Base-promoted Eliminations within Halogenated [*n.m.*1]Propellene Frameworks

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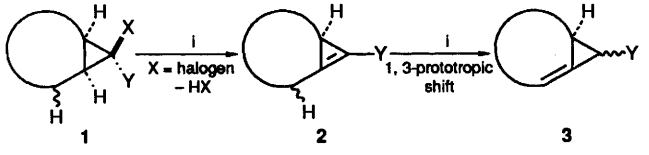
The reactions of halogenated [*n.m.*1]propellenes with potassium *t*-butoxide have been investigated. Propelladiene 9,9-dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene affords 1,6-methano[10]-annulene, 4-methylazulene, and 5*H*-benzocycloheptene, while the related tetracyclic compound 1,1,8,8-tetrachloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene reacts to give 12-chlorotricyclo[5.4.1.$0^{3,5}$]dodeca-1,3(5),6,8,10-pentaene. Treatment of 8,8-dichloro-2,3,4,7-tetrahydro-3a,7a-methano-1*H*-indene with the same base produced a mixture of the chlorodiene 8-chloro-2,3-dihydro-3a,7a-methano-1H-indene, azulene, and 4-methylazulene. The structure of the chlorodiene was established by an X-ray crystallographic study of its Diels–Alder adduct with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione. While reaction of tetracycle 1,1,*syn*-8-trichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene with base failed to produce any characterisable products, under the same conditions epimer 1,1,*anti*-8-trichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene was converted into the cycloproparene tricyclo-[5.4.1.$0^{3,5}$]dodeca-1,3(5),6,8,10-pentaene. Mechanistic proposals which account for the observed conversions have been advanced and are supported by ^{13}C-labelling studies. The initial steps in most of the reaction pathways of the substrates are probably 1,4-elimination processes involving abstraction of an allylic hydrogen, fragmentation of the strained propellene σ-bond, and ejection of the halogen in an *endo*-relationship to the abstracted proton. The primary product of these processes, bridgehead dienes such as bicyclo[4.4.1]undeca-1,3,6(11),8-tetraene, 4,4,12-trichloro-tricyclo[5.4.1.$0^{3,5}$]dodeca-1(11), 7(12),9-triene and 10-chlorobicyclo[4.3.1]deca-1,3,6(10)-triene, then undergo further reaction involving, amongst other things, 1,3-prototropic shifts. Attempts to probe the mode of formation of the C_{11}-4-methylazulene from the C_{10}-precursor 8,8-dichloro-2,3,4,7-tetrahydro-3a,7a-methano-1*H*-indene have uncovered a novel methylation reaction of azulene by the dimsyl anion.

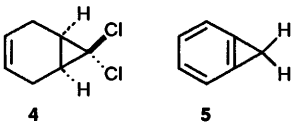
Ring-fused cyclopropanes **1** containing a proton at the ring-junction and a *trans*-related halogen at the apical cyclopropyl carbon can undergo 1,2-elimination of the elements of hydrogen halide on treatment with strong base (Scheme 1).[1] The resulting



1 **2** **3**

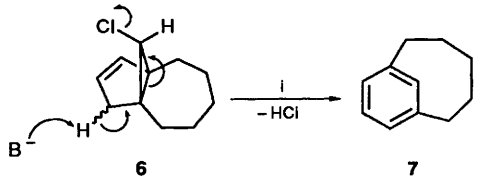
Scheme 1 *Reagents:* i, Base, *e.g.* Bu^{t}O$^-$ K$^+$

1,3-disubstituted cyclopropene **2** may be isolable but frequently this initial reaction product undergoes a base-catalysed 1,3-prototropic shift to give the isomeric and more stable methylenecyclopropane **3**. Further migration of the double bond away from the three-membered ring occurs in some circumstances.[2] This sequence of elimination and rearrangement reactions has found application in various synthetic contexts,[2,3] Perhaps the most notable example involves the base-promoted conversion of the Δ^3-trinorcarene **4** into cyclopropabenzene **5**.[3]



4 **5**

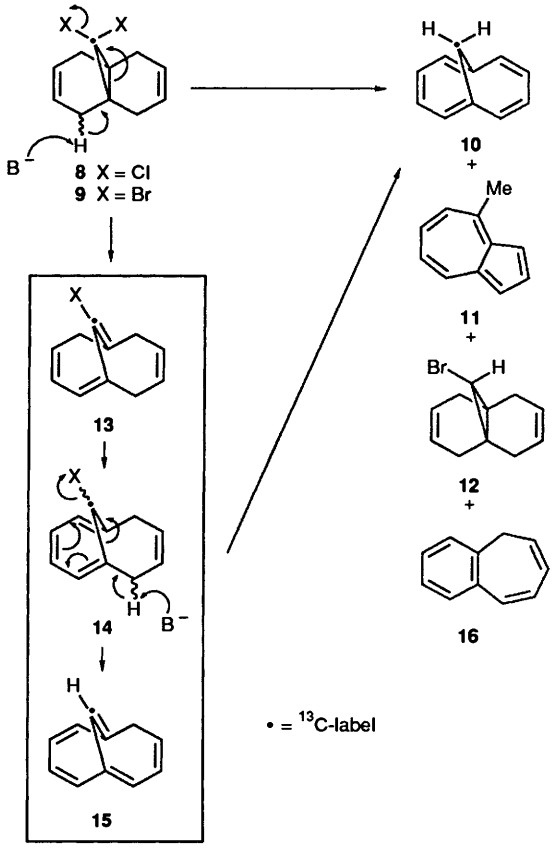
An alternative but less common elimination mode for ring-fused halogenocyclopropanes has been observed. Substrates containing a suitably disposed methylene or methine hydrogen on a carbon adjacent to the three-membered ring can sometimes undergo a base-promoted 1,4-elimination involving concomitant cleavage of the central cyclopropane σ-bond and formation of two new π-bonds to produce either a conjugated diene[4] or a benzene ring.[5,6] A spectacular recent example of such a 1,4-elimination reaction is seen in Bickelhaupt's[5] preparation of [5]metaphane **7** from the [5.3.1]propellene **6** (Scheme 2).



6 **7**

Scheme 2 *Reagent:* i, Bu^{t}O$^-$ K$^+$

In connection with attempts to explore the synthetic utility of 1,4-eliminations, we began investigating the reaction of [4.4.1]propelladienes **8** and **9** with strong base. In a preliminary communication[7] on the outcome of these reactions, we noted that bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (1,6-methano-[10]annulene) **10** and 4-methylazulene **11** are obtained, in low yields, from both substrates **8** and **9** (Scheme 3). A third



Scheme 3 *Reagents and conditions:* i, Bu^{t}O$^-$ K$^+$, Bu^{t}OH (5 mol equiv.), DMSO, 18 °C, 4 h

product, the reductively mono-debrominated compound **12**, was observed when educt **9** was employed. We proposed[7] that compound **10** was derived from an initial 1,4-elimination within the propellene framework of substrate **8** or **9**. The ensuing bridgehead diene **13** experiences a base-catalysed 1,3-prototropic shift to give the more stable tetraene **14** which, in turn, undergoes dehydrohalogenation affording pentaene **15**. Finally, a second 1,3-prototropic shift results in the conversion of intermediate **15** into the aromatic annulene **10**. The mode of formation of azulene **11** in these reactions is less obvious and has been the subject of some speculation.[8,9]

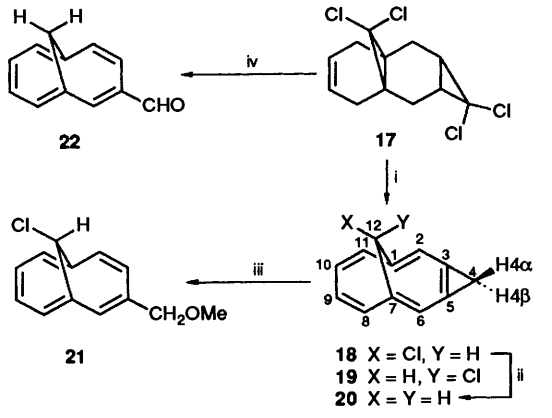
In the present paper, we describe attempts to substantiate the mechanistic proposals that have been advanced[7-9] to account for the formation of products **10** and **11** from substrates **8** and **9**. This work has involved both ^{13}C-labelling studies and an investigation of the reactions of other halogenated [*n.m.*1]-propellenes with strong base. In addition, details of our efforts to explore the scope and utility of reaction sequences involving combinations of 1,2- and 1,4-elimination reactions in conjunction with 1,3-prototropic shifts (all taking place within halogenated [*n.m.*1]propellene frameworks) are reported.

Results and Discussion

1. *Product Studies. Reaction of Propellenes* **8**, **17** *and* **23** *with Base.*—As a prelude to labelling studies, we first re-examined the reaction of the unlabelled [4.4.1]propelladiene **8**[10] with potassium *t*-butoxide, using the originally defined conditions. In addition to the previously reported products **10**[10] (10%) and **11**[11] (12%), 5*H*-benzocycloheptene **16**[12] (19%) (Scheme 3) was also observed in the reaction mixture. Compounds **10** and **16** were inseparable by TLC techniques and it was necessary to resort to preparative GC to obtain reasonably clean samples of each. The high-field ^{1}H and ^{13}C NMR spectra obtained for both products **11** and **16** agreed with the spectral data reported for these compounds by Braun[11] and Kato,[12] respectively. Compound **10** was identical in all respects with an authentic sample of bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene prepared by the method of Vogel *et al.*[10] It is noteworthy that the success of the eliminations involving substrate **8** is critically dependent on using the *t*-butyl alcohol monosolvate of potassium *t*-butoxide as the base for carrying out the reaction. If freshly sublimed potassium *t*-butoxide was used instead, complex mixtures of uncharacterisable products were obtained. We assume that the *t*-butyl alcohol molecules present at the beginning of the reaction provide a high enough proton-donor concentration to ensure that the 1,3-prototropic shift sequences proceed reasonably efficiently.

