Studies in the Synthesis of Polycyclopentanoids: Synthesis, Oxa-di-π-methane Rearrangement of Annulated Bicyclo[2.2.2]octenones and Cyclopropane Ring Cleavage of Tetracyclo[6.3.0.0^{2,4}.0^{3,7}]undecenones

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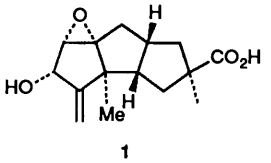
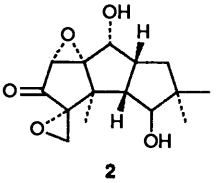
A short, new and general approach for the synthesis of linear polyquinanes having the *cis*:*anti*:*cis* tricyclopentanoidal framework is delineated. The key element of this approach is the photochemical 1,2-acyl shift or oxa-di-π-methane rearrangement of annulated bicyclo[2.2.2]octenones, having β,γ-unsaturated carbonyl chromophoric systems. An efficient method for the synthesis of a variety of annulated bicyclo[2.2.2]octenones *via* inverse demand $\pi^{4s} + \pi^{2s}$ cycloaddition of cyclohexa-2,4-dienones (**9–12**) with olefins (**18–26**) is reported. The structure of the adducts has been established through the study of their high-field ^{1}H NMR and ^{13}C NMR spectra and decoupling experiments. Synthesis of tricyclo[5.2.2.0^{2,6}]undecadienones (**51–57**) from readily available adduct **43** has been achieved. Oxa-di-π-methane rearrangement of various chromophoric systems to polyquinanes (**60–68**) is described. The adduct **32** did not undergo oxa-di-π-methane rearrangement upon sensitized irradiation, while adduct **40** rearranged inefficiently to compound **64**. Studies on the cleavage of the cyclopropane ring of the tetracyclic ketones (**60**, **66**, **67** and **73**) with formic acid and acetyl methanesulfonate is also reported.

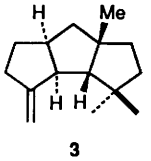
There has been world-wide interest in the chemistry of polycyclopentanoids recently.[1–5] This is partly due to the occurrence and isolation of many natural products having a linearly fused (*cis*:*anti*:*cis*) cyclopentane ring (*e.g.* compounds **1–4**) in their molecular framework and also because many of these products exhibit a wide spectrum of biological activity. For example, hirsutic acid **1** has antibiotic properties,[6] while coriolin **2** shows antibacterial and antitumour activities.[7] The capnellene **3** has been suggested to act as a chemical defence agent[8] to inhibit the growth of micro-organisms. The intricate carbocyclic network coupled with the presence of an array of functional groups in the natural products has further enhanced interest in the polycyclopentanoids and hence they have emerged as target molecules for biological testing as well as for demonstrating new strategies in carbocyclic ring construction.[1–5]



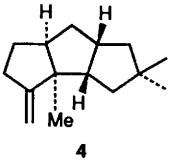
1
Hirsutic acid



2
Coriolin

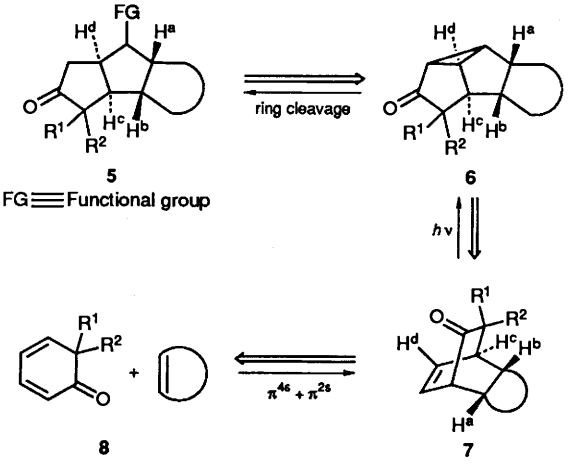


3
$\Delta^{9(12)}$-Capnellene



4
Hirsutene

Though various approaches have been described for the synthesis of triquinanes, the majority of the methodologies used are target oriented, suffer from lack of adaptability, and generate tricyclopentanoidal frameworks after multi-step sequences. The *meta*-photocycloaddition,[3] and 1-3-diyl trapping[4] routes do overcome some of the problems; however, they often lead to regio-and stereo-isomeric mixtures. The photothermal metathetic sequence,[5] though efficient, furnishes *cis*:*syn*:*cis* triquinane ring systems. We therefore initiated an exploratory programme to develop a short and efficient route to linear *cis*:*anti*:*cis*, polyquinane systems and wish to record a complete account[9] of the synthesis and photochemical oxa-di-π-methane rearrangement of various annulated bicyclo[2.2.2]octenones. We also report our studies on electrophile-assisted cleavage of the cyclopropane ring of some of the photoproducts.



5 FG≡Functional group

6

8

7

Scheme 1

Strategy

It was envisaged that functionalized tricyclopentanoidal systems of type **5** could be derived from the tetracyclic precursor **6** through a regioselective cleavage of the carbonyl-conjugated cyclopropane ring. The tetracyclic framework **6** was thought to be amenable from tricyclic system **7** *via* a photochemical reorganization known as an oxa-di-π-methane rearrangement or 1,2-acyl shift.[10] The chromophoric system **7** in turn was thought to be obtained *via* an inverse demand $\pi^{4s} + \pi^{2s}$ cycloaddition between a cyclohexa-2,4-dienone **8** and a suitable dienophile (Scheme 1). Some of the salient features of this

strategy are as follows. The required triquinane framework would be generated in a single stereospecific step with desired *cis*:*anti*:*cis* geometry. Moreover, incorporation of a stereospecific and versatile $\pi^{4s} + \pi^{2s}$ cycloaddition to assemble the chromophoric system provides structural and functional flexibility to the strategy.

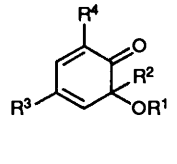
However, it may be noted that a cyclopropane ring is generated during the photorearrangement, which is not required in the synthesis of natural polycyclopentanoids. We contemplated that the carbonyl-conjugated cyclopropane ring can be used as a handle to functionalize the central ring through regioselective cleavage of the peripheral cyclopropane σ-bond since several reagents are known[11] to effect such cleavage.

Results and Discussion

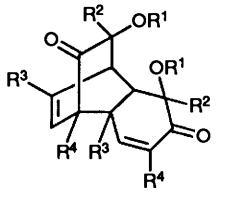
(I) *Synthesis and Structure of Chromophoric System:* $\pi^{4s} + \pi^{2s}$ *Cycloaddition of Cyclohexa*-2,4-*dienones.*—Though a large number of 'normal' Diels–Alder reactions are known,[12–14] the inverse-demand cycloaddition of electron-deficient cyclohexa-2,4-dienones, controlled by $LUMO_{diene}$ $HOMO_{dienophile}$ interactions,[15,16] are not so well known in the literature. While there were some examples of the cycloaddition of cyclohexa-2,4-dienones with highly reactive dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate,[17,18] their cycloaddition with olefins and dienes was relatively unexplored prior to our own preliminary report.[9] It appeared that the relative lack of cycloaddition of cyclohexa-2,4-dienone may be due to its inaccessibility and its propensity towards dimerization and rearrangement.[19] Cyclohexa-2,4-dienones have been known in the literature for a long time; however, there are only a few methods for their preparation. Oxidation of phenols with lead tetraacetate, also known as Wessely oxidation,[20] is a method occasionally employed for the preparation of dienones of type **9**. However, it often proceeds in low yield and furnishes a mixture of products. In our search for an alternative, we explored the possibility of employing the readily available[21] *o*-quinol dimers of type **13** as a source of cyclohexa-2,4-dienones through retro-Diels–Alder reaction of a suitable derivative.

Towards this end, the dimeric dienone **13** was prepared by oxidation of 2,6-dimethylphenol and acetylated with Fritz–Schenk reagent[22] ($HClO_4$–Ac_2O–EtOAc) to give acetoxy dimer **14** in good yield. It should be noted that routine acetylating agents failed to acylate the tertiary hydroxy groups in **13**. Pyrolysis of the diacetate **14** at 140 °C *in vacuo* cleanly gave the monomer **9**, which was stable below 0 °C but which slowly dimerized at room temperature (~30 °C). Therefore, it was immediately treated with freshly cracked cyclopentadiene in refluxing benzene, which gave the cycloadduct **27** as the sole product in 87% yield. Hydrolysis of the keto acetate **27** with KOH in methanol furnished the keto alcohol **28**. Following the above procedure, the Diels–Alder reaction of spiro[4.2]-heptadiene[23] **19**, dimethylfulvene[24,25] **21** and indene **22** with ketone **9** gave the keto acetates **29**, **31** and **33**, respectively, which were hydrolysed with base to furnish the alcohols **30**, **32** and **34**.

