Photochemistry of Substituted Cyclic Enones. Part 5.[1] 3-Aryl-5-(3-phenylprop-2-enyl)cyclopent-2-enones

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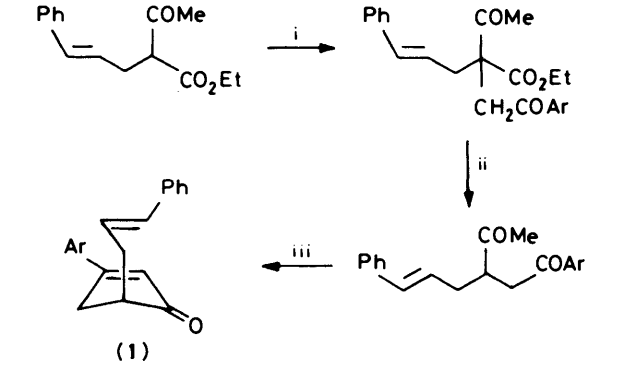
The *E*- and *Z*- compounds (**1**) and (**2**; Ar = Ph, 4-$MeOC_6H_4$, and 4-NCC_6H_4), were synthesised by standard procedures. The *E*- and *Z*-isomers set up a rapid photochemical equilibrium prior to formation of tricyclic [2 + 2]-cycloaddition products, 6-aryl-4-*exo*- and *endo*-phenyltricyclo[3.2.1.$0^{3,6}$]octan-2-ones, (**3**) and (**4**) respectively. The *exo*-tricyclic ketones (**3**) undergo further photolysis to afford the cyclobutanecarbaldehydes (**6**), which rearrange thermally to the enol ethers (**7**). The 6-*endo*-phenyl isomers (**4**) do not photolyse further. Boron trifluoride-assisted rearrangement of compounds (**4**) affords the cyclohexanones (**9**) and, in the case of the 4-cyanophenyl compound, the cyclohexenone (**10c**). Similar rearrangement of compound (**3b**) affords the ketone (**8b**), but compound (**3c**) gives no corresponding ketone (**8c**) but rather, traces of the monocycle (**1c**).

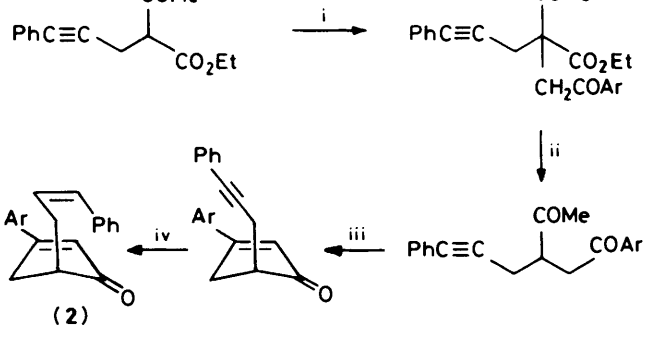
In Part 4,[1] we described the synthesis and photochemistry of 3-aryl-5-allylcyclopentenones, with various alkyl substituents on the allyl sidechain. In every case, we obtained the cage ketones, 6-aryltricyclo[3.2.1.$0^{3,6}$]octan-2-ones, as the primary photoproducts, but these underwent further photolysis to give cyclobutanecarbaldehydes, which themselves rearranged thermally. We decided to investigate the photolysis of analogues in which the allyl side chain was substituted by phenyl in the 3-position. The starting *E*-ketones were synthesised by standard procedures (Scheme 1), and the syntheses require no further comment, other than to mention that the intermediate diketones were isolated and characterised. The *Z*-isomers were prepared from the 5-(3-phenylprop-2-ynyl)cyclopentenones by reduction with hydrogen over Lindlar catalyst, (Scheme 2). We found it best to retain the triple bond until the last stage, as it was found that reduction of the triple bond at an earlier stage and then subjecting the resulting *Z*-alkene to the remaining stages of the synthesis led to some loss of stereochemical integrity at the double bond.



Scheme 1. *Reagents:* i, $ArCOCH_2Br$–OEt^-–DMF; ii, OH^-; iii, NaH–C_6H_6

Photolysis.—Photolysis of the *E*-isomers, (**1a,b**) (Scheme 3) afforded initially a mixture of the *E*- and *Z*-isomers in the ratio 1:1, as shown by n.m.r. tube experiments. Under the same conditions, the *Z*-isomers, (**2a,b**) gave the same ratio of alkenes as their *E*-analogues (n.m.r.). We examined only the *Z*-isomer in the *p*-cyanophenyl series (**2c**) under these conditions, and we could only detect (n.m.r.) the *E*-isomer (**1c**) in the resulting solution. Longer photolysis of the mixture of *E*- and *Z*-isomers in the phenyl and methoxyphenyl series afforded a mixture of 6-aryl-4-*exo*- and 6-aryl-4-*endo*-phenyltricyclo[3.2.1.$0^{3,6}$]octan-2-ones (**3**) and (**4**). In the case of the *p*-methoxy compounds (**1b**) and (**2b**), the ratio of the products (**3b**)* and (**4b**) is the same (1:1) as that of the equilibrating alkenes. In the phenyl series (**1a**) and (**2a**), the ratio of the products (9:10) diverges somewhat from that of the equilibrating alkenes (1:1). In the *p*-cyano series (**1c**) and (**2c**), there is a distinct difference in the two ratios, though further work is required to make a quantitative estimate.

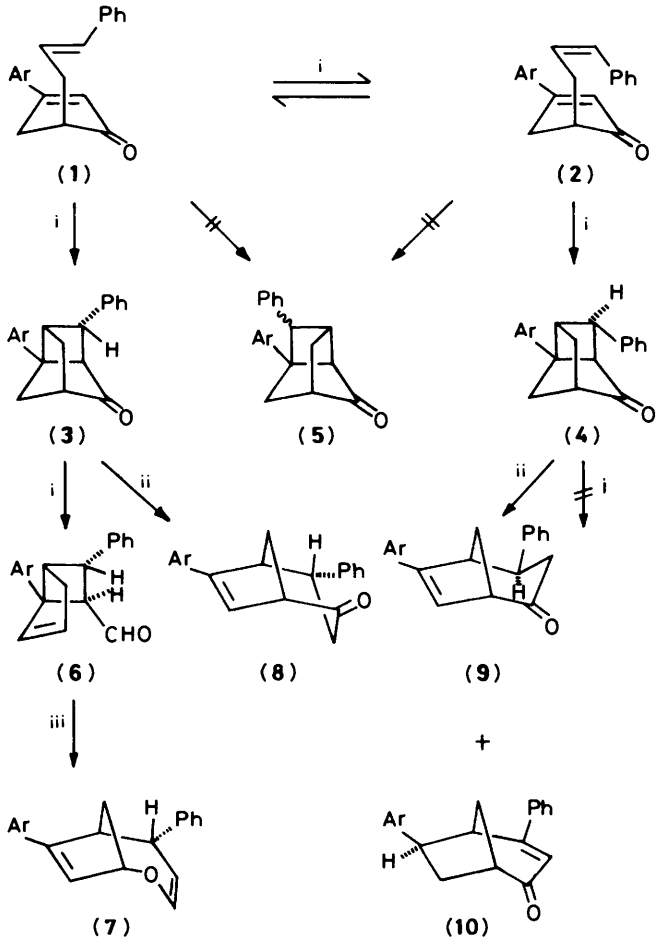
The structures of the tricyclic ketones follow from spectral data. All the ketones show i.r. carbonyl peaks around 1 740 cm^{-1}, rather than at 1 760 cm^{-1}, which would be characteristic of tricyclic ketones of type (**5**).[1,2,3] Comparison of the ^1H spectra of the compounds (**3**) and (**4**) shows that in the latter, the 4-H signal lies downfield at δ_H 4.17. It appears as a 'triplet,' coupled equally to the 3-H and 5-H. In the *exo*-phenyl series, (**3**), the 4-H signal is further upfield, and is hidden in the methylene envelope. Models suggest that a 4-*endo*-hydrogen would be in the shielding zone of the 2-carbonyl, while a 4-*exo*-hydrogen would lie well clear of it.



Scheme 2. *Reagents:* i, NaH–DME–$ArCOCH_2Br$; ii, OH^-; iii, NaH–C_6H_6; iv, H_2–Lindlar catalyst–poison

Further photolysis of the 4-*exo*-phenyl ketones affords initially the cyclobutanecarbaldehydes (**6**). These are unstable to heat and acid, and, as with related compounds,[1] we were unable to obtain analytically pure samples. However, the i.r.

