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# THE REGIOSELECTIVITY OF RHODIUM AND PALLADIUM-CATALYSED CYCLISATIONS OF 2-BROMO-1,6- AND -1,7-DIENES

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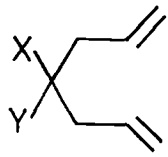
Abstract. 2-Bromo-1,6-dienes are catalytically cyclised to a mixture of the corresponding 3,4-bis(methylene)cyclopentane and 5-methylenecyclohex-3-ene. Wilkinson's catalyst shows good selectivity for the 5-membered ring product whilst palladium catalysts, in general, show little selectivity. Addition of tetraethylammonium salts, especially the chloride, allow the palladium catalysed reactions to be carried out at 30°C in good yield and with high selectivity for the 5-membered ring. 2-Bromo-1,7-dienes are cyclised regiospecifically to 6-membered rings by the same catalysts although some double bond isomerisation also occurs. The mechanism of the catalytic cyclisations is discussed. The 3,4-bis(methylene) cyclopentanes undergo facile Diels-Alder reactions.

We have previously reported the palladium- and rhodium-catalysed cyclisation of 4,4-disubstituted-1,6-dienes (1) to cyclopentenes (2) and exo-methylene cyclopentanes (3) respectively.[1] These cyclisations occur in good yield in chloroform containing hydrogen chloride and are regiospecific for 5-membered rings. The exo-methylene cyclopentanes (3) are isomerised to 1,2-dimethylcyclo pent-1-enes (4) in ethanolic hydrogen chloride containing chlorotris(triphenyl phosphine)rhodium(I). Subsequently Trost reported similar palladium-catalysed reactions for (1, X=Y=$SO_2Ph$) but in this case both 5- and 6-membered products were formed.[2] The palladium-catalysed cyclisation of 1,6-enynes to bis exocyclic dienes (5) has also been reported[3] and $\alpha,\omega$-diynes (6) have been stereoselectively cyclised to E,E-exocyclic dienes (7) in the presence of a titanium reagent.[4]

We have extended our studies to the cyclisation of 2-bromo-1,6- and -1,7-dienes[5] and now report full details of this work. The palladium-catalysed vinylation of aryl, heteroaryl, vinyl or benzyl halides is known as the Heck reaction[6] and has proved to be a valuable method for carbon-carbon bond formation in the appropriate synthetic context. The reaction has a number of synthetic advantages: (a) it provides a facile one-step method for forming carbon-carbon bonds at unsubstituted vinylic positions, (b) it is usually regioselective and stereospecific, (c) it proceeds under mild conditions and (d) it does not require an additional main group metal (e.g. Hg, Sn, Pb, Cu etc) to activate the substrate. At the outset of our studies there were surprisingly few studies of intramolecular Heck reactions and these, apart from one exception[7], all involved aromatic halides, e.g. indoles and oxindoles are formed by the palladium catalysed cyclisation of (8a) and (8b) in moderate to good yield[8] and related cyclisations



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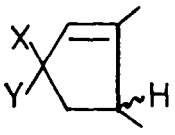

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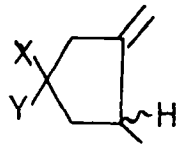

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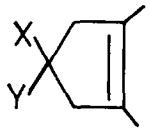

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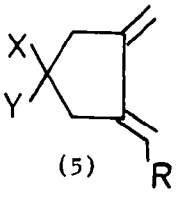

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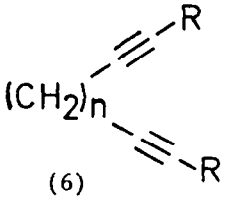

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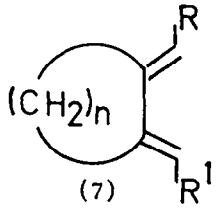

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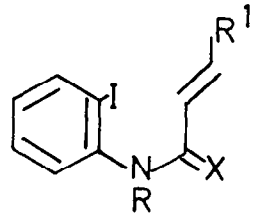
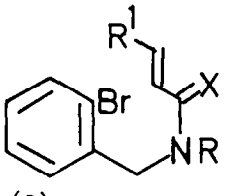


(8) a. X=$H_2$
b. X=O



(9) a. X=$H_2$
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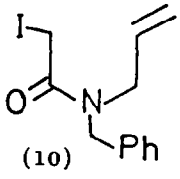

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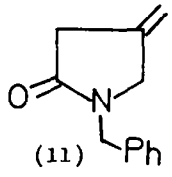

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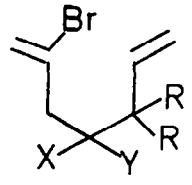
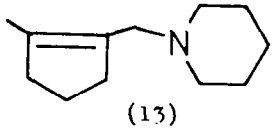


(12) a. X=Y=$CO_2$Et, R=H
b. X Me, Y=COPh, R=H
c. X=Y=COMe, R=H
d. X=Y=R=H
e. X $CO_2$Me, Y=H, R=Me



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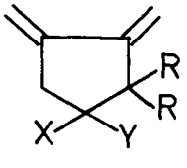
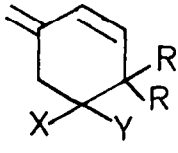
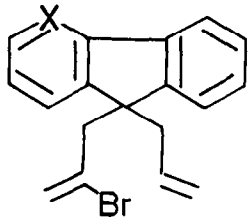


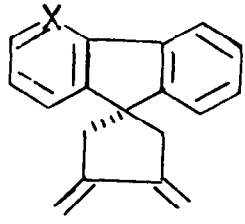


(14) a. X=Y=$CO_2$Et, R=H
b. X=Me, Y=COPh, R=H
c. X=Y=COMe, R=H
d. X=Y=R=H
e. X=$CO_2$Me, Y=H, R=Me

(15)



(16) a. X=CH
b. X=N



(17) a. X=CH
b. X=N

of (9a) and (9b) give dihydroisoquinoline derivatives again in moderate to good yield.[8]

Recently the cyclisation of N-allyl iodoacetamides to γ-lactams (10)⟶(11) in modest yield has been reported and we[10], and later Overman,[11] have reported applications to the synthesis of spiro- and bridged-ring compounds.

Cyclisation of 2-bromo-1,6-dienes.

Our interest in intramolecular Heck reactions arose from the realisation of their potential for generating bis-exocyclic dienes which would, in turn, serve as substrates for Diels-Alder reactions. The synthetic versatility of the Diels-Alder reaction allied to its potential for creating four chiral centres in a single step makes such methodology an attractive goal. Alternative approaches to bis-exocyclic dienes involving a molybdenum(0)-catalysed double bond isomerisation in a bis-allylic acetate[12] or the reaction of π-allylpalladium(II) complexes, derived from two allene molecules, with carbon and nitrogen nucleophiles have been reported.[13] We initially focussed our attention on 2-bromo-1,6-dienes (12a-c). Heck has reported the palladium-catalysed cyclisation of 1- or 2-bromo-1,ω-dienes in the presence of piperidine to give cyclic allylic tertiary amines e.g. (12d)⟶(13).[8] Our initial reactions were carried out in boiling acetonitrile using palladium acetate-triphenylphosphine, tetrakis(triphenylphosphine)palladium(0) or chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) as catalyst and potassium carbonate as base. The products were a mixture of dienes (14) and (15) (table 1).

The results in table 1 show that Wilkinson's catalyst always favours the 5-membered ring (14) over the 6-membered ring (15) by a factor of $\geqslant 5$. When preformed Pd(0) is used as catalyst no clear trend emerges since variation of the substrate results in either a clear preference for (15) (table 1, entry 3), a 1:1 ratio of (14) and (15) (entry 7) or a slight preference for (14) (entry 12). When palladium acetate-triphenylphosphine is used as catalyst in conjunction with an alkali metal carbonate base a slight preference for (14) is usually observed but using triethylamine as base can reverse this preference (entry 6).

The effect of variation of phosphine on the yield and regioselectivity of cyclisation of (12a) was briefly studied using a 1:2 molar ratio of palladium acetate and phosphine and 2-10 mole % of palladium acetate. The monophosphines $(\underline{p}\text{-MeOC}_6\text{H}_4)_3\text{P}$, $(\underline{p}\text{-FC}_6\text{H}_4)_3\text{P}$, the phosphite, $\text{P(OPr}^{\text{i}})_3$, and diphos were all much less effective than $\text{Ph}_3\text{P}$. Other rhodium complexes, $\text{ClRh}[\underline{p}(\text{FC}_6\text{H}_4)_3]$ $\text{ClRh(AsPh}_3)_3$ and $\text{ClRh(CO)(PPh}_3)_2$, were evaluated and found to be less efficient catalysts than Wilkinson's catalyst.

Recently Jeffery[14] reported that the addition of tetrabutylammonium chloride permitted intermolecular Heck reactions to be carried out in DMF at, or near, room temperature in good yield. Consequently, we surveyed the effect of a range of tetraethylammonium salts (1 mol) on the palladium- and rhodium-catalysed cyclisation of (12a). A marked anion effect is observed with the chloride salt emerging as the most effective additive in terms of both yield and regioselectivity. The bromide, fluoride, acetate, tetrafluoroborate and hexafluorophosphate are all much less effective than the chloride. The carbonate and hydroxide salts promote rapid initial reaction but the reaction ceases at ca. 50% conversion of (12a) and addition of further amounts of tetraethylammonium carbonate or hydroxide fails to promote further reaction. In the case of tetraethylammonium hydroxide as additive ca. 20% of diethyl diallylmalonate is also formed. This reduction product arises from water formed in situ since an analogous reduction is observed when (12b) is cyclised in wet acetonitrile.

The tetraethylammonium chloride increases the regioselectivity for the 5-membered product (14a) from 5:1 to 7:1 in the rhodium-catalysed cyclisation.

Table 1. Effect of Catalyst on Regioselectivity of Cyclization of 2-Bromo-1,6-Dienes[a]

| Entry | Substrate | Catalyst (Mol%) | Time(h) | Yield(%)[b] | Ratio 14:15[c] |
|---|---|---|---|---|---|
| 1 | 12a | $Pd(OAc)_2(2),PPh_3(4)$ | 1 | 67 | 5:4 |
| 2 | 12a | $Pd(OAc)_2(4.3),PPh_3(10)$[d] | 48 | 78 | 3:6 |
| 3 | 12a | $Pd(PPh_3)_4(3)$ | 4 | 74 | 1:10 |
| 4 | 12a | $RhCl(PPh_3)_3(5)$ | 6 | 63 | 5:1 |
| 5 | 12b | $Pd(OAc)_2(5),PPh_3(10)$ | 35 | 73 | 2.5:1 |
| 6 | 12b | $Pd(OAc)_2(10),PPh_3(20)$[e] | 48 | 81 | 1:2.5 |
| 7 | 12b | $Pd(PPh_3)_4(5)$ | 6 | 81 | 1:1 |
| 8 | 12b | $RhCl(PPh_3)_3(5)$ | 43 | 45[f] | 6:1 |
| 9 | 12b | $Pd(OAc)_2(10),PPh_3(20)$[g] | 48 | $<10$ | 5:4 |
| 10 | 12c | $RhCl(PPh_3)_3(5)$ | 24 | 55[h] | 10:1 |
| 11 | 12c | $Pd(OAc)_2(5),PPh_3(10)$ | 2.3 | 74[h,i] | 2.8:1 |
| 12 | 12c | $Pd(PPh_3)_4(5)$ | 1.25 | 64[h,j] | 1.5:1 |
| 13 | 12e | $Pd(OAc)(5),PPh_3(10)$ | 18 | 94 | 1.38:1 |
| 14 | 12e | $Pd(PPh_3)_4(5)$ | 12 | 89 | 2.21:1 |
| 15 | 12e | $RhCl(PPh_3)_3$ | 12 | 74 | -[k] |
| 16 | 16a | $Pd(OAc)_2(5),PPh_3(10)$ | 22 | 84 | -[l] |
| 17 | 16a | $Pd(PPh_3)_4(5)$ | 16.5 | 86 | -[l] |
| 18 | 16a | $RhCl(PPh_3)_3(5)$ | 2.5 | 80 | -[l] |
| 19 | 16b | $Pd(OAc)_2(10),PPh_3(20)$ | 0.15 | 90 | -[m] |
| 20 | 16b | $Pd(PPh_3)_4(5)$ | 90 | 50[f] | -[m] |
| 21 | 16b | $RhCl(PPh_3)_3(5)$ | 48 | 70 | -[m] |

(a) Reactions carried out in acetonitrile at 80°C in the presence of $K_2CO_3$ (2 mol).