Independent subjection of each of products **10**, **11** and **16** to the original elimination conditions established that they do not interconvert. These products must therefore lie at the ends of separate reaction pathways.

In order to develop some impression of the scope and utility of 1,4-eliminations within halogenated [*n.m.*1]propellene frameworks, the reaction of propellene **17**,[13] now easily available by sequential additions of dichlorocarbene to isotetralin,[14] with base has been investigated. On treatment with potassium *t*-butoxide in tetrahydrofuran (THF) compound **17** provided the *anti*-12-chloro derivative, **18**, of the known[15] tricyclo-[5.4.1.0^{3,5}]dodeca-1,3(5),6,8,10-pentaene **20** (Scheme 4) in 15%



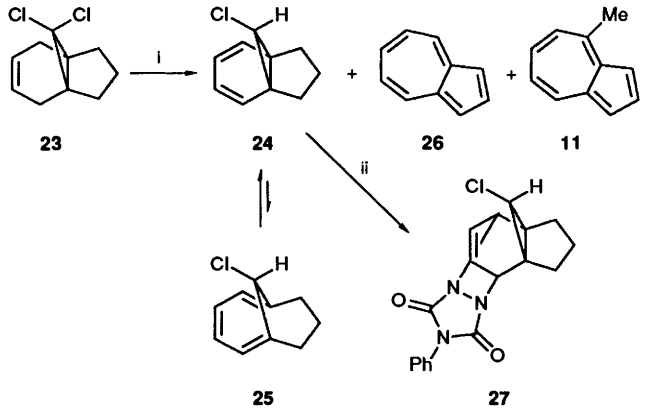
Scheme 4 *Reagents and conditions:* i, Bu^{t}O$^-$ K$^+$ (4 mol equiv.),THF, 18 °C, 20 h; ii, Bu_3SnH, C_6H_{12}, 18 °C, 7 days; iii, $AgNO_3$, MeOH, 18 °C, 4 h; iv, Bu^{t}O$^-$ K$^+$ (12 mol equiv.), THF, 18 °C, 20 h

yield (at 75% conversion). The 100 MHz ^{1}H NMR spectrum of compound **18** displayed an especially diagnostic one-proton singlet at δ 1.62 which has been assigned to the single proton (12-H) on the methano-bridge. The two mutually coupled doublets at δ 2.62 and 3.66 (J 6.9 Hz) represent the AB system expected for the two non-equivalent C-4 protons. The remaining and low-field portion of the spectrum consisted of broad aromatic singlets at δ 7.18 (four protons) and δ 7.32 (two protons). The downfield shift of the C-12 proton in compound **18** relative to the analogous proton in the parent system is of the order of 1.7 ppm. The chemical shifts of the non-equivalent C-4 protons are not influenced by the chlorine as their chemical shifts compared very favourably with those reported[15] for the parent system (δ 2.5 and 3.6). This minimal impact exerted by chlorine on the chemical shifts of the C-4 protons is taken as good evidence for the *anti*-stereochemistry illustrated in structure **18**, *i.e.* the product is less likely to be the epimeric *syn*-compound **19**. Reductive dechlorination of compound **18** with tributyltin hydride afforded the known[15] tricyclo[5.4.1.0^{3,5}]dodeca-1,3(5),6,8,10-pentaene **20** in 80% yield, thereby providing unambiguous evidence for the ring system of compound **18**. Treatment of compound **18** with silver(I) and methanol

afforded the methyl annulenyl ether **21** (75%) typifying the electrophilic ring-opening of a cycloproparene.[3]

In an attempt to ensure complete consumption of propellene **17** and thereby improve the yield of the cycloproparene **18**, the amount of potassium *t*-butoxide used in the elimination was increased to 21 molar equivalents. However, under these conditions the known[15] annulenyl aldehyde **22** (18%) was isolated in place of the expected product **18**.

The readily available[16] [4.3.1]propellene **23** (Scheme 5),



Scheme 5 *Reagents and conditions:* i, Bu^{t}O$^-$ K$^+$, Bu^{t}OH (5.6 mol equiv.), DMSO, 18 °C, 18 h; ii, PTAD, CH_2Cl_2, 18 °C, 0.25 h

when subjected to reaction with potassium *t*-butoxide–*t*-butyl alcohol monosolvate in dimethyl sulfoxide (DMSO), afforded one major and three minor products as determined by GC analysis. The major product was identified as the chlorodiene **24** (60%) on the basis of spectroscopic, chemical and crystallographic studies. The 400 MHz ^{1}H NMR spectrum of compound **24** established the presence of four vinylic and six methylene hydrogens as well as a unique hydrogen giving rise to a one-proton singlet at δ 3.49. The C_2-symmetry associated with this product is clearly evident from the 100 MHz {^{1}H} ^{13}C NMR spectrum which showed only six resonances, including two due to the sp^2-carbons and one at δ 27.4 due to the chlorinated and bridging carbon C-8. These data clearly indicate that compound **24** exists exclusively (at least within the limits of analysis) as the trinorcaradiene rather than as the cycloheptatriene valence bond isomer **25**.[17] The data described above do not, however, provide any information regarding the stereochemical disposition of the chlorine at C-8. Since compound **24** reacted instantaneously with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to produce the crystalline 1:1 Diels–Alder adduct **27**, an X-ray crystal structure of this material was undertaken. The results of this determination, which are shown as an ORTEP plot in Fig. 1, clearly establish that the chlorine is

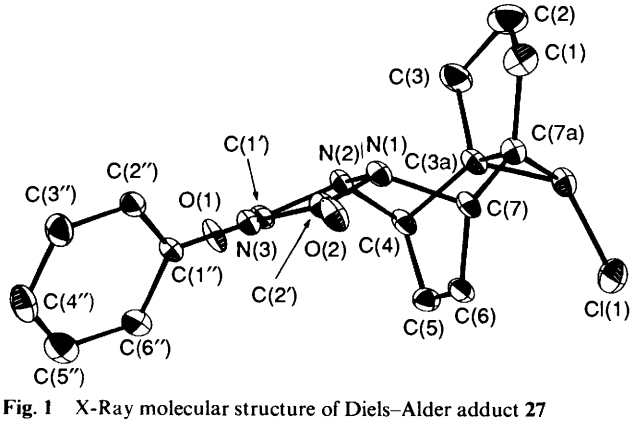
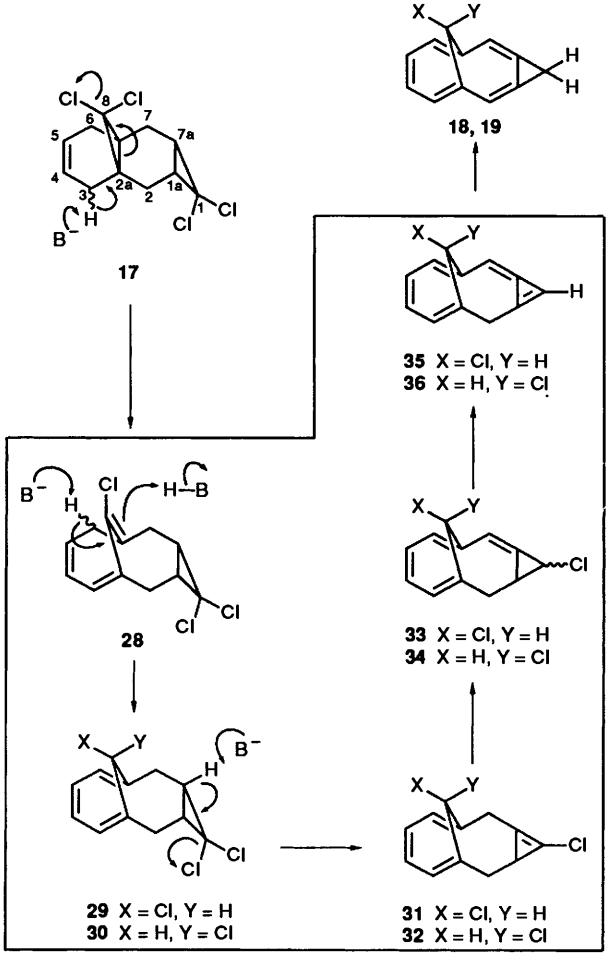


Fig. 1 X-Ray molecular structure of Diels–Alder adduct **27**

in an *anti*-relationship to the five-membered ring in adduct **27** and, by implication, the same stereochemical relationship must hold in precursor diene **24**.

The development of a light blue colouration during and after work-up in the reaction mixture derived from treatment of the propellene **23** with base suggested the presence of azulenoids amongst the products. Indeed, 100 MHz {^{1}H}^{13}C NMR analysis of the reaction revealed the presence of azulene **26** (6%) and its 4-methyl derivative **11** (6%). The third minor component detected by GC remains unidentified.