* Taking into account the further photolysis product (**6**), of (**3**).



Scheme 3. *Reagents:* i, *hν*; ii, BF_3–Et_2O; iii, heat or SiO_2

and ^1H n.m.r. spectra are fully consistent with the structures assigned. They show a peak around 1 720 cm^{-1}, and in the ^1H n.m.r. spectrum of compound (**6a**) the 1-H signal appears as a double doublet at δ 3.75, coupled to the aldehyde proton (*J* 1.45 Hz) and 6-H (*J* 9.1 Hz). The 6-H signal at δ 3.60 is also coupled to 5-H at δ 3.18 (*J* 6.6 Hz). The 4α- and 4β-H resonate at δ 2.88 and 2.55, as a double double triplet, (*J* 16.6, 6.6, 2.0 Hz) and doublet (*J* 16.6 Hz) respectively. The 2-H and 3-H signals occur as a multiplet at δ 5.95, and the aldehyde proton as a doublet at δ9.96. By analogy with earlier cases,[1] the cyclobutanecarbaldehydes rearrange thermally to the enol ethers (**7**). We have detected these in all series, and have isolated the aldehydes (**6a,c**) and the enol ether (**7a**). None of the isomeric tricyclic ketones (**4**) photolyse further. For example, under conditions where compound (**3c**) affords the aldehyde (**6c**), the ketone (**4c**) gives a solution which, at most, contains 4% of an aldehyde.

Boron trifluoride-catalysed rearrangement of the phenyl and methoxyphenyl compounds (**3a,b**), (**4a,b**) affords the bicyclooctenones, (**8**) or (**9**), in which the cyclobutane ring is opened. The ^1H n.m.r. spectra of the compounds (**8**) and (**9**) show differences, as would be expected as the conformation of the six-membered ring is such that the large phenyl group is 'equatorial' in each case. In the case of the 4-cyanophenyl tricyclic ketones, (**3c**) and (**4c**), reaction with boron trifluoride is different. The 4-*endo*-phenyl isomer (**4c**) afforded, in addition to the cyclohexanone (**9c**), the cyclohexenone (**10c**). The latter compound must have been formed by transfer of the 4-*endo*-hydrogen to the 6-position. Such a transfer has been found in other cases,[1,2] and must be linked with an unstable intermediate 6-cation. The 4-*exo*-phenyl isomer (**3c**) afforded a complex mixture containing neither compounds (**8c**) nor (**10c**), but from which a low yield of the *E*-alkene (**1c**) could be isolated. The behaviour of compounds (**3c**) and (**4c**) provides further proof that our assignment of the configuration at the 4-position in the tricyclic ketones is correct. The ^{13}C n.m.r. spectra of the tricyclic ketones described in this paper and in Part 4[1] are listed in the Table. The C-3, -5, -6, and -7 signals are all slightly affected by the stereochemistry of the 4-phenyl group, but the main effect is seen on the C-4 and -8 signals. Indeed, the position of these peaks could be used as a diagnosis of stereochemistry at the 4-position and we used the large shift of one of the triplets to distinguish between, and assign the C-7 and -8 signals.

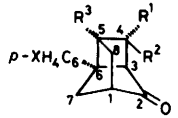
Discussion

Our results raise a number of interesting questions. We are still faced with two possible mechanisms for the isomerisation of the cinnamyl double bond. Clearly from our photolysis this *E-Z* equilibrium is established faster than the cycloaddition. There are many cases recorded in the literature where the stereochemistry of the alkene partner is not fully conserved in intermolecular [2 + 2]-cycloadditions with enones,[4,5] and there are several authenticated cases of this phenomenon in intramolecular cycloadditions.[6] In every case where it has been examined, the starting alkene does not isomerise prior to the [2 + 2]-cycloaddition.[4,7] Our cases appear unique, in this respect. In an earlier paper[2] we seem to preserve stereochemical integrity in the photolysis of the *E*-isomer of the 5-but-2-enyl-3-phenylcyclopentenone, but in the light of our present results, we would reserve judgement on this until we have examined the corresponding *Z*-isomer. However, the cause of the difference between our present results and those of earlier workers may lie in the fact that we have a styryl side-chain as opposed to an alkenyl group.

The first mechanism involves energy transfer from the triplet state of the enone to the styrene chromophore, possibly involving an exciplex. While the energetics of this are favourable for the *E*-alkene [E_t 3-phenylcyclopentenone 259 kJ mol^{-1} (62.0 kcal mol^{-1}),[9] E_t (*E*)-2-methylstyrene 249 kJ mol^{-1} (59.1 kcal mol^{-1})] it is not favourable for the *Z*-alkene [E_t (*Z*)-2-methylstyrene,[10] 293 kJ mol^{-1} (70 kcal mol^{-1})]. While this does not completely rule out this mechanism, we prefer the alternative explanation outlined in Scheme 4 below. This involves the excited triplet enone system (**11**), which collapses presumably *via* an exciplex to a diradical (**12**). This in turn can undergo internal rotation to give the alternative conformation (**13**). The diradical in conformation (**12**) can either collapse to product (**3**) or return to starting material. In conformation (**13**) it can give either product (**4**) or the enone (**2**). Again, the interconversion of the diradical conformations (**12**) and (**13**), and the return of the diradicals to enones (**1**) and (**2**) occur at faster rates than collapse of the diradical to the tricyclic products (**3**) and (**4**). The difference in the photochemical equilibrium ratio of the *E*- and *Z*-alkenes (**1**) and (**2**), and the ratio of the products (**3**) and (**4**) must depend on the inter-relationship of the rates of the various steps in the alkene equilibrium, [2 + 2]-cycloaddition, and in the further photoreaction of the tricyclic products.

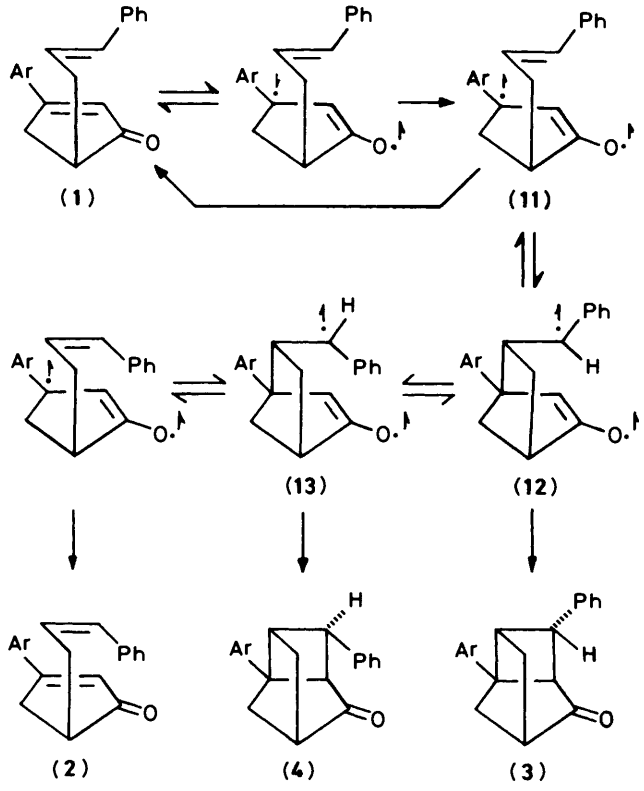
There are analogies in the literature for the failure of the tricyclic ketones (**4**) to undergo further photolysis. In a number of cases where the aromatic ring is held close to the carbonyl group, the compound is not photolabile.[11,12] This appears to be

Table.