(b) Isolated yield

(c) Estimated by p.m.r.

(d) Reaction temperature 25°C.

(e) $NEt_3$ (2 mol) as base.

(f) 50% unreacted starting material.

(g) $Li_2CO_3$ (2 mol) as base.

(h) Estimated by g.l.c. (2m, 5% SGR).

(i) ca. 15% of double bond isomers also formed.

(j) ca. 34% of double bond isomers also formed.

(k) Product is (14e) together with ca. 10% of 3,3-dimethyl-4-methoxycarbonyl-hepta-1,6-diene.

(l) Sole product is (17a).

(m) Sole product is (17b).

In contrast there is marked increase in regioselectivity to 66:1 in favour of (14a) for the palladium-catalysed process together with an increased rate of cyclisation

The catalytic cyclisation of several other substrates has been studied. The fluorenyl derivatives (16a) and (16b) undergo regiospecific 5-exo-trig cyclisation to (17a) and (17b) respectively with both palladium and rhodium catalysts (table 1). Wilkinson's catalyst is particularly effective for the cyclisation of (16a) (table 1, entry 18) whilst with (16b) the cyclisation is slower and, in the case of the palladium catalysed cyclisation, is best achieved by increased amounts of catalyst. Longer reaction times or the requirement for more catalyst presumably reflect interference with the catalytic function by coordination of the metal ion to the pyridine nitrogen atom in (16b). The vinyl bromide (12e) cyclises to a mixture of (14e) and (15e) with palladium catalysts (table 1, entries 13 and 14) whilst Wilkinson's catalyst gives only the 5-exo-trig product (14e) together with a small amount of reduction product 3,3-dimethyl-4-methoxycarbonyl-hepta-1,6-diene (table 1, entry 15). Compared to (12a), compound (12e) requires more catalyst and a longer reaction time.

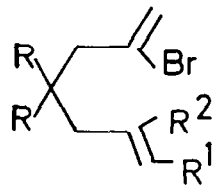
The effect of terminal substitution on the olefin on the palladium-catalysed cyclisation has been briefly investigated. Both (18a) and (18b) cyclise regiospecifically via a 5-exo-trig process to give mixtures of bis-exocyclic dienes (19a) and (19b) with their double bond isomerisation products (20) and (21) respectively, in which the latter invariably predominate (table 2). The isomerisation products (20) and (21) were isolated by subjecting the mixtures to a Diels-Alder reaction with N-phenylmaleimide (NPM) to remove the dienes (19a) and (19b) (see below) followed by preparative t.l.c. of the mother liquors. Their structures are based on interpretation of their p.m.r. spectra and on n.O.e. studies. Thus irradiation of the olefinic methyl group of (20) ($\delta$ 1.95) causes enhancement of both olefinic proton signals at $\delta$ 6.31 (PhCH=) (7%) and $\delta$ 5.98 (CH=CMe) (7%), whilst irradiation of $H_A$ ($\delta$ 6.11) in (21) effects a 6% enhancement of the $CH_2CO_2Me$ signal at $\delta$ 3.19, but no enhancement of the exo-methylene proton signal at $\delta$ 4.88. In contrast to terminal substitution, when a substituent is introduced at the non-terminal olefinic carbon centre (18c) the palladium-catalysed cyclisation is diverted to the 6-endo-trig mode giving an essentially quantitative yield of a 1:1.4 mixture of (22) and (23). Addition of tetraethylammonium chloride allows the cyclisation to take place at 30°C. Wilkinson's catalyst does not effect cyclisation of (18c).

Table 2. Palladium-catalysed cyclisation of 2-bromo-1,6-dienes (18a) and (18b) in acetonitrile containing 2.5 mole $K_2CO_3$

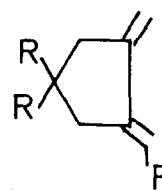
| Substrate | Catalyst mole % | Temp.(°) | Time(h) | Yield(%)[a] | Product Ratio 19a,19b | 20,21 |
|---|---|---|---|---|---|---|
| 18a | $Pd(OAc)_2(5),PPh_3(10)$ | 80 | 6 | 88 | 1 | 1.3 |
| 18a | $Pd(OAc)_2(10),PPh_3(20)$[b] | 30 | 96 | 65 | 1 | 2.6 |
| 18a | $Pd(PPh_3)_4(5)$ | 80 | 10 | 68 | 1 | 1.67 |
| 18b | $Pd(OAc)_2(5),PPh_3(10)$ | 80 | 1 | 50 | 1.6 | 1 |
| 18b | $Pd(OAc)_2(5),PPh_3(10)$ | 30 | 35 | 45 | - [c] | - |
| 18b | $Pd(OAc)_2(5),PPh_3(10)$[b] | 30 | 3.5 | 68 | 1 | 1.8 |

a. Isolated yield; b. 1 mole of $Et_4NCl$ added; c. sole product (19b)

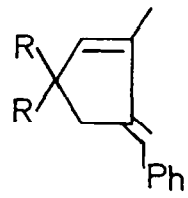
One heterocyclic example, the cyclisation of (24) has been studied. This amide gives a 6:1 mixture of (74%) of (25) and (26) when cyclised with 5 mol.% palladium acetate - 10 mol.% triphenylphosphine (MeCN, 80°C, 2.5h). The amide (24) is not cyclised by Wilkinson's catalyst.



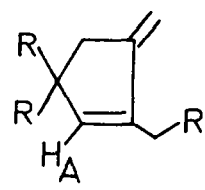
(18) a. $R=CO_2Et$, $R^1=Ph$, $R^2=H$
b. $R=R^1=CO_2Me$, $R^2=H$
c. $R=CO_2Et$, $R^1=H$, $R^2=Me$



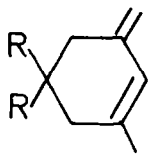
(19) a. $R=CO_2Et$, $R^1=Ph$
b. $R=R^1=CO_2Me$



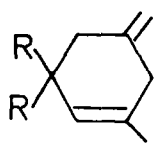
(20) $R=CO_2Et$



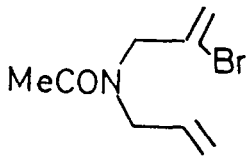
(21) $R=CO_2Et$



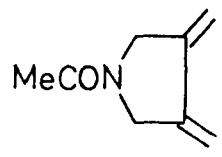
(22) $R=CO_2Et$



(23) $R=CO_2Et$



(24)



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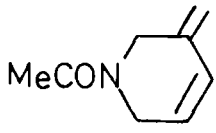

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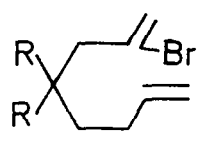
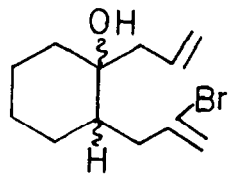


(27) $R=CO_2Et$



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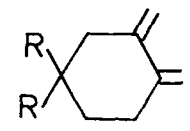

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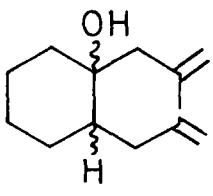
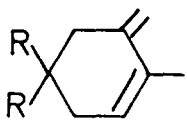
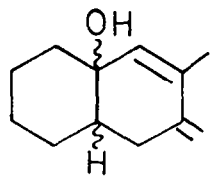


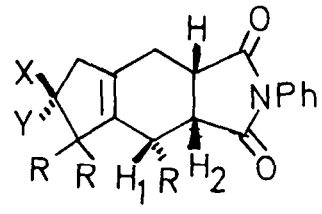
(30)



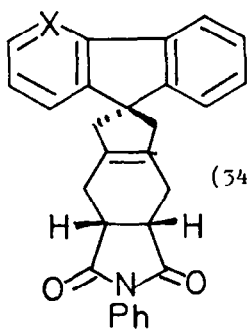
(31) $R=CO_2Et$



(32)



(33) a. X=COPh, Y=Me, $R=R^1=H$
b. X=Y=COMe, $R=R^1=H$
c. $X=CO_2Me$, Y=H, $R^1=Me$
d. $X=Y=CO_2Et$, R=Ph, $R^1=H$
e. $X=Y=R=CO_2Me$, $R^1=H$.



(34) a. X=CH
b. X=N

Cyclisation of 2-bromo-1,7-dienes

The catalytic cyclisation of two examples of 2-bromo-1,7-octadienes (27) and (28) have been studied. Both undergo regiospecific 6-exo-trig cyclisation to give the expected products (29) and (30) respectively, together with the products (31) and (32), of regiospecific double bond isomerisation. No 7-endo-trig cyclisation products were formed.

The cyclisation of (27) with 10 mol % palladium acetate - 20 mol.% triphenylphosphine (MeCN, 80°C, 14h) gives a 4:1 mixture of (29) and (31) in 86% yield. Monitoring the reaction by g.l.c. shows the initial product is (29) which subsequently slowly isomerises to (31). Repeating the reaction with 7.5 mol.% palladium acetate - 15 mol.% triphenylphosphine (MeCN, 30°C, 36h) with the addition of 1 mol. of tetraethylammonium chloride resulted in a lower reaction temperature and less isomerisation and afforded (79%) a 7:1 mixture of (29) and (31). Wilkinson's catalyst (10 mol.%) [$Et_4NCl$ (1 mol.), MeCN, 80°C, 10h] is less effective but gives (29) (42%) as the sole product. The vinyl bromide (28) (isomer mixture) undergoes a palladium-catalysed cyclisation [$Pd(OAc)_2$ (5 mole %), $PPh_3$ (10 mol.%), MeCN, 80°C, 23h] to give a 2.5:1 mixture (66%) of (30) and (32) but fails to cyclise when Wilkinson's catalyst is employed.

