analogous thermolysis of the sodium salt of benzocyclobutenone tosylhydrazone **2** gave 9a,10-dihydrobenz[*a*]azulene **4**. The structure of the ring skeleton of **3** and **4** was confirmed by conversion of each compound into the highly coloured benz[*a*]azulenes **5** and **6** under very mild dehydrogenation conditions, using the two step sequence of hydride ion abstraction by trityl cation followed by deprotonation.[3]

The 90 MHz ^{1}H NMR spectrum of 10-methyl-9a,10-dihydrobenz[*a*]azulene **3** is shown in Fig. 1. Irradiation of the Me doublet caused the doublet of quartets at δ 3.30 to collapse to a doublet; this signal is therefore assigned to H10, with $J_{10,Me} = 7$ Hz and the doublet coupling $J_{10\,9a} = 4$ Hz. This doublet coupling was removed by irradiating the seven line multiplet at δ 2.54, showing that this multiplet is due to H9a. This irradiation also collapsed the doublet of doublets at δ 5.30 to a doublet. The latter signal can therefore be assigned to H9, with $J_{9,8} = 10$ Hz and $J_{9,9a} = 4$ Hz. With the fine coupling to H9a removed, H8 resonated as a clear doublet of doublets at δ 6.06, showing $J_{8,7} = 5$ Hz.

The NMR spectrum of the unsubstituted 9a,10-dihydrobenz[*a*]azulene **4** is shown in Fig. 2. The characteristic doublet of doublets due to the "outer" cycloheptatrienyl proton H9 at δ 5.24 is again evident. The doublet of doublets centred at δ 3.6 is due to one of the benzylic methylene protons H10, as irradiation of H9 leaves it unchanged. The large coupling of 18 Hz to the signal at δ 3.6 must be the geminal coupling $J_{10x,10n}$, while the remaining splitting of 10 Hz is due to the vicinal coupling to H9a. This coupling constant is to be compared with the value of 4 Hz observed for $J_{10,9a}$ in the Me-substituted compound **3**. Inspection of molecular models reveals that the 9a,10-dihydrobenz-[*a*]azulene ring system is conformationally rather rigid. The dihedral angle between the *cis* protons H10x



1 R = Me
2 R = H

3 R = Me
4 R = H

5 R = Me
6 R = H

Scheme 1.

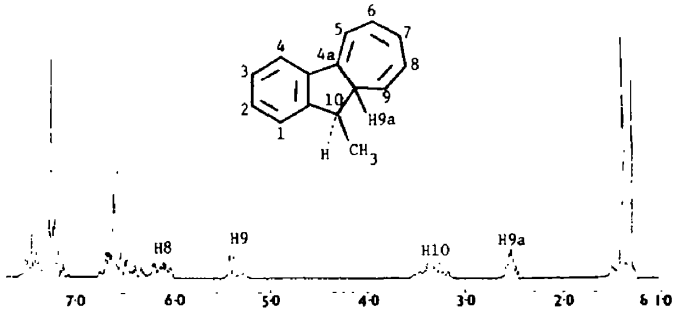


Fig. 1. 90 MHz ^{1}H NMR spectrum of *trans*-10-methyl-9a,10-dihydrobenz[*a*]azulene **3**.

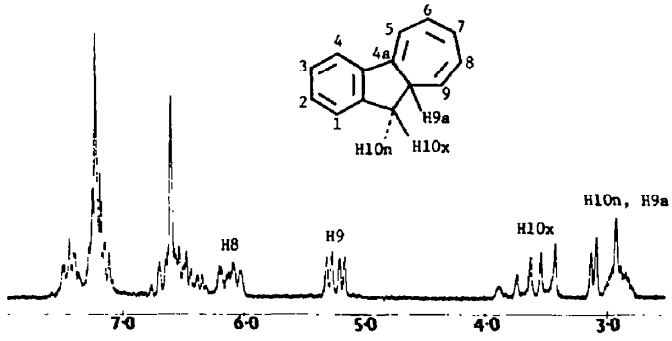


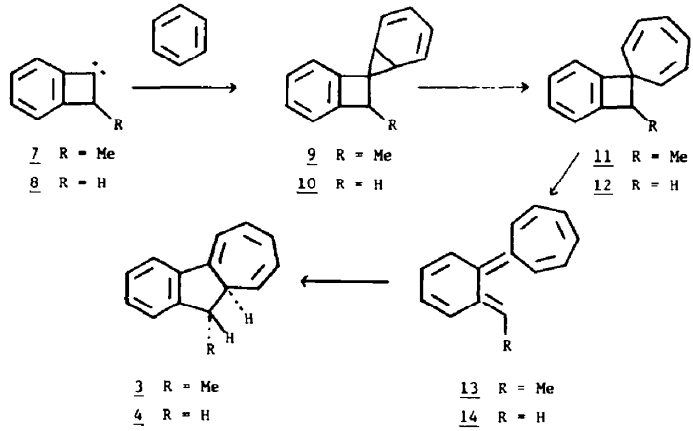
Fig. 2. 90 MHz ^{1}H NMR spectrum of 9a, 10-dihydrobenz[*a*] azulene **4**.

and H9a is close to 0°, while the angle between the *trans* protons H10n and H9a is *ca* 110°. Hence the *cis* coupling constant $J_{10x,9a}$ should be larger than the *trans* coupling constant $J_{10n,9a}$ if the Karplus relationship[4] is assumed to hold. It thus appears that the observed coupling of 4 Hz in **3** is the *cis* coupling constant $J_{10x,9a}$ whereas the observed coupling of 10 Hz in the unsubstituted system **4** is the *trans* coupling constant $J_{10n,9a}$. Hence we assign the *trans* stereochemistry to 10-methyl-9a,10-dihydrobenz[*a*-]azulene, but we emphasise that this is based solely on the above NMR spectral considerations.

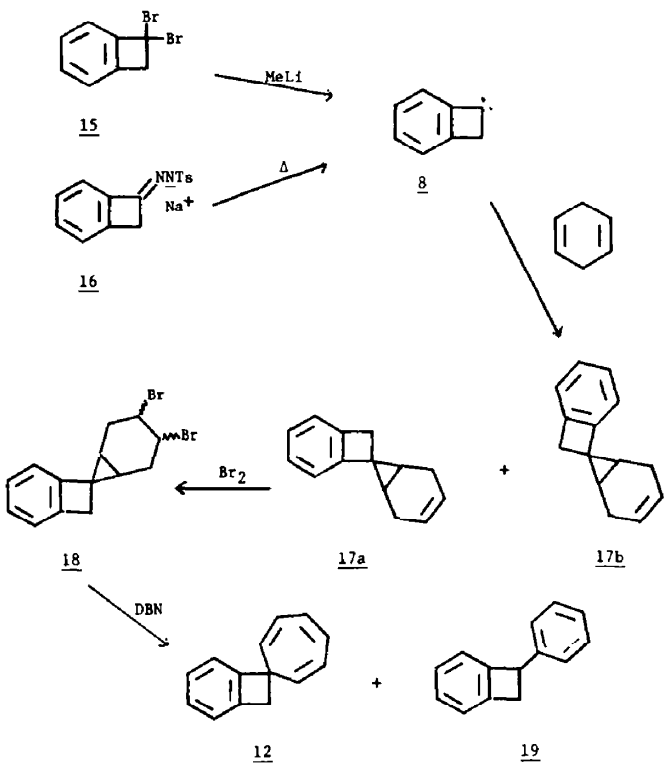
The formation of the 9a,10-dihydrobenz[*a*]azulenes can be rationalised as shown in Scheme 2. The addition of carbene **7** or **8** to the aromatic ring would give the norcaradiene derivative **9** or **10**, which would be expected[5] to isomerise to the respective cycloheptatrienes **11** and **12**. Conrotatory electrocyclic ring opening of the benzocyclobutene moiety of **11** and **12** would afford the extended *o*-xylylene (*o*-quinodimethane) derivatives **13** and **14** (or their equivalent diradicals, see below). Electrocyclic ring closure of **13** and **14** would then give the observed products **3** and **4**.