	X=H $R^1=R^2=R^3=H$	X=OMe $R^1=R^2=R^3=H$	X=CN $R^1=R^2=R^3=H$	X=H $R^1=Me$ $R^2=R^3=H$	X=H $R^2=Me$ $R^1=R^3=H$	X=H $R^1=R^2=Me$ $R^3=H$	X=H $R^1=R^2=H$ $R^3=Me$	X=H $R^1=Ph$ $R^2=R^3=H$	X=H $R^2=Ph$ $R^1=R^3=H$	X=OMe $R^1=Ph$ $R^2=R^3=H$	X=OMe $R^2=Ph$ $R^1=R^3=H$	X=CN $R^1=Ph$ $R^2=R^3=H$	X=CN $R^2=Ph$ $R^1=R^3=H$
C-1	52.2d	52.1d	52.0d	51.4d	52.6d	52.6d	50.2d	53.0d[b]	52.4d[b]	52.5d[b]	52.2d[b]	52.4d[b]	52.3d[b]
C-2	216.6s	216.5s	216.3s	215.5s	*a*	215.6s	216.1s	215.9s	214.6s	215.2s	214.5s	213.5s	212.9s
C-3	49.3d	49.3d	49.1d	54.6d	54.2d	58.4d	45.4d	53.6d[b]	52.2d[b]	53.4d[b]	52.1d[b]	53.3d[b]	52.1d[b]
C-4	37.9t	37.9t	37.8t	45.0d	37.0d	43.2s	42.1t	51.6d	45.5d	51.3d	45.3d	51.4d	45.6d
C-5	39.2d	39.1d	39.6d	44.8d	42.6d	47.0d	44.8s	43.4d	42.8d	43.2d	42.4d	43.7d	43.3d
C-6	57.4s	56.7s	57.6s	56.3s	*a*	54.5s	50.4s	57.2s	54.3s	56.3s	53.8s	57.2s	54.7s
C-7	44.6t	44.7t	44.2t	47.2t	43.7t	44.0t	45.0t	46.8t	44.1t	46.6t	44.0t	46.1t	43.7t
C-8	34.9t	34.8t	34.8t	37.5t	31.4t	32.8t	40.9t	37.6t	31.9t	37.5t	31.2t	37.2t	31.8t
4-*exo*-Me				18.9q		27.6q							
4-*endo*-Me					11.4q	20.5q							
5-Me							22.3q						
OMe		55.3q								55.2q	55.2q		
CN			118.7s									115.9s	112.9s
ArC	126.2	114.3	110.8	126.3		126.2	126.9	126.6	126.3	113.8	114.2		
	126.9	127.6	127.6	126.7	*a*	126.3	128.7	126.9	127.0	126.0	126.0	126.5	126.5
	128.9	132.8	132.6	128.6		128.7		127.2	127.2	127.2	127.2	126.9	127.4
	140.8	158.7	146.5	143.4		143.6	139.6s	127.8	127.4	127.7	127.7	127.5	127.8
								128.6	128.5	128.1	128.1	128.3	128.5
								128.9	128.9	133.4	132.4	132.1	132.8
								141.2	138.7	140.6	138.6	138.9	138.0
								142.2	140.7	158.2	158.6	147.4	143.8

[a] Not detected. [b] The C-1 and C-3 signals in the diaryl series could be interchanged.



Scheme 4.

a deactivation of the triplet excited state, and is reminiscent of the behaviour of other phenyl substituted ketones,[13,14] and also of the deactivation of aldehyde and ketone triplets by aromatic solvents. In this last case, it is believed to involve an exciplex with some charge-transfer characteristics.[15]

Experimental

For general procedures, see Part 1.[16] Photolyses were carried out using a 460 W Hanovia medium pressure lamp. Flash chromatography was carried out as recommended by Still.[17] U.v. spectra were measured in ethanol.

Syntheses

Ethyl (4E)-2-*Acetyl*-2-*benzoylmethyl*-5-*phenylpent*-4-*enoate*.—Ethyl 2-acetyl-5-phenylpent-4-enoate[18] (15 g), phenacyl bromide (12.2 g), sodium ethoxide [from sodium (1.4 g) in dry ethanol (150 ml)], and *N*,*N*-dimethylformamide (150 ml) were stirred at room temperature overnight. Water (500 ml) was then added and the mixture was extracted with ether (3 × 150 ml). The combined ether layers were washed with water and dried ($MgSO_4$). Removal of solvent afforded *ethyl* 2-*acetyl*-2-*benzoylmethyl*-5-*phenylpent*-4-*enoate* as an oil (19.4 g), which was purified by flash chromatography (6% ethyl acetate in hexane), and distillation, b.p. 120 °C at 0.5 mmHg to yield a colourless oil (12.8 g, 57%) (Found: C, 76.1; H, 6.7. $C_{23}H_{24}O_4$ requires C, 75.8; H, 6.6%); $\nu_{max.}$ 1 735, 1 715, and 1 690 cm^{-1}; δ_H 1.23 (t, *J* 7 Hz, ester Me), 2.40 (s, MeCO), 3.0 (dd, $J_{3,5}$ 1.9, $J_{3,4}$ 6.6 Hz, 3-H), 3.70 (s, $PhCOCH_2$), 4.22 (q, *J* 7 Hz, ester CH_2) 5.97 (dt, $J_{4,5}$ 15.4, $J_{4,3}$ 6.6 Hz, 4-H), 6.37 (d, $J_{5,4}$ 15.4 Hz, 5-H) and 7.09—7.21 (m, ArH).

(5E)-3-*Acetyl*-1,6-*diphenylhex*-5-*en*-1-*one*.—Ethyl (4*E*)-2-acetyl-2-benzoylmethyl-5-phenylpent-4-enoate (8 g), ethanol (500 ml), and 1% aqueous sodium hydroxide (160 ml) were stirred at room temperature for 48 h. Ethanol was removed (350 ml) and the mixture was extracted with ether (3 × 150 ml). The combined organic layers were washed with water (250 ml) and dried ($MgSO_4$). Removal of the solvent afforded an oil (5.5 g) which was purified by flash chromatography (12% ethyl acetate in hexane), and crystallisation from ethanol to give (5*E*)-3-*acetyl*-1,6-*diphenylhex*-5-*en*-1-*one* (4.44 g, 69%) m.p. 51—52 °C (Found: C, 82.3; H, 6.85. $C_{20}H_{20}O_2$ requires C, 82.2; H, 6.9%); $\nu_{max.}$ 1 720 and 1 690 cm^{-1}; δ_H 2.27 (s, MeCO), 2.27—2.53 (m, 4-H), 2.64—3.66 (m, 2- and 3-H) 6.08 (dt, $J_{5,4}$ 6.6, $J_{5,6}$ 15.8 Hz, 5-H), 6.40 (d, *J* 15.8 Hz, 6-H), and 7.18—7.93 (m, ArH).

3-*Phenyl*-5-[(2E)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1a**).—3-Acetyl-1,6-diphenylhex-5-en-1-one (3.6 g) and sodium hydride (61%; 1 g) were refluxed in benzene (100 ml) for 3 h under nitrogen. Ethyl acetate (15 ml) and then water (100 ml) were added with caution. The mixture was extracted with benzene and the combined organic layers washed with water (100 ml) and dried ($CaCl_2$). Removal of solvent afforded a red oil (3.21 g) which was purified by flash chromatography (15% ethyl acetate in hexane). Recrystallisation from ethanol of the resultant solid afforded the *cyclopentenone* as colourless needles (2.57 g, 76%), m.p. 57—58 °C (Found: C, 87.7; H, 6.8. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 258 and 285 nm (log ε 4.50 and 4.37 respectively); δ_H 2.30—3.17 (complex m, 4-H, 5-H, $CH_2CH{=}CHPh$), 6.22 (dt, *J* 15.5 and 6.0 Hz, $CH{=}CHPh$), 6.52 (d, *J* 15.5 Hz, $CH{=}CHPh$), 6.57 (t, $J_{2,4}$ < 2 Hz, 2-H), and 7.30—7.78 (m, ArH).

Ethyl 2-*Acetyl*-5-*phenylpent*-4-*ynoate*.—The sodio derivative of ethyl acetoacetate [from sodium (0.87 g, 0.034 mol) and ethyl acetoacetate (25 g, 0.19 mol)] in ethanol (100 ml) was added to a solution of 3-phenylprop-2-ynyl bromide (7.32 g, 0.037 mol) in ethanol (25 ml) at 0 °C. The reaction was set aside overnight, water (200 ml) was added, and the solution was extracted with ether (3 × 75 ml). The combined ether layers were dried ($MgSO_4$). Removal of the solvent afforded a yellow liquid. The excess ethyl acetoacetate was removed by distillation (b.p. 44 °C at 1 mmHg). The residue was the almost pure pentynoate (7.5 g, 82%) which was used without further purification, $\nu_{max.}$ 2 240, 1 740, and 1 720 cm^{-1}; δ_H 1.26 (t, *J* 7.0 Hz, $MeCH_2$), 2.32 (s, MeCO), 2.91 (br d, $J_{3,2}$ 8.0 Hz, 3-H), 3.74 (br t, 2-H), 4.18 (q, $MeCH_2$), and 7.27 (s, ArH).