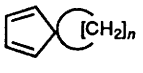
During the cycloaddition, the dienone **9** behaved as a diene (π^4-component) and the olefins **18**–**22** as dienophiles (π^2-



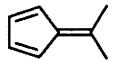
9 R^1 = Ac, R^2 = R^4 = Me, R^3 = H
10 R^1 = H, R^2 = R^3 = R^4 = Me
11 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl
12 R^1 = R^4 = H, R^2 = R^3 = Me



13 R^1 = R^3 = H, R^2 = R^4 = Me
14 R^1 = Ac, R^2 = R^4 = Me, R^3 = H
15 R^1 = H, R^2 = R^3 = R^4 = Me
16 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl
17 R^1 = R^4 = H, R^2 = R^3 = Me



18 *n* = 0
19 *n* = 2
20 *n* = 4



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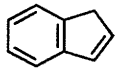

22

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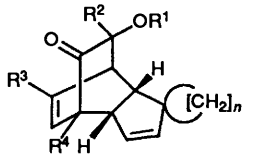
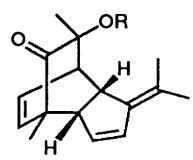
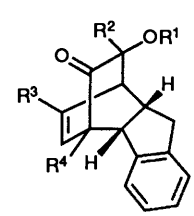


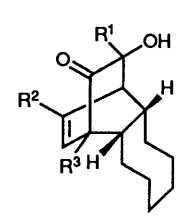
27 R^1 = Ac, R^2 = R^4 = Me, R^3 = H, *n* = 0
28 R^1 = R^3 = H, R^2 = R^4 = Me, *n* = 0
29 R^1 = Ac, R^2 = R^4 = Me, R^3 = H, *n* = 2
30 R^1 = R^3 = H, R^2 = R^4 = Me, *n* = 2
39 R^1 = H, R^2 = R^3 = R^4 = Me, *n* = 2
43 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl, *n* = 0
44 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl, *n* = 2
45 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl, *n* = 4
48 R^1 = R^3 = H, R^2 = R^4 = Me, *n* = 4
50 R^1 = R^4 = H, R^2 = R^3 = Me, *n* = 0



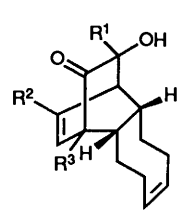
31 R = Ac
32 R = H



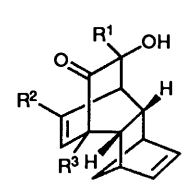
33 R^1 = Ac, R^2 = R^4 = Me, R^3 = H
34 R^1 = R^3 = H, R^2 = R^4 = Me
38 R^1 = H, R^2 = R^3 = R^4 = Me
42 R^1 = R^3 = R^4 = H, R^2 = CH_2Cl



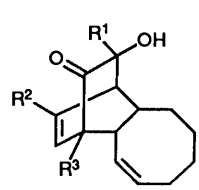
35 R^1 = R^2 = R^3 = Me
40 R^1 = CH_2Cl, R^2 = R^3 = H
46 R^1 = R^3 = Me, R^2 = H



36 R^1 = R^2 = R^3 = Me
41 R^1 = CH_2Cl, R^2 = R^3 = H
47 R^1 = R^3 = Me, R^2 = H



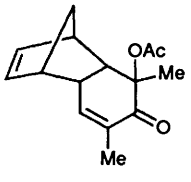
37 R^1 = R^2 = R^3 = Me



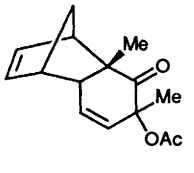
49 R^1 = R^3 = Me, R^2 = H

component). It is interesting to note that no products of type-I or -II cycloaddition were observed. Furthermore, though a single regio- and stereo-specific addition was observed, in principle it could give rise to four different isomeric *endo* cycloadducts (III–VI) as a consequence of four modes of approach between the cyclohexadienone and the dienophile in the transition state. While the gross structure of product **27** was easily discerned from its spectral data, the distinction among the regio- and stereo-isomers III–VI was made as follows. A comparison of the ^{1}H NMR spectra of compounds **27** and **28** revealed that the signal at δ 3.90 due to the bridghead proton H^c in acetate **27** moved upfield to δ 2.95 in the alcohol **28** because the deshielding by the carbonyl function of the acetate group is withdrawn, and the signal at δ 2.78 assigned to H^d in **27** shifted downfield and appeared at δ 3.20 in **28** because of the removal of shielding of this proton by the carbonyl group. The assignments[26] of various signals were confirmed by decoupling experiments.

The signal at δ 2.95 in the ^{1}H NMR spectrum of the alcohol **28** became a broad singlet upon irradiation of the signal at δ 6.26 (assigned to H^b), while irradiation of the signal at δ 3.2 turned the signal at δ 2.85 (H^e) into a broad singlet and removed the finer coupling from the peak at δ 2.95 (H^c), in addition to the changes in the signal at δ 2.55 (assigned to H^i) respectively. The spectral changes observed in compounds **27** and **28**, and the decoupling experiments, clearly established the relationships between various protons and confirmed the formulation of the alcohol **28** (and hence of acetate **27**) as structure III. All other adducts were found to have similar spectral features and hence were assigned the structures **31**–**34**.



(I)



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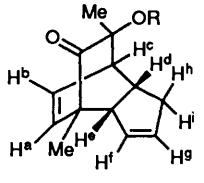
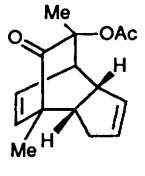
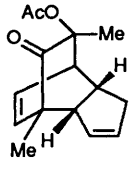


(III)

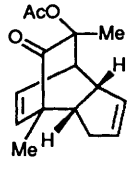
27 R = Ac
28 R = H



(IV)



(V)



(VI)

After having established the structure of the cycloadducts, we explored the possibility of generalizing the cycloaddition route for the synthesis of other chromophoric systems. However, the reaction of acetoxy dienone **9** with dienophiles such as cyclooctene, cyclooctadiene and trinorbornadiene failed under a variety of experimental conditions. Therefore, we thought to explore the cycloaddition between hydroxycyclohexadienones of type **15** and the less reactive dienophiles *via* direct trapping of the hydroxycyclohexa-2,4-dienone **10** generated *in situ* by retro-Diels–Alder reaction of tricycle **15**, since hydroxy dienones of type **10** are more reactive than the corresponding acetoxy derivatives. This contention was an extrapolation of the fact that the hydroxycyclohexadienone undergoes spontaneous cycloaddition with itself.

Indeed, when a solution of cyclooctene **23** and the readily available[27] dimer **15** was heated at 140 °C for 3 h, a smooth cycloaddition occurred to furnish the Diels–Alder adduct **35** in good yield (72%) after chromatography of the crude product. By following this simple modified procedure, annulated bicyclo-[2.2.2]octenones **36**–**39** were synthesized by reaction of dimer **15** with (*Z*,*Z*)-cycloocta-1,5-diene **24**, tricyclo[2.2.1]hepta-2,5-diene **25**, indene **22** and spiro[4.2]heptadiene **19**, respectively. The ease with which tricyclo[2.2.1]hepta-2,5-diene entered into cycloaddition with dimer **15** to furnish the adduct **37** in good yield was remarkable. The generality of this sequence was demonstrated by the synthesis of a variety of annulated bicyclo[2.2.2]octenones. Reaction of the chloro hydroxy dimer **16** with substrates **19** and **21**–**24** gave the corresponding cycloadducts.[28] It is interesting to note that adducts **43** and **50** could be simply obtained by heating of dimers **16** and **17**, respectively, with dicyclopentadiene. Similarly, the adducts **46**–**49** were readily prepared[29] from dihydroxy dimer **13** and the olefins **20**, **23**, **24** and **26**. It may be mentioned that, though exceptionally reactive dienophiles such as dimethyl acetylene-dicarboxylate and maleic anhydride were known to trap cyclohexadienones in a few isolated instances[17,30] trapping with relatively less reactive dienophiles had not previously been recorded in the literature.

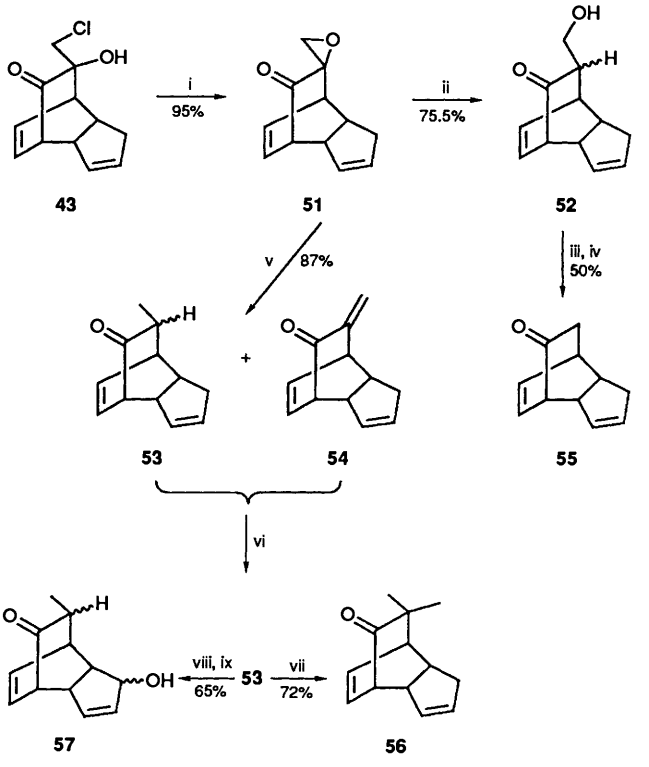
This method of cycloaddition also gave single *endo*-adduct in all the cases, whose structures were determined through their high-field ^{1}H and ^{13}C NMR spectra, followed by comparison with the spectral characteristics of the keto alcohols **28**, **30**, **32** and **34**.