Synthesis of the postulated intermediate spiro[benzocyclobutene-1,7′-cyclohepta-1′,3′,5′-triene] **12**

In order to confirm the intermediacy of the spirocycloheptatriene **12** in the sequence shown in Scheme 2, a synthesis of **12** was undertaken. Benzocyclobutenylidene **8** was generated by thermolysis of **16** in the presence of 1,4-cyclohexadiene to give a hydrocarbon product formulated as a mixture of

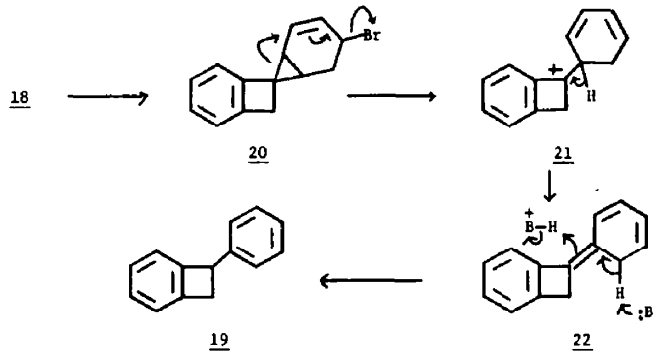


Scheme 2.



Scheme 3.

two stereoisomers† **17a** and **17b**. The NMR spectrum of the product showed two benzylic singlet resonances at δ 3.12 and δ 2.82. Analytical glc revealed two poorly resolved peaks in a ratio of *ca* 7:4. It is probable that the most abundant stereoisomer is **17a** in which the bulky aromatic ring is oriented *exo* with respect to the bicyclo[4.1.0]hept-3-ene ring system. The same hydrocarbon mixture was obtained when 1,1-dibromobenzocyclobutene **15** was treated with methyllithium in the presence of 1,4-cyclohexadiene. This reaction therefore also generates the carbene **8** or a carbenoid species with properties very similar to those of **8**, since the **17a**:**17b** ratio was essentially the same in the two reactions. The isomers **17a** and **17b** were not separated, but reacted with bromine to give a mixture of crystalline dibromides **18** in quantitative yield. Treatment of **18** with the base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in THF at 38° gave a mixture of two hydrocarbons which were separated by chromatography over Al_2O_3–$AgNO_3$. The first eluted material was identified as 1-phenylbenzocyclobutene **19** by comparison with an authentic sample prepared by hydrogenolysis of 1-phenylbenzocyclobutenol. The second product had spectroscopic properties consistent with those expected for spiro[benzocyclobutene-1,7′-cyclohepta-1′,3′,5′-triene] **12**. Thus the NMR spectrum showed a sharp singlet at δ 2.90 for the benzylic protons, a doublet $J = 9.5$ Hz at δ 5.71 for the "outer" cycloheptatrienyl protons H1′ and H6′ and multiplets at δ 6.29–6.06 and δ 6.66–6.54 due to H2′, H5′ and H3′, H4′ respectively.

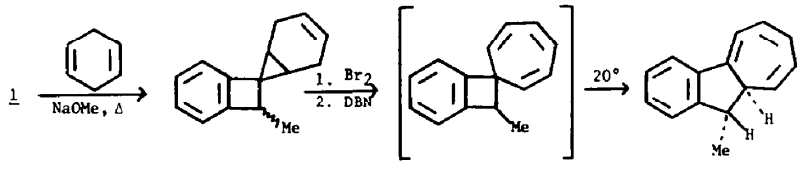


Scheme 4.

†The addition of 4,6-dimethylbenzocyclobutenylidene to simple alkenes has recently been reported.[6] No mention was made of the stereochemical outcome of the addition in the case of cyclic alkenes such as cyclohexene.

The formation of **12** simply involves double dehydrobromination of **18** to give initially the norcaradiene **10** (Scheme 2), which then suffers electrocyclic ring opening. 1-Phenylbenzocyclobutene **19** can arise (Scheme 4) through ring opening of a mono-dehydrobrominated intermediate such as **20** to give initially the carbonium ion **21**, which can undergo proton loss and base-catalysed rearrangement. The **22** → **19** conversion has precedence in the rearrangement of 5-methylenecyclohexa-1,3-diene to toluene which occurs readily at room temperature.[7]

An attempt was also made to isolate spiro[2-methylbenzocyclobutene-1,7′-cyclohepta-1′,3′,5′-triene]- **11** (Scheme 5). Thus the sodium salt of 2-methylbenzocyclobutene tosylhydrazone **1** was decomposed in the presence of 1,4-cyclohexadiene to give the adduct **23** as a mixture of stereoisomers (Scheme 5). Bromination, followed by treatment with DBN at room temperature however did not yield **11** but afforded instead *trans*-10-methyl-9a,10-dihydrobenz[*a*]azulene **3**.

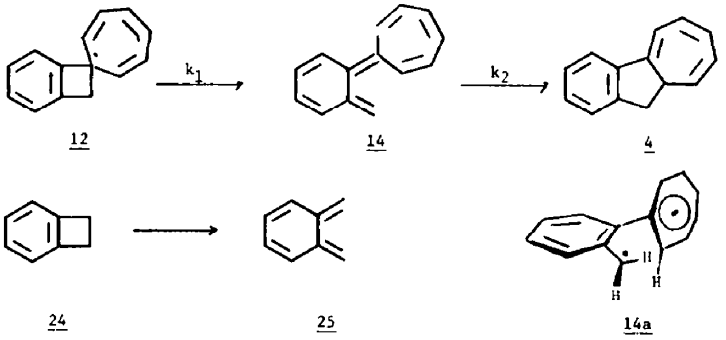


Scheme 5.

Thermal rearrangement of spiro[benzocyclobutene-1,7′-cyclohepta-1′,3′,5′-triene] **12**

When a sample of the spirocycloheptatriene **12** was heated in a sealed NMR tube at 78°, 9a,10-dihydrobenz[*a*]azulene **4** was cleanly obtained as the only product, confirming the intermediacy of **12** in the addition of benzocyclobutenylidene to benzene (Scheme 2). The rate of isomerisation of **12** → **4** was measured in isooctane solution by following the increase in absorption due to **4** at 330 nm as a function of time. Excellent first order kinetics were observed: $k_{59.5} = 8.47 \times 10^{-6}\,sec^{-1}$, $k_{71.8} = 3.97 \times 10^{-5}\,sec^{-1}$, $k_{83.5} = 1.66 \times 10^{-4}\,sec^{-1}$, giving $E_a = (125.9 \pm 0.8)$ Kj mol^{-1} and $A = 1.38 \times 10^{14}\,sec^{-1}$. We assume that $k_2 \gg k_1$ (Scheme 6) in this reaction, i.e. the intermediate *o*-xylylene **14** (or its equivalent diradical, see below) is very short lived and not kinetically significant. Thus the rate constants measured correspond to k_1.

It is instructive to compare the reactivity of **12** with that of the parent benzocyclobutene molecule **24**. Extrapolation of the data of Roth *et al.*[8] gives a value of $k = 1.49 \times 10^{-11}\,sec^{-1}$ for the **24** → **25** isomerisation at 71.8°C. The rate constant for our system **12** at 71.8° is $3.97 \times 10^{-5}\,sec^{-1}$. Thus at this temperature *the ring opening of* **12** → **14** *is* 2.7×10^{6} *times faster than that of* **24** → **25**. This can be explained in terms of intermediate **14** being considerably more stable than **25**. Thus if **14** were to have an essentially planar structure, the *o*-xylylene moiety would be conjugated through to the cycloheptatriene ring. Molecular models indicate however that in a planar structure **14** there is steric clash of the inner methylene hydrogen with the proximate terminal cycloheptatriene hydrogen. It is therefore likely that in the intermediate the cycloheptatriene is tilted at an angle to the benzenoid ring. If this angle of tilt were to approach 90°, conjugation between the two ring systems would be completely disrupted, and the structure of the intermediate would correspond to that of an isolated benzyl radical linked to a cycloheptatrienyl radical **14a**. The actual situation may correspond to something in between two extremes of planar **14** and orthogonal **14a**. It may be noted that for the parent cycloheptatrienyl radical, an empirical resonance energy of 130 KJ mol^{-1} has been determined, and this radical is therefore extensively stabilised.[9] For the formation of an intermediate having some of the diradical character **14a**, this type of stabilisation would be reflected in the transition state for the ring opening, leading to the greatly increased reactivity observed for **12** over the parent benzocyclobutene **24**. The Me substituted spirocycloheptatriene **11** appears to be even more reactive than **12**, since we were unable to isolate **11** under conditions where **12** is stable (Scheme 5). This even greater reactivity can be attributed both to steric destabilisation due to the methyl group in the reactant **11**, and stabilisation of the benzylic centre by methyl substitution at the benzylic centre in the intermediate analogous to **14a**.