Ethyl 2-*Acetyl*-2-*benzoylmethyl*-5-*phenylpent*-4-*ynoate*.—Ethyl 2-acetyl-5-phenylpent-4-ynoate (14.86 g), phenacyl bromide (12.12 g), and sodium hydride (2.38 g) in 1,2-dimethoxyethane (150 ml) were stirred under a nitrogen atmosphere at room temperature for 24 h. Water (100 ml) was added and the mixture extracted with ether (3 × 100 ml). The combined organic layers were washed with water and dried ($MgSO_4$). Removal of the solvent afforded the pentynoate as a yellow oil (17.24 g, 78%) which was used in the next stage without further purification, $\nu_{max.}$ 2 200, 1 740, 1 715, and 1 680 cm^{-1}; δ_H 1.22 (t, *J* 7.0 Hz, $MeCH_2$), 2.38 (s, MeCO), 3.32 (br s, 3-H), 3.93 (br s, $PhCOCH_2$), 4.21 (q, *J* 7.0 Hz, $MeCH_2$), 7.25—7.50, and 7.90—8.05 (m, ArH).

3-*Acetyl*-1,6-*diphenylhex*-5-*yn*-1-*one*.—The above ester (2.1 g), 1% aqueous sodium hydroxide (40 ml), and ethanol (150 ml) were heated at 50 °C for 5 h. Water (150 ml) was added and the mixture extracted with ether (3 × 50 ml). The combined ether layers were washed with water (100 ml) and dried ($MgSO_4$). Removal of the solvent afforded an orange oil (1.2 g, 75%) which was used without further purification, $\nu_{max.}$ 1 710 and 1 680 cm^{-1}; δ_H 2.38 (s, MeCO), 2.73—3.11 (m, 4-H), 3.46—3.69 (m, 2-H, 3-H), and 7.27—7.57, and 7.89—8.04 (m, ArH).

3-*Phenyl*-5-(3-*phenylprop*-2-*ynyl*)*cyclopent*-2-*en*-1-*one*.—The above diketone (0.81 g), sodium hydride (61%; 0.9 g), and benzene (80 ml) were refluxed under nitrogen for 45 min. Ethyl acetate (10 ml) and then water (50 ml) were added cautiously, and the mixture extracted with benzene (3 × 50 ml), and dried ($MgSO_4$). Removal of the solvent afforded a yellow oil which was purified by flash chromatography (14% ethyl acetate in hexane), to give the cyclopentenone as colourless needles (540 mg, 64%), m.p. 84—86 °C (Found: C, 88.4; H, 6.2. $C_{20}H_{16}O$ requires C, 88.2; H, 5.9%); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 287 and 250 nm (log ε 4.45 and 4.20 respectively); δ_H 2.60—2.96 (m, 4-H, 5-H, CH_2C≡CPh), 6.57 (t, $J_{2,4}$ 1.6 Hz, 2-H), 7.26 (br s, ArH), and 7.46—7.76 (m, ArH); δ_C 20.8 (t, CH_2C≡C), 34.2 (t, C-4), 44.5 (d, C-5), 86.5 (s, C≡C), 126.6 (d, C-2), 126.8, 127.7, 128.1, 128.9, 131.3, 131.6 (ArC), 173.1 (s, C-3), and 208.9 (s, C-1).

3-*Phenyl*-5-[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**2a**).—The above propynyl-substituted cyclopentenone (300 mg), Lindlar catalyst (40 mg), pyridine (0.4 ml), and ethanol (300 ml) were stirred at 0 °C for 4 h under a hydrogen atmosphere after which time the mixture was passed through a Celite layer. Removal of the solvent afforded the (*Z*)-cinnamylcyclopentenone (200 mg, 66%) as a solid which was recrystallised from ether–hexane, m.p. 51—53 °C (Found: C, 88.0; H, 6.6. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 285 and 251 nm (log ε 4.34 and 4.12 respectively); δ_H 2.61—3.55 (m, 4-H, 5-H, CH_2CH=CHPh), 5.70 (dt, *J* 11.5 and 6.7 Hz, C*H*=CHPh), 6.55 (t, $J_{2,4}$ 1.4 Hz, 2-H), 6.56 (d, *J* 11.5 Hz, CH=C*H*Ph), and 7.15—7.70 (m, ArH); δ_C 30.4 (t, CH_2CH=CH), 35.0 (t, C-4), 46.3 (d, C-5), 127.5 (d, C-2), 129.5 (d, CH=CH), 127.5, 128.9, 129.5, and 131.9 (ArC), 173.2 (s, C-3), and 210.9 (s, C-1).

Ethyl (4E)-2-*Acetyl*-2-(4-*methoxybenzoylmethyl*)-5-*phenylpent*-4-*enoate*.—Ethyl 2-acetyl-4-(4-methoxyphenyl)-4-oxobutanoate (8.8 g), in *N*,*N*-dimethylformamide (50 ml) was added dropwise to a stirred solution of sodium ethoxide [from sodium (0.73 g) in ethanol (40 ml)] at room temperature. Cinnamyl bromide (6.23 g) in *N*,*N*-dimethylformamide (50 ml) was added in one portion and the mixture stirred at room temperature for 3 h. Water (200 ml) was added and the mixture extracted with ether (3 × 100 ml). The combined organic extracts were washed with water (200 ml) and dried ($MgSO_4$). Removal of solvent afforded a golden oil (8.08 g, 67%), which solidified with time and was recrystallised from ethanol to give the *diketo ester* m.p. 67—69 °C (Found: C, 73.2; H, 6.7. $C_{24}H_{26}O_5$ requires C, 73.1; H, 6.6%); $\nu_{max.}$ 1 740, 1 715, and 1 680 cm^{-1}; δ_H 1.24 (t, *J* 7.15 Hz, *Me*CH_2), 2.38 (s, MeCO), 2.99 (dd, $J_{3,5}$ 3.1, $J_{3,4}$ 7.0 Hz, 3-H), 3.65 (br s, ArCOCH_2), 3.84 (s, OMe), 4.23 (q, *J* 7.15 Hz, MeCH_2), 5.95 (dt, $J_{4,5}$ 15.95, $J_{4,3}$ 7.0 Hz, 4-H), 6.36 (d, $J_{5,4}$ 15.95 Hz, 5-H), 7.23 (br s, Ph), and 7.41 (AA′BB′ system, *J* 9.9 Hz, ArH).

(5E)-3-*Acetyl*-1-(4-*methoxyphenyl*)-6-*phenylhex*-5-*en*-1-*one*.—The above ester (7.5 g), 1% aqueous sodium hydroxide (200 ml) and ethanol (400 ml) were stirred at room temperature for 45 h. The mixture was neutralized with dilute sulphuric acid and ethanol (*ca.* 200 ml) was removed. The mixture was extracted with ether (3 × 100 ml). The organic layers were combined, washed with water (150 ml) and dried ($MgSO_4$). Removal of the solvent gave a yellow solid which on crystallisation from ethanol afforded the *hexenone* (4.53 g, 74%) as fine colourless needles m.p. 96—98 °C (Found: C, 78.1; H, 6.8. $C_{21}H_{22}O_3$ requires C, 78.2; H, 6.9%); $\nu_{max.}$ 1 720 and 1 680 cm^{-1}; δ_H 2.33 (s, MeCO), 2.47 (br dd, $J_{4,5}$ 6.6, $J_{4,3}$ 12.1 Hz, 4-H), 2.90—3.56 (m, 2-H, 3-H), 3.84 (s, OMe), 6.12 (dt, $J_{5,6}$ 15.8, $J_{5,4}$ 6.6 Hz, 5-H), 6.47 (d, $J_{6,5}$ 15.8 Hz, 6-H), 7.29 (s, Ph), and 7.41 (AA′BB′ system, *J* 9.0 Hz, ArH); δ_C 30.2 (q, Me), 34.2 (t, C-4), 39.9 (t, C-2), 47.5 (d, C-3), 55.7 (q, OMe), 126.9 (d, C-5), 133.6 (d, C-6), 114.5, 127.2, 128.1, 129.3, and 131.0 (ArC), 198.0 (s, C-1), and 209.4 p.p.m. (MeCO).