Diels-Alder Reactions of the Bis-exocyclic Dienes

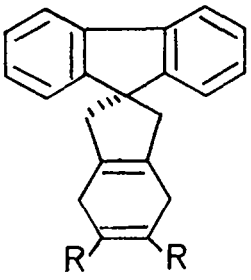
The rigidity and coplanarity of the diene moiety in the 5-membered bis-exocyclic dienes (14) and (19) predisposes them to facile Diels-Alder reactions. As expected they undergo Diels-Alder reactions under mild conditions (25-80°C) with N-phenylmaleimide and other dipolarophiles to give cycloadducts in excellent yield in the majority of cases (table 3). The Diels-Alder reaction provides an effective way of separating mixtures of 5-exo- and 6-endo-trig products arising from the metal catalysed cyclisation of the 2-bromo-1,6-dienes and the mixtures of double bond isomers arising from the cyclisation of the 2-bromo-1,7-dienes.

Table 3. Diels-Alder Cycloadducts of Bis-exocyclic Dienes with Dipolarophiles in Chloroform

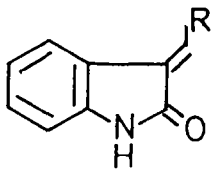
| Diene | Dipolarophile[b] | Temp.(°C) | Time(h) | Product | Yield(%)[a] |
|---|---|---|---|---|---|
| 14b | NPM | 60 | 0.25 | 33a | 90 |
| 14c | NPM | 60 | 0.10 | 33b | 87 |
| 14e | NPM | 80[c] | 0.50 | 33c | 84 |
| 17a | NPM | 25[c] | 6 | 34a | 94 |
| 17a | DMAD | 25 | 96 | 35 | 90 |
| 17a | 36 | 60 | 2 | 37 | 80 |
| 17b | NPM | 60 | 0.33 | 34b | 84 |
| 19a | NPM | 80[d] | 1 | 33d | 36 |
| 19b | NPM | 80[d] | 1 | 33e | 31 |
| 25 | NPM | 60 | 0.10 | 38 | 52 |
| 30 | NPM | 60 | 0.75 | 39 | 44 |

a. Isolated yield; b. NPM = phenylmaleimide; DMAD = dimethyl acetylene dicarboxylate; c. In benzene; d. In acetonitrile.

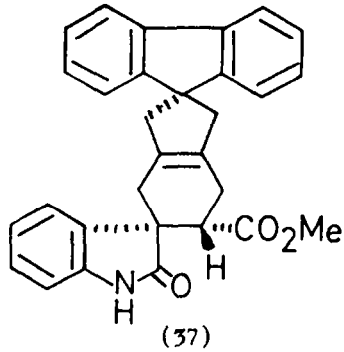
The cycloaddition of (14b) with N-phenylmaleimide (NPM) is diastereofacially specific giving a single cycloadduct. Attempts to establish the stereochemistry of this adduct by n.O.e. experiments were inconclusive and structure (33a) is assigned on the basis of minimising steric interactions in the transition state. The cycloaddition of (14e) and NPM gave a 10:1 mixture of stereoisomers (p.m.r.) from which the major isomer was isolated easily upon crystallisation. The major cycloadduct is assigned stereochemistry (33c) on the basis of minimisation of steric interactions in an endo-transition state. The stereochemistry of cycloadduct (33d) is based on a substantial n.O.e. enhancement of the signal for



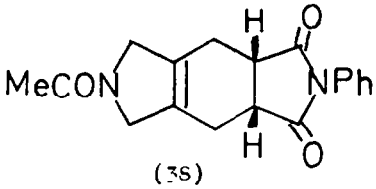
(35) R=$CO_2Me$



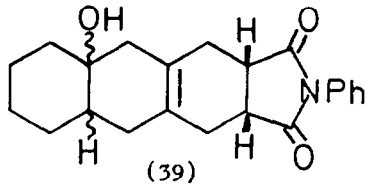
(36) R=$CO_2Me$



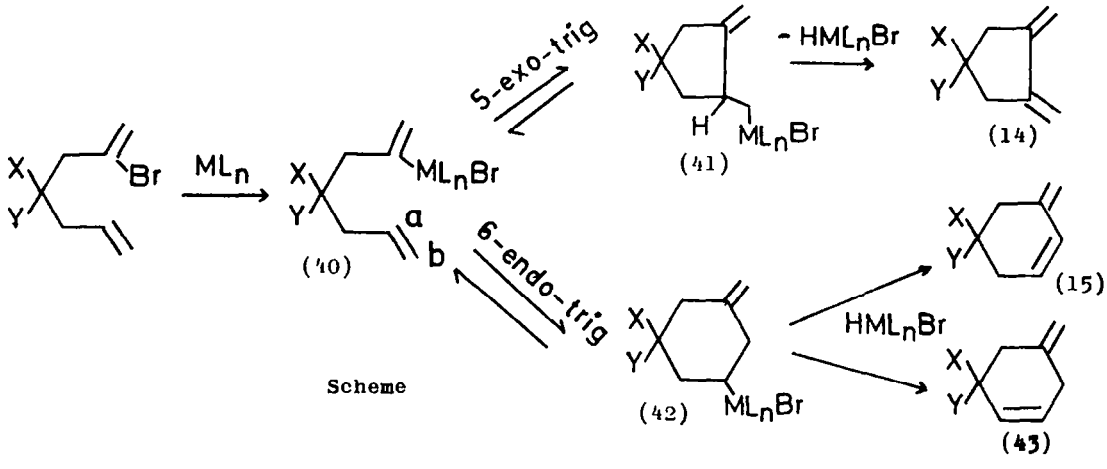
(37)



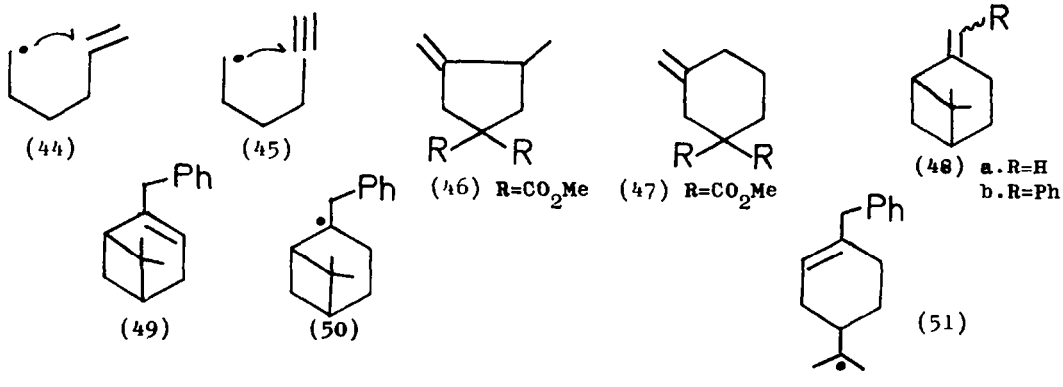
(38)



(39)



Scheme



H-2 (12.5%) when H-1 is irradiated ($J_{H_1H_2}$ 7.1Hz). This stereochemistry corresponds to an endo-transition state and analogous stereochemistry is assigned to (33e) on the basis of a similar coupling constant for H-1/H-2 (J 7.0Hz). Cycloadduct (39) appears to be a single isomer from its p.m.r. data but its precise stereochemistry has not been determined.

Mechanism.

The general mechanistic scheme is illustrated by the case of 2-bromo-1,6-dienes (Scheme).

Oxidative-addition of the vinyl halide to the Pd(0) or Rh(1) species gives the vinylmetal derivative (40) which can undergo a 5-exo- or 6-endo-trig cyclisation by attack at site a or b in (40) to give (41) and (42) respectively. Elimination of $HML_nBr$ from (41) then furnishes the 5-membered product (14) whilst (42) can eliminate $HML_nBr$ in two ways leading to either a conjugated diene (15) or a non-conjugated diene (43). The initial product (42) of the 6-endo-trig cyclisation invariably eliminates $HML_nBr$ to give the conjugate diene (15) although in the cyclisation of (18c) the non-terminal substitution of the olefin apparently results in substantial amounts of the alternative elimination product (23).≠ The slight preference for the 5-exo-trig cyclisation product in palladium catalysed reactions evident in table 1 is markedly accentuated at lower temperature (30°C) in the presence of tetraethylammonium chloride. This is circumstantial evidence for (14) being the kinetically controlled product and (15) the thermodynamically more stable product. However, attempts to observe equilibration of (14) and (15) under a variety of conditions have, thus far, proved futile. The role of the tetraalkylammonium chloride is believed to be that of an anion exchange agent which converts the metallovinyl bromide (40) into the corresponding vinyl $ML_nCl$ species which is more reactive in the cyclisation step and/or the elimination (of $HML_nCl$) step. There are a number of similarities between these metal catalysed cyclisation processes and the cyclisation of the related radical species. Thus although both 5-hexenyl(44) and -hexynyl(45) radicals cyclise regiospecifically by 5-exo- processes, in the absence of substituents other than alkyl at the radical centre[15,16], the cyclisation of the corresponding vinyl radical gives mixtures of 5-exo- and 6-endo-trig products e.g. (12, X=Y=$CO_2Me$, R=H) with tributyltin hydride gives a 3:1 mixture of (46) and (47).[17]

Radical processes have been proposed for the palladium acetate-triphenylphosphine catalysed addition of tetrahalomethanes to alkenes[18] and single electron transfer oxidative additions involving rhodium(1) have been reported.[19] Thus a metal ion mediated radical process could conceivably be operating in the cyclisations reported herein. We therefore looked at the intermolecular Heck reaction between β-pinene (48a) and iodobenzene using our palladium acetate (5 mol.%)-triphenylphosphine (10 mol.%)-potassium carbonate system (2.5 mol., 80°C, 4d). The coupled product (95%) consisted of a ca. 1:1 mixture of (48b, cis- and trans-isomers) and (49). No rearranged products arising via (50)⟶(51) were detected. Radical rearrangements of this type in the β-pinene system are well known.[16] Thus radical processes do not appear to be involved in these palladium catalysed intramolecular Heck reactions.

Experimental

Nuclear magnetic resonance spectra were determined with Varian A-60 (60MHz), Jeol-PMX 60 (60MHz), Bruker WP90 (90MHz), or WH250 (250MHz) instruments using tetramethylsilane as internal standard and $CDCl_3$ as solvent unless otherwise stated. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad. Infrared spectra were recorded with a Perkin Elmer 457 infrared spectraphotometer using potassium bromide

≠ There are other mechanisms for the formation of (23) including elimination involving a methyl group proton followed by isomerisation.

disks unless otherwise stated. Mass spectra were recorded on an AEI MS 902 instrument operating at 70eV. G.l.c. employed Perkin-Elmer F17, F11, F104 and GCD Pye Unicam machines. Peak areas were measured by a Pye Unicam GCD 4 computing integrator. H.p.l.c. was performed on a Perkin-Elmer PE-240 automatic analyser. Melting points were determined with a Kofler hot stage apparatus and are uncorrected. For column chromatography, neutral alumina refers to BDH neutral activated alumina, Brockmann Grade 1, and silica refers to silica gel G (Merck).

