Condensed Cyclic and Bridged-ring Systems. Part IV.[1] Stereochemically Controlled Synthesis of Some *endo*-2-Aryl-6-oxobicyclo[3.2.1]octanes and Related Compounds through Intramolecular Alkylations of γδ-Unsaturated α′-Diazomethyl Ketones

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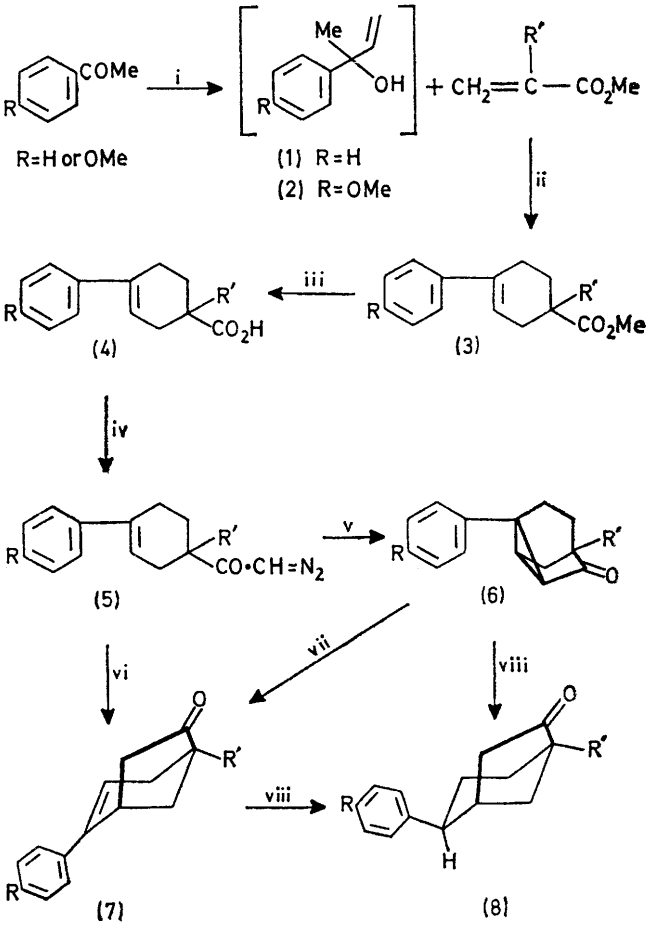
The 4-arylcyclohex-3-enecarboxylic acids (4a—d), prepared through a modified Diels–Alder reaction, have been converted *via* the corresponding diazomethyl ketones (5a—d) into cyclopropyl ketones (6a—d) and the 2-aryl-6-oxobicyclo[3.2.1]oct-2-ene derivatives (7a—d), by oxo-carbenoid addition and boron trifluoride–ether-catalysed cyclisation, respectively, in excellent yields. In addition to the unsaturated ketones (7a and c), the hydroxy-ketones (10a and c) were also obtained in the aqueous tetrafluoroboric acid-catalysed cyclisation of the diazoketones (5a and c). Catalytic reduction of the cyclopropyl ketones and the unsaturated ketones produced the *endo*-2-aryl-6-oxobicyclo[3.2.1]octane derivatives (8a—d) exclusively.

We have previously reported [2] two simple routes to the bicyclo[3.2.1]octan-6-one unit, fused within reduced fluorene and phenanthrene systems, *via* intramolecular alkylations [3,4] of γδ-unsaturated α′-diazomethyl ketones. We describe here the preparation of some *endo*-2-aryl-6-oxobicyclo[3.2.1]octanes (8a—d) and related compounds, as preliminary steps towards the synthesis of simple analogues of gibberellins [5] (Scheme 1).