2. *Mechanistic Proposals and Supporting Experimental and Theoretical Studies.*—A. *Mechanistic proposals relating to the formation of compounds* **10**, **18** *and* **24**. A plausible pathway for the formation of bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10** from dichloride **8** has already been proposed (Scheme 3). Analogous processes can be postulated to account for the formation of the tricyclo[5.4.1.0^{3,5}]dodeca-1,3(5),6,8,10-pentaene **18** and chlorodiene **24** from their respective precursors. Hence, a 1,4-elimination within the framework of tetracycle **17** involving removal of an allylic proton at C-3 (Scheme 6), propellene bond cleavage, and ejection of the *syn*-related chlorine* would provide the bridgehead diene **28**. A 1,3-prototropic shift involving migration of one of the doubly allylic hydrogens would then give either of the epimeric monochlorotrienes **29** or **30**. Each of these could, in turn, undergo two successive 1,2-elimination/1,3-prototropic shift

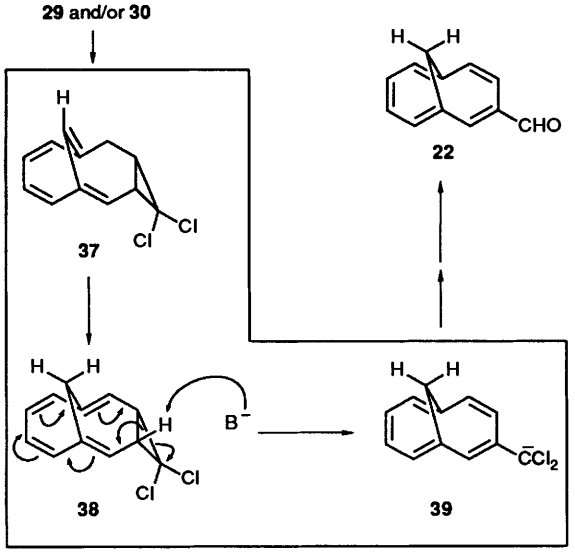


Scheme 6

* The suggestion that this chlorine is lost in the 1,4-elimination process derives from stereoelectronic considerations which will be discussed later.

sequences to provide, *via* **31**–**36**, the epimeric 12-chlorotricyclo[5.4.1.$0^{3,5}$]dodeca-1,3(5),6,8,10-pentaenes **18** and **19**. In principle, base-catalysed epimerisation of *syn*-chloride **19** could result in the observed isomer **18** since the latter compound is probably the thermodynamically more stable epimer because the chlorine is placed in a position remote from the cyclopropyl proton 4-H$^{\alpha}$. Thus the observed stereochemistry about C-12 in the reaction product **18** could be a reflection of the greater stability of this compound or (less likely) of a kinetic preference for the formation of *anti*-product **29** over *syn*-isomer **30** during the prototropic rearrangement of intermediate **28**.

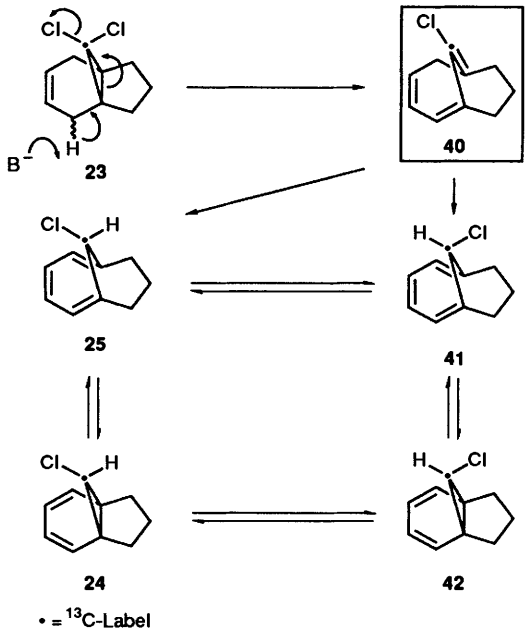
One of a number of possible mechanistic rationalisations for the formation of aldehyde **22** from educt **17** is shown in Scheme 7. Thus, elimination of the elements of hydrogen chloride from either **29** or **30**, intermediates in the proposed pathway leading to the cycloproparene **18** (Scheme 6), would produce tetraene **37** that should undergo base-promoted conversion, *via* isomer **38**, into the [10]annulenyl anion **39**. Finally, protonation and hydrolysis of anion **39** would produce the observed aldehyde **22**.



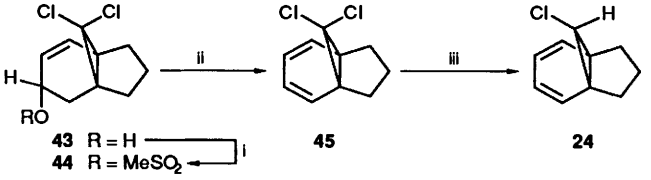
Scheme 7

The proposed mode of formation of chlorodiene **24** from the [4.3.1]propellene **23** is shown in Scheme 8. Triene **40**, the product of the initial 1,4-elimination, could, in principle, undergo a 1,3-prototropic shift to give either of the epimers **25** or **41**. On the basis of Vogel's studies of 1,6-methylene bridged cycloheptatrienes,[17] these latter compounds would be expected to undergo electrocyclic ring-closure to give the epimeric trinorcaradienes **24** and **42**, respectively. Once again, the exclusive formation of *anti*-chloride **24** from reaction of dichloride **23** with base may be a reflection of the greater thermodynamic stability of this product compared with epimer **42**, or it may result from a kinetic preference for formation of *anti*-chloride **25** over *syn*-isomer **41** during prototropic shift involving the initially formed bridgehead diene **40**. Evidence to support the former argument stems from the observation that half-reduction of the dichlorodiene **45** [prepared *via* mesate **44** (Scheme 9) from the known[16] allylic alcohol **43**] using metallic zinc in ethanolic potassium hydroxide[18] afforded epimer **24** (78%) exclusively. In addition, molecular mechanics calculations (using PCMODEL)[19] indicate that compound **24** is ~9.2 kJ mol^{-1} more stable than its C-8 epimer **42**.

B. *Stereochemical requirements of the* 1,4-*elimination.* The stereochemical requirements of the 1,4-eliminations involved in the conversions described above warrant comment. The reactions can be rationalised as thermally allowed outward disrotatory cyclopropyl ring-opening processes[20] which are

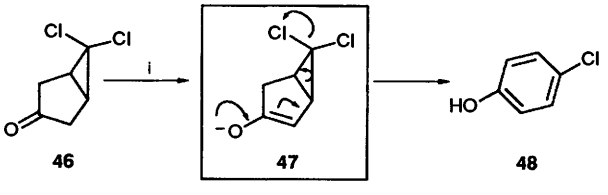


Scheme 8



Scheme 9 *Reagents and conditions:* i, $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C; ii, SiO_2 chromatography; iii, Zn, KOH, ethanol, reflux, 18 h

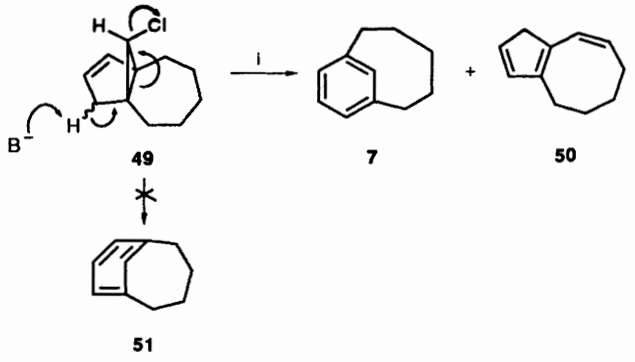
coupled with base-promoted removal of an allylic hydrogen. The well established stereoelectronic demands of the ring-opening processes, together with the need to ensure overlap between the adjacent terminii of the developing 'allylic anionic' and 'allylic cationic' components of this elimination, leads to the conclusion that the proton and chloride ion being lost must come from the same side of the cyclopropane ring. These stereochemical requirements of the 1,4-elimination were first noted by Fleming and Thomas[21] who observed the rapid base-promoted conversion of the bicyclo[3.1.0]hexan-3-one **46** into 4-chlorophenol **48** *via* intermediate enolate **47** (Scheme 10).



Scheme 10 *Reagent:* i, Base

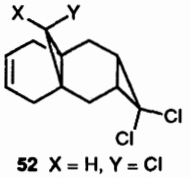
Additional support for these stereoelectronic proposals derives from studies by Bickelhaupt.[5] While the chloro-[5.3.1]propellene **6** underwent 'smooth and quantitative' conversion into [5]metaphane **7** (Scheme 2) on treatment with base, the epimeric compound **49** reacted much more slowly and gave a mixture of the phane **7** and its isomer **50** (Scheme 11). The product of any concerted 1,4-elimination process involving the propellene **49** would provide the highly strained *trans*-metaphane **51** – which is not observed.