Synthesis of Other Chromophoric Systems: Transformations of Chloro Alcohol **43**.—At this stage efforts were directed towards the synthesis of parent tricycloundecadienone **55** and its congeners (Scheme 2) from a common, easily accessible starting material. The cycloadduct **43** appeared suitable for this objective especially because of the disposition of carbonyl, hydroxy and halogen groups at three contiguous centres which may provide a handle for further synthetic manipulation. It was envisaged that the parent chromophoric system **55** could be obtained by oxidation of the keto alcohol **52** followed by subsequent decarboxylation of the resulting β-keto acid. The keto alcohol **52** was thought to be obtainable through zinc reduction of the epoxy ketone **51**, which should be readily derived from chloro hydroxy adduct **43**. Thus, the chlorohydrin **43** was converted into epoxide **51** by treatment with aqueous KOH in chloroform containing cetyltrimethylammonium bromide (CTAB) as a phase-transfer catalyst. Reduction of epoxide **51** with activated zinc[31] in dry methanol containing ammonium chloride, at 60 °C, gave, however, a mixture of products **52** and **53**. It was found that the required alcohol **52** could be obtained selectively by reaction of epoxide **51** with zinc in aqueous methanol, while reduction of the keto epoxide in refluxing 1,4-dioxane gave deoxygenated products **53** and **54** as major products.† The mixture of enones **53** and **54** was converted solely into dienone **53** upon further reduction with zinc (Scheme 2).

The keto alcohol **52** was oxidized with Jones' reagent[33] and the resultung β-keto acid was decarboxylated with aqueous barium hydroxide[34,35] to give the desired dienone **55** (50%). Further, the ketone **53** was alkylated[36] with methyl iodide in the presence of sodium hydride in tetrahydrofuran (THF), to give the dimethyl-substituted ketone **56** (72%). In order to functionalize the cyclopentene ring of compound **53**, it was treated with *N*-bromosuccinimide (NBS)[37] and the resulting bromo derivative was immediately hydrolysed with sodium hydrogen carbonate‡ in aqueous acetone to give the hydroxy

† The origin of the *syn*:*anti* mixture, stereochemistry and mechanism of the zinc reduction has been briefly discussed.[32]

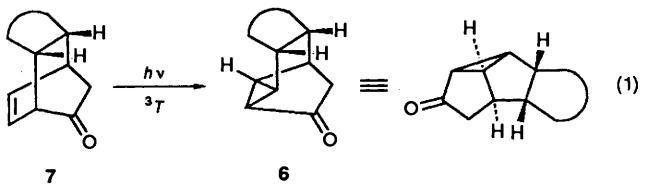
‡ The hydrolysis of the allylic bromide with aq. $NaHCO_3$ was developed in our laboratory.[38]



Scheme 2 *Reagents and conditions:* i, CTAB, $CHCl_3$, aq. KOH, room temp.; ii, Zn, aq. MeOH, NH_4Cl, room temp.; iii, Jones' reagent; iv, $Ba(OH)_2$, water, heat; v, Zn, 1,4-dioxane, heat; vi, Zn, MeOH, NH_4Cl, heat; vii, NaH, THF, MeI; viii, NBS, CCl_4, $(BzO)_2$, *hν*; ix, aq. $NaHCO_3$, acetone

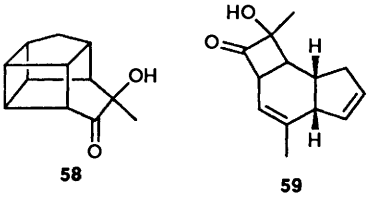
ketone **57**. The overall sequence of reactions employed for synthesis of compounds **51**–**57** from the chlorohydrin **43** is outlined in Scheme 2.

II(a). *Photochemical Oxa-di-π-methane Rearrangement of Annulated Bicyclo*[2.2.2]*octenones: Synthesis of Polyquinanes.*— β,γ-Unsaturated ketones undergo two major types of photoreaction upon electronic excitation.[10] The sensitized irradiation (T_1, π–π*) of β,γ-unsaturated ketones constrained in a rigid framework causes a stereospecific[39] 1,2-acyl shift with the concurrent formation of a cyclopropyl ketone, known as an oxa-di-π-methane rearrangement. Direct irradiation (S_1, π–π*) of β,γ-unsaturated ketones leads to a 1,3-acyl shift to give cyclobutanone derivatives.[10] We realized that oxa-di-π-methane (ODPM) rearrangement of tricyclic system **7** with a β,γ-unsaturated carbonyl chromophore would provide a direct entry into a variety of polyquinane frameworks (*e.g.*, **6**), depending upon the nature of the ring annulated onto the bicyclic framework. Further, since the stereochemistry at the ring junction in the rearranged product would be governed by the orientation of the annulated ring, the rearrangement would produce a *cis*:*anti*:*cis* triquinane framework if the annulated ring is *endo* [equation (1)].

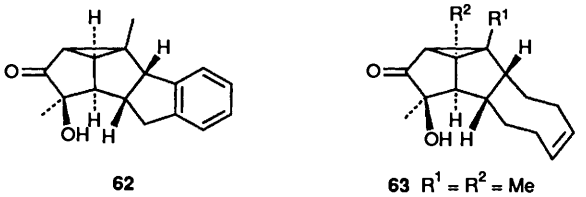


Though photochemical rearrangement of β,γ-unsaturated ketones has been studied in detail, earlier investigations were mainly focussed on its mechanistic aspects and the singlet–triplet dichotomy.[10,40,41] The synthetic potential of the oxa-di-π-methane rearrangement, however, was not realized until recently.[9,42] Although Demuth and co-workers have recently employed ODPM rearrangement towards the synthesis of natural products, most of their studies were limited to simple bicyclo[2.2.2]octenones[42] leading to diquinane systems. However, some examples of oxa-di-π-methane rearrangement leading to angular triquinanes appeared[43] during our investigation. Though the scope of oxa-di-π-methane rearrangement appears to be wide, it is quite sensitive to the nature of both functional groups and substituents.[42] Considering the structural and functional complexity of the above chromophoric systems, many photochemical reactions such as intramolecular cycloaddition,[44] photoreduction,[45] epimerization,[46] 1,3-shift, and oxa-di-π-methane rearrangement can be expected. In view of the above, the behaviour of tricycloundecadienones and other tricycles **28**, **30**, **32**, **34**, **36**, **40**, **50**, **52**, **53** and **57** towards sensitized irradiation was explored.

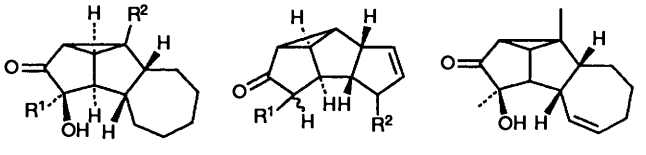
Towards this end, an acetone solution of the tricycloundecadienone **28** was irradiated, with a mercury vapour lamp (250 W, Bajaj), for 3.5 h under nitrogen. Removal of solvent followed by column chromatography of the crude product on silica gave a crystalline photoproduct **60** in good yield (55%) along with some unchanged starting material. It was surprising that no products such as the cage molecule **58** or the cyclobutanone **59** were obtained as a result of intramolecular $\pi^{2s} + \pi^{2s}$ cycloaddition and 1,3-acyl shift, respectively. The spectral and analytical data of the photoproduct was consistent with the structure **60** and clearly ruled out alternative possibilities (**58**/**59**).



60 R^1 = Me, R^2 = H, *n* = 0
61 R^1 = Me, R^2 = H, *n* = 2
65 R^1 = H, R^2 = Me, *n* = 0
71 R^1 = Me, R^2 = H, *n* = 4



63 R^1 = R^2 = Me
70 R^1 = Me, R^2 = H



64 R^1 = CH_2Cl, R^2 = H
69 R^1 = R^2 = Me

66 R^1 = CH_2OH, R^2 = H
67 R^1 = Me, R^2 = H
68 R^1 = Me, R^2 = OH
73 R^1 = CH_2OAc, R^2 = H

72

After having observed ODPM rearrangement of the compound **28**, the annulated bicyclooctenones **30**, **32**, **34**, **36**, **40**, **50**, **52**, **53** and **57** were subjected to sensitized irradiation in acetone. All the adducts except **32** underwent the oxa-di-π-methane rearrangement to give the corresponding polyquinanes **61**–**68**.

It should be noted that irradiation of the α-methyltricycloundecadienone **53** in acetone solution for 4 h gave the rearranged product **67** in only trace amounts. However, its irradiation in dry acetone containing benzophenone as sensitizer[41] gave the corresponding polyquinane in 38% yield. This difference is apparently a reflection of the E_T-value of the ketone which probably matches that of benzophenone.[10]

The structure of the polyquinanes **61–68** was derived from spectral and analytical characteristics and by comparison with the spectral features of compound **60**. In order to attempt generalization of this oxa-di-π-methane rearrangement, some more chromophoric systems (substrates **46–49**) were subjected to sensitized irradiation and were transformed into polyquinanes **69–72**.[29] It was interesting, however, to note that the dimethylfulvene adduct **32** did not undergo the desired oxa-di-π-methane rearrangement under a variety of experimental conditions. Furthermore, while the adduct **40** having a chloromethyl group underwent oxa-di-π-methane rearrangement inefficiently to give the corresponding polyquinane **64** (20% yield), its congeners **41–44** were inert to sensitized irradiation.