Diels–Alder reactions of the dienes generated from the crude carbinols (1) and (2), prepared from the appropriate aryl methyl ketones through a modified route [2c] (see Experimental section), with methyl acrylate in benzene in the presence of catalytic amounts of iodine, hydroquinone, and quinoline afforded crystalline ester adducts. Saponification of these esters gave the corresponding known acids (4a) [6] and (4b) [7] in *ca.* 50% yield, based on the starting ketones. Similarly the reactions of the carbinols (1) and (2) with methyl methacrylate produced the corresponding ester adducts, which on saponification yielded the respective acids (4c and d) as the only isolable products in *ca.* 45% overall yield. Repeating the Diels–Alder reaction in toluene or xylene produced considerable amounts of high-boiling products with little improvement in the yields of the desired ester adducts. The high regioselectivities observed in these [$_{\pi}4 + _{\pi}2$] cycloadditions,[8] in contrast to other systems [2c,9] are notable.

The diazo-ketones (5a—d), derived from the respective acids in the usual manner,[2] underwent smooth intramolecular oxo-carbenoid addition by thermal decomposition in the presence of ' activated CuO catalyst ' [2b]



(3)–(8) a; R=H, R′=H
b; R=OMe, R′=H
c; R=H, R′=Me
d; R=OMe, R′=Me

SCHEME 1 Reagents: i, CH_2:CHMgBr–THF; ii, quinoline–hydroquinone–I_2–benzene; iii, KOH–H_2O (ethanol or ethylene glycol); iv, NaOEt–EtOH, $(COCl)_2$–pyridine–benzene, CH_2N_2–Et_2O–Et_3N; v, ' activated CuO '–cyclohexane–THF(*hν*); vi, BF_3–Et_2O–$ClCH_2$·CH_2Cl; vii, HCl–$CHCl_3$; viii, Pd–C(10%) in EtOH

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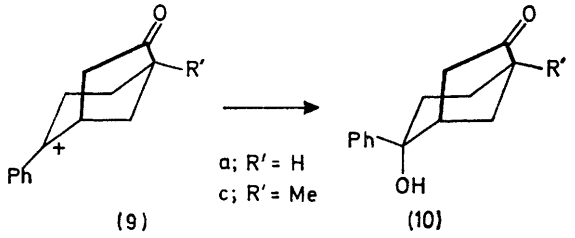
under irradiation with tungsten lamps to afford the cyclopropyl ketones (6a—d) in high yields. Thermal decompositions [2] of the diazoketones with ' activated CuO catalyst ' in the absence of light or with anhydrous copper sulphate gave the cyclopropyl ketones in lower yields. Fragmentations [2] of the cyclopropyl ketones (6a—d) by treatment with dry hydrogen chloride in chloroform produced the corresponding styrenoid ketones (7a—d) in excellent yields. These were also obtained in high yields by direct boron trifluoride–ether-catalysed cyclisation of the diazo-ketones. When aqueous tetrafluoroboric acid in nitromethane was used as the cyclisation reagent, the diazo-ketones (5a and c) afforded a mixture, from which careful chromatographic separation on basic alumina gave the unsaturated ketones (7a and c) in 30 and 26% yields, respectively, along with the corresponding hydroxy-ketones (10a and c) in 21 and 18% yields. The hydroxy-ketones were identified from the spectral and analytical data. Their stereochemistry has been tentatively assigned from the mode of their formation, evidently from the intermediate cations (9a and c) through nucleophilic attack of water from the less hindered *exo*-face.[10]



SCHEME 2

In accord with our previous findings [2] with similar systems, high stereo- and regio-selectivity was observed in the catalytic hydrogenolysis of the cyclopropyl ketones (6a—d) over palladium–charcoal (10%) in ethanol, to produce the *endo*-2-aryl ketones (8a—d) in high yields as the only isolable products. Catalytic hydrogenation of the unsaturated ketones (7a—d) under similar conditions again produced only the respective *endo*-aryl ketones (8a—d) in high yields. The stereochemistry of these ketones was assigned by analogy with similar systems.[2] Further transformations of some of these bridged ketones towards B-seco-gibberellin models are being pursued.

EXPERIMENTAL

The compounds described are racemic forms. M.p.s were taken for samples in open capillaries in a sulphuric acid bath. The homogeneity of all compounds was checked by t.l.c. on silica gel G (Merck) (*ca.* 0.2 mm). Spots were located by exposing the dried plates to iodine vapour. U.v. spectra were determined for solutions in 95% ethanol with a Beckmann DU spectrometer, and i.r. spectra for solutions in chloroform with a Perkin-Elmer 21 spectrometer (by Mr. A. Ghosal). 60 MHz ^{1}H N.m.r. spectra were recorded with a Varian T-60A instrument for solutions in CCl_4 with tetramethylsilane as internal standard. Analyses were carried out by Mrs. C. Dutta, of this laboratory. Petroleum refers to the fraction of b.p. 60—80°.