In the present work, there is good evidence for the same stereochemical requirements to hold. The epimeric trichloropropellenes **52** and **53** have been prepared[14] from compound **8** by half-reduction (to the chloro congener of the propellene **12**)



Scheme 11 *Reagent:* i, $Bu^tO^- K^+$

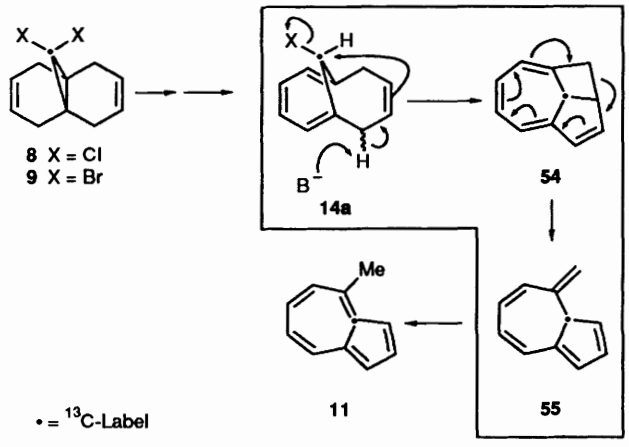
and highly selective π-facial additions to the double bond *syn* with respect to the remaining chlorine. Thus dichlorocarbene addition delivers compound **52** in 72% yield whereas initial expoxidation to the α-face of the *syn*-double bond, carbene addition to the *anti*-double bond and deoxygenation leads to epimer **53** in 53% overall yield.[14] The trichloropropellene **52** is recovered in 80% yield upon treatment with potassium *t*-butoxide and no other products were either detected or isolated. In contrast the epimer **53**, with the chlorine substituent *syn* to the double bond, afforded ~7% (at 75% conversion) of the cyclopropparene tricyclo[5.4.1.$0^{3,5}$]dodeca-1,3(5),6,8,10-pentaene **20** under the same conditions. It should be noted that a range of bases, including potassium *t*-butoxide, failed to catalyse the interconversion of epimers **52** and **53**. Reaction product **20** was found to be much more labile than the chloro derivative **18** isolated earlier and it could only be characterised by GC/MS techniques.



52 X = H, Y = Cl
53 X = Cl, Y = H

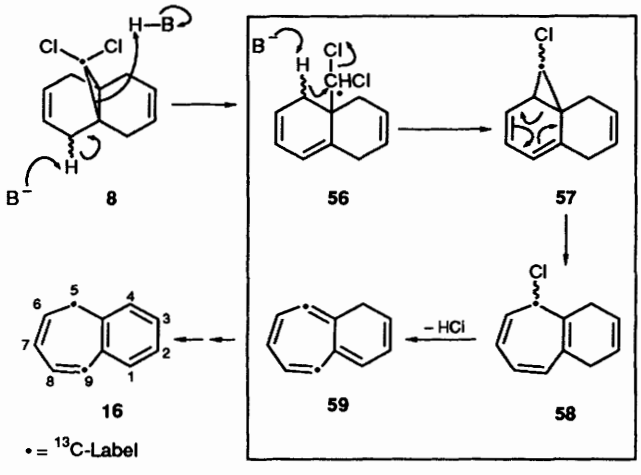
C. *Mechanistic proposals relating to the formation of compounds* **11**, **16** *and* **26**. As noted earlier, there has been some speculation[8,9] in the literature regarding the mode of formation of 4-methylazulene **11** from the propelladiene **8**. The proposed route is shown in Scheme 12 and involves exactly the same first two steps suggested (Scheme 3) in the mechanism for formation of bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10**. Thus, the tetraene **14a** is an intermediate common to both pathways and on the azulene route base-promoted intramolecular carbon–carbon bond formation between C-7 and C-11 (of **14a**) results in the generation of the tricyclic system **54**. Thermally allowed [π8s + σ2s] electrocyclic ring-opening would then provide the pentaene **55** which, under the basic conditions employed, would isomerise to give the observed product **11**.

A possible mechanism for the formation of 5*H*-benzocycloheptene **16** from the propellene **8** is shown in Scheme 13. Base-catalysed isomerisation of substrate **8** by a process involving cleavage of one of the two equivalent non-propellene side bonds of the cyclopropyl group would produce the dichloromethyl product **56**. Base-promoted 1,3-elimination involving this intermediate **56** would then deliver the ring-fused trinorcaradiene **57** which, upon electrocyclic ring-opening, would produce the benzocycloheptene **58**. Elimination of the elements of a second molecule of hydrogen chloride (to give alkene **59**, for example) and a subsequent prototropic shift

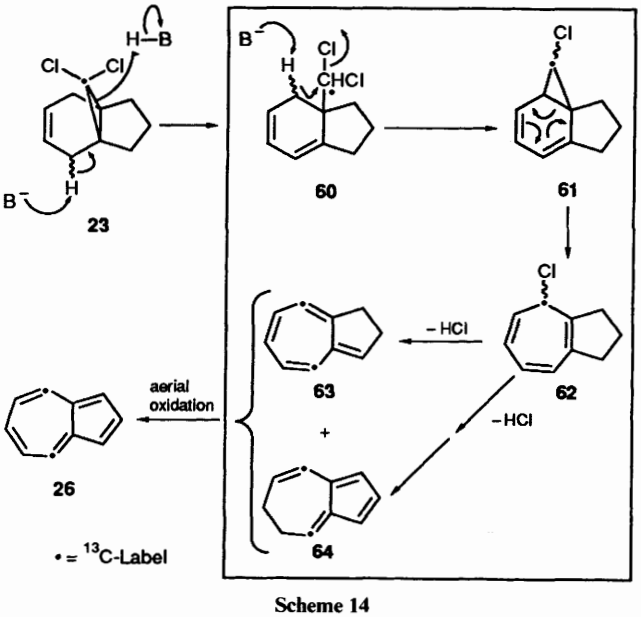


Scheme 12

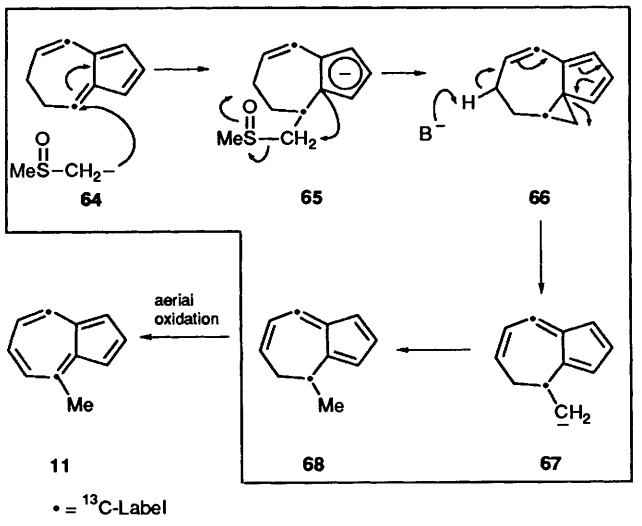
would then result in the observed aromatic product **16**. An analogous pathway (Scheme 14) can be used to rationalise the formation of azulene **26** from the propellene **23**. The key additional feature of this conversion is that the initial products of reaction will be a series of dihydroazulenes (*e.g.*, **63** and **64**) which then lead to azulene **26** after aerial oxidation during work-up. Indeed, and as noted above, the characteristic blue colour of



Scheme 13



Scheme 14



Scheme 15

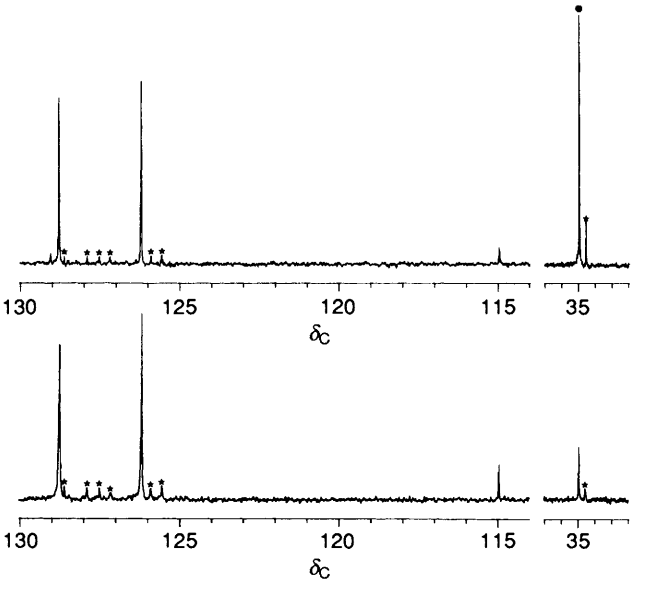


Fig. 2 100 MHz $\{^1H\}$ ^{13}C NMR spectra of unlabelled (lower spectrum) and ^{13}C-Labelled (upper spectrum – ' represents labelled carbon) bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10** (the resonances marked by a star are due to traces of 5*H*-benzocycloheptatriene **16**)

azulenes only develops after commencement of the isolation of azulene **26** from this reaction.