Palladium acetate was supplied by Engelhardt Ltd. Tetrakis(triphenyl) phosphine)palladium(0), Wilkinson's catalyst [$RhCl(PPh_3)_3$], tris(tri(p-fluoro phosphine)rhodium(I) chloride, tris[tri(p-methoxyphenylphosphine)]rhodium(I) chloride, $RhCl(AsPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and tris(triphenylphosphine) ruthenium(II) dichloride were synthetised according to the literature methods. Tetraethylammonium carbonate was synthesised by reacting tetraethylammonium hydroxide with carbon dioxide[20].

2-Bromo-1,6-dienes

2-Bromo-4,4-di(ethoxycarbonyl)hepta-1,6-diene (12a). Diethyl allyl malonate (5.0g, 2.5mmol) was slowly added with stirring to sodium ethoxide (from 0.62g sodium, 2.7mmol), in ethanol (50ml) under a nitrogen atmosphere and the resulting solution was stirred for 15 min. 2,3-Dibromopropene (5.8g, 2.9mmol) was then added dropwise over 10 min. and the resulting mixture was boiled under reflux overnight. The mixture was then cooled, water (100ml) added, the mixture extracted with ether (100ml), dried ($MgSO_4$) and concentrated. Fractional distillation gave the product (6.0g, 75%), b.p. 92-95°C/0.1mmHg (Found: C, 49.10; H, 6.05; Br, 24.95. $C_{13}H_{19}BrO_4$ requires C, 48.90; H, 6.00; Br, 25.05%); $\delta$ 5.6 (1H, m, $CH{=}CH_2$), 5.59 and 5.60 (2 x 1H, 2 x br s, $CBr{=}CH_2$), 4.20 (4H, 2 x q, 2 x $CH_2Me$), 3.15 (2H, br s, $CH_2CBr$), 2.73 (2H, d, $CH_2{-}CH{=}CH_2$), and 1.26 (6H, t, 2x$MeCH_2$); $\nu_{max}$(film) 3070, 1730, 1622, 920 and 899 $cm^{-1}$; m/z(%) 320 ($M^+$,2), 319(2), 239(100) and 165(35).

Phenyl 1-methylbut-3-enyl ketone. n-Butyllithium (1.6M in hexane) (250ml, 0.4mol) was added to a solution of diisopropylamine (41g, 0.4mol) in dry THF (400ml) under $N_2$ at -63°C. The mixture was stirred for 15min and then propiophenone (47.2g, 0.35mol) was added and stirring continued at -63°C for 1.5h. Allyl bromide (42g, 0.32mol) was then added over 5min and the mixture stirred at -63°C for 1.5h followed by 4h at room temperature. Water (50ml) was then added, the THF evaporated under reduced pressure and a further portion of water (50ml) added. The resulting mixture was extracted with ether (2 x 100ml), dried ($MgSO_4$) and concentrated. Distillation of the residual oil gave the product (45g, 73%) as a colourless oil b.p. 93-97°C/2.5mmHg (Found: C, 82.50; H, 8.05. $C_{12}H_{14}O$ requires, C, 82.70; H, 8.10%); $\delta$ 7.71 (5H, m, ArH), 5.79 (1H, m, $CH{=}CH_2$), 5.04 (2H, m, $CH{=}CH_2$), 3.55 (1H, m, $CHMe$), 2.56 and 2.20 (2 x 1H, 2 x m, $CH_2{-}CH{=}CH_2$) and 1.21 (3H, d, Me); $\nu_{max}$(film), 3065, 3050, 2965, 2910, 2900, 2860, 1684, 1635, 1590, 1573, 1440, 1370, 1350, 1204 and 700 $cm^{-1}$; m/z(%) 174 ($M^+$,16), 105(100) and 77(24).

2-Bromo-4-benzoyl-4-methylhepta-1,6-diene (12b). n-BuLi (1.6M, 125ml, 0.2mol) was added to a solution of diisopropylamine (22g, 0.22mol) in dry THF at -78°C and the mixture stirred for 15min when HMPA (78ml) was added and stirring continued for a further 15min. Phenyl 1-methylbut-3-enyl ketone (30g, 0.17mol) in THF (10ml) was then added over 5min., the mixture stirred for 40 min and then 2,3-dibromopropene (45g, 0.23mol) in THF (10ml) added. The resulting mixture was stirred at -78°C for 45min and allowed to warm to room temperature over 3h. Water (50ml) was then added and THF removed under reduced pressure. Aqueous ammonium chloride solution (20ml) was added to the residue and the mixture extracted with ether (100ml). The ether extract was washed with water (50ml), dried ($MgSO_4$), and concentrated to give an oil (52g) which comprised a 1:1 mixture of starting material and product. Distillation gave the product (5.9g, 10%) as a colourless oil, b.p. 93-94°C/ 0.05mmHg. (Found: C, 61.45; H, 5.85. $C_{15}H_{17}BrO$ requires C, 61.45; H, 5.75%); $\delta$ 7.45 (5H, m, ArH), 5.69 (1H, m, $CH{=}CH_2$), 5.61 (2H, m, $C(Br){=}CH_2$), 5.06 (2H, m, $CH{=}CH_2$), 3.24 and 2.80 (2 x 1H, d, J 15.1Hz, $CH_2{-}CBr$), 2.67 and 2.40 (2 x 1H, d, J 14.0Hz, $CH_2{-}CH{=}CH_2$) and 1.39 (3H, s, Me); $\nu_{max}$(film) 3070, 3050, 2970, 2930, 2910, 1670, 1635, 1620, 1455, 1440 and 700 $cm^{-1}$; m/z(%) 294 ($M^+$, 1), 292(1), 213(24), 105(100) and 77(23).

2-Bromo-4,4-diacetylhepta-1,6-diene (12c)

A mixture of allylacetylacetone (3.5g, 0.025mol), potassium carbonate (3.41g, 0.025mol) and 2,3-dibromopropene (5.3g, 0.026mol) was boiled under reflux in acetone (20ml) under a nitrogen atmosphere for 22h. The mixture was filtered and filtrate concentrated. Distillation of the residual oil gave the product (4.52g, 70%) as a colourless oil, b.p. 100°C/1.25mmHg (Found: C, 51.00; H, 5.85. $C_{11}H_{15}BrO_2$ requires C, 51.15; H, 6.05%); $\delta$ 5.63 and 5.57 (2 x 1H, 2 x d, $CH_2{=}C(Br)$), 5.54 (1H, m, $CH{=}CH_2$), 5.15 (2H, m, $CH{=}CH_2$), 3.18 (2H, d, $CH_2{-}CBr$), 2.83 (2H, d, J 7.2Hz, $CH_2{-}CH{=}CH_2$), and 2.18 (2 x 3H, s, Me); $\nu_{max}$ (film) 3065, 2995, 2965, 2910, 1695, 1620, 1420 and 1350 $cm^{-1}$; m/z(%) 260 ($M^+$, 0.5), 258(0.5), 216(10), 179(63), 137(32), 97(29), 95(21), and 43(100).

2-Bromo-4-carbomethoxy-5,5-dimethylhepta-1,6-diene (12e).

Methyl 3,3-dimethylpent-4-enoate (14.2g, 0.1mol) was added to a solution of LDA [from 2.6M n-BuLi (40ml, 0.1mol) and diisopropylamine (10.12g, 0.1mol)] in THF (8ml). The mixture was kept at -78°C for 30min when 2,3-dibromopropene (22g, 0.11mol) dissolved in HMPA (5.4g, 0.03mol]) was added maintaining the temperature at -78°C. The work up was described previously. The product (10.4g, 39%) distilled as a colourless oil, b.p. 79-81°C/2mmHg (Found: C, 50.65; H, 6.80;

Br, 30.30. $C_{11}H_{17}BrO_2$ requires C, 50.60; H, 6.55; Br, 30.60%); $\delta$ 5.84 (1H, m, CH=$CH_2$), 5.57 and 5.39 (2 x 1H, 2 x t, C(Br)=$CH_2$), 5.02 (2H, m, CH=$CH_2$), 3.66 (3H, s, MeO), 2.79 (1H, t, CH-$CH_2$), 2.68 and 2.45 (2 x 1H, m and d, $CH_2$-C(Br)), and 1.07 (6H, s, 2 x Me); $\nu_{max}$(film) 3075, 2960, 2940, 2835, 1730, 1625, 1430, 1123, 1150, 1015, 990 and 845 $cm^{-1}$; m/z(%) 262 ($M^+$, 0.2), 181(80), 69(100) and 41(48).

9-Allyl-9-(2-bromoallyl)fluorene (16a). Freshly prepared phenyl lithium [from bromobenzene (52.3g, 0.33mol) and lithium shot (5.0g, 0.8mol)] in dry ether (250ml) was slowly added to a solution of 9-allylfluorene[21] (36.6g, 0.14mol) in dry ether (300ml) at room temperature under a dry nitrogen atmosphere. An immediate dark red colour indicated that the anion had formed. The mixture was stirred for 40min and then 2,3-dibromopropene (30g, 0.15mol) was added over 10min causing the red colour of the anion to discharge. The mixture was boiled under reflux for 20min., water (200ml) added and the organic layer separated, dried ($MgSO_4$) and concentrated. Distillation of the residual oil gave the product (26g, 59%) as a colourless viscous oil, b.p. 116-120°C/0.1mmHg (Found: C, 70.20; H, 5.35; Br, 24.45. $C_{19}H_{17}Br$ requires C, 70.15; H, 5.25; Br, 24.65%); $\delta$ 7.7-7.3 (8H, ArH), 5.19 (1H, m, CH=$CH_2$), 5.09 and 4.86 (2 x 1H, 2 x s, C(Br)=$CH_2$), 4.85 and 4.77 (2 x 1H, 2 x d, CH=$CH_2$), 3.19 (2H, s, $CH_2CBr$), and 2.72 (2H, d, $CH_2$=$CH_2$); m/z(%) 326 ($M^+$, 9), 324(9), 285(21), 283(21), 205(100), and 203(51).

9-Allyl-4-azafluorene. t-Butyllithium (42ml of a 2M hexane solution, 8.4mmol) was added to a solution of 4-azafluorene (12.54g, 7.5mmol) in THF (300ml) at 78°C under a nitrogen atmosphere to give a red solution of the anion. After stirring for 30 min. at -78°C allyl bromide (18g, 15mmol) was added over 5 min. The mixture was stirred at -78°C for a further 1h and then allowed to warm to room temperature over 3h. The THF was then removed and the residue partitioned between ether and water. The dried ($MgSO_4$) ether extract was evaporated and the residual oil distilled to afford the product (11.9g, 76%), b.p. 112-115°C/0.09mmHg (Found: C, 85.95; H, 6.50; N, 6.60. $C_{15}H_{13}N$ requires C, 86.90; H, 6.30; N, 6.75%); $\delta$ 7.85 (7H, m, ArH), 5.73 (1H, m, CH=$CH_2$), 5.02 (2H, m, CH=$CH_2$), 3.97 (1H, t, ArCH) and 2.68 (2H, m, $CH_2$); m/z(%) 207 ($M^+$, 28), 167(27), 166(100), 140(14), and 139(12).