Vinyl Bromide.—A solution of vinyl bromide in dry tetrahydrofuran (THF) was prepared by the following modification of the methods of Kogermann [11] and Schick *et al.*[12] 1,2-Dibromoethane (194 g, 1.03 mol) was added dropwise to a stirred solution of potassium hydroxide (120 g, 2.14 mol) in water (62 ml) and ethylene glycol (115 ml) maintained at 65—75 °C. The generated vinyl bromide gas was dried over fused calcium chloride and phosphorus pentaoxide and was condensed into dry THF (115 ml) cooled in an ice–salt bath (*ca.* 80—90% yield). This solution was used directly for the preparation of the Grignard reagent; it could be preserved at 0 °C for several weeks.

4-Phenylcyclohex-3-enecarboxylic Acid (4a).—Vinylmagnesium bromide was prepared through the following modified procedure (*cf.* ref. 13). A stirred suspension of magnesium turnings (16 g, 0.67 g atom) in dry THF (80 ml) containing a crystal of iodine was externally warmed at 60—65° under nitrogen and treated with a few drops of methyl iodide. The aforementioned vinyl bromide solution [from 1,2-dibromoethane (194 g)] was then added dropwise. Soon a vigorous reaction commenced, the heating source was removed, and the addition rate was adjusted so that gentle refluxing was maintained. When the addition was complete (*ca.* 40 min) the stirred mixture was refluxed for 1 h and cooled in an ice-bath, and to it a solution of acetophenone (60 g, 0.5 mol) in dry THF (50 ml) was added during 1 h. The mixture was stirred at 25 °C for 2 h, refluxed for 2 h, and left overnight. The THF was recovered (the recovered THF can be reused after distillation over lithium aluminium hydride) by distillation on a steam-bath. The complex was chilled in ice, treated with benzene (100 ml), and decomposed with ice-cold aqueous ammonium chloride. The organic layer was separated and the aqueous layer was repeatedly extracted with benzene (4 × 100 ml). The combined extracts were washed with water and dried (Na_2SO_4). A small portion of the solution was evaporated under reduced pressure to afford a pale yellow oil, $\nu_{max.}$ 3 450br cm^{-1} (OH) (no C=O band).

The benzene solution of the carbinol (1) was refluxed for 9 h with freshly distilled methyl acrylate (86 g, 1 mol), iodine (2 crystals), quinoline (0.5 ml), and hydroquinone (30 mg) under a Dean–Stark water separator. The cooled mixture was washed with water, aqueous 5% sodium thiosulphate, aqueous 5% sodium carbonate, and water again, dried (Na_2SO_4), and concentrated *in vacuo*, and the residual oil was distilled to afford the ester adduct (3a) (65 g), b.p. 133—135° at 0.2 mmHg, as an oil which solidified, m.p. 58° (lit.,[6] 58°); $\lambda_{max.}$ 247 nm (log ε 4.1); $\nu_{max.}$ 1 725s and 1 600w cm^{-1}; δ 2.67 (7 H, m), 3.65 (3 H, s), 6.0br (1 H, t), and 7.2br (5 H, s). A mixture of the ester (3a) (65 g), potassium hydroxide (60 g), water (80 ml), and ethanol (520 ml) was refluxed for 5 h under nitrogen. The solution was diluted with water (150 ml) and most of the alcohol was distilled off. After removal of the neutral matter the aqueous layer was acidified in the cold with hydrochloric acid (6N). The separated acid was extracted with ether and the extract was washed with brine, dried, and evaporated. The residual solid (52.5 g) on two recrystallisations from 95% ethanol

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afforded the pure acid (4a) (49.8 g, overall yield 50% based on acetophenone), m.p. 155—156° (lit.,[6] 155—156°), $\lambda_{max.}$ 247 nm (log ε 4.19), $\nu_{max.}$ 1 700s and 1 600m cm^{-1}.