Scheme 6.

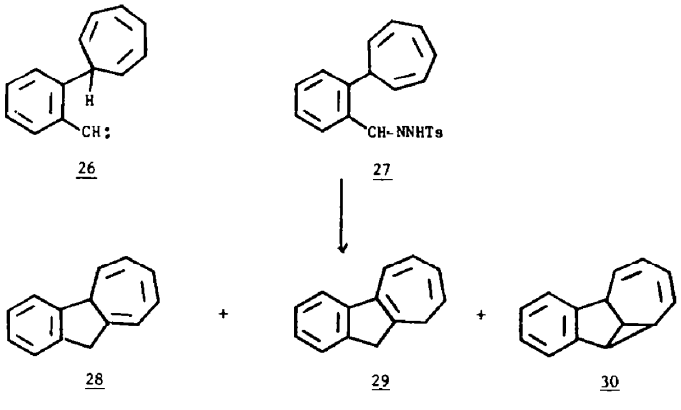
Further evidence against the intermediacy of an approximately planar *o*-xylylene intermediate **13** or **14** comes from the observed *trans* stereochemistry of the product **3** arising from the Me substituted spirocycloheptatriene **11**. It is reasonable to assume that **11** would undergo conrotatory ring opening to give **13** having the Me group in the less crowded "outer" environment. Orbital symmetry considerations[10] demand that a concerted 10 (or 14) Π electron cyclisation of **13** take place in a disrotatory mode to give *cis*-10-methyl-9a,10-dihydrobenz[*a*]azulene. The formation of the more stable *trans* isomer **3** mitigates against the intermediacy of planar **13**, and is readily explained in terms of a least motion bonding in an intermediate having considerable diradical character. Thus overall the formation of **3** from **11**, and presumably **4** from **12** constitute further examples of thermally "forbidden" electrocyclic reactions.[11]

Finally, we note that we have been unable to trap the hypothetical *o*-xylylene intermediate **14**. Thus when the spirocycloheptatriene **12** was heated in the presence of either dimethyl fumarate or dimethyl acetylenedicarboxylate, clean rearrangement to 9a,10-dihydrobenz[*a*]azulene occurred, and no Diels–Alder adducts derived from **14** were detected. It may of course be argued that these dienophiles are not sufficiently reactive to intercept **14**, but the use of more reactive dienophiles was precluded since these reacted with the cycloheptatriene Π-system of **12**.

Decomposition of the sodium salt of 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)-*benzaldehyde tosylhydrazone* **27**

It was felt that 2-(7′-cyclohepta-1′,3′,5′-trienyl-) phenylcarbene **26** possessed the potential to also give rise to spiro[benzocyclobutene-1,7′-cyclohepta-1′,3′,5′-triene] **12** by insertion of the carbenic centre into the benzylic C–H bond. Accordingly, the tosylhydrazone **27** was prepared, and the decomposition of its sodium salt was investigated under various conditions (Scheme 7). These reactions yielded three isomeric hydrocarbons which were identified as 4a, 10-dihydrobenz [*a*]azulene **28**, 9,10-dihydrobenz[*a*-] azulene **29** and 8,9-benzotricyclo[5.3.0.^{2,10}]dexa-3,5,8-triene **30**. Compound **28**, a colourless oil when freshly purified, rapidly acquired a blue-green colour on standing, probably due to the formation of trace amounts of benz[*a*]azulene. The NMR spectrum of **28** showed H4a as a broad structureless multiplet at δ 3.5, upfield from the methylene singlet at δ 3.93, due to shielding resulting from it being in the 7 position of the cycloheptatriene ring.[12] When the H4a signal was irradiated, the doublet of doublets at δ 5.12 became a doublet, which can therefore be assigned to H5, with $J_{5,4a} = 4$ Hz and $J_{5,6} = 10$ Hz. Little effect was observed on the spectrum when the methylene protons H10 were irradiated, as expected from their isolated position. Evidence for the non-conjugated nature of **28** is provided by its electronic spectrum which shows much lower extinction coefficients when compared with the spectra of the conjugated isomers **4** and **29** (see below).

9,10-Dihydrobenz[*a*]azulene **29** is a low melting solid, which tends to turn green on standing. The NMR spectrum of **29** shows a doublet at δ 2.86 attributable to H9, which is shielded due to its position in the cycloheptatriene ring,[12] relative to the benzylic protons which resonate as a singlet at δ 3.35. A well-defined doublet of triplets at δ 5.5 is clearly due to H8 as irradiation of H9 reduced it to a doublet. Two other sets of vinylic resonances are present as doublet of doublets at δ 6.14 and 6.60 due to H7 and H6 respectively. Another possible structure which would appear to fit these data is **31**. This structure is rejected on mechanistic grounds (see below) and on the basis of the chemical shift of the remaining vinylic proton which occurs in the aromatic region of the spectrum. This resonance can be assigned to H5 in structure **29**, since that proton is deshielded due to its proximity to



26 27

28 + 29 + 30

Conditions for decomposition of Na salt of 27	Product Ratio 28 : 29 : 30
Diglyme, 120°	1 : 1.5: 5
Diglyme, Cu_2Cl_2, 120°	1 : 1.3: 5
Benzene, 100°	1 : 1.6: 3.2
THF, hν, 0°	2.3: 1 : 2.9
Pyridine, 60°	1 : 4.8: 6.5

Scheme 7.

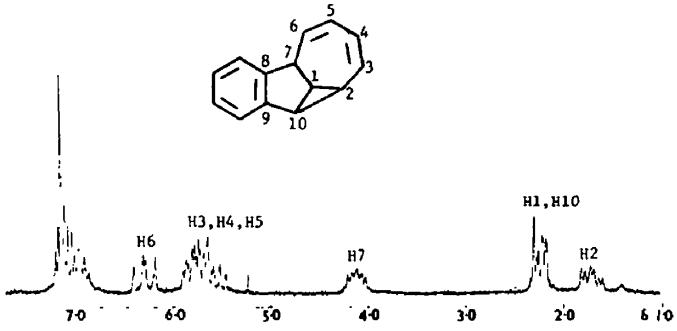


Fig. 3. 90 MHz ^{1}H NMR spectrum of 8,9-benzotricyclo-[5.3.0.0^{2,10}]deca-3,5,8-triene **30**.

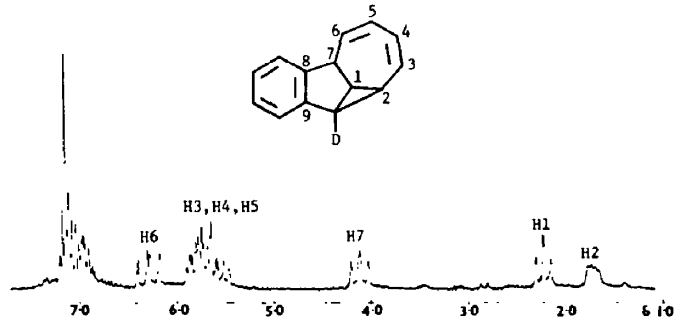


Fig. 4. 90 MHz ^{1}H NMR spectrum of 8,9-benzotricyclo-[5.3.0.0^{2,10}] deca-3,5,8-triene-10-D$_1$ **32**.

the aromatic ring, as is the analogous proton in 9a,10-dihydrobenz[*a*]azulene **4**, while no such deshielding influence on a vinylic proton would be expected for **31**.