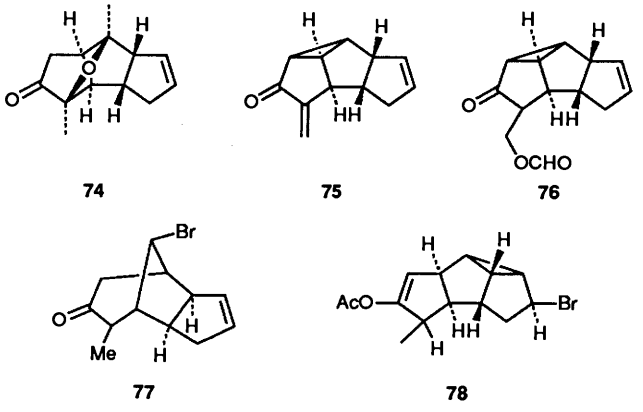
Though the unreactivity of adduct **32** towards ODPM rearrangement upon sensitized irradiation could be rationalized as being due to a quenching effect[10] of the diene moiety present in the annulated ring, it is difficult to explain the inefficiency or inertness of substrates **40** and **41–46**, respectively. This is in accord with the literature wherein the efficiency of ODPM was found to be dependent on the substitution pattern.[47–49] Several reasons have been suggested[47,48] to explain this behaviour but it appears that photochemical reactivity *versus* inertness is influenced by very subtle differences in the substitution pattern.

II(b). *Cyclopropane Ring Cleavage of Tetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undecenones*.—In order to extend the scope of the cycloaddition–oxa-di-π-methane strategy towards the synthesis of natural tricyclopentanoids it was desirable to develop methods for peripheral cleavage of the cyclopropane ring of the tetracyclic products resulting through oxa-di-π-methane rearrangements. We therefore briefly investigated cyclopropane ring cleavage of the tetracyclic polyquinanes **60**, **66**, **67** and **73**.

There are two principal modes for the opening of cyclopropyl ketones: (a) electrophile-mediated 1,4-addition and (b) reductive opening, and both modes have been thoroughly studied.[11,50] The stereoelectronic requirements of the process have been found to control the rupture of cyclopropane bonds.[51] However, the nature of the molecular framework, functional groups present on the cyclopropane ring, and the nature of the reagents have a profound effect on the mode of opening.[11,52] The majority of these studies, however, deal with bicyclic systems. We first attempted electrophile-assisted cleavage of the ketones **60** and **66** with formic acid[53] and ketone **67** with acetyl methanesulfonate,[54] since both reagents are known to affect cleavage of the peripheral cyclopropane bond with simultaneous introduction of the functional group.

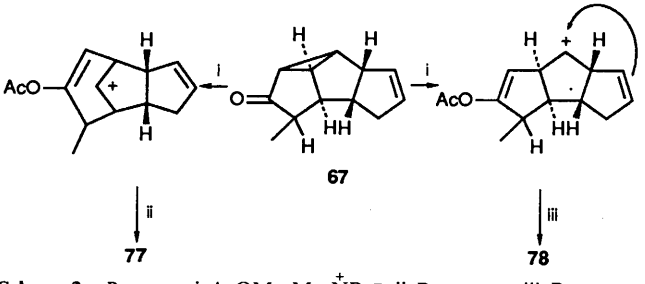
Treatment of compound **60** with formic acid furnished the product **74** wherein peripheral cleavage was selectively observed. However, the intramolecular attack of the tertiary hydroxy group during the cleavage led to the formation of the keto ether in 46% yield. Treatment of the hydroxy ketone **66** with formic acid at 80 °C for 30 min, however, yielded two compounds, the enone **75** and the formate ester **76** in a 5:4 ratio without cleavage of cyclopropane bonds. The structure of compounds **74**, **75** and **76** was established with the help of spectral and analytical data.

In order to avoid the undesired elimination and ester formation, we prepared the keto acetate **73** by acetylation of the corresponding alcohol **66** with acetic anhydride in pyridine and treated it with acetyl methanesulfonate.[54] However, the reaction gave a mixture of products. After these results, the α-methyl ketone **67** was subjected to cleavage with acetyl methanesulfonate in the presence of tetrabutylammonium bromide.[54] Careful chromatography of the product mixture first gave the bromo compound **77** (m.p. 122 °C) followed by another compound (**78**) (m.p. 142 °C). The structure of the bromo ketone **77** was deduced from its spectral data and was confirmed by X-ray analysis.*



The more polar compound **78** was only briefly investigated and its structure was tentatively assigned on the basis of limited data. The absence of olefinic protons of the cyclopentene ring in the NMR spectrum clearly indicated its involvement during the cleavage. We, therefore, proposed the structure **78**, on the basis of mechanistic considerations and spectral data.

The mechanism of formation of products **77** and **78** is depicted in Scheme 3. Compound **77** is obtained *via* cleavage of the internal cyclopropane bond, followed by capture of the resultant carbonium ion by bromide. We believe that compound **78** is formed *via* desired peripheral cleavage, followed by attack of the π-bond of the third ring.



Scheme 3 *Reagents:* i, AcOMs, $Me_4\overset{+}{N}Br^-$; ii, Br^-, water; iii, Br^-

It is difficult to rationalize the results obtained above, especially the formation of compound **77** as a major product; a detailed investigation is probably required. These results do, however, suggest that regioselective peripheral cleavage of a cyclopropane ring may be achieved. The mode of cleavage, however, is controlled by subtle structural features and it is further complicated by the presence of other functional groups.

Conclusions.—To summarize, a new general protocol for the synthesis of various annulated bicyclo[2.2.2]octenones, having a β,γ-unsaturated carbonyl chromophore, through inverse-demand $\pi^{4s} + \pi^{2s}$ cycloaddition has been developed. Photo-

* The results of X-ray analysis will be published in due course. We are thankful to Dr. K. Venkatsubrayamanyam, CSMCRI, Bhavnagar, for the X-ray analysis.

chemical oxa-di-π-methane rearrangement of the chromophoric systems thus synthesized was explored and its application towards general efficient synthesis of the *cis*:*anti*:*cis*-triquinane framework has been successfully demonstrated. Peripheral cleavage of the cyclopropane ring of the oxa-di-π-products has been partially achieved. We are continuing our efforts towards the synthesis of natural tricyclopentanoids.

Experimental

General Remarks.—IR spectra were recorded on a Shimadzu IR-408 spectrometer (solids as KBr, liquids as thin films). UV spectra were recorded on a Shimadzu UV-240 spectrometer. ^{1}H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32, or at 270 MHz on a Bruker WH 270, or at 300 MHz on a Varian XL-300 instrument. *J*-Values are given in Hz. ^{13}C NMR spectra were recorded at 25 MHz on a JEOL FX 100, or at 22.5 MHz on a JEOL FX 90Q, or at 75 MHz on a Varian XL-300 instrument. All the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. M.p.s were measured on a Gallenkamp micromelting point apparatus MF-350 and are uncorrected; elemental analyses were performed on a Collman instrument. All organic extracts were dried over anhydrous Na_2SO_4. Chromatographic separations were done on silica gel and the spots were visualized with iodine vapour.

9-*Acetoxy*-7,9-*dimethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **27**.—A solution of freshly prepared acetoxy dienone[9] **9** (3.5 g, 20 mmol) and cyclopentadiene **18** (5 g, 8 mmol, excess) in dry benzene (50 cm^3) was refluxed for 6 h under nitrogen. Removal of solvent under reduced pressure and chromatography of the residue over silica gel furnished the *tricyclic keto acetate* **27** (4.2 g, 87%), m.p. 105 °C; ν_{max}/cm^{-1} 3050, 2900, 1750, 1735 and 1585; λ_{max}(MeOH)/nm 303; δ_H(270 MHz) 6.25 (1 H, superimposed dd, *J* 8, 10-H), 5.75 (2 H, m, 4-, and 11-H), 5.55 (1 H, dd, *J* 6.5 and 4-, 5-H), 3.90 (1 H, d with structure, *J* 10, 1-H), 2.90 (1 H, d, *J* 10, 6-H), 2.78 (1 H, m, 2-H), 2.55 (1 H, ddd, *J* 17.5 and 8.5, 3-H^{exo}), 2.05 (3 H, s, Ac) 2.0 (1 H, md, *J* 17.5, 3-H^{endo}), 1.53 (3 H, s, Me) and 1.38 (3 H, s, Me) (Found: C, 71.8; H, 7.1. $C_{15}H_{18}O_3$ requires C, 71.40; H, 7.10%).