The formation of 4-methylazulene **11**, a product containing eleven carbons, from the ten-carbon-containing precursor **23** seems impossible at first sight. However, it is known[22] that under strongly basic conditions dimethyl sulfoxide can act as a methylating agent. In light of this we began to suspect that 4-methylazulene arises *via* dimethyl sulfoxide-mediated methylation of a dihydroazulene such as compound **64**. One possible pathway for this methylation reaction is shown in Scheme 15 and involves the dimsyl anion acting as a nucleophile which attacks compound **64** at C-4 to give the adduct **65** containing the aromatic cyclopentadienyl anion moiety. This latter species then undergoes a favoured 3-*exo-tet*[23] cyclisation with ejection of the methanesulfenate anion to give the cyclopropane **66**. Compound **66** can, in turn, react with base to give the anion **67**. Upon work-up, intermediate **67** would be protonated to give compound, **68** which would then be oxidised in air to give the observed azulenoid **11**. Some support for this proposal stems from the observation that on subjecting azulene **26** to reaction with potassium *t*-butoxide in dimethyl sulfoxide or dimsyl sodium in dimethyl sulfoxide a ~ 68% yield of 4-methylazulene **11** (together with small amounts of 6-methylazulene[24]) is obtained. This novel reaction provides a rather useful method for the synthesis of 4-methylazulene and is competitive with other procedures.[25]

D. ^{13}C-*Labelling studies*. Since a ^{13}C-labelled carbon can be readily introduced into the bridging cyclopropyl carbons of the propellenes **8** and **23** by addition of ^{13}C-labelled dichlorocarbene (generated by treatment of ^{13}C-labelled chloroform with base) to the appropriate alkene precursors, a simple means of probing the mechanistic proposals outlined above was available. To these ends, the appropriate substrates were produced in which C-9 of compound **8**[26] contained ~9% ^{13}C-label and C-8 of compound **23** contained ~ 16% ^{13}C-label. Although the precise level of ^{13}C-enrichment in propellenes **8** and **23** could not be determined spectroscopically because the labelled centres are quaternary and various attempts to obtain integrated spectra were unsuccessful, the quoted values have been correlated with the concentration of the label in the [^{13}C]chloroform used to generate dichlorocarbene. In addition, certain of the products of reaction of these compounds with base have the same (and now determinable) concentrations of label at a single site.

Subjection of the ^{13}C-labelled propellene **8** to treatment with potassium *t*-butoxide under the reaction conditions used earlier provided the labelled products **10**, **11** and **16**. Comparison of the 100 MHz ^{13}C NMR spectrum of labelled and unlabelled **10** (Fig. 2) clearly showed significant enhancement of the signal at δ 35.0 which is assigned to C-11. In the 400 MHz ^1H NMR spectrum, integration of the ^{13}C-satellites associated with the signal at δ −0.45 (and due to the highly shielded protons on C-11) established a ~9% ^{13}C content at C-11 in compound **10**. The outcome of this labelling study is fully consistent with the mechanistic proposals outlined in Scheme 3 for the conversion of propellene **8** into **10**.

The only significant difference between the ^{13}C NMR spectra of labelled and unlabelled 4-methylazulene **11** (Fig. 3) was the dramatic enhancement, in the former spectrum, of the signal at δ 137.5. As a result of extensive work by Braun *et al.*[11] on the analysis of the ^{13}C NMR spectra of various azulenes including the 4-methyl derivative **11**, this signal can be assigned to C-3a, the carbon that would be labelled if the mechanism shown in Scheme 12 were operative.

The outcome of the labelling study pertaining to the formation of 5*H*-benzocycloheptene **16** is slightly more complex although still fully consistent with the mechanistic proposals outlined in Scheme 13. Hence, a comparison of the appropriate ^{13}C NMR spectra (Fig. 4) revealed ^{13}C isotope enrichment at C-9 (δ 133.5) and C-5 (δ 32.5) in labelled **16**. The labelling sites could be assigned with confidence since the two-proton doublet (J 6.5 Hz) and associated satellites centred at δ 3.04 must be due to 5-H^{α} and 5-H^{β}, the only alicyclic protons in compound **16**. The one-proton doublet (J 11.5 Hz) and associated satellites at δ 7.09 must, by virtue of the observed chemical shift and simple spin-spin coupling, be assigned to 9-H. The 4% level of ^{13}C-label at these sites was readily determined by integration of the ^1H NMR signals and associated satellites mentioned above. The mechanism shown in Scheme 13 is consistent with this outcome since it predicts that the labelled carbon of the starting material **8** will appear at both C-5 and C-9 in the product **16**. Thus, base-promoted elimination of the elements of hydrogen chloride from **58** can occur by two alternative pathways both of which give product **59**, differing only in the position of labelled carbon. The conversion of **58** into **59** would be degenerate in the absence of such a labelled carbon.

Subjection of the ^{13}C-labelled propellene **23** to treatment with potassium *t*-butoxide provided the expected labelled products **11**, **24** and **26**. Propelladiene **24** contained the ^{13}C-label

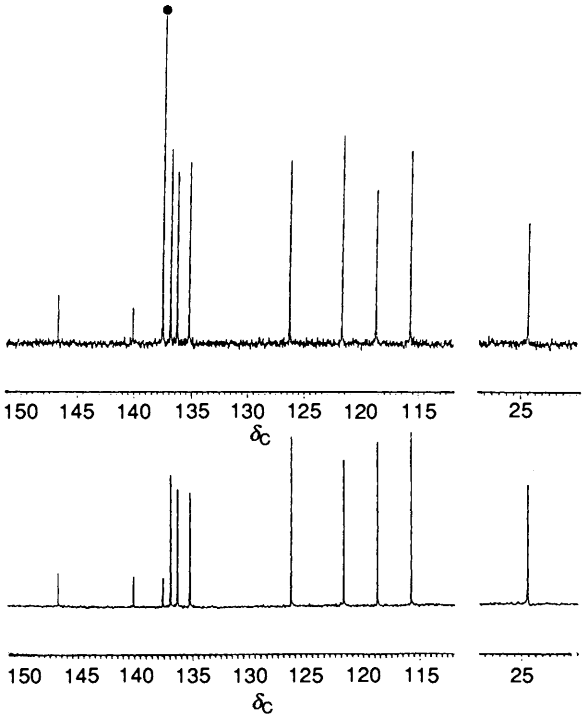


Fig. 3 100 MHz {^{1}H} ^{13}C NMR spectra of unlabelled (lower spectrum) and ^{13}C-labelled (upper spectrum – * represents labelled carbon) 4-methylazulene **11**

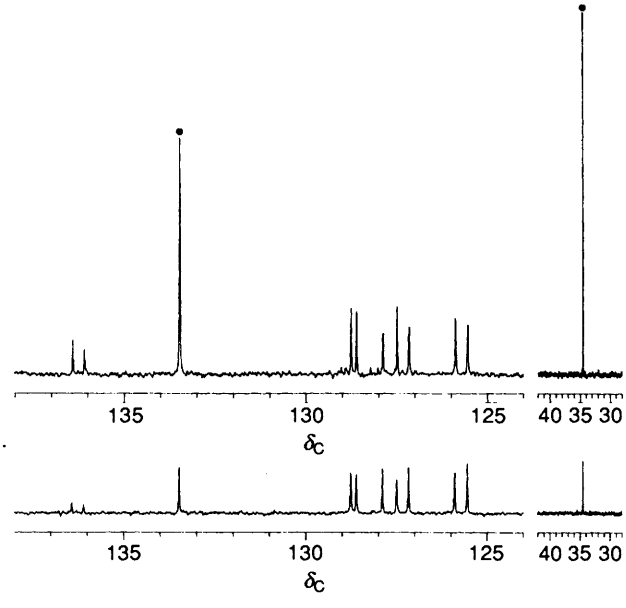


Fig. 4 100 MHz {^{1}H} ^{13}C NMR spectra of unlabelled (lower spectrum) and ^{13}C-labelled (upper spectrum – * represents labelled carbons) 5*H*-benzocycloheptatriene **16**

(16%) exclusively at the bridging cyclopropyl carbon (C-8) as predicted by the mechanistic proposal outlined in Scheme 8. The ^{13}C NMR spectrum of the labelled azulene **26** revealed that only the signal at δ_C 136.4, which has been assigned to C-4 and -8, was enhanced. The analogous spectrum of 4-methylazulene **11** established that the label was equally distributed between C-4 (8%) and C-8 (8%). Both of these outcomes support the proposals shown in Schemes 14 and 15.

Experimental

General Details.—M.p.s were recorded on a Kofler hot-stage and are uncorrected. Microanalyses were carried out in the Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand or the Australian Mineral Development Laboratories, Melbourne, Australia. IR spectra were recorded on a Perkin–Elmer 938G spectrometer. Samples were analysed either as thin liquid films on sodium chloride plates or as KBr discs. Unless otherwise specified, ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform on a JEOL GX 400 spectrometer. ^{1}H NMR chemical shifts (δ_H) are reported downfield from tetramethylsilane as internal standard, while ^{13}C NMR chemical shifts (δ_C) were referenced to the central peak (δ_C 77.0) associated with the signals due to deuteriochloroform. All *J*-values are in Hz. High- and low-resolution mass spectra were recorded on a VG Micromass 7070F using positive ion electron impact techniques.

Analytical TLC was conducted on aluminium-backed 0.2 mm-thick silica gel 60 GF_{254} plates supplied by Merck and the chromatograms were visualised under a 254 nm UV lamp and/or with anisaldehyde–sulfuric acid–ethanol (2:5:93) spray reagent. Preparative TLC (PLC) was conducted using 20 × 20 cm glass plates loaded with Merck Kieselgel 60 GF_{254} (35 g plate^{-1}) and developed with the solvent system indicated. The components were located under 254 nm UV light and extracted with the solvents indicated. GC analyses were carried out on a Perkin-Elmer Sigma 3B gas chromatograph equipped with a 4 mm (i.d.) × 2 m glass column containing 3% Dexil on Chromasorb W. A nitrogen carrier gas flow rate of 16.2 cm^3 min^{-1} was used. A standard temperature program, *viz.* 70 °C (5 min)/heat at 10 °C min^{-1}/300 °C (10 min), was used. Retention times are quoted in seconds. Preparative GC was carried out on a Hewlett-Packard 5790A gas chromatograph equipped with a 4 mm (i.d.) × 3.6 m glass column containing 25% Dexil on Chromasorb W. A flame ionisation detector fitted with a 100:1 splitter and a nitrogen carrier gas flow rate of 153 cm^3 min^{-1} were used. Both the preparative and analytical gas chromatographs were interfaced with a Spectra-Physics SP4270 reporting integrator.