8,9-Benzotricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene **30** has previously been reported[13,14] as the major product of the Ag^+ catalysed reaction between benzyne and cyclooctatetraene. This reaction was repeated, and the product found to be identical with the third hydrocarbon obtained from tosylhydrazone **27**. The NMR spectrum of **30** shows certain unusual features, and is reproduced in Fig. 3. The signal due to H2 appears as an approximately first order doublet of doublets of doublets centred at δ 1.74. Irradiation of the upfield portion of the vinylic multiplet, which is likely to contain H3, caused the H2 signal to become a doublet of doublets (apparent triplet). This revealed the coupling constants $J_{2,3} = 3$ Hz, $J_{2,1} = 8$ Hz and $J_{2,10} = 8$ Hz. Irradiation of H2 itself only caused some sharpening of the upfield vinylic pattern, the H1 and H10 resonances being too close to H2 to be observed under decoupling conditions. The vinylic doublet of doublets centred at δ 6.28 is due to H6, as this proton would feel most the deshielding influence of the aromatic ring. When H6 was irradiated, the 7 line resonance at δ 4.11 became a broad structureless multiplet as expected for H7. Irradiation of H7 collapsed the H6 vinylic signal to a doublet, revealing the couplings $J_{6,5} = 11$ Hz and $J_{6,7} = 8$ Hz. This irradiation also produced an unexpected effect on the remaining 2 proton resonance centred at δ 2.27. This irregular multiplet, which must be due to H1 and H10, became a clean doublet, with a separation of 8 Hz, corresponding to the coupling of each of these protons to H2. Conversely irradiation of the signal at δ 2.27 caused H7 to collapse to a doublet, with $J_{7,6} = 8$ Hz. The above observations would seem to indicate that *the benzylic proton H*10 *and the central proton H*1 *have identical chemical shifts*. This unusual situation was not further clarified by a 270 MHz spectrum, but was confirmed by examination of the spectrum of the C10 deuterated compound **32** (Fig. 4). This material was obtained from the deuterated tosylhydrazone prepared from 2-(7′-cyclohepta-1′,3′,5′-trienyl)benzaldehyde formyl-D1 (Experimental). In the spectrum of **32**, the position of the deuterium is apparent both from the integration and from the appearance of the peaks in the aliphatic region. The signal at δ 2.3, now due to H1 only, is a doublet of doublets (apparent triplet), as is the H7 signal, although the latter is broadened. When H7 was irradiated, H1 became a doublet with $J_{1,2}$ *ca* 7 Hz, and therefore $J_{1,7}$ is also *ca* 7 Hz. The broad hump at δ 1.74 due to H2 became a broad doublet with $J_{2,1} = 7.5$ Hz when the upfield region of the vinylic multiplet was irradiated.

Mechanism of formation of the hydrocarbons **28**, **29** *and* **30** *from tosylhydrazone* **27**

A control experiment established that 9a,10-dihydrobenz[*a*]azulene **4** is thermally stable in diglyme, and it is therefore unlikely that the isomeric dihydrobenz[*a*]azulenes **28** and **29** are formed via **4** in the thermal decompositions (Scheme 7). Irradiation of **4** does however lead to quantitative conversion into **28** by means of a suprafacial 1,7-hydrogen shift, a process

well-documented in cycloheptatrienes.[15] In **28** the cycloheptatriene chromophore is not conjugated with the aromatic ring, and this leads to shorter wavelength absorption maxima for **28**. This explains why the potentially photoreversible equilibrium **4** ⇄ **28** is not established, but **4** is cleanly isomerised to **28**. Although the appropriate control experiment has not been carried out, it is probably that **29** can also be photoisomerised to **28**, and it is therefore possible that the increased proportion of **28** (at the expense of **29**) observed in the photochemical decomposition of the sodium salt of tosylhydrazone **27** results from **29** → **28** isomerisation. However, since products **28**, **29** and **30** only are formed in all the decompositions, it is highly probable that a common reaction pathway exists for the thermal and photochemical reactions, and that **4** is not an intermediate in the formation of **28** or **29**.

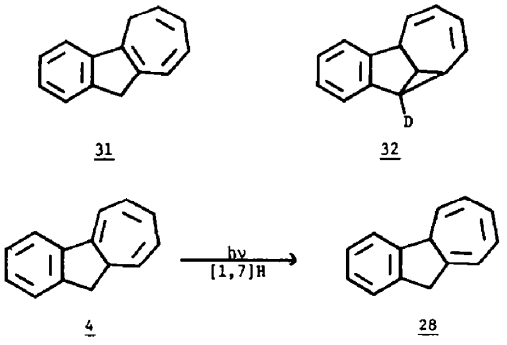
The most likely mechanism for the decomposition of the sodium salt of **27** is not one proceeding via carbene **26** (since this should give rise to some 9a,10-dihydrobenz[*a*]azulene **4**), but one involving a pyrazoline intermediate **34** (Scheme 9). The latter could readily arise from an intramolecular 1,3-dipolar cycloaddition of the CHN_2 group of diazo compound **33** onto the proximate cycloheptatriene Π-bond. An attempt was made to detect the postulated intermediates **33** and **34** by warming the tosylhydrazone **27** with NaOMe in pyridine at 60°, conditions which are known, for example, to yield phenyldiazomethane from benzaldehyde tosylhydrazone.[16] Only hydrocarbons **28**, **29** and **30** were detected even under these mild conditions, suggesting that the **33** → **34** reaction and subsequent decomposition of **34** occur very rapidly.† Loss of nitrogen from pyrazoline **34** would give diradical **35**, which can readily give rise to the cyclopropane derivative **30**. Formation of 4a,10-dihydrobenz[*a*]azulene **28** can occur by intramolecular H atom transfer from C9a to C10, while C9a → C9 H atom transfer would give compound **36**, which, as a substituted indene derivative, would be expected to isomerise under the reaction conditions to the conjugated isomer **29**. Thus the absence of **4**, and the formation of **28**, **29** and **30** can readily be explained in terms of this mechanism in which intramolecular 1,3-dipolar addition in **33** is more efficient than nitrogen loss to give carbene **26**.

EXPERIMENTAL

General directions are given in the accompanying paper.[1]

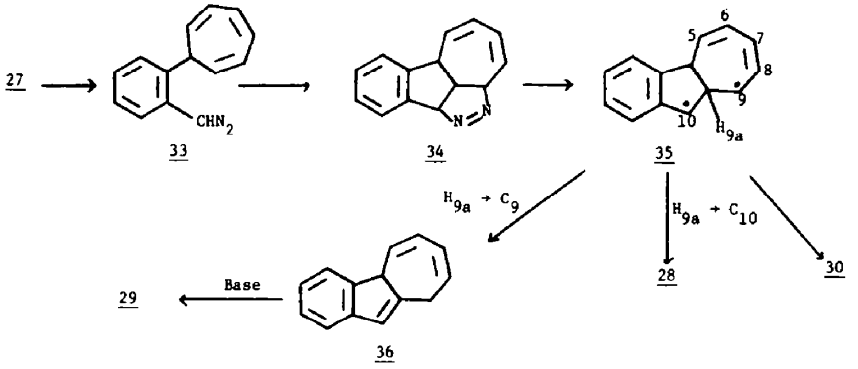
Thermolysis of the sodium salt of 2-methylbenzocyclobutenone tosylhydrazone in benzene

NaH (105 mg of 80%, 3.5 mmol) was added to a soln of the tosylhydrazone **1**[1] (1.0 g, 3.3 mmol) in THF (20 ml) under N_2. The mixture was stirred at room temp for 15 min, and the



31 32 4 28

Scheme 8.



33 34 35 28 30 29 36

Scheme 9.

†Preliminary attempts to prepare the diazo compound **33** by oxidation of 2-(7′-cycloheptatrienyl)benzaldehyde hydrazone have also been unsuccessful. Hydrocarbons **28**, **29** and **30** were again formed.