1-Methyl-4-phenylcyclohex-3-enecarboxylic Acid (4c).—The carbinol (1) prepared from acetophenone (60 g), on Diels–Alder reaction with methyl methacrylate (100 g, 1 mol) under the above conditions, afforded an ester adduct (64.7 g), b.p. 135—140° at 0.2 mmHg, $\lambda_{max.}$ 247 nm (log ε 4.15), $\nu_{max.}$ 1 725s and 1 600w cm^{-1}; the ^1H n.m.r. spectrum showed the Me and CO_2Me singlets δ 1.20 and 3.58 due to the ester (3c) along with very weak singlets at δ 1.13 and 3.66, possibly due to the isomeric ester (*ca.* 5—7%). The ester (3c) (64.6 g) was saponified by refluxing for 5 h with potassium hydroxide (60 g) in water (80 ml) and ethylene glycol (520 ml) under nitrogen. The usual work-up and recrystallisation from aqueous ethanol gave the *acid* (4c) (48.6 g, 45% based on acetophenone), m.p. 136°, $\lambda_{max.}$ 247 nm (log ε 4.2), $\nu_{max.}$ 1 700 cm^{-1} (Found: C, 77.7; H, 7.5. $C_{14}H_{16}O_2$ requires C, 77.8, H, 7.5%).

4-(p-Methoxyphenyl)cyclohex-3-enecarboxylic Acid (4b).—*p*-Methoxyacetophenone (75 g, 0.5 mol) was treated with a solution of vinylmagnesium bromide [from magnesium (16 g, 0.67 g atom)] in THF as described above and the resulting carbinol (2) was treated with methyl acrylate (86 g, 1 mol) as before. The crude crystalline adduct, on recrystallisation once from benzene–petroleum, afforded the ester (3b) (69.4 g), m.p. 114°, $\lambda_{max.}$ 254 nm (log ε 4.2), $\nu_{max.}$ 1 725 cm^{-1}, δ 0.7—2.45 (7 H, m), 3.67 (3 H, s), 3.74 (3 H, s), 5.9 (1 H, m), and 6.93 (4 H, ABq, J_{AB} 8 Hz). This ester (69.4 g) was saponified by refluxing for 5 h with potassium hydroxide (70 g) in 90% ethanol (700 ml) under nitrogen. The usual work-up and recrystallisation from 90% ethanol gave the acid (4b) (59.7 g, 52% based on *p*-methoxyacetophenone), m.p. 204—205° (lit.,[7] 202—204°), $\lambda_{max.}$ 254 nm (log ε 4.29), $\nu_{max.}$ 1 700s and 1 600m cm^{-1}.

4-(p-Methoxyphenyl)-1-methylcyclohex-3-enecarboxylic Acid (4d).—The crude vinyl carbinol (2) prepared from *p*-methoxyacetophenone (75 g), on Diels–Alder reaction with methyl methacrylate (100 g) under the above conditions, yielded the adduct (3d) (71 g) as a pale yellow oil, b.p. 150—155° at 0.15 mmHg. Saponification with potassium hydroxide (70 g), ethylene glycol (610 ml), and water (90 ml) by refluxing for 5 h under nitrogen afforded the *acid* (4d) (54.2 g, 44% based on *p*-methoxyacetophenone) after recrystallisation once from 90% ethanol; m.p. 139—140°, $\nu_{max.}$ 1 700s and 1 595m cm^{-1}, $\lambda_{max.}$ 255 nm (log ε 4.28) (Found: C, 73.0; H, 7.4. $C_{15}H_{18}O_3$ requires C, 73.1; H, 7.4%).