All solvents were purified according to literature procedures[27] and freshly dried anhydrous solvents were stored over activated 4Å molecular sieves in tightly stoppered vessels out of sunlight. [^{13}C]Chloroform solutions were prepared by diluting 90% [^{13}C]chloroform (Stohler Isotope Chemicals) with the appropriate quantities of spectroscopic-grade chloroform. Potassium *t*-butoxide/*t*-butyl alcohol monosolvate was prepared by reaction of freshly cut and clean potassium metal with an excess of anhydrous *t*-butyl alcohol under nitrogen. After completion of the reaction excess of *t*-butyl alcohol was removed by vacuum distillation (25 °C/2 mmHg) to yield a solid. Titration of this material with dil. hydrochloric acid established it was the *t*-butyl alcohol monosolvate of potassium *t*-butoxide. Immediately prior to use portions of this material were crushed in a glove bag under dry nitrogen and the resulting fine powder was dispensed into the appropriate reaction vessel.

(4aα,8aα)-9,9-*Dichloro*-1,4,5,8-*tetrahydro*-4a,8a-*methanonaphthalene* **8**.—The title compound was prepared according to the method described by Vogel *et al.*[10] and was obtained as crystals, m.p. 90–91 °C (lit.,[10] 90–91 °C); δ_H 5.53 (4 H, t, *J* 1.2, 2-, 3-, 6- and 7-H) and 2.3–2.6 (8 H, m, 1-, 4-, 5- and 8-H); δ_C 123.6 (C-2, -3, -6 and -7), 74.2 (C-9), 30.4 (C-1, -4, -5 and -8) and 24.8 (C-4a and -8a). Compound **8** containing a ^{13}C-label at C-9 was synthesized by the same method as employed above but using 9% [^{13}C]chloroform in the dichlorocarbene-addition step. Comparison of the ^{13}C NMR spectra of the unlabelled and labelled materials indicated a significant enhancement of the signal at δ_C 74.2 (C-9) in the latter case (Found: M$^+$, 215.0345. $^{13}C^{12}C_{10}H_{12}{}^{35}Cl_2$ requires M, 215.0345); *m/z* (70 eV) 217 (1%), 216 (4), 215 (2) and 214 (7) (M$^+$).

Dehydrochlorination of Propelladiene **8**. *Formation of Compounds* **10**, **11** *and* **16**.—A solution of the propelladiene **8** (1.0 g, 4.7 mmol) in degassed DMSO (20 cm^3) was added in a dropwise fashion (syringe pump) to a stirred suspension of potassium *t*-butoxide–*t*-butyl alcohol monosolvate (4.37 g, 23 mmol) in DMSO (30 cm^3) maintained under dry nitrogen. The resultant black reaction mixture was stirred at ambient temperature for 4 h then diluted with water (300 cm^3) and extracted with hexane (4 × 100 cm^3). The combined organic extracts were washed with water (2 × 100 cm^3), then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a dark purple oil. This material was subjected to PLC (hexane solvent) and two major chromophoric bands, A and B, were obtained.

Extraction (dichloromethane) of band A (R_F 0.4) afforded 4-methylazulene **11**[11] (80 mg, 12%) as a dark purple oil (Found: M^+, 142.0781. Calc. for $C_{11}H_{10}$: M, 142.0782); δ_H 8.35 (1 H, d, *J* 9.5, 8-H), 7.83 (1 H, t, *J* 3.9, 2-H), 7.53 (1 H, t, *J* 10.1, 6-H), 7.42 (1 H, d, *J* 3.9, 3-H), 7.38 (1 H, dd, *J* 3.7 and 1.5, 1-H), 7.17 (1 H, d, *J* 10.1, 7-H), 7.12 (1 H, t, *J* 9.5, 5-H) and 2.92 (3 H, s, Me); δ_C 146.8 (C-4), 140.2 (C-8a), 137.5 (C-3a), 136.9 (C-8), 136.3 (C-6), 135.2 (C-2), 126.3 (C-5), 121.7 (C-7), 118.7 (C-1), 115.7 (C-3) and 24.5 (Me); ν_{max}(NaCl)/cm^{-1} 3081, 1588, 1556, 1429, 1357 and 1454; *m*/*z* (70 eV) 143 (12%) and 142 (100) (M^+) and 141 (78) (M^+ − H).

Extraction (dichloromethane) of band B (R_f 0.6) yielded a mixture of bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10** (64 mg, 10%) and 5*H*-benzocycloheptene **16** (128 mg, 19%). These two components were separated by subjecting the mixture to preparative GC (column temperature 180 °C). 5*H*-Benzocycloheptene **16**[12] (GC t_R 1800 s) was obtained as a clear oil, δ_H 7.15–7.30 (4 H, complex m, H1–4), 7.09 (1 H, d, *J* 11.5, 9-H), 6.48 (1 H, dd, *J* 5.3 and 11.5), 6.03 (1 H, dd, *J* 5.6 and 10), 5.80 (1 H, m) and 3.04 (2 H, d, *J* 6.5, 5-H_2); δ_C 136.4, 136.1, 133.5, 128.8, 128.6, 127.9, 127.5, 127.2, 125.9, 125.5 and 32.5; ν_{max}/cm^{-1} 3017, 2950, 1632, 1556, 1486 and 1449; *m*/*z* (70 eV) 143 (18%) and 142 (93) (M^+) and 141 (100) (M^+ − H).

Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10**[10] (GC t_R 2400 s) was obtained as a clear oil and was contaminated with small (<5%) quantities of compound **16**, δ_H 7.44 (4 H, m), 7.10 (4 H, m) and −0.45 (2 H, s, 11-H_2); δ_C 128.8, 126.2, 115.0 and 35.0 (C-11); ν_{max}/cm^{-1} 3038, 2996, 1692, 1594, 1511, 1485, 1445 and 1398; *m*/*z* (70 eV) 143 (9%) and 142 (77) (M^+) and 141 (100) (M^+ − H).

Subjection of the labelled propelladiene **8** to the elimination conditions specified above provided the corresponding labelled products. Comparison of the ^{13}C NMR spectra of the unlabelled and labelled 4-methylazulene **11** (Fig. 3) suggested a significant enhancement of the signal at δ_C 137.5 (C-3a) in the latter case; *m*/*z* (70 eV) 143 (19%) and 142 (100) (M^+), 141 (87) (M^+ − H) and 115 (29) (M^+ − C_2H_3) (Found: M^+, 143.0818. Calc. for $^{13}C^{12}C_{10}H_{10}$: M, 143.0816). Comparison of the ^1H and ^{13}C NMR spectra of the unlabelled and *labelled* 5H-*benzocycloheptene* **16** (Fig. 4) indicated a ~four-fold enhancement of the signals at δ_C 133.5 (C-9) and 32.5 (C-5) in the latter case (Found: M^+, 143.0817. $^{13}C^{12}C_{10}H_{10}$ requires M, 143.0816); δ_H 7.15–7.3 (m, H1–4), 7.09 (1 H, td, J_{CH} 84, $J_{3,4}$ 11.5, 9-H), 6.48 (1 H, dd, *J* 5.3 and 11.5), 6.03 (1 H, dd, *J* 5.6 and 10), 5.80 (1 H, m), 3.04 (2 H, td, J_{CH} 83, $J_{7,6}$ 6.5, 5-H_2); *m*/*z* (70 eV) 143 (18%) 142 (100) (M^+), 141 (96) (M^+ − H) and 115 (44) (M^+ − C_2H_3). Comparison of the ^1H and ^{13}C NMR spectra of the unlabelled and labelled bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10** (Fig. 2) indicated a ~eight-fold enhancement of the signal at δ_C 35.0 (C-11) in the latter case; δ_H 7.44 (4 H, m), 7.10 (4 H, m) and −0.45 (2 H, t, J_{CH} 70, 11-H_2); *m*/*z* (70 eV) 143 (9%) and 142 (77) (M^+), 141 (100) (M^+ − H) and 115 (37) (M^+ − C_2H_3). The spectra of labelled bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene **10** were identical in all respects with the spectra obtained on an authentic sample of labelled **10** available from earlier work.[26]

Dehydrochlorination of Propellenes **17** *and* **52**. *Formation of Elimination Products* **18**, **20** *and* **22**.—A solution of compound **17**[13,14] (0.5 g, 1.7 mmol) in THF (12 cm^3) was added dropwise during 30 min to a chilled (ice–salt) and magnetically stirred suspension of freshly sublimed potassium *t*-butoxide (0.75 g, 6.8 mmol) in THF (20 cm^3) maintained under oxygen-free nitrogen. The resultant mixture was stirred at ambient temperature for 20 h and was then concentrated under reduced pressure to give an oily solid, which was partitioned between diethyl ether (200 cm^3) and water (50 cm^3). The organic phase was washed with additional water (4 × 50 cm^3) and the combined aq. phases were acidified with hydrochloric acid (5 drops of a 10 mol dm^{-3} aqueous solution) and re-extracted with diethyl ether (2 × 30 cm^3). The combined organic extracts were washed with water (1 × 50 cm^3), then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an oily solid. Subjection of this material to PLC (hexane) afforded three bands, A, B and C.