9-*Hydroxy*-7,9-*dimethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **28**.—A solution of the keto acetate **27** (3.0 g, 12 mmol) in methanol (100 cm^3) was treated with aq. NaOH (20 cm^3; 10%). After the reaction mixture had been stirred for 3 h at room temp. (~32 °C), it was acidified with conc. hydrochloric acid and methanol was removed under reduced pressure. The residue was extracted with diethyl ether (3 × 50 cm^3), washed with brine (15 cm^3), and dried. Removal of solvent, followed by chromatography, yielded the *alcohol* **28** (2.2 g, 90%), m.p. 85 °C; ν_{max}/cm^{-1} 3450, 3050, 2950, 2900, 1710, 1615 and 1455; λ_{max}(MeOH)/nm 303; δ_H(270 MHz) 6.25 (1 H, dd, *J* 8, 10-H), 5.72 (2 H, m, 4- and 11-H), 5.53 (1 H, dd, *J* 6 and 4, 5-H), 3.2 (1 H, m, 2-H), 2.95 (1 H, d with structure, *J* 10, 1-H), 2.85 (1 H, d with structure, *J* 10, 6-H), 2.55 (1 H, qd, *J* 17.5 and 8.5, 3-H^{exo}), 2.38 (1 H, s, OH), 2.00 (1 H, md, *J* 17.5, 3-H^{endo}) and 1.25 (6 H, s, 2 × Me); δ_C(75 MHz) 215.44 (C=O), 134.32, 133.28, 133.20, 128.39, 72.87 (C–O), 56.11, 51.91, 48.38, 38.74, 34.76, 26.24 and 15.52; *m*/*z* 204 (M$^+$) and 186 (M − H_2O) (Found: C, 76.65; H, 7.8. $C_{13}H_{16}O_2$ requires C, 76.47; H, 7.48%).

The adducts **29**–**34** were prepared following the above procedure and their spectral and analytical data have been reported.[9]

12-*Hydroxy*-10,12,13-*trimethyltricyclo*[8.2.2.0^{2,9}]*tetradec*-13-*en*-11-*one* **35**.—The diol dimer **15** (0.5 g, 1.64 mmol) and cyclooctene **23** (2 cm^3, 1.7 g, 15.45 mmol) in *o*-phenylene dichloride (12 cm^3) were heated at 140 °C for 3 h. Removal of solvent and excess of cyclooctene, followed by chromatography of the residue, afforded the *adduct* **35** (0.62 g, 72%), m.p. 164 °C; ν_{max}/cm^{-1} 3550, 2950, 2800, 1715 and 1450; λ_{max}(MeOH)/nm 216 and 308; δ_H(300 MHz) 5.35 (1 H, s, =CH), 2.55 (1 H, dd, *J* 9, CH), 2.4 (1 H, br s, CH), 2.35 (1 H, br s, OH), 1.9 (3 H, s, 13-Me), 1.7–1.4 (8 H, m, 4 × CH_2), 1.3–1.2 (5 H, m, 2 × CH_2 and CH), 1.2 (3 H, s, Me) and 1.18 (3 H, s, Me); δ_C(25 MHz) 217.07 (C=O), 143.42 and 124.12 (olefinic carbons), 73.41, 59.06, 52.41, 46.48, 38.35, 31.17, 30.88, 26.28, 25.76, 24.29, 23.35, 22.82 and 16.64 (for methyls, methylenes and methines); *m*/*z* 263 (M$^+$ + H) and 245 (M$^+$ + H − H_2O) (Found: C, 77.5; H, 9.65. $C_{17}H_{26}O_2$ requires C, 77.86; H, 9.90%).

12-*Hydroxy*-10,12,13-*trimethyltricyclo*[8.2.2.0^{2,9}]*tetradeca*-5,13-*dien*-11-*one* **36**.—Following the above procedure, the diol dimer **15** (1.0 g, 3.28 mmol) and (*Z*,*Z*)-cycloocta-1,5-diene **24** (3 cm^3, 2.64 g, 24.4 mmol) gave *title compound* **36** (1.32 g, 78%), which was recrystallized from ethyl acetate–light petroleum (60–80 °C) (20:80), m.p. 143 °C; ν_{max}/cm^{-1} 3500, 2900, 1715 and 1450; λ_{max}(MeOH)/nm 220 and 310; δ_H(300 MHz) 5.72 (2 H, m, =CH), 5.32 (1 H, br s, =CH), 2.76 (1 H, superimposed dd, *J* 9.5, CH), 2.37 (4 H, m), 2.17 (2 H, s), 2.1–1.6 (8 H, complex m, CH_2 s, OH and 13-Me), 1.18 (3 H, s, Me) and 1.15 (3 H, s, Me); δ_C(25 MHz) 213.08 (C=O), 143.83, 131.53, 131.52 and 123.82 (sp^2 carbons), 72.00 (COH), 57.29, 51.94, 45.23, 36.88, 32.70, 27.28, 26.28, 25.94, 24.41, 23.39 and 16.23; *m*/*z* 261.1 (M$^+$ + H) and 243.1 (M$^+$ + H − H_2O) (Found: C, 78.8; H, 9.0. $C_{17}H_{24}O_2$ requires C, 78.46; H, 9.22%).

10-*Hydroxy*-8,10,11-*trimethyltetracyclo*[6.2.2.1^{3,6}.0^{2,7}]-*trideca*-4,11-*dien*-9-*one* **37**.—Freshly distilled tricyclo[2.2.1]-hepta-2,5-diene **25** (2 cm^3, 1.8 g, 18.4 mmol, excess) and the dimeric dienone **15** (0.7 g, 2.3 mmol) were refluxed in *m*-xylene (10 cm^3) for 4 h. Removal of the excess of diene and the xylene, and chromatography, gave the *crystalline adduct* **37** (0.8 g, 72%), m.p. 153 °C; ν_{max}/cm^{-1} 3450, 3010, 2900, 1710 and 1455; λ_{max}(MeOH)/nm 210 and 308; δ_H(300 MHz) 6.28 (1 H, dd, *J* 6 and 3, =CH), 6.10 (1 H, dd, *J* 5.5 and 3, =CH), 5.30 (1 H, br s, 12-H), 2.79 (1 H, br s, CH), 2.62 (2 H, m, CH), 2.50 (1 H, md, *J* 8, CH), 2.38 (1 H, s, OH), 2.25 (1 H, d, *J* 9, CH), 1.85 (3 H, d, *J* 1.7, 11-Me), 1.54 (1 H, d, *J* 8, CH_2), 1.24 (3 H, s, Me), 1.23 (3 H, s, Me) and 1.01 (1 H, d, *J* 8, CH_2); δ_C(22.5 MHz) 214.9 (C=O), 144.0, 141.5, 138.7 and 124.8 (olefinic C), 73.4 (COH), 51.9, 51.0, 47.2, 45.8, 44.5, 42.0, 40.0, 25.0, 22.9 and 16.0; *m*/*z* 245 (M$^+$ + H), 227 (M$^+$ + H − H_2O) and 217 (Found: C, 79.1; H, 8.3. $C_{16}H_{20}O_2$ requires C, 78.70; H, 8.20%).

12-*Hydroxy*-1,12,15-*trimethyltetracyclo*[9.2.2.0^{2,10}.0^{3,8}]-*pentadeca*-3,5,7,14-*tetraen*-13-*one* **38**.—Following the above procedure, indene **22** (3.0 cm^3, 3.0 g, 2.58 mmol, excess) and the diol dimer **15** (0.5 g, 1.64 mmol) gave the *adduct* **38** (0.62 g, 70%, m.p. 181 °C; ν_{max}/cm^{-1} 3450, 2950, 1715 and 1450; λ_{max}(MeOH)/nm 235, 270 and 308; δ_H(300 MHz) 7.28–7.1 (4 H, m, ArH), 5.18 (1 H, br s, 14-H), 3.52 (1 H, m, CH), 3.33 (1 H, d, *J* 9, CH), 3.11 (1 H, dd, *J* 17 and 10.5, 9-H^{exo}), 2.83 (1 H, m, CH), 2.6 (1 H, dd, *J* 17.6, 9-H^{endo}), 2.48 (1 H, br s, OH), 1.86 (3 H, d, *J* 1.6, 15-Me), 1.42 (3 H, s, Me) and 1.29 (3 H, s, Me); δ_C(25 MHz) 215.54 (CO) 145.30, 143.12, 142.20, 127.30, 126.48, 125.94, 124.71. 124.48, 72.47, 53.23, 53.06, 52.18, 37.06, 36.41, 24.94, 24.06 and 16.11 (Found: C, 80.55; H, 7.45. $C_{18}H_{20}O_2$ requires C, 80.59; H, 7.46%).

9-*Hydroxy*-7,9,10-*trimethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-3-*spirocyclopropan*-8-*one* **39**.—The reaction of dione **15** (0.8 g, 2.63 mmol) and spiro[2.4]hepta-4,6-diene **19** (4 cm^3, excess) furnished the *adduct* **39** (0.79 g, 62%), m.p. 107 °C; ν_{max}/cm^{-1} 3500, 3010, 1715 and 1455; λ_{max}(MeOH)/nm 208 and 310; δ_H(300 MHz) 5.42 (1 H, dd, *J* 5.6 and 2.1, =CH), 5.29 (1 H,

br s with structure, 11-H), 5.25 (1 H, dd, *J* 5.6 and 1.7, =CH), 3.08 (1 H, d, *J* 9, CH), 2.9 (1 H, dd, *J* 8.8 and 3, 2-H), 2.49 (1 H, d, *J* 2.4, 1-H), 2.28 (1 H, s, OH), 1.95 (3 H, d, *J* 1, 10-Me), 1.25 (3 H, s, Me), 1.23 (3 H, s, Me), 0.90 (2 H, m, cyclopropane CH_2) and 0.65 (2 H, m, cyclopropane CH_2); δ_C(25 MHz) 215.97 (C=O), 142.71, 142.36, 125.65 and 124.77 (=Cs), 72.41 (COH), 55.82, 51.89, 51.35, 41.09, 33.65, 24.76, 22.59, 15.53, 14.76 and 10.05 (Found: C, 78.3; H, 8.1. $C_{16}H_{20}O_2$ requires C, 78.68; H, 8.19%).