3-(4-*Methoxyphenyl*)-5-[(2E)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1b**).—The above diketone (5.45 g), sodium hydride (61%; 1.23 g), and benzene (200 ml) were heated under a nitrogen atomosphere at 50 °C for 4 h. Ethyl acetate (20 ml) and then water (200 ml) were added cautiously. The mixture was extracted with benzene (3 × 75 ml). The combined organic layers were washed with water (100 ml) and dried ($CaCl_2$). Removal of the solvent afforded a red oil (4.1 g). Flash chromatography (15% ethyl acetate in hexane) yielded the *cyclopentenone* which was crystallised from ethanol to give fine needles (2.2 g, 43%), m.p. 106 °C (Found: C, 82.7; H, 6.5. $C_{21}H_{20}O_2$ requires C, 82.7; H, 6.6%); $\nu_{max.}$ 1 680 cm^{-1}; $\lambda_{max.}$ 316 and 248 nm (log ε 4.32 and 4.18 respectively); δ_H 2.14—3.50 (complex m, 4-H, 5-H, CH_2CH=CHPh), 3.84 (s, OMe) 6.18 (dt, *J* 15.75 and 6.0 Hz, C*H*=CHPh), 6.45 (t, $J_{2,4}$ 1.6 Hz, 2-H), 6.50 (d, *J* 15.75 Hz, CH=C*H*Ph), 7.20—7.40 (m, Ph), and 7.26 (AA′BB′ system, *J* 9.0 Hz, ArH); δ_C 35.1 (t, CH_2CH=CH), 35.4 (t, C-4), 46.4 (d, C-5), 55.3 (OMe), 125.2 (d, C-2), 127.7 (d, CH=CHPh), 128.0 (d, CH=CHPh), 114.9, 126.7, 129.1, 129.3, 132.7 (ArC), 173.8 (s, C-3), and 209.8 (s, C-1).

Ethyl 2-*Acetyl*-2-(4-*methoxybenzoylmethyl*)-5-*phenylpent*-4-*ynoate*.—Ethyl 2-acetyl-4-(4-methoxyphenyl)-4-oxobutanoate (10.0 g) in *N*,*N*-dimethylformamide (50 ml) was added dropwise to a stirred solution of sodium ethoxide [from sodium (0.827 g) in ethanol (50 ml)], at room temperature. 3-Phenylprop-2-ynyl bromide (7.02 g) in *N*,*N*-dimethylformamide (50 ml) was added dropwise and the mixture stirred at room temperature for 3 h. Water (200 ml) was added and the mixture extracted with ether (3 × 100 ml). The combined ether extracts were washed with water (200 ml) and then dried ($MgSO_4$). Removal of the solvent afforded an oil (13.1 g, 93%) which was used without further purification, $\nu_{max.}$ 1 740, 1 715, and 1 680 cm^{-1}; δ_H 1.24 (t, *J* 7.15 Hz, CH_2*Me*), 2.36 (s, MeCO), 3.30 (br, s, 3-H), 3.83 (s, OMe), 3.89 (br s, ArCOCH_2), 4.24 (q, *J* 7.15 Hz, CH_2Me), 7.26 (br s, Ph), and 7.45 (AA′BB′ system, *J* 8.8 Hz, Ar-H).

3-*Acetyl*-1-(4-*methoxyphenyl*)-6-*phenylhex*-5-*yn*-1-*one*.—The above ester (4.08 g), 1% aqueous sodium hydroxide (100 ml), and ethanol (120 ml) were stirred at room temperature for 48 h. The mixture was neutralised with dilute sulphuric acid, water (100 ml) was added and the mixture extracted with ether (3 × 100 ml). The combined ether extracts were washed with water (150 ml) and dried ($MgSO_4$). Removal of the solvent afforded a brown solid. Purification by flash chromatography (12% ethyl acetate in hexane) and recrystallisation yielded the *hexynone* as needles (2.13 g, 64%), m.p. 80—82 °C (Found: C, 78.9; H, 6.2. $C_{21}H_{20}O_3$ requires C, 78.7; H, 6.3%); $\nu_{max.}$ 1 710 and 1 680 cm^{-1}; δ_H 2.40 (s, MeCO), 2.65—2.74 (m, 4-H), 3.21—3.54 (m, 2-H, 3-H), 3.84 (s, OMe), 7.32 (m, Ph), and 7.49 (AA′BB′ system, *J* 9.0 Hz, ArH); δ_C 21.5 (t, C-4), 29.5 (q, Me), 39.5 (t, C-2), 46.2 (d, C-3), 55.2 (MeO), 86.4 (C-5, C-6) 113.7, 127.8, 128.1, 130.2, and 131.5 (ArC), 196.3 (C-1), and 209.4 (MeCO).

3-(4-*Methoxyphenyl*)-5-(3-*phenylprop*-2-*ynyl*)*cyclopent*-2-*en*-1-*one*.—The above diketone (4.1 g), sodium hydride (61%; 0.92 g), and benzene (80 ml) were heated at 50 °C under nitrogen for 5 h. Ethyl acetate (10 ml) and then water (80 ml) were added cautiously. The mixture was extracted with benzene (3 × 50 ml), and the combined organic layers were washed with water (50 ml) and dried ($MgSO_4$). Removal of the solvent afforded a red oil which was purified by flash chromatography (15% ethyl

acetate in hexane), and crystallisation from ethanol, to yield the *cyclopentenone* (2.39 g, 62%) as needles m.p. 97—98 °C (Found: C, 83.3; H, 5.8. $C_{21}H_{18}O_2$ requires C, 83.4; H, 6.0%); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 315 and 250 nm (log ε 4.33 and 4.22 respectively); δ_H 2.67—3.29 (m, 4-H, 5-H, $CH_2C{\equiv}C$), 3.86 (s, OMe), 6.50 (t, $J_{2,4}$ 1.65 Hz, 2-H), 7.18—7.41 (m, Ph), and 7.31 (AA'BB' system, J 9.2 Hz, ArH); δ_C 21.6 ($CH_2C{\equiv}C$), 35.0 (t, C-4), 45.2 (d, C-5), 55.8 (MeO), 82.6 ($CH_2C{\equiv}CPh$), 87.6 ($CH_2C{\equiv}CPh$) 125.4 (d, C-2), 115.2, 128.6, 129.11, 129.6, and 132.6 (ArC), 173.6 (s, C-3), and 209.6 (s, C-1).

3-(4-*Methoxyphenyl*)-5-[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one*-(**2b**).—The above prop-2-ynyl-substituted cyclopentenone (100 mg), Lindlar catalyst (10 mg), quinoline (4 drops), and ethanol (50 ml) were stirred at 0 °C for 4 h under a hydrogen atmosphere, after which time the mixture was filtered through Celite. Removal of the solvent afforded a solid which was recrystallised from ethanol to give the Z-*alkene* as needles (62 mg, 62%), m.p. 97—98 °C (Found: C, 82.9; H, 6.4. $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 316 and 234 nm (log ε 4.40 and 4.15 respectively); δ_H 2.42—3.35 (m, 4-H, 5-H, $CH_2CH{=}CHPh$), 3.85 (s, OMe), 5.65 (dt, J 13.4 and 7.0 Hz, $CH_2CH{=}CHPh$), 6.46 (t, $J_{2,4}$ 2.0 Hz, 2-H), 6.53 (d, J 13.4 Hz, $CH{=}CHPh$), 7.25 (AA'BB', system J 9.0 Hz, ArH), and 7.28 (s, Ph); δ_C 29.9 (t, $CH_2CH{=}CH$), 34.4 (t, C-4), 45.6 (d, C-5), 55.1 (OMe), 124.9 (d, C-2), 128.8 (d, $CH{=}CHPh$), 129.3 (d, $CH{=}CHPh$), 114.4, 126.8, 128.3, 128.9, and 131.2 (ArC), 173.2 (s, C-3), and 211.0 (s, C-1).

Ethyl (4E)-2-*Acetyl*-2-(4-*cyanobenzoylmethyl*)-5-*phenylpent*-4-*enoate*.—Ethyl 2-acetyl-4-(4-cyanophenyl)-4-oxobutanoate (5 g) in *N,N*-dimethylformamide (50 ml) was added dropwise to a stirred solution of sodium ethoxide [from sodium (440 mg) and dry ethanol (50 ml)] at room temperature. Cinnamyl bromide (3.16 g) in *N,N*-dimethylformamide (50 ml) was then added, and the mixture was stirred for 2 h. Water (200 ml) was added and the mixture was extracted with ether (3 × 50 ml). The combined ether layers were washed with water and dried. Removal of the solvent and chromatography of the residue on silica gave *ethyl* (4E)-2-*acetyl* 2-(4-*cyanobenzoylmethyl*)-5-*phenylpent*-4-*enoate* (7 g, 98%) m.p. 86—88 °C (Found: C, 74.3; H, 5.6. $C_{24}H_{23}NO_4$ requires C, 74.0; H, 5.95%); $\nu_{max.}$ 2 220, 1 730, 1 710, and 1 690 cm^{-1}; δ_H 1.26 (t, J 7.2 Hz, CH_2Me), 2.40 (s, MeCO), 2.93—3.04 (m, 3-H), 3.65 (s, $PhCOCH_2$), 4.25 (q, J 7.2 Hz, CH_2Me), 5.93 (dt, J 15.6 and 7.1 Hz, 4-H), 6.37 (d, J 15.6 Hz, 5-H), and 7.23—7.75 (m, ArH).