Extraction (dichloromethane) of band A (R_f 0.7) gave starting material **17** (152 mg, 25% recovery) as shown by ^1H NMR and m.p. analyses.

Extraction (dichloromethane) of band B (R_f 0.6) furnished anti-12-*chlorotricyclo*[5.4.1.$0^{3,5}$]*dodeca*-1,3(5),6,8,10-*pentaene* **18** (34 mg, 15%) as a pale yellow solid, m.p. 27–28 °C (Found: M^+, 188.0393. $C_{12}H_9{}^{35}Cl$ requires M, 188.0393); δ_H 7.32 (2 H, br, s), 7.18 (4 H, br, s), 3.66 (1 H, d, *J* 6.9), 2.62 (1 H, d, *J* 6.9) and 1.62 (1 H, s, 12-H); δ_C 132.7 and 131.6 (C-1, -3, -5 and -7), 126.9, 124.9 and 119.2 (C-2, -6, -8, -9, -10 and -11), 29.7 (C-12) and 18.11 (C-4); *m*/*z* (70 eV) 190 (11%) and 188 (34) (M^+), 153 (87) (M^+ − Cl) and 152 (100) (M^+ − HCl).

Extraction (acetone) of band C (R_f 0) afforded a black tar which contained solely aliphatic material as shown by ^1H NMR spectral analysis.

Treatment of the tetrachloropropellene **17** (0.5 g, 1.7 mmol) under the same conditions as described above but using a larger excess of potassium *t*-butoxide (2.3 g, 21 mmol) afforded a black oil on work-up. Subjection of this material to PLC [(10:1) hexane–ethyl acetate] afforded two bands, A and B.

Extraction (Et_2O) of band A (R_f 0.3) afforded bicyclo-[4.4.1]undeca-1,3,5,7,9-pentaene-3-carbaldehyde **22**[15] (52 mg, 18%) as an oil. The ^1H NMR data were in agreement with those published previously;[15] *m*/*z* (70 eV) 170 (29%) (M^+) and 141 (100) (M^+ − CHO).

Extraction (acetone) of band B (R_f 0) gave black tar material which showed a broad signal at δ 1.50 in the ^1H NMR spectrum.

The crude product arising from treatment of (1aα,2aβ,6aβ,7-aα)-1,1, *anti*-8-trichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene **52**[14] (445 mg, 1.7 mmol) with potassium *t*-butoxide–*t*-butyl alcohol monosolvate (0.75 g, 7 mmol) was extracted with hexane (150 cm^3). The organic phase was washed with water (2 × 20 cm^3), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to near dryness. Column chromatography (60–100 mesh Florisil, hexane elution) under oxygen-free nitrogen gave starting material **52** (120 mg, 27% recovery) (identity determined by m.p. and ^1H NMR analyses) and a yellow oily solid (80 mg). GC/MS analysis of a benzene solution of this oily solid showed it to consist of a 5:1 mixture of hydrocarbon **20** (t_R 950 s) and starting material **52** (t_R 1190 s). Subsequent isolation of substrate **52** (68 mg, 9% recovery) by radial chromatography (hexane) allowed the yield of compound **20** to be calculated as ~7%. The mass spectrum of compound **20** [*m*/*z* (70 eV) 154 (58%) (M^+), 153 (100) (M^+ − H), 152 (90) (M^+ − 2H) and 128 (21) ($C_{10}H_8$)] was consistent with that reported in the literature.[15]

Reductive Dechlorination of anti-12-*chlorotricyclo*[5.4.1.$0^{3,5}$]-*dodeca*-1,3(5),6,8,10-*pentaene* **18**.—The cycloproparene **18** (15 mg, 0.08 mmol) and tributyltin hydride (1.0 g, 3.4 mmol) were stirred in hexane (5 cm^3) under oxygen-free nitrogen for 7 days. Concentration of the reaction mixture under reduced pressure and subjection of the residue to flash chromatography (neutral alumina, hexane elution) afforded tricyclo[5.4.1.$0^{3,5}$]dodeca-1,3(5),6,8,10-pentaene **20**[15] (10 mg, 80%).

anti-11-*Chloro*-3-(*methoxymethyl*)*bicyclo*[4.4.1]*undeca*-1,3,5,7,9-*pentaene* **21**.—To a solution of silver nitrate (6 mg, 0.034 mmol) in methanol (8 cm^3) was added a solution of cycloproparene **18** (13 mg, 0.07 mmol) in methanol (17 cm^3). After the mixture had been stirred in the dark for 4 h, the solvent was removed under reduced pressure, the residue was dissolved in diethyl ether (50 cm^3), and the solution washed with water (3 × 10 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure to give a light yellow solid. Subjection of this material to PLC [(1:15) ethyl acetate–hexane] afforded a single major chromophoric band (R_f 0.6), which upon extraction (dichloromethane) and treatment with activated charcoal furnished anti-11-*chloro*-3-(*methoxymethyl*)*bicyclo*[4.4.1]*undeca*-1,3,5,7,9-*pentaene* **21** (12 mg, 75%) as crystals, m.p. 32–34 °C (Found: C, 70.7; H, 6.3; Cl, 16.0. $C_{13}H_{13}ClO$ requires C, 70.7; H, 6.0; Cl 16.1%); δ_H 7.10–7.30 (7 H, complex m), 4.6 (2 H, d, *J* 3.2, ArCH_2OMe), 3.41 (3 H, s, OMe) and 1.80 (s, 12-H); δ_C 137.5 (C-3), 127.6, 127.4, 127.1, 126.7 and 124.9 (all CH), 126.8 (2 × CH), 116.9 and 116.6 (C-1 and -6), 77.6 (ArCH_2OMe), 57.8 (CHCl) and 55.0 (OMe); *m/z* (70 eV) 222 (0.5%) and 220 (1.5) (M^+), 185 (100) (M^+ − Cl), and 177 (5) and 175 (13) (M^+ − CH_2OMe).

(3aα,7aα)-8,8-*Dichloro*-2,3,4,7-*tetrahydro*-3a,7a-*methano*-1H-*indene* **23**.—The title compound was prepared according to the method described by Banwell[16] and obtained as crystals, m.p. 51–51.5 °C (lit.,[16] 51–51.5 °C); δ_H 1.2–2.2 (6 H, m, 1-, 2- and 3-H_2), 2.3 (4 H, s, 4- and 7-H_2) and 5.6 (2 H, s, 5- and 6-H); δ_C 123.3 (C-5 and -6), 75.9 (C-8), 37.5 (C-4 and -7), 36.1 (C-3a and -7a), 26.2 (C-1 and -3) and 25.5 (C-2).

Compound **23** containing a ^{13}C-label at C-8 was synthesized by the same method as employed above but using 16% [^{13}C]chloroform in the dichlorocarbene-addition step (Found: M^+, 203.0348. $^{13}C^{12}C_9H_{12}Cl_2$ requires M, 203.0349). Comparison of the ^{13}C NMR spectra of the unlabelled and labelled materials indicated a ~15-fold enhancement of the signal at δ_C 75.9 (C-8) in the latter case; *m/z* (70 eV) 205 (1%), 204 (3), 203 (1) and 202 (5) (M^+) and 169 (32) and 167 (92) (M^+ − Cl).

Dehydrochlorination of Propellene **23**. *Formation of Elimination Products* **11**, **24** *and* **26**.—A solution of the propellene **23** (1.0 g, 5 mmol) in degassed DMSO (20 cm^3) was added in a dropwise fashion (syringe pump) to a magnetically stirred suspension of potassium *t*-butoxide–*t*-butyl alcohol monosolvate (5.20 g, 28 mmol) in DMSO (30 cm^3) maintained under dry nitrogen. The resultant red solution was stirred at ambient temperature for 18 h, then diluted with water (300 cm^3) and extracted with hexane (4 × 100 cm^3). The combined extracts were washed with water (2 × 100 cm^3), then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a dark purple oil. This material was subjected to PLC (hexane) and afforded a single major band (R_f 0.4), which by GC analysis consisted of four components in the proportions 82:7:7:4. ^{13}C NMR and GC analysis of this mixture (including a comparison with ^{13}C NMR spectra and GC traces of authentic materials) indicated that the first three components were diene **24** (60%), azulene **26** (6%), and 4-methylazulene **11** (6%). The fourth and least abundant component of the reaction mixture was not identified.