Preparation of the Diazo-ketones (5a—d).—The acid (4a) (4 g, 0.02 mol) in dry ethanol was neutralised with a dilute solution of sodium ethoxide in ethanol (phenolphthalein as indicator). The solvent was removed *in vacuo*. The sodium salt, dried by repeated addition of dry benzene followed by distillation, was suspended in dry benzene (50 ml) and pyridine (0.3 ml), cooled in ice, and treated with oxalyl chloride (3 ml). The mixture was kept at 0 °C for 30 min with occasional shaking, then at room temperature for 30 min, and finally warmed at 55—60 °C for 1 h. The precipitate was filtered off and the filtrate concentrated *in vacuo*. The crude acid chloride was dissolved in dry ether (60 ml) and added slowly to a stirred solution of an excess of ice-cold ethereal diazomethane [from *N*-methyl-*N*-nitrosourea] containing dry triethylamine (1 ml), and the mixture was left overnight. The solution was filtered and concentrated and the product purified by passing through a column of neutral alumina (15 g) with ether–petroleum (1 : 1) or ether to obtain the diazo-ketone (5a) (4.16 g, 92%) as a yellow low-melting solid, $\nu_{max.}$ 2 125s and 1 640m cm^{-1}, which was used without further characterisation. The diazo-ketones (5b—d) were prepared similarly in 90—95% yields.

Carbenoid Addition Reaction of the Diazo-ketone (5a).—*Method A. Photoinduced decomposition in the presence of 'activated* CuO *catalyst'.* The diazo-ketone (5a) (4.5 g, 0.02 mol) in dry cyclohexane (900 ml) was heated and stirred under reflux over 'activated CuO catalyst'[2b] (18 g) with irradiation by two 250 W tungsten lamps until the i.r. band at *ca.* 2 130 cm^{-1} had disappeared (*ca.* 3 h). The mixture was filtered and the filtrate evaporated under reduced pressure; the residual oil was chromatographed on activated neutral alumina (50 g). Petroleum (1.2 l) eluted *2-phenyltricyclo*[3.2.1.$0^{2,7}$]*octan-6-one* (6a) as a yellowish liquid (3.15 g, 80%), $\nu_{max.}$ (film) 1 715s and 1 600w cm^{-1}, δ 1.1—2.57 (9 H, m) and 7.13 (5 H, s). Evaporative distillation gave a sample of b.p. 135° (bath temp.) at 0.4 mmHg (Found: C, 84.5; H, 7.3. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%).

Method B. Thermal decomposition in the presence of 'activated CuO *catalyst'.* The above experiment was repeated with the diazo-ketone (5a) (4.1 g) in the absence of an additional light source; 5 h were required for completion of the reaction. The bridged ketone (6a), identical (i.r. and n.m.r.) with the sample described above, was obtained in 70% yield.

Method C. Thermal decomposition in the presence of anhydrous copper sulphate. Thermal decomposition of the diazo-ketone (5a) (5 g, 0.022 mol) in dry cyclohexane (900 ml) in the presence of anhydrous copper sulphate (20 g) required *ca.* 9 h for completion; the bridged ketone (6a) (2.5 g, 57%), identical with the sample described above, was isolated by the usual work-up and purified by chromatography.

Decomposition of the Diazo-ketone (5c).—Decomposition of the diazo-ketone (5c) (4.8 g, 0.02 mol) according to method A required *ca.* 3 h for completion; the product, after chromatography on neutral alumina (40 g), afforded *5-methyl-2-phenyltricyclo*[3.2.1.$0^{2,7}$]*octan-6-one* (6c) (3.73 g, 88%) as plates, m.p. 60—61° (from petroleum), $\nu_{max.}$ 1 715s and 1 600w cm^{-1}, δ 0.93 (3 H, s), 1.21—2.47 (8 H, m), and 7.2 (5 H, s) (Found: C, 84.9; H, 7.7. $C_{15}H_{16}O$ requires C, 84.9; H, 7.6%).

Decomposition of the Diazo-ketone (5b).—Decomposition of the diazo-ketone (5b) (5.1 g, 0.02 mol) in anhydrous cyclohexane–THF (3 : 1; 900 ml) according to Method A required *ca.* 4 h for completion. The crude product was chromatographed on neutral alumina (50 g) and *2-(p-methoxyphenyl)-tricyclo*[3.2.1.$0^{2,7}$]*octan-6-one* (6b) was eluted with benzene–petroleum (1 : 20). Recrystallisation from petroleum gave pure material (3.63 g, 80%), m.p. 107°, $\nu_{max.}$ 1 710s and 1 600m cm^{-1}, δ 2.0 (9 H, m), 3.73 (3 H, s), and 6.88 (4 H, ABq, J_{AB} 8 Hz) (Found: C, 78.9; H, 7.0. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%).