(5E)-3-*Acetyl*-1-(4-*cyanophenyl*)-6-*phenylhex*-5-*en*-1-*one*.—The above ester (3.1 g), 1% aqueous sodium hydroxide (62 ml), and ethanol (310 ml) were set aside for 3 h. The mixture was acidified, diluted with water and extracted with ether (3 × 100 ml). The combined ether layers were washed with water and dried ($MgSO_4$). Removal of the solvent gave the diketone as an oil (2.2 g, 87%) which was used without further purification, $\nu_{max.}$ 2 220, 1 710, and 1 690 cm^{-1}; δ_H 2.34 (s, MeCO), 2.13—3.72 (m, 2-H, 3-H, and 4-H), 6.07 (dt, J 16.0 and 7.0 Hz, 5-H), 6.45 (d, J 16.0 Hz, 6-H), 7.29 (m, Ph), and 7.85 (AA'BB' system, C_6H_4CN-*p*).

3-(4-*Cyanophenyl*)-3-[(2E)-5-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1c**).—The crude diketone (2.1 g), sodium hydride (2 g), and benzene (100 ml), were refluxed under nitrogen for 36 h. Water was added carefully and the organic layer separated. The aqueous layer was extracted with ether, and the combined organic layers were dried ($MgSO_4$). Removal of the solvent followed by column chromatography gave 3-(4-*cyanophenyl*)-5-[(2*E*)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1c**) (970 mg, 50%), m.p. 110—111 °C (Found: C, 83.8; H, 6.1. $C_{21}H_{17}NO$ requires C, 84.2; H, 5.7%); $\nu_{max.}$ 2 200 and 1 695 cm^{-1}; $\lambda_{max.}$ 259 and 290 nm (log ε 4.03 and 4.15 respectively); δ_H 2.21—3.44 (m, 4-H, 5-H, $CH_2CH{=}CH$), 6.15 (dt, J 16.0 and 6.2 Hz, $CH_2CH{=}CH$), 6.51 (d, J 16.0 Hz, $CH_2CH{=}CH$), 6.61 (m, 2-H), 7.29 (m, Ph), and 7.72 (s, C_6H_4CN-*p*).

Ethyl 2-*Acetyl*-2-(4-*cyanobenzoylmethyl*)-5-*phenylpent*-4-*ynoate*.—Ethyl 2-acetyl-4-(4-cyanophenyl)-4-oxobutanoate (7.91 g) in ethanol (360 ml), and *N,N*-dimethylformamide (40 ml) was added dropwise to a stirred, ice-cooled solution of sodium ethoxide [from sodium (667 mg) in ethanol (200 ml)]. 3-Phenylprop-2-ynyl bromide (5.65 g) in ethanol (100 ml) was added and the mixture stirred at room temperature for 24 h. Ethanol was removed (*ca.* 250 ml), water (200 ml) added, and the mixture was extracted with ether (3 × 150 ml). The combined ether layers were washed with water and dried ($MgSO_4$). Removal of the solvent afforded a red oil (10.06 g) which was purified by flash chromatography (17% ethyl acetate in hexane), to yield a yellow oil (4.82 g, 43%), $\nu_{max.}$ 2 210, 1 735, 1 720, and 1 690 cm^{-1}; δ_H 1.25 (t, J 7.15 Hz, CH_2Me), 2.38 (s, MeCO), 3.29 (br s, 3-H), 3.87 (br s, $COCH_2$), 4.25 (q, J 7.15 Hz, CH_2Me), 7.27 (s, Ph), and 7.92 (AA'BB' system, J 8.6 Hz, ArH).

3-*Acetyl*-1-(4-*cyanophenyl*)-6-*phenylhex*-5-*yn*-1-*one*.—Ethyl 2-acetyl-2-(4-cyanobenzoylmethyl)-5-phenylpent-4-ynoate (2.81 g), ethanol (300 ml), and 1% aqueous sodium hydroxide (250 ml) were stirred for 20 min and then neutralised with dilute sulphuric acid. Water (150 ml) was added and the mixture was extracted into ether (3 × 100 ml). The combined ether extracts were washed with water and dried ($MgSO_4$), and removal of the solvent afforded a yellow oil which was purified by flash chromatography (18% ethyl acetate in hexane). The *hexynedione* (1.6 g, 70%) was recrystallised from ethanol, m.p. 96 °C (Found: C, 80.3; H, 5.6; N, 4.4. $C_{21}H_{17}NO_2$ requires C, 80.0; H, 5.4; N, 4.4%); $\nu_{max.}$ 2 250, 1 720, and 1 695 cm^{-1}; δ_H 2.41 (s, MeCO), 2.72—2.79 (m, 4-H), 3.28—3.74 (m, 2-H, 3-H), 7.26—7.36 (m, Ph), and 7.91 (AA'BB' system, J 8.5 Hz, ArH).

3-(4-*Cyanophenyl*)-5-(3-*phenylprop*-2-*ynyl*)*cyclopent*-2-*en*-1-*one*.—The above diketone (2.7 g), sodium hydride (61%; 2.7 g), and benzene (150 ml), were refluxed under nitrogen for 15 h. Ethyl acetate (15 ml) and then water (200 ml) were added cautiously. The mixture was extracted with benzene (3 × 50 ml) and the combined organic layers washed with water and dried ($CaCl_2$). Removal of the solvent afforded a red oil. Purification by flash chromatography (25% ethyl acetate in hexane) afforded 3-(4-*cyanophenyl*)-5-(3-*phenylprop*-2-*ynyl*)*cyclopent*-2-*en*-1-*one* (1.6 g, 63%) m.p. 133—134 °C (Found: C, 84.5; H, 5.2; N, 4.6. $C_{21}H_{15}NO$ requires C, 84.8; H, 5.1; N, 4.6%); $\nu_{max.}$ 2 200 and 1 690 cm^{-1}; $\lambda_{max.}$ 289 and 249 nm (log ε 4.5 and 4.41 respectively); δ_H 2.75—3.28 (m, 4-H, 5-H, $CH_2C{\equiv}C$), 6.67 (t, $J_{2,4}$ 2.0 Hz 2-H), 7.26 (br s, Ph), and 7.76 (br s, ArH); δ_C 21.3 (t, $CH_2C{\equiv}C$), 34.7 (t, C-4), 45.1 (d, C-5), 86.4 (s, $C{\equiv}C$), 114.6 ($C{\equiv}N$), 127.5 (C-2), 128.0, 128.4, 129.4, 131.8, and 132.8 (ArC), 173.1 (s, C-3), and 208.2 (s, C-1).

3-(4-*Cyanophenyl*)-5-[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**2c**).—The above propynyl-substituted cyclopentenone (250 mg), ethanol (300 ml), and Lindlar catalyst (50 mg) were stirred at 0 °C for 4 h under a hydrogen atmosphere, after which time the mixture was passed through a Celite layer. Removal of the solvent afforded the 3-(4-*cyanophenyl*)-5-[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (250 mg, 99%), m.p. 132—133 °C (Found: C, 84.4; H, 5.4; N, 4.5. $C_{21}H_{17}NO$ requires C, 84.3; H, 5.7; N, 4.7%); $\nu_{max.}$ 2 200 and 1 690 cm^{-1}; $\lambda_{max.}$ 288 and 245 nm (log ε 4.41 and 4.20 respectively); δ_H 2.86—3.13 (m, 4-H, 5-H, $CH_2CH{=}CHPh$), 5.64 (dt, J 7.4 and 11.8 Hz, $CH{=}CHPh$),

6.57 (d, J 11.8 Hz, CH=C*H*Ph), 6.64 (t, $J_{2,4}$ 1.4 Hz, 2-H), 7.27—7.35 (m, Ph), and 7.70—7.72 (m, ArH).

Photolysis Experiments

Photolysis of 3-*phenyl*-5-[(2E)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one*.—(*a*) The above ketone (5 mg) in [$^2H_6$]-benzene (1 ml) was placed in an n.m.r. tube and irradiated for 1 h. The n.m.r. spectrum of the resulting mixture showed that it consisted of an approximately 1:1 mixture of *E* and *Z*-ketones, (**1a**) and (**2a**) with very little (0.5%) cycloaddition product.