9-*Hydroxy*-9,10-*dimethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **50**.—The diol **17** (1.2 g, 5.88 mmol) and dicyclopentadiene (4 cm^3, excess) gave *title compound* **50** (0.66 g, 77%), m.p. 86 °C; ν_{max}/cm^{-1} 3450, 1715 and 1615; δ_H(300 MHz) 5.68 (1 H, dd, *J* 8 and 4, =CH), 5.55 (1 H, d, *J* 8, =CH), 5.35 (1 H, md, *J* 7, 11-H), 3.2–3.05 (3 H, m, CH), 2.7 (1 H, s, OH), 2.55 (2 H, md, *J* 10, 3-H), 2.50 (1 H, md, *J* 10, 3-H), 1.9 (3 H, d, *J* 1, 10-Me), 1.25 (3 H, s, 9-Me) (Found: C, 76.55; H, 7.8. $C_{13}H_{16}O_2$ requires C, 76.47; H, 7.84%).

Tricyclo[5.2.2.0^{2,6}]*undeca*-3,10-*diene*-8-*spirooxiran*-9-*one* **51**.—To a stirred solution of the chloro alcohol **43** (0.5 g, 2.22 mmol) and cetyltrimethylammonium bromide (0.05 g, 0.018 mmol) in chloroform (50 cm^3) was added aq. KOH (10 cm^3; 1 mol dm^{-3}) at room temperature (~25 °C). After 10 min (TLC), the organic layer was separated, and washed successively with water (2 × 20 cm^3) and brine (2 × 20 cm^3), and was then dried. Removal of solvent, and chromatography of the residue over silica gel, gave the *epoxide* **51** (0.397 g, 95%), ν_{max}/cm^{-1} 3050, 2900, 1740, 1620 and 1360; λ_{max}(MeOH)/nm 214 and 305; δ_H(90 MHz) 6.35 (1 H, superimposed dd, *J* 8, 11-H), 6.15 (1 H, superimposed dd, *J* 8, 10-H), 5.75 (1 H, m, =CH), 5.55 (1 H, m, =CH), 3.55 (2 H, md, *J* 8, CH), 2.9 (2 H, AB, *J* 8, OCH_2), 2.60 (3 H, m, 2 × CH and 5-H) and 2.0 (1 H, m, 5-H); *m/z* 189 (M^+ + H), 171.0 and 154.0 (Found: C, 76.2; H, 6.7. $C_{12}H_{12}O_2$ requires C, 76.59; H, 6.38%).

9-*Hydroxymethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **52**.—The keto epoxide **51** (0.36 g, 1.9 mmol) was treated with zinc (1.39 g, 0.02 mg) and ammonium chloride (0.03 g, 0.6 mmol) in methanol (20 cm^3) containing water (3 cm^3) for 6 h at room temperature. Work-up and chromatography [ethyl acetate–light petroleum (60–80 °C) (20:80)] gave first a mixture of ketones **53** and **54** (0.020 g, 5.6%). Continued elution with ethyl acetate–light petroleum (60–80 °C) (20:80) gave an epimeric mixture of β-*hydroxy ketone* **52** (0.274 g, 75.5%) as a thick liquid, b.p. 163 °C/0.6 mmHg; ν_{max}/cm^{-1} 3400, 3050, 2900 and 1720; λ_{max}(MeOH)/nm 210 and 300; δ_H(270 MHz) 6.45 and 6.35 (total 1 H, superimposed dd, *J* 7, 10-H), 6.05 (1 H, superimposed dd, *J* 7, 11-H), 5.65 (1 H, ddd, *J* 5.5, 2 and 1.8, =CH), 5.40 (1 H, dd, *J* 5.5 and 2, =CH), 3.90 and 3.70 (total 2 H, dd, *J* 11 and 8, OCH_2), 3.59 (1 H, d, *J* 7, CH), 3.15–3.0 (3 H, m, 2 × CH and OH), 2.70 (1 H, m), 2.50 (1 H, m), 2.30 (1 H, m) and 2.0 (1 H, md, *J* 14, 3-H); *m/z* 190 (M^+) and 172 ($M^+ - H_2O$) (Found: C, 75.4; H, 7.3. $C_{12}H_{14}O_2$ requires C, 75.78; H, 7.36%).

9-*Methyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **53**.—To a suspension of zinc (2.1 g, 0.032 mol) and ammonium chloride (0.054 g, 0.93 mmol) in dry 1,4-dioxane (20 cm^3) was added a solution of epoxide **51** (0.5 g, 2.66 mmol) in 1,4-dioxane (5 cm^3) and the reaction mixture was refluxed for 4 h. Work-up and chromatography [ethyl acetate–light petroleum (60–80 °C) (5:95)] gave a mixture of ketones **53** and **54** (0.295 g, 63.8%), ν_{max}/cm^{-1} 1720 and 1640. This mixture was further reduced with zinc to give dienone **53** as follows.

A mixture of dienone **53** and trienone **54** (0.14 g), zinc (4.0 g, 0.06 g-atom) and ammonium chloride (0.07 g, 0.014 mmol) in dry methanol (20 cm^3) was refluxed for 8 h. The usual isolation procedure, followed by chromatography, gave an epimeric mixture of the *title compound* **53** (0.13 g, 93%) as a liquid, b.p. 120 °C/0.6 mmHg; ν_{max}/cm^{-1} 3000, 2950 and 1720; λ_{max}(MeOH)/nm 208 and 300; δ_H(270 MHz) 6.40 and 6.30 (total 1 H, superimposed dd, *J* 7, 10-H), 6.05 (1 H, superimposed dd, *J* 7, 11-H), 5.65 (1 H, m, =CH), 5.40 (1 H, m, =CH), 3.1 (2 H, br m, CH), 2.8 (2 H, br m, CH), 2.5 (1 H, m, CH), 2.1 (1 H, md, *J* 18, 3-H^{exo}), 2.0 (1 H, md, *J* 18, 3-H^{endo}) and 1.15 and 1.05 (total 3 H, d, *J* 8, 9-Me); *m/z* 174 (M^+) and 118 (Found: C, 82.3; H, 8.0. $C_{12}H_{14}O$ requires C, 82.76; H, 8.04%).

Tricyclo[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **55**.—To a stirred solution of the alcohol **52** (1.2 g, 6.32 mmol) in acetone (30 cm^3) was added Jones' reagent dropwise at room temperature (~28 °C). The addition was stopped after complete conversion (TLC). Acetone was removed under reduced pressure, water was added to the residue, and the aqueous layer was extracted with ethyl acetate (4 × 20 cm^3). The combined extract was washed successively with water (2 × 15 cm^3) and brine (2 × 15 cm^3), and was then dried. Removal of solvent under reduced pressure left a pale yellow residue, which was chromatographed on silica gel to give the corresponding acid, as a solid (1.1 g, 85%) m.p. 194 °C; ν_{max}/cm^{-1} 3350.

The β-keto acid thus obtained (0.46 g, 2.45 mmol) was taken up in aq. barium hydroxide (15 cm^3; 20%) and the mixture was refluxed for 3 h. The reaction mixture was acidified (pH ~ 3, measured with pH paper) with HCl (1:1), saturated with NaCl, and extracted with diethyl ether (4 × 20 cm^3). The combined ether layer was washed successively with aq. $NaHCO_3$ (5%; 2 × 10 cm^3), water (2 × 10 cm^3) and brine (2 × 10 cm^3), and was then dried. Removal of solvent and chromatography of the residue gave the *ketone* **55** (0.320 g, 50%) as a liquid, ν_{max}/cm^{-1} 2900 and 1730; λ_{max}(MeOH)/nm 208 and 310; δ_H(90 MHz) 6.30 (1 H, superimposed dd, *J* 8.5, 10-H), 6.05 (1 H, superimposed dd, *J* 8.5, 11-H), 5.75 (1 H, m, =CH), 5.45 (1 H, m, =CH), 3.05 (2 H, m, CH), 2.75–2.15 (4 H, cluster, 2 × CH and CH_2) and 2.1–1.75 (2 H, m, 3-H_2) (Found: C, 89.8; H, 7.4. $C_{11}H_{12}O$ requires C, 90.00; H, 7.50%).