A pure sample of diene **24** was obtained in the following way: a portion of the crude reaction product(~200 mg) was added to a solution of 1,3,5-trinitrobenzene (1,3,5-TNB) (70 mg) in ethanol (1 cm^3) and the resulting mixture was heated at 70 °C for 0.5 h, then was cooled to room temperature, and the precipitated 1,3,5-TNB complexes of the azulenes **26** and **11** were removed by filtration. The filtrate was cooled to −78 °C and the resulting solid was collected by vacuum filtration (whilst maintaining the filtration apparatus at low temperature) to give (3aα,7aα)-anti-8-*chloro*-2,3-*dihydro*-3a,7a-*methano*-1H-*indene* **24** as crystalline plates, m.p. 29 °C (Found: M^+ − Cl, 131.0858. $C_{10}H_{11}$ requires *m/z*, *M* − Cl, 131.0861); δ_H 6.17 (2 H, dd, *J* 2.7 and 7.6) and 5.89 (2 H, dd, *J* 2.7 and 7.3) (together 4-, 5-, 6- and 7-H), 3.49 (1 H, s, 8-H), 2.25 (2 H, complex m, 1- and 3-H^a), 1.83 (2 H, complex m, 1- and 3-H^b), 1.59 (1 H, complex m, 2-H^b) and 1.27 (1 H, complex m, 2-H^a); δ_C 123.5 (d) and 122.6 (d) (C-4, -5, -6, and -7), 42.9 (s) (C-3a and -7a), 33.3 (t) (C-1 and -3), 27.4 (d) (C-8) and 19.8 (t) (C-2); ν_{max}(KBr)/cm^{-1} 3034, 2955, 2931, 2858, 1452, 1444 and 1388; *m/z* (70 eV) 131 (100%) (M^+ − Cl).

Dehydrohalogenation of the ^{13}C-labelled propellene **23** gave the same products in the same approximate proportions as obtained above. ^{13}C-Labelled monochlorodiene **24**: δ_C 123.4, 122.6, 42.8, 33.3 and 27.3 (C-8, 16-fold enrichment) and 19.8; *m/z* (70 eV) 167 (1%) and 166 (2) (M^+) and 131 (100) (M^+ − Cl). ^{13}C-Labelled azulene **26**: δ_C 140.2 (C-3a and -8a), 136.9 (C-2 and -6), 136.4 (C-4 and -8, 16-fold enrichment), 122.6 (C-5 and -7) and 118.1 (C-1 and -3); *m/z* 129 (29%) and 128 (100) (M^+). ^{13}C-Labelled 4-methylazulene **11**: δ_C 146.4 (C-4, 8-fold enrichment), 140.1 (C-8a), 137.6 (C-3a), 136.7 (C-8, 8-fold enrichment), 136.0 (C-6), 135.2 (C-2), 126.1 (C-5), 121.6 (C-7), 118.8 (C-1), 115.8 (C-3) and 24.2 (Me); *m/z* (70 eV) 143 (21%) and 142 (100) (M^+) and 141 (M^+ − H).

Reaction of Monochlorodiene **24** *with PTAD. Formation of Diels–Alder Adduct* **27**.—To a stirred solution of the diene **24** (30 mg, 0.18 mmol) in dichloromethane was added PTAD (31 mg, 0.18 mmol) in one portion and the resulting solution was stirred until the crimson colour of the dienophile had been discharged (*ca.* 15 min). The solution was concentrated under reduced pressure and the resultant solid was recrystallised (ethyl acetate) to yield *adduct* **27** (60 mg, 98%) as a solid, m.p. 185 °C (Found: C, 63.1; H, 4.6; Cl, 10.6; N, 12.1. $C_{18}H_{16}ClN_3O_2$ requires C, 63.4; H, 4.4; Cl, 10.4; N, 12.3%); δ_H 7.44 (4 H, m), 7.38–7.33 (1 H, complex m), 6.33 (2 H, m), 5.26 (2 H, t, *J* 3.2), 3.32 (1 H, s), 2.20 (2 H, m), 1.95 (2 H, m) and 1.61–1.48 (2 H, complex m); δ_C 157.4, 131.2, 129.1, 128.3, 128.2, 125.6, 56.4, 43.1, 34.7, 28.4 and 27.3; ν_{max}(KBr)/cm^{-1} 3088, 2957, 2930, 2857, 1781, 1713, 1693, 1501, 1431, 1239 and 1019; *m/z* (15 eV) 131 (100%) (M^+ − PTAD − Cl).

Synthesis of Authentic Sample of (3aα,7aα)-8-*Chloro*-2,3-*dihydro*-3a,7a-*methano*-1H-*indene* **24**.—Methanesulfonyl chloride (332 mm^3, 4.3 mmol) was added in a dropwise fashion to a stirred and chilled (0 °C) solution of allylic alcohol **43**[16] (400 mg, 1.83 mmol) and NEt_3 (760 mm^3) in dichloromethane (15 cm^3). After the reaction mixture had been stirred at 0 °C for 2 h it was poured into water (20 cm^3) and extracted with dichloromethane (2 × 10 cm^3). The combined extracts were washed with HCl (2 × 5 cm^3 of a mol dm^{-3} aq. solution), then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford a light yellow oil. Subjection of this material to PLC (hexane) afforded a single major chromophoric band (R_f 0.9), which upon extraction (dichloromethane) afforded diene **45**[28] (291 mg, 79%) as a crystalline solid, m.p. 56–57 °C (Found: M^+, 200.0159. Calc. for $C_{10}H_{10}{}^{35}Cl_2$: M, 200.0159); δ_H 6.09 (2 H, complex m), 5.88 (4 H, complex m, 4-, 5-, 6- and 7-H), 2.48 (2 H, complex m, 1- and 3-H^a), 2.05 (2 H, complex m, 1- and 3-H^b), 1.75 (1 H, complex m, 2-H^b) and 1.65 (1 H, complex m, 2-H^a); δ_C 123.9 and 122.9 (C-4, -5, -6 and -7), 68.1 (C-8), 49.3 (C-3a

and -7a), 35.6 (C-1 and -3) and 24.9 (C-2); ν_{max}(KBr)/cm^{-1} 3036, 2968, 2936, 2866, 1549, 1445, 1378, 1173, 883 and 868; *m/z* (70 eV) 204 (0.5%), 202 (5) and 200 (8) (M^+), 167 (35) and 165 (100) $M^+ - Cl$).

To a stirred solution of diene **45** (291 mg, 1.44 mmol) and KOH (1.26 g) in EtOH (5 cm^3) was added finely divided zinc dust (1.47 g). The resulting mixture was heated at reflux for 18 h, then cooled and quenched with water (40 cm^3), and extracted with dichloromethane (3 × 30 cm^3). The combined organic phases were washed successively with HCl (2 × 20 cm^3 of a 2 mol dm^{-3} aq. solution) and water (1 × 20 cm^3), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford monochlorodiene **24** (90 mg, 78%) as a clear oil which crystallised on storage to give a crystalline solid, m.p. 29 °C. This material was identical in all respects with the monochlorodiene obtained from reaction of dichloride **23** with potassium *t*-butoxide–*t*-butyl alcohol monosolvate.

Reaction of Azulene **26** *with Potassium t-Butoxide in DMSO. Formation of* 4-*Methylazulene* **11**.—A solution of azulene **26** (40 mg, 0.30 mmol) in deoxygenated DMSO (1 cm^3) was added in a dropwise fashion (syringe pump) to a stirred suspension of potassium *t*-butoxide–*t*-butyl alcohol monosolvate (180 mg, 1 mmol) in DMSO (2 cm^3) maintained under dry nitrogen. The resultant yellow-orange solution was stirred at ambient temperature for 18 h, then diluted with water (12 cm^3) and extracted with hexane (4 × 6 cm^3). The combined extracts were washed with water (2 × 6 cm^3), then was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a dark purple oil. This material was subjected to PLC (hexane) to give a single purple band (R_f 0.4). Extraction (dichloromethane) of this band gave a ~5:1 mixture of 4- and 6-methylazulene (32 mg, 75%) as determined by ^{13}C NMR analysis (including a comparison with ^{13}C NMR spectra of authentic materials).

Reaction of Azulene **26** *with Dimsyl Sodium in DMSO. Formation of* 4-*Methylazulene* **11**.—A mixture of DMSO (10 cm^3) and NaH (72 mg, 3.0 mmol) was heated to 75 °C until the evolution of hydrogen had ceased (*ca.* 45 min). The resulting solution was cooled to room temperature and a solution of azulene **26** (50 mg, 0.38 mmol) in DMSO (2 cm^3) was added in a dropwise fashion. The resulting green-black solution was stirred magnetically for 18 h by which time it had become orange-black in colour. The reaction mixture was quenched with water (200 cm^3) and extracted with hexane (3 × 100 cm^3). The combined organic fractions were dried ($MgSO_4$), then filtered, and concentrated under reduced pressure to give a purple oil (20 mg). ^{13}C NMR analysis of this material established that it was a ~8:1 mixture of 4- and 6-methylazulene.

Single-Crystal X-Ray Diffraction Analysis of Diels–Alder Adduct **27**.—*Crystal data:* $C_{18}H_{16}ClN_3O_2$ crystallises in space group *P*1 (No. 2) with a = 6.248(3), b = 12.402(2), c = 20.954(4) Å, α = 78.59(2), β = 87.77(3), λ = 87.63(3)°, D_c = 1.428, D_m (flotation) = 1.45(2) g cm^{-3}, Z = 4, V = 1589.3 Å^3. Intensity data out to θ = 22° were collected using ω–5θ scans on a CAD4 four-circle diffractometer employing graphite-monochromated Mo-Kα (λ = 0.7107 Å) radiation. The structure was solved by direct methods and refined by blocked-matrix least-squares techniques to yield final discrepancy factors of R = 0.036 and R_w = 0.041 on 2697 F with $I > 2.5\sigma(I)$.*

* *Supplementary data* (see section 5.6.3 of Instructions for Authors, January issue). Tables of atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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