Decomposition of the Diazo-ketone (5d).—Decomposition of the diazo-ketone (5d) (5.5 g, 0.02 mol) in anhydrous cyclohexane–THF (3 : 1; 900 ml) according to Method A required *ca.* 3 h for completion. The crude product was chromatographed on neutral alumina (60 g) and *2-(p-methoxyphenyl)-5-methyltricyclo*[3.2.1.$0^{2,7}$]*octan-6-one* (6d) was eluted with benzene–petroleum (1 : 5). Recrystallisation from petroleum gave pure material (4.29 g, 87%), m.p. 92°, $\nu_{max.}$ 1 715s and 1 605m cm^{-1}, δ 0.93 (3 H, s), 1.41—2.41 (8 H, m), 3.71 (3 H, s), and 6.88 (4 H, ABq, J_{AB} 8 Hz) (Found: C, 79.2; H, 7.35. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%).

Synthesis of the Unsaturated Ketones (7a—d) *and the Hydroxy-ketones* (10a *and* c). 2-*Phenylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (7a).—(a) *Cleavage of the cyclopropyl ketone* (6a). Through a solution of the ketone (6a) (1 g) in anhydrous chloroform (50 ml) was bubbled a stream of dry hydrogen chloride at room temperature for 2 h. Removal of solvent *in vacuo* left a solid which was filtered through a short column of alumina in petroleum. The *unsaturated ketone* (7a) (900 mg, 90%), m.p. 67—68°, crystallised as needles (from petroleum), $\nu_{max.}$ 1 735 cm^{-1}, $\lambda_{max.}$ 247 nm (log ε 4.12), δ 2.0—2.6 (7 H, m), 3.17br (1 H, s), 5.73br (1 H, t, *J* 4 Hz), and 7.23br (5 H, s) (Found: C, 84.6; H, 7.3. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%).

(b) *Boron trifluoride–ether-catalysed intramolecular alkylation of the diazo-ketone* (5a). To a stirred solution of the diazo-ketone (5a) (5.5 g, 0.024 3 mol) in anhydrous ethylene chloride (100 ml), cooled in ice–salt (*ca.* −10 to −5 °C), freshly distilled boron trifluoride–ether (1 ml) was added. After 2 h the solution was washed with water, 5% sodium carbonate solution, and water, dried (Na_2SO_4), and evaporated. The residue was dissolved in a minimal volume of benzene and chromatographed on neutral alumina (70 g). Elution with petroleum and benzene–petroleum (1 : 9) yielded the ketone (7a) (3.57 g, 74%), m.p. and mixed m.p. 67—68° (from petroleum).

(c) *Tetrafluoroboric acid-catalysed cyclisation of the diazo-ketone* (5a). To a stirred solution of the diazo-ketone (5a) (2.5 g) in nitromethane (40 ml), cooled in ice–salt, aqueous tetrafluoroboric acid (50%; 1 ml) in nitromethane (10 ml) was added dropwise. After stirring for 1½ h the solution was washed with water, aqueous 5% sodium carbonate, and water, dried ($CaCl_2$), and evaporated. The residue was chromatographed on activated basic alumina (40 g). Petroleum and benzene–petroleum (1 : 9 to 1 : 4) eluted the unsaturated ketone (7a) (720 mg, 30%), m.p. 68—69°, identical (mixed m.p. and i.r.) with the sample described above. Benzene (800 ml) eluted exo-2-*hydroxy*-endo-2-*phenylbicyclo*[3.2.1]*octan*-6-*one* (10a) (510 mg, 21%) as needles, m.p. 117° (from benzene–petroleum), $\lambda_{max.}$ 250 (log ε 1.96), 256 (2.1), and 262 nm (1.94); $\nu_{max.}$ 3 550br, m and 1 735s cm^{-1}, δ 1.47—2.9 (10 H, m) and 7.3 (5 H, m) (Found: C, 77.6; H, 7.3. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.4%). When nitroethane was used as the reaction medium similar results were observed.