9,9-*Dimethyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **56**.—To a suspension of dry sodium hydride (0.3 g, 11 mmol) in THF (30 cm^3) was added a solution of the ketone **53** (1.05 g, 6.03 mmol) in THF (5 cm^3). Methyl iodide (5 cm^3, excess) was added to the reaction mixture, which was then refluxed for 16 h, during which more methyl iodide (5 cm^3) was added. THF was removed under reduced pressure, and water (20 cm^3) and diethyl ether (20 cm^3) were added to the residue. The organic layer was separated and the aqueous layer was further extracted with diethyl ether (3 × 15 cm^3). The combined organic extract was washed successively with aq. ammonium chloride (10%; 20 cm^3), water (2 × 20 cm^3), and brine (2 × 15 cm^3). Drying, and removal of solvent under reduced pressure, gave a pale yellow residue, which was chromatographed to give the *title compound* **56** (0.504 g, 72%), b.p. 138 °C/0.6 mmHg; ν_{max}/cm^{-1} 3050, 2900, 1720 and 1615; δ_H(300 MHz) 6.35 (1 H, superimposed dd, *J* 8, 10-H), 6.05 (1 H, superimposed dd, *J* 8, 11-H), 5.65 (1 H, m, =CH), 5.45 (1 H, m, =CH), 3.1 (1 H, dd, *J* 7 and 1.8, CH), 3.05 (1 H, dd, *J* 4.5 and 1.2, CH), 2.98 (1 H, m, CH), 2.69 (1 H, br m, CH), 2.5 (1 H, dd with structure, *J* 17 and 10, 3-H^{exo}), 1.98 (1 H, md, *J* 17, 3-H^{endo}), 1.12 (3 H, s, 9-Me) and 1.05 (3 H, s, 9-Me) (Found: C, 82.6; H, 8.2. $C_{13}H_{16}O$ requires C, 82.96; H, 8.50%).

3-*Hydroxy*-9-*methyltricyclo*[5.2.2.0^{2,6}]*undeca*-4,10-*dien*-8-*one* **57**.—A solution of ketone **53** (1.1 g, 6.34 mmol) in carbon tetrachloride (50 cm^3), freshly crystallized NBS (2.2 g, 14.4 mmol) and benzoyl peroxide (0.04 g) was irradiated for 40 min. The floating succinimide was removed by filtration and the solvent was removed under reduced pressure to obtain the

α-bromo compound (0.8 g, 50%), which was directly subjected for hydrolysis as follows.

A solution of the above compound (0.5 g, 1.98 mmol) in acetone (30 cm^3) and aq. $NaHCO_3$ (10%; 30 cm^3) was stirred at room temperature for 3 h. The reaction mixture was filtered over a Celite pad, acetone was removed under reduced pressure, and the aqueous solution was saturated with NaCl and extracted with diethyl ether (4 × 30 cm^3). The combined ether layer was washed successively with aq. $NaHCO_3$ (10%; 2 × 20 cm^3), water (20 cm^3), and brine (20 cm^3). Drying, and removal of solvent, followed by chromatography of the residue over silica gel, afforded the *allylic alcohol* **57** (0.24 g, 65%) as a thick liquid, b.p. 160 °C/0.5 mmHg; ν_{max}/cm^{-1} 3450, 2950 and 1720; δ_H(90 MHz) 6.35 (1 H, superimposed dd, *J* 8, 10-H), 6.20 (1 H, superimposed dd, *J* 8, 11-H), 5.9–5.7 (2 H, m, =CH), 4.40 (1 H, br s, 3-H), 3.55–3.00 (2 H, m, CH), 2.85 (1 H, m, CH), 2.6 (1 H, m, CH), 2.3–2.0 (2 H, br m, CH, OH) and 1.15 (3 H, d, *J* 8, 9-Me) (Found: C, 75.4; H, 7.5. $C_{12}H_{14}O_2$ requires C, 75.79; H, 7.37%).

Oxa-di-π-methane Rearrangement of Annulated Bicyclo[2.2.2]*octenones. General Procedure.*—A solution (0.4%) of an adduct in dry acetone (both as a solvent and as a sensitizer) was irradiated by a 250 W mercury vapour lamp in a Pyrex immersion well under nitrogen. After 3–5 h the solvent was removed under reduced pressure and the residue was chromatographed [ethyl acetate–light petroleum (60–80 °C) (10:90)] on silica gel to give some unchanged starting material followed by the rearrangement product.

6-*Hydroxy*-2,6-*dimethyltetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **60**.—Irradiation of the keto alcohol **28** (0.80 g, 4 mmol) gave the *polyquinane* **60** (0.44 g, 55%), m.p. 95 °C; ν_{max}/cm^{-1} 3450, 3050 and 1715; λ_{max}(MeOH)/nm 294; δ_H(300 MHz) 5.75 (1 H, br s, =CH), 5.65 (1 H, br s, =CH), 3.00 (1 H, dd, *J* 10.5 and 7, CH), 2.85 (1 H, br s, OH), 2.70 (1 H, br s, CH), 2.50 (2 H, d merged with m, C*H* and CH*H*), 2.35 (1 H, br m, CH), 2.15 (1 H, md, *J* 14, C*H*H), 1.75 (1 H, d, *J* 3, CH), 1.30 (3 H, s, Me), 1.12 (3 H, s, Me); δ_C(75 MHz) 215.02, 131.50, 130.50, 82.69, 53.00, 52.50, 46.98, 43.42, 38.81, 38.00, 37.50, 26.74 and 19.26; *m*/*z* 204 (M^+) (Found: C, 76.6; H. 7.6. $C_{13}H_{16}O_2$ requires C, 76.50; H, 7.80%).

Similarly, compounds **61** and **62** were obtained from substrates **30** and **34** in 60 and 50% yield, respectively.[9]

6-*Hydroxy*-2,3,6-*trimethyltetracyclo*[6.6.0.$0^{2,4}$.$0^{3,7}$]*tetradec*-11-*en*-5-*one* **63**.—Irradiation of compound **36** (0.53 g, 2.03 mmol) for 4 h furnished the *title compound* **63** (0.24 g, 45%), m.p. 184 °C; ν_{max}/cm^{-1} 3420, 3050 and 1720; λ_{max}(MeOH)/nm 279; δ_H(300 MHz) 5.60 (1 H, md, *J* 8, =CH), 5.45 (1 H, dd with structure, *J* 8 and 4, =CH), 2.65 (1 H, superimposed dd, *J* 8, CH), 2.60 (1 H, md, *J* 8, CH), 2.50 (1 H, d, *J* 10, CH), 2.30 (1 H, s, OH), 2.20 (1 H, dd, *J* CH), 2.0 (3 H, m, CH_2 and C*H*H), 1.85 (1 H, dd, *J* 12 and 7, C*H*H), 1.75 (1 H, md, *J* 8, C*H*H), 1.65 (1 H, md, *J* 8, CH*H*), 1.55 (2 H, br s, CH_2), 1.45 (3 H, s, Me), 1.25 (3 H, s, Me) and 1.15 (3 H, s, Me) (Found: C, 78.1; H, 9.0. $C_{17}H_{24}O_2$ requires C, 78.46; H, 9.23%).

6-*Chloromethyl*-6-*hydroxytetracyclo*[6.6.0.$0^{2,4}$.$0^{3,7}$]-*tetradecan*-5-*one* **64**.—Irradiation of compound **40** (0.60 g, 2.24 mmol) gave *title compound* **64** (0.12 g, 20%), m.p. 95 °C; ν_{max}/cm^{-1} 3400, 2900 and 1720; δ_H(90 MHz) 3.48 (2 H, s, CH_2Cl), 3.00 (2 H, br s, CH), 2.50 (2 H, d overlapped with another signal, *J* 4.5, CH and OH), 2.35 (1 H, md, *J* 9, CH), 2.1 (2 H, dd, *J* 9 and 4.5, CH), 1.90–1.52 (6 H, br m, CH_2) and 1.50–1.10 (6 H, br m, CH_2) (Found: C, 67.4; H, 8.0. $C_{15}H_{21}ClO_2$ requires C, 67.04; H, 7.82%).

6-*Hydroxy*-3,6-*dimethyltetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **65**.—Irradiation of compound **50** (1.0 g, 5 mmol) for 5 h gave *title compound* **65** (0.40 g, 40%), m.p. 131 °C; ν_{max}/cm^{-1} 3480, 2950 and 1725; δ_H(300 MHz) 5.75 (1 H, m, =CH), 5.68 (1 H, m, =CH), 3.00 (1 H, dd, *J* 12 and 7, CH), 2.85 (1 H, d, *J* 12, CH), 2.65 (1 H, md, *J* 12, CH), 2.55 (1 H, d with structure, *J* 12, CH), 2.30 (1 H, s, OH), 2.25 (1 H, md, *J* 12, CH), 1.80 (1 H, part of AB, *J* 10, C*H*H), 1.65 (1 H, part of AB, *J* 10, CH*H*), 1.58 (3 H, s, Me) and 1.30 (3 H, s, Me) (Found: C, 77.4; H, 7.3. $C_{13}H_{16}O_2$ requires 77.77; H, 7.40%).

6-*Hydroxymethyltetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **66**.—Irradiation of compound **52** (*syn*:*anti* mixture) (0.40 g, 2.1 mmol) for 4 h gave *title compound* **66** as an epimeric mixture (0.22 g, 55%), b.p. 165 °C/0.6 mmHg; ν_{max}/cm^{-1} 3490 and 1715; δ_H(270 MHz) 5.74 (2 H, br s, =CH), 3.82 (2 H, complex m, CH_2OH), 3.60 and 3.54 (total 1 H, d, *J* 5, CH), 2.90 (1 H, m, CH), 2.86–2.48 (4 H, complex m, CH), 2.28 (1 H, m, CH), 2.09 (1 H, s, OH), 1.90 (1 H, dd, *J* 9 and 4.5, C*H*H) and 1.74 (1 H, m, CH*H*); *m*/*z* 191.1 (M^+ + H) and 173.1 (M^+ + H − H_2O).