THF was then evaporated and replaced by benzene (200 ml). The mixture was refluxed for 3 hr. The benzene was evaporated and the residue partitioned between ether and water. Acidification of the aqueous layer followed by ether extraction gave unchanged tosylhydrazone (380 mg). The original ether layer afforded a yellow oil, which was subjected to preparative tlc to give from the fast moving band *trans*-9*a*,10-*dihydro*-10-*methylbenz*[a]*azulene* **3** as an oil (170 mg, 26%, or 42% based on unrecovered tosylhydrazone), b.p. 115°/0.25 mm (Found: C, 92.9; H, 7.4. $C_{15}H_{14}$ requires: C, 92.7; H, 7.3%). NMR ($CDCl_3$) δ: 7.56–7.0 (m, 4 H, ArH), 6.72–5.94 (m, 4 H, vinyl), 5.30 (dd, $J_{9,9a}$ 4 Hz, $J_{9,8}$ 10 Hz, 1 H, H9), 3.30 (dq, $J_{10,9a}$ 4 Hz, $J_{10,Me}$ 7 Hz, 1 H, H10), 2.54 (m, 1 H, H9a), 1.36 (d, J 7 Hz, 3 H, methyl) (Fig. 1). MS: 194 (M^+, 30%), 180 (15), 179 (100), 178 (45), 165 (10), 152 (8), 115 (5), 89 (18), 76 (10). UV (EtOH) λ_{max} 211 (log ε 3.77), 241 (3.75), 331 (3.56) nm.

Benzocyclobutenone tosylhydrazone **2**

A soln of benzocyclobutenone[17] (2.27 g, 19 mmol) and tosylhydrazine (3.58 g, 19 mmol) in the minimum volume of MeOH containing a few drops of dil HCl was kept at room temp overnight. The mixture was then cooled and the ppt collected and recrystallised from MeOH–H_2O to give the *tosylhydrazone* **2** (4 g, 73%) as colourless prisms, m.p. 156–7° (Found: C, 63.0; H, 5.1. $C_{15}H_{14}N_2O_2S$ requires: C, 62.9; H, 4.9%). NMR ($CDCl_3$) δ: 8.1–7.8 and 7.5 7.2 (m, 9 H, ArH and NH), 3.75 (s, 2 H, benzylic), 2.40 (s, 3 H, methyl). MS (120°): 286 (M^+, 33%), 285 (16), 222 (16), 221 (123), 155 (7), 147 (20), 139 (16), 131 (100), 118 (27), 116 (67), 104 (40), 102 (60), 91 (60), 89 (30), 77 (57), 65 (30), 63 (20).

Thermolysis of the sodium salt of benzocyclobutene tosylhydrazone in benzene

NaH (130 mg, 4.3 mmol) was added to a soln of the tosylhydrazone **2** (510 mg, 1.8 mmol) in THF (15 ml) under N_2. The mixture was stirred at room temp for 15 min and then benzene (140 ml) was added, and the mixture refluxed for 70 hr. The benzene was removed by distillation and the residue partition between ether and water. Acidification of the aqueous layer followed by ether extraction gave unchanged tosylhydrazone (230 mg). The original ether layer was washed with water, dried and evaporated to give a brown oil (260 mg). Preparative tlc gave 9*a*,10-*dihydrobenz*[a]*azulene* **4** (89 mg, 27%, or 51% based on unrecovered starting material) as an oil, b.p. 88°/0.03 mm, which went green on storage (Found: C, 93.4; H, 6.8. $C_{14}H_{12}$ requires: C, 93.3; H, 6.7%). NMR ($CDCl_3$) δ: 7.56–7.05 (m, 4 H, ArH), 6.55 6.30 (m, 3 H, vinyl), 6.22–6.00 (m, 1 H, vinyl), 5.24 (dd, $J_{9,9a}$ 4 Hz, $J_{9,8}$ 9.5 Hz, 1 H, H9), 3.60 (dd, $J_{10x,10n}$ 18 Hz, $J_{10x,9a}$ 10 Hz, 1 H, H10x), 3.18–2.78 (m, 2 H, H10n, H9a) (Fig. 2). MS: 180 (M^+, 100%), 179 (100), 178 (60), 165 (55), 152 (17), 115 (8), 89 (25), 76 (25). UV (EtOH) λ_{max} 217 (log ε 4.53), 250 sh (3.91), 330 (3.94) nm.

Preparation of benz[a]*azulene* **6** *and* 10-*methylbenz*[a]*azulene* **5**

(i) A soln of triphenylmethyl hexafluorophosphate (300 mg, 0.77 mmol) in the minimum volume of CH_2Cl_2 was added to a soln of 9a,10-dihydrobenz[a]azulene (132 mg, 0.73 mmol) in CH_2Cl_2 (3 ml) under N_2. After 10 min the yellow ppt which had formed was collected and washed with anhydrous ether to give the *tropylium hexafluorophosphate* as pale yellow crystals (140 mg, 59%), m.p. *ca* 130° (dec). NMR (CH_3CN) δ: 9.63–7.46 (m, 9 H, ArH and tropylium H), 4.63 (s, 2 H, benzylic). The salt was partitioned between ether and 50% aqueous Me_3N soln, and the dark blue ether layer washed with water, dried and evaporated to give a dark green solid (100 mg). Recrystallisation from EtOH gave *benz*[a]*azulene* **6** as dark green plates (67 mg, 51% overall), m.p. 189–190° (sealed capillary) (lit.[18] 188°) after sublimation at 120–140°/0.2 mm. The NMR and UV spectra were identical with those reported.[19,20]

(ii) A soln of triphenylmethyl hexafluorophosphate (282 mg, 0.73 mmol) in CH_2Cl_2 (8 ml) was added to a soln of 3 (140 mg, 0.72 mmol) under N_2. The soln went dark but no ppt had appeared after 15 min at room temp. Trimethylamine (25%, 15 ml) was added, and the mixture extracted with CH_2Cl_2. The blue organic extract was washed with water, dried and evaporated to give a blue solid. Preparative tlc failed to separate triphenylmethane from the product. Accordingly the mixture was dissolved in light petroleum and extracted several times with 85% H_3PO_4 soln. The light petroleum extract yielded triphenylmethane (85 mg). The yellow acid extract was poured onto ice and extracted with ether. The blue ether layer was washed with water, dried and evaporated to give a dark green solid (74 mg). Recrystallisation from EtOH–H_2O gave 10-*methylbenz*[a]*azulene* **5** as dark green needles (60 mg, 39%), m.p. 80° after sublimation at 75°/0.1 mm (Found: C, 93.6; H, 6.6. $C_{15}H_{12}$ requires: C, 93.7; H, 6.3%). NMR (CCl_4) δ: 8.28 (m, 6 H, ArH), 7.05–6.05 (m, 3 H, ArH), 2.5 (s, 3 H, methyl). MS: 192 (M^+, 100%), 191 (87), 165 (20). UV (cyclohexane) λ_{max} 251 (log ε 3.94), 261 (3.97), 298 (4.77), 3.07 (4.79), 350 (3.14), 367 (2.46), 387 (3.58), 408 (3.30) nm.

1,1-*Dibromobenzocyclobutene* **15**

Benzocyclobutenone[17] (4.0 g, 34 mmol) was added under N_2 to a slurry of PBr_5 (22.5 g, 52 mmol) in CH_2Cl_2 (50 ml), and the mixture was refluxed for 24 hr. The solvent was evaporated, and the residue stirred with 20% $NaHCO_3$ soln (400 ml) for 30 min, and then worked up by ether extraction. Removal of the solvent followed by distillation gave the *dibromide* **15** as a colourless oil (6.55 g, 79%), b.p. 59°/0.3 mm (lit.[21] 85°/0.5 mm). NMR (CCl_4) δ: 7.4–6.8 (m, 4 H, ArH), 4.16 (s, 2 H, benzylic). MS: 264, 262 (M^+, 3%), 184 (63), 182 (55), 102 (100), 101 (29), 75 (34), 50 (39), 51 (45).