5-*Methyl*-2-*phenylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (7c). (*a*) Cleavage of the cyclopropyl ketone (6c) (600 mg) as in the preceding experiment gave the *product* (7c) (550 mg, 93%), m.p. 70° (from petroleum), $\lambda_{max.}$ 247 nm (log ε 4.10), $\nu_{max.}$ 1 735 cm^{-1}, δ 1.13 (3 H, s), 1.77—2.47 (6 H, m), 3.13 (1 H, m), 5.73 (1 H, t, *J* 4 Hz), 7.23br (5 H, s) (Found: C, 85.0; H, 7.4. $C_{15}H_{16}O$ requires C, 84.9; H, 7.6%).

(*b*) The diazo-ketone (5c) (5 g, 0.02 mol) was cyclised with boron trifluoride–ether (1 ml) as described above to afford the ketone (7c) (3.53 g, 80%), m.p. and mixed m.p. 70°.

(*c*) The diazo-ketone (5c) (2.5 g) was cyclised with tetrafluoroboric acid (50%; 1.2 ml) as described above to afford the unsaturated ketone (7c) (560 mg, 26%), m.p. and mixed m.p. 70°, and the *hydroxy-ketone* (10c) (440 mg, 18%), obtained as prisms, m.p. 97°, $\lambda_{max.}$ 250 nm (log ε 2.86), $\nu_{max.}$ 3 550wbr and 1 735s cm^{-1}, δ 1.0 (3 H, s), 1.80—2.65 (10 H, m), and 7.3 (5 H, m) (Found: C, 78.4; H, 8.1. $C_{15}H_{18}O_2$ requires C, 78.25; H, 7.8%).

2-(p-*Methoxyphenyl*)*bicyclo*[3.2.1]*oct*-2-*en*-6-*one* (7b). (*a*) Cleavage of the cyclopropyl ketone (6b) (500 mg) as described above gave the *product* (7b) (480 mg, 96%), m.p. 86°, after direct crystallisation of the product from petroleum, $\lambda_{max.}$ 258 nm (log ε 4.2), $\nu_{max.}$ 1 740 cm^{-1}, δ 2.0—2.6 (7 H, m), 3.15 (1 H, m), 3.75 (3 H, s), 5.61 (1 H, t, *J* 5 Hz), and 6.95 (4 H, ABq, J_{AB} 8 Hz) (Found: C, 79.0; H, 7.4. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1%).

(*b*) Cyclisation of the diazo-ketone (5b) (2.55 g, 0.01 mol) with boron trifluoride–ether (0.6 ml) as above afforded the ketone (7b) (1.86 g, 82%), m.p. and mixed m.p. 86°.

2-(p-*Methoxyphenyl*)-5-*methylbicyclo*[3.2.1]*oct*-2-*en*-6-*one* (7d). (*a*) Cleavage of the cyclopropyl ketone (6d) (200 mg) as described above gave the *product* (7d) (185 mg, 93%), m.p. 95—96° (from petroleum), $\lambda_{max.}$ 260 nm (log ε 4.29), $\nu_{max.}$ 1 735s and 1 610m cm^{-1}, δ 1.13 (3 H, s), 1.87—2.47 (6 H, m), 3.13 (1 H, m), 3.75 (3 H, s), 5.65 (1 H, t, *J* 4 Hz), and 6.6—7.3 (4 H, dd) (Found: C, 79.0; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%).

(b) Cyclisation of the diazoketone (5d) (5.5 g, 0.02 mol) with boron trifluoride–ether as above afforded the ketone (7d) (4.19 g, 85%), m.p. and mixed m.p. 95—96°.