6-*Methyltricyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **67**.—Irradiation of compound **53** (*syn*:*anti* mixture; 0.42 g, 2.23 mmol) in dry acetone containing benzophenone as sensitizer gave *title compound* **67** (epimeric mixture) (0.16 g, 38%), b.p. 135 °C/0.6 mmHg; ν_{max}/cm^{-1} 2950 and 1725; λ_{max}(MeOH)/nm 227; δ_H(90 MHz) 5.7 (2 H, br s, =CH), 2.85 (2 H, m, CH), 2.70 (2 H, d, *J* 7, CH), 2.5 (3 H, m, CH), 1.9 (1 H, dd, *J* 12 and 8, C*H*H), 1.7 (1 H, dd, *J* 12 and 7, CH*H*) and 1.1 and 0.98 (total 3 H, d, *J* 8, Me) (Found: C, 82.5; H, 7.85. $C_{12}H_{14}O$ requires C, 82.76; H, 7.95%).

9-*Hydroxy*-6-*methyltetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **68**.—Irradiation of compound **57** (mixture of stereoisomers; 0.42 g, 2.21 mmol) in acetone for 4 h gave *title compound* **68** (0.19 g, 45%) as a mixture of stereoisomers, b.p. 160 °C/0.6 mmHg; ν_{max}/cm^{-1} 3490 and 1715; δ_H(270 MHz) 5.92 (1 H, dd, *J* 5.3 and 2.5, =CH), 5.76 (1 H, dd, *J* 5.3 and 4, =CH), 4.76 and 4.62 (total 1 H, br s, *H*COH), 3.26 (1 H, br s, OH), 3.09–2.9 (1 H, m, CH), 2.83 (1 H, m, CH), 2.56 (2 H, m, CH), 2.39 (1 H, m, CH), 2.28 (1 H, m, CH), 1.94 (1 H, m, CH) and 0.96 and 0.92 (total 3 H, d, *J* 6, Me); *m*/*z* 190.4 (M^+) and 172.1 (M^+ − H_2O).

6-*Acetoxymethyltetracyclo*[6.3.0.$0^{2,4}$.$0^{3,7}$]*undec*-10-*en*-5-*one* **73**.—The keto alcohol **66** (1.8 g, 9.47 mmol) was stirred in a mixture of pyridine (10 cm^3) and acetic anhydride (1.4 g, 13.7 mmol) for 6 h. The reaction mixture was poured into cold, aq. sodium hydrogen carbonate (30 cm^3) and extracted with ethyl acetate (4 × 25 cm^3). The combined extract was washed successively with HCl (10%; 2 × 25 cm^3), aq. sodium hydrogen carbonate (5%; 20 cm^3), water and brine. Drying and removal of solvent gave a pale oil, which was chromatographed and distilled to give *title compound* **73** (1.62 g, 74%), b.p. 138 °C/1.0 mmHg; ν_{max}/cm^{-1} 2950, 1750 and 1715; δ_H(90 MHz) 5.7 (2 H, br s, =CH), 4.15 (2 H, m, CH_2OAc), 3.1 (1 H, d, *J* 8, CH), 2.98–2.70 (2 H, m, CH), 2.68–2.50 (2 H, m, CH), 2.42 (1 H, br s, CH), 2.25 (1 H, m, CH), 2.05 (3 H, s, Ac) and 1.95 (2 H, m, CH) (Found: C, 72.1; H, 6.5. $C_{14}H_{16}O_3$ requires C, 72.41; H, 6.89%).

1,8-*Dimethyl*-12-*oxatetracyclo*[6.3.1.$0^{2,9}$.$0^{3,7}$]*dodec*-5-*en*-11-*one* **74**.—The tetracyclic ketone **60** (0.055 g, 0.27 mmol) was heated in formic acid (80%; 5 cm^3) at 55 °C for 1 h. The reaction mixture was poured onto cooled, aq. $NaHCO_3$ (40 cm^3) and extracted with ethyl acetate (4 × 15 cm^3). The combined extract was washed successively with aq. $NaHCO_3$ (5%; 2 × 10 cm^3), water (2 × 15 cm^3), and brine (20 cm^3), and dried. Removal of solvent under reduced pressure, and column chromatography [ethyl acetate–light petroleum (60–80 °C) (10:90)] of the residue, yielded the *keto ether* **74** (0.025 g, 46%), m.p. 82 °C; ν_{max}/cm^{-1} 2950 and 1760; δ_H(500 MHz) 5.84 (1 H, ddd, *J* 6, 2 and 2, =CH), 5.48 (1 H, dd with structure, *J* 6 and 3,

=CH), 3.15 (1 H, br d, *J* 5.5, CH), 2.82 (1 H, md, *J* 17 and 8, CH), 2.73 (1 H, ddd, *J* 18 and 8, and 3, CH), 2.42 (1 H, dd, *J* 2.2 and 4.8, CH), 2.36 (1 H, d, *J* 18, CH), 2.21 (1 H, dd, *J* 18, 5 C*H*H), 2.14 (1 H, md, *J* 18, CH*H*), 1.92 (1 H, d, *J* 2, CH), 1.25 (3 H, s, Me) and 1.24 (3 H, s, Me); δ_C(75 MHz) 208.4 (C=O), 134.3, 129.07, 87.80, 85.30, 63.40, 56.90, 41.50, 39.60, 34.4, 33.40, 15.20 and 10.40 (Found: C, 76.7; H, 8.0. $C_{13}H_{16}O_2$ requires C, 76.47; H, 7.84%).

6-Methylenetetracyclo[6.3.0.0^{2,4}.0^{3,7}]*undec-10-en-5-one* **75** *and 6-Formyloxymethyltetracyclo*[6.3.0.0^{2,4}.0^{3,7}]*undec-10-en-5-one* **76**.—The keto alcohol **66** (0.4 g, 2.1 mmol) was heated in formic acid (80%; 10 cm^3) at 80 °C for 30 min under nitrogen. Work-up as described earlier and chromatography of the residue first gave the *enone* **75** (0.170 g, 50%) as a liquid, ν_{max}/cm^{-1} 1720 and 1645; λ_{max}(MeOH)/nm 225; δ_H(500 MHz) 5.76 (3 H, m, =CH), 5.17 (1 H, br s, =CH), 3.31 (1 H, d, *J* 4.2, CH), 3.04 (1 H, d, *J* 5, CH), 2.72 (1 H, dd, *J* 11 and 5.5, CH), 2.60 (1 H, m, CH), 2.56 (1 H, d, *J* 9.2, CH), 2.36 (1 H, dd, *J* 11 and 5, CH), 2.06 (1 H, dd, *J* 9.6 and 5.3, C*H*H) and 1.86 (1 H, dd, *J* 9.6 and 6, CH*H*) (Found: C, 89.4; H, 6.8. $C_{12}H_{12}O$ requires C, 89.53; H, 6.97%).

Further elution of the column gave the formate **76** (0.184 g, 40%), ν_{max}/cm^{-1} 1730 and 1170; δ_H(90 MHz) 8.0 (1 H, s, OCHO), 5.7 (2 H, br s, =CH), 4.25 (2 H, d, *J* 8, CH_2O), 3.0 (1 H, br d, CH), 2.8–2.1 (4 H, complex m, CH), 2.0–1.8 (2 H, m, CH_2) and 1.3 (2 H, br m, CH). Its structure was further confirmed by methanolysis with NaOMe–MeOH, which gave the starting material **66**.

11-Bromo-8-methyltricyclo[5.3.1.0^{2,6}]*undec-3-en-9-one* **77** *and 10-Acetoxy-5-bromo-9-methyltetracyclo*[6.3.0.0^{2,4}.0^{3,7}]*-10-ene* **78**.—To a solution of ketone **67** (0.130 g, 0.75 mmol) in acetonitrile (8 cm^3) was added acetyl methanesulfonate (0.20 g, 1.4 mmol) and tetramethylammonium bromide (0.25 g, 1.67 mmol) and the mixture was stirred for 20 h at room temp. (~32 °C), then was filtered, the solvent was removed, and the residue was taken up in diethyl ether. The ethereal solution was washed successively with water and brine, and dried. Removal of solvent gave a residue, which was chromatographed to give title compound **77** as a solid (0.083 g, 44%), m.p. 122 °C; ν_{max}/cm^{-1} 1730 and 1610; δ_H(90 MHz) 5.7 (2 H, br s, =CH), 4.6 (1 H, br s, HCBr), 3.08 (1 H, m, CH), 2.6 (6 H, complex m, 2 × CH and 2 × CH_2), 2.25 (2 H, m, CH) and 1.15 (3 H, d, *J* 6, Me). Its structure was further confirmed by X-ray analysis.

Continued elution of the column gave title compound **78** as a solid (0.04 g, 18%), m.p. 142 °C; ν_{max}/cm^{-1} 1720; δ_H(90 MHz) 4.8 (1 H, br s, =CH), 3.85 (1 H, br m, HCBr), 2.9 (1 H, br m, CH), 2.7–2.4 (8 H, 6 × CH and CH_2), 2.25 (3 H, s, Ac) and 1.12 and 1.05 (total 3 H, d, *J* 8, Me).

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