(*b*) The above *E*-ketone (780 mg) in dry benzene was irradiated for 6 h. Removal of the solvent afforded, after chromatography, the cyclobutanecarbaldehyde (**6a**) (190 mg, 24%) (see below), 4-exo, 6-*diphenyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one* (**4a**) as an oil (90 mg, 20%) characterised as the 2,4-*dinitrophenylhydrazone*, m.p. >210 °C (Found: C, 68.6; H, 4.7; N, 12.0. $C_{26}H_{22}N_4O_4$ requires C, 68.7; H, 4.9; N, 12.3%). The ketone gave $\nu_{max.}$ 1 740 cm^{-1}; δ_H 1.91 (br s, 7-H), 2.27 (m, 8-H), 2.73—3.34 (m, 1-H, 3-H, 4-H, 5-H), and 7.00—7.12 (Ph); and 4-endo, 6-*diphenyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one* (**3a**) (300 mg, 38%) m.p. 106—107 °C (Found: C, 87.5; H, 6.65. $C_{20}H_{12}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 740 cm^{-1}; δ_H 2.05 (br s, 7-H), 2.15 (br s, 8-H), 2.75 (br s, 1-H), 3.25 (m, 3-H, 5-H), 4.17 (t, J 7.0 Hz, 4-H), and 7.1—7.6 (m, ArH).

(*c*) 3-Phenyl-5-[(2*E*)-3-phenylprop-2-enyl]cyclopent-2-en-1-one (400 mg) in benzene (400 ml) was irradiated for 8 h. The solvent was removed and the residue chromatographed on silica gel to give, in order, 5-endo, 7-*diphenyl*-2-*oxabicyclo*[4.2.1]-*nona*-3,7-*diene* (**7a**) (80 mg, 20%) as an oil, b.p. 105 °C/0.5 mmHg (Found: C, 87.65; H, 6.7. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 650 cm^{-1}; δ_H 2.06—2.18 (m, 2-H, 9-H), 3.42 (m, 6-H), 3.92 (m, 5-H), 4.17 (ddd, J 8.4, 5.1, 1.1 Hz, 4-H), 5.16 (m, 1-H), 6.04 (dd, J 8.4, 1.5 Hz, 3-H), 6.09 (d, J 2.9 Hz, 8-H), and 7.33 (m, ArH); this was followed by 1,6-*exo*-diphenylbicyclo-[3.2.0]hept-2-ene-7-*endo*-carbaldehyde (**6a**) (25 mg, 6%) as an oil, $\nu_{max.}$ 1 720 cm^{-1}; δ_H 2.55 (d, J 16.5 Hz, 4-*endo*-H), 2.88 (ddt, J 16.5, 6.6 and 2.0 Hz, 4-*exo*-H), 3.18 (t, J 6.6 Hz, 5-H), 3.60 (dd, J 9.0, 6.6 Hz, 6-H), 3.75 (dd, J 9.0, 1.4 Hz, 7-H), 5.95 (m, 2-H, 3-H), 7.29 (m, ArH), and 9.96 (d, J 1.4 Hz, CHO); and 4-*endo*, 6-diphenyltricyclo[3.2.1.0^{3,6}]octan-2-one (**3a**) (250 mg, 62%), m.p. 106—107 °C.

Photolysis of 3-*Phenyl*-5-[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**2a**).—The *Z*-isomer (5 mg) in [$^2H_6$]benzene (1 ml) was placed in an n.m.r. tube and irradiated for 20 min. The ^1H n.m.r. spectrum of the product showed that the resulting mixture was a 1:1 mixture of the *E*- and *Z*-ketones, (**1a**) and (**2a**) with very little (0.5%) cycloaddition product.

5-exo, 6-*Diphenylbicyclo*[3.2.1]*oct*-6-*en*-2-*one* (**9a**).—The 4-*endo*-phenyl ketone (**4a**) (400 mg), freshly distilled boron trifluoride–diethyl ether (4 ml) and dry dichloromethane (25 ml) were refluxed for 6 h. The reaction mixture was cooled, and was washed with 10% aqueous sodium hydrogen carbonate and water. The organic layer was dried ($MgSO_4$), and removal of the solvent and chromatography of the residue over silica afforded 4-exo, 6-*diphenylbicyclo*[3.2.1]*oct*-6-*en*-2-*one* (**9a**) (250 mg, 62%), b.p. 122 °C/0.5 mmHg (Found: C, 87.7; H, 6.6. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%); $\nu_{max.}$ 1 710 cm^{-1}; δ_H 2.31 (m, 8-H), 2.64 (dd, J 17.2, 3.0 Hz, 3-*endo*-H), 3.03 (dd, J 17.2, 8.8 Hz, 3-*exo*-H), 3.29—3.35 (m, 1-H, 5-H), 3.55 (br d, J 8.8 Hz, 4-H), 6.25 (d, J 3.0 Hz, 7-H), and 7.1—7.5 (m, ArH); δ_C 36.5 (t, C-8), 40.5 (t, C-3), 40.9 (d, C-4), 47.1 (d, C-5), 56.1 (d, C-1), 125.4 (d, C-7), 150.3 (s, C-6), and 209.1 (s, C-2).

When this ketone (100 mg) in dioxane (4 ml), and a solution of sodium methoxide [from sodium (20 mg)] in monodeuteriomethanol (4 ml) and dioxane (4 ml) were refluxed for 6 h, the product was the 3-[3,3-$^2H_2$]ketone, δ_H 2.31 (m, 8-H), 3.29—3.35 (m, 1-H, 5-H), 2.53 (br s, 4-H), 6.25 (d, 3.0 Hz, 7-H), and 7.2—7.7 (m, ArH). The ^{13}C spectrum lacks the peak at δ_C 40.5.

Photolysis of 3-(4-*methoxyphenyl*)-5-[(2E)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1b**).—(*a*) The 3-methoxyphenyl ketone (5 mg) in [$^2H_6$]benzene (1 ml) was placed in an n.m.r. tube, and irradiated for 1 h. The n.m.r. spectrum of the resulting mixture showed that it consisted of the *E*- and *Z*-cinnamyl ketones in the ratio 1:1.

(*b*) 3-(4-methoxyphenyl)-5-[(2*E*)-3-phenylprop-2-enyl]cyclopent-2-en-1-one (400 mg) in benzene (500 ml) was irradiated for 20 h. Removal of the solvent and chromatography of the residue on silica gel afforded 6-(4-*methoxyphenyl*)-4-endo-*phenyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one* (**4b**) (160 mg, 40%), m.p. 98—100 °C (Found: C, 82.8; H, 6.5. $C_{21}H_{22}O_2$ requires C, 82.9; H, 6.6%); $\nu_{max.}$ 1 740 cm^{-1}; δ_H 1.92 (m, 7-H), 2.06 (m, 8-H), 2.72 (m, 1-H), 3.1—3.29 (m, 3-H, 5-H), 3.79 (s, OMe), 4.13 (t, J 7.0 Hz, 4-H), and 7.0—7.4 (m, ArH); this was followed by 6-(4-*methoxyphenyl*)-4-exo-*phenyltricyclo*[3.2.1.0^{3,6}]*octan*-2-*one* (**3b**) (160 mg, 40%), b.p. 115 °C/0.5 mmHg (Found: C, 82.9; H, 6.6%); $\nu_{max.}$ 1 740 cm^{-1}; δ_H 1.83 (m, 1-, 3-, 4-*endo*-, 5-H), 3.68 (s, OMe), and 7.0—7.3 (m, ArH).

Photolysis of 3-(4-*Methoxyphenyl*)-5[(2Z)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**2b**).—(*a*) The *Z*-isomer (**2b**) (5 mg) in [$^2H_6$]benzene was irradiated for 1 h in an n.m.r. tube. The n.m.r. of the resulting mixture showed that it contained the *E*- and *Z*- isomers in the ratio 1:1.

(*b*) 3-(4-methoxyphenyl)-5-[(2*Z*)-(3-phenylprop-2-enyl]-cyclopent-2-en-1-one (500 mg) in benzene (500 ml) was irradiated for 15.5 h. Removal of the solvent and flash chromatography of the residue (8% ethyl acetate in hexane) afforded 6-(4-methoxyphenyl)-4-*endo*-phenyltricyclo[3.2.1.0^{3,6}]octan-2-one (**4b**), (180 mg, 36%) followed by 6-(4-methoxyphenyl)-4-*exo* phenyltricyclo[3.2.1.0^{3,6}]octan-2-one (**3b**), (175 mg, 35%). Both compounds were identified by m.p., mixed m.p., or b.p. and by their i.r. and ^1H and ^{13}C n.m.r. spectroscopic properties.