Synthesis of the Saturated Bridged-ring Ketones (8a—d).—endo-2-*Phenylbicyclo*[3.2.1]*octan*-6-*one* (8a). (a) *Catalytic hydrogenolysis of the cyclopropyl ketone* (6a). The ketone (6a) (2.5 g) was hydrogenated over palladium–carbon (10%; 100 mg) in ethanol (30 ml). Uptake was complete within 15—20 min. The usual work-up gave the *product* (8a) as an oil, which was distilled (b.p. 125—130° at 0.2 mmHg; yield 2.4 g, 96%), $\nu_{max.}$ (neat) 1 735 cm^{-1}; δ 1.3—3.21 (11 H, m) and 6.96—7.3 (5 H, m) (Found: C, 83.8; H, 7.9. $C_{14}H_{16}O$ requires C, 84.0; H, 8.0%). The 2,4-*dinitrophenylhydrazone* crystallised from ethyl acetate; m.p. 192° (Found: C, 63.2; H, 5.6. $C_{20}H_{20}N_4O_4$ requires C, 63.2; H, 5.3%).

(b) *Catalytic hydrogenation of the unsaturated ketone* (7a). The ketone (7a) (1.15 g) was hydrogenated in ethanol (20 ml) over palladium–carbon (10%; 70 mg) to afford the ketone (8a) (1.10 g, 96%), identical with the sample described above (i.r. spectrum and mixed m.p. of 2,4-dinitrophenylhydrazone).

5-*Methyl*-endo-2-*phenylbicyclo*[3.2.1]*octan*-6-*one* (8c). (*a*) Hydrogenolysis of the cyclopropyl ketone (6c) (900 mg) in ethanol (15 ml) over palladium–carbon (10%; 70 mg) gave an oil which was evaporatively distilled at 130 °C (bath temp.) and 0.4 mmHg. The *ketone* (8c) (810 mg, 90%) solidified; m.p. 55° (from petroleum), $\lambda_{max.}$ 258 nm (log ε 2.45), $\nu_{max.}$ 1 730 cm^{-1}, δ 0.97 (3 H, s), 1.23—3.2 (10 H, m), and 7.1 (5 H, s) (Found: C, 84.0; H, 8.5. $C_{15}H_{18}O$ requires C, 84.1; H, 8.45%); the 2,4-*dinitrophenylhydrazone* had m.p. 220° (from ethyl acetate) (Found: C, 63.6; H, 5.8. $C_{21}H_{22}N_4O_4$ requires C, 63.9; H, 5.6%).

(*b*) Catalytic hydrogenation of the unsaturated ketone (7c) (400 mg) gave the saturated ketone (8c) (380 mg, 95%), m.p. and mixed m.p. 55°.

endo-2-(p-*Methoxyphenyl*)*bicyclo*[3.2.1]*octan*-6-*one* (8b). (*a*) Hydrogenation of the cyclopropyl ketone (6b) (300 mg) in ethanol (15 ml) over palladium–carbon (10%; 50 mg) afforded the *ketone* (8b) (290 mg, 97%), m.p. 81—82° (from petroleum), $\nu_{max.}$ 1 735 cm^{-1}, δ 1.47—2.7 (10 H, m), 2.7—3.1 (1 H, m), 3.67 (3 H, s), and 6.75 (4 H, ABq, *J* 9 Hz) (Found: C, 78.3; H, 7.9. $C_{15}H_{18}O_2$ requires C, 78.2; H, 7.9%).

(*b*) Hydrogenation of the unsaturated ketone (7b) (300 mg) gave the ketone (8b) (94%), m.p. and mixed m.p. 81—82°.

endo-2-(p-*Methoxyphenyl*)-5-*methylbicyclo*[3.2.1]*octan*-6-*one* (8d). (*a*) Hydrogenolysis of the cyclopropyl ketone (6d) (1.5 g) in ethanol (40 ml) over palladium–carbon (10%; 100 mg) afforded the *ketone* (8d) (1.45 g, 97%), m.p. 71°

(from petroleum), $\nu_{max.}$ 1 730 cm^{-1}, δ 1.0 (3 H, s), 1.3—2.3 (9 H, m), 2.9 (1 H, m), 3.7 (3 H, s), and 6.86 (4 H, ABq, J 8 Hz) (Found: C, 78.4; H, 8.3. $C_{16}H_{20}O_2$ requires C, 78.6; H, 8.2%).

(*b*) Hydrogenation of the unsaturated ketone (7d) (1.5 g) gave the ketone (8d) (96%), m.p. and mixed m.p. 71°.

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