Trapping of benzocyclobutenylidene with 1,4-*cyclohexadiene*

(i) To a soln of benzocyclobutenone tosylhydrazone (500 mg, 1.8 mmol) in THF (15 ml) contained in a thick walled ampoule was added NaH (100 mg, 3 mmol). The gel-like ppt was stirred for 90 min, and then most of the THF was evaporated using a stream of N_2. A mixture of 1,4-cyclohexadienenbenzene (34:76, 3.4 g) was added, and the sealed ampoule was heated at 140° for 2 hr. The cooled mixture was diluted with water and worked up by ether extraction to give a brown oil (280 mg). Distillation gave anti and syn-*spiro*[*benzocyclobutene*-1,7′-*bicyclo*[4.1.0]*hept*-3′-*ene*] **17a** and **17b** (180 mg, 56%), b.p. 60°/0.2 mm as a pale yellow oil, which turned green on standing (Found: C, 92.5; H, 7.65. $C_{14}H_{14}$ requires: C, 92.25; H, 7.75%). NMR (CCl_4) δ: 7.2–6.32 (m, 4 H, ArH), 5.52–5.37 (m, 2 H, vinyl), 3.10 and 2.81 (2 × s, 2 H, benzylic), 2.7 1.8 (m, 4 H, methylene), 1.67–1.35 (m, 2 H, cyclopropane). From the heights of the signals at δ 3.10 and 2.81, the ratio of **17a**:**17b** was *ca* 7:4. MS: 182 (M^+, 50%), 167 (100%), 165 (55), 128 (85), 115 (60), 104 (75), 77 (55).

(ii) A soln of 1,1-dibromobenzocyclobutene **15** (15 g, 57 mmol) in 1,4-cyclohexadiene-benzene (72:28, 40 ml) was cooled under N_2 to −5°, and ethereal MeLi (53 ml, 1.1 M) was added with stirring over 90 min. Stirring was continued at room temp for 3 hr, and then the mixture was treated with ice-water, and worked up by ether extraction to give a pale yellow oil (5.83 g, 56%), whose NMR spectrum was essentially identical with the material prepared under (i).

Bromination-dehydrobromination of adduct **17**

Preparation of spiro[*benzocyclobutene*-1,7′-*cyclohepta*-1′,3′,5′-*triene*] **12**. To a soln of the alkene mixture **17** (1.5 g, 8.2 mmol) in CH_2Cl_2 (5 ml) was added at 0° under N_2 a soln of Br_2 (1.3 g, 8.2 mmol) in CH_2Cl_2 (15 ml) over 30 min. The solvent was evaporated to give the *dibromide* **18** (2.8 g, 100%) as a crystalline solid. A small sample was recrystallised from light petroleum to give needles, m.p. 93–6° (Found: C, 49.0; H, 4.3. $C_{14}H_{14}Br_2$ requires: C, 49.2; H, 4.1%). NMR (CCl_4) δ: 7.22–6.75 (m, 4 H, ArH), 4.6–4.0 (m, 2 H, bromomethine), 3.10 (m, 2 H, benzylic), 3.0 2.3 (m, 4 H, methylene), 1.8–1.3

(m, 2 H, cyclopropyl). A soln of the dibromide **18** prepared as above (7.3 g, 21 mmol) in THF (45 ml) was treated with DBN (40 g, 322 mmol) and the mixture was stirred at 38° for 48 hr. The soln was diluted with H_2O, extracted with ether, and the ether extracts washed successively with H_2O, dil HCl and $NaHCO_3$ soln. Solvent removal at 5° from the dried extract gave a yellowish oil (3.43 g) which was chromatographed on 10% $AgNO_3$–Al_2O_3 (100 g). Elution with light petroleum gave 1-*phenylbenzocyclobutene* **19** (495 mg, 13%) as a colourless oil, spectroscopically identical with a sample prepared as described below. Elution with 5–50% EtOAc–light petroleum gave the *spirocycloheptatriene* **12** (409 mg, 11%) as a colourless oil, b.p. 40°/0.01 mm (Found: C, 93.3; H, 7.0. $C_{14}H_{12}$ requires C, 93.3; H, 6.7%). NMR (CCl_4) δ: 7.2–6.8 (m, 4 H, ArH), 6.66–6.56 (m, 2 H, H3', H4'), 6.29–6.06 (m, 2 H, H2', H5'), 5.71 (d, J = 9.5 Hz, 2 H, H1', H6'), 2.90 (s, 2 H, benzylic). MS: 180 (M^+, 60%), 179 (100), 178 (80), 165 (60), 152 (20), 88 (30), 76 (30), 63 (20). UV (isooctane) λ_{max} 215 (log ε 3.95), 267 (3.64), 273 (3.62) nm.

1-*Phenylbenzocyclobutene* **19**

A soln of 1-phenylbenzocyclobutenol[22] (330 mg) in MeOH (8 ml) was stirred with 10% Pd-C (100 mg) under H_2 at room temp for 6.5 hr. The mixture was diluted with ether, filtered and the filtrate evaporated. The residue was filtered through a short column of Al_2O_3 in light petroleum to 1-*phenylbenzocyclobutene* **19** (292 mg, 78%), b.p. 60°/0.05 mm. This compound has been reported previously,[23] but does not seem to have been characterised adequately. (Found: C, 93.5; H, 7.0. $C_{14}H_{14}$ requires: C, 93.3; H, 6.7%). NMR ($CDCl_3$) δ: 7.39–7.05 (m, 9 H, ArH), 4.68 (dd, J 3 Hz, 5 Hz, 1 H, H1), 3.71 (dd, J 5 Hz, 14 Hz, 1H, H2 *trans* to H1), 3.05 (dd, J 3 Hz, 14 Hz, 1H, H2 *cis* to H1).

Trapping of 2-methylbenzocyclobutenylidene with 1,4-cyclohexadiene

To a soln of NaOMe from Na (300 mg) in MeOH (15 ml) was added 2-methylbenzocyclobutenone tosylhydrazone (2.15 g). The soln was stirred at 40° for 30 min, and then the MeOH was removed under vacuum and replaced by 1,4-cyclohexadiene-benzene (72:28, 20 ml). The resulting mixture was refluxed for 24 hr, diluted with water and worked up by ether extraction to give an oil, which was filtered through a short column of Al_2O_3 to give *spiro[2-methylbenzocyclobutene-1,7'-bicyclo[4.1.0]hept-3'-ene]* **23** as an oil (140 mg, 11%), b.p. 90°/0.1 mm. (Found: C, 91.5; H, 8.1. $C_{15}H_{16}$ requires C, 91.8; H, 8.2%). NMR (CCl_4) δ: 7.1–6.4 (m, 4 H, ArH), 5.7–5.4 (m, 2 H, vinyl), 2.27 and 3.33 (q, J 7 Hz, total 1 H, benzylic), 2.8–2.1 (m, 4 H, methylene), 1.38 and 1.20 (d, J 7 Hz, total 3 H, methyl), 1.7–1.3 (m, 4 H, cyclopropane).

Bromination-dehydrobromination of adduct **23**

To a soln of the adduct mixture **23** (210 mg, 1.07 mmol) in CH_2Cl_2 (5 ml) at 0° was added a soln of Br_2 (173 mg, 1.08 mmol) in CH_2Cl_2 (5 ml) over 20 min. The solvent was evaporated and the residue dissolved in THF (5 ml), treated with DBN (3.2 g, 2.5 mmol) and stirred at room temp (20–25°) for 2.5 days. The mixture was diluted with water, extracted with ether, and the ether extract washed with dil HCl, $NaHCO_3$ soln and dried. Removal of the ether at room temp gave a faintly green oil (55 mg), shown by NMR analysis to contain mainly *trans-10-methyl-9a,10-dihydrobenz[a]azulene*, and another component, possibly 1-methyl-2-phenylbenzocyclobutene. The mixture was chromatographed on 10% $AgNO_3$–Al_2O_3 (30 g). Elution with light petroleum gave a trace of material which was not further investigated. Elution with 5–25% EtOAc–light petroleum gave pure trans-10-*methyl*-9a,10-*dihydrobenz[a]azulene* **3** (30 mg). The NMR spectrum was identical with that obtained from the thermolysis of the sodium salt of tosylhydrazone **1** in benzene (Fig. 1) except that the small impurity doublet at δ 1.47 was lacking.