Reaction of 6-(4-*Methoxyphenyl*)-4-endo-*phenyltricyclo*-[3.2.1.0^{3,6}]*octan*-2-*one with Boron Trifluoride–Diethyl Ether*.—The *endo*-phenyl ketone (100 mg), freshly distilled boron trifluoride–diethyl ether (1 ml), and dry dichloromethane (10 ml) were refluxed for 6 h. The mixture was cooled, washed with 10% aqueous sodium hydrogen carbonate and water, and then dried. Removal of the solvent, and chromatography of the residue over silica gel afforded 6-(4-*methoxyphenyl*)-4-exo-*phenylbicyclo*[3.2.1]*oct*-6-*en*-2-*one* (**9b**) (40 mg, 40%) as an oil (Found: C, 82.6; H, 6.5. $C_{21}H_{22}O_2$ requires C, 82.9; H, 6.6%); $\nu_{max.}$ 1 710 cm^{-1}; δ_H 2.34 (m, 8-H), 2.80 (dd, J 17.2, 2.5 Hz, 3-*endo*-H), 3.03 (dd, J 17.2, 8.8 Hz, 3-*exo*-H), 3.15 (m, 1-H, 5-H), 3.55 (br d, J 8.8 Hz, 4-H), 3.80 (s, OMe), 6.23 (d, J 3.1 Hz, 7-H), and 7.0—7.6 (m, ArH).

Reaction of 6-(4-*Methoxyphenyl*)-4-exo-*phenyltricyclo*-[3.2.1.0^{3,6}]*octan*-2-*one with Boron Trifluoride–Diethyl Ether*.—The *exo*-phenyl ketone (100 mg), freshly distilled boron trifluoride–diethyl ether (1 ml), and dichloromethane (10 ml) were refluxed for 6 h. The mixture was cooled, washed with 10% aqueous sodium hydrogen carbonate and water, and then dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on silica gel afforded 6-(4-*methoxyphenyl*)-4-endo-*phenylbicyclo*[3.2.1]*oct*-6-*en*-2-*one* (**8b**) (40 mg, 40%) as an oil (Found: C, 82.6; H, 6.55. $C_{21}H_{22}O_2$ requires C, 82.9; H, 6.6%); $\nu_{max.}$ 1 710 cm^{-1}; δ_H 2.58 (d, J 10.6 Hz, 8-*endo*-H), 2.65 (m, 3-*endo*- and 8-*exo*-H), 3.37 (m, 4-H, 5-H), 3.71 (s, OMe), 6.3 (d, J 3.3 Hz, 7-H), and 7.0—7.6 (m, ArH).

Photolysis of 3-(4-*Cyanophenyl*)-5-[(2E)-3-*phenylprop*-2-*enyl*]*cyclopent*-2-*en*-1-*one* (**1c**).—The *E*-isomer (1.5 g) in benzene (500 ml) was irradiated for 4 h. The solvent was removed and the residue chromatographed on silica gel to give, in order, 6-(4-*cyanophenyl*)-4-endo-*phenyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (**4c**) (130 mg, 9%) m.p. 102—105 °C (Found: C, 84.65; H, 5.8. $C_{21}H_{17}NO$ requires C, 84.25; H, 5.7%); $\nu_{max.}$ 2 220 and 1 740 cm^{-1}; δ_H 2.0 (m, 7-H), 2.14 (m, 8-H), 2.8 (m, 1-H), 3.14 (dd, *J* 1.0 Hz, 4-*exo*-H), and 7.28—7.66 (m, ArH); this was followed by 6-(4-*cyanophenyl*)-4-exo-*phenyltricyclo*[3.2.1.$0^{3,6}$]*octan*-2-*one* (**3c**) (800 mg, 53%) characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 218—220 °C (Found: C, 67.25; H, 4.3. $C_{27}H_{21}N_5O_4$ requires C, 67.6; H, 4.4%); $\nu_{max.}$ (of ketone) 2 215 and 1 740 cm^{-1}; δ_H 1.91 (s, 7-H), 2.28—2.54 (m, 8-H), 3.05—3.55 (m, 1-, 3-, 4-*endo*-, and 5-H), and 6.97—7.2 (m, ArH).

Photolysis of 3-(4-*Cyanophenyl*)-5-[(2Z)-*phenylprop*-2-*enyl*]-*cyclopent*-2-*en*-1-*one* (**1c**).—(*a*) The *Z*-isomer (5 mg) in [$^2H_6$]-benzene (1 ml) was irradiated in an n.m.r. tube for 20 min. The n.m.r. spectrum of the resulting solution only showed the presence of the *E*-isomer.

(*b*) The *Z*-isomer (240 mg) in benzene (500 ml) was irradiated for 11.5 h. Removal of the solvent and flash chromatography of the residue (16% ethyl acetate in hexane) afforded the cyclobutanecarbaldehyde (**6c**) (50 mg, 21%), 6-(4-cyanophenyl)-4-*endo*-phenyltricyclo[3.2.1.$0^{3,6}$]octan-2-one (**4c**) (56 mg, 23%), followed by 6-(4-cyanophenyl)-4-*exo*-phenyltricyclo-[3.2.1.$0^{3,6}$]octan-2-one (**3c**), (76 mg, 32%). Both compounds were identified by m.p., mixed m.p., or b.p. and by their i.r. and ^1H n.m.r. spectroscopic properties.

Photolysis of 6-(4-*cyanophenyl*)-4-exo-*phenyltricyclo*-[3.2.1.$0^{3,6}$]*octan*-2-*one* (**3c**).—The tricyclic ketone (300 mg) in benzene (500 ml) was irradiated for 16 h. The solvent was removed and the product chromatographed to afford 1-(4-cyanophenyl)-6-*exo*-phenylbicyclo[3.2.0]hept-2-ene-7-*endo*-carbaldehyde, (60 mg, 20%), $\nu_{max.}$ 2 220 and 1 710 cm^{-1}; δ_H 2.59 (br d, *J* 16.0 Hz, 4-*endo*-H), 2.95 (ddt, *J* 16.0, 6.2, 1.0 Hz, 4-*exo*-H), 3.18 (br t, *J* 6.2, 6.0 Hz, 5-H), 3.48—3.79 (m, 6-H, 7-H), 5.93 (m, 3-H), 6.03 (m, 2-H), 7.27—7.49 (m, ArH), and 9.93 (d, *J* 1.5 Hz, CHO). Under the same conditions the 4-*endo*-phenyl isomer (**4c**) gave less than 4% aldehyde, as determined by n.m.r. spectroscopy.

Reaction of 6-(4-*Cyanophenyl*)-4-endo-*phenyltricyclo*-[3.2.1.$0^{3,6}$]*octan*-2-*one with Boron Trifluoride–Diethyl Ether*.—The tricyclic ketone (**4c**) (130 mg), freshly distilled boron trifluoride–diethyl ether (2 ml) and dichloromethane (12 ml) were refluxed for 48 h. The mixture was cooled, washed with 10% aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of the solvent, and chromatography of the residue on silica afforded, in order 6-(4-cyanophenyl)-4-*exo*-phenylbicyclo[3.2.1]oct-6-en-2-one (**9c**) (30 mg, 23%); $\nu_{max.}$ 2 230 and 1 710 cm^{-1}; δ_H 2.37 (m, 8-H), 2.63 (dd, *J* 17.2, 3.0 Hz, 3-*endo*-H), 3.06 (dd, *J* 17.2, 8.4 Hz, 3-*exo*-H), 3.35 (m, 1-H, 5-H), 3.50 (br d, *J* 8.4 Hz, 4-H), 6.58 (d, *J* 3.3 Hz, 7-H), and 7.31—7.68 (ArH); this was followed by 6-*exo*-(4-cyanophenyl)-4-phenylbicyclo[3.2.1]oct-3-en-2-one (**10**) (20 mg, 15%), $\nu_{max.}$ 2 230 and 1 665 cm^{-1}; δ_H 2.24—2.37 (m, 7-H, 8-H), 3.14—3.53 (m, 1-H, 5-H, 6-H), 6.42 (t, *J* 1.3 Hz, 3-H), and 6.96—7.74 (m, ArH).

Reaction of 6-(4-*Cyanophenyl*)-4-exo-*phenyltricyclo*-[3.2.1.$0^{3,6}$]*octan*-2-*one with Boron Trifluoride–Diethyl Ether*.—The *exo*-tricyclic ketone (170 mg), freshly distilled boron trifluoride–diethyl ether (1.5 ml) and dichloromethane (12 ml) were refluxed for 24 h. Work-up as above afforded the *E*-alkene (**1c**) (10 mg, 6%) identified by m.p., mixed m.p., and its n.m.r. spectrum.

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