9-Allyl-9-(2-bromoallyl)-4-azafluorene (16b). t-Butyl lithium (31.0ml of a 1.6N solution in hexane, 0.062mol) was added to a solution of 9-allyl-4-azafluorene (10.5g, 0.051mol) in THF (200ml) at -50°C under a nitrogen atmosphere to give a red-violet solution of the anion. This solution was stirred at -50°C for 30min and then 2,3-dibromopropene (20g, 0.10mol) in THF (10ml) was added over 5min. The mixture was stirred at -30 to -40°C for 30 min and then allowed to warm to room temperature over 2.5h. Water (20ml) was then added, the THF removed under reduced pressure, a further portion of water (100ml) added and the mixture extracted with ether (2 x 100ml), dried ($MgSO_4$) and concentrated. Distillation of the residual oil gave the product (12.4g, 65%) as a colourless viscous oil b.p. 150-153/0.01mmHg (Found: C, 66.0; H, 5.05; N, 4.15. $C_{18}H_{16}BrN$ requires C, 66.25; H, 4.95; N, 4.25%); $\delta$ 8.57 (1H, m, ArH), 8.05 - 7.19 (6H, m, ArH), 5.25 (1H, m, CH=$CH_2$), 5.13 and 4.96 (2 x 1H, 2 x s, $CH_2$=CBr), 4.82 (2H, m, $CH_2$=CH), 3.2 (2H, s, $CH_2CBr$), and 2.75 (2H, m, $CH_2$-CH=$CH_2$); $\nu_{max}$(film) 3075, 2980, 2900, 1685, 1618, 1580, 1560, 1530, 1495 and 1416 $cm^{-1}$.

Diethyl 3-phenylprop-2-enylmalonate. Diethyl malonate (20g, 0.125mol) was slowly added with stirring to a solution of sodium ethoxide [from sodium (2.00g, 8.7mmol)] in ethanol (320ml). After the addition was complete stirring was continued for a further 15min and cinnamyl bromide (22g, 0.112mol) was then added dropwise over 10min and the resulting mixture stirred at room temperature for 15h. The mixture was then concentrated to ca.100ml under reduced pressure, poured into water (500ml), extracted with ether (3x), the ether extracts dried ($MgSO_4$), the solvent removed and the residue distilled to afford the product (16g, 52%) as a colourless oil, b.p. 137-141°C/0.45 mmHg (Found: C, 69.50; H, 7.15. $C_{16}H_{20}O_4$ requires C, 69.55; H, 7.30%); $\delta$ 7.19 (5H, m, ArH), 6.40 (1H, d, J 15.8Hz, PhCH=CH), 6.08 (1H, m, PhCH=CH), 4.11 (2 x 2H, q, $CH_2$Me), 3.42 (1H, t, CHCH$_2$), 2.72 (2H, m, $CH_2$CH=C), and 1.18 (2 x 3H, t, $CH_2$Me); $\nu_{max}$(film) 3075, 3050, 3020, 2975, 2930, 2900, 2865, 1730, 1593, 1445, 915, 860, 745 and 695 $cm^{-1}$; m/z(%) 276 ($M^+$, 26), 202(41), 157(16), 130(18), 129(100), 117(48), 115(22), and 91(17).

2-Bromo-4,4-di(ethoxycarbonyl)-7-phenylhepta-1,6-diene (18a). Using the same procedure as above diethyl 3-phenylprop-2-enylmalonate (15g, 5.4mmol), sodium ethoxide [from sodium (1.5g, 6.5mmol)] and 2,3-dibromopropene (13.0g, 6.5mmol) in ethanol (250ml) gave the product (18.9g, 84%) as a colourless oil, b.p. 165-167°C/0.03mmHg (Found: C, 57.75; H, 5.90; Br, 20.15. $C_{19}H_{23}BrO_4$ requires C, 57.75; H, 5.85; Br, 20.20%); $\delta$ 7.27 (5H, m, ArH), 6.42 (1H, dd, $J_{AB}$ 15.1Hz, PhCH), 6.04 (1H, m, PhCH=CH), 5.72 and 6.63 (2 x 1H, 2 x d, $CH_2$=CBr), 4.21 (4H, m, MeC$H_2$), 3.20 (2H, s, $CH_2CBr$), 2.93 (2H, dd, $CH_2$CH=CHPh), and 1.26 (2 x 3H, t, 2 x MeC$H_2$). $\nu_{max}$(film) 3070, 3050, 3020, 2975, 2928, 2898, 1725, 1620, 1425, 1410, 1210, 1385, 740 and 692 $cm^{-1}$; m/z(%) 396 ($M^+$, 4), 394(4), 315(9), 275(25), 269(11), 241(38), 230(29), 229(71), 183(13), 167(18), 117(100), 115(59), and 91(42).

Dimethyl (2-bromoallyl)malonate

Dimethyl malonate (5.3g, 4mmol) was added to a solution of sodium (0.75g, 3.3mmol) in MeOH (50ml). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 15min and then 2,3-dibromopropene (6.6g, 3.3mmol) was slowly added. The mixture was boiled under reflux for 3h, cooled, and water (10ml) added. The ethanol was then removed by a rotary evaporator and the remaining solution partitioned between ether and $H_2O$. The ether layer was

separated, dried ($MgSO_4$), evaporated, and the residue distilled to afford the product (2.81g, 34%) as a colourless oil, b.p. 82-84°C/0.5mmHg; $\delta$ 5.70 and 5.49 (2 x 1H, 2 x t, $CH_2$=CBr), 3.83 (1H, t, CH), 3.76 (2 x 3H, s, 2 x MeO), 3.03 (2H, dd, $CH_2$).

2-Bromo-4,4,7-tri(methoxycarbonyl)hepta-1,6-diene (18b). Prepared from dimethyl (2-bromoallyl)malonate (2.75g, 1.1mmol), sodium methoxide [from sodium (0.25g, 1.1mmol)] and methyl 4-bromocrotonate (2.0g, 1.1mmol) in methanol (50ml) by the same procedure as above. The product (1.4g, 37%) distilled as a colourless oil, b.p. 156-160°C/0.5mmHg (Found: C, 44.65; H, 4.75. $C_{13}H_{17}BrO_6$ requires C, 44.70; H, 4.90%); $\delta$ 6.78 (1H, m, $CH_2$CH=), 5.93 and 5.87 (1H, 2 x t, $CH_2CH$=CH) 5.70 and 5.63 (2 x 1H, t and d, $CH_2$=CBr), 3.76 (2 x 3H, s, 2 x MeO), 3.73 (3H, s, MeO), 3.17 (2H, d, $CH_2CBr$), and 2.92 (2H, dd, $CH_2CH$=); m/z(%) 291(49), 289(48), 171(100), 139(26), 111(32), 91(21) and 59(43). $\nu_{max}$(film) 3100, 3000, 2950, 2840, 1725, 1645, 1620, and 1435 $cm^{-1}$.

2-Bromo-4,4-di(ethoxycarbonyl)-6-methylhepta-1,6-diene (18c). Using the above procedure, diethyl(2-methylallyl)malonate (6.3g, 3mmol), sodium ethoxide [from sodium (0.6g, 3mmol)], and 2,3-dibromopropene (5.9g, 2.9mmol) in ethanol (50ml) gave the product (5.55g, 56%) as a colourless oil, b.p. 95-96°C/0.03mmHg (Found: C, 50.60; H, 6.35; Br, 23.75. $C_{14}H_{21}BrO_4$ requires C, 50.45; H, 6.35; Br, 24.00%); $\delta$ 5.69 and 5.59 (2 x 1H, m, $CH_2$=CBr), 4.88 and 4.77 (2 x 1H, s, $CH_2$=CMe), 4.20 (2 x 2H, q, 2 x $MeCH_2$), 3.21 (2H, d, $CH_2CBr$), 2.82 (2H, s, $CH_2$Me) 1.57 (3H, s, Me), and 1.26 (2 x 3H, t, 2 x $MeCH_2$); $\nu_{max}$(film) 3065, 2970, 2925, 2900, 2860, 1730, 1620, 1440, 1210, 1185 and 900 $cm^{-1}$; m/z(%) 334 ($M^+$, 2), 332(2), 253(100), 207(29), 179(65), 167(45), and 151(43).

N-Allyl-N-(2-bromoallyl)acetamide (24). n-Butyl lithium (84ml of a 1.45M solution in hexane, 12mmol) was slowly added to a solution of diisopropylamine (12g, 12mmol) in THF (250ml) at -78°C and stirred under a nitrogen atmosphere for 15min. The mixture was then cooled to -90°C and N-allylacetamide (10g, 11mmol) in THF (10ml) added. The mixture was stirred for 1h and then 2,3-dibromopropene (24g, 12mmol) was slowly added keeping the temperature at -80° to -90°C for 1h and then allowed to warm to room temperature with stirring over 3h. The THF was removed under reduced pressure and the residue partitioned between ether and water. The ether extract was dried ($MgSO_4$), evaporated, and the residual oil distilled to give the product as a colourless oil (15.7g, 60%), b.p. 60-62°C/0.1mmHg (Found: C, 44.15; H, 5.55; N, 6.35. $C_8H_{12}BrNO$ requires C, 44.05; H, 5.55; N, 6.40%); $\delta$ 5.47 (5H, m, CH=$CH_2$ and $CH_2$=CBr), 4.25 and 4.08 (2 x 1H, 2 x s, $CH_2N$), 4.0 and 3.94 (2 x 1H, 2 x d, $CH_2N$), and 2.15 N, 6.35. $C_8H_{12}BrNO$ requires C, 44.05; H, 5.55; N, 6.40%); 5.47 (5H, m, CH=$CH_2$ and $CH_2$=CBr), 4.25 and 4.08 (2 x 1H, 2 x s, $CH_2N$), 4.0 and 3.94 (2 x 1H, 2 x d, $CH_2N$), and 2.15 (3H, s, Me); $\nu_{max}$(film) 3290, 3070, 3000, 2970, 2910, 1645, 1410, 1240, 985 and 920 $cm^{-1}$; m/z(%) 219(1), 217(1), 138(100), 96(325), 56(27), 43(59), 42(8), 41(42), and 39(27).

2-Bromo-1,7-dienes

2-Bromo-4,4-di(ethoxycarbonyl)octa-1,7-diene (27). Using the same procedure as above, diethyl (but-3-enyl)malonate (20g, 9mmol)[22], sodium ethoxide [from sodium (2.3g, 10mmol), and 2,3-dibromopropene (22g, 11mmol) in dry ethanol (200ml) were reacted to afford the product (22.4g, 73%), as a colourless oil, b.p. 88°C/0.01mmHg (Found: C, 50.20; H, 6.35; Br, 23.75. $C_{14}H_{21}BrO_4$ requires C, 50.45; H, 6.35; Br, 24.00%); $\delta$ 5.76 (1H, m, CH=$CH_2$), 5.66 and 5.57 (2 x 1H, 2 x s, $CH_2$=CBr), 4.18 (4H, q, 2 x $CH_2$Me), 3.17 (2H, s, $CH_2CBr$), 1.98 ($CH_2CH$=), 1.91 (2H, m, $CH_2$), and 1.26 (6H, t, 2 x $CH_2$Me); m/z(%) 335 ($M^+$, 0.5), 333(0.5), 253(100) and 199(34).