Thermal rearrangement of the spirocycloheptatriene **12** *to* 9a,10-*dihydrobenz[a]azulene* **4**

(i) A soln of **12** (50 mg) in C_6D_6 (0.5 ml) was sealed in an NMR tube with TMS as internal standard. The soln was heated at 78° and the spectrum was scanned intermittently. Signals due to **4** were observed to appear, while those due to starting material **12** decreased in intensity. After 5 hr, only signals due to **4** were discernible. NMR (C_6D_6) δ: 7.4–6.7 (m, 4 H, aromatic), 6.6–5.7 (m, 4 H, vinyl), 5.1–4.8 (m, 1 H, vinyl), 3.3–2.5 (m, 3 H, benzylic). The C_6D_6 was evaporated to give **4** as a faint green oil (50 mg), whose NMR spectrum in CCl_4 was identical with that of the material obtained from the addition of benzocyclobutenylidene to benzene (Fig. 2).

(ii) For the rate measurements, **12** (19.71 mg) was dissolved in isooctane (250 ml) and the soln was thoroughly deoxygenated with a stream of N_2. Small portions (*ca* 4 ml) were sealed in ampoules, which were wrapped in foil to exclude visible light. This is essential since in this dilute solution the photochemical isomerisation of the product **4** → **28** (see below) occurs readily in daylight or laboratory light. The ampoules were placed in a constant temp both regulated to ±0.05°. After 10 min the first ampoule was removed, rapidly cooled to −40°, and then allowed to warm to room temp. The electronic spectrum and optical density of the soln at 330 nm was recorded. A plot of log ($OD_x - OD_t$) vs time (t), where OD_t is the optical density at time = t, and OD_x is the optical density at time = "infinity", i.e. after 10 half lives gave excellent straight lines. Rate constants were evaluated from the slopes by application of the Texas Instruments SR-56 least squares programme. The rate constants observed with the mean deviations were: 59.5°C k = (8.47 ± .30) × 10^{-6} sec^{-1}; 71.8°C k = (3.97 ± .08) × 10^{-5} sec^{-1}; 83.5°C k = (1.66 ± .01) × 10^{-4} sec^{-1}. A least squares plot of log k against T^{-1} gave the activation energy E_a = (125.9 ± 0.8) KJ mol^{-1} (30.1 ± .2 Kcal mol^{-1}) and the frequency factor A = 1.38 × 10^{14} sec^{-1}.

Attempted trapping of the o-*xylylene* **14**

(i) A soln of **12** (11 mg, 0.06 mmol) and dimethyl fumarate (9 mg, 0.06 mmol) in C_6D_6 (0.4 ml) was sealed in an NMR tube, and heated at 77°. The spectrum was checked periodically, and at the end of 5 hr the soln contained only **4** and dimethyl fumarate.

(ii) A soln of **12** (74 mg) in freshly distilled dimethyl acetylenedicarboxylate (0.5 ml) was sealed in an NMR tube and heated at 80°. The aromatic region of the spectrum was scanned periodically, but only signals ascribable to **4** could be discerned. After 6 hr most of the dimethyl acetylenedicarboxylate was removed by careful distillation in a vacuum. The residue consisted chiefly of **4** (NMR) and no signals attributable to any cycloadduct being present.

Preparation of 2-(7'-cycloheptatrienyl)benzaldehyde tosylhydrazone **27**

A soln of 2-(7'-cyclohepta-1',3',5'-trienyl)benzaldehyde[18] (1.28, 6.5 mmol) and tosylhydrazine (1.1 g, 5.9 mmol) in the minimum volume of MeOH was allowed to stand at room temp overnight. Crystallisation was induced by cooling and dropwise addn of H_2O. Recrystallisation from MeOH (charcoal) gave the *tosylhydrazone* **27** as pale brown crystals (1.12 g, 47%), m.p. 130°. (Found: C, 68.8; H, 5.5. $C_{21}H_{20}N_2O_2S$ requires: C, 69.2; H, 5.5%). NMR ($CDCl_3$) δ: 8.0–7.6 (m, 4 H, ArH, CH=N and NH, decrease in area on D_2O exchange), 7.5–7.0 (m, 6 H, ArH), 6.75–6.52 (m, 2 H, H3', H4'), 6.3–5.95 (m, 2 H, H2', H5'), 5.2 (dd, 2 H, H1', H6'), 2.94 (br t, 1 H, H7'), 2.38 (s, 3 H, methyl). MS: 194 (13%), 180 (65), 179 (100), 178 (70), 165 (50), 156 (22), 152 (13), 139 (13), 92 (35), 91 (50).

Decomposition of the sodium salt of tosylhydrazone **27**

(i) NaH (88 mg of 80%, 2.9 mmol) was added to a soln of **27** (870 mg, 2.4 mmol) in diglyme (70 ml) under N_2. The mixture was then stirred at 120–130° until gas evolution ceased

(20 min). The mixture was filtered, diluted with H_2O and worked up by ether extraction to give a brown oil (470 mg). NMR analysis showed the presence of the hydrocarbons **28**, **29** and **30** in the ratio 1:1.5:5. Chromatography on Al_2O_3 (10 g) in light petroleum gave early fractions which were mixtures, followed by a low melting solid (43 mg, 10%) which was distilled at 95°/0.01 mm to give 9,10-*dihydrobenz*[*a*]*azulene* **29** as a pale green oil which solidified on cooling. (Found: C, 93.5; H, 7.1. $C_{14}H_{12}$ requires: C, 93.3; H, 6.7%). NMR ($CDCl_3$) δ: 7.5–6.94 (m, 5 H, ArH, H5), 6.60 (dd, $J_{6,7}$ 11 Hz, 1 H, H6), 6.14 (dd, $J_{7,6}$ 6 Hz, $J_{7,8}$ 10 Hz, 1 H, H7), 5.49 (dtr, $J_{8,9}$ 6 Hz, $J_{8,7}$ 10 Hz, 1 H, H8), 3.35 (s, 2 H, H10), 2.86 (d, $J_{9,8}$ 6.3 Hz, 2 H, H9). MS: 180 (M^+, 93%), 179 (73), 178 (60), 177 (13), 166 (20), 165 (100), 152 (23), 151 (13), 89 (30), 76 (27). UV (EtOH) λ_{max} 211 (log ε 4.3), 252 (4.37), 300 (3.77) nm. Some of the earlier fractions (100 mg) were combined and subjected to preparative tlc using multiple elution with hexane. The high R_f band gave 4a,10-*dihydrobenz*[*a*]*azulene* **28** (10 mg) as a colourless oil, b.p. 91°/0.7 mm. (Found: C, 93.3; H, 6.9. $C_{14}H_{12}$ requires: C, 93.3; H, 6.7%). NMR ($CDCl_3$) δ: 7.56–6.9 (m, 4 H, ArH), 6.56 (m, 2 H, H7, H8), 6.3 (m, 1 H, H9), 6.12 (m, 1 H, H6), 5.12 (dd, $J_{5,4a}$ 4 Hz, $J_{5,6}$ 10 Hz, 1 H, H5), 3.93 (br s, 2 H, H10), 3.5 (br m, 1 H, H4a). MS: 180 (M^+, 74%), 179 (100), 178 (65), 177 (13), 166 (13), 165 (43), 152 (17), 151 (13), 89 (26), 76 (25). UV (EtOH) 212 (log ε 4.2), 267 (3.18), 274 (3.24) nm. The lower R_f band contained 8,9-*benzotricyclo*[5.3.0.0^{2,10}]*deca*-3,5,8-*triene* **30** as a pale blue oil (30 mg). NMR ($CDCl_3$) δ: 7.28–6.83 (m, 4 H, ArH), 6.28 (dd, $J_{6,7}$ 8 Hz, $J_{6,5}$ 11 Hz, 1 H, H6), 5.94–5.42 (m, 3 H, H5, H4, H3), 4.11 (7 line m, 1 H, H7), 2.27 (7 line m, 2 H, H10, H1), 1.74 (ddd, $J_{2,3}$ 3 Hz, $J_{2,1}$ 8 Hz, $J_{2,10}$ 8 Hz, 1 H, H2) (see Fig. 3). MS: 180 (M^+, 77%), 179 (100), 178 (62), 177 (12), 166 (11), 165 (58), 152 (19), 151 (10), 89 (20), 76 (15). UV (EtOH) λ_{max} 210 (log ε 4.09), 230 sh (3.83), 252 (3.41), 272 (3.32), 281 (3.20).