1-Allyl-2-(2-bromoallyl)cyclohexanol (28). Allyl magnesium bromide [from allyl bromide (3.5g, 2.9mmol), magnesium turnings (1.69g, 7mmol) in ether (20ml)] was added dropwise to a solution of 2-bromoallylcyclohexanone (5.0g, 2.3mmol)[23] in dry ether (20ml) under a nitrogen atmosphere, at such a rate that the ether gently boiled. After the addition the mixture was heated under reflux for 30min and then allowed to stand for 1h. The magnesium complex was decomposed by the addition of ice (12g) and conc. HCl (1.9ml) followed by the addition of water (50ml) and extraction with ether (3 x 50ml). The ether extracts were dried ($MgSO_4$), concentrated, and the residue distilled to afford the product (3g, 50%) as a colourless oil, b.p. 73-74°C/0.1mmHg (Found: C, 55.60; H, 7.40. $C_{12}H_{19}BrO$ requires C, 55.45; H, 7.45%); $\delta$ 5.84 (1H, m, CH=$CH_2$), 5.57 and 5.42 (2H, 2 x t, $CH_2$=CBr), 5.15 (2H, m, CH=C$H_2$), 2.79 [1H, m, CHC(OH)], 2.30 (4H, m, $CH_2CH$= and $CH_2CBr$), and 1.51 (9H, m, 4 x $CH_2$ and OH); $\nu_{max}$(film) 3470, 3070, 3000, 2970, 2930, 2850, 1624, 1445, and 1430 $cm^{-1}$; m/z(%) 219 ($M^+$, 39), 217(40), 137(100), 95(40), 43(46) and 41(43).

Cyclisation of 2-Bromo-1,6- and -1,7-dienes

General Procedure

The catalyst (5 or 10mole %) (tables 1 and 3) was added to a mixture of the 2-bromo-1, -diene and anhydrous potassium carbonate in dry acetonitrile. The reaction mixture was stirred at 30°C or boiled under reflux under a nitrogen atmosphere monitoring the reaction by g.l.c. (2.5 or 5% SGR, 2 or 5M). After the reaction was complete inorganic salts were removed by filtration and the filtrate concentrated and passed through a short column of silica or alumina (neutral) eluting with ether and 40-60° petroleum ether to remove dissolved salts.

When tetraethylammonium salts were added the hydrated salts were dehydrated by boiling under reflux with excess 2,2-dimethoxypropane under a nitrogen atmosphere for 16h.

Diethyl 3,4-bis(methylene)cyclopentane-1,1-dicarboxylate (14a) and diethyl 5-methylenecyclohex-3-ene-1,1-dicarboxylate (15a). A 5:4 mixture of (14a) and (15a) is a colourless oil, b.p. 66-68°C/0.05mmHg whilst (15a) has b.p. 73-74°C/0.15mmHg. [Found (mixture): C, 65.35; H, 7.20. $C_{13}H_{18}O_4$ requires C, 65.55; H, 7.60%]. Pure samples of both isomers were obtained by preparative t.l.c. ($SiO_2$) eluting with 9:1 v/v 40-60° petroleum ether-ether.
(14a) Colourless oil. $\delta$ 5.39 and 4.97 (2 x 2H, 2 x s, 2 x C=$CH_2$), 4.17 (4H, q, 2 x $CH_2$Me), 3.03 (4H, s, 2 x $CH_2$), and 1.24 (6H, t, 2 x $CH_2$Me); m/z(%) 238 ($M^+$,14), 193(10), 165(23), 164(76), and 91(100).
(15a) Colourless oil. $\delta$ 5.86 and 5.62 (2 x 1H, d and m, CH=CH), 4.83 (2H, m, C=$CH_2$), 4.19 (4H, q, $CH_2$Me), 2.96 (2H, d, $CH_2$), 2.57 (2H, s, $CH_2$), and 1.24 (6H, t, $CH_2$Me); m/z(%) 238 ($M^+$, 14), 193(11), 165(23), 164(76) and 91(100).
1-Benzoyl-1-methyl-3,4-bis(methylene)cyclopentane (14b) and 1-benzoyl-1-methyl-5-methylenecyclohex-3-ene (15b). The reaction mixture was a pale yellow oil which was separated by column chromatography ($SiO_2$) eluting with 1:3 v/v 40-60° petroleum ether-ether. The cyclopentane (14b) was characterised as its Diels-Alder adduct with N-phenylmaleimide (below).
(14b) Pale yellow oil. $\delta$ 7.61 (5H, m, ArH), 5.44 and 4.96 (2 x 2H, d and t, C=$CH_2$), 3.07 and 2.60 (2 x 2H, m and d, $CH_2$C=$CH_2$) and 1.39 (3H, s, Me).
(15b) Pale yellow oil. m/z $M^+$ 212.1201, $C_{15}H_{16}O$ requires 212.1201; $\delta$ 7.49 (5H, m, ArH), 6.10 and 5.66 (2 x 1H, 2 x m, CH=CH), 4.81 and 4.73 (2 x 1H, 2 x s, $CH_2$=C), 2.91 and 2.14 (2H, m, CH=CH$CH_2$), 2.75 and 2.37 (2H, 2 x d, $CH_2$=C$CH_2$), and 1.27 (3H, s, Me); $\nu_{max}$(film) 3050, 3010, 2960, 2920, 2885, 1715, 1665, 1450 and 1260 $cm^{-1}$; m/z(%) 212 ($M^+$,1), 107(31), 106(35), 105(100), and 77(30).
1,1-Diacetyl-3,4-bis(methylene)cyclopentane (14c) and 1,1-diacetyl-5-methylene cyclohex-3-ene (15c). The isomeric products were separated by h.p.l.c. (25cm x 16mm 7 m Lichrosorb Si60 column eluting with 1:9 v/v ether-hexane. (Found (mixed isomers): C, 73.85; H, 8.15. $C_{11}H_{14}O_2$ requires C, 74.15; H, 7.90%).
(14c) Colourless oil. $\delta$ 5.40 and 4.98 (2 x 2H, 2 x t, C=$CH_2$), 2.97 (2 x 2H, 2 x t, $CH_2$-C=$CH_2$) and 2.14 (2 x 3H, s, Me).
(15c) Colourless oil. $\delta$ 6.12 and 5.80 (2 x 1H, 2 x m, CH=CH), 4.95 (2H, q, C=$CH_2$), 2.88 (2H, t, $CH_2$-C= ), 2.66 (2H, m, $CH_2$C= and 2.13 (2 x 3H, s,Me); $\nu_{max}$(film) 3050, 2960, 2920, 2850, 1710, 1620, 1445 and 1120 $cm^{-1}$; m/z(%) 178 ($M^+$,6), 160(12), 136(17), 135(58), 93(16), 91(15) and 43(100).
Methyl 2,2-dimethyl-3,4-bis(methylene)cyclopentene-1-carboxylate (14e) and methyl 2,2-dimethyl-5-methylenecyclohex-3-ene-1-carboxylate (15e). The products were both colourless oils and the 1.38:1 mixture of (14e) and (15e) had b.p. 70-90°C/1.5mmHg (molecular distillation) [Found (mixed isomers) C, 73.00; H, 9.10. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.95%].
(14e) $\delta$ 5.41, 4.94, and 5.38, 4.82 (4 x 1H, 2 x br s and 2 x s, 2 x $CH_2$=C), 3.71 (3H, s, MeO), 2.83 (1H, m, CHCO), 2.59 (2H, m, $CH_2$), and 1.29 and 0.9 (2 x 3H, 2 x s, 2 x Me); $\nu_{max}$(film) 3060, 2940, 2195, 2860, 1720, 1428, 1155, 1192 and 1155 $cm^{-1}$.
(15e) $\delta$ 6.01 and 5.50 (2 x 1H, 2 x d, J 9.8Hz, CH=CH), 4.85 and 4.83 (2 x 1H, 2 x d, $CH_2$=C), 3.70 (3H, s, MeO), 2.66 (1H, m, CH), 2.50 (2H, m, $CH_2$), and 1.17 and 1.0 (2 x 3H, 2 x s, 2 x Me); $\nu_{max}$(film) 3020, 2925, 2840, 1720, 1420 and 1150 $cm^{-1}$; m/z(%) 180 ($M^+$,18), 121(100), 105(31) and 91(25).
9,9-Spiro[3,4-bis(methylene)cyclopentyl]fluorene (17a). The product crystallised from benzene (some decomposition) as colourless prisms, m.p. 141-144°C (Found: C, 93.45; H, 6.60. $C_{19}H_{16}$ requires C, 93.40; H, 6.60%); $\delta$ 7.46 (8H, m, ArH), 5.62 and 5.04 (4H, 2 x t, 2 x C=$CH_2$), and 2.87 (4H, t, 2 x $CH_2$); $\nu_{max}$ 3070, 3020, 2941, 1620, 1470 and 889 $cm^{-1}$; m/z(%) 244 ($M^+$,100), 229(57), 215(35), and 178(14).
9,9-Spiro[3,4-bis(methylene)cyclopentyl]-4-azafluorene (17b). Obtained as colourless plates, m.p. 94-96°C, by preparative t.l.c. ($SiO_2$) eluting with 4:1 v/v 40-60° petroleum ether-ether (Found: C, 88.10; H, 6.20; N, 5.60. $C_{18}H_{15}N$ requires C, 88.15; H, 6.15; N, 5.70%); $\delta$ 8.55 and 8.04 (2 x 1H, 2 x m, ArH), 7.41 (4H, m, ArH), 5.65 and 5.08 (2 x 2H, 2 x s, 2 x $CH_2$=C), and 2.99 and 2.78 (2 x 2H, 2 x d, J 16Hz, $CH_2$-C=$CH_2$); $\nu_{max}$ 3070, 3035, 3010, 2965, 2915, 2892, 2845, 2820, 1585, 1575, 1563, 1405, 795, 760 and 740 $cm^{-1}$; m/z(%) 245 ($M^+$,41), 230(21), 207(23), 206(100), 204(38), 179(11), 178(12), and 166(28).
Diethyl 3-benzylidene-4-methylenecyclopentane-1,1-dicarboxylate (19a) and diethyl 3-methyl-4-benzylidenecyclopent-2-ene-1,1-dicarboxylate (20). The mixed isomers comprised a colourless oil which decomposed on attempted distillation. Characterisation of (19a) was thus achieved as its Diels-Alder adduct with N-phenylmaleimide (below) and pure (20) was isolated from the mother liquors of this reaction by preparative t.l.c. ($SiO_2$) eluting with 4:1 v/v 40-60° petroleum ether-ether.
(19a) $\delta$ 7.33 (5H, m, ArH), 6.88 (1H, m, PhCH), 5.50 and 5.0 (2 x 1H, t and br s, $CH_2$=C), 4.21 (2 x 2H, q, $CH_2$Me), 3.35 and 3.07 (2 x 2H, d and t, $CH_2$C=C), and 1.27 (2 x 3H, t, $CH_2$Me).
(20) Colourless oil (Found: C, 72.45; H, 7.10. $C_{19}H_{22}O_4$ requires C, 72.60; H, 7.05%); $\delta$ 7.33 (5H, m, ArH), 6.31 (1H, t, PhCH), 5.98 (1H, br s, CH=CMe), 4.21 (2 x 2H, q, 2 x MeC$H_2$), 3.49 (2H, d, $CH_2$), 1.95 (3H, br d, =CMe), and 1.27 2 x 3H, t, 2 x MeC$H_2$); $\nu_{max}$(film) 3070, 3040, 3010, 2970, 2930, 1723, 1440, 1245, 1180, 1060, 750 and 695 $cm^{-1}$; m/z(%) 314 ($M^+$,2), 241(18), 173(25), 129(18), 128(17), 127(24), 105(100), 91(17), 77(36) and 76(28).

Dimethyl 3-carbomethoxymethylidene-4-methylenecyclopentane-1,1-dicarboxylate (19b) and dimethyl 3-carbomethoxymethyl-4-methylenecyclopent-2-ene-1,1-dicarboxylate (21). The mixed isomers comprised a colourless oil. Characterisation of (19b) was achieved as its Diels-Alder adduct with N-phenylmaleimide (below) whilst (21) was isolated by preparative t.l.c. ($SiO_2$, 40-60° petroleum ether-ether) of the mother liquors of this latter reaction.
(19b) $\delta$ 6.11 (1H, br s, $CHCO_2Me$), 5.57 and 5.13 (2 x 1H, t and br s, $CH_2=C$), 3.68 (2 x 3H, s, MeO), 3.64 (3H, s, MeO) and 3.48 and 2.90 (2 x 2H, m and br s, $CH_2C=C$).
(21) Colourless oil (Found: C, 58.70; H, 6.10. $C_{13}H_{16}O_6$ requires C, 58.20; H, 6.00%); $\delta$ 6.11 (1H, br s, C=CH), 4.88 (2H, m, $C=CH_2$), 3.68 (2 x 3H, s, 2 x MeO), 3.64 (3H, s, MeO), 3.19 (2H, d, $CH_2C=CH$), and 3.15 (2H, t, $CH_2C=CH_2$); $\nu_{max}$(film) 1730, 1710, 1595, 1435 and 1390 $cm^{-1}$; m/z(%) 268 ($M^+$,42), 236(27), 209(100), 208(48), 177(48), 149(91), 119(21), 105(42), and 91(80).
Diethyl 3-methyl-5-methylenecyclohex-3-ene-1,1-dicarboxylate (22) and diethyl 3-methyl-5-methylenecyclohex-2-ene-1,1-dicarboxylate (23). The product was a colourless oil which comprised a 1:1.4 mixture (p.m.r.) of (22) and (23), b.p. 35-50°C/0.1mmHg (molecular distillation) [Found (mixed isomers): C, 66.80; H, 7.90. $C_{14}H_{20}O_4$ requires C, 66.65; H, 8.00%]; m/z(%) (mixed isomers) 252 ($M^+$,15), 180(14), 179(100), 178(32), 151(23), 150(24), 149(17), 133(13), 107(57), 106(19), 105(71), and 91(39).
(22) $\delta$ 5.55 (1H, s, CH=CMe), 4.82 and 4.79 (2 x 1H, 2 x s, $C=CH_2$), 4.11 (4H, m, 2 x $MeCH_2$), 2.69 and 2.63 (2 x 2H, 2 x s, 2 x $CH_2$), 1.71 (3H, s, Me), and 1.18 (6H, t, 2 x $MeCH_2$); max 231 (11,400)
(23) $\delta$ 5.85 (1H, s, CH=CMe), 4.73 (2H, s, $C=CH_2$), 4.10 (4H, m, 2 x $MeCH_2$), 2.74 and 2.50 (2 x 2H, 2 x s, $CH_2$), 1.74 (3H, s, MeC=CH), and 1.16 (6H,t,2 x $MeCH_2$).
N-Acetyl-3,4-bis(methylene)pyrrolidine (25) and N-acetyl-5-methylene-1,2,5,6-tetrahydropyridine (26). The product (74%) was a colourless oil which comprised a 6:1 mixture (p.m.r.) of (25) and (26), b.p. 30-40°C/0.01mmHg (molecular distillation). Characterisation of (25) was achieved as its Diels-Alder adduct with N-phenylmaleimide (below), whilst (26) was isolated by preparative t.l.c. ($SiO_2$, 40-60° petroleum ether-ether) of the mother liquors of this latter reaction.
(25) $\delta$ 5.54 and 5.04 (2 x 2H, 2 x m, $CH_2=C$), 4.28 (2 x 2H, d, $NCH_2$), and 2.08 (3H, 2 x s, Me, amide isomers).
(26) Colourless oil (Found: C, 69.95; H, 8.30; N, 10.00. $C_8H_{11}NO$ requires C, 70.05; H, 8.10; N, 10.20%); $\delta$ 6.29 (1H, m, $CH=CHCH_2$), 5.84 (1H, m, $CH=CHCH_2$), 4.97 (2H, m, $CH_2=C$), 4.28 and 4.17 (2 x 1H, 2 x s, $NCH_2$), 4.09 and 4.04 (2 x 1H, 2 x m, $NCH_2CH$), and 2.14 and 2.12 (3H, 2 x s, MeCO); $\nu_{max}$(film) 2950, 2910, 2840, 1625, 1420, 1307, 1025 and 800 $cm^{-1}$; m/z(%) 137 ($M^+$,61), 95(38), 94(100), 82(20), 67(18), 65(10), 57(20), 56(21), and 43(64).
Diethyl 3,4-bis(methylene)cyclohexane-1,1-dicarboxylate (29) and diethyl 4-methyl-5-methylenecyclohex-3-ene-1,1-dicarboxylate (31). The 4:1 mixture (86%) of (29) and (31) was a colourless oil, b.p. 60°C/0.01mmHg, whilst pure (31) had b.p. 60°C/0.005mmHg. The minor isomer (31) was separated by preparative t.l.c. ($SiO_2$) eluting with 9:1 v/v 40-60° petroleum ether-ether.
(29) Colourless oil (Found: C, 66.80; H, 7.95. $C_{14}H_{20}O_4$ requires C, 66.65; H, 8.00%); $\delta$ 4.98, 4.91, 4.72 and 4.63 (4 x 1H, 4 x s, 2 x $C=CH_2$), 4.13 (4H, q, 2 x $CH_2Me$), 2.70 (2H, s, ring $CH_2$), 2.23 (2H, m, allyl $CH_2$), 2.08 (2H, t, ring $CH_2$), and 1.2 (6H, t. 2 x $CH_2Me$); $\nu_{max}$(film) 3070, 2975, 2931, 1730, 1633, 1182, 1121, 1050, and 795 $cm^{-1}$; m/z(%) 252 ($M^+$,17), 179(25), 178(52), and 105(100).
(31) Colourless oil. (Found: C, 66.85; H, 8.15. $C_{14}H_{20}O_4$ requires C, 66.65; H, 8.00%); $\delta$ 5.60 (1H, m, ring C=CH), 4.99 and 4.89 (2H, 2 x s, $C=CH_2$), 4.14 (4H, q, 2 x $CH_2Me$), 2.87 (2H, s, ring $CH_2$), 2.77 (2H, d, ring $CH_2$), 1.79 (3H, s, Me), and 1.22 (6H, t, 2 x $CH_2Me$); $\nu_{max}$(film) 3075, 2985, 1730, 1640, 1172, 1127, and 782 $cm^{-1}$; m/z(%) 252 ($M^+$,42), 207(18), 179(64), and 105(100).
2,3-Bis(methylene)-9-hydroxydecalin (30) and 2-methylene-3-methyl-9-hydroxy 3-decalin (32). The reaction product (66%) was a colourless oil, b.p. 65-75°C/0.03mmHg, which comprised a 2.5:1 mixture (p.m.r.) of (30) and (31). Characterisation of (30) was achieved by formation of its Diels-Alder adduct with N-phenylmaleimide (below), whilst (32) was isolated by preparative t.l.c. ($SiO_2$, 40-60° petroleum ether-ether) of the mother liquors of this latter reaction.
(30) $\delta$ 5.08, 4.95, 4.76 and 4.68 (4 x 1H, 4 x br s, $CH_2=C$), and 1.71 (15H, m, 6 x $CH_2$, OH, and 2 x CH).
(32) Colourless oil. (Found: C, 80.60; H, 10.30. $C_{12}H_{18}O$ requires C, 80.85; H, 10.20%); $\delta$ 5.57 (1H, br s, CH=CMe), 4.99 and 4.90 (2 x 1H, m, $CH_2=C$), 1.83 (3H, d, Me), and 1.71 (13H, m, 5 x $CH_2$, OH and 2 x CH); $\nu_{max}$(film) 3470, 3070, 2925, 2850, 1630, 1600, 1443, 985, 952, and 890 $cm^{-1}$; m/z(%) 178 ($M^+$,21), 163(44), 145(26), 135(34), 121(76), 107(61), 93(46), 91(82), 79(62) and 77(64).
Diels-Alder Reactions. The reaction conditions are summarised in table 4.
Cycloadduct from 1-Benzoyl-1-methyl-3,4-bis(methylene)cyclopentane (14b). Prepared by reacting a 2.5:1 mixture of (14a) and (14b) (110mg) and N-phenylmaleimide (50mg) in chloroform (1ml) (table 4). The cycloadduct (33a) (100mg, 90%) crystallised from chloroform-ether as colourless rods, m.p. 106-108°C (Found: C, 77.75; H, 6.05; N, 3.65. $C_{25}H_{23}NO_3$ requires C, 77.90; H, 6.00; N, 3.65%); $\delta$ 7.74 (2H, m, ArH), 7.37 (8H, m, ArH), 3.36 (2 x 1H, m, 2 x $CH_2CHCO$), 3.18 and 2.38 (2 x 2H, 2 x br d, cyclopentenyl $CH_2$), 2.55 (2 x 2H, m, 2 x $CH_2CHCO$), and 1.45

(3H, s, Me); $\nu_{max}$(film) 3060, 2970, 2940, 2885, 2845, 1705, 1660, 1590, 1495, 1445, 1435, 1370, 760, 715, and 688 $cm^{-1}$; m/z(%) 385 ($M^+$,26), 370(13), 280(75), 174(23), 105(100), 91(25), and 77(44).

Cycloadduct from 1,1-diacetyl-3,4-bis(methylene)cyclopentane (14c). The product (33b) (67mg, 87%) crystallised from methanol-ether as colourless rods, m.p. 138-140°C (Found: C, 70.30; H, 6.05; N, 3.80. $C_{21}H_{21}NO_4.0.5H_2O$ requires C, 70.00; H, 5.85; N, 3.90%); $\delta$ 7.36 (5H, m, ArH), 3.30 (2 x 1H, m, 2 x $CHCH_2$), 2.89 (2 x 2H, m, 2 x $CH_2C{=}C$), 2.63 and 2.48 (2 x 2H, d and br d, $J_{gem}$ 16.2Hz, 2 x $CH_2CH$), and 2.13 and 2.09 (2 x 3H, 2 x s, Me); $\nu_{max}$ 3060, 2905, 1705, 1690, 1590, 1490, 1385, 750, 705 and 690 $cm^{-1}$; m/z(%) 351 ($M^+$,0.5), 309(24), 308(100), 266(21), 119(12), 117(10), 91(10), 77(7) and 43(62).