(ii) NaH (47 mg, 1.6 mmol) and Cu_2Cl_2 (20 mg) were added to a soln of **27** (440 mg, 1.2 mmol) in diglyme (30 ml) under N_2. After 20 min, the mixture was immersed in an oil bath at 120° and heated until gas evolution ceased (10 min). The mixture was cooled, filtered, diluted with water and worked up by ether extraction to give a brown oil (274 mg), shown by NMR analysis to contain **28**, **29** and **30** in a ratio of 1:1.3:5.

(iii) NaH (17 mg, 0.57 mmol) was added to a soln of **27** (135 mg, 0.37 mmol) in THF (5 ml) under N_2. The mixture was stirred for 10 min, the THF evaporated and replaced by benzene (25 ml), and the mixture immersed in an oil bath at 100° for 30 min. Dilution with water and work-up by ether extraction gave a yellow oil (66 mg), shown by NMR analysis to consist of hydrocarbons **28**, **29** and **30** in the ratio 1:1.6:3.2.

(iv) NaH (51 mg, 1.7 mmol) was added to a soln of **27** (330 mg, 0.9 mmol) in THF (15 ml) under N_2. The mixture was stirred for 10 min, diluted with THF (160 ml), cooled in an icebath and irradiated for 20 min. The theoretical volume of N_2 was evolved after 15 min. The mixture was concentrated, diluted with water and worked up by ether extraction to give a brown oil (166 mg). Preparative tlc gave a pale blue oil (80 mg) shown by NMR analysis to contain **28**, **29** and **30** in the ratio 2.3:1:2.9.

(v) NaOMe (23 mg, 0.43 mmol) was added to a soln of **27** (150 mg, 0.41 mmol) in pyridine (3 ml) under N_2. The mixture was stirred at 60°, and the initially clear soln became cloudy and after 15 min deposited colourless crystals of sodium *p*-toluenesulphinate. At no stage could the characteristic colour of an aryldiazomethane be detected. After 40 min the mixture was cooled, diluted with water and worked up by ether extraction to give a semisolid (75 mg). Preparative tlc gave from the lower band unchanged **27** (46 mg), and the higher R_f band (18 mg) contained by NMR analysis hydrocarbons **28**, **29** and **30** in a ratio of 1:4.8:6.5.

Control experiment

Attempted isomerisation of 9a,10-*dihydrobenz*[*a*]*azulene* **4**. A soln of **4** (47 mg) in diglyme (15 ml) was heated with NaH (15 mg) under N_2 at 120° for 30 min. Work-up by ether extraction gave a green oil (45 mg) identified as **4** by its NMR spectrum.

Photochemical isomerisation of 9*a*,10-*dihydrobenz*[*a*]*azulene* **4**

(i) A soln of **4** (25 mg) in CCl_4 (0.4 ml) was sealed in an NMR tube and irradiated with 350 nm radiation for 4 hr. The NMR spectrum indicated that complete isomerisation to **28** had occurred.

(ii) A soln of **4** (1.5×10^{-4} M) in isooctane was kept in a silica cuvette exposed to laboratory light (daylight plus fluorescent). After 6 hr the electronic spectrum of **4** was replaced by that due to **28**.

Reaction of benzyne with cyclooctatetraene[13,14]

o-Benzenediazonium carboxylate, prepared from anthranilic acid (5 g, 36.5 mmol), was suspended in a soln of freshly distilled cyclooctatetraene (19 g, 183 mmol) in MeCN (25 ml). $AgBF_4$ (130 mg, 0.67 mmol) was added and the mixture was heated at 50–60° until gas evolution ceased (2.5 hr). Volatile material was removed under vacuum, and the dark viscous residue was adsorbed onto Al_2O_3 and chromatographed on that adsorbent using light petroleum. The early fractions yielded essentially pure 8,9-*benzotricyclo*[5.3.0.0^{2,10}]*deca*-3,5,8-*triene* **30** (318 mg, 5%) as a clear oil, spectroscopically identical to the material obtained from **27**.

Preparation of 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)*benzaldehyde formyl*-D_1 *tosylhydrazone*

o-Bromobenzaldehyde (6.64 g, 36 mmol), KCN (4.66 g, 72 mmol), dry ether (40 ml), and D_2O (40 ml) were vigorously stirred at room temp for 40 hr[24]. The layers were separated, the D_2O layer was washed twice with dry ether, and the combined ether extract was dried, and concentrated to 25 ml. This layer was then stirred with fresh D_2O (30 ml) and KCN (2.3 g) for a further 48 hr. Work-up as above gave *o-bromobenzaldehyde formyl*-D_1 (5.87 g, 88%) as an oil. NMR analysis revealed 96% D in the formyl position. The deuterated aldehyde was converted into the ethylene acetal, and thence into the Grignard reagent which was reacted with 7-methoxycycloheptatriene as described for the undeuterated material.[18] This afforded 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)-*benzaldehyde formyl*-D_1 *ethylene acetal* as an oil, whose NMR spectrum was identical with that of the undeuterated material,[18] except for the absence of the acetal methine signal. A soln of the above deuterated acetal (1.6 g) in THF (20 ml) was treated with HCl (10%, 1 ml) and kept at room temp for 40 hr. Dilution with water and work-up by ether extraction gave 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)*benzaldehyde formyl*-D_1 (1.36 g) as an oil. The NMR spectrum was similar to that of the undeuterated aldehyde except that the formyl proton resonance was too small to be accurately integrated. The above aldehyde was converted into 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)*benzaldehyde formyl* D_1 *tosylhydrazone*, m.p. 128°, as described for the undeuterated material.

Thermolysis of the sodium salt of 2-(7′-*cyclohepta*-1′,3′,5′-*trienyl*)*benzaldehyde formyl*-D_1 *tosylhydrazone*

NaH (40 mg, 1.3 mmol) was added to a soln of the deuterated tosylhydrazone (392 mg, 1.1 mmol) in diglyme (40 ml) under N_2. The mixture was stirred at room temp for 25 min and then in an oil bath at 130° for 35 min. The mixture was filtered, diluted with H_2O and worked up by ether extraction to give a brown oil (200 mg). This was separated chromatographically as described previously to give (i) 4a,10-*dihydrobenz*[*a*]*azulene*-10-D_1 (10 mg). NMR δ: 7.6–6.9 (m, 4 H, ArH), 6.7–6.0 (m, 4 H, vinyl), 5.12 (dd, 0.95 H, H5), 3.9 (brs, 0.9 H, H10), 3.5 (brs, 0.95 H, H4a). MS: 181 (M^+, 82%), 180 (100), 179 (76), 178 (29), 167 (12), 166 (50), 165 (18), 153 (20), 152 (20), 89 (24).

(ii) 9,10-*Dihydrobenz*[*a*]*azulene*-10-D_1 (14 mg). NMR ($CDCl_3$) δ: 6.95 (m, 5 H, ArH, H5), 6.58 (dd, 0.97 H, H6), 6.12 (dd, 0.86 H, H7), 5.48 (dt, 0.86 H, H8), 3.45 (brs, 0.92 H, H10), 2.86 (d, 1.56 H, H9). MS: 181 (M^+, 87%), 180 (100), 179 (76),

178 (37), 177 (18), 176 (13), 167 (14), 166 (92), 165 (30), 153 (18), 152 (21), 151 (12), 89 (24), 77 (18).

(iii) 8,9-*Benzotricyclo*[5.3.0.0^{2,10}]*deca*-3,5,8-*triene*-1-D$_1$ (67 mg). NMR ($CDCl_3$) δ: 7.3–6.8 (m, 4H, ArH), 6.28 (dd, 0.85H, H6), 5.95–5.4 (m, 3H, H5, H4, H3), 4.11 (br t, 0.80H, H7), 2.34 (br t, 0.92H, H1), 1.74 (br m, 0.82H, H2) (Fig. 4). MS: 181 (M^+, 75%), 180 (100), 179 (75), 178 (24), 167 (8), 166 (40), 165 (18), 153 (14), 152 (14). In each NMR integral, peak areas are based on the assumption that the aromatic multiplet contains the whole number of protons indicated.

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