Cycloadduct from methyl 2,2-dimethyl-3,4-bis(methylene)cyclopentane-1-carboxylate (14e). Prepared (84%) from a 1.38:1 mixture of (14e) and (15e) and N-phenylmaleimide in benzene (80°C, 0.5h). The product (33c) crystallised from ether-acetonitrile as colourless plates, m.p. 140-142°C (Found: C, 71.15; H, 6.55; N, 4.00. $C_{21}H_{23}NO_4$ requires C, 71.35; H, 6.55; N, 3.95%); $\delta$ 7.35 (5H, m, ArH), 3.76 (1H, m, $OCCHCH_2$), 3.7 (3H, s, MeO), 3.31 (2 x 1H, m, $CHCHCH_2$), 2.78 (3 x 2H, m, 3 x $CH_2$), and 1.18 and 0.88 (2 x 3H, s, 2 x Me); $\nu_{max}$ 3062, 3007, 2950, 2920, 2845, 1730, 1700, 1592, 1495, 1387, 1182, 776, 770, 702 and 690 $cm^{-1}$; m/z(%) 353 ($M^+$,100), 338(78), 306(46), 293(54), 278(48), 277(21), 262(20), 174(25), 131(89) and 91(67).

Cycloadducts from 9,9-spiro[3,4-bis(methylene)cyclopentyl]-4-azafluorene (17a).

(a). With N-phenylmaleimide. The product (34a) (94%) crystallised from ether as colourless rods, m.p. 242-245°C (Found: C, 83.20; H, 5.65; N, 3.40. $C_{29}H_{23}NO_2$ requires C, 83.45; H, 5.55; N, 3.35%); $\delta$ 7.45 (13H, m, ArH), 3.45 (2H, m, CH), 2.96 and 2.60 (4H, m, 2 x $CH_2CH$), and 2.80 (4H, m, 2 x $CH_2C{=}$); $\nu_{max}$ 3050, 3025, 2905, 2890, 2827, 1710, 1443, 1375, 770, 735 and 700 $cm^{-1}$; m/z(%) 417 ($M^+$,100), 229(16), 178(31), 165(30) and 91(17).

(b) With dimethyl acetylenedicarboxylate. The product (35)(90%) crystallised from benzene-ether as colourless rods, m.p. 195-197°C (Found: C, 77.60; H, 5.80. $C_{25}H_{22}O_4$ requires C, 77.70; H, 5.75%); $\delta$ 7.47 (8H, m, ArH), 3.83 (2 x 3H,s,Me) and 3.14 and 2.83 (2 x 4H, s, $CH_2C{=}$); $\nu_{max}$ 3050, 3025, 2940, 2825, 1730, 1715, 1647, 1435, 1425, 765 and 730 $cm^{-1}$; m/z(%) 386 ($M^+$,56), 354(15), 326(5), 295(8), 267(16), 265(15), 178(54) and 176(100).

c. With methyl 3-isatylideneacetate. The product (37) (80%) crystallised from methanol as colourless needles, m.p. 243-244°C (Found: C, 80.60; H, 5.45; N, 3.00. $C_{30}H_{25}NO_3$ requires C, 80.70; H, 5.40; N, 3.15%); $\delta$ 7.36 (12H,m,ArH), 3.55 (3H, s, OMe), 3.04 (1H, d, $CHCO_2Me$), 2.80 (7H, m, 3 x $CH_2$, $HCHCHCO_2Me$) and 2.1 (1H, d, CH of ring methylene); $\nu_{max}$ 3175, 3150, 3130, 3030, 3010, 2940, 2900, 2880, 2830, 1725, 1697, 1615, 1465, 1433, 1440, 765, 755, 735, and 730 $cm^{-1}$; m/z(%) 447 ($M^+$,100), 415(45), 388(13), 387(24), 386(39), 270(24), 244(22), 243(23), 242(43), 229(39), 204(38) and 178(44).

Cycloadduct from 9,9-spiro[3,4-bis(methylene)cyclopentyl]-4-azafluorene (17b). The cycloadduct (34b) (84%) crystallised from methanol-chloroform as colourless rods, m.p. 228-230°C (Found: C. 78.95; H, 5.35; N, 6.60. $C_{28}H_{22}N_2O_2.0.5H_2O$ requires C, 78.65; H, 5.40; N, 6.55%); $\delta$ 8.53 and 7.99 (2 x 1H, 2 x m, ArH), 7.28 (10H, m, ArH), 3.44 (2 x 1H, m, 2 x CHCO), and 2.79 (4 x 2H, m, 4 x $CH_2C{=}$); $\nu_{max}$ 3040, 2900, 2890, 2840, 2830, 1709, 1490, 1400, 1375, 765, 740, and 695 $cm^{-1}$; m/z(%) 418 ($M^+$,100), 270(12), 244(15), 230(12) and 180(23).

Cycloadduct from diethyl 3-benzylidene-4-methylenecyclopentane-1,1-dicarboxylate (19a). Prepared from a 1:1.3 mixture of (19a) and (20). The product (33d) (36%) was obtained as a colourless solid, m.p. 166-168°C (Found: C, 71.25; H, 6.05; N, 2.80. $C_{29}H_{29}NO_6$ requires C, 71.45; H, 6.00; N, 2.85%); $\delta$ 7.24 (6H, m, ArH), 7.02 and 6.33 (2 x 2H, m, ArH), 4.22 and 4.11 (2 x 2H, 2 x q, $CH_2Me$), 3.97 (1H, d, PhCH), 3.49 (1H, t, PhCHCH), 3.39 (1H, m, CHCO), 3.11 [4H, m, 3H, $(EtOCO)_2CCH_2$ and 1H of $CH_2CHCO$], 2.75 [1H, br d, $(C_2H_5OCO)_2CCHH$], 2.58 (1H, m, CHCO), and 1.26 and 1.15 (2 x 3H, 2 x t, 2 x $CH_2Me$); $\nu_{max}$ 2970, 2950, 2910, 2840, 1715, 1698, 1487, 1380, 745 and 700 $cm^{-1}$; m/z(%) 487 ($M^+$,100), 414(63), 413(81), 367(42), 340(29), 193(51), and 167(56).

Cycloadduct from dimethyl 3-carbomethoxymethylidene-4-methylenecyclopentane-1,1-dicarboxylate (19b). Prepared (acetonitrile, 80°C, 1h) from a 1:1.2 mixture of (19b) and (21), and N-phenylmaleimide. The product (33e) (31%) was obtained as a colourless solid from ether-methylene chloride, m.p. 144-146°C (Found: C, 58.85; H, 5.10; N, 2.60. $C_{23}H_{23}NO_8.0.5\ CH_2Cl_2$ requires C, 58.40; H, 5.00; N, 2.90%); $\delta$ 7.31 (5H, m, ArH), 3.76 (1H, m, CHCO), 3.69, 3.67 and 3.59 (3 x 3H, 3 x s, 3 x MeO), 3.63 (1H, m, CH), 3.25 [5H, m, CHCO, 1H of CHCHCON, 3H of $(MeO_2C)_2CCH$], and 2.58 [2H, m, 1H of $(MeO_2C)_2CCHH$ and 1H of $HCHCHCO$]; $\nu_{max}$ 2950, 2920, 1705, 1498, 1390, 1260 and 1200 $cm^{-1}$; m/z(%) 441 ($M^+$,44), 174(24), 115(21), 91(11), 83(100), 59(22), and 43(21).

Cycloadduct from N-acetyl-3,4-bis(methylene)pyrrolidine (25). Prepared (chloroform, 60°C, 10min.) from a 6:1 mixture of (25) and (20) and N-phenylmaleimide. The product (38) (52%) crystallised from ether-chloroform as light yellow rods, m.p. 217-220°C (Found: C, 60.35; H, 5.30; N, 6.95. $C_{18}H_{18}N_2O_3$. 0.5 $CHCl_3$ requires C, 60.05; H, 5.05; N, 7.55%); $\delta$ 7.35 (5H, m, ArH), 4.2 (2 x 2H, s, $NCH_2$), 3.39 (2H, m, CHCO), 2.59 (4H, m, 2 x $CH_2CHCO$), and 2.06 (3H, s, MeCO); $\nu_{max}$ 3050, 2955, 2920, 2845, 1705, 1635, 1495, 1380, 755 and 690 $cm^{-1}$; m/z(%) 310 ($M^+$,7), 277(25), 173(99), 123(55), 109(45), 108(35), 105(29), 94(29), 93(28), 91(25), 80(34), 78(36), and 77(35).

Cycloadduct from 2,3-bis(methylene)-9-hydroxydecalin (30). Prepared (chloroform, 60°C, 45 min.) from a 2.5:1 mixture of (30) and (32), and N-phenylmaleimide. The product (39) (44%) crystallised from ether-chloroform as colourless rods, m.p. 151.5-152.5°C (Found: C, 74.60; H, 7.10; N, 3.85. $C_{22}H_{25}NO_3$ requires C, 75.20; H, 7.15; N, 4.00%); $\delta$ 7.33 (5H, m, ArH), 3.25 (2 x 1H, m, 2 x CHCO), and 1.86 (19H, m, 8 x $CH_2$, OH and 2 x CH); $\nu_{max}$ 3045, 2910, 2840, 1690, 1493, 1375, 745 and 690 $cm^{-1}$; m/z(%) 351 ($M^+$,4), 334(24), 333(100), 304(37), 254(39), 129(27), 107(54), 98(45) and 91(86).

Palladium Catalysed Coupling of Bromobenzene and $\beta$-Pinene. A mixture of bromobenzene (1.6g, 1.0mmol), palladium acetate (110mg, 0.05mmol), triphenyl phosphine (260mg, 0.1mmol), potassium carbonate (3.5g, 2.5mmol), and $\beta$-pinene (1.36g, 1.0mmol) in acetonitrile (20ml) was boiled under reflux under a nitrogen atmosphere for 4 dy. The inorganic salts were then removed by filtration, the filtrate concentrated and passed through a short column ($Al_2O_3$) eluting with 3:1 v/v 40-60°C petroleum ether-ether. Evaporation of the eluate afforded the product (2.02g, 95%) as a ca. 1:1 mixture (p.m.r.) of (48b) and (49). Distillation gave a colourless oil (1.87g, 88%), b.p. 134-140°C/7.0mmHg, in which the ratio of (48b) and (49) had altered to ca. 3:1 in favour of (49) [Found (mixed isomers): C, 90.50; H, 9.45. $C_{16}H_{20}$ requires C, 90.50; H, 9.50); m/z(%) (mixed isomers) 212 ($M^+$,28), 197(13), 169(23), 168(20), 155(14), 154(70), 153(22), 121(26) and 91(100).

(48b) $\delta$ 7.37 (5H, m, ArH), 6.3 and 6.0 (2 x 1H, 2 x m, CH=C, both isomers), 2.49 (3H, m, CHC= and $CH_2C$=), 1.96 (5H, ring $CH_2$ and CH), and 1.32, 1.27, 1.17 and 0.9 (4 x s, Me, both isomers).

(49) $\delta$ 7.37 (5H, m, ArH), 5.22 (1H, m, CH=), 3.26 (2H, m, $PhCH_2$), 2.29 (3H, m, CHCH= and $CH_2C$=), 1.96 (3H, CH and $CH_2$), and 1.19 and 0.74 (2 x 3H, 2 x s, Me).

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